

Development of some visible light active spinel and perovskite based novel nanocomposite photocatalysts for hazardous pollutants degradation and electrocatalytic application

Thesis submitted for the Degree of
DOCTOR OF PHILOSOPHY (SCIENCE)

Submitted By

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CERTIFICATE FROM THE SUPERVISORS

This is to certify that the thesis entitled "*Development of some visible light active spinel and perovskite based novel nanocomposite photocatalysts for hazardous pollutants degradation and electrocatalytic application*" submitted by **Mr. Kalyan Ghorai** who got his name registered on 27th June, 2017 for the award of Ph.D. (Science) degree of Jadavpur University, is absolutely based upon his own work under the joint supervision of **Dr. Arup Gayen** and **Dr. Md. Motin Seikh** and neither this thesis nor any part of it has been submitted for either any degree/ diploma or any other academic award anywhere before.

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DECLARATION

I hereby declare that the work embodied in the present thesis entitled “*Development of some visible light active spinel and perovskite based novel nanocomposite photocatalysts for hazardous pollutants degradation and electrocatalytic application*” is the result of investigations carried out by me in the Department of Chemistry of Jadavpur University under the joint supervision of **Dr. Arup Gayen**, Department of Chemistry, Jadavpur University and **Dr. Md. Motin Seikh**, Department of Chemistry, Visva-Bharati University and neither this thesis nor any part of this thesis has been submitted for any degree earlier anywhere.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made whenever the work described has been based on the findings of the other investigators. Any omission which might have occurred by oversight or error in judgment is regretted.

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**Dedicated
To
My Teachers**

Acknowledgement

Introducing myself into the life of a doctoral researcher and the subsequent completion of my Ph.D. thesis work was a very challenging task for me. I faced many ups and downs in this journey. But there were many people whose constant motivation and support helped me to choose the right direction in this journey. I would like to express my heartiest respect to all of them.

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Thesis abstract

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Thesis Title: “*Development of some visible light active spinel and perovskite based novel nanocomposite photocatalysts for hazardous pollutants degradation and electrocatalytic application*” – Submitted by Kalyan Ghorai

Pure spinel and perovskite oxide materials alone are supposedly not an active member in the photocatalyst family due to their low band gap energy values and very high electron-hole pair recombination tendency, although they show a good visible light absorption activity. But surprisingly their combinations with other semiconductor materials forming a nanocomposite heterojunction system can act as a potential photocatalyst material with promising visible light absorption activity. In such nanocomposite photocatalysts, the catalytic performance is effectively increased due to improvement of charge separation via Type I, Type II, SER (surface plasma resonance), S-scheme, and Z-scheme mechanisms. Based on this background knowledge about the advantage of nanocomposite photocatalyst over single spinel oxide or single perovskite oxide, we have motivated to fabricate some spinel or perovskite oxide based nanocomposite photocatalyst materials for wastewater treatment and electrochemical oxygen evolution. The research work included in this thesis is based on the synthesis and development of some potential spinel and perovskite oxide based visible light active nanocomposite photocatalyst materials that are applied as an active photocatalyst for photocatalytic degradation of hazardous pollutants such as industrial colorful azo dyes like Rhodamine B (RhB), methylene blue (MB), methyl orange (MO), and reactive black 5 (RB5) as well as colorless antibiotics like tetracycline hydrochloride (TC-HCl), and norfloxacin (NORF) with the aid of visible light irradiation from a domestic light emitting diode (LED) light. These nanocomposite materials are also used as an active electrocatalyst for electrochemical oxygen evolution reaction (OER) under dark and light (visible) condition.

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A general introduction on the basics of photocatalysis and its operation mechanism, photocatalyst, oxide based nanocomposite as photocatalyst and preparation methods of these materials, different types of charge transfer mechanisms in the nanocomposite heterojunction, and details of CuCr_2O_4 spinel and LaNiO_3 perovskite oxide systems which are the backbones of this research work is presented in **Chapter 1** that ends with the scope of the present investigation.

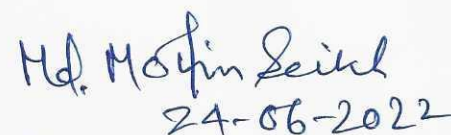
To achieve the targeted goal we have employed different synthetic routes for the preparation of pure components as well as their nanocomposite materials. The research methodology, the various types of characterization techniques and fabrication of photocatalytic reactor setup are discussed in **Chapter 2**.

In **Chapter 3**, we have discussed the findings on synthesis, characterization, and photocatalytic activity of $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ (CCO/BiOBr) nanocomposite photocatalyst for the degradation of RhB and TC-HCl using household LED light. In this nanocomposite system, sol-gel combustion made spherical shaped CuCr_2O_4 nanoparticles are decorated on BiOBr plates in a single step via coprecipitation method using cetyltrimethylammonium bromide (CTAB) as the Br-source as well as the template. The synthesized materials are subsequently characterized by employing several techniques such as powder X-ray diffraction (PXRD), Brunauer-Emmett-Teller (BET) surface area, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray (EDX) spectroscopy, elemental mapping, selective area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), UV visible diffusion reflectance spectroscopy (UV-Vis DRS), photoluminescence (PL) spectroscopy and Raman spectroscopy. The 20% $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ composite exhibits high degradation efficiency for both RhB (96% in 15 min) and TC-HCl (96.7% in 300 min) in presence of LED light with good recycling behavior. Based on the band modification at the interface of the composite materials and radical trapping analyses a plausible mechanistic path of the photocatalytic degradation process is presented.

Chapter 4 deals with the synthesis of $\text{CuCr}_2\text{O}_4/\text{CeO}_2$ (CCO/ CeO_2) nanocomposite materials as a highly active heterogeneous Fenton like photocatalyst for the degradation of harmful azo dyes under domestic LED light irradiation. The catalysts have been synthesized via a simple co-precipitation method followed by heat treatment and is subsequently characterized thoroughly. The 10%CCO/ CeO_2 nanocomposite sample exhibits high degradation activity and it could effectively degrade RhB (99% in 15 min), MB (98% in 20


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min) and MO (96% in 30 min) with a very high rate. The radical trapping and coumarin based fluorescence probe methods suggest the generation of $\cdot\text{OH}$ (hydroxyl radical) in the catalytic pathways and based on the reactive species trapping analysis, band positions and degradation results, we have established a detailed photocatalytic degradation mechanism. The recycling activity is also discussed.

Chapter 5 is based on the studies on photocatalytic Fenton like activity of Anatase TiO_2 decorated CuCr_2O_4 nanocomposite material. In this chapter, we have discussed the surprising performance of $\text{CuCr}_2\text{O}_4/\text{anatase-TiO}_2$ (CCO/ TiO_2) nanocomposite as a Fenton like catalyst with potential impact on sustainable design and environmental protection. A series of $\text{CuCr}_2\text{O}_4/\text{TiO}_2$ nanocomposites was synthesized by sonochemical mixing method followed by heat treatment. All the materials are thoroughly characterized by numerous physical and chemical techniques. The 100% CCO-loaded nanocomposite material (100%CCO/ TiO_2) obtained by heat-treatment at 400 $^\circ\text{C}$ is found as high performance catalyst towards the degradation of azo dyes like RhB (97% in 15 min), MB (99% in 15 min) and MO (90% in 15 min), antibiotics like TC-HCl (99% in 15 min) and NORF (97% in 75 min), and a promising Pt-free candidate for photoelectrocatalytic oxygen evolution reaction under domestic LED light irradiation. The details of recycling behavior, chemical stability, and photocatalytic mechanism are also discussed.

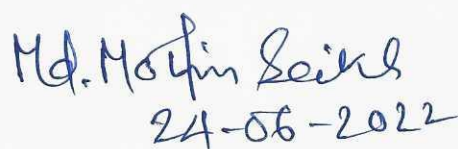
In **Chapter 6**, we have included our studies on Z-scheme type $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ (LNO/g-CN) photocatalyst for pollutants degradation under natural sunlight irradiation. The major issues in this chapter are (i) development of nanocomposite photocatalyst working through Z-scheme charge transfer pathway across the heterojunction, (ii) utilization of direct sunlight as the photo-source, (iii) prospect of ligand-hole in photocatalysis through enhanced sub-band gap absorption. The $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ nanocomposite photocatalysts are synthesized via a facile solid state mixing route followed by thermal treatment and are characterized by using several physicochemical techniques. The photocatalytic performance of Z-scheme photocatalyst (100%LNO/g-CN being the best photocatalyst) for the degradation of hazardous pollutants such as RB5 (94% in 60 min), MB (98% in 180 min) and colorless antibiotic-pollutant TC-HCl (96% in 300 min) in presence of natural sunlight is discussed here. The details of active species trapping, recycling activity and charge separation mechanism are also elucidated.

In **Chapter 7**, we have dealt with the synthesis, characterization and photoelectrochemical behavior of $\text{CuCr}_2\text{O}_4/\text{BiVO}_4$ (CCO/BVO) nanocomposite system. The


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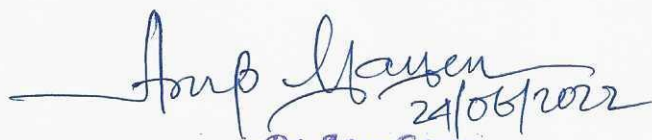

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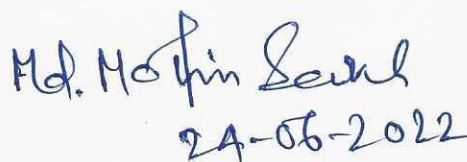
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synthesized materials have been characterized by various physical and chemical techniques. The hydrothermally synthesized electrocatalyst has been used as an active material for electrochemical oxygen evolution reaction under visible light and dark condition. 10 mole % CCO loaded sample (10%CCO/BVO) shows the best electrocatalytic (OER current density = 22.5 mA cm^{-2}) and photoelectrocatalytic (OER current density = 36.9 mA cm^{-2}) OER activity among whole nanocomposite series. The OER activity is effectively improved under visible LED irradiation.

In the end we have made concluding remarks with critical insights of this research work in **Chapter 8** and advocated for the necessity to continue further research in this very important and emerging area of heterogeneous photocatalysis and photoelectrocatalysis.


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Chapter 1

A brief overview on nanostructured metal oxides and their composites for heterogeneous photocatalysis applications

1.1. Introduction

The present and future challenges of our society are to achieve environmental sustainability of the modern Earth and meet simultaneously the energy crisis. In other word, to meet the growing energy demand without comptonization of environmental sustainability is long a standing issue. Accordingly, the trends of modern research are largely focused on the energy issues. The rapid growth of industries, the use of coal, oil and natural gas, fossil fuel, and other human activities produces many harmful gases and untreated wastewater which causes environmental pollution [1]. The condition of water resources is becoming worse day by day due to its rapid contamination with pollutants and human waste. The rapidly increasing concentration of greenhouse gases is responsible for global warming. Thus, at the expense of huge environmental taxation we fulfill our energy demand. Therefore, it is very much essential to solve these global problems to address the issues of clean energy and clean environment. It demands development of novel and feasible protocol to eliminate the contaminants from water resources and to produce sustainable clean energy. Solar energy is an alternative sustainable energy source that is clean, easily available, and accessible [2]. So, the use of solar energy is a renewable energy resource to replace fossil fuel in the future. However, the transformation of solar energy into clean energy through the photovoltaic cell, solar thermal processes, artificial photosynthesis, and solar plant have been extensively studied but the use of such evergreen energy is faced with several challenges till now. Although solar energy has many advantages such as, ample availability in the major continents, zero cost, unlimited lifetime, and unlimited resources but it is not available on the earth for the whole day, and it also depends on the weather conditions. Thus, trapping and storage of solar energy is highly essential for continuous application purpose. Solar energy harvesting takes place by three different approaches namely, photothermal, photovoltaic, and photocatalysis which are mainly involved in the generation of clean energy. Among these three, photocatalysis is an emerging technique that has a huge potential to form energy-rich products such as H_2 , CH_4 , CH_3OH , C_2H_5OH , and NH_3 , etc, from rich resources like H_2O , CO_2 , O_2 , and N_2 by the process of water splitting, pollutants degradation, CO_2 reduction, N_2

fixation and many more [3]. The applications of photocatalysis in various fields of science and technology are represented schematically in **Fig. 1.1**. Employing the photocatalytic pollutants degradation process for wastewater treatment, the solar energy can be used, and, in this process, many useful energy-rich compounds are formed such as hydrogen, hydrocarbons, and ammonia [4]. The sunlight energy is mainly the combination of three different light energy radiations namely ultraviolet (UV), visible (Vis), and near-infrared (NIR), and depending on the light absorption activity of the working photocatalyst, the specific light energy of sunlight can be used. Due to this limitation of using the sunlight, researchers are also using the UV, the Vis, and the NIR energy radiation from external sources instead of sunlight.

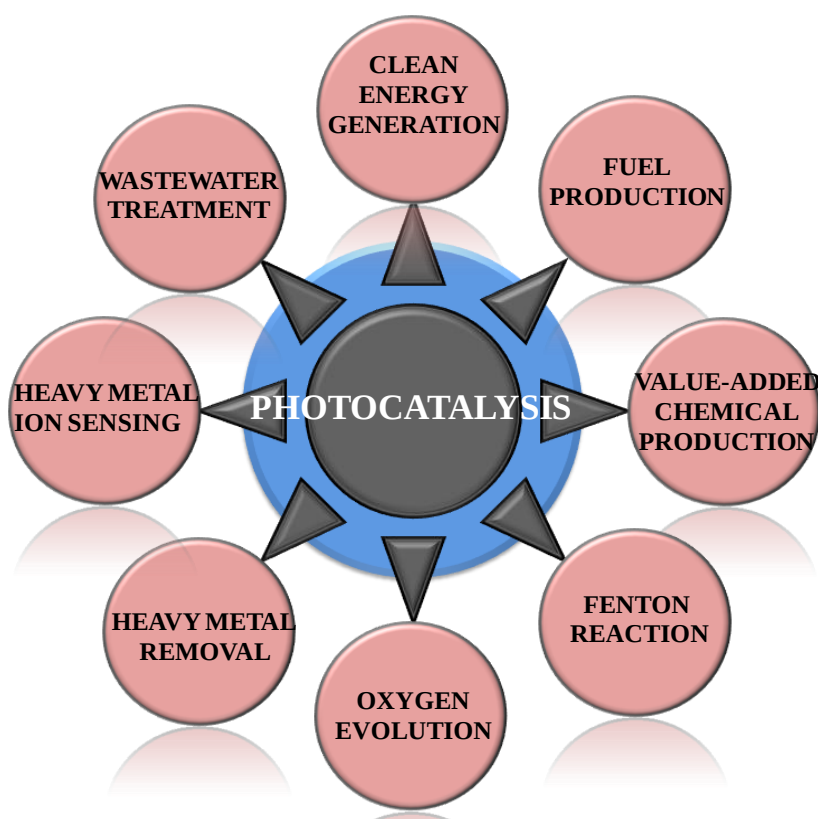


Fig. 1.1: Applications of photocatalysis in different fields of science and technology.

Therefore, photocatalysis is an advanced technique for environmental decontamination and energy conversions that uses light energy by using a suitable semiconductor photocatalyst [5]. Photocatalysis is a green and promising way to fight against global problems and energy crisis. This technique can oxidize and reduce the pollutants by photogenerated holes on the valence band and photogenerated electrons on the conduction band of photocatalyst, respectively. In this technique, the photogenerated electrons generate

the reactive oxygen species (ROS), like hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\cdot\text{O}_2^-$), and singlet oxygen that is responsible for pollutants degradation to form value-added products [6]. It is used for clean and green energy production like H_2 generation and CO_2 reduction to fuel products by using photogenerated electrons.

If we look at the history of photocatalysis, two famous scientists, Honda and Fujishima in the year 1972 reported the electrochemical photocatalytic H_2 and O_2 production by the splitting of water using the benchmark photocatalyst TiO_2 under the ultraviolet light irradiation [7]. The first concept of photocatalysis originated from this pioneering work performed by Honda and Fujishima. According to Prof. Fujishima, the benefits of science and technology should be shared by everyone. He says “*The primary aim of science and technology is to create a society where people can have healthy, comfortable and long lives. The crucial thing in science and technology is to develop a new innovation that can be applied to actual products and services, and these new products and services will make people happy*”. By making use of his discovery of photocatalyst, he came forward to create such a society.

The fundamental of photocatalysis involves three steps, firstly the absorption of a suitable wavelength of light energy by the semiconductor photocatalyst which is greater than its corresponding band gap energy to form photoexcited electron-hole charge carriers, and secondly, photogenerated electron-hole charge carriers are separated into reductive electrons and oxidizing holes into the conduction band and valence band, respectively and thirdly, participation of photoinduced charge carriers to trigger the redox reaction of oxidation or reduction reaction in the semiconductor photocatalyst. In general, the photo-induced electrons and holes with sufficient thermodynamic energy operate the reduction and oxidation reactions, respectively, and consequently showing high photocatalytic activity. So, it is most likely to expect that photocatalysis has the potential impact for utilization of natural sunlight and artificial light energy for environmental decontamination like pollutants degradation, chemical transformation reaction like CO_2 photoreduction, CO photooxidation, and clean energy generation like H_2 production and O_2 evolution. Unfortunately, poor utilization of visible light energy, low quantum efficiency, and low stability of photocatalyst disrupt the advancement of heterogeneous photocatalysis [8]. In this regard, the modifications of photocatalyst with improved photocatalytic activity, recycling activity, and stability is the prime priority to develop heterogeneous photocatalysts [9]. The modification of photocatalyst materials is generally involved by (i) the doping of metal and nonmetal ions [10], (ii) the

formation of nanocomposite system via the coupling of other semiconductor metal oxide [11], (iii) the formation of composite system with carbon-based polymer [12], and (iv) changing the morphology of photocatalyst materials [13].

Generally, in the case of photocatalysis, the appropriate thermodynamic energies of the photoinduced electrons and holes are the prime causes to promote the redox reaction. The major number of visible light active metal oxide-based photocatalysts has strong oxidation ability due to the photogenerated holes but owing to the fact that the conduction band of metal oxide generally lies below 0 eV (vs. NHE), the reduction ability of the photogenerated electrons are poor. Therefore, it is necessary to achieve effective visible light response photocatalyst by the formation of heterojunction via the coupling with suitable band gap semiconductor oxide material to form a thermodynamically favorable energy platform that can facilitate the charge separation and migration. On the other hand, the shifted electron has sufficient energy to participate in the reduction reactions feasibly. Therefore, an efficient heterojunction photocatalyst is primarily the nanocomposite type materials which are mainly composed of the combination of two different metal oxide systems or the combination of one metal oxide with other semiconductor materials.

1.2. Major sources of water pollution

Water is a very important resource of our environment. Life on the earth fully depends on water. In other words, it is said that water is the key source of surviving life on earth. Water has regenerative nature in the sense that it can absorb a certain level of pollution load without changing its nature [14]. When an excess of pollution load surpasses the regenerative capacity of water resources, the water gets polluted [15]. Water pollution has been listed as a top priority worldwide political agenda due to its undesirable effects on global health and the environment from the last decades of nineteenth century [16]. Various research studies on water pollution indicate that the contaminants released from industries, agricultural, horticultural and human activities are the prime causes of water pollution, which creates a bad impact on the entire water bodies of the ecological system [17]. Research studies also proved that chemical compounds such as industrial dyes and textile dyes are responsible for the ever increasing global threats. It has been reported that approximately 10-20% of the total dye in the world is released as textile waste during industrial manufacturing processing. Moreover, according to the global scale, production over 0.7 million tons of artificial organic dyes in every year mainly for the utilization in the textile, leather, painting,

plastic, detergent, food sector, cosmetics, electronic sector, agriculture, horticulture, printing, paper, medical equipment industries, man-made activity and many more [18-19]. **Fig. 1.2** presents a few live photographic images which show how water resources get polluted with various reasons or activities.



Fig. 1.2: Snapshots of various industrial and man-made activities that is responsible for water pollution.

Furthermore, millions of colored chemical compounds were manufactured in the last century, and out of these more than 10,000 were produced for textile and leather industries. The pollutants from textile waste are highly suspended solid powder, high chemical oxygen demand (COD), and very toxic. Furthermore, textile industries release large amounts of dyes into the water that creates ecological problems. Textile, paper, plastic, leather, tanning, paint industries, and many other industries actively use organic dye as a coloring agent. The pollutions from such industries come from dyeing and finishing processes [20]. In the textile industries, nearly 21-377 m³ of water is used per ton of textile products and can form large quantities of wastewater from the steps of the dyeing and finishing process. Generally, the

coloring agent can be categorized into two parts namely, dyes and pigments (see **Fig. 1.3** and **Fig. 1.4**). The distinct difference between dyes and pigments is as follows: dyes are fully or partly soluble in water whereas pigments are insoluble substances. Day by day an increasing number of industrial chemical products are contributing contamination in industrial wastewater. The wastewater released from the textile sector is marked as the most wanted polluting source among all other industrial sectors due to the utilization of more than 10,000 dyes and pigment compounds of which nearly about 50% are azo dyes [21]. Dyes molecules are categorized based on their structure and functional group or both (see Fig. 1.3). Also, the dye can be classified into acid, basic, cationic, anionic, reactive, direct, disperse, etc. On the other side, the pigments are classified as organic pigments and inorganic pigments (see Fig. 1.4). The organic pigments are structured by long carbon chains and carbon rings which generally are categorized as different classes like azo pigments, polycyclic pigments, anthraquinone pigments, dioxazine pigments, triaryl carbonium pigments, and quinophthalone pigments. On the other hand, inorganic pigments are non-carbon-based chemical compounds that are formed by the precipitation of metallic salts. Inorganic pigments are classified as white pigments, black pigments, special pigments, and color pigments.

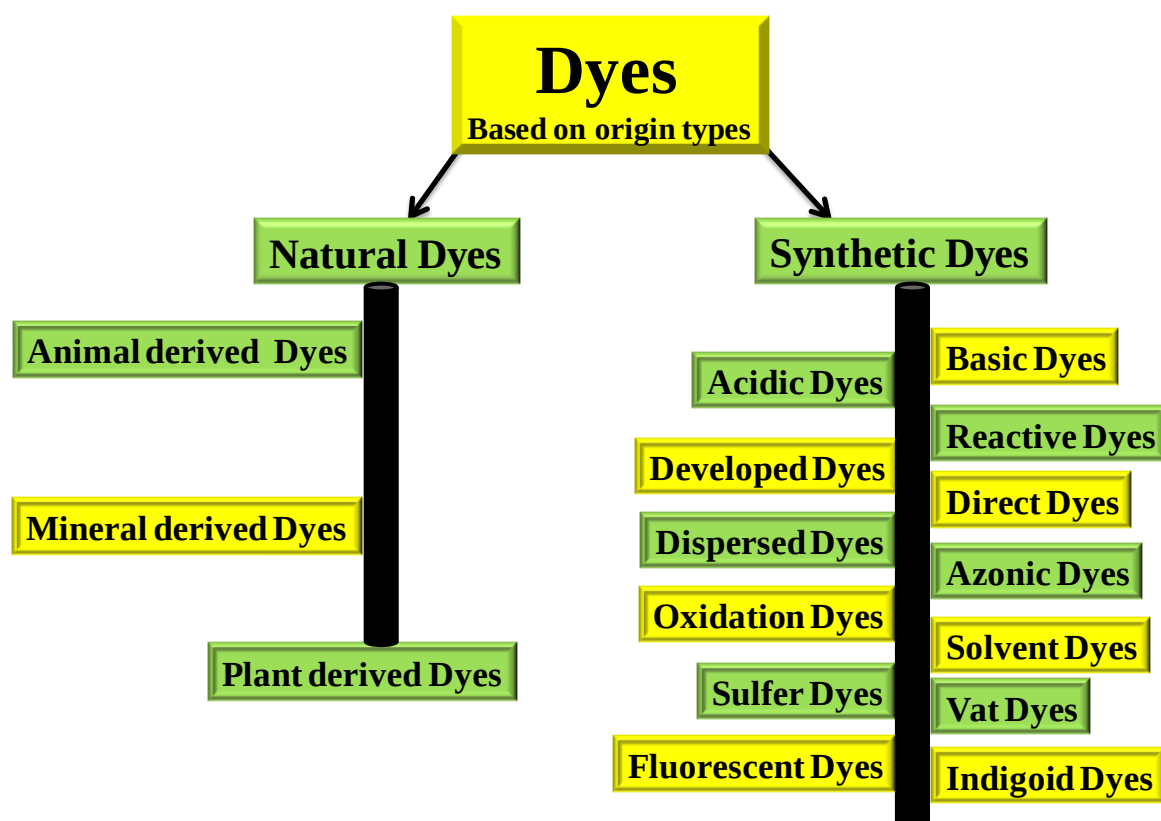


Fig. 1.3: Classification of dyes based on their origin and their chemical constitution.

Among all other industrial waste, the textile wastewater produces a large number of serious problems which are as follows: (i) presence of very high total dissolved solid content in the wastewater, (ii) presence of toxic metals such as Cr, Cu, As, Sb, Cd, etc., (iii) presence of free chlorine and silica, (iv) presence of non-biodegradable organic dyes, and (v) most of the dyes present in the textile wastewater are stable to light because dyes have a complex aromatic molecular system which makes it more stable and difficult to degrade in the environment [22].

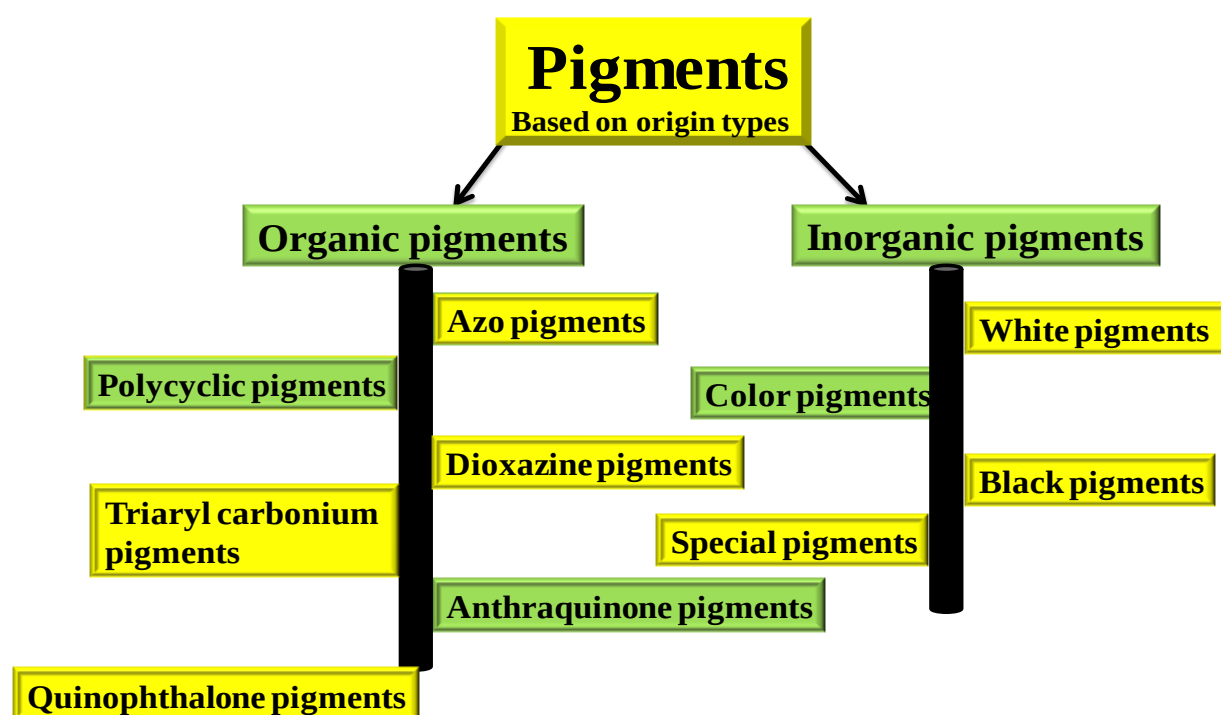


Fig. 1.4: Classification of pigments based on the carbon chains and non-carbon based chemical compounds.

1.3. Advanced oxidation process (AOPs) for environmental remediation

The advanced oxidation processes are considered as an alternative method for wastewater treatment. Degradation, detoxification, and removal of various toxic, hazardous pollutants in wastewater are possible only by AOPs [23]. The basic principle of AOPs is to produce reactive oxygen species (ROS) such as superoxide and hydroxyl radicals in aqueous medium that work as powerful oxidants to oxidize a wide range of pollutants without any selectivity [24]. AOPs are very effective for the treatment of highly concentrated industrial wastewater and treatment of trace contaminants [25]. AOPs are generally carried out by the

activator such as UV light, visible light, transition metals, microwave, electrical, and ultrasonication and oxidants like H_2O_2 , persulfate ion, and O_3 . Various kinds of ROS can be generated that mainly including the formation of hydroxyl radicals, sulfate radicals, superoxide radicals, which exhibit strong oxidation capabilities [26]. Among these AOPs, the Fenton reaction, Fenton like reaction, photo Fenton like reaction, and photocatalysis techniques are environment-friendly strategies to produce stronger oxidants (ROS) [27]. AOPs have many advantages like low or non-toxicity, simple operation, low cost, and time-saving process. These ROS are highly effective and unselective to degrade many harmful pollutants into less harmless or harmless species and even CO_2 , H_2O , or other inorganic salts.

1.4. Reason behind the choice of photocatalysis for environment remediation

The choice of photocatalysis for environmental protection is due to the following advantages:

- It is an ecofriendly green technology to tackle environmental issues.
- The catalysts used in photocatalysis are easy to synthesize.
- Photocatalysis is a very simple, cost-effective, time-saving process and requires lesser chemical input.
- It requires a very simple reaction setup with a mild reaction condition.
- Photocatalysis deals with several environmental issues like degradation of various organic and inorganic pollutants from wastewater, reforming reaction for hydrogen production, H_2O_2 generation, hydrogen and oxygen evolution, clean energy generation, CO_2 reduction, CO oxidation, water splitting, antibacterial activity, various organic transformation reactions (C-C coupling, C-N coupling, and many more) for valuable chemical production, production of fuels and so on.
- It is applied to control air pollution and is also used extensively in the medical field.
- In heterogeneous photocatalysis, a photocatalyst can be easily recovered by simple washing and drying and can be used for the next cycle with high activity.
- Minimal quantity of secondary pollutants is generated after the completion of photocatalysis.
- Photocatalysis is by far the best alternative technique to replace the energy-intensive conventional methods like adsorption on activated carbon, ultrafiltration, reverse

osmosis, coagulation by chemical reagent, and ion exchange on synthetic adsorbent resins, etc.

- It is a suitable method for the formation of harmless and eco-friendly products. The traditional treatment methods transfer the pollutant phase to another pollutant phase.
- This technique can be used to destroy various classes of hazardous pollutant compounds.

1.5. A brief introduction to photocatalysis

Photocatalysis is a gifted and extraordinary method to science and technology which can be used for various environmental safety issues such as degradation of various organic and inorganic pollutants in wastewater, production of hydrogen energy, purification of air, the evolution of oxygen, antibacterial activity, organic transformation reaction to form valuable chemicals, production of fuels and so on. It is a rapidly growing method to solve environmental issues and drawing more attention of the researchers due to its many advantages like low cost, easy operation technique, high efficiency, time effectiveness, and requires a simple reaction setup [28]. Photocatalysis is the combined effect of photochemistry and catalysis where the concept of photochemistry is applied to enhance the catalysis [29]. The term photocatalysis is rooted from the Greek language and is composed of two parts, namely photo that means light energy, and catalysis which is a reaction process where a substance (called catalyst) is involved in the reaction which increases the rate of a transformation of the reactants by reducing the activation energy without being changed at the end of the reaction. Therefore, photocatalysis is a technique where light energy and catalyst are used together to boost or speed up a chemical reaction. The catalyst used in photocatalysis is named as photocatalyst. So “*the catalysis which is accelerated by light energy*” is called photocatalysis. In general, photocatalysis can be defined as an improvement of the rate of chemical reactions in presence of photocatalyst under the assistance of light energy.

The fundamental steps of photocatalysis operated in the semiconductor materials are expressed below:

- ❖ Firstly, the different light energy in terms of photons falls on the semiconductor surface and if the energy of incident light is greater than the band gap energy of the semiconductor, then the electrons on the VB are excited and move to the CB of the semiconductor material.

- ❖ Secondly, holes would be left on the VB of the semiconductor. These holes are very oxidative and react with water to form hydroxyl radical which is a very powerful oxidizing agent to oxidize various pollutants. Furthermore, holes can directly react with compounds present in the reaction medium.
- ❖ The electrons on the CB of the semiconductor react with the dissolved oxygen to produce the superoxide radicals. These CB electrons participate in the oxidation reaction.

So, these excitons are very much able to conduct oxidation and reduction reactions with any compound which might be adsorbed on the semiconductor surface to give the expected products. A representative photocatalytic mechanism is presented schematically in **Fig. 1.5**.

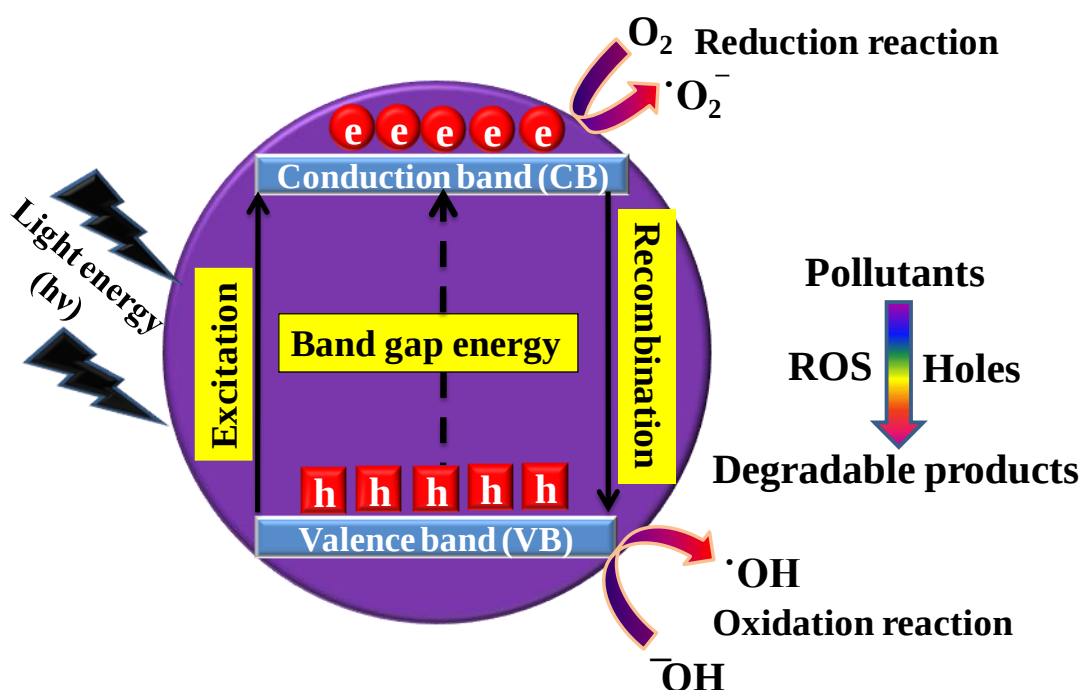


Fig. 1.5: Schematic representation of the basic steps of photocatalytic mechanism of a semiconductor photocatalyst.

1.6. Types of photocatalysis

Photocatalysis is classified into two types, homogeneous photocatalysis and heterogeneous photocatalysis. Homogeneous photocatalysis is commonly used in various metal complexes as photocatalyst such as iron complex, copper complex, and chromium complex, etc [30]. In this process, the higher oxidation state of metal ions in the complex under light and thermal conditions produces hydroxyl radicals which lead to degrade the toxic materials. While heterogeneous photocatalysis is an advanced technical method, in

which photocatalyst and reactant remain in different phases, and it can be easily recovered after completion of the photocatalytic reaction [31]. The heterogeneous photocatalysis has many advantages like high photocatalytic efficiency, low cost, formation of eco-friendly products, no issues for the formation of a secondary pollutant, requirement of mild reaction condition, and very high recycling efficiency. For example, the semiconductor materials like TiO_2 , ZnO , WO_3 , SnO_2 , CeO_2 , Bi_2O_3 , etc., are mainly used in heterogeneous photocatalysis due to suitable electronic structure where a filled valence band and vacant conduction band, suitable optical property, great charge transfer property, and high excited states lifetime of excitons [32]. An ideal semiconductor photocatalyst should be light active, easily able to absorb visible or UV light, eco-friendly, chemically inert, stable towards photo corrosion, inexpensive, and nontoxic. The heterogeneous photocatalysis with semiconductor photocatalyst emerges to be a promising technology for environmental safety.

In AOPs, heterogeneous photocatalysis in presence of semiconductor metal-oxide and semiconductor metal-oxide based nanocomposite materials is an efficient candidate for mineralizing a wide range of pollutants in water into environment-friendly and harmless products like CO_2 , N_2 , O_2 , H_2O , and a variety of inorganic salts, etc. Heterogeneous photocatalysis has been widely investigated and is a promising technique for the applications of self-cleaning, antibacterial activity as well as the application of the photocatalytic process for purification of wastewater through removing various pollutants and bacteria. The physicochemical properties of metal-oxide and oxide based nanocomposite materials are a crucial factor for the high photocatalytic efficiency of heterogeneous photocatalysts which mainly depends on the composition, size, and morphology of materials [33].

1.7. Factors affecting the photocatalysis process

As it has been mentioned above that the photocatalysis process involves several steps and intermediate chemical species, it is sensitive to the different factors. The photocatalytic process primarily depends on the following parameters:

1.7.1. Structure, morphology, size, involved phases, and surface area of photocatalysts

The structure of photocatalysts plays an important role in achieving improved photocatalytic activity. For example, TiO_2 photocatalyst contains three phases namely anatase, rutile, and brookite. But the most sensitive and active phase of TiO_2 is the anatase phase having improved photocatalytic efficiency due to its stability, suitable adsorption

power, the proper position of the conduction band, and a higher degree of hydroxylation [34]. Moreover, the previously published reports support that morphology of photocatalyst also acts as a considerable factor for improved photoactivity because morphology controls the active site, surface area, and adsorption power of a photocatalyst [35]. Saravanan et al. reported that spherical-shaped ZnO photocatalyst shows higher photocatalytic activity than that of needle-shaped and rod-shaped ZnO [36]. Generally, the nanomaterials having a larger surface area with a smaller size can effectively show higher photocatalytic activity [37]. It is observed that the nanosized TiO₂ material acts as a highly efficient photocatalyst compared with its bulk phase due to the smaller size [38]. When the size of the photocatalyst is smaller, a large number of atoms are accumulated on the catalyst surface that increases their surface to volume ratio and as a result there occurs an enhancement in the number of active sites as well as the charge transfer rate, thereby achieving improved photocatalytic activity. Furthermore, the photocatalytic redox reaction takes place on the photocatalyst surface so that the surface properties of the photocatalyst greatly affect the activity of the photocatalyst.

1.7.2. Reaction temperature

In general, the photocatalytic efficiency of a photocatalyst does not depend on the reaction temperature. Although, it is true that during the photocatalytic reaction, an optimum temperature can enhance the electron-hole pair separation which is the key factor to show improved photocatalytic activity. For example, during the photocatalytic reaction of TiO₂ material, when the reaction temperature is increased above 80 °C, the charge separation is enhanced but due to desorption of adsorbed reactant species, the overall photocatalytic activity is decreased [39]. Because of photonic activation, heat is not required to initiate the photocatalytic reaction and it can easily operate at room temperature. It is reported that the optimum reaction temperature for the photocatalytic activity of TiO₂ falls in the range of 20 °C to 70 °C that depends on the activation energy of photocatalyst material [40].

1.7.3. pH of the medium

Since the photocatalytic activity of a photocatalyst depends on the surface charge properties of the photocatalyst material, so in this case, the photocatalytic activity of the photocatalyst can be influenced by the pH factor. Previously published works reported that the change in pH significantly affects the photocatalytic activity of photocatalyst towards pollutant degradation [41]. Neppolian et al. reported that the reactive blue 4 degradation

under different pH conditions over TiO_2 photocatalyst shows different photocatalytic activity [42]. The degradation data indicated that the lower degradation activity in the acidic pH ($\text{pH} \leq 5$) is due to the higher concentration of proton and on the other hand, in the alkaline pH ($\text{pH} \geq 8$) condition, the existence of hydroxyl radicals increases the degradation efficiency of the photocatalytic reaction. Unfortunately, the unexpected drop of degradation efficiency in the very high alkaline pH ($\text{pH} = 11-14$) is due to the scavenging of $\cdot\text{OH}$, as reported by Neppolian et al. [42]. The effect of pH on the photocatalytic reaction is explained in terms of electrostatic interactions of charged photocatalyst with pollutant molecules which influences the rate of adsorption and subsequently the surface properties.

1.7.4. Intensity of light

Since the primary step of photocatalysis is the generation of electron-hole pairs by the irradiation of light energy on the photocatalyst surface, so the degradation rate of photocatalytic reaction depends on the light intensity [43]. The quanta of light absorbed by the photocatalyst are given by the quantum yield which is the ratio of the rate of reaction to that of absorption of radiation. Many published works have investigated the effects of varied light intensity on the photocatalytic efficiency of photocatalyst [44]. The photocatalytic reaction rate is inversely related to the intensity of irradiated light. The high light intensity promotes more electron-hole recombination causing a decrease in photocatalytic reaction rate.

1.7.5. Quantity of catalyst

The amount of photocatalyst mass is also an influencing factor on the efficiency of the photocatalyst. In every photocatalytic reaction, there is an optimum amount of photocatalyst mass where the photocatalytic activity is reached to maximum values. If there is an increase in the amount of photocatalyst mass, the number of active sites on the catalyst surface increases which in turn produce an increased number of ROS [45] and as a result, the photocatalytic activity is increased because the activity is directly related to the formation of ROS. However, the general findings indicate that when the catalyst loading amounts are beyond the optimum amounts, the photocatalytic activities are unfavorable due to the decrease in the light penetration depth into the reacting solution and consequently diminishes the light scattering [46].

1.7.6. Type and concentration of pollutant

Another important factor that affects photocatalytic activity is the type of pollutants and its concentration in the reaction mixture [47]. Many published reports have addressed the photocatalytic activity under similar operating conditions with the same catalyst but variation in the preliminary concentration of pollutants in the reaction solution and as result the different times required to attain complete degradation [48]. For example, TiO_2 material exhibits different degradation percentages under similar reaction conditions with the use of different concentrations of Acid Orange 7 from 25 to 600 mg L^{-1} , and the observed results indicated that complete mineralization of Acid Orange 7 was achieved for the concentration of 25 to 100 mg L^{-1} and the degradation rate decreased at higher concentration (200-600 mg L^{-1}). A similar trend has been agreed upon by other published reports [49].

1.8. Limitations of photocatalysis

Photocatalysis has the following limitations that need attention of the researchers for improving photocatalysis efficiency.

- ❖ Interfacial charge transfer.
- ❖ Need to develop a suitable semiconductor photocatalyst.
- ❖ Adsorption of reactants on the catalyst surface.
- ❖ Light adsorption activity, band gap energy, and conduction band position of the photocatalyst.
- ❖ Stopping of electron-hole pair recombination rate or improved charge separation.

1.9. Basic requirements in choosing a photocatalyst

The perfect choice of a heterogeneous photocatalyst is guided by the following factors:

- Photocatalysts should be able to use in heterogeneous photocatalysis.
- The synthetic route of photocatalyst should be very simple and cost-effective.
- The photocatalyst should be stable before and after the photocatalytic reaction.
- It should be able to absorb light energy in a wide range of wavelengths from UV to the visible range.
- Charge separation of photocatalyst should be very high.
- Photocatalyst must have sufficient surface area for the availability of active sites.
- It should have high recycling activity.

1.10. A brief history of transition metal oxides

Generally, the transition metal oxides are composed of oxygen atoms that are attached to transition metals. They are commonly famous for their utilization in homogeneous and heterogeneous catalysis, photocatalysis, and photoelectrocatalysis. Transition metal oxides have good chemical and physical stability, optical properties, electrical properties, magnetic properties, and semiconductor properties. It has a wide variety in its surface structures which can affect the surface energy, chemical property, and catalytic efficiency. The relative acidity and basicity of the surface atoms of metal oxide are also influenced by the coordination of the metal cation and oxygen anion which also affect their catalytic properties. Metal oxide shows great conductive properties and response to electromagnetic radiations which makes it a useful candidate for many redox reactions, isotope exchange, and surface reactions.

The oxide materials can be categorized as fluorite (AO_2 or ABO_2), spinel (AB_2O_4), scheelites (ABO_4), perovskite (ABO_3), pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$), palmeirites ($\text{A}_3\text{B}_2\text{O}_8$), Ruddlesden–Popper oxides (A_2BO_4), etc. These oxides and their nanocomposites have very important catalytic applications towards photocatalysis for environmental remediation. We have mainly focused on novel transition metal based fluorite, perovskite, and spinel oxide systems because one of these oxides is a member of our synthesized nanocomposite systems.

1.10.1. Fluorite

It is a binary metal oxide system whose space group is $\text{Fm}\bar{3}\text{m}$ and having a general formula of AO_2 and ABO_2 , where A and B is a metal cation having the oxidation state of +4 or +2 and oxygen atoms acts as anions having the oxidation state of -2. The fluorite oxide structure contains oxygen atoms in simple cubic packing. The metal cations are occupying the center of cube, and oxygen atoms are coordinated in a tetrahedral fashion with the metal cations. Examples of AO_2 type cubic fluorite are ZrO_2 , CeO_2 , PrO_2 , etc and CuFeO_2 , CuCrO_2 , CuBO_2 , etc are the example of ABO_2 type fluorite.

1.10.2. Perovskite

The perovskite oxide material is an important class of functional oxide materials and formulated as ABO_3 ($\text{Pm}\bar{3}\text{m}$ space group) that exhibits a range of different stoichiometries and crystal structures. In the perovskite structure, the A-site cations whose oxidation state is +2 or +3 and exist in 12-fold coordination with oxygen atoms. On the other hand, the B-site cation exists in +4 or +3 oxidation state, and it is occupied in 6-fold coordination with oxygen

atoms. In this structural framework, A is a larger cation situated on the edge of the structure and B is a smaller cation located in the center of the octahedron. In the perovskite, the cationic radii of A and B are greater than 0.09 and 0.051 nm, respectively. Additionally, several elements of the periodic table can be adjusted at A and B sites to form a large number of perovskite materials. Due to the difference in cationic radii of A and B atoms, a lattice distortion occur which can change the structural symmetry to orthogonal, tetrahedral, monoclinic, rhombohedral, and triclinic structures. The photocatalytic properties, photo-excitation, and charge transfer can also be affected by these factors. Moreover, the compositional and symmetry change by the doping of metal, nonmetal, composite formation, cation vacancy, and oxygen vacancy can improve the band structure, optical property, adsorption activity, and photocatalytic efficiency of the perovskite materials. Therefore, the photocatalytic activity of perovskite can be tailored easily due to the availability of lattice sites.

1.10.3. Spinel

The spinel oxides are generally a group of ternary oxide which is formulated as AB_2O_4 , where A and B are both cation and their oxidation states are +2 and +3, respectively, whereas the oxidation state of oxygen is -2 which act as an anion. In the crystal structure of spinel oxide, cations are occupied in some or all of the octahedral and tetrahedral lattice sites and oxygen atoms are occupied in a cubic closed packed lattice site. The spinel oxide belongs to the $Fd3m$ space group. Depending on the crystal field stabilization energy (CFSE), the A^{2+} and B^{3+} cations are distributed in the octahedral (Oh) or tetrahedral (Td) lattice sites and based on the occupancy of Oh and Td sites, the spinel oxide is classified into three categories, namely, normal spinel, inverse spinel, and mixed spinel. In the normal spinel structure, all the A^{2+} and B^{3+} cations are occupied in the tetrahedral and octahedral sites, respectively and it can be represented as $A_{Td}^{2+}B_{Oh}^{3+}_2O_4$. $ZnFe_2O_4$ is an example of this type of spinel. In the inverse spinel, all the A^{2+} and half of B^{3+} cations are occupied in the octahedral site, and the rest half of B^{3+} cations are occupied in the tetrahedral site and it is represented as $[B^{3+}]_{Td}[A^{2+}B^{3+}]_{Oh}O_4$. Fe_3O_4 , $CoFe_2O_4$, $CuFe_2O_4$, $NiFe_2O_4$, etc. are the examples of this class of spinel. In the mixed spinel structure, both A^{2+} and B^{3+} metal cations are distributed in Td and Oh lattice sites. The structural formula of the mixed spinel is represented as $[A^{2+}_{1-d}B^{3+}_d]_{Td}[A^{2+}_dB^{3+}_{1-d}]_{Oh}O_4$, where d is the degree of inversion. $MnFe_2O_4$ is an example of this

type of spinel where $d = 0.2$ and its structural formula is $[\text{Mn}^{2+}_{0.8}\text{Fe}^{3+}_{0.2}]_{\text{Td}}[\text{Mn}^{2+}_{0.2}\text{Fe}^{3+}_{0.8}]_{\text{Oh}}\text{O}_4$.

Spinel oxide materials are classified into following groups

❖ Aluminium spinels (Aluminate):

MAl_2O_4 (M = Be, Ba, Mg, Mn, Fe, Co, Ni, Cu, Zn etc.)

❖ Iron spinels (Ferrite):

MFe_2O_4 (M = Mn, Fe, Co, Ni, Cu, Zn etc.)

❖ Chromium spinels (Chromite):

MCr_2O_4 (Mn, Fe, Co, Ni, Cu, Zn etc.)

❖ Others with spinel structure:

Coulsonite: FeV_2O_4 , Magnesiocoulsonite: MgV_2O_4 , Ringwoodite: $(\text{Mg, Fe})_2\text{SiO}_4$

Thus, there is a large variety of spinel oxide and perovskite oxide material. In this study, we have focused our attention only on the lanthanum nicolate (LaNiO_3) and chromite spinel especially for copper chromite (CuCr_2O_4); their structural properties, nanocomposite materials and interesting applications including photocatalysis are discussed in **section 1.15**.

1.11. Basic notion of nanocomposite

The nanocomposite system is a mixture of two or more semiconductor materials that are used for various applications in science and technology fields. In the nanocomposite system, the two phases of the pure materials form a heterojunction interface between them. This interface promotes charge separation through different kinds of charge transfer mechanisms to reduce the electron-hole pair recombination which increases the photocatalytic reaction rate of nanocomposite. Therefore, nanocomposite type photocatalyst is the benchmark of photocatalyst in the photocatalysis field which is supported by many previously published works [50-51].

1.11.1. Advantages of metal oxide based nanocomposite systems

Following advantages of metal oxide based nanocomposite systems contribute to ever increasing interest of the researchers in this fascinating area of photocatalysis:

- ❖ Metal oxide photocatalyst is very much suitable for heterogeneous catalysis.
- ❖ Metal oxide has high thermal stability and its crystal phases generally remain unchanged before and after photocatalytic reaction.

- ❖ These oxides have a very high light absorption activity within a wide range of wavelengths.
- ❖ The synthetic procedure of metal oxides is very simple, low cost, time-saving and suitable for large-scale synthesis.
- ❖ Metal oxide can easily form a tight contact with other semiconductor materials to generate a nanocomposite system.
- ❖ A large number of metal oxides with various types of band gaps are available from which it is easy to fabricate any type of nanocomposite photocatalyst.
- ❖ In the metal oxide-based nanocomposite system, electron-hole pair is separated via different kinds of charge transfer mechanisms like Type I, Type II, Type III, S-scheme, Z-scheme, and surface plasma resonance (discussed in details in section 1.11) so that the charge separation is significantly increased and this is the basic need for improving the photocatalytic activity. These photocatalytic mechanisms operate at the heterojunction of metal oxides which fully depend on the band edge positions (VBs and CBs) of the two partners.
- ❖ Metal oxide based nanocomposite type photocatalyst is the best alternative option of classical Fenton reagent. Furthermore, the Fenton reaction rate over the metal oxide based nanocomposite type photocatalyst was significantly improved by the light energy, and it is called photo Fenton reaction.
- ❖ The recycling activity of metal oxide based nanocomposite is higher than that of other catalysts.
- ❖ Metal oxide based nanocomposite photocatalysts is applicable to a broad range of photocatalysis fields.
- ❖ Finally, in the metal oxide based nanocomposite type photocatalyst, the major limitations of the photocatalysis like low charge separation, recycling performance, stability can be overcome and fulfill all the basic requirements of photocatalyst.

1.11.2. Metal and nonmetal doped metal oxide system

The recent research trends on photocatalysis indicated that the photocatalytic activity of metal oxide is improved by the doping of metal ions, nonmetal ions, or when both these two are doped into the metal oxide system [52]. In the major cases, doping of metal or nonmetal ions increases the charge separation due to the formation of oxygen or metal ion vacancy, changing of structure, morphology, surface properties, optical property, spin state,

and band gap energy, etc [53-54]. Generally, the doping of appropriate metal ions into an appropriate material can enhance photocatalytic performance. Many research reports explained the easy and short synthetic protocols for metal or nonmetal ions doped semiconductor nanomaterials which would be very useful for the improvement of visible light active photocatalysts and photovoltaic devices [55]. When transition metals like Cu, Co, Mn, V, and Fe are substituted for Zn in ZnO, materials with lower band gap (compared with pure ZnO (3.2 eV)) forms due to the spin-exchange interaction leading to their improved photocatalytic activity under visible light irradiation [56]. Co-doping in ZnO leads to surface oxygen vacancy and the material shows an improved methylene blue degradation activity under visible light irradiation [57]. When the surface of TiO₂ is doped with vanadium metal ion, the optical absorption edge of TiO₂ is shifted from UV to visible region and as expected improved photocatalytic activity is observed at a very low vanadium doping percentage. At a very high vanadium doping percentage, the excess vanadium ions cover the TiO₂ surface and facilitate the electron-hole pair recombination leading to lower photocatalytic activity [58]. Besides metal ion doping, photocatalysts doped with nonmetals like B, N, C, and S have also boosted the photocatalytic activity. Doping of nonmetals in TiO₂ increases the photocatalytic activity under visible light due to the synergetic effect [59]. Shifu et al. reported that the photocatalytic efficiency of N-doped ZnO material is higher than that of pure ZnO due to conductivity conversion and as a result higher activity under visible light irradiation [60]. The degradation of methylene blue and phenol dye by N and S-doped TiO₂ photocatalyst is significantly increased due to the formation of oxygen vacancies in the TiO₂ surface [61].

1.11.3. Versatility of nanocomposite materials

The application of the nanocomposite system is very vast because the nanocomposite system was already in use in a large number of research fields. So it is a suitable candidate to be used as a photocatalyst in various types of application due to its fulfillment of basic and advanced criteria of both photocatalysis and photocatalyst. According to the recent trends in photocatalysis, the nanocomposite system is a landmark of the photocatalyst. The applications of nanocomposite towards the photocatalysis field are huge, some of the important applications are as follows (i) wastewater treatment, (ii) CO₂ reduction, (iii) clean energy production, (iv) organic transformation reaction, (v) reforming reaction, (vi) urea oxidation, (vii) ammonia degradation, (viii) heavy metal detection and reduction, (ix) metal

ion sensing, (x) methane conversion, (xi) various photoelectrocatalytic applications like oxygen evolution, hydrogen evolution, alcohol oxidation, sensing, and so on [62-67].

1.11.4. Strategies of improving the photocatalytic activity

The current scenario of photocatalysis demands modifications of photocatalysts to achieve enhanced photocatalytic activity. A photocatalyst with low electron-hole pair recombination tendency shows high photocatalytic activity. The modification is carried out by the coupling of semiconductor material with other semiconductor materials of suitable band gap energy or metal ions or carbon-based polymers (i.e., different types of composite formation) or metal/nonmetal doping with the semiconductor materials [68]. Research trends indicate that composite materials which are formed by the combination of semiconductor oxide materials are the best modified photocatalyst candidates for improved photocatalytic activity. In these composite systems different types of semiconductor materials have the effect of diminishing the band gap that in turn improve the visible light absorption, charge separation as well as photocatalytic activity [50-51].

1.11.5. Literature survey of nanocomposite systems with special relevance to photocatalyst

The coupled materials of nanocomposite systems have different energy levels which play a leading role to improve the charge separation. The nanocomposite systems encompass a broad area with a large number of materials of which the most popular composite systems such as metal oxide/ metal ion, metal oxide/ metal oxide, metal oxide/ carbon-based polymer system, metal oxide/non-carbon based polymer, different phases of the same metal oxide (for example, anatase/rutile TiO_2 , α/β Bi_2O_3 , etc.) and metal oxides with different morphologies (for example, rod-like/ plate-like ZnO , plate-like/ sphere-like BiOBr , etc.) have been successfully synthesized and reported to show encouraging photocatalytic activity behavior [69-71]. Researchers have synthesized the composite systems which contain Au/TiO_2 , ZnO/CdO , Au/CeO_2 , $\text{g-C}_3\text{N}_4/\text{LaNiO}_3$, $\text{CuCr}_2\text{O}_4/\text{BiOBr}$, graphene oxide/ TiO_2 , PANI/ZnO , CeO_2/ZnO , $\text{BiVO}_4/\text{CeO}_2$ and many more [72-78]. The conjugated polymers like $\text{g-C}_3\text{N}_4$, graphene oxide, and PANI in the nanocomposite system act as electron mediators which can delay the electron-hole pair recombination and thereby increasing the photocatalytic activity [76]. When metal ions are used in the nanocomposite systems, the surface plasma resonance effect increases the charge separation as well as photocatalytic activity [79]. On the other

hand, in nanocomposite system of two metal oxides, the charge separation is increased due to the reduction of photoexcited electron-hole pair recombination rate via different charge transfer mechanisms such as Type I, Type II, Type III, Z-scheme, and S-scheme [80]. Cun et al. explained that the ZnO/SnO₂ nanocomposite system shows greater photocatalytic activity compared to pure ZnO and SnO₂ due to the higher charge separation in the ZnO/SnO₂ system via Type II mechanism [81].

1.12. Photocatalytic mechanisms for maximization of charge separation

The photocatalytic activity depends on many factors and the primary challenge for enhancing photocatalytic efficiency is to reduce the electron-hole pair recombination rate. The general trend indicates that pure semiconductor materials show lower photocatalytic activity, the main reason is their very high electron-hole recombination tendency. Progress in this area of research indicates that coupling of two or more semiconductor materials with a suitable band gap energy forming a heterojunction that can reduce the electron-hole pair recombination and so composite system formation may be the best option for photocatalyst modification. In the composite system, the electron-hole recombination is reduced via different kinds of pathways in the heterojunction called photocatalytic mechanism. These photocatalytic mechanisms are Type I, Type II, Type III, Z-scheme, S-scheme, and surface plasma resonance (SPR). These different kinds of mechanisms have a strong impact on the overall photocatalytic pathway and thus play a leading role in photocatalysis.

1.12.1. Type I mechanism

As shown in **Fig. 1.6 (a)**, Type I heterojunction contains two semiconductors where the first semiconductor 1 (Sem 1) has a highly negative CB and a highly positive VB potential values so that the CB and VB bands of the second semiconductor 2 (Sem 2) reside in between the first semiconductor. Generally, this type of heterojunction suffers from favorable photocatalysis due to the lower accumulation of photogenerated charges on the second semiconductor.

1.12.2. Type II mechanism

The schematic diagram of the photocatalytic mechanism of Type II heterojunction is presented in **Fig. 1.6 (b)**. It is a very common type of photocatalytic mechanism for charge separation. The electrons of both Sem 1 and Sem 2 are excited from the VB to the CB by the

treatment of light energy whereas holes are left on their VB. Depending on the band edge positions of VBs and CBs, the photoexcited electrons are transferred from semiconductors of higher CB to semiconductors of lower CB, and holes are shifted from semiconductors with lower VB to semiconductors with higher VB. In this way the rapid charge transfer on Type II heterojunction reduces the electron-hole recombination of photogenerated excitons, thereby enhancing the photocatalytic activity of photocatalyst. The optimum band edge positions of semiconductor in the Type II heterojunction provides efficient photogenerated electron-hole pairs.

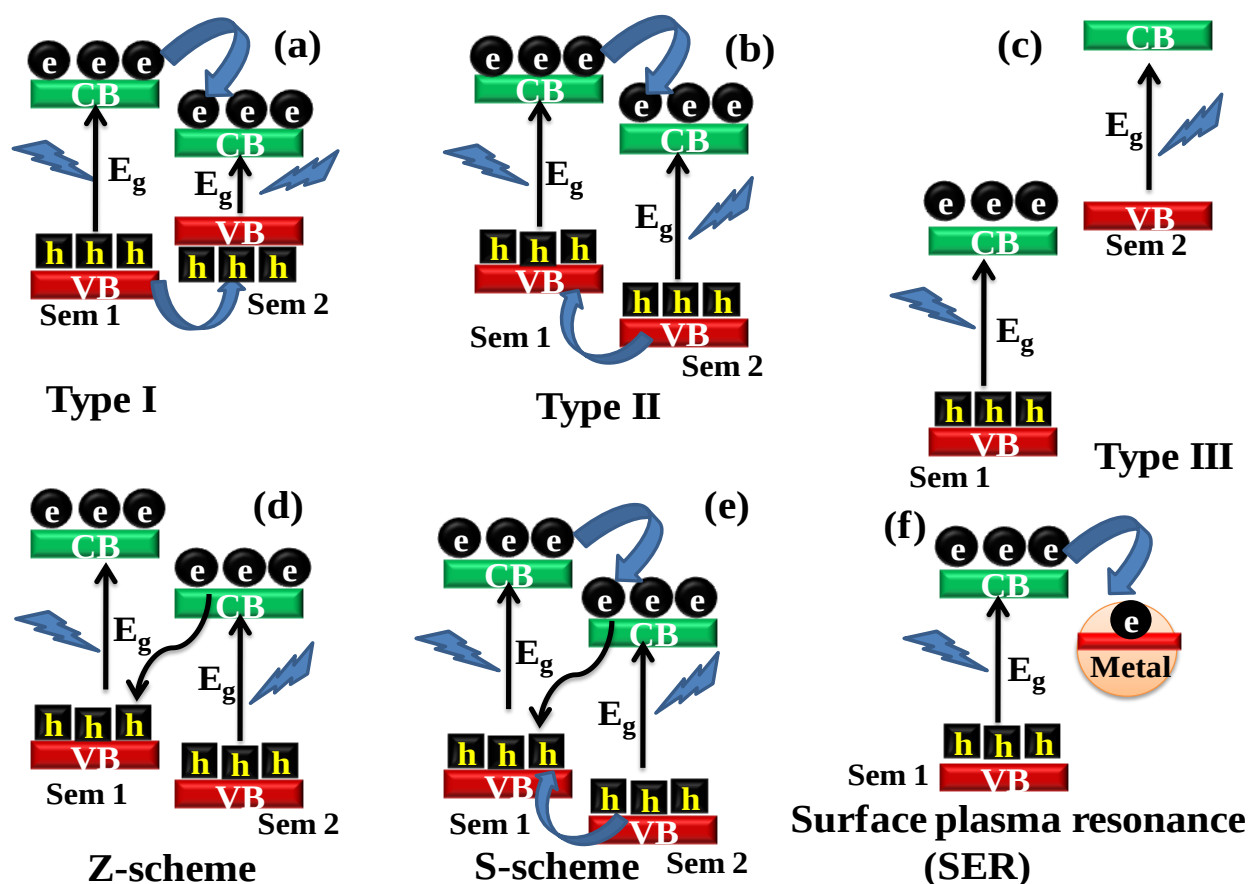


Fig. 1.6: Schematic diagram of charge transfer mechanism of six types of heterojunction in the composite systems: (a) Type I, (b) Type II, (c) Type III, (d) Z-scheme, (e) S-scheme, and (f) Surface plasma resonance.

1.12.3. Type III mechanism

Another photocatalytic mechanism for the enhanced photocatalytic reaction is the Type III heterojunction which is represented in **Fig. 1.6 (c)**, and it is generally a broken type

heterojunction. In type-III heterojunction, the difference between the VB and CB positions of the two semiconductors is very high in comparison to the conventional Type II heterojunction. The photogenerated electrons on the CB of Sem 1 combines with the holes on the VB of Sem 2. On the other hand, the photogenerated electrons on the CB of Sem 2 and the holes are lefts on the VB of Sem 1 participate respectively in the reduction reaction and oxidation reaction.

1.12.4. Z-scheme mechanism

The photocatalytic process via the Z-scheme mechanism shown in **Fig. 1.6 (d)** is associated with a high photocatalytic activity. In this mechanism, the electrons of both Sem 1 and Sem 2 are photoexcited from the VB to CB, and holes are left on their VB. Afterward, the photoexcited CB electrons of semiconductors with lower reducibility are transferred to the VB of other semiconductors, and photoexcited electrons of semiconductors with weak reduction tendency are recombined with the weak oxidizing holes of another semiconductor. Following this mechanistic pathway, the electrons with higher reducing capability and holes with higher oxidizing capability are retained. Generally, the Z-scheme photocatalyst is the combination of two semiconductors with close surface contact and the excitons transportation pathway is similar to the capital English letter “Z”. This type of photocatalyst has a high efficiency of electron-hole pairs and an optimized redox potential value. Furthermore, the formation of the internal electric field in the contact zone of two semiconductors is a favorable path for the electrons transportation which facilitates the recombination of electron-hole pairs with lower redox abilities and preserves the electron-hole pairs with higher redox abilities. It is well known that the internal electric field is generated due to the difference in the work function of semiconductors. The electrons are shifted from the semiconductor with a smaller work function to the semiconductor with a higher work function, so both the semiconductors are trying to balance their Fermi levels when they come into contact. Therefore, the one side that gives electrons and the other side that accepts electrons are charged positively and negatively, respectively and thus forming an internal electric field.

1.12.5. S-scheme mechanism

The S-scheme or Step-scheme mechanism is a new type of charge transfer route operated in the heterojunction structure of two semiconductor materials which was discovered by Xu et al. [82]. The composite type photocatalyst with S-scheme heterojunction

possesses an oxidation and a reduction photocatalytic system with a staggered band structure. The S-scheme mechanism is similar to the Type-II heterojunction mechanism, but with a different charge transfer pathway as shown in **Fig. 1.6 (e)**. According to the mechanism, when two semiconductor materials are in intimate contact with each other, the electrons in the lower CB semiconductor are spontaneously diffused to the higher CB semiconductor, creating the electron accumulation and electron depletion layer near the interfaces of two semiconductors, respectively. Thus in the interface, one side is negatively charged and another side is positively charged and an internal electric field directed from the positively charged side to the negatively charged side is formed. The band bending allows the photogenerated CB electrons of semiconductors with higher CB values and holes in the VB of another semiconductor at the heterojunction to be recombined. Therefore, the excess charge carrier is neutralized by recombination while the photogenerated electrons with higher reducing ability in the CB of semiconductor and the holes with higher oxidizing ability in the VB of another semiconductor are preserved to take part in the photocatalytic reaction. In this S-scheme mechanism, the higher redox capability and efficient charge separation are collectively achieved.

1.12.6. Surface plasma resonance (SPR) mechanism

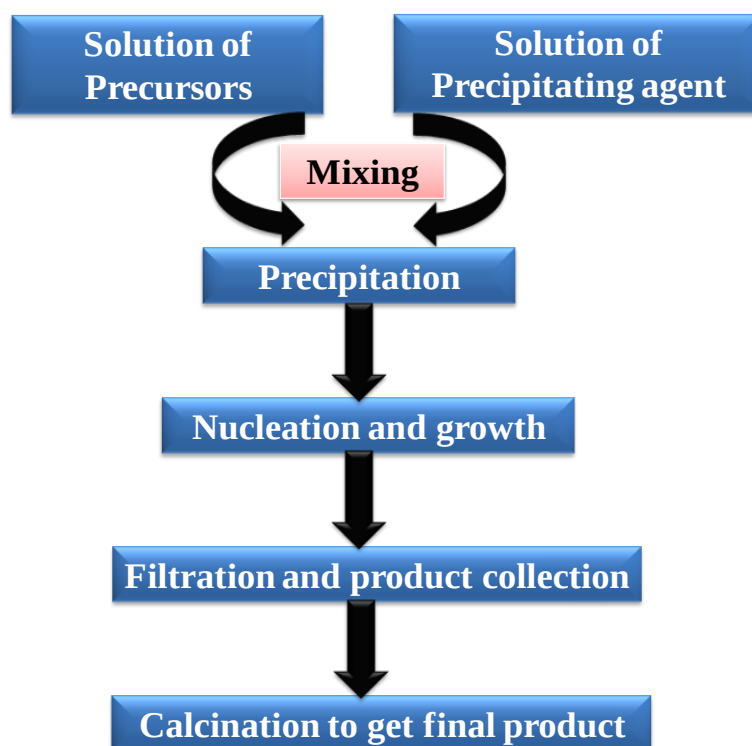
The schematic diagram of the photocatalytic mechanism for the charge transportation route in the Schottky heterojunction is presented in **Fig. 1.6 (f)**, and the mechanism is known as surface plasma resonance. The Schottky heterojunction is formed in the composite type photocatalyst when a metal ion is combined with a semiconductor material. When the photocatalyst is irradiated with the light source, a large number of photogenerated electrons are transferred from the VB of the semiconductor to its CB, whereas the holes are left on its VB and results in the formation of photogenerated electron-hole pairs. Afterward, the photogenerated electrons are transferred from the CB of semiconductor materials to the metal surface, and the reduction reaction takes place on the metal surface. The lower interface voltage and rectification characteristics of Schottky heterojunction can control the generation and flow of photogenerated electrons. These effects significantly promote their charge separation efficiency, thus improving the photocatalytic activity. In addition, the photocatalytic activities can improve by restrained electron-hole recombination by aligning their Fermi energy levels.

1.13. Synthesis of metal oxides and their nanocomposites

Metal oxide, mixed metal oxide, and especially the nanocomposite materials of these two are well accepted and a benchmark type photocatalyst in the applications of the vast field of visible light active photocatalysis. These fascinated outcomes motivate researchers to synthesize various types of new nanocomposite materials with a variety of compositions thus producing unique properties for environmental safety. Although the preparation methods of metal oxide, mixed metal oxide, and the nanocomposite materials are the same and these are sol-gel, co-precipitation, hydrothermal, solid state, precipitation via template, microwave irradiation, sonochemical, chemical vapor deposition, pulsed laser, plasma, soft chemical treatment, solution combustion synthesis (SCS), microemulsions, thermal decomposition, electrochemical, photochemical, gamma radiation and some others. The overall summaries of synthetic routes by which the materials of this work have been fabricated are discussed below.

1.13.1. Coprecipitation method

The coprecipitation method for the preparation of photocatalyst materials is one of the best and mostly used wet chemical methods (see **Scheme 1.1**). It is a very effective synthetic route for the synthesis of active photocatalyst materials including nanocomposite materials. This



Scheme 1.1: General synthetic route of coprecipitation method.

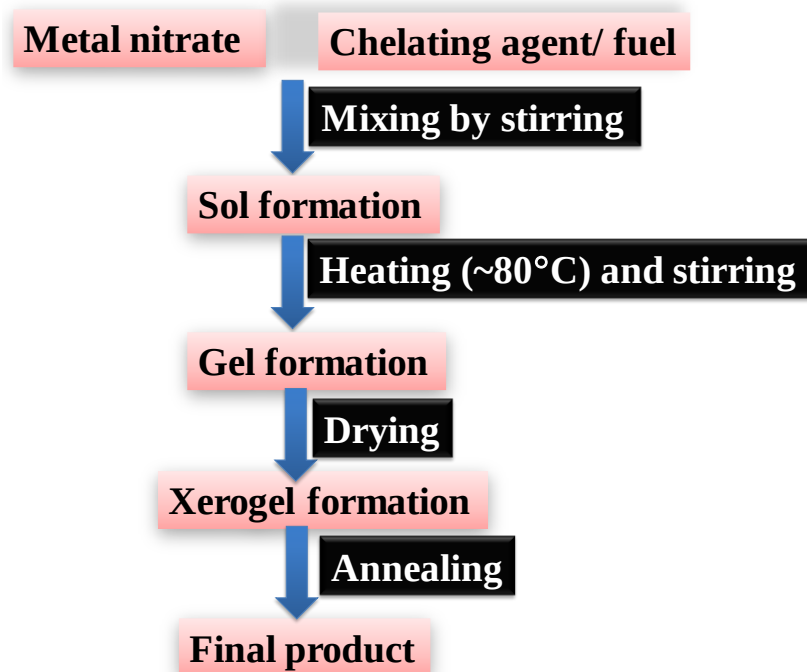
method is based on the bottom-up approach which is very simple, low cost, and time saving process. In surfactant assisted coprecipitation method, the surfactant is used as template and structure directing agent as well as element source and due to this reason the chemical consumption is less that is another important advantage of this synthetic method. Additionally, it is a very useful and a popular one for the synthesis of nanocomposite material because the parent phases can readily form a good heterojunctional contact.

In this typical procedure, the metal precursors (acetate or nitrate) are used to precipitate in an aqueous solution. The precipitation reactions are performed by their precursors or by adding an alkaline solution as precipitating agent. The following reaction steps are involved in the coprecipitation method: (i) the parent's precursors reach a supersaturating condition by mixing with ultrapure water, (ii) nucleation of precursors, (iii) growth of precursor nuclei, (iv) aggregation of nuclei, (v) separation of precipitate from aqueous solution followed by drying and finally (vi) calcination of dry precipitate to form the target materials.

1.13.2. Sol-gel method

The potential and conventional chemical method for the synthesis of photocatalyst materials is the sol-gel method because this approach yields materials of uniform size and specific morphology. It is predominantly used to prepare nanocomposite as well as its pure components. This synthetic method is very famous in the nanotechnology field due to its simplicity. In this approach, it is possible to switch the morphology and particle size by varying the pH, annealing temperature, and by adding a reaction modifier. In this typical method, hydrolysis and polycondensation of alkoxide-based metal precursors form an inorganic bridging network. The term “sol” means the solvated metal precursors forming via a colloidal type suspension. The produced sol is then converted into a polymeric network form in a liquid phase known as “gel”. In this synthetic technique, two different metal precursors and chelating agents are dissolved in an appropriate volume of ultrapure water to form a sol. In some cases metal precursors are chemically unstable in water in natural pH which causes agglomeration and in this case diluted acid is added to avoid this issue. During mild heating (~ 70 °C), water is slowly evaporated from the sol to form gel. After that, the obtained gel is dried at 80 °C to 100 °C for 2 to 4 h and finally, the collected solid mass products are ground and transferred into a muffle furnace for calcination at various

temperatures for various times to get the targeted material. A synthetic outline of the sol-gel technique is displayed in **Scheme 1.2**.

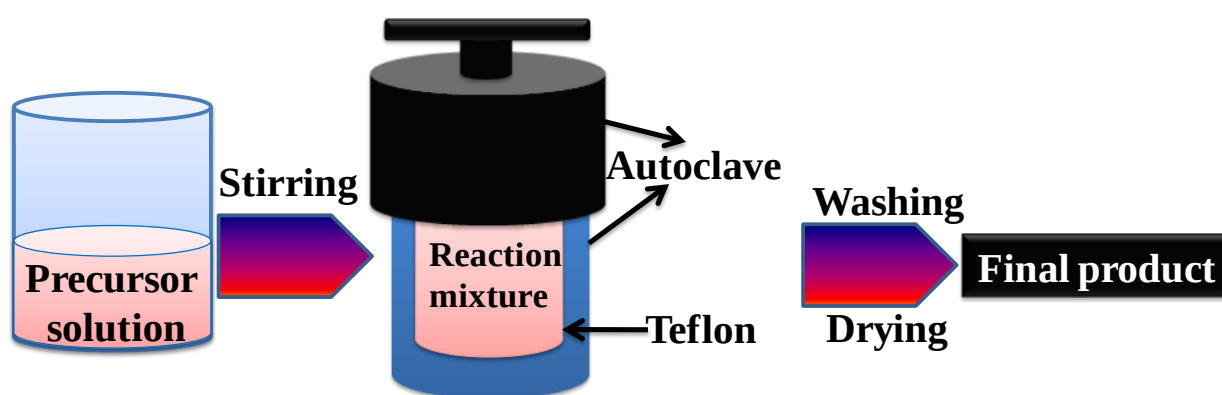


Scheme 1.2: General synthetic route of sol-gel method.

1.13.3. Hydrothermal method

The hydrothermal method is a chemical reaction that is performed under a certain condition of high temperature and high level of water pressure involved to synthesize the metal oxide, mixed metal oxide, and also their nanocomposite system. A specific reactor apparatus is used in this technique known as “autoclave” or “bomb” which is build up by good quality stainless steel and a beaker of Teflon material is used in the inner core of the “autoclave” to avoid any contamination (see **Scheme 1.3**). This type of synthetic technique requires water or any other non-explosive solvent to synthesize various types of photocatalyst materials with distinct morphologies and particle size. The hydrothermal reaction is generally performed at a temperature above 100 °C and very high pressure. In this typical procedure, the metal precursors with exact stoichiometry are fully dissolved in water or in other solvents and the mixture solution are stirred vigorously to get a homogenized solution. It is to be noted that when other solvents are used instead of water, then it is called the solvothermal method. The homogenized solution is then transferred to the Teflon-lined stainless steel autoclave. The autoclave is locked carefully and put into an oven maintained at a specific temperature for different times. After the completion of the reaction, the final product is washed with

water and alcohol several times and is dried finally in an oven to get the target material. The hydrothermal route has more benefits than the other wet chemical routes to prepare nanocomposite materials for various photocatalytic applications. The method has numerous advantages: (i) it is a cost-effective method and very famous for the synthesis of mixed metal oxide nanocomposite, (ii) it has rapid reaction kinetics, (iii) it leads to varieties of morphology, surface area, and particle size, (iv) it can be used to fabricate a new type of composite materials at nano region, (v) it is a pollutant-free synthetic route as the reaction is performed in a closed environment, (vi) it is associated with large scale production rate with high purity of materials, (vii) this synthetic route does not need any specific booster reagent, hazardous surfactant, and seed solution.



Scheme 1.3: General representation of hydrothermal reaction route.

1.13.4. Solid state mixing method

The solid state method is a simple chemical route for the synthesis of metal oxide based photocatalysts. It is the conventional and most commonly used method for the synthesis of various types of nanocomposite materials as well as their pure counterparts due to its simplicity. In this method, the pre-synthesized parent materials /components of the nanocomposite are physically mixed by grinding in a pestle mortar (~ 1 to 2 h is generally sufficient) followed by drying at low temperature (~80 to 100 °C) to synthesize the desired nanocomposite and then it is used directly for catalytic application purpose. However, the lower extent of mixing between the parent components reduced the catalytic activity of nanocomposite. To overcome these problems many authors have used a heat treatment or ultrasonication of the mixture of parent components in a suitable solvent such as alcohol, water, ether, etc. followed by evaporation of solvent at ~80 °C, and finally, the solid mass is calcined at 400-800 °C that leads to better mixing between the parent phases of the

nanocomposite. Note that, in the case of nanocomposite synthesis by heat treatment, the temperature does not exceed the original synthesis temperature of the parent materials because of possibility of formation of individual metal oxide.

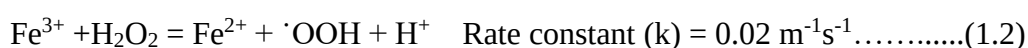
1.13.5. Sonochemical method

The sonochemical mixing method is comparatively a recent method used by many research groups (2006 onwards) and is considered as a new effective technique in nanoscience for the synthesis of nanocomposite materials. Among the various chemical methods, the sonochemical method follows a simple and straightforward approach. The major advantages of this process are: (1) increase in the effective surface areas as well as active sites, (2) formation of highly homogeneously distributed nanoparticles, (3) very simple, low cost and time saving process, (4) effective technique for the formation of nano-sized catalyst, and (5) very hard mixing is occur between the parent components in the nanocomposite system. In this typical procedure, the parent sources of the metal oxide components of the nanocomposite are first mixed with a suitable solvent followed by stirring with a magnetic stirrer. After that, the mixture solution is ultra-sonicated for the desired time followed by the slow addition of the precipitating agent. Then the collected product is dried and heated at the required temperature to get the final product. Since the nanocomposite formation depends on the extent of mixing that is connected with the dispersion, so, well dispersed parent materials can form an effective nanocomposite material by the sonochemical mixing process.

1.14. Homogeneous and heterogeneous Fenton reaction for wastewater treatment: Necessity for upgrading to heterogeneous photo Fenton reaction

In recent times, advanced oxidation processes have been widely studied and accepted as important tools for wastewater treatment and other environmental remediation. AOPs are very popular for the degradation of toxic and non-biodegradable chemicals like pesticides, aromatics compounds, pharmaceuticals, beauty products, personal care products, and heavy metals [83]. AOPs are an advanced and extraordinary technique for the permanent treatment of highly concentrated industrial wastewater and trace contaminants [84]. These AOPs are commonly performed in presence of different activators like UV light, transition metals, heat energy, microwave, and ultrasonication as well as different oxidants like hydrogen peroxide,

persulfate, and ozone [24, 83-84, 85]. Various types of ROS can be formed, including hydroxyl radicals, sulfate radicals, superoxide radicals, and others, which are very strong oxidants than the adopted pristine oxidants [26, 83-84]. Among all other AOPs, Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), Fenton like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$), and photo Fenton ($\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$) are well accepted techniques as they are environment friendly, low toxicity, simple and cost-free techniques that produces highly oxidative hydroxyl radicals [27, 86]. The overall concepts of Fenton's reaction follow the following reaction steps.



The formation rate of highly oxidative hydroxyl radicals is rapid because of the direct *in situ* reaction between ferrous ions and H_2O_2 (**equation (1.1)**). On the other hand, the produced ferric ions are reduced slowly by the H_2O_2 to regenerate ferrous ions (**equation (1.2)**). Since the homogeneous Fenton reaction is based on free iron metal ions dissolved in water, so it suffers from two major drawbacks. Firstly, it demands a lower pH range of nearly 3 to maintain ferrous and ferric ions solubility in the solution for showing optimum performance, so it consumes a higher volume of acid [87]. Secondly, severe iron sludge is produced due to the formation of insoluble solid iron hydroxide/ oxide, which works as a secondary pollutant [88]. To overcome these drawbacks of the Fenton process, a variety of research developments have been made including the application of chelating agents like EDTA (ethylenediamine tetraacetate), EDDS (ethylenediamine-N,N'-disuccinic acid), and NTA (nitrilotriacetic acid) to coordinate iron ions. These chelating agents of the iron complex maintain the iron ions soluble at neutral pH, the H_2O_2 activation and regeneration of ferrous ions [89], but these iron complex compounds can react with formed radicals that compete with the contaminants in wastewater. On the other side, some residual complexes (e.g. EDTA) are non-biodegradable. Furthermore, very low iron recycling and iron sludge formation at high pH is a largely unsolved part of the Fenton reaction. Therefore the research development on Fenton reaction is shifted from homogeneous Fenton reaction to heterogeneous Fenton reaction where insoluble solid Fe material is used as Fenton catalyst instead of soluble Fe salt. Research studies on heterogeneous Fenton reaction indicate that it is suitable for the treatment of highly concentrated wastewater under solution pH conditions, and solid catalyst can easily be separated from the reaction mixture via sedimentation, filtration, or magnetic separation [90]. The heterogeneous catalyst can be used for several

cycles with high catalytic efficiency. Transition metal based oxide materials are commonly used as catalyst for heterogeneous Fenton reaction in which the surface of solid catalyst activates H_2O_2 , and free iron ions play a little role. Therefore, for homogeneous Fenton reaction, the reaction takes place between free soluble iron ions and H_2O_2 , whereas the heterogeneous Fenton reaction highly depends on the solid surface of iron ions (Fe^{2+}) which interacts with H_2O_2 to generate ROS. In recent times, detailed studies for the developments of catalyst, reactions mechanism, and the various applications of heterogeneous Fenton reaction have been published on both synthetic iron containing catalysts and natural iron minerals including magnetite, ferrihydrite, ferrite, hematite, and so on [87-90]. In addition to natural minerals, zero-valent iron, porous materials, layered materials, activated carbons, immobilizing iron species with support materials, and supported iron catalyst have also attracted considerable interest [91]. However, heterogeneous Fenton reactions have some serious drawbacks including low reaction performances, low ferrous ion regeneration kinetics, high H_2O_2 consumptions, and iron sludge generation. These drawbacks are mainly due to the high dependency of heterogeneous Fenton reactions on the interface of the catalyst. In such surface reactions, the electron transfer rate for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ reaction cycle is regarded as the limiting step for H_2O_2 dissociation. So, one of the major challenges in heterogeneous Fenton reactions is developing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ reaction cycle of this limiting step to improve the dissociation rate of H_2O_2 as well as photocatalytic efficiency. To tackle these limitations, a variety of iron catalysts have been synthesized with a change of nominal composition, electronic properties, morphology, and structure to optimize the density and stability of active sites [92]. Furthermore, the application of some external fields such as electrical, electrochemical, ultrasonic, microwave, and light energy driven force to promote the Fenton reaction.

The heterogeneous Fenton reaction assisted with light energy (known as heterogeneous photo Fenton reaction) is very famous because it is economical and also highly promising to enhance the charge separation to boost the Fe^{2+} regeneration and H_2O_2 dissociation. This enhancement can be explained based on the photo assisted synergistic effects because the photo Fenton reaction is the combined effect of photocatalysis and interfacial Fenton reaction.

Several attempts such as electric field, UV/ visible light irradiation, microwave irradiation, and ultrasound treatment have been made to facilitate electron transfer in the catalyst surface [92]. This improved charge separation enhances the H_2O_2 activation

performance and thereby increasing the heterogeneous Fenton reaction efficiency. Currently the hot research topic in photocatalysis, especially for wastewater treatment where the effective utilization of UV light, solar light, or visible light is highly promising, is called the photo Fenton reaction which is energy saving and hence cost-effective. In the homogeneous photo Fenton process, the UV light reduces the ferric ions to ferrous ions and $\cdot\text{OH}$. The formed ferrous ions then readily react with H_2O_2 to form more $\cdot\text{OH}$. In the heterogeneous photo Fenton process, various iron materials like iron ions, iron clusters, iron hydroxides, iron sulfides, and iron oxides can act as active sites for H_2O_2 activation [93]. The photoexcited electrons accumulated in the catalyst surfaces are transferred to the bulk phase of the catalyst to accelerate the formation of the ferrous ions. Therefore, light energy plays a key role in promoting ferric/ ferrous ions circulation/ cycling. Although most of the iron based materials are semiconductor types with a narrow band gap that can respond to visible light, unfortunately, ferric/ ferrous ions circulation rate is very slow due to the extremely fast electron hole recombination which decreases the heterogeneous photo Fenton activity of catalyst [93]. So, it is highly desirable to search for effective strategies to increase the charge separation by reducing the lifetime of electrons at an excited state. To overcome this limitation, the fabrication of well dispersed iron species on suitable support of photo or non-photosensitive materials is regarded as a promising catalyst. More and more focus is drawn on the construction of composite / hybrid materials by the combination of iron material with other semiconductors to build up heterogeneous photo Fenton systems. On the other hand, the research focus is also drawn towards Fenton like materials and composite of Fenton like materials to improve the photocatalytic activity for wastewater treatment. Fenton like materials are those materials other than Fe^{2+} ions which show Fenton type reaction with H_2O_2 activation to generate $\cdot\text{OH}$. The examples of Fenton like materials contain the following metal ion pairs, $\text{Cu}^{2+}/\text{Cu}^+$, $\text{Ce}^{4+}/\text{Ce}^{3+}$, $\text{Ti}^{4+}/\text{Ti}^{3+}$, etc [94-95]. Heterogeneous photo Fenton or photo Fenton like system plays dual roles of photocatalysis and surface heterogeneous Fenton catalysis. It is noted that in some particular photo Fenton/ Fenton like systems, the H_2O_2 can be generated in-situ in presence of light energy. In this special type of reaction, the photogenerated electrons and holes react with dissolved oxygen or water to produce H_2O_2 [96-97], and thus lowering the H_2O_2 consumption or avoid the necessity of adding extra H_2O_2 in the reaction medium. The photo Fenton activity of a composite materials based Fenton catalyst or Fenton like catalyst, which is the upgradation of Fenton catalyst mainly depends on two predominating factors. The first factor is the perfect interfacial contact of component

materials of the composite system which improves the charge separation as well as preventing metal ion leaching. The second factor is the dispersive nature of materials which increases the availability and accessibility of catalyst active sites.

1.15. Present status of CuCr_2O_4 (CCO), LaNiO_3 (LNO) and their nanocomposite materials in photocatalysis

Copper chromate is an important spinel material and a p-type semiconductor photocatalyst. It shows very high visible light activity due to its lower band gap energy of nearly 1.4 eV [98]. Spinel CCO is a versatile photocatalyst because of its structural stability, physical, chemical properties, thermal stability, and easy synthetic methodology. The application of CCO is growing very vast including hydrogenation [99], dehydrogenation [100], oxidation [101], hydrogen production [102], reforming [103], organic transformation [104], photocatalytic pollutants degradation [105-106], Fenton like reaction [107]. Surprisingly, the photocatalytic activity of CCO is not satisfactory when compared with the recent trends of photocatalysis due to its very high electron-hole pair recombination [105-107]. Therefore, the photocatalysis areas of CCO are shifted towards its composite system and it is seen that the photocatalytic activity of CCO is tremendously increased in composite form [75]. Several reports related to CCO composite materials like $\text{BiVO}_4/\text{CuCr}_2\text{O}_4$ [98], $\text{CuO}/\text{CuCr}_2\text{O}_4$ [108], $\text{CeO}_2/\text{CuCr}_2\text{O}_4$ [94], $\text{BiOBr}/\text{CuCr}_2\text{O}_4$ [75], $\text{TiO}_2/\text{CuCr}_2\text{O}_4$ [109], $\text{g-C}_3\text{N}_4/\text{CuCr}_2\text{O}_4$ [110], $\text{SnO}_2/\text{CuCr}_2\text{O}_4$ [111], $\text{rGO}/\text{CuCr}_2\text{O}_4$ [112], $\text{CaFe-LDO}/\text{CuCr}_2\text{O}_4$ [113], and many more have been published where the improved photocatalytic activity is mainly due to high charge separation in the composite system. These composite systems are applied to various photocatalytic applications like different kinds of organic pollutants degradation, hydrogen and oxygen evolution, clean energy production, and other photocatalytic applications.

Perovskite oxides have drawn more attention as versatile photocatalyst material to the researchers because this system has extraordinary structural stability [114]. Among the large number of perovskite oxides, lanthanum nickelate (LaNiO_3) is a very important one due to its unique structural features, high thermal stability, excellent electronic as well as ionic conductivity and low cost and easy to synthesize material. In this perovskite, +3 oxidation state of Ni and oxygen vacancy play key role for its higher reactivity [115]. Likewise CCO, LNO is a p-type semiconductor material with band gap energy of nearly 2.1 eV, and because

of its lower band gap, there is significant interest in using it as a visible light active photocatalyst. The photocatalytic activity of this perovskite is unsatisfactory like CCO with respect to recent view of photocatalyst and photocatalysis research due to lower charge separation, so it needs modification [116]. It has been proved that the composite system of LNO is the best modification that gives very much satisfactory outcomes in terms of its photocatalytic activity. Literature survey indicates that its composite materials are successfully used as highly active photocatalyst for different field of photocatalysis applications in presence of visible light due to its suitable band gap and excellent electronic properties [117]. Many reports on LaNiO₃-based composite system such as g-C₃N₄/LaNiO₃ [117], TiO₂/LaNiO₃ [118], SnS₂/LaNiO₃ [119], graphene oxide/LaNiO₃ [120], Co(OH)₂/LaNiO₃ [121], MoS₂/LaNiO₃ [122], ZnIn₂S₄/LaNiO₃ [123], Ni₃C/LaNiO₃ [124], AgBr/C₃N₄/LaNiO₃ [125] etc, have been applied in varieties of photocatalytic applications.

Whole of this research work is based on binary nanocomposite materials for photocatalytic applications where one of the components is either CCO or LNO. Such a choice stems from the following advantages of CCO and LNO.

- CCO and LNO are very attractive for their unique physical and chemical properties.
- Pure as well as their respective nanocomposite materials can be synthesized by low cost and time-saving easy synthetic routes with the provision of large-scale synthesis.
- The thermal stability of these pure materials is high and hence they can maintain their structural stability in the nanocomposite system.
- The significantly higher photocatalytic efficiency of CCO or LNO based nanocomposite materials are due to higher charge separation in their nanocomposite system.
- CCO and LNO-based nanocomposite materials are easily separable (via magnetic or simple washing) from the photocatalytic reaction mixture and can be applied for recycling test with very high activity.
- The nanocomposites as well as the pure components have very high visible light absorption activity due to the smaller band gap energy of CCO and LNO.
- CCO or LNO related nanocomposite materials are active in environment-friendly visible light sources such as domestic LED light and sunlight for photocatalytic application.
- The CCO or LNO related nanocomposite systems show very high recycling performance.

- CCO related nanocomposite materials can be used in visible LED light assisted photo Fenton like reaction.
- While few reports on the nanocomposite system of these materials in photocatalysis purpose have already been published in the open literature, there are no reports on visible light assisted photo Fenton like reaction of their nanocomposites raising hope for research on the synthesis of novel nanocomposite materials with promising photocatalytic activity behavior.

1.16. Objective and scope of the present investigation

From the above discussion, it is evident that there is a huge opportunity in the area of synthesis and development of nanocomposite systems based on two or more semiconductors materials including metal oxide, metal sulfide, etc. and carbon or nitrogen based polymeric material. These synthesized materials are promising candidates for use as visible light active photocatalysts for various photocatalytic applications such as pollutants degradation, Fenton like reaction, photochemical reactions for synthesis of valuable chemicals, various photooxidation and photoreduction reactions, bacteria destruction, metal ions detection, sensing, and so on.

With the increasing pace of urbanization along with the associated growth of various types of industries leading to exhaustive use of industrial products, environment pollution has reached at an alarming level. Our water resources have been seriously affected by the contamination of pollutants from industrial wastewater and man-made activities. Pollutants are various classes of color compounds such as pigments, dyes, etc. These pollutants should be degraded to save our water resources. So, pollutants degradation is a promising research topic. Degradation of these pollutants via photocatalysis is a promising technique because of its simplicity, high performance, eco-friendly nature, and a time-saving technique. In order to meet the criteria, a highly active photocatalyst is required which should have enough physical and chemical stability, environmentally friendly, low cost, easy synthetic route, etc. From this point of view, metal oxide based nanocomposite photocatalyst materials are projected as the best choice.

There are many advantages of metal oxide based nanocomposite materials in photocatalysis: (i) in the nanocomposite system both the component metal oxides play an individual role for enhancement of photocatalytic efficiency and their crystal phases remain the same after photocatalytic reaction, and (ii) physico-chemical properties of parent metal

oxides are improved in their composite system. (iii) it is easily separated from the reaction mixture by simple filtration, sedimentation, washing, or drying method, (iv) it shows very high recycling activity, (v) its photocatalytic efficiency as well as charge separations is very promising,

In view of this present state of photocatalysis and ways to contribute further in the development of the field, our present research is focused on the synthesis of metal oxide based nanocomposite systems via different kind of synthetic approaches such as sol-gel, coprecipitation, surfactant-assisted coprecipitation, hydrothermal, thermal polymerization, and solid-state mixing methods. All these synthesized materials have been characterized thoroughly by various techniques like powder X-ray diffraction (PXRD), BET surface area, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), photocurrent, and photoluminescence spectroscopy (PL). The photocatalytic activity of photocatalyst was tested for the degradation of azo dyes like methylene blue (MB), rhodamine-B (RhB), methyl orange (MO); reactive dyes like reactive black 5 (RB5), reactive blue (RB); and antibiotics like tetracycline hydrochloride (TC-HCl) and norfloxacin (NORF). Domestic visible LED light and natural sunlight are used as eco-friendly light sources for photocatalytic experiments of pollutants degradation. The photocatalysts have also been used for the photoelectrochemical oxygen evolution reaction (OER) under visible LED light irradiation.

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Chapter 2

Synthetic routes, materials, characterization techniques and photocatalytic activity test

Chapter abstract

This chapter focuses on the synthetic routes of preparing pure oxide and nanocomposite materials with the anticipation to act as active photocatalyst. The sol-gel method, coprecipitation method, solid state mixing method, sonochemical method and hydrothermal method are extensively used in studies embedded in this thesis. Numerous modern instrumental techniques like PXRD, FESEM, TEM, HRTEM, EDX, elemental mapping, XPS, UV-Vis DRS, photoluminescence spectroscopy, photocurrent, and Raman spectroscopy that are used to characterize the various physical and chemical properties of the projected synthesized photocatalyst materials are elaborated in detail. The heterogeneous photoreactor setup and photocatalytic reaction procedure and analysis are discussed subsequently. Furthermore, the radical trapping and fluorescence probe methods for reactive species detection as well as recycling activity test are discussed in the end of this chapter.

2.1. Introduction

It is always a very challenging task for researchers to fabricate a highly efficient heterogeneous catalyst material for the technology application to protect our environment [1]. The applications of these catalyst materials are also very important for the various industrial viewpoints [2]. Therefore, the primary requirements of these catalyst materials are: (i) high catalytic activity, (ii) simple and short time of preparation, and (iii) it must be cost effective. The secondary requirements are the properties of the catalyst material that includes the surface area, surface metal oxidation state, particle size, optical property, charge transfer property, chemical composition, chemical stoichiometry, physical and chemical stability, active phase stability, surface defect, structural defect, and surface morphology. So, the construction and synthesis protocol play a critical role to control all the segments of the primary and the secondary requirements of the catalyst materials. The main objective is to improve the electric, optical, charge transfer, and photocatalytic activity of various classes of novel nanocomposite material. In recent times, researchers have used different types of simple and cost-effective techniques to fabricate various active nanocomposite type photocatalyst materials [3]. The nanocomposite materials have been synthesized by coprecipitation method [4], surfactant-assisted coprecipitation method [5], hydrothermal/solvothermal method [6], sol-gel method [7], microemulsion method [8], solid

state method [9], freeze-drying method [10], combustion method [11], and sonochemical method [12].

Furthermore, the detailed characterizations of the synthesized catalyst materials are also an important part of material science. Without any characterization, the research progress of catalyst, as well as catalysis in the application of science and technology cannot be made meaningful. Therefore, the right characterization tools make the right strategy for the construction of highly active catalyst materials. Therefore, sample characterization is an important tool that connects the actual structure and physical properties of synthesized materials with their catalytic activity. Furthermore, it helps better designing or modification for the synthesis of highly active nanocomposite materials for the targeted catalytic application.

This chapter discusses the different synthetic approaches adopted in this doctoral research to prepare the photoactive nanocomposite materials as well as their pure components followed by the details of several sophisticated instrumental techniques used for their characterization. The photocatalytic reactor set up and photocatalysis procedure for applications such as photocatalytic dye and antibiotic pollutants degradation, photo and dark Fenton like reaction for wastewater treatment, electrocatalytic oxygen evolution reaction under visible light as well as dark condition, and also sunlight assisted photocatalytic test are elaborated afterwards.

2.2. Chemicals

Analytical grade chemicals $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ceric ammonium nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$), bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), ammonium metavanadate (NH_4VO_3), titanium isopropoxide (TTIP), cetyltrimethylammonium bromide (CTAB), acetic acid, citric acid (CA), tartaric acid (TA), melamine, reactive black-5 (RB5), methylene blue (MB), rhodamine B (RhB), methyl orange (MO), tetracycline hydrochloride (TC-HCl), norfloxacin (NORF), benzoquinone (BQ), isopropyl alcohol (IPA), ethylenediaminetetraacetic acid disodium salt dihydrate ($\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$), coumarin ($\text{C}_9\text{H}_6\text{O}_2$), silver nitrate (AgNO_3), and hydrogen peroxide were purchased from Sigma-Aldrich, Merck and SD Fine and were used without any further purification. Ultrapure water (Milli-Q) and double distilled water were used as solvent.

2.3. Preparation of nanocomposite photocatalysts

There are various types of preparation methods for the synthesis of photocatalyst nanomaterials as discussed in **Chapter 1**. Details about the preparation of pure vis-à-vis nanocomposite photoactive materials of this study are discussed below

2.3.1. Synthesis of CuCr_2O_4 (CCO)

Synthesis of CuCr_2O_4 was done by sol-gel combustion process in which tartaric acid served the purposes of both a chelating agent and a fuel by maintaining the molar ratio of metal nitrate salts and tartaric acid at $\text{Cu} : \text{Cr} : \text{TA} = 1 : 2 : 2$. Typically, 0.9057 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 3 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were homogenized thoroughly in 80 mL of ultrapure water by stirring for about 15 min. This was followed by the slow addition of 3.3755 g of TA under continuous stirring and under hot condition ($\sim 80^\circ\text{C}$) in order to form a spongy type mass. The crude mass collected in the end was ground thoroughly and then calcined in static air at 700°C for 4 h to get the target oxide material CCO.

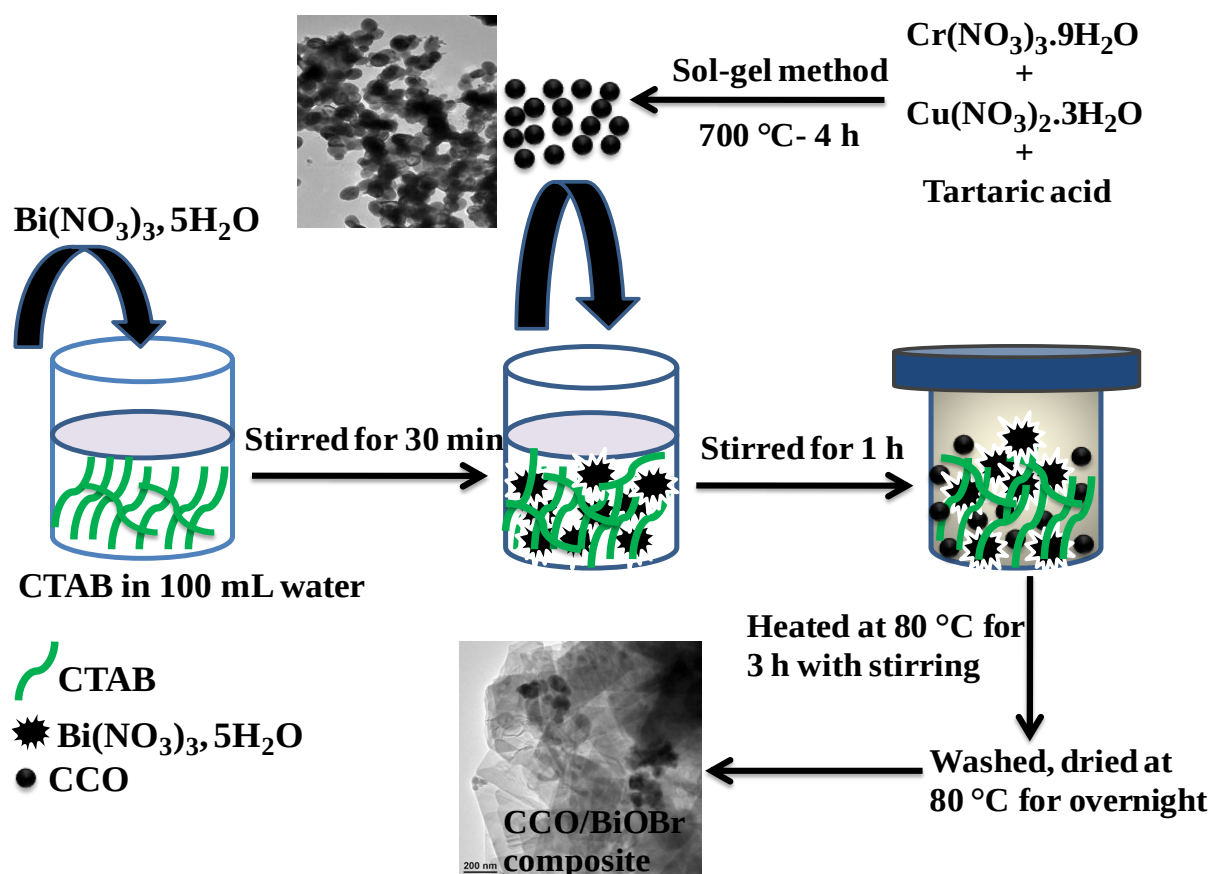
2.3.2. Synthesis of LaNiO_3 (LNO)

The nano-sized LNO was synthesized by citrate sol-gel method reported by Zhong et al. [13]. In brief, 2 g of $\text{La}(\text{NO}_3)_3$ and 1.343 g of $\text{Ni}(\text{NO}_3)_3$, corresponding to 1:1 molar ratio were at first dissolved in 100 mL of ultrapure (Milli-Q) water with continuous stirring (RPM ~ 400) by a magnetic stirrer (REMI, India). After 15 min of stirring, 3.55 g of citric acid (metal nitrate : CA ratio of 1:4) was added and the resulting solution was kept under stirring condition at $\sim 80^\circ\text{C}$ for the formation of a green colored gel. The gel is subsequently heated to get black spongy type mass, which was collected and crushed in a mortar to get a black powder. The black powder was initially heated at 500°C for 3 h followed by final calcination at 700°C for 3 h to get LNO nanoparticles.

2.3.3. Synthesis of CCO/BiOBr nanocomposite

The CCO/BiOBr composite materials were synthesized by a facile single pot precipitation method for BiOBr in presence of previously synthesized CCO as shown in **Scheme 2.1**. We have used the surfactant CTAB which acts both as a template and as the Br source. In a typical synthesis, 1.2 g of CTAB was initially dissolved in 100 mL ultrapure water taken in a 250 mL beaker followed by the addition of 1.6 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and the

whole mixture was stirred for 30 min. Different amounts of CCO (0.05 g, 0.1 g, 0.2 g and 0.3 g) dispersed in 30 mL ultrapure water by ultrasonication for 15 min in a 100 mL beaker were then added slowly to the above mixture under constant stirring. The resulting mixture was then covered with a petri dish and stirred continuously under heating at 80 °C for another 3 h. After cooling to the room temperature, the final product was centrifuged (8000 rpm for 10 min) and washed with ultrapure water and ethanol for three times followed by drying at 80 °C for overnight. The composite samples of CCO/BiOBr obtained so and containing 0.05 g, 0.1 g, 0.2 g and 0.3 g of CCO per g of BiOBr are henceforth denoted as 5%CCO/BiOBr, 10%CCO/BiOBr, 20%CCO/BiOBr and 30%CCO/BiOBr, respectively. For comparison, pure BiOBr was synthesized via the same procedure without adding CCO.

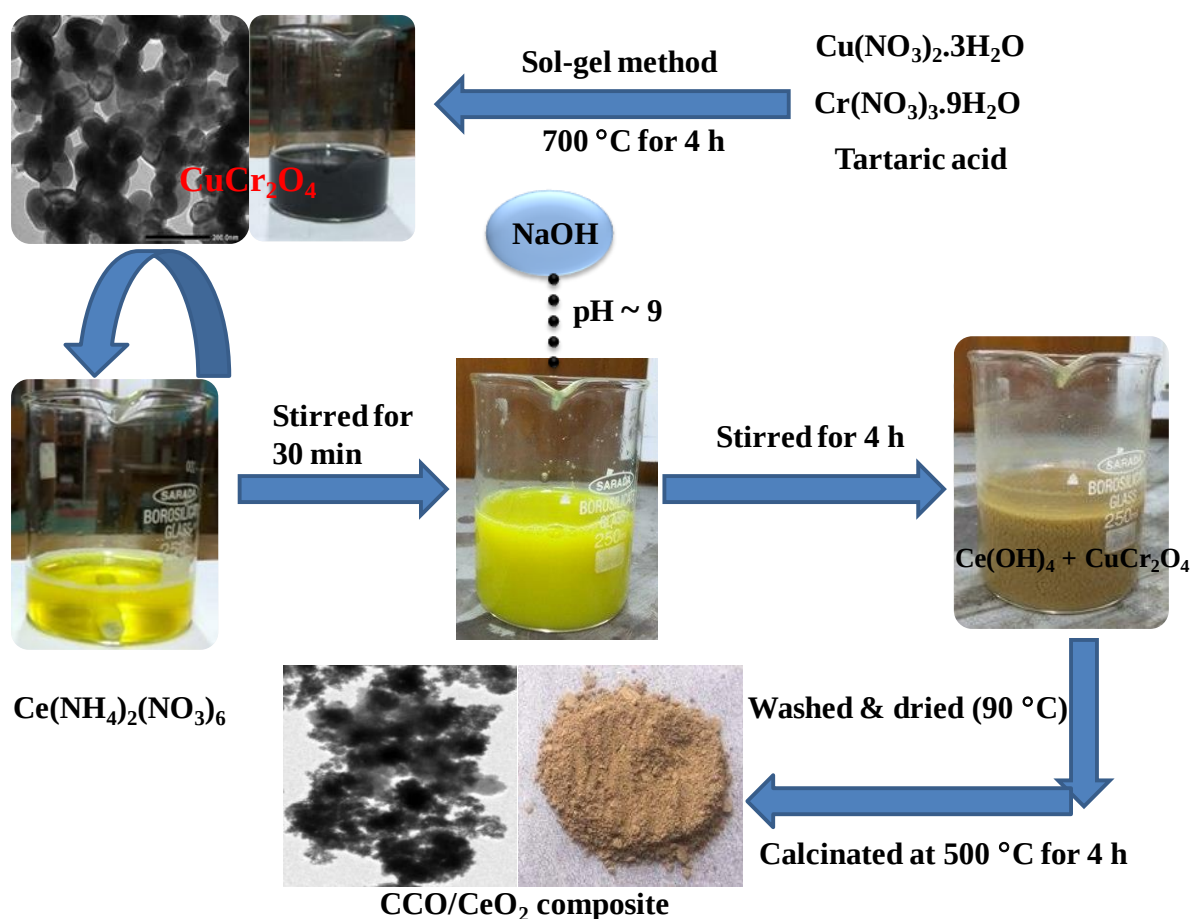


Scheme 2.1. Synthetic diagram showing the preparation of CCO/BiOBr composite.

2.3.4. Synthesis of CCO/CeO₂ nanocomposite

Scheme 2.2 presents the synthesis procedure of CCO/CeO₂ nanocomposite. In a typical procedure, 3.21 g of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ was dissolved in 50 mL of Milli-Q water in a

beaker placed on a magnetic stirrer and then 50 mL dispersed solution (by ~ 5 min ultrasonication) of 0.1 g of pre-synthesized CCO was added slowly to it. The stirring was continued for 30 min followed by the addition of 3 N NaOH solution to adjust the pH of the resulting solution at ~ 9. The reaction mixture was left under stirring condition for ~ 4 h. It was then allowed to settle and the precipitate obtained so was centrifuged and washed with Milli-Q water and isopropanol for three times each and then dried at 90 °C for overnight. Finally, the dry precipitate was crushed to powder form and calcined subsequently at 500 °C for 4 h in air to get 10%CCO/CeO₂ (0.1 g of CCO with 1 g of CeO₂ formed on calcination) nanocomposite. The 5%CCO/CeO₂ and 20%CCO/CeO₂ composites were also synthesized similarly by adding 50 mL dispersed solution of 0.05 g and 0.2 g CCO, respectively in the synthesis procedure. For comparison, pure CeO₂ was synthesized following the same procedure without adding CCO.



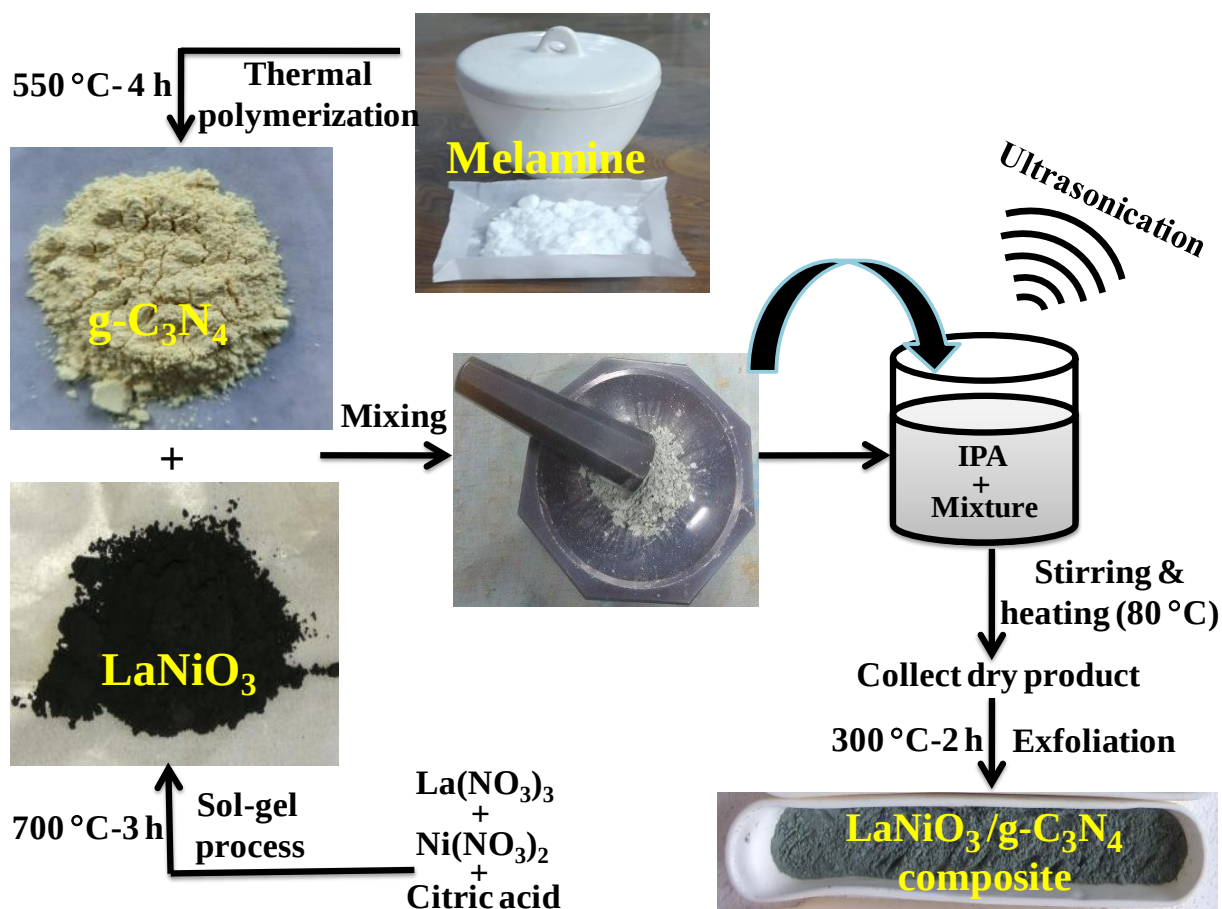
Scheme 2.2. Schematic representation of the synthesis procedure of CCO/CeO₂ nanocomposite.

2.3.5. Thermal polymerization method for synthesis of g-C₃N₄ (g-CN)

The graphitic carbon nitride was synthesized by thermal polymerization of melamine [14]. In a typical preparation, 5 g of melamine was placed in a silica crucible with a lid and heated at ~ 550 °C in a muffle furnace for 4 h and after completion of polymerization reaction the yellow solid product is crushed into fine powder in a pestle mortar to get the g-CN material. The g-CN is also synthesized from urea following the same procedure.

2.3.6. Synthesis of LNO/g-CN nanocomposite

LNO/g-CN photocatalyst was synthesized by simple physical mixing of the two components by mass followed by calcination as shown in **Scheme 2.3**. At first, 1 g of previously synthesized g-CN and different masses of LNO (0, 0.1, 0.5, 1, and 1.5 g) that leads to LNO/g-CN mass percentages (with respect to g-CN content) in the corresponding nanocomposites of 0%, 10%, 50%, 100%, 150% LNO, respectively were mixed by grinding in a mortar for 30 min. The mixture was then transferred to a beaker containing 100 mL of

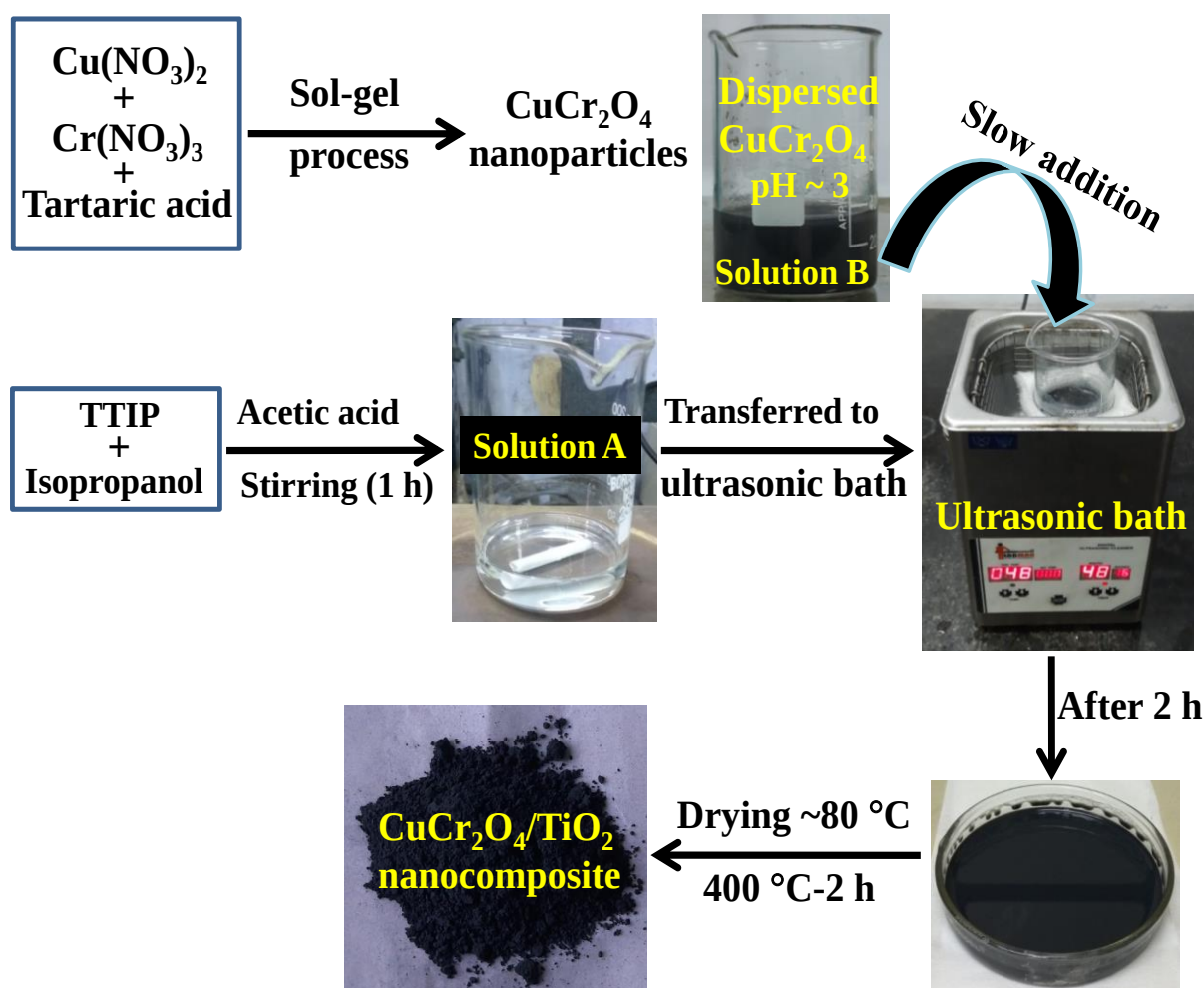


Scheme 2.3. Synthesis protocol of LNO/g-CN nanocomposite.

isopropanol, exposed to ultrasound treatment for 10 min and the whole contents were stirred at 80 °C to evaporate isopropyl alcohol. The residue formed was collected and heated at 300 °C for 2 h under air to get x% LNO/g-CN nanocomposite (x= 0%, 10%, 50%, 100% and 150%).

2.3.7. Synthesis of CCO/TiO₂ nanocomposite

The typical synthesis protocol of CCO/TiO₂ nanocomposite is shown schematically in **Scheme 2.4**. In the first step of nanocomposite synthesis, 3 mL of TTIP was homogenized in 80 mL of isopropanol in a beaker and then 1 mL of acetic acid was added under stirring condition (rpm ~400). The mixture solution was left under stirring for 1 h and was marked as solution A. In a separate beaker, 0.05 g of previously synthesized CCO nanoparticles was dispersed well in 50 mL ultrapure water by sonication for 30 min and then the pH of the solution was adjusted at



Scheme 2.4. Schematic diagram of the synthetic protocol followed for the preparation of CCO/TiO₂ nanocomposite.

about 3 by conc. HNO_3 addition and the resulting solution was marked as solution B. Solution A was subsequently placed under constant sonication in an ultrasonic bath and then solution B was added slowly drop by drop to it. After two hours of ultra-sonication, the total solution mixture was collected and dried in a hot air oven at $80\text{ }^\circ\text{C}$ for overnight. Finally, the black colored dry mass was calcined at $400\text{ }^\circ\text{C}$ for 2 h to get 6.25%CCO/ TiO_2 nanocomposite. The other samples, namely 12.5%CCO/ TiO_2 , 50%CCO/ TiO_2 , 100%CCO/ TiO_2 and 200%CCO/ TiO_2 nanocomposite materials were prepared similarly by adding 0.1 g, 0.4 g, 0.8 g and 1.6 g of CCO nanoparticles, respectively in the synthesis process. The pure TiO_2 was synthesized by a similar method of nanocomposite synthesis without adding CCO nanoparticles.

2.3.8. Synthesis of CCO/ BiVO_4 (CCO/BVO) nanocomposite

In the typical synthetic procedure of CCO/BVO nanocomposite synthesis, 1.9045 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 50 mL ultra pure water and after stirring for 15 min, 0.460 g NH_4VO_3 was added to it. Then dispersed solution of 0.1 g pre-synthesized CCO in 30 mL ultra pure water was added slowly to the whole mixture followed by constant stirring for 1 h. After stirring, whole mixture solution was transferred to a 100 mL Teflon lined autoclave. Finally, the autoclave was kept in a hydrothermal oven and heated at $180\text{ }^\circ\text{C}$ for 12 h. After completion of hydrothermal reaction, product was collected and washed with water/ethanol followed by drying for overnight at $80\text{ }^\circ\text{C}$ to get CCO/BVO nanocomposite in which CCO: BVO mole ratio is 0.1:0.9 and named as 10%CCO/BVO. Similarly, 5%CCO/BVO, 20%CCO/BVO and 30%CCO/BVO samples were also prepared by using the calculated amounts of CCO, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 . Pure BVO was synthesis by the same method without the involvement of CCO.

2.4. Characterization of synthesized material

In this section all the characterization techniques used to investigate the physical and chemical properties of our synthesized materials are discussed in detail.

2.4.1. PXRD study

Powder X-ray diffraction data were recorded under normal conditions in a Bruker D8 advance diffractometer system using $\text{Cu K}\alpha$ radiation of $\lambda = 1.5418\text{ \AA}$ with the voltage and

ampere setting of respectively 40 kV and 40 mA and one dimensional (1D) position sensitive Lynxene detector with the scanning rate of 0.2 to 1 s per step.

The average crystallite size of the materials is determined by using Scherrer's formula:

$$\tau = \frac{0.9\lambda}{\beta \cos \theta} \dots\dots\dots(2.1)$$

where τ is the average crystallite size of the phase under investigation, λ is the wavelength of X-ray, β is the full-width at half maximum (FWHM) of the diffraction peak and θ is the Bragg angle.

2.4.2. TEM, HRTEM, EDX and elemental mapping study

The microstructural and morphological analyses were done with FEG-TEM (JEOL JEM 2100 F electron microscope) of ultrahigh resolution housed with a 200 kV electron source. The same instrument was used to perform the selected area electron diffraction analyses. The experimental samples were prepared by pouring a drop of highly dispersed aqueous sample solution onto a carbon coated Cu-grid (300 mesh size from Ted Pella) followed by its drying in a vacuum desiccator for 40 to 50 h before the actual analysis. The energy dispersive X-ray analyses and elemental mapping of the photocatalyst samples was analyzed using the same instrument.

2.4.3. FESEM study

The surface morphology of the samples was characterized by field emission scanning electron microscopy images with FEI inspect S50 instrument using carbon coated paper after gold coating the synthesized samples.

2.4.4. XPS study

XPS technique has been employed to evaluate the surface compositions and elemental oxidation states of synthesized nanocomposite materials as well as their pure components. XPS spectra were recorded using PHI-5000 VersaProbe III ULVAC-PHI Inc. fitted with a monochromatic Al K α radiation (1486.6 eV) as an X-ray source and operated at 150 W (15 kV and 10 mA). For referencing purpose, the C 1s spectral peak was fixed at the binding energy of 284.6 eV in our whole work. The pass energy of 40 eV and step increment of 0.05 eV were used to obtain individual core level spectra of metal and non metal elements. The analysis was performed by mounting the pellet form (diameter ~9 mm) of each specimen and

leaving it for overnight in the sample preparation chamber under an ultra-high vacuum of 5×10^{-6} mbar. The sample was transferred the following day into the analyzing chamber maintained at the vacuum level of 5×10^{-9} mbar and the XPS data were recorded. The core level spectra of elements present in the catalyst sample were recorded and curve-fitted into a number of components Gaussian peaks using Peakfit v.11 program after subtracting a linear background. Fitting parameters like peak positions, spin-orbit separations, intensity ratio of doublet, and FWHM were permitted to vary marginally as available in the literature.

2.4.5. BET surface area study

The porosity data, namely BET specific surface area (S_{BET}), pore size distribution and pore volume of the synthesized materials were determined from the analyses of N_2 adsorption isotherms. Before each measurement, the samples were first degassed under vacuum at 100 °C in the FLOVAC Degasser unit of an Autosorb iQ2 gas sorption instrument (Quantachrome Instruments, USA). The Non-Local Density Functional Theory (NLDFT) method was used to determine the pore volume and pore size distribution values.

2.4.6. UV-Vis DRS study

The optical properties of the photocatalyst materials are analyzed from UV-Vis diffuse reflectance spectroscopy using powdered form of solid photocatalyst materials. An UV-Vis DRS (Perkin-Elmer Lambda-35) instrument with integrating sphere arrangement has been used to study the optical properties of the samples in the wavelength range of 200–800 nm. In this typical characterization technique, some amount of solid sample (~ 70 to 100 mg) in fine powder form was spread on the surface of a thin quartz slide (spherical shape) and then the slide was sealed carefully with its sample holder. It was then placed into the DRS instrument for taking UV-Vis spectra of solid sample.

2.4.7. Bandgap study

2.4.7.1. Bandgap from UV-Vis DRS analysis

The bandgap energy value was determined from the Tauc plot analysis based on the UV-Vis DRS data of the respective photocatalyst materials. The Tauc plots are obtained according to equation 2.2

$$(\alpha h\nu)^{2/n} = A (h\nu - E_g) \dots\dots\dots(2.2)$$

where α , h , ν , E_g and A are the absorption co-efficient, the Planck constant, the light frequency, bandgap energy and a constant, respectively. The value of n depends on the nature of semiconductor, $n = 1$ for direct semiconductor and $n = 4$ for indirect semiconductor. The bandgap values are obtained by extrapolating the straight portion of $(\alpha h\nu)^2$ vs. $h\nu$ or $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots to the $\alpha = 0$ point.

2.4.7.2. Bandgap from electrochemical analysis (Cyclic voltammogram studies)

Cyclic voltammetry (CV) is a well-known method to measure the oxidation and reduction potentials of any materials in a precise manner. The relative energy positions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of synthesized materials as well as their bandgap energies have also been calculated thorough simple electrochemical measurements. An electrochemical set up have been made to determine the position of HOMO-LUMO energy levels of synthesized material in presence of suitable redox couple with the help of CHI600A electrochemical analyzer using standard three electrode system, namely glassy carbon (GC) as a working electrode, Pt-wire as an auxiliary electrode and an Ag/AgCl as the reference electrode. Cyclic voltammograms were performed in a cell containing 20 mL of 0.1 M KCl/Ferrocene mixture solution in CH₃OH as the supporting electrolyte with different scan rates of 10, 20, 200, 500 mV s⁻¹ to understand the reproducibility with dispersed materials in methanol. Prior to measurement, the solution was purged with pure nitrogen and the same environment was maintained throughout the experiment.

The synthesized material was well-dispersed in methanol for 30 min by an ultrasonic bath before CV scans. Auxiliary electrode (cleaned thoroughly with 0.1 M H₂SO₄), GC counter electrode and the reference electrode (kept in 1.0 M KCl) were introduced into the electrochemical system at room temperature. At the time of experiment 1 mL dispersed solution of synthesized material was injected into the electrochemical system.

The energy level of Ferrocene/Ferrocenium (Fc/Fc⁺) redox couple that acted as an internal standard was supposed to be -4.8 eV near vacuum level. The half-wave potential of the Fc/Fc⁺ redox couple was estimated from $E_{1/2, Fc/Fc^+} = (E_{ap} + E_{cp})/2$, where E_{ap} and E_{cp} are the anodic and cathodic peak potentials, respectively. The half-wave potential of Fc/Fc⁺ was found to be +0.49 V in reference to the Ag/AgCl reference electrode. The HOMO and LUMO energy levels of prepared material were obtained from the following equations [15]:

$$\text{HOMO} = - e[E_{\text{ox}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}}] - 4.8 \text{ eV} \dots\dots\dots(2.3)$$

$$\text{LUMO} = - e[E_{\text{red}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}}] - 4.8 \text{ eV} \dots\dots\dots(2.4)$$

E_{ox} , E_{red} , and $E_{\text{ferrocene}}$ are the oxidation, reduction potential and onset potential of ferrocene.

2.4.8. Raman spectroscopy study

Raman spectra of the synthesized samples were recorded from the wave number range of 30 to 500 cm^{-1} using 514 nm laser sources in a micro-Raman spectrometer (AGILTRON photonwares co. USA).

2.4.9. Photoluminescence (PL) study

The PL spectral studies of the photocatalyst materials have been carried out in a RF-5301PC spectrofluorophotometer (Shimadzu, Japan) in the wavelength range of 250 to 600 nm. The PL spectral analyses give the information about the charge separation of photocatalyst materials. In the other words, it describes about the electron hole pair recombination rate of photocatalyst which is the key factor responsible for improved activity. The electron hole pair recombination efficiency and photocatalytic activity are having a reciprocal relationship. The higher intensity of photocatalyst materials in the PL plot (intensity Vs wavelength) means a higher electron hole pair recombination and vice versa. In this study, certain amounts (~ 25 to 30 mg) of solid sample is dispersed by ultrasonication in a certain volume (~ 15 to 20 mL) of mili-Q water or double distilled water and 2.5 mL solution is put in the PL cell and recorded the data using a suitable excitation wavelength. In general, the light absorption edge and absorption maxima in UV-Vis DRS spectra of material give a rough idea of suitable excitation wavelength.

2.4.10. Photocurrent/ photoresponse study

2.4.10.1. By means of device fabrication

To study the photoresponse of the synthesized photocatalyst materials, thin film devices were fabricated based on each of the materials. The fabrication was done in an Aluminium/material thin film/ITO sandwich type configuration. ITO coated glass substrates were cleaned with soap solution, acetone, ethanol and distilled water in an ultrasonic bath. Then well dispersed solutions of the materials were prepared in ethanol medium by ultrasonication and thin film of the same was deposited by spin coating on pre-cleaned ITO

coated glasses. The film thickness was $\sim 1\ \mu\text{m}$ as measured by surface profiler. Thereafter, aluminium was deposited on the films by thermal evaporation technique to complete the device fabrication. Effective device area was $7.065 \times 10^{-6}\ \text{m}^2$.

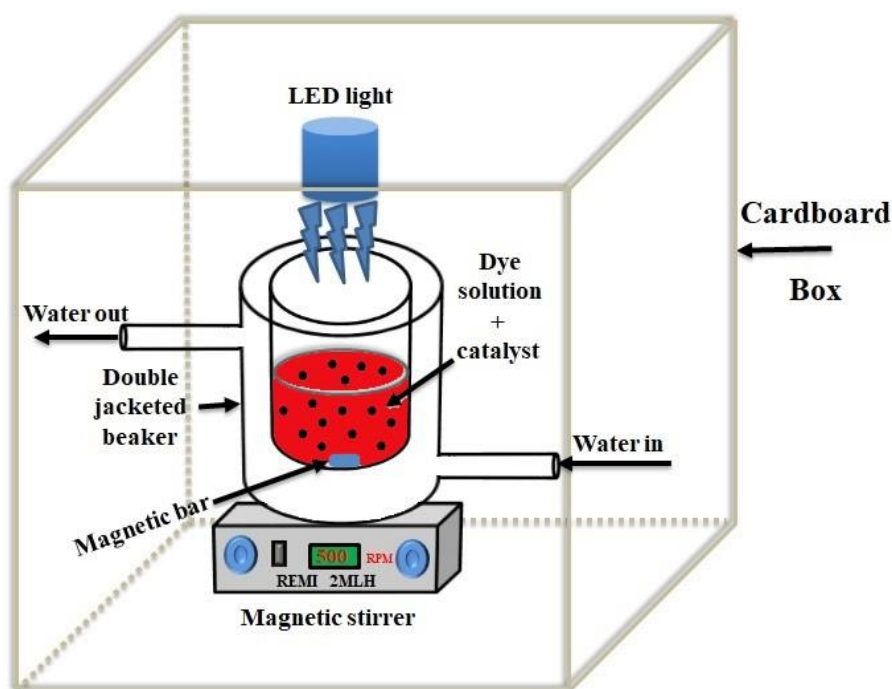
2.4.10.2. By means of electrochemical chronoamperometric measurements

The photoelectrochemical response of the nanocomposite sample and their pure components was measured in a three-electrode system using a computer-aided potentiostat/galvanostat instrument (AUTOLAB) under visible light irradiation at room temperature. In order to fabricate the working electrode, the as-synthesized catalyst materials were deposited on graphite carbon support by the 'drop and dry' technique of chemical solution (concentration: $2\ \text{g.L}^{-1}$) [16]. The area of the working electrode obtained so was $0.12\ \text{cm}^2$. A Pt foil of area $1 \times 1\ \text{cm}^2$ and an Ag/AgCl electrode are used as the counter electrode and the reference electrode, respectively. A $0.5\ \text{M}\ \text{Na}_2\text{SO}_4$ solution ($\text{pH} = 7$) was used as the electrolyte. In photocurrent response study, light irradiation was periodically interrupted in every 20 s interval during chronoamperometric measurements, and this process is known as electrochemical chopping. A 50 W visible LED light (intensity = $350 \times 100\ \text{LUX}$) was used as the light source.

2.5. Photocatalysis study

2.5.1. Fabrication of the photocatalytic reactor for pollutants degradation

The photocatalytic activities of the as synthesized samples were tested in a simple lab made photoreactor shown in **scheme 2.5**, where a domestic 50 W COOL LED light (Phillips) was used as the visible light source. The photocatalytic degradation experiments were carried out in a 100 mL capacity borosilicate double jacketed beaker with a water circulation system to avoid the little temperature effect of LED light that was placed vertically at a separation of $\sim 13\ \text{cm}$ from the surface of reaction solution. The double jacketed beaker was placed on a magnetic stirrer (REMI 1MLH) and the whole system was enclosed within a cardboard box of dimension $50\ \text{cm} \times 15\ \text{cm} \times 15\ \text{cm}$, the inner and outer surfaces of which were covered with black chart paper. A door of dimension $\sim 4\ \text{cm} \times 3\ \text{cm}$ was made available in the front face of the box for collecting the sample solution during experiments.



Scheme 2.5. Diagrammatic representation of fabricated photocatalytic reactor for pollutants degradation.

2.5.2. Photocatalytic activity test for pollutant degradation and analysis

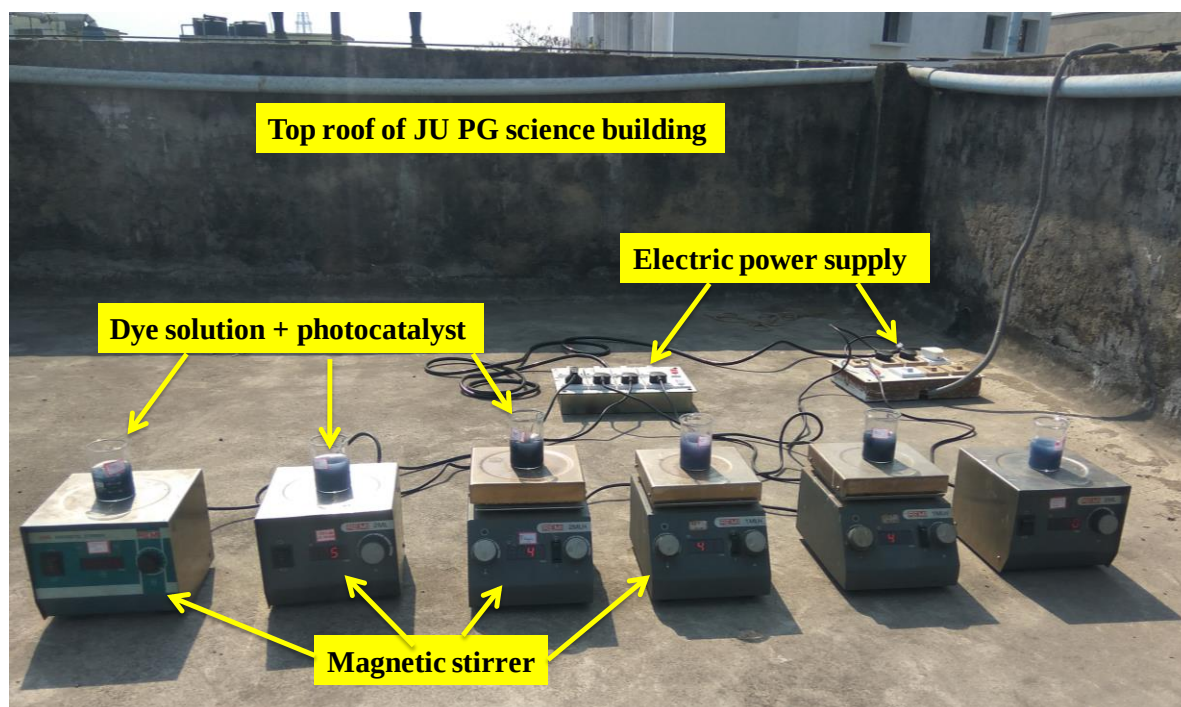
In a typical photocatalytic experiment for the degradation of pollutants, certain amount (in general, 25 mg to 125 mg) of photocatalyst was added into certain volume (60 to 100 mL) with a fixed concentration (10 to 20 ppm) of pollutants solution under ultrasonication (~60 s) in the double jacketed beaker. Before light irradiation, the obtained suspension was stirred in the dark for 30 to 60 min to reach the adsorption-desorption equilibrium. The time requires for adsorption-desorption equilibrium is fully depends on nature of catalyst surface which may vary catalyst to catalyst, but it was seen equilibrium is reached within 60 min. Once the equilibrium is reached, the suspension was irradiated and photodegradation was initiated. For analysis, 2 mL of light irradiated solution (reaction solution) was withdrawn at every 5 min interval, centrifuged at 8000 rpm and absorbance of pollutant was measured for the supernatant solution by UV–Vis spectrophotometer (JASCO, V-630). The degradation percentage is calculated using the following equation:

$$\% \text{ degradation} = \left(1 - \frac{C_t}{C_0} \right) \times 100 \quad \dots\dots\dots(2.5)$$

where C_0 and C_t are the initial concentration and concentration at time t of pollutant, respectively.

2.5.3. Sunlight assisted photocatalytic activity test for the degradation of reactive black 5 and methylene blue

The natural sunlight assisted photocatalytic activity tests (see **Scheme 2.6**) were carried out in a sunny day of May to July months at the roof top of PG Science Building, Jadavpur University, Kolkata situated at the latitude and the longitude coordinates of, respectively, 22.5726 ° N, 88.3639 ° E in between 10.30 AM–2.30 PM. The intensity of natural sunlight measured by a digital LUX meter (model no. LX-101A) was $\sim 550 \times 100$ to 600×100 LUX. A 50 ppm of 60 mL of RB5 and 10 ppm of 60 mL of MB solution were taken for photocatalytic experiments. Before starting the photocatalytic experiments, pre-fixed amount of photocatalyst was added to the dye solution followed by sonication for 2 min and finally the mixture solution was stirred for 45 min in the dark for adsorption-desorption equilibrium. After reaching the equilibrium, the mixture solution was quickly irradiated with natural sunlight under stirring condition. To analyze the extent of degradation, 2 mL of sample solution was withdrawn from the reaction mixture at every 15 and 30 min interval for RB5 and MB, respectively. The solution was centrifugated at 2000 RPM for separating the catalyst from reaction solution and the concentration of the resulting dye solution was calculated by measuring the absorbance at the wavelengths of 597 and 664 nm for RB5 and MB, respectively, using UV spectrophotometer according to **equation (2.5)**.



Scheme. 2.6. Sunlight assisted photocatalytic activity test set up.

2.5.4. Photo Fenton and dark Fenton like (PFL and DFL) activity test for the degradation of azo dyes and antibiotics

The visible LED light assisted photo Fenton like activity of synthesized nanocomposite and its parent materials were investigated through the degradation of industrial organic dyes viz., MB, RhB and MO as well as antibiotics like TC-HCl and NORF using the same 50 W domestic LED light source. In a typical PFL reaction, 50 mg of catalyst was added to 10 ppm of 60 mL dye/ antibiotics solution followed by ultrasonication (~ 60 s). Then the mixture solution was stirred continuously for about 30 min in dark condition for establishing the adsorption-desorption equilibrium. Once the equilibrium was reached, 4 mM of H₂O₂ (30% v/v) was added to the mixture solution and then the entire mixture solution was irradiated by the visible LED light. During the visible LED light irradiation process, 3 mL of reaction aliquot was withdrawn at an interval of 5 min and then centrifuged (~8000 rpm) immediately to separate the solid catalyst mass from the mixture solution. The relevant data of concentration at the particular instant of time was determined from the recorded value of the absorbance of MB, RhB, MO, TC-HCl and NORF at their corresponding λ_{max} values of 664, 553, 460, 357 and 276 nm using JASCO V-630 spectrophotometer. The experimental procedure of DFL reaction is the same as PFL reaction where the overall reaction was investigated in complete dark condition instead of a light condition. The dye degradation efficiency was calculated according to the **equation (2.5)**.

2.5.5. Photoelectrocatalytic activity test and analysis

The photoelectrochemical measurement was also carried out in the same electrochemical workstation of AUTOLAB used for photoresponse studies. The three-electrode system was consisted of the as prepared samples as the working electrode with area 0.12 cm², a platinum metal foil of area 1 cm² as the counter electrode, and an Ag/AgCl electrode as the reference electrode. An aqueous solution of 1 M NaOH solution acted as the electrolyte, while a 50 W domestic LED light was used as the visible light source.

2.5.6. Fluorescence probe method for $\cdot\text{OH}$ detection in PFL and DFL reaction

The experimental evidence of $\cdot\text{OH}$ formation in photo Fenton like reaction was tested by using a coumarin fluorescence probe method [17]. In this method, fluorescence inactive coumarin reacts with $\cdot\text{OH}$ to form highly fluorescent 7-hydroxy coumarin. In a typical experiment of $\cdot\text{OH}$ detection in photocatalytic reaction, optimum amount of synthesized

catalyst was dispersed well in 60 mL of coumarin solution (20 ppm) in a 100 mL beaker and stirred vigorously for about 30 min in dark condition. Optimum amount of H_2O_2 (30% w/w) was then added and the mixture solution was irradiated fast by the visible LED light. During the experimental process, 2 mL of fluorescence probe reaction solution was withdrawn at every 5 min intervals and then centrifuged (8000 rpm) to separate the solid catalyst component. Then 1 mL of the supernatant solution was added to fluorescence cell holding 1 mL of Milli-Q water. The experimental procedure for the involvement of $\cdot\text{OH}$ formation in DFL photocatalytic reaction and normal photocatalytic reaction are similar to the PFL reaction where the whole experiment was investigated in dark condition and in the absence of H_2O_2 , respectively. The fluorescence intensity of 7-hydroxy coumarin was determined at 456 nm by using the excitation wavelength of 332 nm in a RF-5301PC spectrofluorophotometer (Shimadzu, Japan).

2.5.7. Radical detection technique

The reactive species or radical detection technique is an important aspect because various reactive species play a crucial role in the photocatalytic reaction as well as mechanism [18]. The reactive species generated in the catalytic process are mainly responsible for dye degradation. Therefore, radical trapping experiments for reactive species have been conducted to determine the roles of various active species involved in the photocatalytic process. In this typical technique, different types of trapping agents namely, benzoquinone (BQ), disodium ethylenediaminetetraacetic acid disodium salt dihydrate ($\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$), isopropanol (IPA) and silver nitrate (AgNO_3) are used to identify the active species, superoxide radical, hole, hydroxyl radical and electron, respectively [19]. In general, optimized catalyst amount, 1 mL of 0.1 M solution of trapping agent and 60 mL solution of pollutant (10 ppm) were used in this experiment. These trapping agents are added individually to the photocatalytic reaction medium with an optimum concentration and the responsible reactive species is identified if the respective trapping agent significantly reduced the rate of photocatalytic reaction by capturing that specific reactive species.

2.5.8. Recycling activity test of photocatalysis

The recycling activity of synthesized photocatalyst is a big concern in the photocatalytic applications of science and technology as well as industrial purposes [20]. The practicability of a photocatalyst relies upon on its recycling behavior. In this respect, washing

of photocatalyst is a crucial factor. In our study of recycling test, the solid catalyst materials were washed three to four times each with alcohol (ethanol or isopropanol) and ultrapure water very carefully followed by drying to clean the catalyst surface from the adsorbed products generated during the photocatalytic reaction [21]. In some cases, additional heat treatment was required to remove the adsorbed carbon or nitrogen containing compounds from the solid catalyst surface [22]. In this case, the temperature and time of heating were not allowed to exceed the actual synthesis temperature and time of the photocatalyst synthesis. Finally, after successfully recovery of photocatalyst, the recycling activity test was performed following the same procedure adopted for the fresh catalyst.

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Chapter 3

Studies on photocatalytic activity of $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ nanocomposite photocatalyst

Chapter abstract

This chapter describes the synthesis, characterization, and photocatalytic activity of $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ (CCO/BiOBr) nanocomposites photocatalyst system used for the degradation of RhB and TC-HCl by employing household visible light emitting diode source. In these nanocomposites, sol-gel combustion made spherical shaped CCO nanoparticles are decorated on BiOBr plates in single pot via precipitation method using CTAB as the Br source and the template. Among the whole nanocomposite series, 20%CCO/BiOBr sample exhibits high degradation efficiency for both RhB (96% in 15 min) and TC-HCl (96.7% in 300 min) with good recycling behavior. The structural and optical characterizations of all the samples were investigated by different instrumental techniques. The optical data have revealed significant improvement in visible light absorption of CCO/BiOBr nanocomposite. Based on the band modification and radical trapping analyses a plausible mechanistic path of the entire photocatalytic degradation process is presented.

3.1. Introduction

As elaborated in chapter 1, the removal of high molecular mass dyes from wastewater is an important issue for environmental safety [1–3]. These dyes have harmful effect on human health and aquatic life [4]. Photocatalytic degradation is one of the most valuable and common methods for chemical pollutants removal from wastewater [1-3, 7, 10, 13–18]. In most of the reports on photocatalysis, high power xenon lamp [1, 2, 6, 14, 15], halogen lamp [13], UV lamp [7, 8] or high pressure mercury vapor lamp [19] are used as light sources, which are having certain benefits, but are harmful, costly and difficult to handle. However, it would be convenient to use household light emitting diode (LED) light as the radiation source for the purpose of photodegradation of such organic pollutants [10, 11].

According to the literature, the most extensively studied photocatalyst is TiO_2 [18, 20]. Unfortunately, its large band gap of about 3.2 eV imposes limitation to its applicability in visible light driven (VLD) photoactivity. Subsequently, the Bi (III) based semiconductors are reported as non-titania type VLD photocatalysts for wastewater treatment [10, 14, 15, 21–23]. The lowering of band gap in such Bi-based semiconductors has been attributed to the effective overlap of $6s^2$ orbital of Bi^{3+} with 2p orbital of oxygen. Several other Bi-based photocatalysts and their composite systems with other semiconductor materials such as BiOX ($\text{X} = \text{Cl, Br, I}$) [12], Bi_2O_3 [24], BiOBr/BiOI [25], BiOBr/ Bi_2O_3 [26], $\text{Bi}_2\text{WO}_6/\text{Ta}_3\text{N}_5$ [27],

Bi₂MoO₆/WO₃ [28], Bi₂MoO₆/Ta₃N₅ [29], and Bi₂WO₆/Ag₆Si₂O₇ [30] have been developed to serve the purpose of VLD photocatalyst. Among these, BiOX (X= Cl, Br, I) related photocatalysts with lower photo-induced electron-hole recombination rate have attracted attention of researchers to consider as alternatives to non-TiO₂ photocatalysts. In this regard, particularly BiOBr is found to be the most promising one due to its smaller band gap (2.7 eV), chemical stability and structural feature. The lamellar type structure of BiOBr with [Bi₂O₂]²⁺ slabs interleaved by Br⁻ is suggested to be crucial for its enhanced photocatalytic activity [2]. Over the past few decades, several attempts have been made to improve the photocatalytic performance of BiOBr such as by doping with metals and non-metals [31, 32], or by forming a heterojunction of BiOBr with transition metal oxides (TMOs) of dissimilar band gaps [33, 34]. Attempts are also made to improve the catalytic performance of BiOBr through controlling their shape, size and morphologies [1, 35-36]. Moreover, the VLD photocatalytic activity of BiOBr is found to increase when coupled with lower band gap materials like NiFe₂O₄, CoFe₂O₄ [37, 38].

Recently, there are several reports showing better photocatalytic performance of composite materials, where transition metal oxides (TMOs) can play a role as an important component. Moreover, TMOs apart from their intriguing physical properties like electrical, magnetic and other multifunctional behaviour have attracted significant interest due to their potential applications in various areas of modern interest like explosive and gas sensing [39, 40], reforming [41], dye degradation as well as adsorption [42-44], photocatalytic hydrogen production [45, 46], burn rate modifier [47], organic transformation [48, 49] and so on. Several spinel based composites like ZnO/NiFe₂O₄ [50], CuFe₂O₄/CdS [51], CuFe₂O₄/Bi₄Ti₃O₁₂ [52], CuCr₂O₄/g-C₃N₄ [10] have been reported to show better photocatalytic performance and it has been attributed to the probable *p-n* type heterojunction formation at the interface of the components. In this regard, CuCr₂O₄ with a low band gap of 1.4 eV can be considered as an important material. Such lower band gap material should exhibit effective absorption of visible light [53]. Unfortunately, its photocatalytic performance is significantly weak due to its high electron-hole pair recombination tendency.

Bearing all these in mind we have considered that it would be of worth investigating CuCr₂O₄/BiOBr nanocomposite system as photocatalyst. In this nanocomposite material, the spherical CCO nanoparticles spread over the plate like BiOBr can very efficiently degrade the hazardous pollutants in presence of LED light.

3.2. Results and discussion

3.2.1. Structural analysis

The powder XRD patterns of CCO, BiOBr and the whole series of CCO/BiOBr nanocomposites are presented in **Fig. 3.1**. It is clearly evident that all the samples are highly crystalline. The diffraction peaks for pure CCO positioned at the 2θ values 18.5° , 29.6° , 30.9° , 35.17° , 37.7° and 42.4° correspond to (101), (200), (112), (211), and (202) reflections, respectively and corroborate to the JCPDS file no. 88-0110. Similarly, the major (001), (002), (101), (102), (110), (003), and (111) reflections for BiOBr are positioned at the 2θ values of 10.9° , 21.9° , 25.1° , 31.7° , 32.2° , 33.1° , 34.1° , and 46.2° , respectively, and it is in good agreement with JCPDS file no. 85-0862. All composite samples exhibit the combined diffractions of the parent phases without appearance of any traces of impurity. This result suggests that pure CCO/BiOBr composites are formed successfully without any decomposition of mother phases. However, the relative intensity of the peaks depends on the phase fraction of the components.

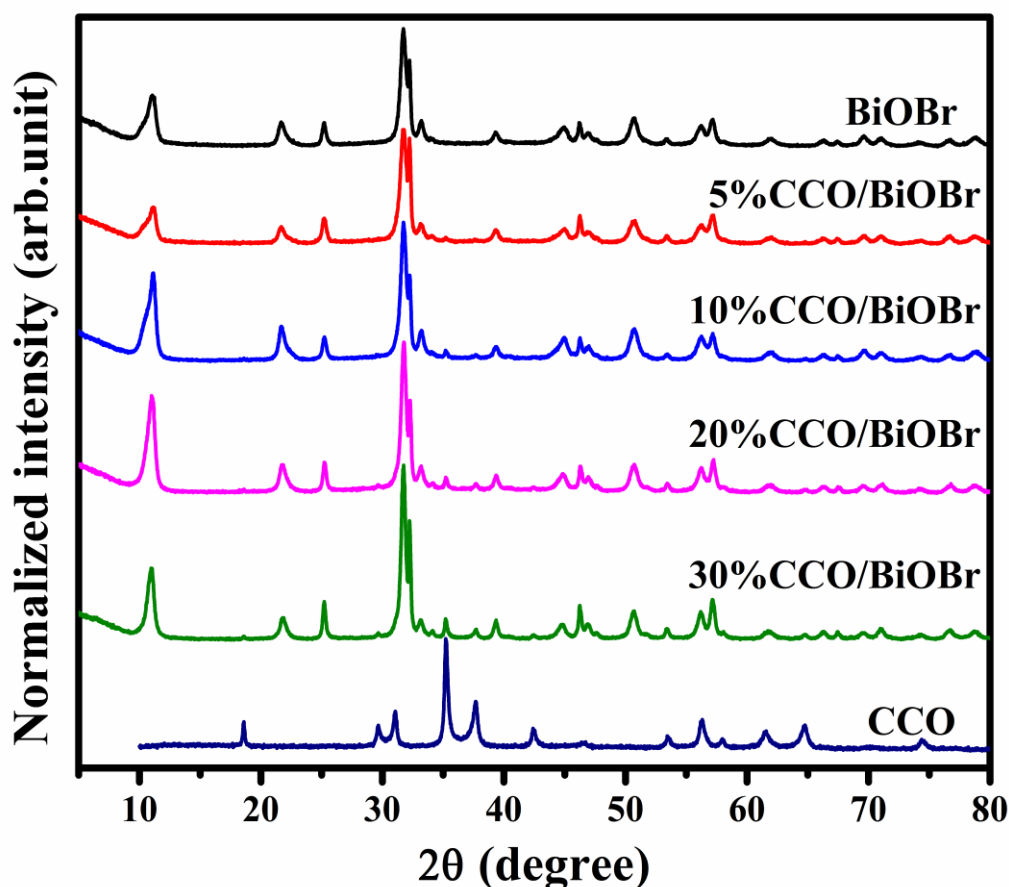


Fig. 3.1: Normalized powder XRD patterns of pure CCO and BiOBr along with the CCO/BiOBr nanocomposites.

3.2.2 Morphology and microstructural analysis

In **Fig. 3.2**, FESEM micrographs of the synthesized samples are reported. The images of CCO samples (**Fig. 3.2(a, b)**) reveal typical irregular spherical like morphology with agglomerated particles and the sizes of CCO particles range from 30 nm to 80 nm. An irregular sheet or platelet-like morphology with unique layered structure and smooth surface is observed for BiOBr (see **Fig. 3.2(c, d)**). It can be seen from **Fig. 3.2(e, f)** that spherical CCO nanoparticles are highly decorated on the surface of BiOBr plates in the composite material and all these observations are consistent with the findings of the TEM analysis presented below.

The low resolution TEM suggests the morphology of BiOBr to be characterized by the presence of a number of aggregated square or rectangular type nanosheets (see **Fig. 3.3(a)**). While pure CCO is constituted by an irregular shaped spherical particles (see **Fig. 3.3(b)**). The TEM image of the composite, shown in **Fig. 3.3(c)**, indicates that the CCO spheres are highly decorated in between BiOBr nanosheets in agreement to the FESEM findings. A HRTEM image of CCO/BiOBr nanocomposite is shown in **Fig. 3.3(d)**. Sharp and continuous lattice fringes along two different directions with d spacing of 0.28 nm and 0.3 nm correspond to the (102) planes of BiOBr and (220) planes of CCO, respectively [55, 56]. The EDX spectrum of composite, shown in **Fig. 3.3(e)**, confirms the presence of Bi, O, Br, Cu and Cr. In the EDX table (see **Fig. 3.3(f)**) of atomic% and weight% of the respective elements, the highest amount of Cu in comparison to the other elements in each case is caused due to contribution from the copper grid used in TEM analysis. The SAED pattern of the composite sample shown in **Fig. 3.3(g)** appears as a number of concentric rings that can be marked as (001), (102), (112), (200) and (411) planes for BiOBr and (220) plane for CCO. This is a definitive signature of the polycrystalline nature of the nanocomposite.

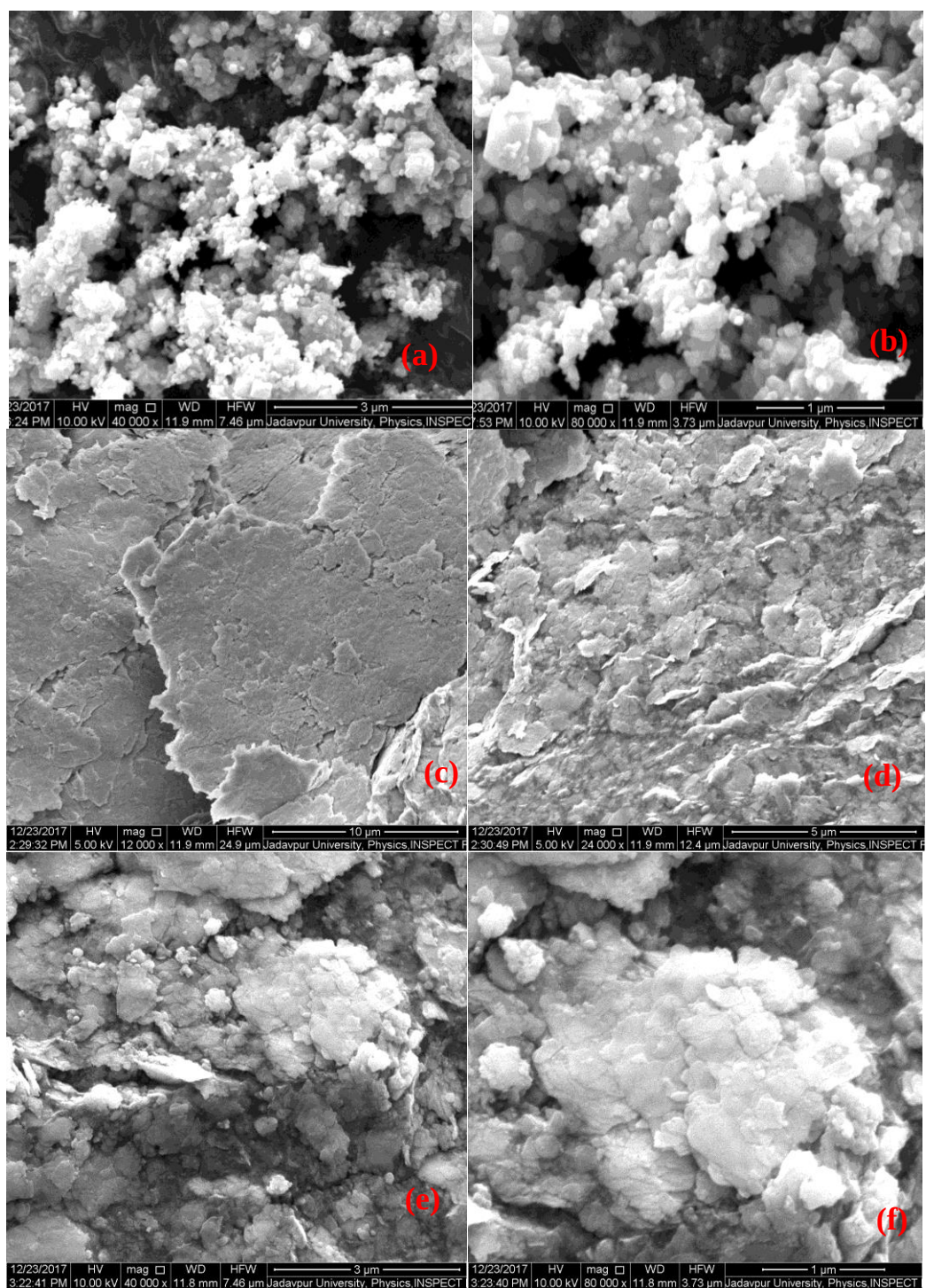


Fig. 3.2: FESEM images of (a, b) CCO, (c, d) BiOBr and (e, f) 20%CCO/BiOBr nanocomposite.

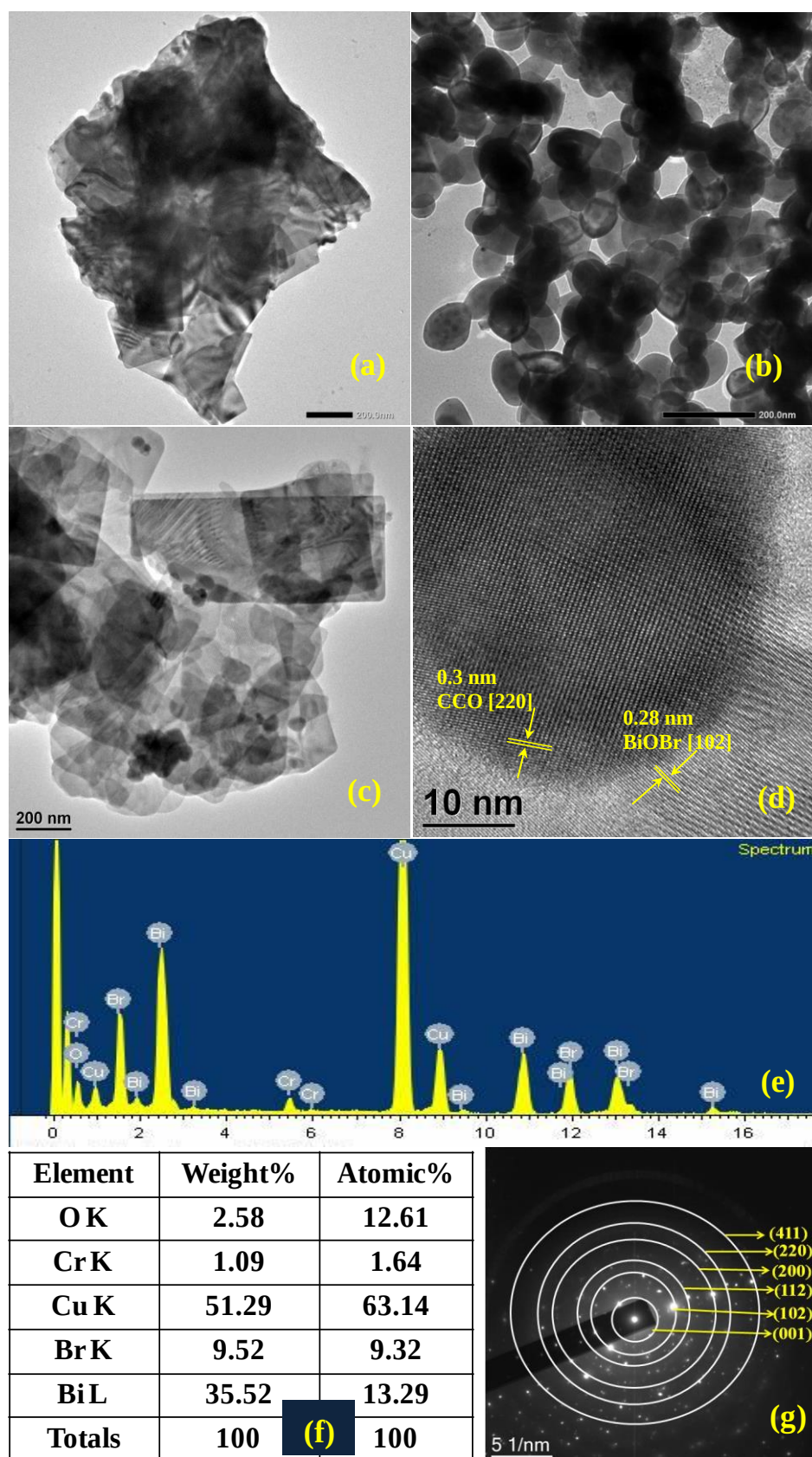


Fig. 3.3: (a-c) TEM images of BiOBr, CCO and 20%CCO/BiOBr and (d) HRTEM, (e) EDX spectra, (f) EDX table of the elements for their atomic% and weight% and (g) SAED pattern of 20%CCO/BiOBr nanocomposite sample.

3.2.3. BET analyses

The BET N_2 adsorption-desorption isotherms of CCO, BiOBr and CCO/BiOBr composites are displayed in **Fig. 3.4**, while their pore size distributions are shown in the inset. The specific surface area and porosity data of all the samples are listed in **Table 3.1**. According to the IUPAC classification, the nature of isotherms of the synthesized samples in the relative pressure range from 0 to 1 exhibits type IV isotherm with a H3 hysteresis loop because the amounts of N_2 gas adsorption is lower at low relative pressure and increased gradually at high relative pressure. The surface area of pure BiOBr is low, $\sim 9.0 \text{ m}^2 \text{ g}^{-1}$, while pure CCO exhibits a little higher surface area of $12.3 \text{ m}^2 \text{ g}^{-1}$. Loading of a lower amount (5%) of CCO in BiOBr essentially does not have any effect ($S_{\text{BET}} \sim 8.8 \text{ m}^2 \text{ g}^{-1}$). A gradual increase of the surface areas of the nanocomposites occur for the 10–20%CCO-loaded catalysts, the 20%CCO-loaded catalyst exhibiting the highest surface area of $15.0 \text{ m}^2 \text{ g}^{-1}$. Further increase in CCO loading to 30% has the effect of decreasing the overall area of the nanocomposite ($S_{\text{BET}} \sim 10.9 \text{ m}^2 \text{ g}^{-1}$). The highest surface area of 20%CCO/BiOBr nanocomposite among all the other samples is expected to be reflected in the photodegradation activity pattern of the nanonanocomposite samples.

Table 3.1: Surface area and porosity data of CCO, BiOBr and CCO/BiOBr nanocomposites.

Sample name	Surface area ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore size (nm)
CCO	12.3	0.026	1.45
5%CCO/BiOBr	8.8	0.034	2.72
10%CCO/BiOBr	11.6	0.044	2.38
20%CCO/BiOBr	15.0	0.050	1.66
30%CCO/BiOBr	10.9	0.040	1.66
BiOBr	9.0	0.027	1.66

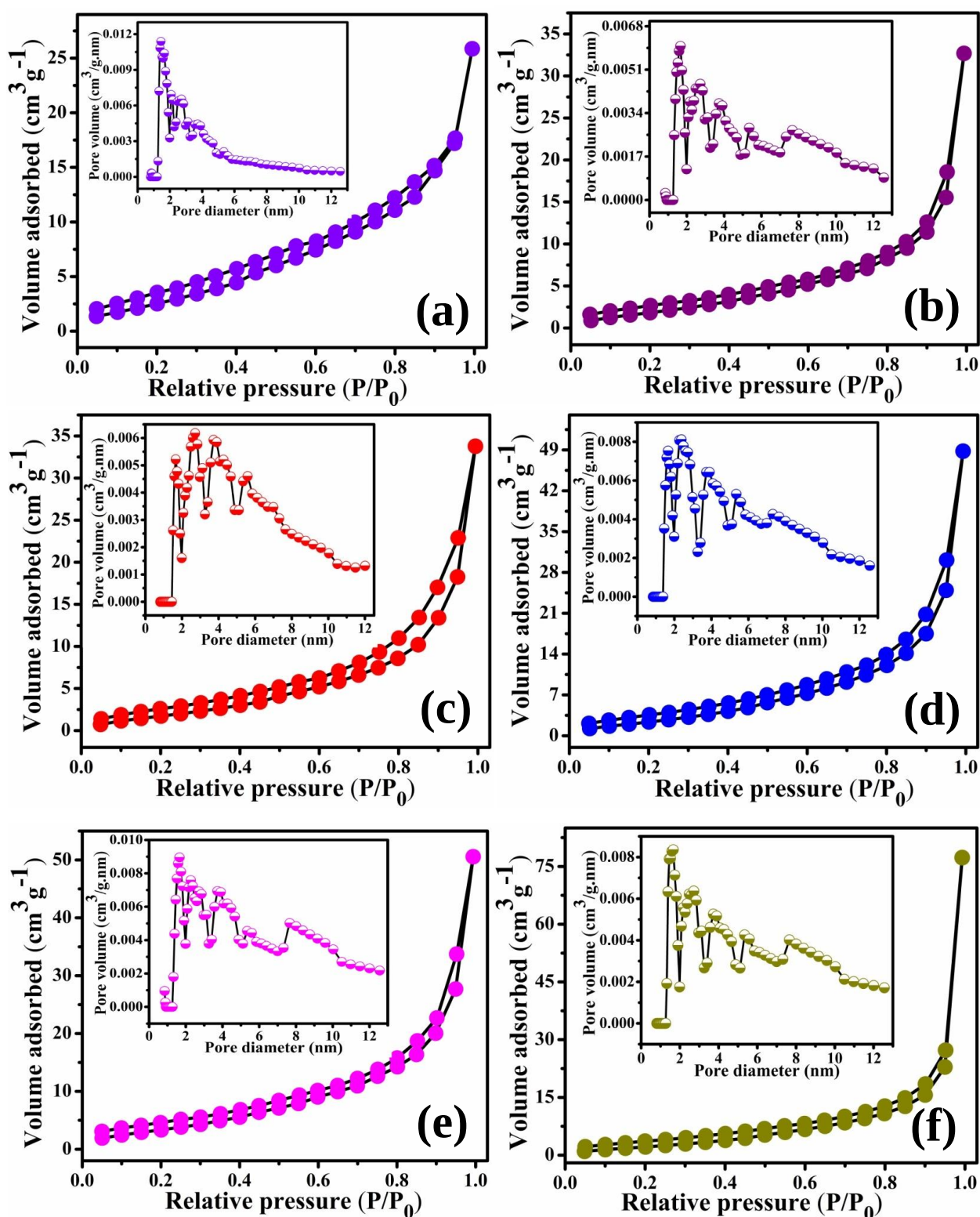


Fig. 3.4: Nitrogen adsorption-desorption isotherms and pore size distribution curves (in the inset) of (a) CCO, (b) BiOBr, (c) 5%CCO/BiOBr, (d) 10%CCO/BiOBr, (e) 20%CCO/BiOBr and (f) 30%CCO/BiOBr.

3.2.4. XPS analysis

XPS is one of the important tools to study the surface composition and elemental oxidation states of materials. It can provide information about metal binding energy change because of different coordination environment with oxygen ions [57, 58]. Generally, in AB_2O_4 spinel structure, A is in +2 oxidation state with tetrahedral coordination and B is in +3 oxidation state with octahedral coordination for a normal spinel. $CuCr_2O_4$ adopts spinel structure wherein Cu is fully in tetrahedral coordination sites and Cr occupies octahedral sites. Cu 2p core level spectrum of CCO is broad indicating the presence of different Cu species which is decomposed into different component peaks by curve-fitting as shown in **Fig. 3.5(a)**. Accordingly, Cu $2p_{3/2,1/2}$ peaks at 933.1 and 953.6 eV with characteristic satellite peaks and spin-orbit separation of 19.5 eV are attributed to Cu^{2+} species present in CCO material. Satellite peaks are special features of oxidized transition metals such as Fe, Co, Ni and Cu. It is well established that an additional excitation of a second electron takes place during creation of a hole in a core level by photoelectron emission. Sudden hole creation in Cu $2p^6$ filled orbital from Cu^{2+} ion present in the catalyst forms Cu^{3+} ion which is unstable. Therefore, an electron transfer from O 2p level to Cu 3d level occurs resulting in satellite peaks in the Cu 2p core level spectrum as observed in the figure. In addition to these peaks, intense $2p_{3/2,1/2}$ component peaks at 935.4 and 955.6 eV are also observed in the Cu 2p spectrum. It has been reported in the literature that Cu 2p binding energy decreases when changing from tetrahedral to octahedral sites corresponding to increase in Cu coordination number with oxygen ions [59-61]. Therefore, Cu $2p_{3/2,1/2}$ peaks at 933.1 and 953.6 eV are assigned for Cu^{2+} species in octahedral sites and Cu $2p_{3/2,1/2}$ peaks at 935.4 and 955.6 eV are related to Cu^{2+} species in tetrahedral coordination environment in CCO structure. High intense peak observed around 962 eV corresponds to satellite peak of Cu $2p_{1/2}$ core level and Cr LMM Auger peak. Cu 2p core level spectrum of CCO/BiOBr nanocomposite is broad and curve-fitted into several component species which is presented in **Fig. 3.5(b)**. Curve-fitted peaks are assigned to Cu^{2+} species in octahedral and tetrahedral coordination sites. However, intensity of Cu 2p core level spectrum is observed to decrease in CCO/BiOBr nanocomposite. Intensity ratio of tetrahedral to octahedral Cu^{2+} species in CCO is 1.8 and that in CCO/BiOBr nanocomposite is 2.4 indicating that tetrahedral species are the major species in the CCO and its nanocomposite.

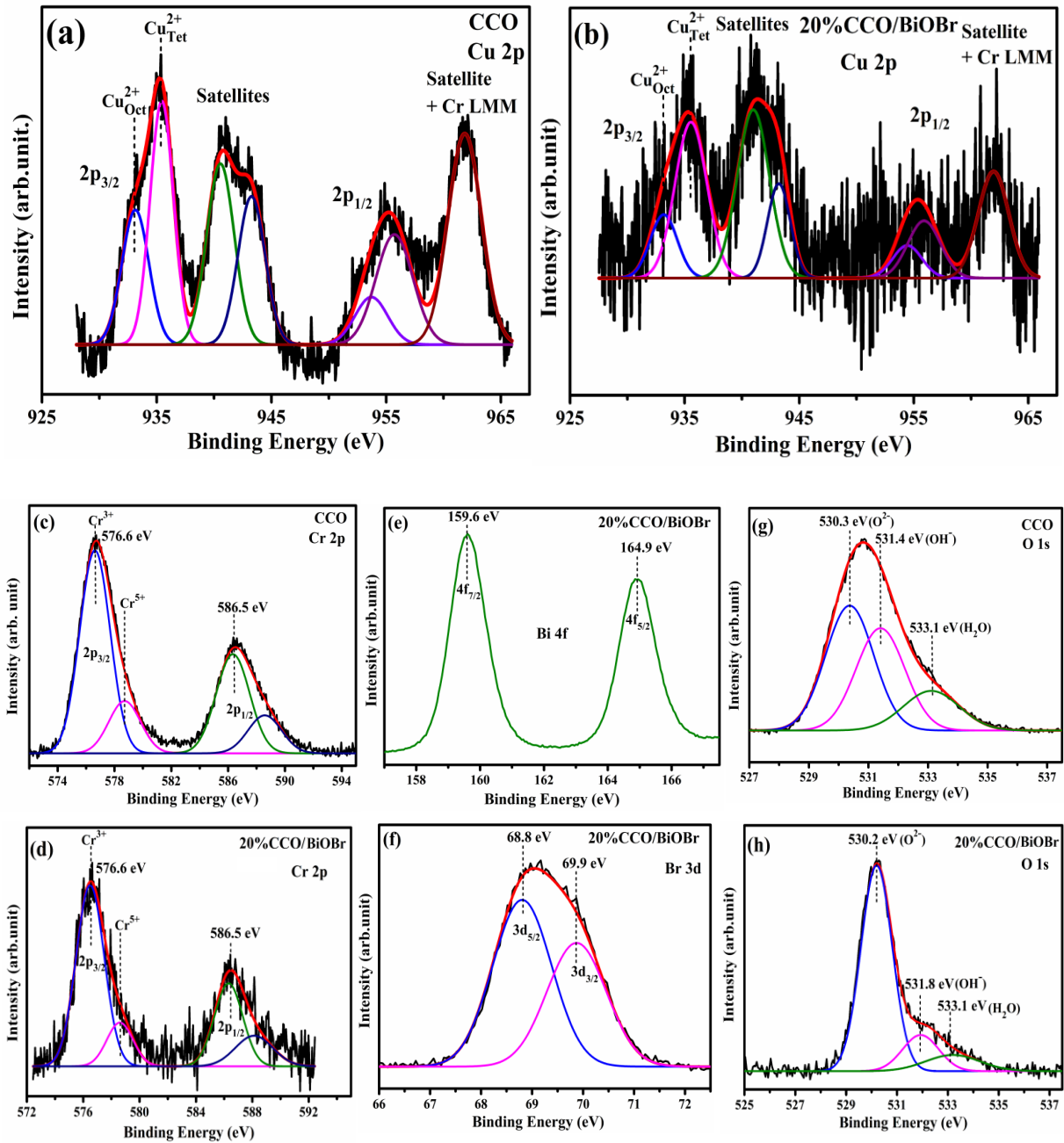


Fig. 3.5: X-ray core level spectra of CCO and 20%CCO/BiOBr sample: (a, b) Cu 2p, (c, d) Cr 2p, (e) Bi 4f, (f) Br 3d, (g, h) O 1s regions.

Cr 2p core level spectrum of CCO shown in **Fig. 3.5(c)** contains a long tail in the higher binding energy region indicating the presence of different Cr species which are resolved by curve-fitting. Observed Cr $2p_{3/2,1/2}$ peaks around 576.6 and 586.5 eV with 9.9 eV spin-orbit separation correspond to Cr^{3+} species [62]. There are weak component peaks at 578.7 and 588.6 eV that correspond to higher chromium oxide species such as Cr^{5+} [63]. Therefore, concentration of octahedral Cr^{3+} species decreases to some extent. It is to be noted that according to crystal field theory, formation of Cr^{3+} species in tetrahedral sites is very

difficult. In this sense, some amount of Cu^{2+} species occupy octahedral sites because of formation of higher chromium oxide species (Cr^{5+}) which is reflected in Cu 2p core level spectrum. Cr is also observed to be present in +3 oxidation state in CCO/BiOBr nanocomposite along with Cr^{5+} species as displayed in **Fig. 3.5(d)**. The Cr 2p spectral intensity also decreases in the nanocomposite sample.

Bi 4f core level spectrum in the CCO/BiOBr nanocomposite is shown in **Fig. 3.5(e)**. Observed $4f_{7/2,5/2}$ peaks at 159.6 and 164.9 eV are assigned for Bi^{3+} species in the nanocomposite [64]. Binding energy values of Br $3d_{5/2,3/2}$ peaks noticed at 68.8 and 69.9 eV as presented in **Fig. 3.5(f)** agree well with this type of material reported in the literature [65].

Spectral characteristics of O 1s core level are broad suggesting that several oxygen component species are present in the CCO. Spectrum is decomposed into different peaks by curve-fitting and is presented in **Fig. 3.5(g)**. Component peak at 530.4 eV is assigned for oxide species and peak around 531.4 eV stands for hydroxyl species. Weak component peak with binding energy above 533.1 eV is related to adsorbed water species present in the catalysts. These binding energy values agree well with the literature [62]. However, oxide species is found to be a major species in comparison with other two species. A sharp oxide peak at 530.2 eV along with OH^- and H_2O peaks are noticed in the O 1s core level spectrum of the nanocomposite material (**Fig. 3.5(h)**).

3.2.5. Optical spectral analyses

3.2.5.1. UV-Vis DRS and band gap analyses

Fig. 3.6 shows the UV-Vis DRS spectra of CCO, BiOBr and CCO/BiOBr nanocomposites. Pure BiOBr shows absorption edge at ~ 450 nm. On the other hand, pure CCO exhibits its very high visible light absorption property over the whole visible range without any absorption edge like BiOBr. From **Fig. 3.6**, it is evident that the visible light absorption ability of BiOBr is remarkably improved in composite form with 5%CCO/BiOBr. This increased visible light absorption ability for CCO/BiOBr composites is partially due to the superposition effect of the mixture. There is a slight blue shift in the absorption edge of BiOBr in nanocomposite phase. The shift in absorption edge could be due to band deformation across the interface of the components. The gradual increase of intensity and shift of absorption edge in the nanocomposite with the increase of CCO loading suggests beneficial effect of CCO, presence of which seems to improve the visible light absorption

property effectively. The shifting of band edge below 450 nm for BiOBr effectively widens the visible absorption range.

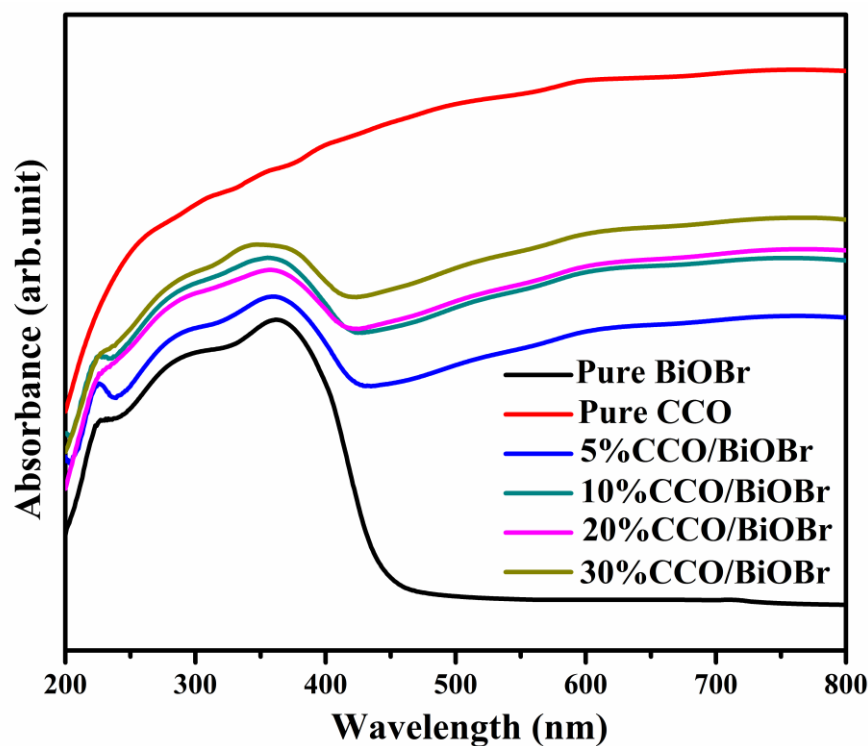


Fig. 3.6: UV-Vis DRS spectra of BiOBr, CCO and CCO/BiOBr nanocomposites.

According to previously reported literature, the n value of CCO is 1, a direct semiconductor [54] and it is 4 for BiOBr, an indirect semiconductor [25]. For the CCO/BiOBr nanocomposites, the value of n is considered to be 4 because of its similar UV-DRS characteristics pattern to BiOBr and higher content of BiOBr in the nanocomposite system. The calculated band gap (E_g) values of CCO, BiOBr, 5%CCO/BiOBr, 10%CCO/BiOBr, 20%CCO/BiOBr and 30%CCO/BiOBr determined so are 1.48 eV, 2.62 eV, 2.42 eV, 2.38 eV, 2.2 eV and 2.28 eV, respectively (see six representative plots in **Fig. 3.7**). The optical band gap energies of CCO/BiOBr nanocomposites are decreased from that of pure BiOBr after the introduction of different amounts of CCO, showing a maximum reduction of band gap value for the 20%CCO/BiOBr sample that shows maximum RhB degradation activity over all the other samples as will be shown later.

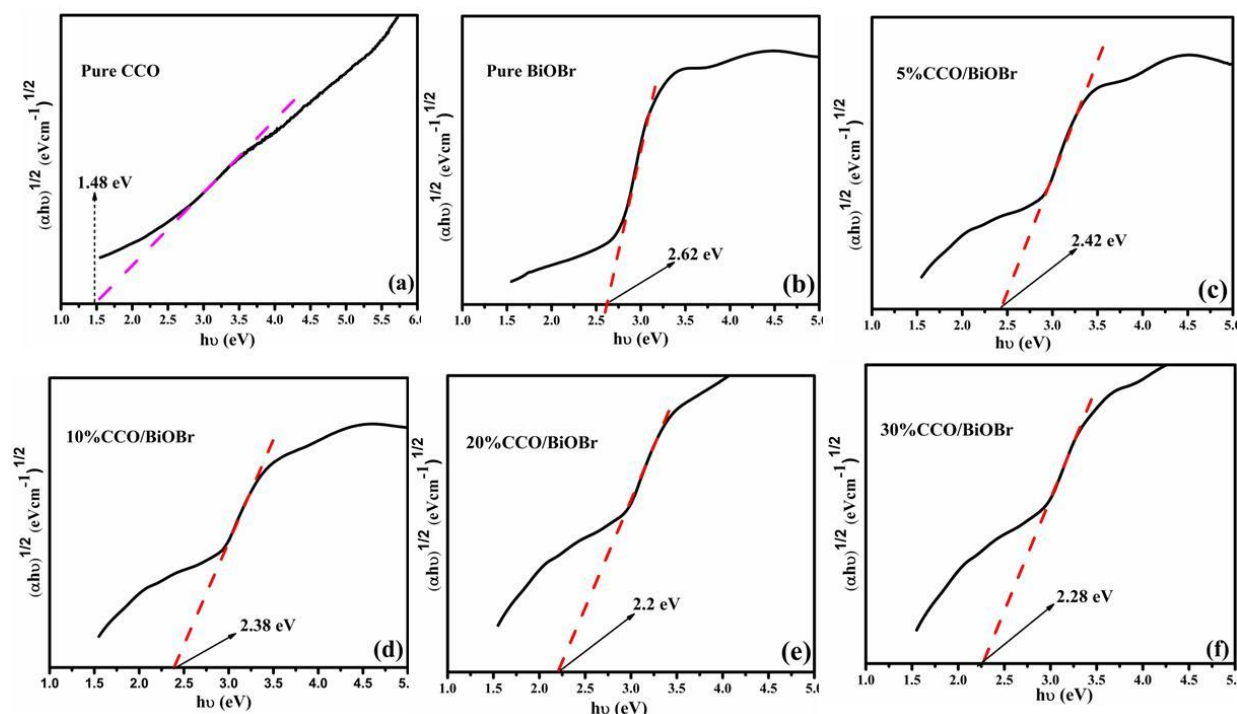


Fig. 3.7: Tauc plots of (a) CCO, (b) BiOBr, (c) 5%CCO/BiOBr, (d) 10%CCO/BiOBr, (e) 20%CCO/BiOBr and (f) 30%CCO/BiOBr.

3.2.5.2. HOMO-LUMO of BiOBr, CCO and CCO/BiOBr nanocomposite for electrochemically analysis of band gap

The half-wave potential of Fc/Fc^+ was found to be +0.49 V in reference to the Ag/AgCl reference electrode (see Fig. 3.8). The oxidation potential corresponding to electron extraction from the HOMO level can be correlated with the ionization potential, while the

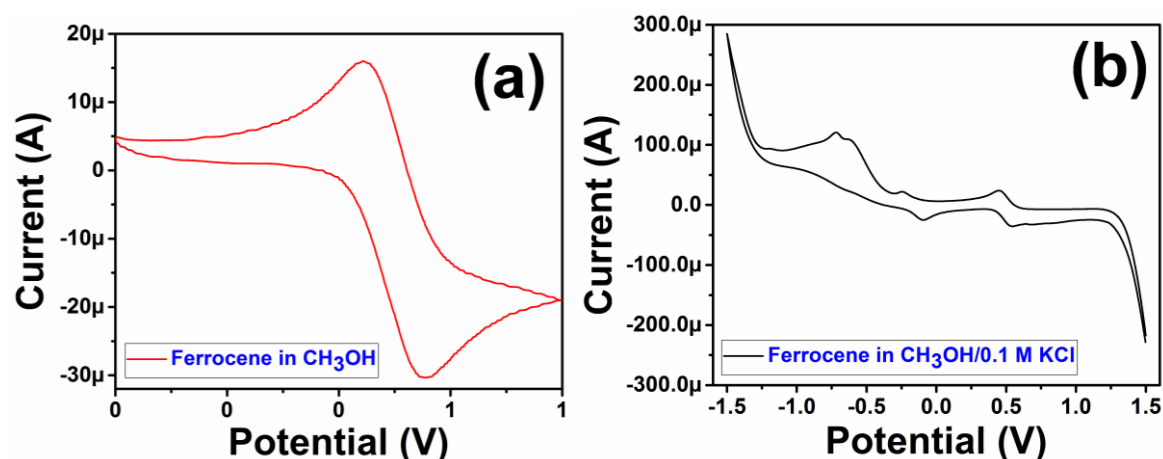


Fig. 3.8: Cyclic voltammograms of Ferrocene (a) in CH_3OH and (b) in 0.1 M KCl/ CH_3OH ($E^\circ = +0.49$ V; GC as the working electrode, Pt-wire as the counter electrode and Ag/AgCl as the reference electrode).

reduction potential is associated with the electron affinity and indicates the LUMO level of the corresponding materials. Cyclic voltammograms of dispersed solutions of BiOBr, CCO, and 20%CCO/BiOBr at different scan rates viz., 20, 50, 200 and 500 mV s^{-1} represent the reproducibility of anodic and cathodic peak potentials (see **Fig. 3.9**). These materials show slight changes in the oxidation and reduction potentials at a definite condition. HOMO levels are found to be -5.27 eV, -5.21 eV and -5.24 eV for BiOBr, CCO and 20%CCO/BiOBr, respectively and the corresponding LUMO levels are -2.97 eV, -3.12 eV and -2.98 eV. The assessed band gap energy values of three materials are tabulated in **Table 3.2**. The estimated values of HOMO-LUMO from the electrochemical analysis are comparable with those obtained from the optical data. Slight deviations between the optical and the electrochemical data are ascribed to the solid-liquid interfacial tension.

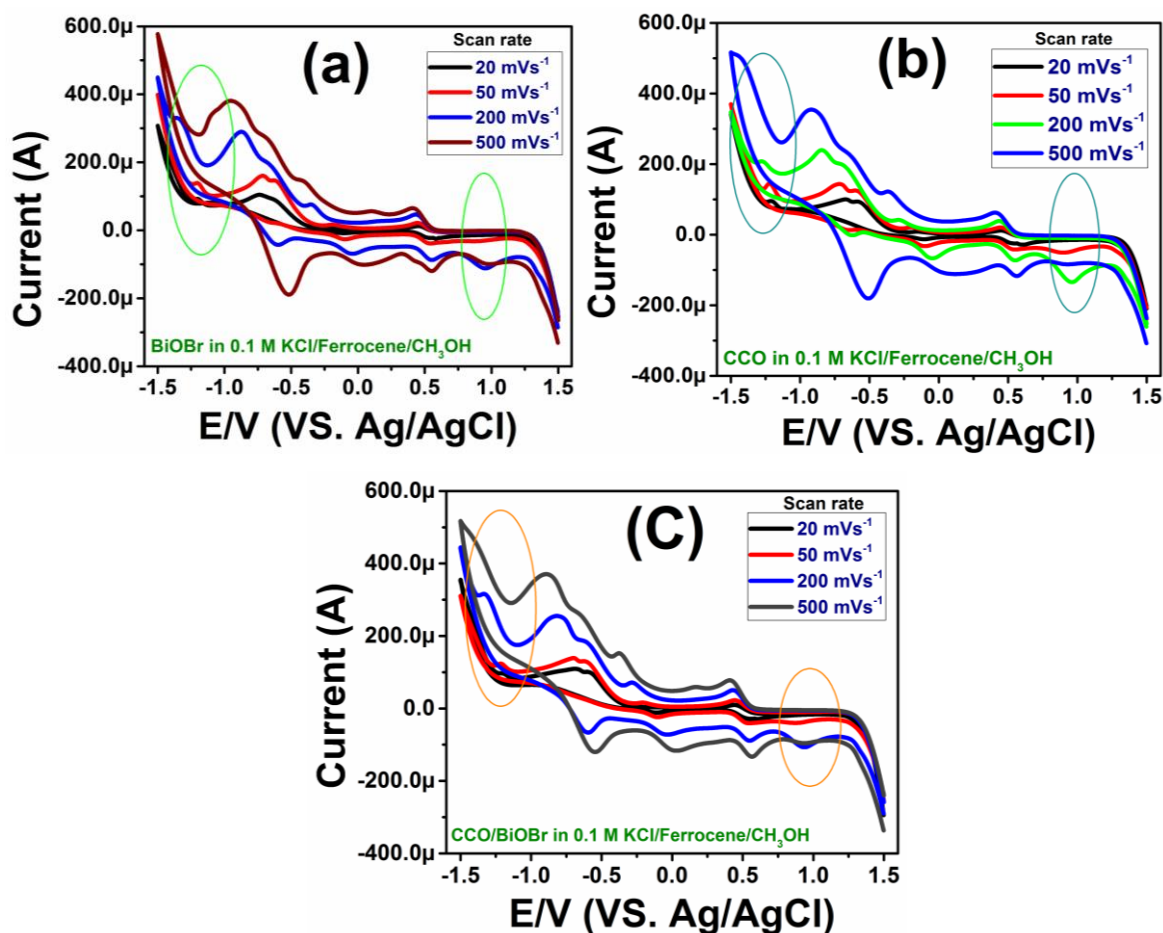


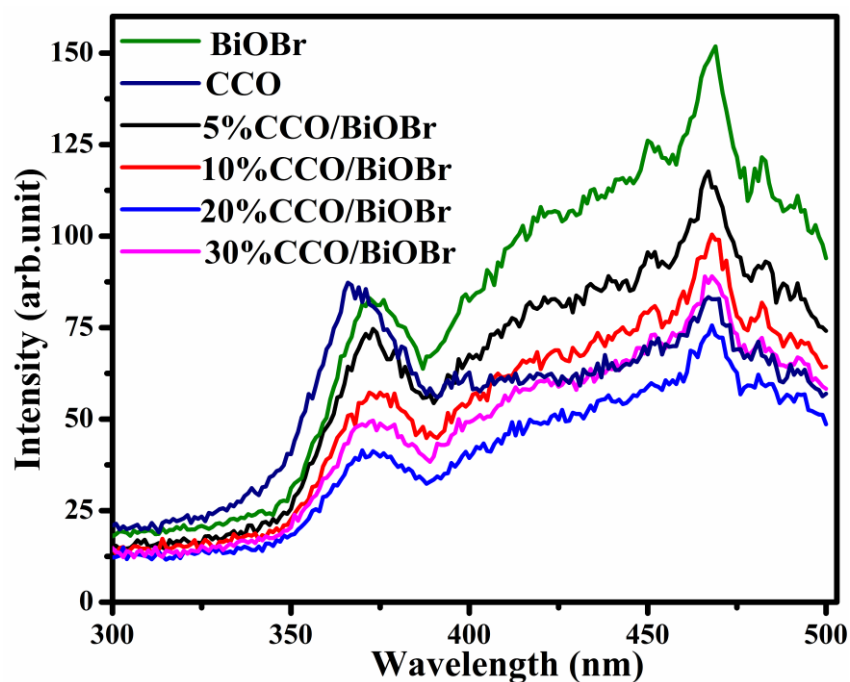
Fig. 3.9: Cyclic voltammograms of (a) BiOBr (b) CCO and (c) 20%CCO/BiOBr in 0.1 M KCl/ CH_3OH /Ferrocene with GC as the working electrode, Pt-wire as the counter electrode and Ag/AgCl as the reference electrode, the marked region represents change in the potential in each case.

Table 3.2: Assessed band gap energy values of BiOBr, CCO and 20%CCO/BiOBr.

Materials	Optical value (eV)	Electrochemical value (eV)	Reported value (eV)	Ref.
BiOBr	2.62 ($\lambda_{\max} \sim 474$ nm)	2.30	1.75-2.5	[66]
CCO	1.48 ($\lambda_{\max} \sim 800$ nm)	2.09	2.12	[67]
20%CCO/BiOBr	2.20 ($\lambda_{\max} \sim 540$ nm)	2.26	2.20	This work

3.2.6. PL spectroscopy analyses

PL spectral analysis was carried out to understand the effect of CCO on electron-hole pair recombination rate of BiOBr (see **Fig. 3.10**). While pure BiOBr exhibits emission peaks at ~ 468 nm and ~ 374 nm upon excitation at the wavelength of 260 nm, pure CCO shows emission peaks at 366 nm and 468 nm under the same excitation wavelength of BiOBr. The higher PL intensity means lower electron-hole pair separation and vice-versa [68-70]. A lower PL intensity was observed for CCO/BiOBr composite system compared to pure BiOBr that clearly suggests significant increase of electron-hole pair separation rate in the composite after introduction of CCO. The PL intensity of BiOBr in the composite system decreased gradually on CCO loading and the 20%CCO-loaded BiOBr composite sample shows the lowest PL intensity. Therefore, this composite has the maximum electron-hole separation ability among the whole composite series.

**Fig. 3.10:** PL spectra of CCO, BiOBr and CCO/BiOBr nanocomposites.

3.2.7. Transient photocurrent measurement

Then photocurrents produced by the fabricated devices (see **Chapter 2, Section 2.4.10.**) were investigated under a white light of intensity 100 mW/cm² and a bias voltage of +1 V. The **Fig. 3.11** shows the transient photocurrent response (Current vs time) for all the devices. The photocurrents were reproducible for several light on-light off cycle. Clearly, the photoresponse of 20%CCO/BiOBr composite is significantly higher than the other two.

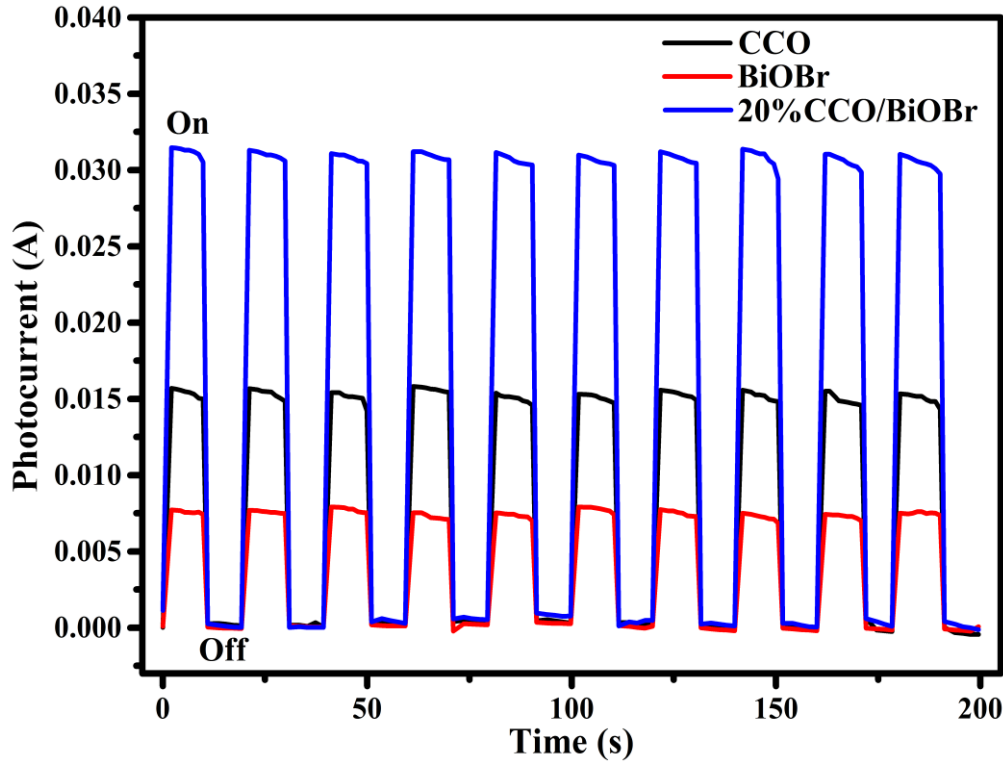


Fig. 3.11: Transient (I-t) photocurrent response for the CCO, BiOBr and 20%CCO/BiOBr.

To have a better insight of this improvement, the photosensitivity (S) and responsivity (R) were calculated. The photosensitivity has been extracted from the following equation [71-72]

$$S = \frac{I_{Ph}}{I_{Dark}} \quad (3.1)$$

Where, $I_{Ph} (= I_{Light} - I_{Dark})$ is the photocurrent, I_{Dark} is the dark current. The photosensitivity was 2.97 for CCO, 2.20 for BiOBr and 3.61 for the 20%CCO/BiOBr nanocomposite. Further, the responsivity was determined by using [72]:

$$R = \frac{I_{Ph}}{P.A} \quad (3.2)$$

Where, P is the incident optical power per unit area and A is the effective device area. The responsivity of the CCO, BiOBr and 20%CCO/BiOBr were found to be 2.13 A/W, 0.90 A/W and 4.17 A/W. So, the photosensitivity of the nanocomposite was at least 21% higher compared to one of the pure materials and the responsivity was at least 96% higher. The results indicate better potential of the 20%CCO/BiOBr for optoelectronic applications.

3.2.8. Raman spectroscopy analysis

Raman spectra have been employed for BiOBr and CCO/BiOBr composites to explore the effect of CCO on the surface properties of the composite, as shown in **Fig. 3.12**. Both BiOBr and CCO/BiOBr composite samples exhibit two Raman active modes at 57 cm^{-1} and 91 cm^{-1} corresponding to external A_{1g} and internal A_{1g} first order vibrational modes of Bi metal [17], while the band at 162.4 cm^{-1} is related to E_{1g} internal stretching mode of Bi–Br [65, 73]. On the other side, the strong Raman band at 111.8 cm^{-1} match with the A_{1g} internal Bi-Br stretching mode [17]. The Raman spectral bands of CCO/BiOBr composites show sharp reduction of peak intensity with the increase of CCO content and the two major bands experiences certain shift towards higher wave number (see **Fig. 3.12 (b)**). The decreased intensity indicates lowering of crystallinity subsequent to composite formation. Thus, the surfaces of CCO/BiOBr composites change subsequent to formation of an interface between CCO and BiOBr.

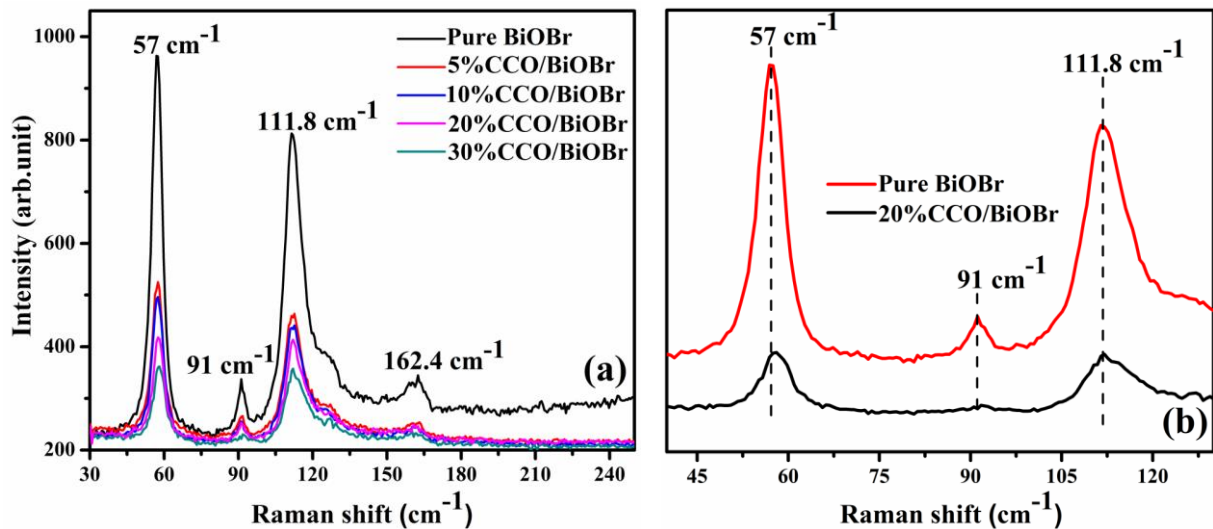


Fig. 3.12: Raman spectra of (a) BiOBr and CCO/BiOBr composites and (b) enlarged view of the most important members of the family.

3.2.9. Photocatalytic properties

3.2.9.1 Degradation of RhB

The visible light enhanced photocatalytic activities (see **Fig. 3.13**) of CCO/BiOBr nanocomposite series with respect to the parent phases have been evaluated through degradation of RhB by using a household white visible 50 W LED bulb. A blank test for RhB degradation performed in presence of visible light without any photocatalyst suggests no degradation of RhB. BiOBr shows highest dye adsorption activity after establishment of adsorption-desorption equilibrium (~30 min) under dark condition. While CCO shows very poor degradation behavior, converting nearly 1.94% after 15 min of visible LED light irradiation, pure BiOBr degrades as high as 68.78% of RhB. In presence of the nanocomposites, the observed degradations are 85.68%, 91.11%, 95.97% and 89.85%, respectively for 5%CCO/BiOBr, 10%CCO/BiOBr, 20%CCO/BiOBr and 30%CCO/BiOBr nanocomposites. These results clearly indicate that photocatalytic activity of BiOBr is enhanced after introduction of CCO in BiOBr reaching a maximum for 20% loading of CCO. Such improvement of photocatalytic activity can be explained by considering the effect of visible light absorption, band gap reduction and p-n type heterojunction of CCO/BiOBr nanocomposites.

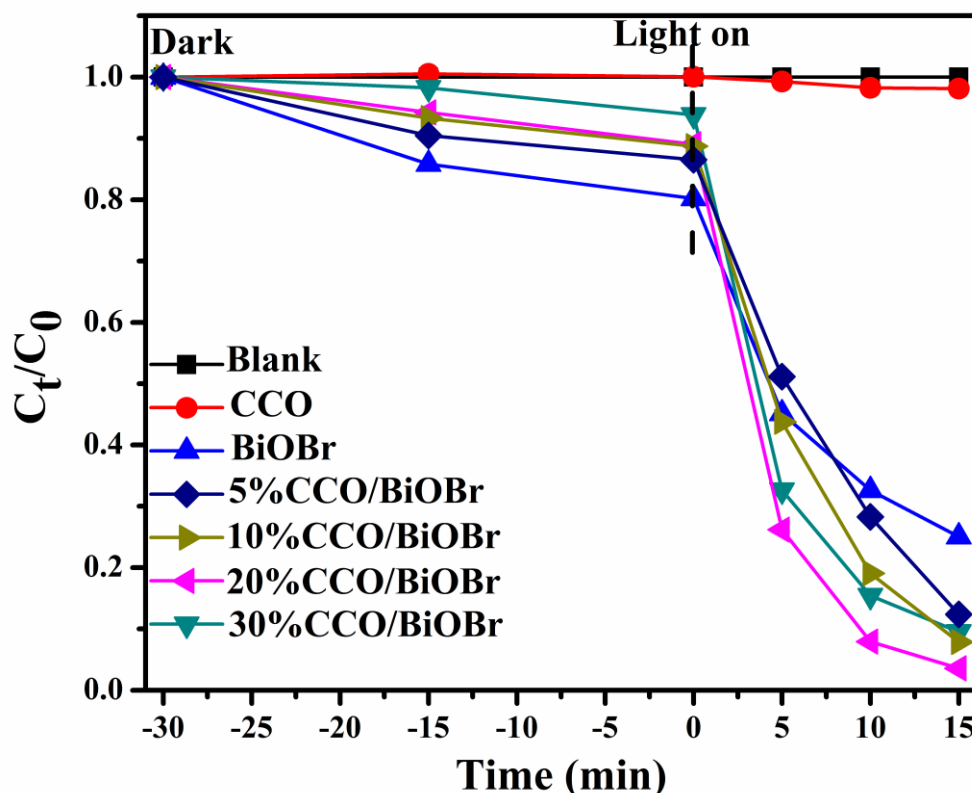


Fig. 3.13: Photocatalytic degradation behavior of BiOBr, CCO and CCO/BiOBr nanocomposites.

The degradation pathway was decided from the analysis of the time resolved spectra of RhB depicted in **Fig. 3.14** for the 20%CCO/BiOBr nanocomposite. It is clearly evident that there occurs a blue shift of RhB absorbance maxima from 553 nm to 506 nm after 15 min of light irradiation suggesting degradation of RhB via N-demethylation and N-deethylation processes [74].

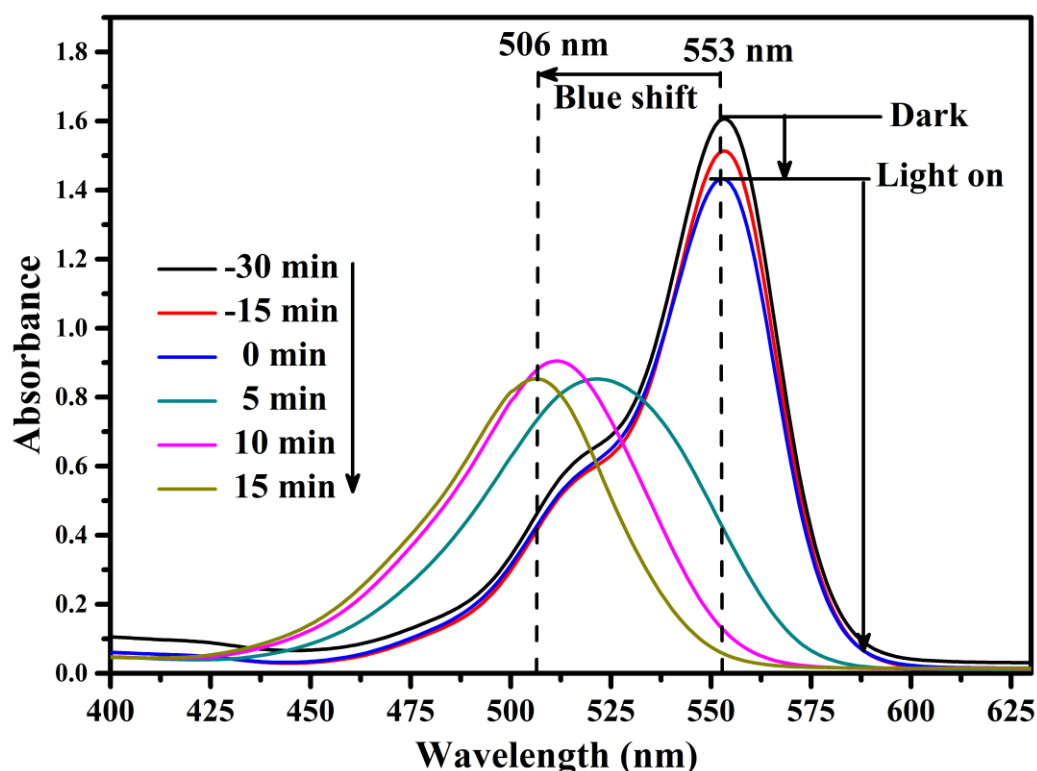


Fig. 3.14: Evidence of N-demethylation and N-deethylation processes in the photocatalytic RhB degradation for the 20%CCO/BiOBr nanocomposite sample.

The effect of catalyst mass on RhB degradation has also been investigated with optimum catalytic nanocomposite sample 20%CCO/BiOBr by varying the catalyst mass from 20 mg (0.33 g/L) to 50 mg (0.83 g/L), as shown in **Fig. 3.15**. It is observed that the degradation increases from 20 mg (0.33 g/L) to 25 mg (0.41 g/L) and then starts decreasing with further increase of catalyst mass, more particularly beyond 5 min of degradation and for the highest catalyst mass of 50 mg (0.83 g/L) where a portion of light might get reflected in presence of higher catalyst mass.

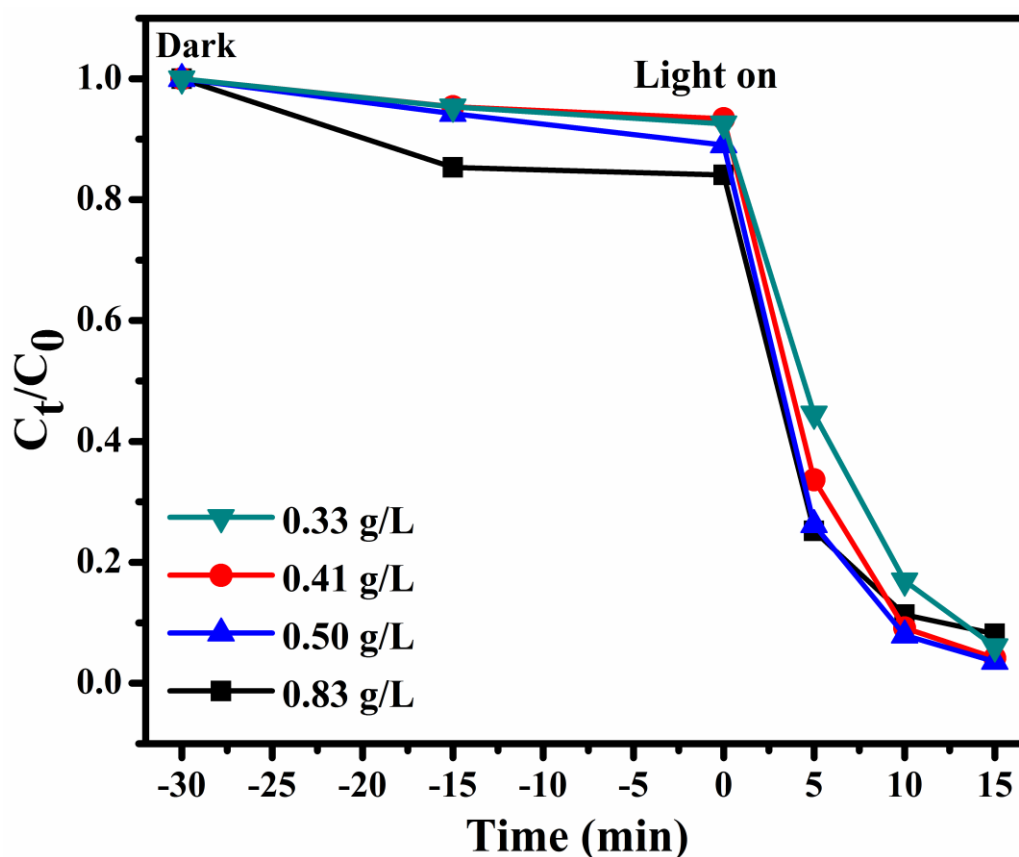


Fig. 3.15: Effect of catalyst amounts on photocatalytic RhB degradation using 20%CCO/BiOBr nanocomposite.

Kinetic behavior has been studied to quantify the photocatalytic ability of the samples. The pseudo first order reaction model has been used to investigate the kinetics of decomposition of RhB according to the following equation:

$$-\ln(C_t / C_0) = kt \quad (3.3)$$

where k , C_0 and C_t are reaction rate constant, initial concentration and concentration at time t of RhB, respectively. The values of rate constant (k) are calculated from the respective slopes of first order linearly fitted plots. As can be seen from **Fig. 3.16**, all the composite samples exhibit higher values of compared to the pure BiOBr. The rate constants of RhB photodegradation follow the order: 20%CCO/BiOBr > 30%CCO/BiOBr > 10%CCO/BiOBr > 5%CCO/BiOBr > BiOBr > CCO. The 20%CCO/BiOBr sample shows the highest k value of 0.22427 min^{-1} , which is 2.67 times higher than that of pure BiOBr confirming again the role of CCO in the composites.

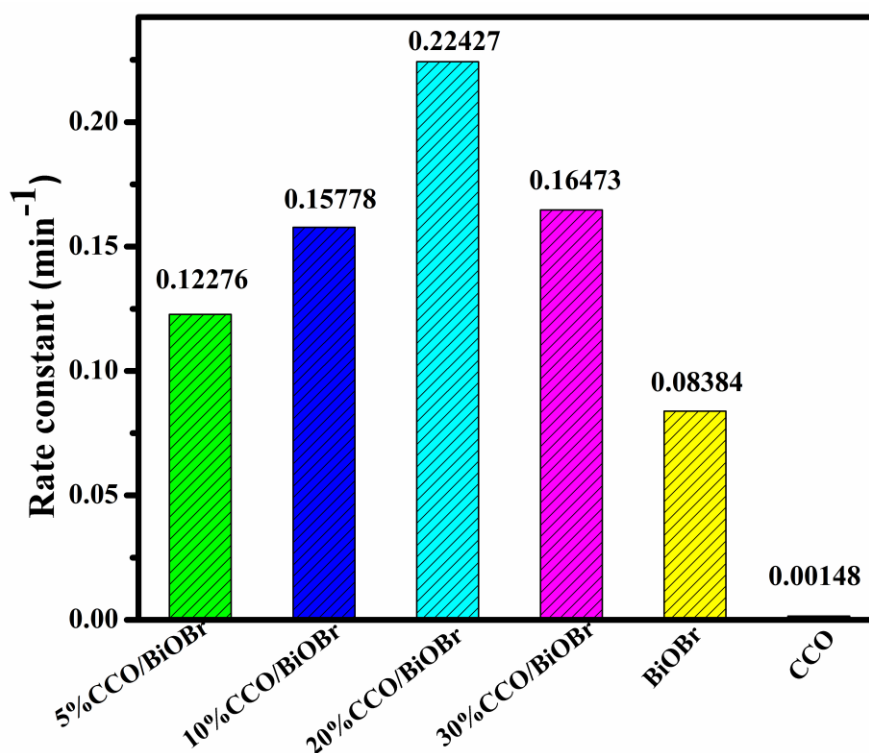


Fig. 3.16: Rate constants for various composite samples calculated for the photocatalytic RhB degradation reaction assuming first order reaction kinetics.

3.2.9.2 Comparison of RhB degradation behavior of the present nanocomposite catalyst with other relevant photocatalysts

A comparative study of RhB degradation activity behavior of various BiOBr and CCO related photocatalyst systems with CCO/BiOBr nanocomposite system for RhB degradation using various light sources (see **Table 3.3**) is presented below to support the excellent photocatalytic activity of CCO/BiOBr nanocomposite. From **Table 3.3** it is seen that N-doped BiOBr/carbon fibers [32], BiOBr/BiOI [25], BiOBr/Bi₂S₃ [15] and BiOBr/BiPO₄ [14] composite type photocatalysts require a minimum of 60 to 100 min for near complete degradation of RhB (ranging from 10 to 20 mg/L) under 500 W xenon lamp irradiation as visible light source. On the other hand, α -Fe₂O₃/BiOBr [33], NiFe₂O₄/BiOBr [37], Bi nano sphere/3D BiOBr [6], BiOBr/TiO₂ [2] and BiF₃/BiOBr [76] photocatalysts also show good catalytic activity towards RhB degradation and the complete degradation of RhB takes place in 20 to 120 min under a 300 W xenon lamp irradiation. Here it may be mentioned that the use of xenon lamp has some disadvantages like high cost, harmful and moreover its use requires a cooling system for lamp operation. Although the g-C₃N₄-NS/CuCr₂O₄ [10] photocatalyst can degrade RhB (25 mg/L) completely under 50 W LED light irradiation, it demands high catalyst mass (1000 mg) and long duration (210 min) for

Table 3.3: Comparison of photocatalytic activity behaviour (data corresponding to the optimized composition) of various BiOBr and CCO related photocatalyst systems for RhB degradation.

Photocatalyst	Light source	RhB conc. (mg/L) and volume (mL)	Catalyst dosage (mg)	Time (min) and maximum degradation (%)	Ref.
N-doped BiOBr/Carbon Fibers	500 W high pressure Xe lamp	10 and 50	30	60 and 99	[32]
α -Fe ₂ O ₃ /BiOBr	300 W Xe lamp	20 and 100	100	40 and 95	[33]
NiFe ₂ O ₄ /BiOBr	300 W Xe lamp	10 and 100	100	120 and 96	[37]
Bi nano sphere/3D BiOBr	300 W Xe lamp	5 and 100	20	40 and ~100	[6]
BiOBr/TiO ₂	300 W Xe lamp	10 and 100	25	20 and ~100	[2]
BiOBr/BiOI	500 W Xe lamp	15 and 50	50	60 and 90	[25]
g-C ₃ N ₄ -NS/CuCr ₂ O ₄	50 W LED light	25 and 250	1000	210 and 98.8	[10]
BiF ₃ /BiOBr	300 W Xe lamp	20 and 200	2000	40 and ~100	[76]
Ti doped BiOBr	11 W daylight lamp	10 and 50	50	180 and ~100	[31]
BiOBr/Bi ₂ S ₃	500 W Xe lamp	20 and 200	40	100 and ~98	[15]
BiOBr/BiPO ₄	500 W Xe lamp	10 and 300	3000	90 and 97.5	[14]
CuCr ₂ O ₄ /BiOBr	50 W domestic LED light	10 and 60	25	15 and ~96	This work

complete degradation of RhB. On the contrary, the presently reported 20%CuCr₂O₄/BiOBr photocatalyst can degrade RhB (10 mg/L) completely within a very short time (15 min) and requires much lower catalyst mass (25 mg) under 50 W domestic LED light irradiation.

3.2.9.3 Degradation activity of 20%CCO/BiOBr for colorless antibiotic-pollutant

The photocatalytic activity of CCO/BiOBr composite was also investigated for the degradation of tetracycline hydrochloride (C₂₂H₂₅ClN₂O₈, TC-HCl) under visible LED light irradiation to underscore the usefulness of this nanocomposite catalyst for the degradation of colorless pollutants. The TC-HCl is a very stable colorless antibiotic-pollutant molecule where the aromatic rings are fused together. It shows absorption peaks at 270 nm and 358 nm. In the typical TC-HCl degradation process, 25 mg of the nanocomposite photocatalyst was added to 60 mL of TC-HCl solution (10 ppm) and stirred for ~30 min in dark for adsorption-desorption equilibrium and the mixture solution was subsequently irradiated with LED light for 300 min. The TC-HCl degradation behavior of CCO/BiOBr composite is also compared with its parent components under the same conditions to understand the beneficial effect of the nanocomposite catalyst. The degradation activities and the corresponding rate constants are displayed in **Fig. 3.17(a, b)**. The figure also includes the data of a blank test to understand the effect of LED light on TC-HCl degradation in the absence of photocatalyst. The finding of blank test indicates negligible degradation of TC-HCl. On the other hand, the TC-HCl degradation percentages after 300 min of LED light irradiation are 96.7%, 56.6% and 15% for 20%CCO/BiOBr, BiOBr and CCO, respectively. Moreover, the rate constant value of 20%CCO/BiOBr is respectively ~ 19 times and 3.6 times higher than that of the parent phases CCO and BiOBr. So, the present nanocomposite catalyst is a novel catalyst that has the capability to degrade not only the harmful colored organic dye pollutants like RhB, but also the colorless highly stable antibiotic-pollutants like TC-HCl.

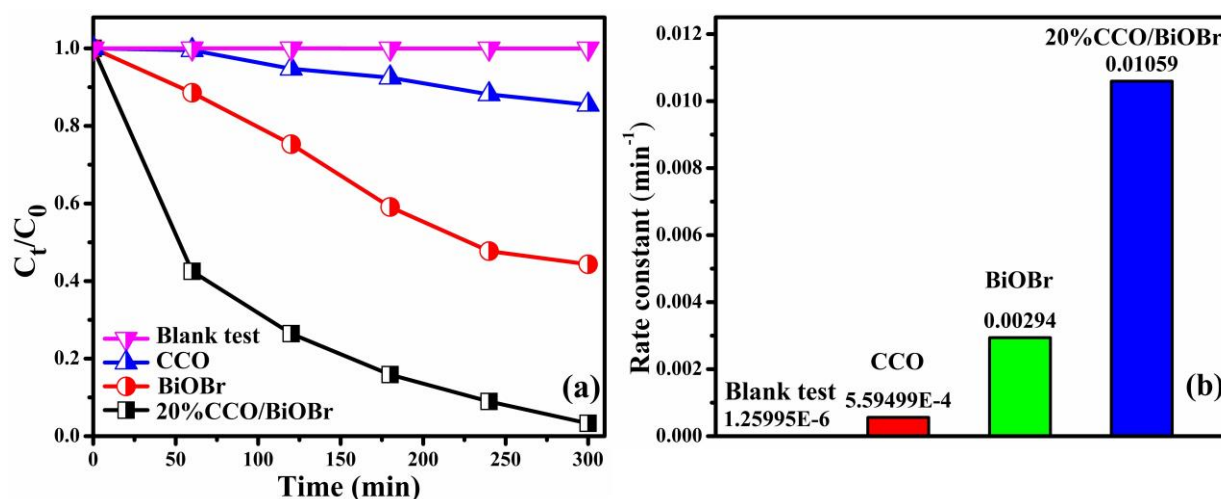


Fig. 3.17: (a) Photocatalytic activity and (b) rate constants of 20%CCO/BiOBr along with the pristine components for the degradation of TC-HCl under LED light irradiation.

3.2.9.4 Trapping of reactive species

The outcome of the radical trapping experiments shown in **Fig. 3.18** clearly suggests that RhB photodegradation efficiencies decreased significantly in presence of BQ and Na_2EDTA . Thus, both superoxide radical and hole play key role in photodegradation. The effect of quenching is marginal in presence of IPA and AgNO_3 , indicating only a little role of hydroxyl radical and electron in the present photocatalytic dye degradation.

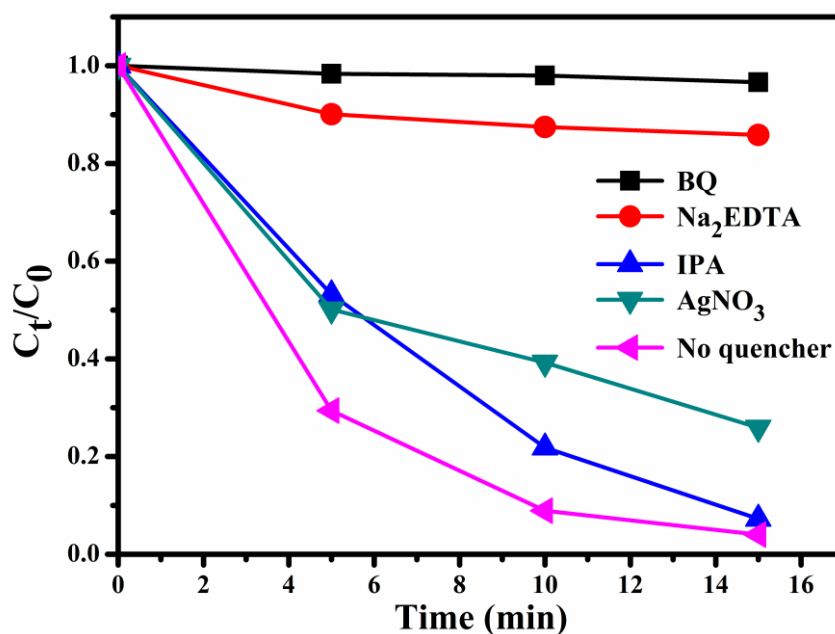


Fig. 3.18: Results of reactive species trapping experiments in the photocatalytic degradation of RhB over 20%CCO/BiOBr under LED irradiation.

3.2.9.5 Mechanism of photodegradation

To explain the photodegradation mechanism of RhB over the CCO/BiOBr composite, it is necessary to determine the band edge position of CCO and BiOBr. The band edge position of VB and CB of a semiconductor material can be calculated by using the following empirical equations:

$$E_{VB} = \chi - E^e - 0.5E_g \quad (3.4)$$

$$E_{CB} = E_{VB} + E_g \quad (3.5)$$

where E_{VB} and E_{CB} are respectively the valence band and conduction band edge potentials, χ is the M ulliken electronegativity of semiconductor material which is the geometric mean of the electronegativities of the constituent atoms present in the semiconductor. The χ values of CCO and BiOBr are 5.71 eV and 6.17 eV, respectively [54, 75]. E^e is the energy of electrons on the hydrogen scale, approximately 4.5 eV. E_g is the band gap energy of the corresponding semiconductor. The E_{VB} and E_{CB} values for BiOBr are calculated to be 2.98 eV and 0.36 eV, respectively and those of CCO are estimated to be 1.95 eV and 0.47 eV, respectively.

On the basis of these bands edge positions, photodegradation as well as radical trapping experimental data, a plausible photocatalytic degradation mechanism based on improved photo electron-hole separation and migration efficiency of the CCO/BiOBr composite is schematically illustrated in the upper panel of **Fig. 3.19**. Since, CCO is a p-type semiconductor [54], its Fermi energy level is located near to the VB, while BiOBr is an n-type semiconductor [12] whose Fermi energy level lies close to its CB. When the p-n heterojunction is formed between CCO and BiOBr, the electrons from BiOBr diffuse into CCO, and the holes from CCO diffuse into BiOBr. These flows of electrons and holes create a negatively charged region in the CCO side and positively charged region in the BiOBr side at the heterojunction together with the formation of a region depleted of electrons and holes, called depletion region at the interface. At equilibrium, the Fermi energy levels of both the semiconductor materials coincide and this has the effect of rearranging the VBs and CBs of CCO and BiOBr. Thus the VB and CB energies of BiOBr and CCO are shifted downward and upward, respectively. Under visible LED irradiation, the CCO and BiOBr are both excited simultaneously and the excited electrons of CCO in its CB are transferred to the CB of BiOBr and the holes of BiOBr in its VB migrate to the valence band of CCO. This is the main reason for the lowering of electron-hole pair recombination, which in effect enhances

the involvement of the reactive species in the photocatalytic degradation process thereby increasing the photoactivity of the composite catalyst.

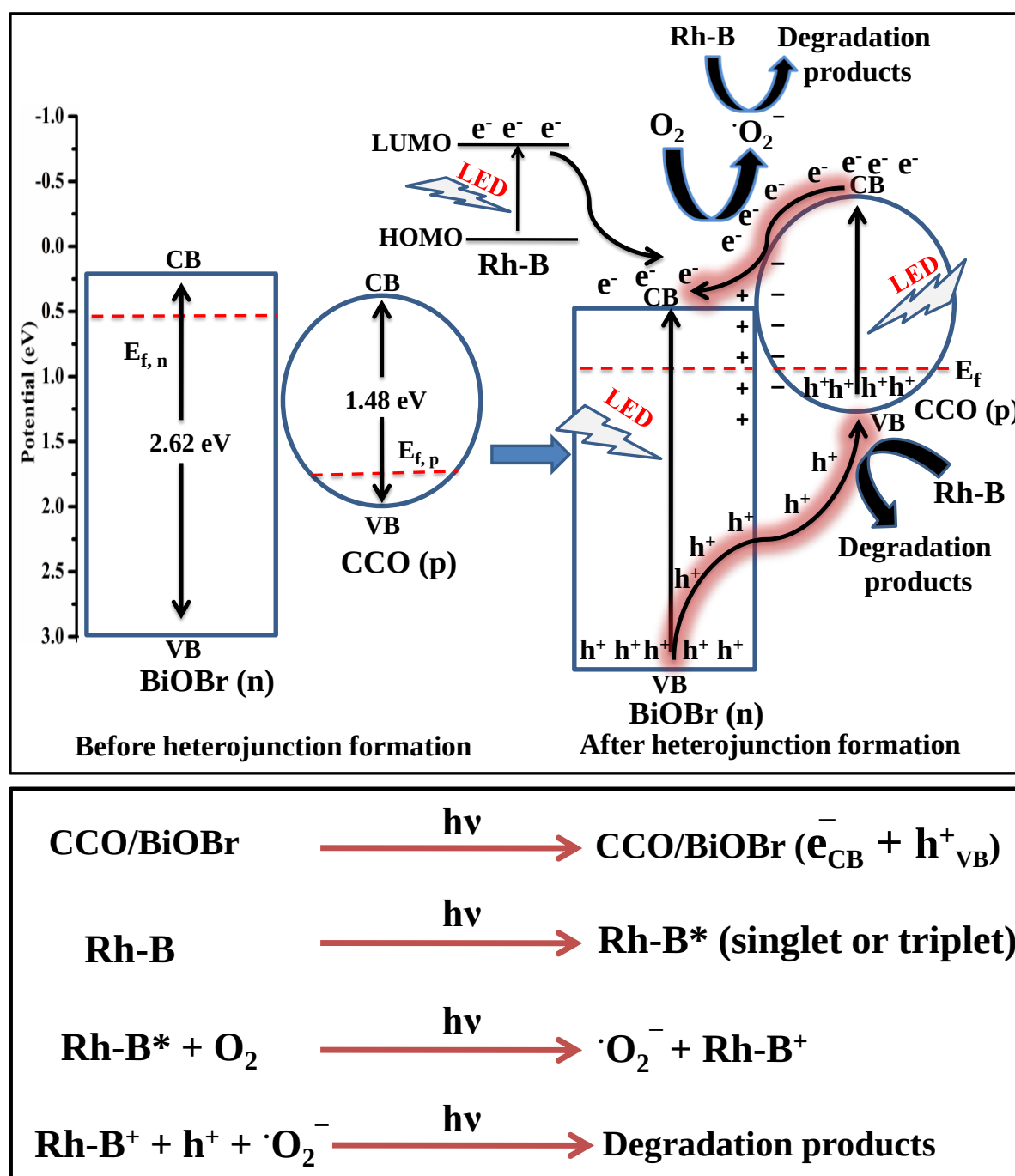


Fig. 3.19: Proposed pathway of photocatalytic RhB degradation (upper panel) and the essential steps of photodegradation (lower panel) in CCO/BiOBr composite under visible LED irradiation.

In addition, a dye sensitized photocatalytic reaction may also occur in this composite system [76]. Under the visible LED irradiation, the RhB dye molecules are excited into a singlet or triplet state (RhB^*) and excited RhB^* is more effective to oxidize degradation because the reduction potential of RhB^* is lower than that of $\text{O}_2/\bullet\text{O}_2^-$ (-1.42 V vs -0.33V). The excited electrons on the dye molecules can easily be transferred to the catalyst surface which reacts with the adsorbed oxygen to form super oxide radicals. As the VB and CB energies of CCO and BiOBr are higher than the HOMO-LUMO energies of RhB^* , the photo-excited electrons of RhB in LUMO are preferentially transferred to the catalyst surface rather than recombining with its HOMO facilitating the reduction of abundant oxygen to superoxide radicals. In the absence of any photocatalyst, the newly generated electrons of RhB in the LUMO quickly combine with its HOMO, suggesting a very negligible role of RhB self-degradation.

Since the VB potential of CCO (1.95 eV) is higher than the HOMO of RhB (0.80 eV), so the holes in CCO can also degrade the RhB dye directly. Thus the two major reactive species formed during the photocatalytic degradation process are hole and superoxide radical, which is already supported by the radical trapping experiment. The essential steps of RhB degradation can thus be represented as listed in the lower panel of **Fig. 3.19**.

3.2.9.6 Recycling characteristics

The recycling activity and hence the stability of catalyst is an important feature of photocatalysis and it was evaluated by using the optimal 20%CCO/BiOBr catalyst for four consecutive cycles under the same conditions. Before every run, the catalyst was separated by centrifugation and washed with Milli-Q water and isopropanol for three times and then dried at $80\text{ }^\circ\text{C}$ for 2 h. The activity data are shown in **Fig. 3.20(a)**. As can be seen from the figure, RhB degradation percentage is decreased by 10% after the 4th run and this is ascribed to be due to deactivation of surface active sites caused primarily by the deposition of small organic molecules produced from RhB degradation together with minor role of loss of some catalyst amount during the washing process that cannot be avoided.

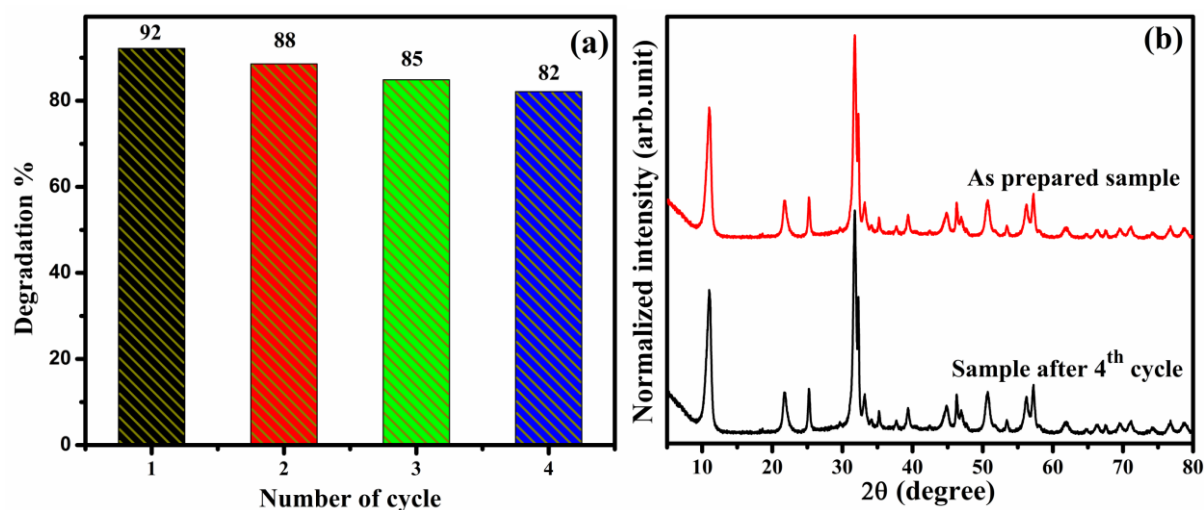


Fig. 3.20: (a) Recycling activity and (b) normalized XRD patterns of recycled (after 4th run) catalyst along with the as prepared sample of 20%CCO/BiOBr catalyst.

The bulk crystalline phase of the catalyst remains unchanged as evident from the powder XRD data of the sample collected after the fourth cycle of operation (see **Fig. 3.20(b)**). Therefore, our study suggests CCO/BiOBr composite catalyst as an efficient photocatalyst for the treatment of industrial wastewater containing harmful dyes like RhB due to its high recycling performance and phase stability.

3.3. Conclusions

In conclusion, spherical shaped CCO has been synthesized by tartaric acid sol-gel method. These CCO spheres have been successfully decorated onto BiOBr plates in a single pot co-precipitation method to synthesize CCO/BiOBr composite. All the parent and composite phases have been characterized using several physicochemical techniques. The XRD patterns confirm high crystallinity and purity of all the samples. FESEM, TEM, HRTEM and EDX analysis substantiate the morphologies, shape, size, crystallinity and chemical composition as well as chemical homogeneity of the samples. XPS analysis validates the chemical environment of the cations in all the samples. The detailed optical investigations using UV-Vis DRS, PL and Raman scattering substantiate the electronic states and associated changes in band structure in composites. There is huge improvement in visible light absorption of BiOBr in presence of CCO. Such well characterized samples have been employed to investigate the photocatalytic degradation of RhB and TC-HCl in presence of a domestic LED light. Our investigations underscore the remarkable improvement in photocatalytic degradation of RhB and TC-HCl using the CCO/BiOBr nanocomposite

photocatalyst. The maximum efficiency is achieved for 20%CCO/BiOBr sample. All the composites exhibit reasonable recycling behaviour. A plausible mechanistic path of the whole photocatalytic process based on intermediate trapping experiments has been presented. It is believe that the present finding reveals a leap to wastewater treatment specially to degrade the harmful organic dye RhB and colorless antibiotic TC-HCl using conventional household light source and cheap nanocomposite catalyst.

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Chapter 4

Studies on $\text{CuCr}_2\text{O}_4/\text{CeO}_2$ nanocomposite photocatalyst for Fenton like degradation behavior of azo dyes

Chapter abstract

This chapter is focused on the CCO/CeO_2 nanocomposite system as a highly active and recyclable heterogeneous Fenton like catalyst for the degradation of azo dyes like RhB, MB, and MO under domestic LED light irradiation. Extensive characterizations of the samples were performed using several physicochemical techniques. A careful monitoring of photo-activities reveals the best performance of 10% CCO/CeO_2 sample showing complete degradation of 10 ppm RhB, MB, and MO dyes within 15, 20 and 30 min, respectively, in presence of 4 mM of H_2O_2 . The CCO/CeO_2 nanocomposite material shows an enhanced visible light absorption. The radical trapping and fluorescence methods suggest the generation of $\cdot\text{OH}$ in the catalytic pathways. The Fenton like catalytic behavior of marginally active CeO_2 is dramatically enhanced in presence of CCO in the nanocomposite due to larger creation of oxygen vacancy. Finally, plausible mechanistic pathways for Fenton like degradation have been presented at the end.

4.1. Introduction

Plentiful inorganic compounds from different classes of materials have been investigated by the materials researchers till date for their suitability in varieties of catalytic applications including photocatalysis [1-10]. Apart from their plethora of different properties, the TMOs are one of those promising materials exhibiting potential photocatalytic application as well. Furthermore, the driving force of vast amount of research on TMOs arises from their abundance, chemical as well as thermal stability under the operating conditions and ease of synthesis due to plenty of available synthetic methods. The spinel type $[\text{A}]_t[\text{B}_2]_o\text{O}_4$ oxides are of special significance in this regard and are extensively investigated. The spinel structure can accommodate a wide range of metal ions in their variable oxidation states (+1 to +6) in both the tetrahedral and the octahedral coordination. This structural feature provides an excellent opportunity to bring different metal ions of catalytically active binary oxides into a single structural network. They exhibit attractive photocatalytic activities due to their narrow optical bandgap causing efficient absorption of light in the visible region [1-2, 9]. In the past few decades, transition metal based spinel oxide materials have received major attention of many researchers because of their potential to solve the major problems of environmental water pollution [1–4], energy storage [5, 6], liquid phase organic transformation [7, 8] and hydrogen production [9, 10]. Among the transition metals based spinel oxides, CuCr_2O_4 is

regarded as a prominent candidate for its wide range of applications in photocatalytic dye degradation for wastewater treatment [11–13], photocatalytic H₂ production [14, 15], supercapacitor [16], organic transformation [17–19] and glycerol hydrogenolysis [20]. However, recombination rate of the photogenerated electron-hole pair is high for CuCr₂O₄ [12] which restrict the performance of CuCr₂O₄ in photocatalytic application like degradation of harmful dyes present in wastewater from different sources. Consequently, various attempts have been made to improve the photocatalytic activity of CuCr₂O₄, for instance in situ formation of heterojunction with other oxide [11], composite formation with nonmetals like g-C₃N₄ [21] or by changing the morphology of CuCr₂O₄ through modification of synthesis conditions [22].

Use of CeO₂ in heterogeneous Fenton like reaction primarily relies upon its easy availability and involvement of the stable Ce³⁺/Ce⁴⁺ redox couple [23–30]. The Fenton like mechanism of CeO₂–H₂O₂ system is very interesting and different from the classical Fenton reaction with Fe²⁺–H₂O₂ system [31–36]. The improved Fenton like activity is directly related to surface oxygen defect, redox reaction, and the Ce³⁺ ion concentration on the CeO₂ surface [37–44]. Many research groups have been attempting to improve the Fenton like catalytic activity of CeO₂ by doping of metals [37–41, 45–52] or through composite formation with other semiconductor oxides [46, 53–54]. The modulation of effective interaction and redox reaction at the interface of composite is responsible for improved functionality [47, 55]. Researchers have thus capitalized the photo Fenton like reaction ability of CeO₂ based Fenton like system for further improvement of its Fenton like activity where the oxidation/ reduction reaction is enhanced by the photoexcited electrons [23, 56–57]. So a composite formation with other semiconductor oxides like CuCr₂O₄ is expected to be a better choice for greater charge separation in CeO₂.

Bearing all the beneficial effect of the pristine CuCr₂O₄ and CeO₂ oxides in mind, we have investigated a series of CuCr₂O₄/CeO₂ nanocomposites to exploit their interfacial phenomena for improved functionality with emphasis on photocatalytic dye degradation for wastewater treatment. We were encouraged to notice that the visible light absorption is dramatically enhanced in CuCr₂O₄/CeO₂ nanocomposites, which is definitely an indicator of potentially novel photoactivity of the nanocomposite material. The well characterized nanocomposites have subsequently been applied as catalyst in heterogeneous Fenton like reaction with H₂O₂ activation for the degradation of azo dyes such as RhB, MB, and MO under household visible LED light irradiation. Such enhanced catalytic behavior has been

attributed to the band bending, redox reaction, improved charge separation and oxygen vacancy in the nanocomposite system.

4.2. Results and discussion

4.2.1. Powder X-ray diffraction analyses

The powder XRD patterns of CeO₂, CCO and their nanocomposites are shown in **Fig. 4.1**. CeO₂ adopts in fluorite type structure and the corresponding pattern matches to JCPDS file no. 34-0394. On the other hand, unlike other spinels, CCO crystallizes in non-cubic tetragonal structure due to the presence of Jahn-Teller (JT) active Cu²⁺ ions and corresponds to JCPDS file no. 72-1212. In the CCO/CeO₂ nanocomposite system, the diffraction peaks with 2θ values of 28.55°, 32.93°, 47.4°, 56.3°, 59°, 69.4° and 76.7° correspond to fluorite type CeO₂ and the 2θ values of 31°, 35.1°, 37.7° and 42.2° are attributed to CCO. Hence, the powder XRD results indicate that CCO/CeO₂ nanocomposite system contains both CeO₂ and CCO phases without any additional phase (s) as impurity. Here it may be noted that the peaks for 5% and 10%CCO/CeO₂ nanocomposites at the above-mentioned 2θ values of CCO aren't obvious, while those of 20%CCO/CeO₂ are clearly distinguishable. This is ascribed to be due to finely dispersed nanodimensional CCO in the synthesized composites of lower CCO loading. Such apparent disappearance of diffraction peak could be due to its smearing out in the background for huge broadening of finely dispersed particles of smaller amounts of CCO. At 20%CCO loading, it appears that some of the CCO are bit agglomerated and hence they contribute to CCO related peaks with detectable intensity in the diffraction pattern of the corresponding composite. Evidence of highly dispersed CCO presence in 10%CCO/CeO₂ nanocomposite will be made clearer from HRTEM and EDS elemental mapping analyses as well as XPS studies in the following sections. The average particle size obtained from powder patterns using Scherrer's formula are ~14 and 9 nm for pure CCO and CeO₂, respectively. The size of the nanocomposite particles that are dominated by CeO₂ ranges from 10 to 14 nm for all the samples.

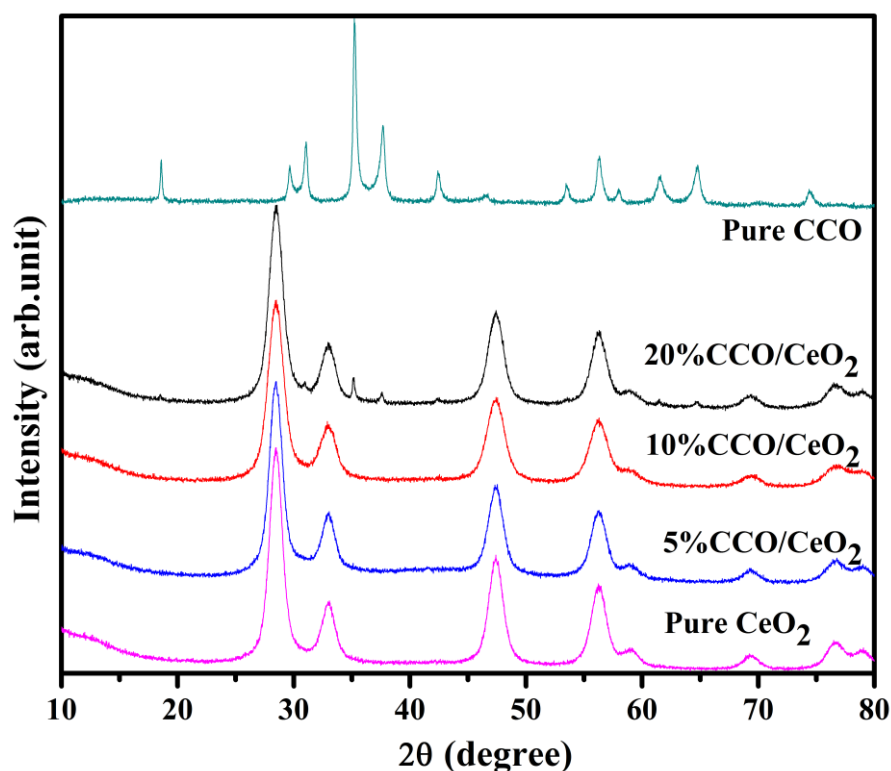


Fig. 4.1: Powder XRD patterns of as-synthesized CCO, CeO₂ and CCO/CeO₂ nanocomposites.

4.2.2. Morphology and microstructure analyses

Figs. 4.2(a-c) show the low resolution TEM images of CCO, CeO₂ and 10%CCO/CeO₂ nanocomposite. The sol-gel synthesized CCO particles are mostly agglomerated in nature, semi-spherical in shape and sizes of about 15 nm with narrow size distribution (**Fig. 4.2(a)**). The TEM image of CeO₂ indicates a spherical like morphology with smaller sized particles of ~10 nm and the particles are also present in an aggregated form (**Fig. 4.2(b)**). However, the nanocomposites are predominated by much smaller sized (4–6 nm) spherical shaped particles of CeO₂ obtained through coprecipitation in presence of dispersed CCO (see **Fig. 4.2(c)**). **Fig. 4.2(d)** shows a representative HRTEM image of CeO₂ in which the lattice-fringe analysis unveils a *d*-spacing of nearly 0.318 nm corresponding to the (111) lattice plane of CeO₂. **Fig. 4.2(e)** shows a detailed HRTEM image of 10% CCO/CeO₂ in which two kinds of lattice fringe patterns can be clearly distinguished. Consequently, the *d* spacing of about 0.318 and 0.3 nm correspond to (111) and (220) planes of CeO₂ and CCO, respectively. The chemical homogeneity of the nanocomposite sample is substantiated from the EDS elemental mapping shown in **Fig. 4.2(f-i)**. It shows the homogeneous distribution of Ce, Cu, Cr and O in the nanocomposite.

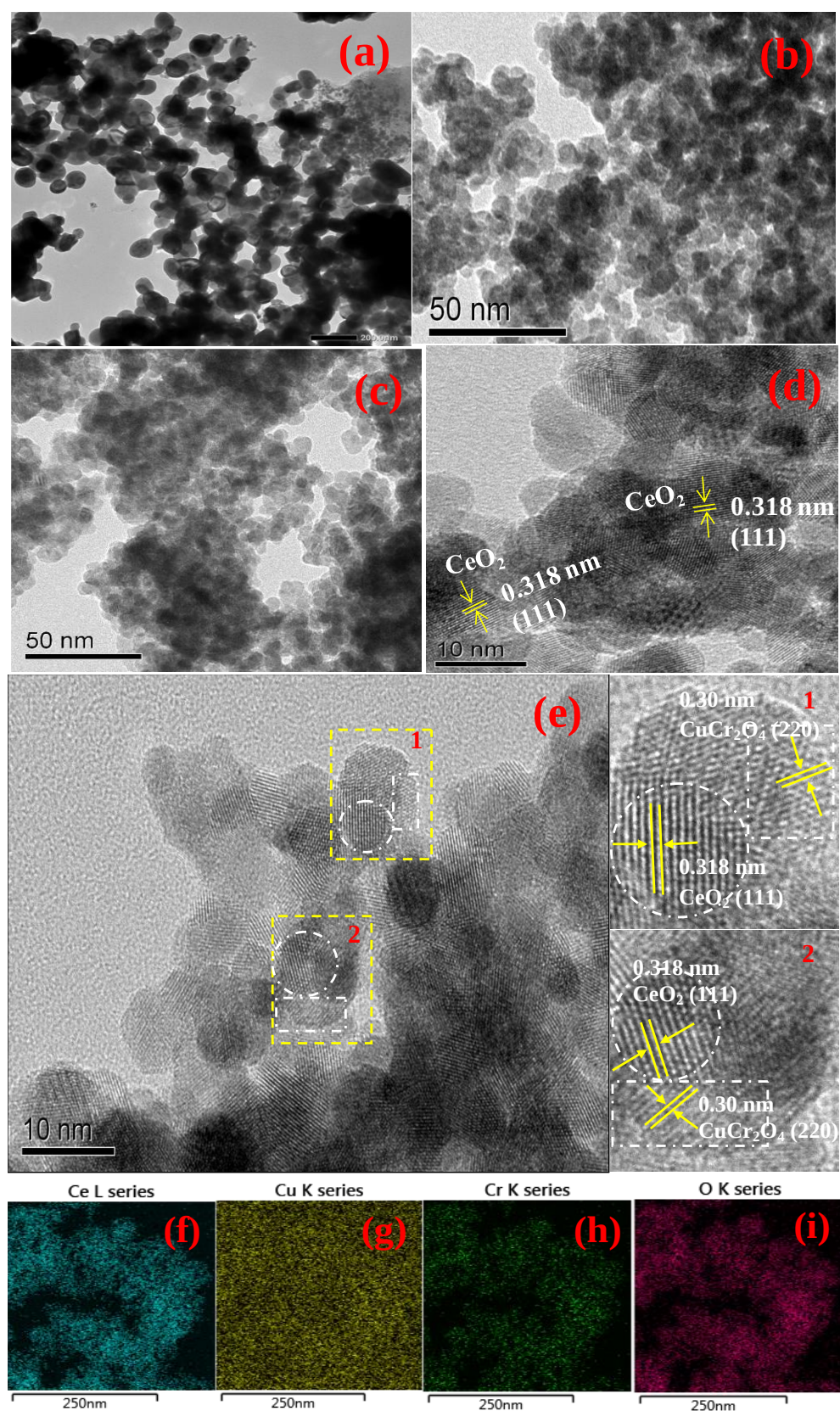


Fig. 4.2: Low resolution TEM images of (a) CCO, (b) CeO₂ and (c) 10%CCO/CeO₂; HRTEM images of (d) CeO₂ and (e) 10%CCO/CeO₂ and (f-i) EDS elemental mapping analysis of 10%CCO/CeO₂ nanocomposite.

4.2.3. BET surface area analyses

The porous structural parameters are listed in **Table 4.1**, while the adsorption–desorption isotherm of all the photocatalysts are shown in **Fig. 4.3** and the corresponding pore size distribution results are shown in the insets of **Fig. 4.3**. The S_{BET} 's of bare CeO_2 and CCO are 91 and 12 $\text{m}^2 \text{g}^{-1}$, respectively. Subsequent to nanocomposite formation, the S_{BET} decreases considerably to 55 $\text{m}^2 \text{g}^{-1}$ for 5–10%CCO/ CeO_2 that decreases further to 48 $\text{m}^2 \text{g}^{-1}$ for 20%CCO/ CeO_2 . These results demonstrate that the S_{BET} of CeO_2 decreases in subsequent nanocomposite materials with increase in the amounts of CCO. It is evident from the TEM and HRTEM images of 10%CCO/ CeO_2 nanocomposite that the surface of smaller CeO_2 particles is mostly covered by the larger CCO particles. This results in higher aggregation between CCO and CeO_2 in the nanocomposite form causing a lowering of surface areas. While loading of 5–10%CCO causes major decrease, the effect of 20%CCO loading is comparatively small.

Table 4.1: Textural and structural characteristics of CeO_2 , CCO and CCO/ CeO_2 nanocomposites.

Sample name	Scherrer size (nm)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore size (nm)	$I_{600}/I_{465.6}$
CeO_2	9	91	0.158	1.324	0.055
CCO	14	12	0.045	1.324	–
5%CCO/ CeO_2	10	55	0.111	1.385	0.295
10%CCO/ CeO_2	12	55	0.090	1.324	0.509
20%CCO/ CeO_2	14	48	0.095	1.324	0.405

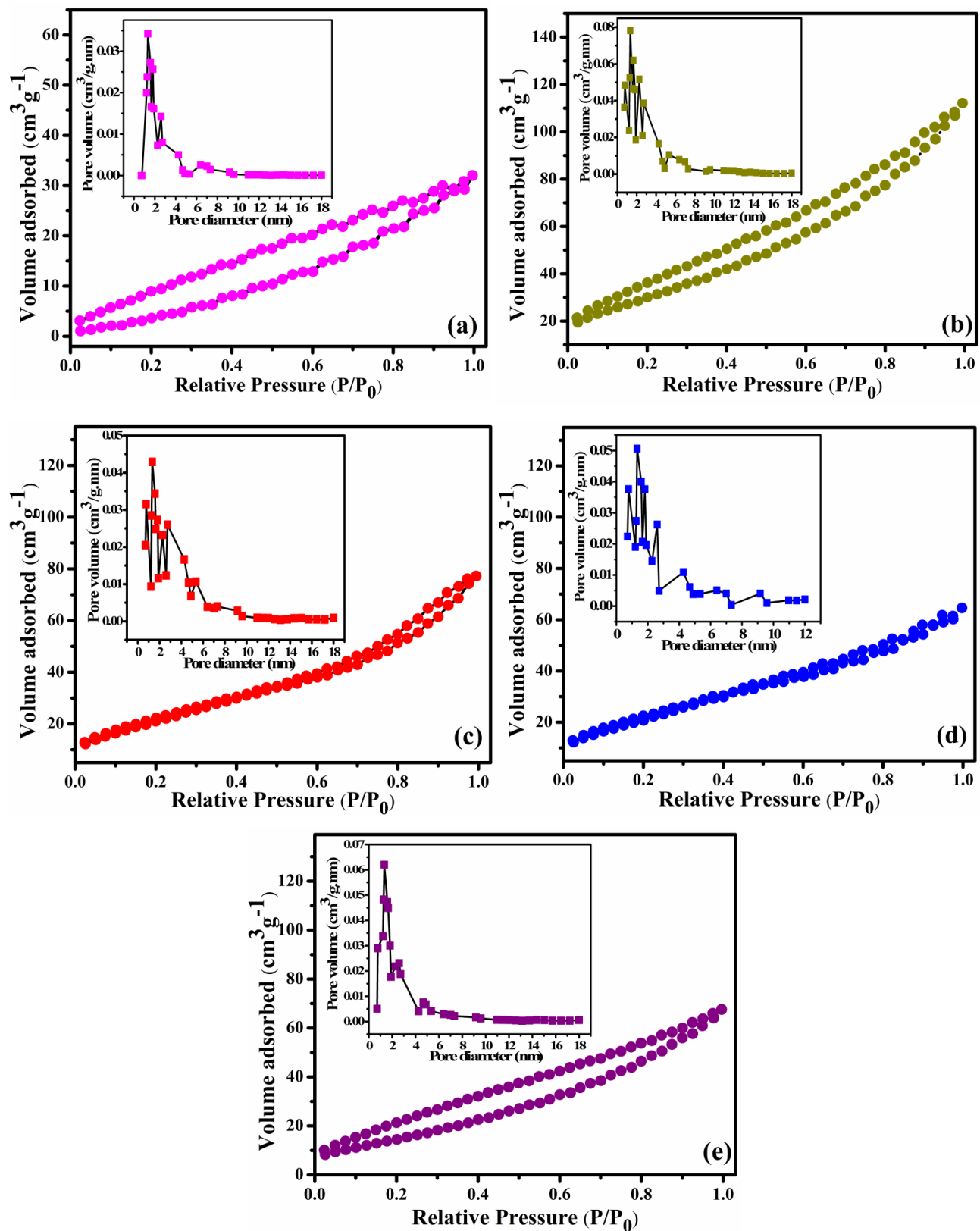


Fig. 4.3: Nitrogen adsorption-desorption isotherms and pore size distribution curves (in the inset) of (a) CCO, (b) CeO_2 , (c) 5%CCO/ CeO_2 , (d) 10%CCO/ CeO_2 and (e) 20%CCO/ CeO_2 sample.

4.2.4. Raman spectroscopy analyses

The Raman spectroscopy was investigated to characterize the structural defect (surface and bulk) of CeO₂ and CCO/CeO₂ nanocomposite samples. The spectral results are shown in **Fig. 4.4(a, b)**. A highly intense Raman band at 465.6 cm⁻¹ is observed for bare CeO₂ (see **Fig. 4.4(a)**) which represents the first order F_{2g} mode of the cubic fluorite structure. The peak intensity of this F_{2g} mode of CeO₂ in the CCO/CeO₂ nanocomposite is considerably reduced and shifted towards the lower wave number from 465.6 to 462.2 cm⁻¹ (see **Fig. 4.4(b)**). This suggests that the structural property (mainly oxygen vacancy) of CeO₂ is affected by CCO. The Raman band at 600 cm⁻¹ observed for CeO₂ and all the nanocomposite corresponds to the defect induced band (D band) which is directly related to the oxygen vacancy of CeO₂. The concentration of oxygen vacancies was determined by taking the intensity ratio of Raman band at 600 cm⁻¹ to that at 465.6 cm⁻¹ (i.e., I₆₀₀/I_{465.6}) [58]. The I₆₀₀/I_{465.6} values of all the samples are listed in **Table 4.1**. The relative intensity ratio of the nanocomposite is increased after the introduction of CCO onto CeO₂ surface, which suggests that CCO can enhance the surface oxygen vacancy of CeO₂ in the nanocomposite. The value of I₆₀₀/I_{465.6} is found to increase from 5%CCO/CeO₂ to 10%CCO/CeO₂, where it is having the maximum value of 0.509, and then it is decreased for the highest CCO loaded sample, 20%CCO/CeO₂ nanocomposite.

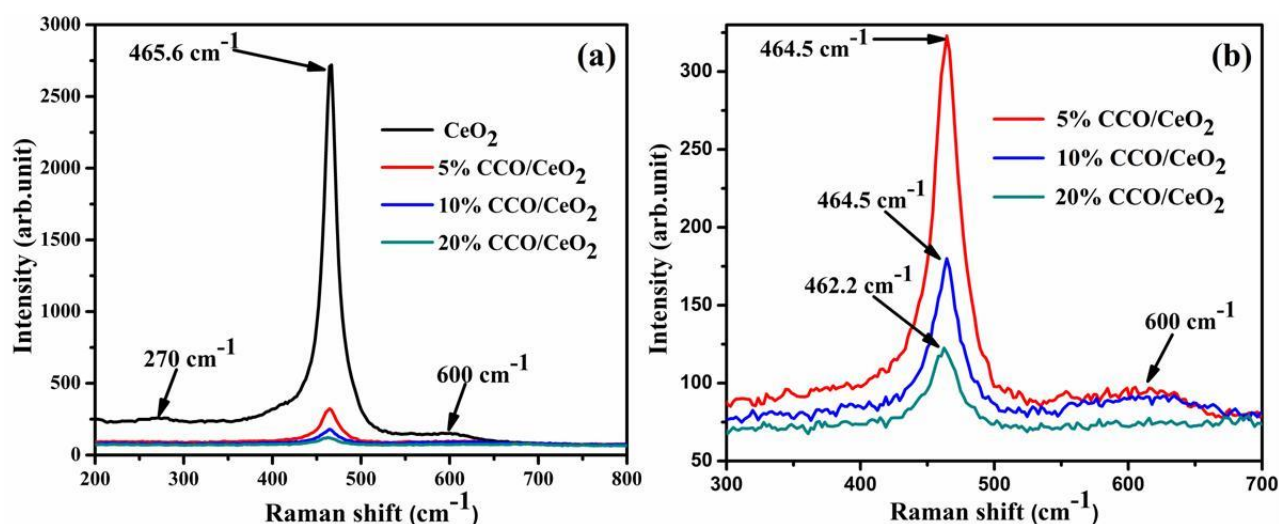


Fig. 4.4: Raman spectra of (a) CCO, CeO₂ and various CCO/CeO₂ nanocomposites and (b) enlarged spectral view of all the nanocomposites.

4.2.5. XPS analyses

XPS of CeO₂ and 10%CCO/CeO₂ nanocomposite have been recorded to understand the nature of surface species in the catalysts. Ce 3d, Cu 2p, Cr 2p and O 1s core level spectra of respective photocatalysts are displayed in **Fig. 4.5**. The observed broad nature of Ce 3d spectral envelopes of CeO₂ and 10%CCO/CeO₂ as shown in **Fig. 4.5(a)** indicates the presence of Ce⁴⁺ and Ce³⁺ species in the photocatalysts and they are decomposed into several Ce 3d_{5/2,3/2} spin-orbit doublets by curve-fitting. The curve-fitted Ce 3d core level spectra show 10 peaks wherein each 5 doublet peaks are associated with 3d_{5/2} (marked as v) and 3d_{3/2} (marked as u) components. The three sets of doublet peaks at 882.6 and 901.0 eV (marked as v–u), 888.5 and 906.9 eV (marked as v'–u') and 898.1 and 916.5 eV (marked as v''–u'') represent Ce⁴⁺ species in the samples. Peaks at 881.3 and 899.2 eV (marked as v₀–u₀) and 885.4 and 903.6 eV (marked as v'–u') correspond to Ce³⁺ species. Observed binding energy peak values agree well with the literature values [59-60]. Comparatively well separated u'' peak at 916.5 eV from the rest of the peaks in the spectrum signifies the presence of Ce⁴⁺ species in Ce compounds. Observed peaks of v'' and u'' are related to primary photoionization from Ce⁴⁺ with Ce3d⁹4f⁰O2p⁶ final state. Lower binding energy peaks of v'–u' and v–u correspond to the Ce3d⁹4f¹O2p⁵ and Ce3d⁹4f²O2p⁴ final states shake-down satellite features [59-60]. Satellites are caused by the facilitation of ligand O 2p to metal Ce 4f charge transfer by primary photoionization process. In Ce³⁺ related peaks, higher binding energy v'–u' spin-orbit doublets are attributed to main photoionization from Ce3d⁹4f¹O2p⁶ final state, whereas lower binding energy v₀–u₀ peaks stand for Ce3d⁹4f²O2p⁵ final state shake-down satellites [59-60]. Peak areas (A) of Ce⁴⁺ and Ce³⁺ components are commonly used to estimate their relative concentrations (C) in the samples using the following equations [59].

$$A_{\text{Ce}^{3+}} = A_{v_0} + A_{u_0} + A_{v'} + A_{u'} \quad (4.1)$$

$$A_{\text{Ce}^{4+}} = A_v + A_u + A_{v''} + A_{u''} + A_{v'''} + A_{u'''} \quad (4.2)$$

$$C_{\text{Ce}^{3+}} = \frac{A_{\text{Ce}^{3+}}}{A_{\text{Ce}^{4+}} + A_{\text{Ce}^{3+}}} \quad (4.3)$$

Accordingly, surface concentrations of Ce⁴⁺ species in CeO₂ and 10%CCO/CeO₂ are estimated to be 78 and 68%, respectively and rest amount are Ce³⁺ species. Thus, XPS analysis demonstrate that concentration of Ce³⁺ species gets enhanced in 10%CCO/CeO₂ nanocomposite in comparison with CeO₂.

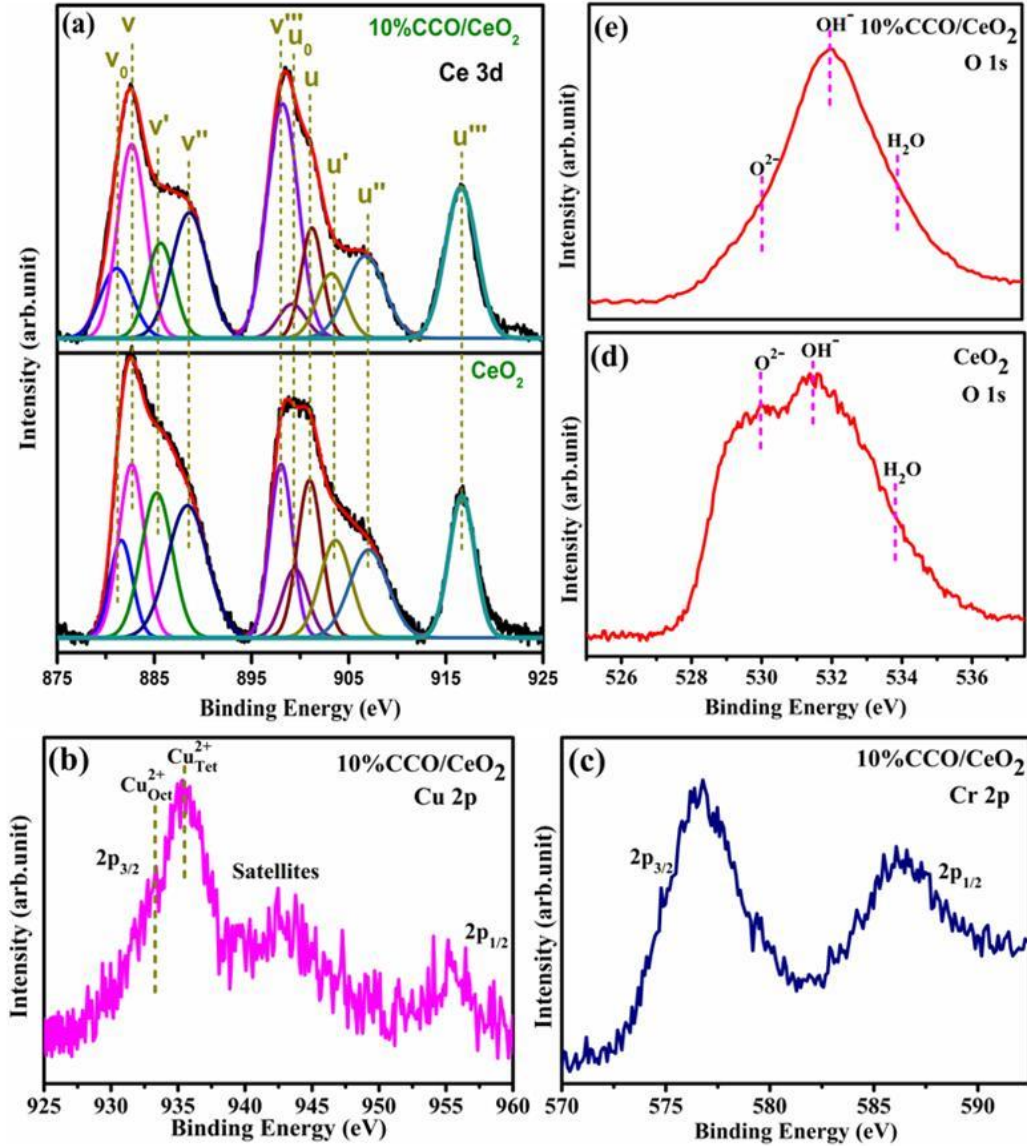


Fig. 4.5: (a) Ce 3d, (b) Cu 2p, (c) Cr 2p and (d, e) O 1s core level spectra of CeO₂ and 10%CCO/CeO₂ nanocomposite.

Broad nature of Cu 2p core level spectrum of CCO indicates the occurrence of different Cu species which is decomposed into component peaks by curve-fitting as shown in **Fig. 4.5(b)**. Accordingly, Cu 2p_{3/2} peaks at 933.6 and 935.5 eV with characteristic satellite peaks correspond to different Cu²⁺ species present in CCO material. Accordingly, the Cu 2p_{3/2,1/2} peaks at 933.6 and 953.7 eV are attributed to Cu²⁺ species in octahedral sites and Cu 2p_{3/2,1/2} peaks at 935.5 and 955.6 eV are associated with Cu²⁺ species in tetrahedral coordination environment in CCO structure [61-64]. Cr 2p core level spectrum of CCO presented in **Fig. 4.5(c)** contains Cr 2p_{3/2,1/2} peaks around 576.6 and 586.5 eV with 9.9 eV spin-orbit separation and are ascribed for Cr³⁺ species in octahedral environment [65].

Asymmetric spectral characteristics of O 1s core levels of CeO₂ and 10%CCO/CeO₂ indicate the presence of several oxygen species in the photocatalysts as presented in **Fig. 4.5(d, e)**. In CeO₂, component peak at 530.0 eV is assigned for oxide Ce⁴⁺ species associated with CeO₂ and the peak around 531.6 eV stands for hydroxyl species [59, 60, 65]. A weak component peak with binding energy above 533.5 eV is related to adsorbed water species present in the catalysts. However, binding energy related to oxide species is slightly higher in 10%CCO/CeO₂ nanocomposite photocatalyst which may be because of CCO present in the nanocomposite.

In agreement with the Raman spectroscopy analyses, the XPS analyses also support the higher oxygen vacancy in the 10%CCO/CeO₂ nanocomposite compared with bare CeO₂.

4.2.6. UV-Vis DRS and band gap analyses

The UV–Vis DRS spectra of CeO₂, CCO and CCO/CeO₂ nanocomposite are shown in **Fig. 4.6**. The band gaps are calculated from UV-Vis DRS data by using Tauc plots, depicted in **Fig. 4.7**. The absorption edge of pure CeO₂ is found to be at 465 nm. Pure CCO sample shows very high visible light absorption. After loading of CCO on CeO₂, the absorption edge of CeO₂ is red shifted with very high visible light absorption [51]. Specifically, addition of just 5%CCO considerably increases the adsorption of pure ceria and is red-shifted. Doubling the dosage of CCO increases the absorption certainly, but not so much, specifically above 600 nm. Loading of 20%CCO is nearly similar to that of pure CCO. The UV–Vis DRS results clearly demonstrate that introduction of CCO on CeO₂ increases the visible light absorption and the absorption edge of CeO₂ is shifted towards the visible region. The estimated band gap energy values of CeO₂, CCO, 5%CCO/CeO₂, 10%CCO/CeO₂ and 20%CCO/CeO₂ are 2.81, 1.48, 2.78, 2.75 and 1.72 eV, respectively. Here it may be noted that the band gap values of 5% and 10%CCO/CeO₂ show no significant change, however, when the CCO content increases to 20%, the value decreases evidently. This variation tendency is mostly likely due to the mass ratio of CCO.

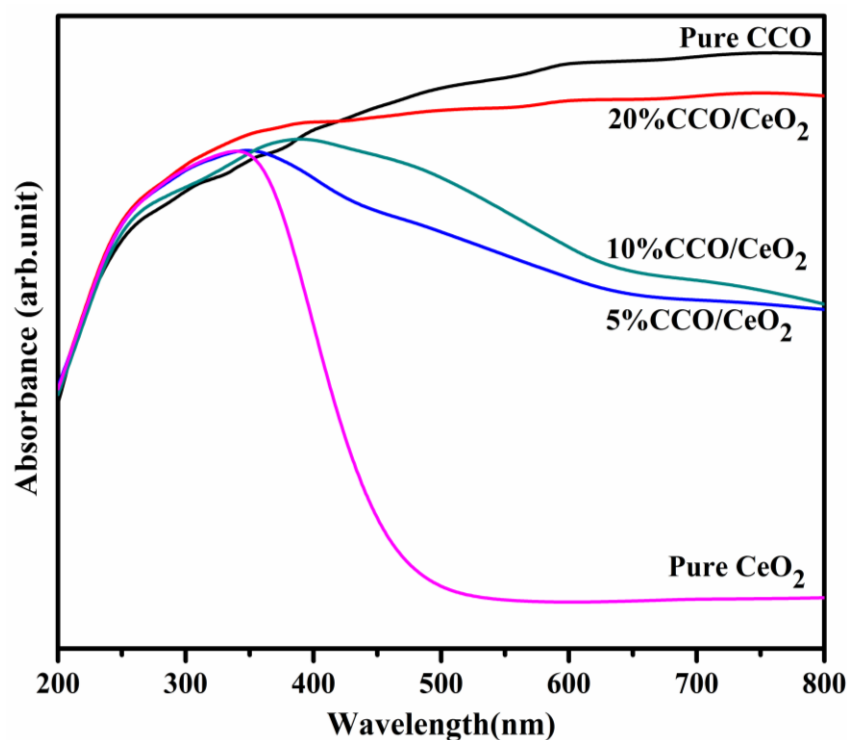


Fig. 4.6: UV-Vis DRS spectra of CCO, CeO_2 and CCO/ CeO_2 nanocomposite series.

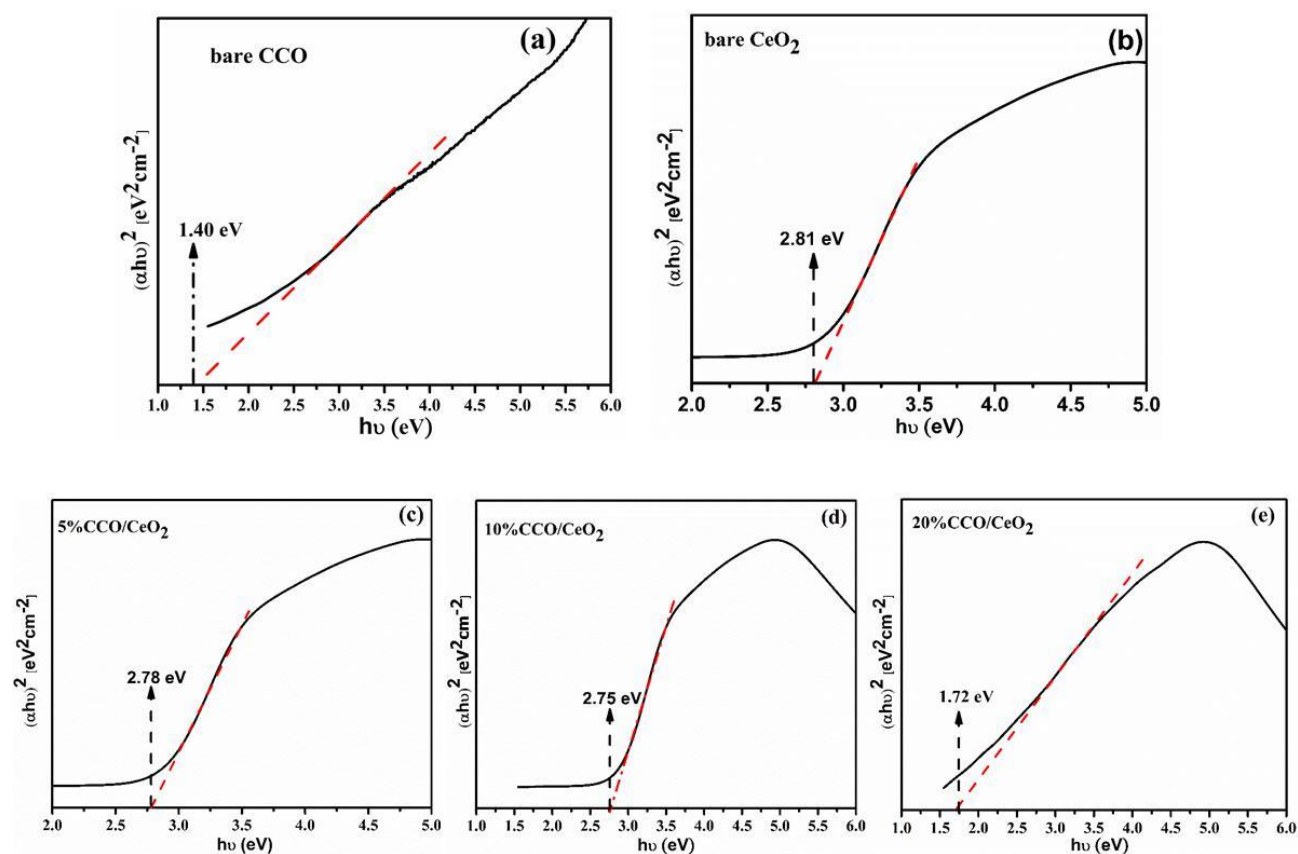


Fig. 4.7: Tauc plots of (a) CCO, (b) CeO_2 , (c) 5% CCO/ CeO_2 , (d) 10% CCO/ CeO_2 , and (e) 20% CCO/ CeO_2 nanocomposite.

4.2.7. PL spectroscopy and electron-hole pair recombination analyses

PL spectra of pure CeO_2 , 5%CCO/ CeO_2 , 10%CCO/ CeO_2 and 20%CCO/ CeO_2 have been recorded at an excitation wavelength of 340 nm, which are shown in **Fig. 4.8(a)**. It is observed that the recombination rate for 10%CCO/ CeO_2 nanocomposite is the lowest i.e., having maximum lifetime of the excited state. This originates from its maximum oxygen vacancy among all the samples as supported by the Raman spectroscopy and XPS analyses. In fact, oxygen vacancy is the determining factor for the electron-hole pair recombination rate of a semiconductor [66]. Another way to tune the excited state lifetime is thermal annealing of the composite. Accordingly, the 10%CCO/ CeO_2 nanocomposite has been annealed at different temperatures and subsequently PL spectra have been recorded (see **Fig. 4.8(b)**).

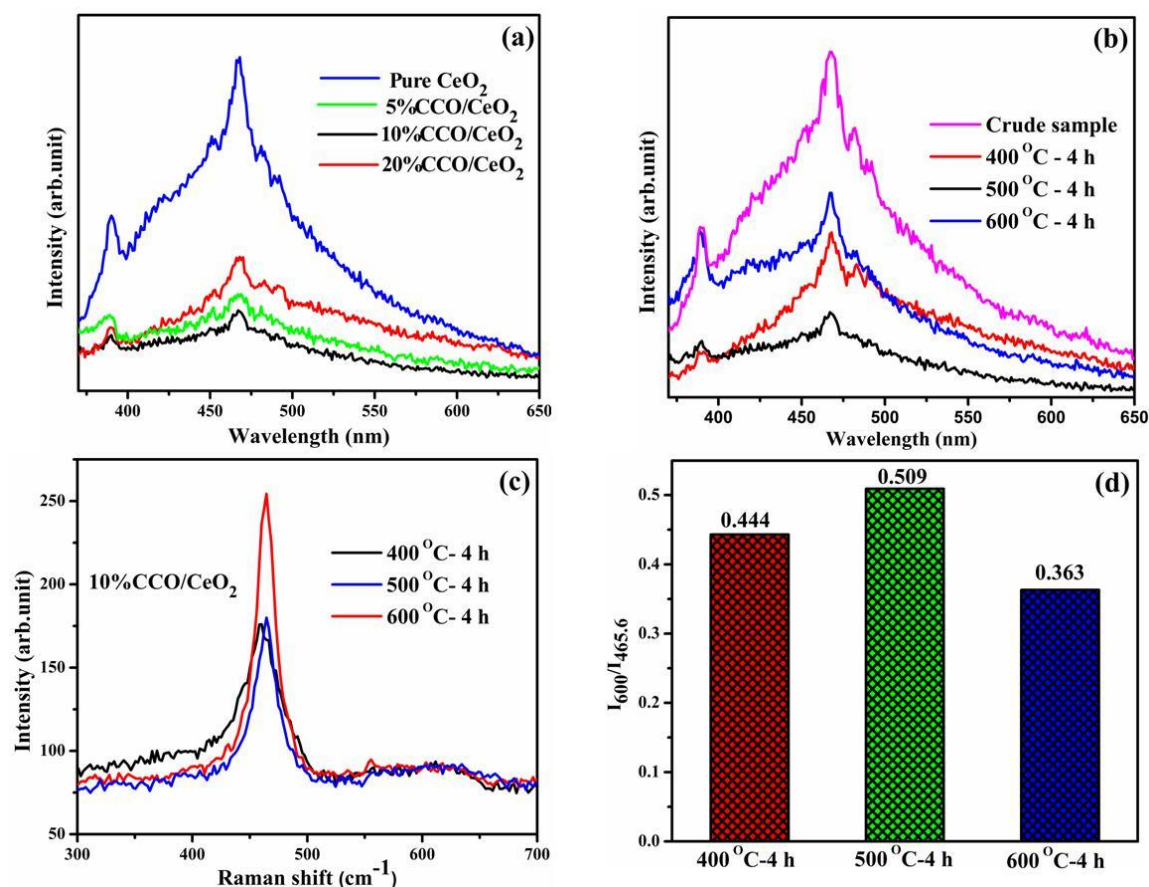


Fig. 4.8: PL spectra of (a) CeO_2 and CCO/ CeO_2 nanocomposite samples, (b) 10%CCO/ CeO_2 nanocomposite sample annealed at different temperatures, (c) Raman spectra and (d) oxygen vacancy of 10%CCO/ CeO_2 nanocomposite sample annealed at different temperatures.

The minimum PL intensity is observed for the sample annealed at 500 °C suggesting it to be the most efficient photocatalyst for dye degradation, which will be discussed in the following

section. Similar variation in lifetime with annealing temperature has been reported for extrinsic semiconductor heterojunction [67]. The Raman spectroscopic analysis of 10%CCO/CeO₂ nanocomposite annealed at these temperatures have suggested the sample annealed at 500 °C to possess the highest oxygen vacancy (see **Fig. 4.8 (c, d)**). Hence, this particular sample is expected to show highest charge separation ability and hence highest catalytic activity in perfect concurrence with the PL analyses.

4.2.8. Photocatalytic properties

4.2.8.1. Degradation of RhB

The Fenton like degradation activity of CeO₂, CCO and CCO/CeO₂ nanocomposites were investigated using RhB as a model organic pollutant under visible LED light irradiation. **Fig. 4.9(a)** shows the time dependent PFL RhB degradation activity of bare CeO₂, CCO and CCO/CeO₂ nanocomposites. **Fig. 4.10** shows respective change of absorbance of RhB with time during PFL degradation over pure and nanocomposite samples. The results demonstrate that in absence of Fenton like catalyst, RhB exhibits good stability (suffers only 1.3% degradation in 15 min) in presence of H₂O₂ under visible LED irradiation. It is observed that CCO/CeO₂ nanocomposites exhibit a remarkably enhanced PFL performance compared to its pure counterparts. For the CCO/CeO₂ nanocomposites series, the degradation efficiency increases with the increase of CCO loading on CeO₂ and the optimal PFL activity is observed for the 10%CCO/CeO₂ nanocomposite sample. The RhB degradation percentages obtained after 15 minutes of LED irradiation for CCO, CeO₂, 5%CCO/CeO₂, 10%CCO/CeO₂ and 20%CCO/CeO₂ samples are 17%, 5%, 95%, 99%, and 92%, respectively. In case of DFL activity (i.e., in the absence of LED light irradiation), a significant lowering of the Fenton like performance is noticed (see **Fig. 4.9(c)**). In the dark condition and after 15 minutes, the RhB degradation percentages of CCO, CeO₂, 5%CCO/CeO₂, 10%CCO/CeO₂ and 20%CCO/CeO₂ samples are 3.3%, 0.6%, 46.8%, 60% and 43%, respectively. It is also evident from **Fig. 4.9(a, c)** that pure CCO and CeO₂ respectively show low and negligibly small Fenton like activity in visible light and in dark condition. Since the oxygen vacancy of CeO₂ in nanocomposite enhances its catalytic activity, it may thus be concluded that CCO/CeO₂ nanocomposites show the better catalytic activity than bare CeO₂ due to the higher oxygen vacancy of CeO₂ in the nanocomposite (see the results of Raman spectroscopy analyses in **section 4.2.4** and XPS analyses in **section 4.2.5** that support increase of oxygen vacancy of CeO₂ subsequent to nanocomposite formation).

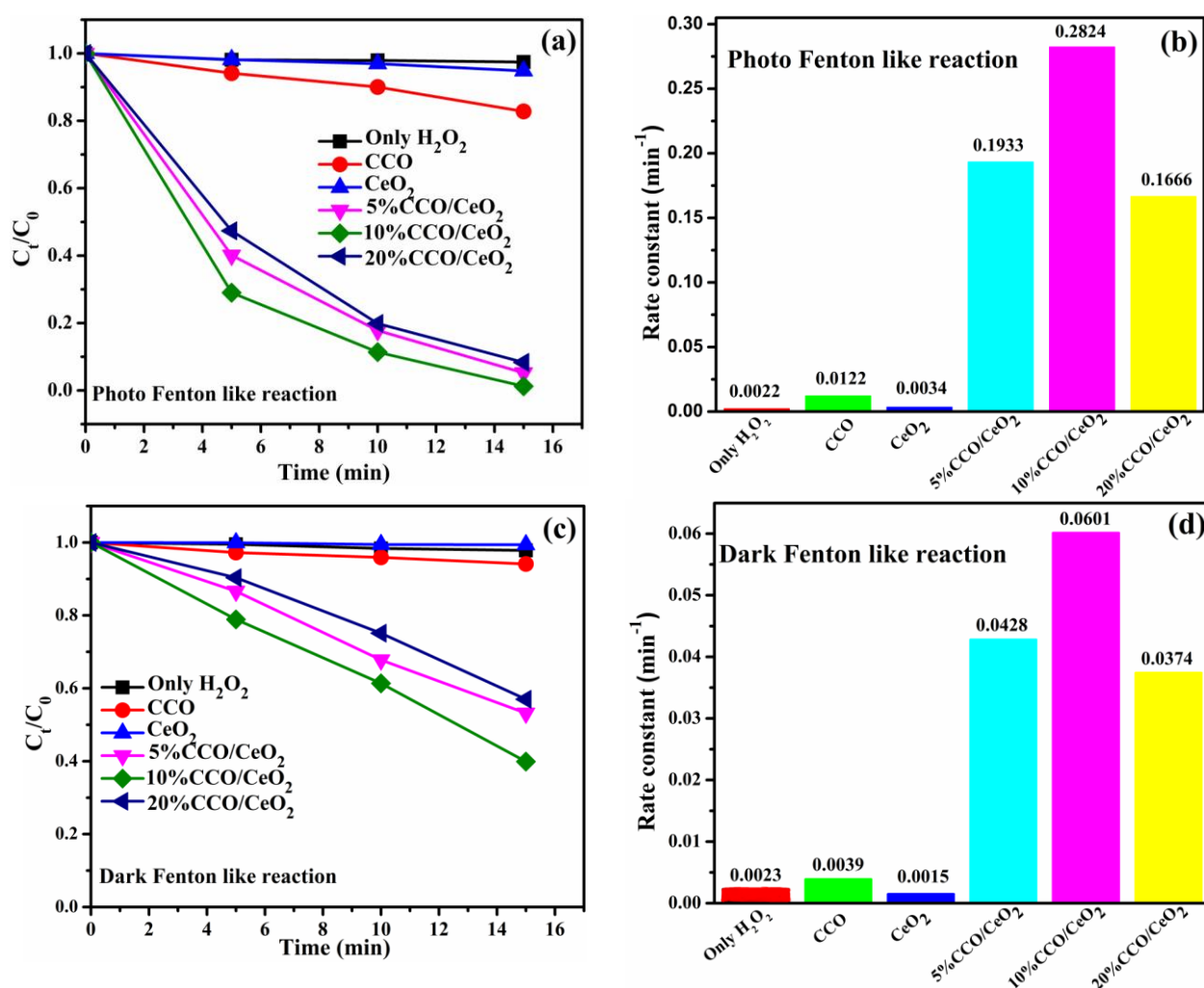


Fig. 4.9: Fenton like RhB dye degradation activity and rate constant of CCO, CeO_2 and CCO/ CeO_2 nanocomposites for (a, b) PFL reaction and for (c, d) DFL reaction.

The RhB degradation following pseudo first order reaction kinetics was also investigated to study the photo and dark Fenton like reaction efficiencies of CCO/ CeO_2 nanocomposites. The values of k are presented in **Fig. 4.9(b,d)**. The values of k of all the CCO/ CeO_2 nanocomposite are very much higher than that of bare CCO and CeO_2 for both PFL and DFL reactions. These values are also significantly higher in PFL reaction than in DFL reaction.

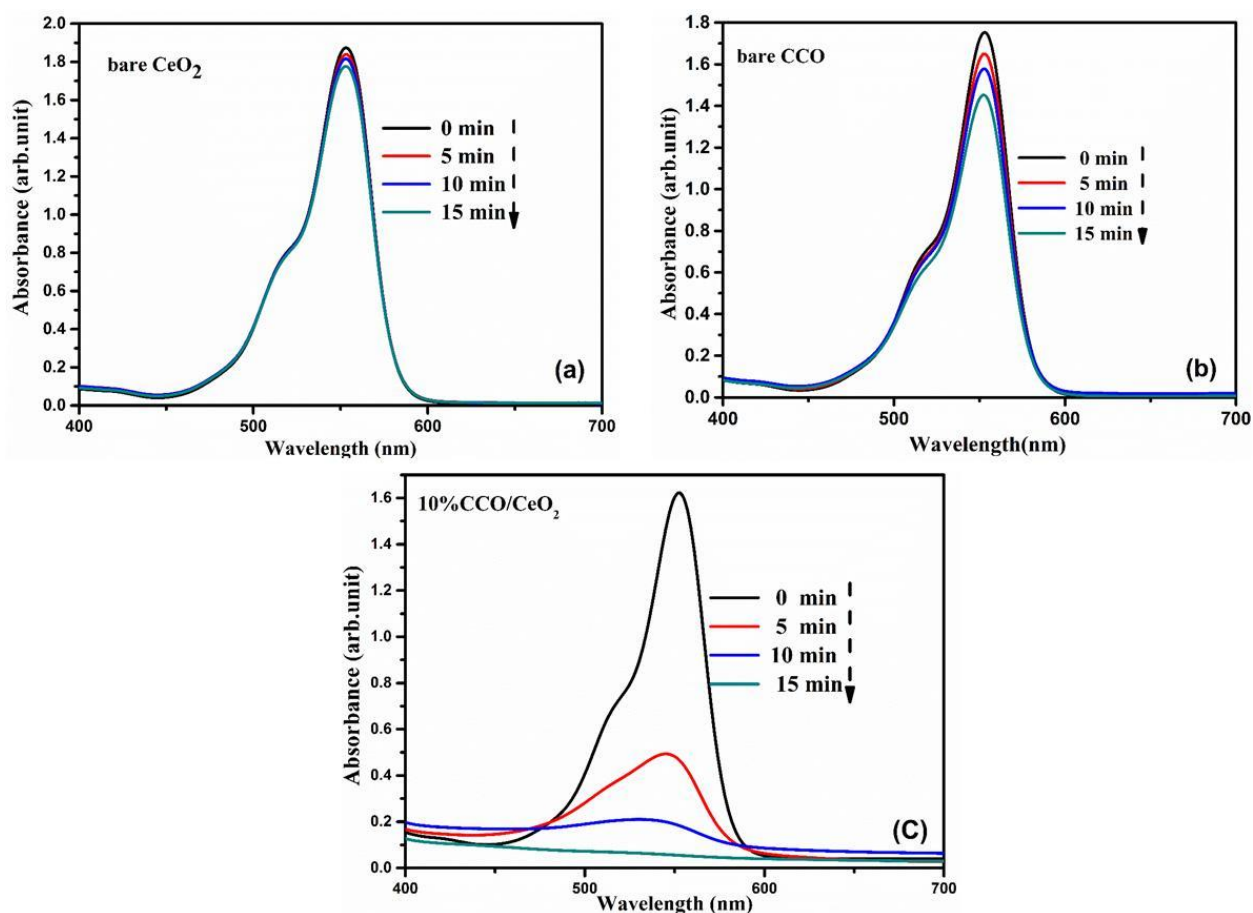


Fig. 4.10: Variation of absorbance of RhB dye during the PFL reaction in presence of (a) CeO_2 , (b) CCO and (c) 10%CCO/ CeO_2 composite.

4.2.8.2. Effect of variation of catalyst mass on PFL activity

To standardize the catalyst amount for the specified reaction condition, RhB degradation with varied amounts of the most efficient catalyst 10%CCO/ CeO_2 has been performed. **Fig. 4.11(a)** shows the time evolution of RhB degradation at different catalyst masses. It is observed that the maximum efficiency is attained for 50 mg of catalyst, which can be considered to provide optimum active sites to produce $\cdot\text{OH}$. Further increase in catalyst quantity decreases the degradation efficiency. This could be due to failure of incident light to make excitation of the underlying catalyst for higher thickness of increased mass or superimposition of catalyst active sites to generate $\cdot\text{OH}$.

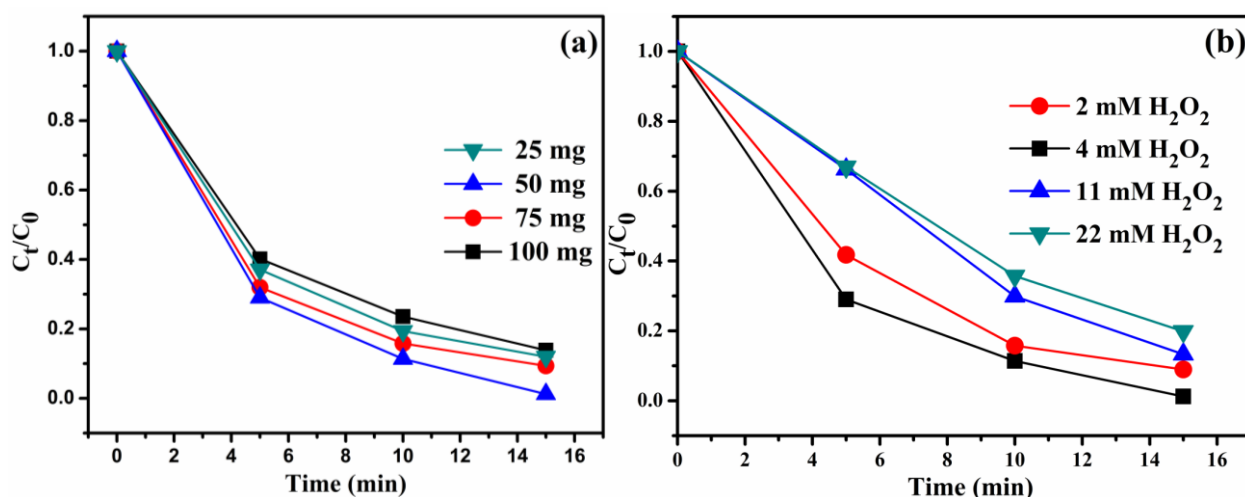


Fig. 4.11: Effects of the variation of (a) catalyst mass and (b) H₂O₂ concentration with 10%CCO/CeO₂ nanocomposite catalyst in PFL reaction.

4.2.8.3. Effect of variation of H₂O₂ concentration on PFL activity

In order to get the optimized concentration of H₂O₂ under the reaction condition, RhB degradation has been carried out using 10%CCO/CeO₂ nanocomposite. Maximum efficiency is observed for 4 mM of H₂O₂ (**Fig. 4.11(b)**). Further increase in H₂O₂ results a lowering in PFL activity. This decrease of RhB degradation at high H₂O₂ concentrations could be due to self-scavenging of $\cdot\text{OH}$ by H₂O₂ followed by the formation of less reactive $\cdot\text{OOH}$ ($\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \cdot\text{OOH} + \text{H}_2\text{O}$).

4.2.8.4. Effect of calcination temperature on PFL activity of the nanocomposite

The effect of annealing temperature on the lifetime of photoexcited electron-hole pairs across the grain boundary of the nanocomposite materials has been mentioned in the preceding section 4.2.7. Experimental observation based on the PL studies has been elaborated here by considering the most efficient Fenton like catalyst i.e., 10%CCO/CeO₂ nanocomposite. This nanocomposite was synthesized at 400 °C, 500 °C, and 600 °C by annealing for 4 h. The PFL degradation of RhB with the elapse of time using these annealed samples as catalysts is shown in **Fig. 4.12(a)**. The most efficient degradation is achieved for 500 °C annealed nanocomposites. To confirm this observation, coumarin based PL probing method has been carried out. Actually, in the catalytic pathway the nanocomposite produces $\cdot\text{OH}$, the main responsible species for Fenton like activity (discussed with details in trapping

experiment), from H_2O_2 and better the production of $\cdot\text{OH}$, more efficient is the catalytic performance. In presence of $\cdot\text{OH}$, coumarin reacts to form 7-hydroxy coumarin, which gives an intense PL peak at 456 nm upon excitation at 332 nm. Thus, evolution of PL intensity with time will provide a measure of $\cdot\text{OH}$ generation by the catalyst. The time evolution of PL intensity for 400 °C, 500 °C, and 600 °C annealed nanocomposites are shown in **Fig. 4.12(b)**. The maximum intensity is obtained for the sample annealed at 500 °C, which is consistent with its highest RhB degradation activity.

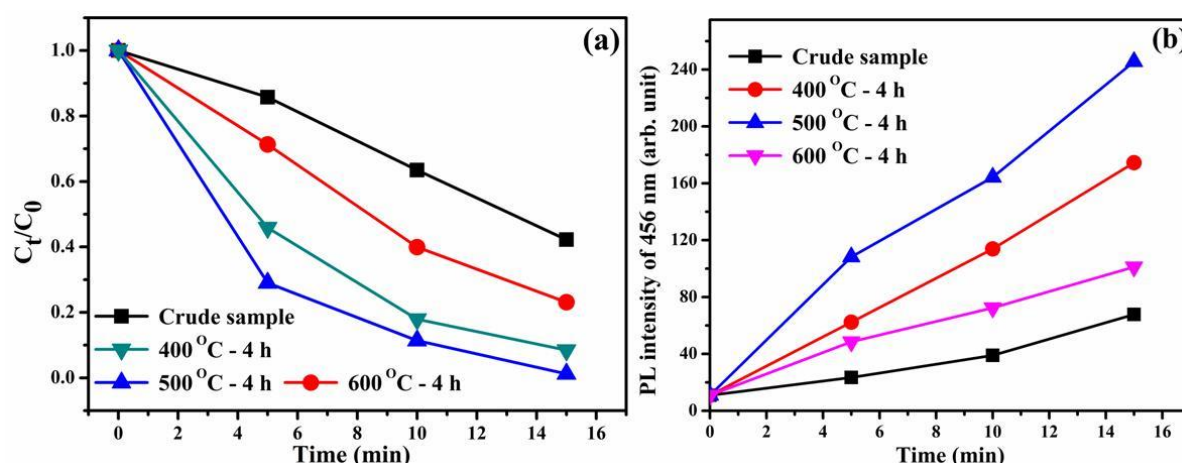


Fig. 4.12: Effect of calcination temperature of 10%CCO/CeO₂ nanocomposite on (a) PFL RhB degradation activity and (b) $\cdot\text{OH}$ formation activity (obtained from the analysis of time evolved intensity of PL peak at 456 nm upon excitation at 340 nm).

4.2.8.5. Radical trapping experiments

Radical trapping experiments were carried out in order to determine the reactive species formed in the catalytic process of dye degradation for both PFL and DFL reaction. The results of radical trapping experiment of PFL process are shown in **Fig. 4.13(a)**. From the figure it is clearly seen that the RhB degradation efficiency over 10%CCO/CeO₂ nanocomposite sample reached 99% with 15 min of LED light irradiation in the absence of any radical trapper, but the RhB degradation efficiency decreased to 9%, 61% and 74% in the presence of IPA, Na₂EDTA.2H₂O and BQ, respectively. This observation strongly suggests that $\cdot\text{OH}$ is formed as the major active species in PFL process. Furthermore, both $\cdot\text{O}_2^-$ and hole also contribute a little to the overall photocatalytic process.

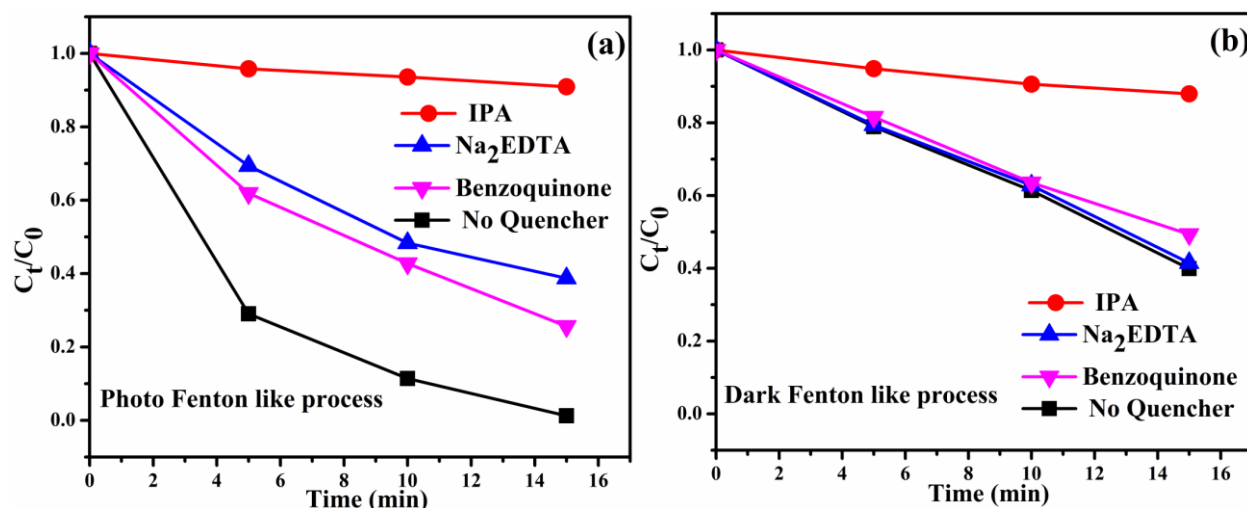


Fig. 4.13: Radical trapping experiment of (a) PFL and (b) DFL processes by using 10%CCO/CeO₂ nanocomposite.

The radicals trapping experiments were also carried out for DFL process (i.e., in presence of H₂O₂, but without LED irradiation) and the experimental results are shown in **Fig. 4.13(b)**. The RhB degradation efficiency over 10%CCO/CeO₂ nanocomposite without any radical trapper is 60% after 15 min, while the degradation efficiency is reduced respectively to 12%, 58% and 50% when IPA, Na₂EDTA.2H₂O and BQ is used as the radical trapper. These findings again point to $\cdot\text{OH}$ as the main responsible species even in the DFL process.

4.2.8.6. Optimization of IPA dosage

Since $\cdot\text{OH}$ is the primary reactive species, so optimization of IPA dosage is necessary in both the PFL and DFL reactions under identical condition. **Fig. 4.14(a)** displays the effect of IPA dosage on the PFL RhB degradation. It is observed from the figure that IPA dosage significantly influences the RhB degradation that is decreased as the IPA dosage is increased and almost no degradation of RhB is observed when 20 μL of IPA is added. This phenomenon indicates that at sufficiently high IPA dosage, the generated $\cdot\text{OH}$ is almost completely trapped by IPA and hence the catalyst loses its PFL activity. A similar trend is observed for the DFL process (see **Fig. 4.14(b)**) where the RhB degradation is almost negligible when ~ 10 μL (about half of earlier dosage) of IPA is added to the reaction medium. These comparative studies on the variation of IPA dosage in RhB degradation under photo and dark condition thus in turn supports the higher $\cdot\text{OH}$ generation during the PFL process.

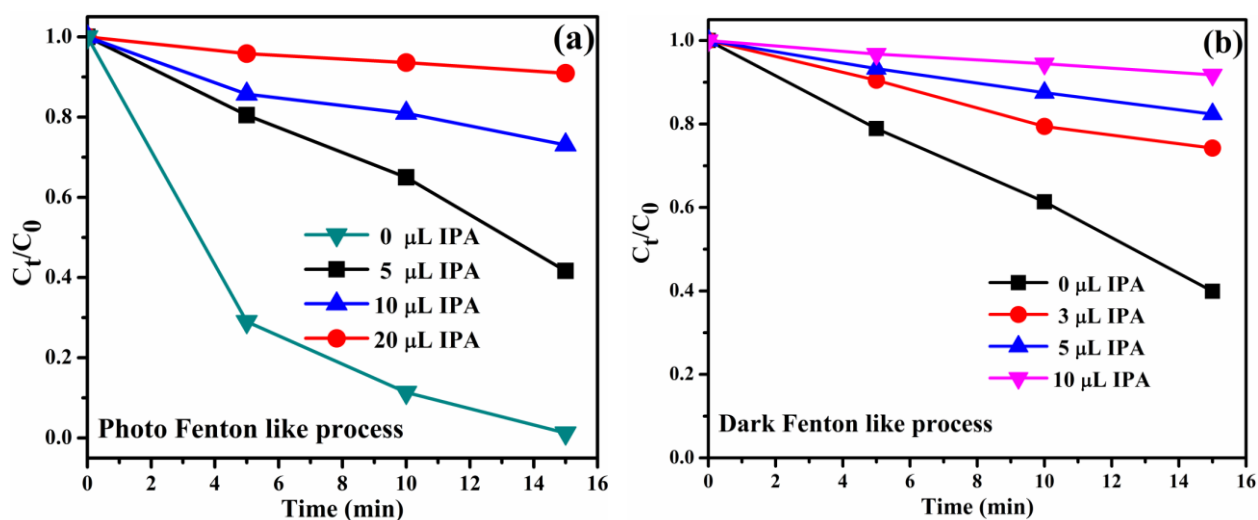


Fig. 4.14: Effect of IPA dosage on RhB degradation in (a) photo and (b) dark Fenton like reaction over 10%CCO/CeO₂ nanocomposite.

4.2.8.7. $\cdot\text{OH}$ detection by fluorescence technique

To further verify the evidence of $\cdot\text{OH}$ formation in both the photo and dark Fenton like processes of RhB degradation, coumarin based fluorescence probe experiment was performed and the experimental results are displayed in **Fig. 4.15**. It is observed from the figure that the fluorescence intensity of the peak at 456 nm corresponding to fluorescence active 7-hydroxy coumarin is increased significantly with time (up to 15 min) for 10%CCO/CeO₂ nanocomposite when compared with bare CCO and CeO₂ (see **Fig. 4.15 (a-e)**). The experimental results also show that the intensity of fluorescence peak is higher in presence of LED irradiation than in its absence (see **Fig. 4.15 (a, b, e)**), which strongly suggests higher generation of $\cdot\text{OH}$ in the PFL reaction than in the DFL reaction. This in turn explains higher RhB degradation in the PFL process. At this point it is worth mentioning that the possible reason for very poor efficiency of pure CeO₂ as a Fenton like catalyst towards the degradation of RhB could be related to the negligible formation of the crucial species $\cdot\text{OH}$. This can be ascribed to the formation of peroxo complex of Ce³⁺ with H₂O₂. Such complexation is manifested through the visual color change of pure CeO₂ suspension, where the white colored suspension turns yellow on addition of H₂O₂ (see **Scheme 4.1**). However, such change is not observed for the nanocomposite system. This suggests the change in electronic states of CeO₂ surface on composite formation with CCO. Thus, the efficient formation of $\cdot\text{OH}$ in the nanocomposite system is not hampered and hence better photocatalytic performance is observed.

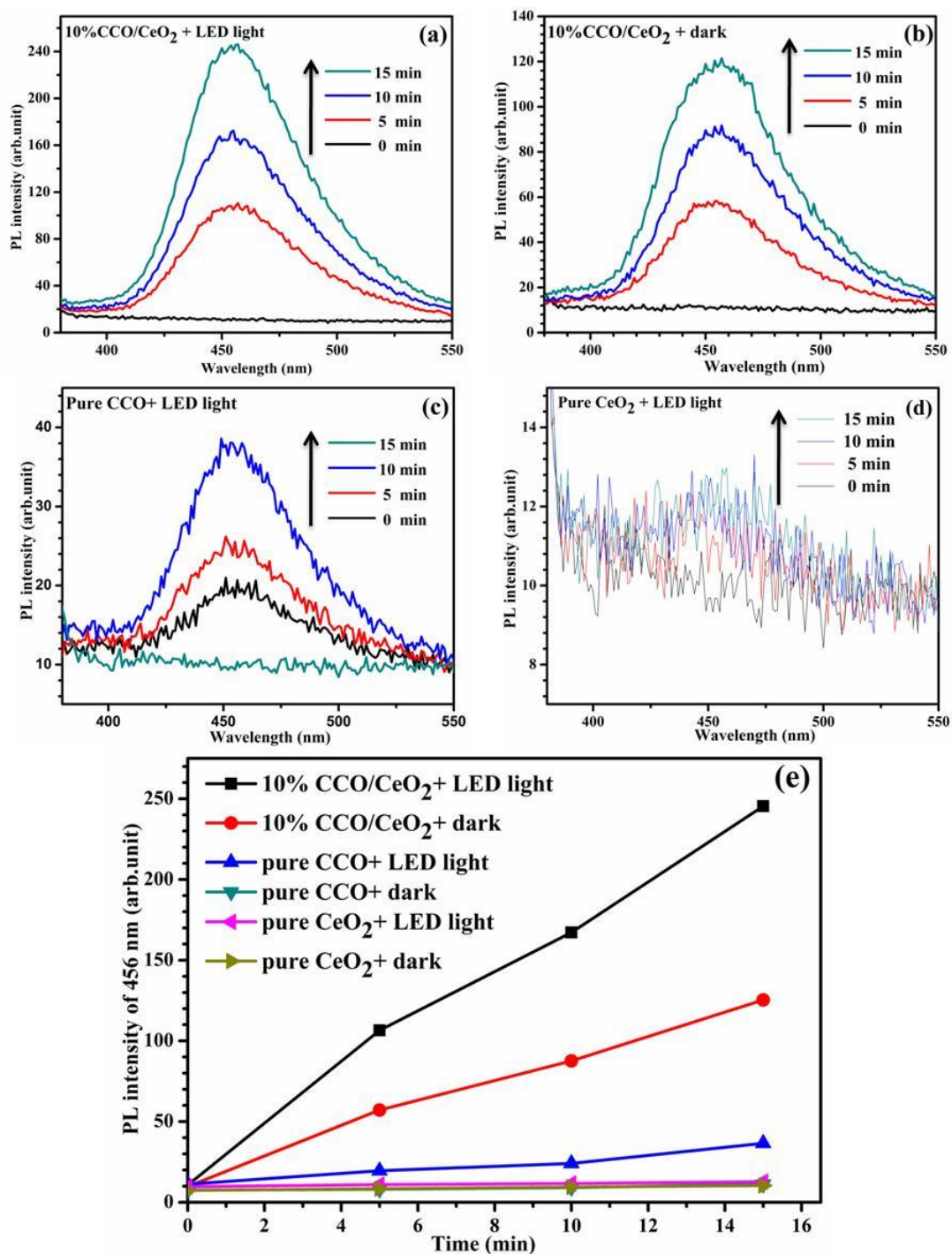
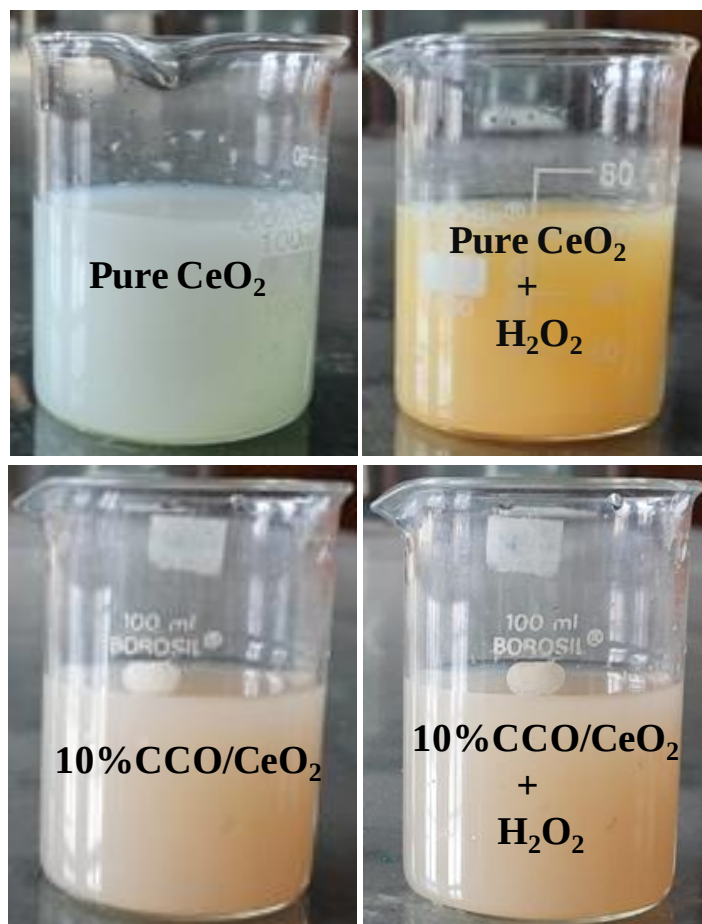


Fig. 4.15: Fluorescence spectra of the formation of 7-hydroxy coumarin in presence of 10%CCO/CeO₂ under visible LED light (a), in dark (b), and those of pure CCO (c) as well as pure CeO₂ (d) in presence of visible LED. The change in PL intensity of 7-hydroxy coumarin at 456 nm with time for CCO, CeO₂ and 10%CCO/CeO₂ nanocomposite under visible LED light and in dark (e).



Scheme 4.1: live images of color change of pure CeO_2 and 10%CCO/ CeO_2 nanocomposite suspensions before and after the addition of H_2O_2 .

4.2.8.8. Fenton like activity of 10%CCO/ CeO_2 nanocomposite for MB and MO degradation

In order to see whether the nanocomposite catalyst also really works for MB and MO with different light absorption bands, we performed degradation tests with these two dyes under the optimized experimental conditions of RhB degradation. The results are shown in **Fig. 4.16** for both the photo and dark Fenton like processes along with the respective values of pseudo first order rate constants in the inset. Noting the degradation data of RhB from **Fig. 4.9** and those of MB and MO from **Fig. 4.16**, the degradation activity of 10%CCO/ CeO_2 nanocomposite for the three dyes follows the order $\text{RhB} > \text{MB} > \text{MO}$. For example, at the fixed degradation time of 15 min, RhB degrades almost entirely (99%), MB degrades by about 85% and 60% of MO can get degraded. A maximum of 98% of MB can be degraded in 20 min (**Fig. 4.16(a)**), while a slightly lower percentage (96%) of degradation for MO can be achieved at a higher time of 30 min (**Fig. 4.16(b)**) by using the nanocomposite catalyst. The DFL processes also follow the expected trend. For RhB it was 60% in 15 min, while the

respective values for MB and MO are 50% in 20 min and 42% in 30 min. **Fig. 4.17** shows representative change of absorbance of MB and MO with time during PFL and DFL degradation over the nanocomposite catalyst.

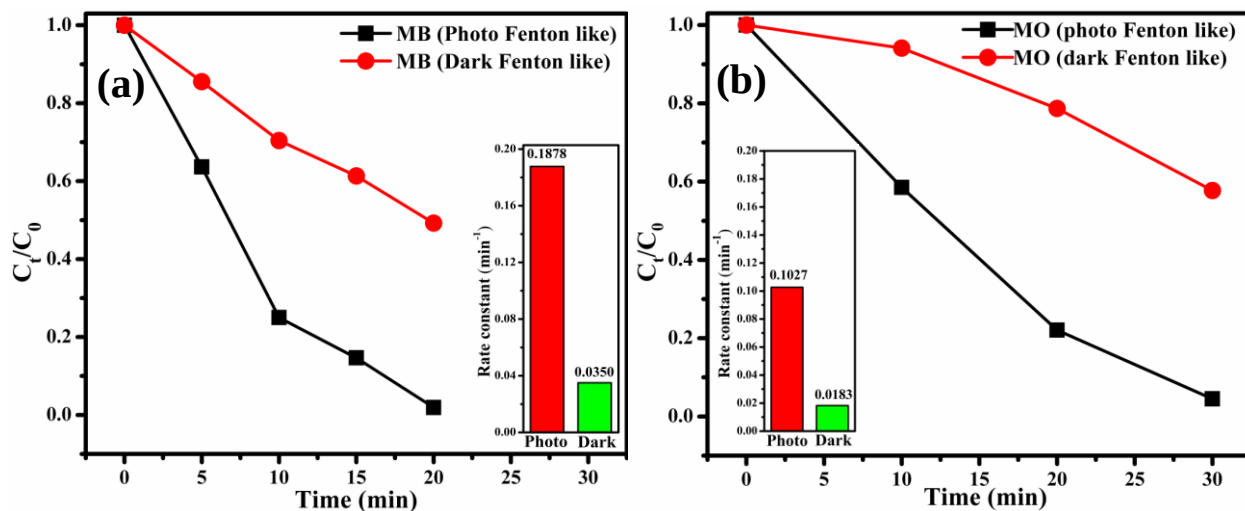


Fig. 4.16: PFL as well as DFL activities and rate constants (as inset) of 10%CCO/CeO₂ nanocomposite for (a) MB and (b) MO degradation.

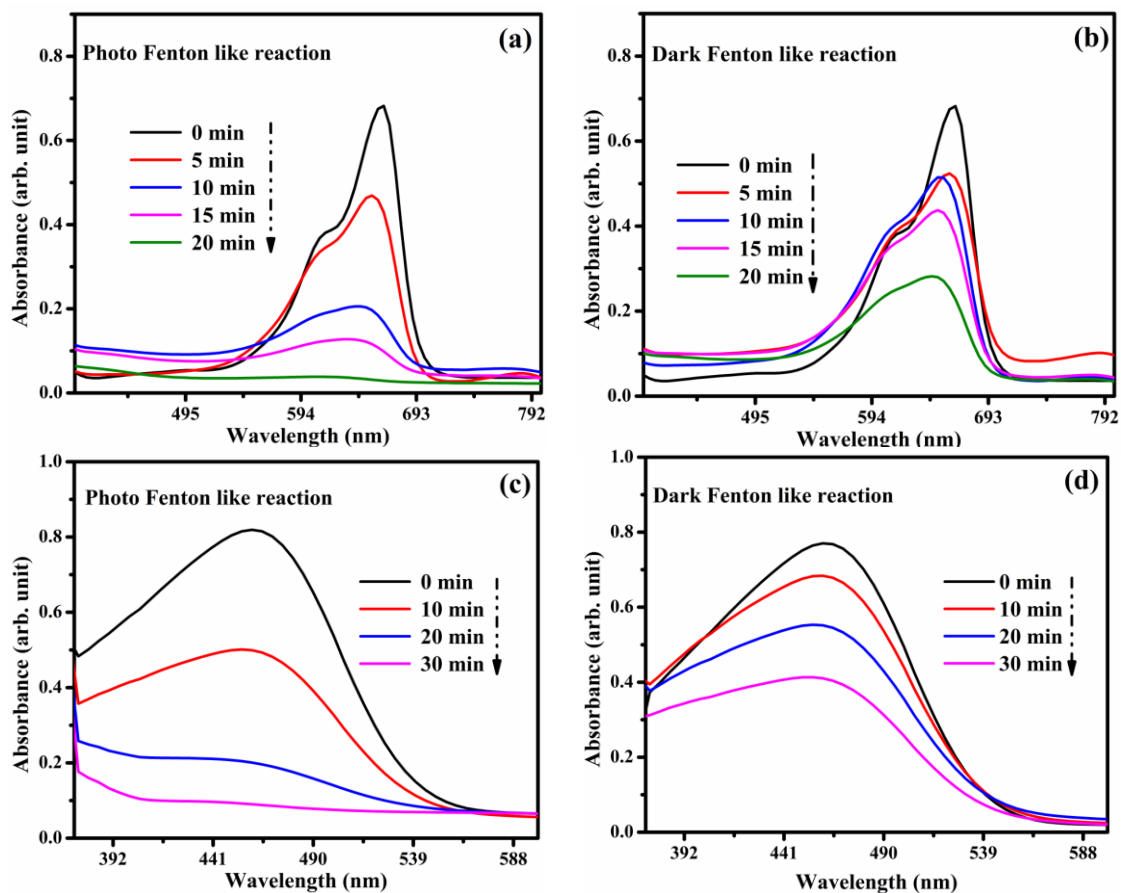
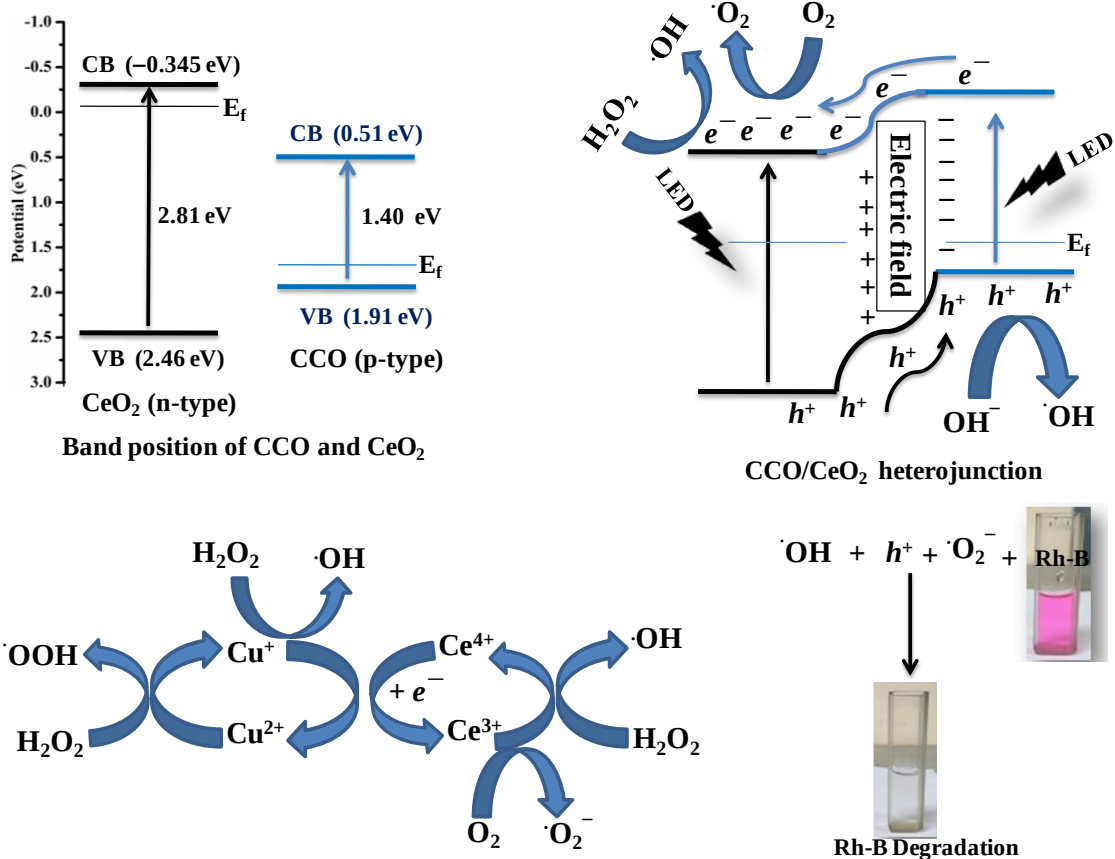


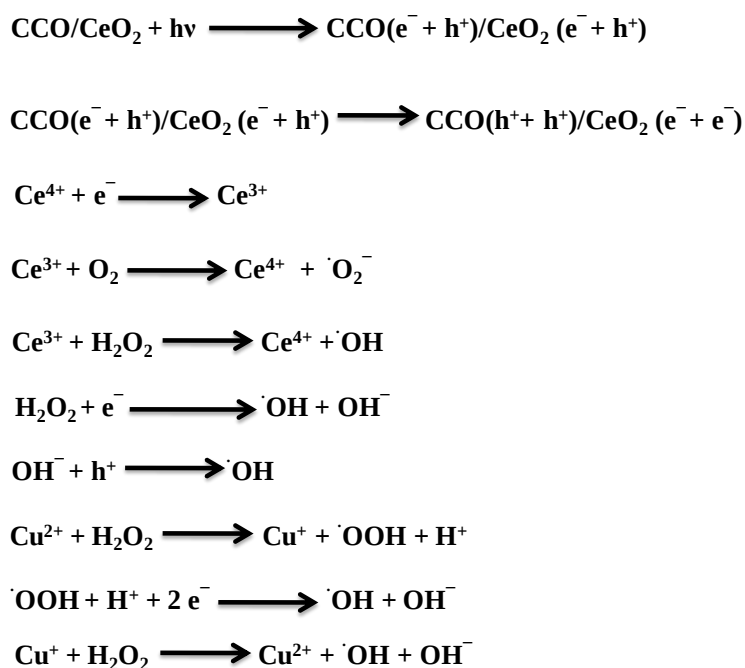
Fig. 4.17: Variation of absorbance during the photo and dark Fenton like degradation of (a, b) MB and (c, d) MO dyes in presence of 10%CCO/CeO₂ nanocomposite catalyst.

4.2.8.9. Mechanism of PFL reaction over CCO/CeO₂ nanocomposite

Photocatalytic mechanism is established (see **Scheme 4.2**) by determining the VB and CB energy values of CCO and CeO₂ with the help of their χ and E_g values using standard equations as discussed in chapter 3. The χ values of CCO and CeO₂ of respectively 5.71 eV and 5.56 eV [12, 33], while E_g values of respectively 1.40 eV and 2.81 eV. The calculated band edge energies of VB and CB of CCO are 1.91 eV and 0.51 eV, respectively and those of CeO₂ are 2.46 eV and -0.345 eV, respectively. Under visible LED irradiation, the excited electrons on the CB of CCO are transferred to the CB of CeO₂ and the holes on the VB of CeO₂ are easily shifted to the VB of CCO. Such transitions of photogenerated electrons and holes in the CCO/CeO₂ heterojunction reduce the electron-hole recombination probability thereby increasing the lifetime of the charge carriers. On the other hand, in presence of H₂O₂, the electronic structure as well as proportions of the redox couples Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺ of CCO/CeO₂ heterojunction can get modified [68, 69]. The electrons in the CB of CeO₂ are trapped by the Ce⁴⁺ ions to produce Ce³⁺ ions which react respectively with dissolved oxygen and H₂O₂ to form superoxide radicals and hydroxyl radical and itself gets oxidized to Ce⁴⁺ ions. Meanwhile, H₂O₂ can react directly with the excited electrons to form OH⁻ and [•]OH, between which OH⁻ is oxidized to [•]OH by the reaction with holes. On the other hand, Cu²⁺ in the CCO/CeO₂ nanocomposite reacts with H₂O₂ to form [•]OOH, which reacts further with the excited electrons to form [•]OH and itself gets reduced to Cu⁺. The Cu⁺ ion formed so in turn reacts rapidly with H₂O₂ to generate [•]OH and itself gets reoxidized to Cu²⁺. The overall process is greatly enhanced by the presence of photo-excited electrons [70]. Additionally, photogenerated holes can react directly with RhB to degrade it. Thus, presence of H₂O₂ and improved charge separation facilitate the oxidation-reduction cycle of Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺ pairs in the composite that greatly enhances the [•]OH formation activity of the nanocomposite system during the photocatalytic process. Therefore, the CCO/CeO₂ heterojunction play an important role in the formation of [•]OH, [•]O₂⁻ and holes. The necessary steps of PFL process are summarized in **Scheme 4.3**.

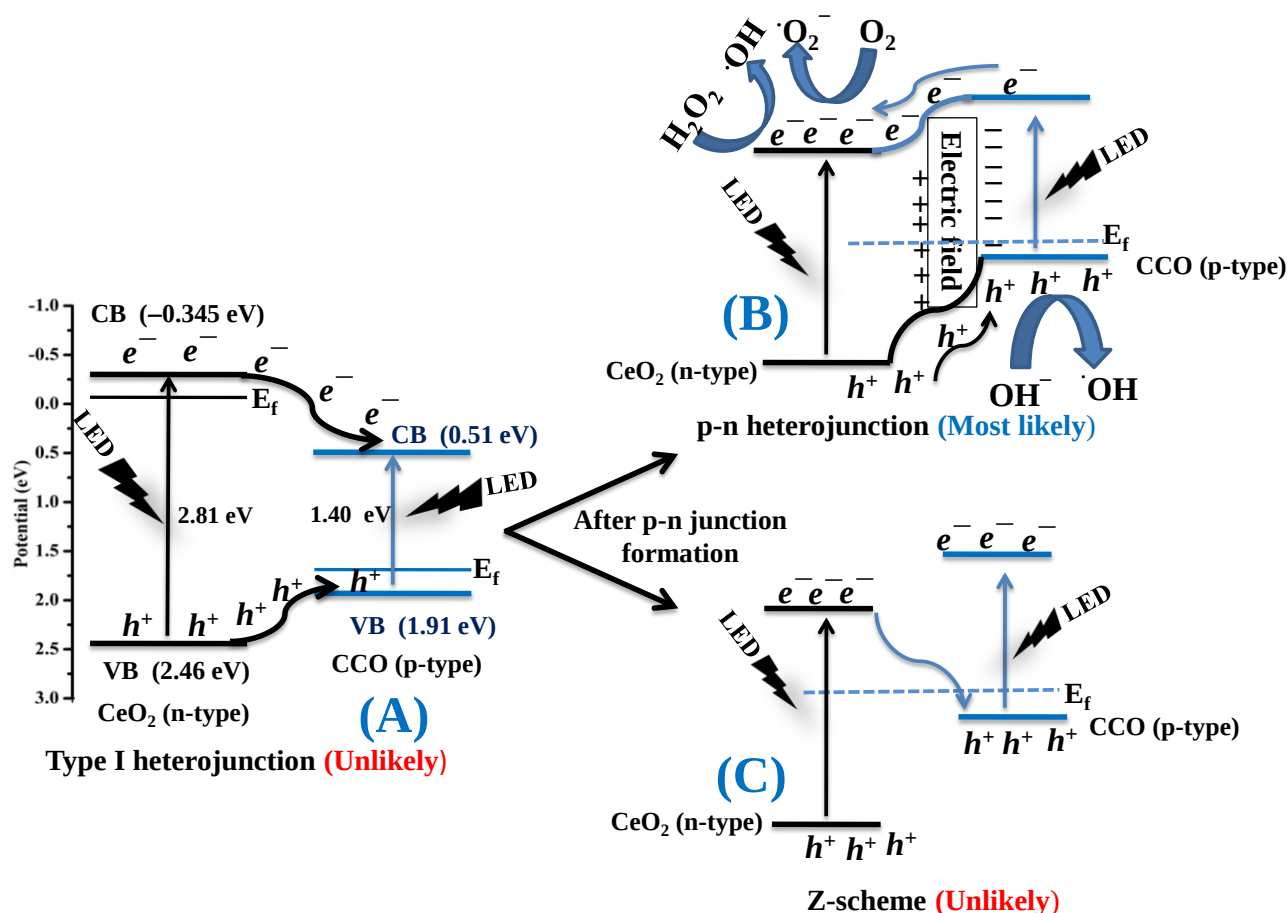


Scheme 4.2: Schematic presentation of PFL mechanism of CCO/CeO₂ nanocomposite for dye degradation.



Scheme 4.3: Plausible reaction steps involved in PFL reaction.

To further elucidate the involvement of the above mechanism in the photocatalytic reaction, we have made a comprehensive scrutiny of the possible Type I heterojunction, Z-scheme process together with the *p-n* heterojunction mechanism. These three processes are schematically shown in **Scheme 3.4**. The consideration of all these three types of possible mechanistic pathways is fully based on the calculated band edge energies of VBs and CBs and nature of semiconductors, i.e., *p*-type CCO and *n*-type CeO₂, two components of the nanocomposite photocatalyst.



Scheme 4.4: Possible mechanistic pathways of PFL reaction over CCO/CeO₂ nanocomposite. (A) Type I heterojunction, (B) p-n heterojunction and (C) Z-scheme.

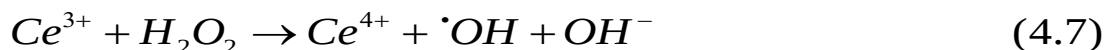
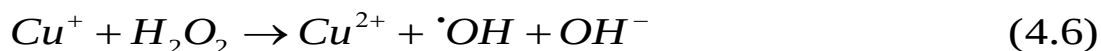
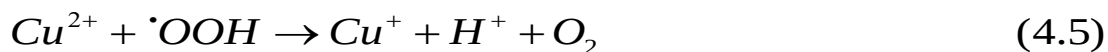
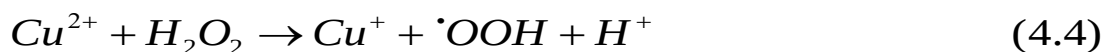
In Type I heterojunction mechanism (**Scheme 4.4(A)**), the relative positions of the VBs and CBs suggest accumulation of electrons only at the CB of the CCO site. This means that the population of electrons at the CeO₂ site is hampered and its positive role, an experimental finding, is not given due consideration. So involvement of this photocatalytic pathway is not a good choice for proper explanation of the PFL behavior of the nanocomposite catalyst and hence it is unlikely to act.

When the possibility of the *p-n* heterojunction pathway (**Scheme 4.4(B)**), briefed from **Scheme 4.2**) is taken into consideration, the electrons and holes can follow a cyclic pathway. Predominance of this type of mechanism maintains the population of electrons at both the CCO and CeO₂ sites as detailed above. So it has been considered to be the most reasonable mechanism for the explanation of PFL behavior of the CCO/CeO₂ nanocomposite system.

When one considers the Z-Scheme route (**Scheme 4.4(C)**), the electrons on the CB of CeO₂ are shifted to the VB of CCO so that the population of electrons again becomes higher at the CB of CCO site than that of the CeO₂ site. Hence the Z-scheme mechanism is not considered as a reasonable mechanism for explanation of the present PFL reaction. Based on the above discussion, the *p-n* heterojunction mechanism proposed here turns out to be most likely mechanism for the investigated nanocomposite catalyst system.

4.2.8.10. Mechanism of DFL reaction over CCO/CeO₂ nanocomposite

Based on the experimental studies of radical trapping and coumarin based fluorescence probe method for $\cdot\text{OH}$ detection, the following plausible mechanism for H₂O₂ decomposition over the CCO/CeO₂ nanocomposite in the DFL process is suggested. The mechanism possibly involves two pathways. The dissociation of H₂O₂ by Cu²⁺ in CCO as the first pathway; while its dissociation by Ce³⁺ in CeO₂ as the second pathway. In the first pathway, H₂O₂ reacts with the surface Cu²⁺ ions of CCO in the CCO/CeO₂ nanocomposite to generate $\cdot\text{OOH}$ (**Eq. (4.4)**) and these $\cdot\text{OOH}$ react further with Cu²⁺ to produce Cu⁺ (**Eq. (4.5)**). Then the DFL process for RhB degradation is initiated with $\cdot\text{OH}$ formation via decomposition of H₂O₂ on the nanocomposite surface by the reaction of Cu⁺ and H₂O₂ (**Eq. (4.6)**). The DFL can also be initiated by the reaction of H₂O₂ with Ce³⁺ of CeO₂ in the nanocomposite to produce $\cdot\text{OH}$ (**Eq. (4.7)**) as the second pathway in which Ce³⁺ gets oxidized to Ce⁴⁺. The redox potentials of Ce⁴⁺/Ce³⁺ and Cu²⁺/Cu⁺ couples are 1.44 and 0.15 V, respectively. So, the reoxidation of Cu⁺ to Cu²⁺ takes place via the thermodynamically spontaneous reaction with Ce⁴⁺/Ce³⁺ pair (**Eq. (4.8)**). This spontaneous redox reaction can steadily form Cu⁺ and Ce³⁺ ions, which can generate more of $\cdot\text{OH}$ via H₂O₂ decomposition and improve the Fenton like activity of CCO/CeO₂ nanocomposite. The $\cdot\text{OH}$ generated on the surface of CCO/CeO₂ nanocomposite can enter into the solution phase through diffusion and take part in the degradation of RhB present at catalyst surface and in the solution phase.



4.2.8.11. Recycling behavior of CCO/CeO₂ nanocomposite

Fig. 4.18(a) presents the recycling behavior of 10%CCO/CeO₂ nanocomposite for RhB degradation. A significant deactivation of catalyst was observed during the first cycle. For instance, the degradation of RhB is decreased from 99% for the fresh catalyst to 29% in the cycled catalyst. The decrease in degradation may be due to deposition of small organic compounds with low molecular weight on the catalyst surface generated from the degradation of RhB [43]. Another probable reason for such type of deactivation may be caused by the reduction of oxygen vacancies on the catalyst surface by the $\cdot OH$ produced from the dissociation of H₂O₂ [71]. To understand these aspects and to decide how to make a nanocomposite with good regeneration characteristics, the deposited organic compounds on the catalyst surface is removed by introducing an intermediate thermal treatment step. Before every run, the 10%CCO/CeO₂ nanocomposite was washed with Milli-Q water and isopropanol for three times each and then heated at 500 °C for 4 h in presence of air and then the Fenton like activity of the nanocomposite was assessed. As expected, the Fenton like activity can be recovered considerably as can be found in other reports [43, 71]. Nevertheless, the RhB degradation behavior is decreased by 10.6% after the third cycle (see **Fig. 4.18(b)**). It may also be noted that the results of phase analysis of 10%CCO/CeO₂ nanocomposite catalyst show no change in the bulk structure before and after the heat treatment (see **Fig. 4.18(c)**). So, the decrease is apparently due to blocking of the active sites by the deposited organics from degradation and not due to any structural change of the nanocomposite. A thermal treatment is good enough to remove those unwanted species and make available a clean surface for continuation of further dye degradation. Such an intermediate heat treatment is also shown to be effective in recovering oxygen vacancy on the catalyst surface that helps regaining the activity in the consecutive cycles of degradation [71].

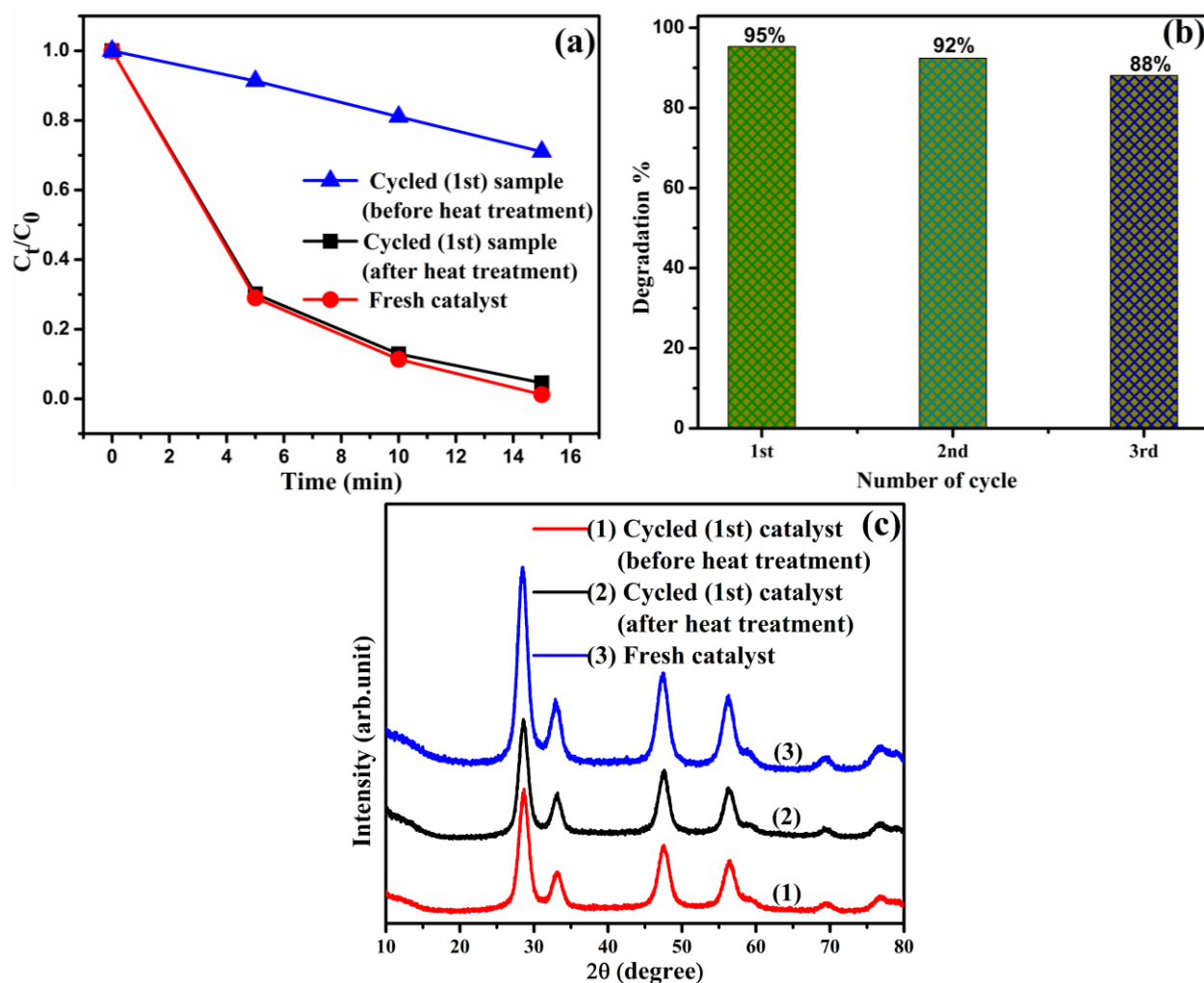


Fig. 4.18: (a) Degradation behavior of 10%CCO/CeO₂ nanocomposite sample collected after first run under two conditions, before and after heat treatment at 500 °C for 4 h along with the degradation activity of the fresh catalyst, (b) recycling behavior of the nanocomposite subsequent to thermal cleaning and (c) XRD patterns of the nanocomposite catalyst before and after heat treatment at 500 °C for 4 h and that of the fresh catalyst.

4.3. Conclutions

CCO, CeO₂ and a series of CCO/CeO₂ nanocomposites are synthesized respectively by tartaric acid sol-gel, co-precipitation and a combination of these two methods. The BET specific surface area of CeO₂ decreases considerably on forming composite with CCO due to strong aggregation between the component oxides. Powder XRD results suggest presence of nanosized CeO₂ and CCO phases in the nanocomposite samples without any additional phase (s) as impurity. The TEM and HRTEM analyses supplement the XRD findings, while EDS elemental mapping analysis shows chemical homogeneity of the nanocomposite. The detailed

XPS analyses demonstrate expected variable oxidation states for cerium with enhancement of Ce^{3+} concentration due to nanocomposite formation in comparison with CeO_2 . RhB dye with 10 ppm concentration is completely degraded by the most active 10%CCO/ CeO_2 nanocomposite within 15 min. However, the Fenton like activity of CCO is much lower, while that of ceria is rather peripheral. Thus, the improved Fenton like activity of CCO/ CeO_2 nanocomposite can be ascribed as a remarkable synergistic effect between the two components CeO_2 and CuCr_2O_4 . Both the Raman and XPS analyses support a higher oxygen vacancy in the 10%CCO/ CeO_2 nanocomposite compared with bare CeO_2 that is attributed to be a determining factor for its better PFL activity than bare CeO_2 . The photoluminescence studies indicate the lowest electron-hole pair recombination rate for 10%CCO/ CeO_2 nanocomposite sample annealed at 500 °C and hence it is having the maximum lifetime of the excited state suggesting it to be the most efficient photocatalyst for RhB degradation. Radical trapping and coumarin fluorescence probe experiments have confirmed that $\cdot\text{OH}$ plays the main role in RhB degradation. The $\cdot\text{OH}$ formation is higher in presence of visible LED light than in dark during Fenton like reaction. DFL reaction is initiated by thermodynamically favorable redox reaction between $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Cu}^{2+}/\text{Cu}^{+}$ redox couples. The low molecular weight compounds formed on degradation are strongly deposited on the catalyst active sites and put a restriction on the reusability of the catalyst. However, this drawback can be overcome by heating the cycled catalyst in presence of air to remove the deposited compounds. The degradation behavior of the heat-treated catalyst is not widely different than the as-synthesized composite. These findings on the $\text{CuCr}_2\text{O}_4/\text{CeO}_2$ nanocomposite system and their role in RhB degradation are expected to motivate further research in this important area of wastewater treatment. The dramatic improvement of catalytic activity of the nanocomposite in comparison to the parent phases can be ascribed to the band bending across the grain boundary of the composite phases. The change in interaction of the nanocomposite phases at the interface by varying calcination temperature modifies the excited state lifetime of the electron-hole pair, which has direct impact on the photocatalytic performance. Based on a comprehensive analysis of the possible mechanistic pathways for the photocatalytic process we have concluded that the p-n heterojunction mechanism is the most suitable pathway to rationalize the photodegradation behavior of the investigated nanocomposite catalyst. The generality of catalytic activity of this nanocomposite tested with MB and MO dyes have revealed the novelty of the photocatalyst. Interestingly, MB and MO dyes can be degraded by 98% in 20 min and by 96% in 30 min,

respectively. It is highly expected that the present finding will motivate the researchers to discover more new transition metal oxide-based Fenton like catalysts as well as their theoretical exploration.

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Chapter 5

Studies on photocatalytic Fenton like activity of anatase TiO₂ decorated CuCr₂O₄ nanocomposite photocatalyst

Chapter abstract

This chapter deals with the surprising performance of CCO/anatase-TiO₂ nanocomposite system as a highly recyclable Fenton like catalyst with potential impact for sustainable design and environmental protection. All the materials were thoroughly characterized by numerous physical and chemical techniques. A series of CCO/TiO₂ nanocomposite was synthesized by sonochemical method followed by heat treatment. The 100% CCO-loaded nanocomposite material obtained by heat-treatment at 400 °C is found to exhibit high performance towards degradation of azo dyes like MB, RhB and MO, antibiotics like TC-HCl and NORF, and a promising Pt-free candidate for photoelectrocatalytic oxygen evolution reaction under domestic LED light irradiation. Both the components of the nanocomposite play a specific role for improved charge separation and visible light absorption. TiO₂ plays two primordial roles, namely, it acts as an electron receiver to improve the charge separation in the nanocomposite and secondly, it participates in the Fenton like reaction.

5.1. Introduction

The archetypal TiO₂ photocatalyst serves the purpose of AOP with many advantages over other AOPs. In addition, TiO₂ exhibits excellent properties like electrical [1], optical [2], dielectric [3], piezoelectric [4] and gas sensing [5]. Moreover, TiO₂ possesses the fabulous features like low price, ease of synthesis, high chemical inertness, and biologically benign. Remarkably, at ambient condition TiO₂ exists in three polymorphic forms namely, rutile, brookite and anatase depending on the mode of connectivity of TiO₆ building blocks. The octahedral edge sharing feature increases from two, three to four in rutile, brookite and anatase, respectively leading to the stability order rutile>brookite>anatase. Due to such structural modification, TiO₂ shows variable band gap. The band gap values of different polymorphs of TiO₂ are 3.0 eV (~413 nm), 3.2 eV (~387.5 nm) and 3.3 eV (~375.7 nm), respectively for rutile, anatase and brookite. In addition, different surfaces of TiO₂ exhibit different band gaps as well [6]. Accordingly, photocatalytic activity of TiO₂ appears in the violet to near ultraviolet region of the electromagnetic spectrum. Among these polymorphs, brookite is less explored as photocatalyst. Though the band gap of anatase TiO₂ is larger than rutile, the relative position of conduction band of anatase is lower than that of the rutile [7].

For the efficient catalytic performance, the photoexcited electrons, rather excitons should effectively diffuse to reach the surface. The superior exciton mobility from interior towards the surface in anatase polymorph makes it a better photocatalyst compared to the rutile form [8]. In addition, several studies revealed that TiO_2 exhibits crystallographic orientation dependent photocatalytic anisotropies [9-11].

The main two strategies towards increase in photocatalytic activity of TiO_2 were amplification in surface area and combination of polymorphic phases (rutile, brookite and anatase) [12-14]. Mixed phase TiO_2 is reported to show enhanced photocatalytic activity compared to the pure phase [7]. The mixed phase anatase/brookite exhibits high performance towards removal of methylene blue [12]. However, diverse activities are undertaken to broaden the spectral absorption region of TiO_2 to the visible light, such as doping with transition metal, coupling of nanoparticles or making composites with other semiconductor materials [15-16]. The enhanced photoactivity requires delayed recombination of the photogenerated charge carriers. Thus, it demands to put more effort for developing smart photocatalysts with enhanced exciton life-time and high performance under visible light irradiation. We have recently developed the nanocomposites $\text{CuCr}_2\text{O}_4/\text{CeO}_2$ [17] and $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ [18] with excellent performance towards dye degradation. These findings highly motivated us to investigate the $\text{CuCr}_2\text{O}_4/\text{TiO}_2$ nanocomposite.

We observed that $\text{CuCr}_2\text{O}_4/\text{TiO}_2$ composite (CCO/TiO_2) exhibits both the photo and dark Fenton like activity with much more superior performance and versatility as photocatalyst towards degradation of complex azo dyes like MB, RhB and MO as well as degradation of antibiotics such as tetracycline hydrochloride and norfloxacin with the aid of a domestic visible LED light source. These composites have been realized to be promising photoelectrocatalyst for the oxygen evolution reaction under domestic LED light irradiation. In CCO/TiO_2 nanocomposite, both CCO and TiO_2 participate in Fenton reaction requiring H_2O_2 activation. The improved charge separation can be attributed to the transfer of electrons from the CB of CCO to CB of TiO_2 under light irradiation. In this nanocomposite, the TiO_2 has been realized to play two primary roles. Firstly, it acts as an electron acceptor to improve the charge separation in the nanocomposite system and secondly, it may participate in the Fenton like reaction. The improved charge separation facilitated the turnover of $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ pair.

5.2. Results and discussion

5.2.1 Powder X-ray diffraction study

The complete XRD patterns of TiO_2 , CCO and the CCO/ TiO_2 nanocomposites are displayed in **Fig. 5.1(a)**. The XRD pattern of TiO_2 corresponds to tetragonal anatase phase which is well matched to JCPDS file no. 99-0008. On the other hand, the XRD pattern of CCO well corresponds to JCPDS file no.72-1212 suggesting its tetragonal type structure. Consequently, in the CCO/ TiO_2 nanocomposite system the peaks at the 2θ values of 25.34° , 37.8° , 47.97° , 54.18° and 62.65° can be indexed to (101), (004), (200), (105) and (118) planes of anatase type TiO_2 and those at 31° , 35.2° , 37.7° and 42.2° correspond to (112), (211), (202) and (220) planes of CCO. Hence from the XRD results, it is observed that the CCO/ TiO_2 nanocomposite system contains both TiO_2 and CCO phases without any additional impurity phase(s). The average sizes of particles obtained from the XRD patterns using Scherrer's formula are ~ 30.1 and 10.9 nm for pure CCO and TiO_2 , respectively. The average particle sizes of the CCO/ TiO_2 nanocomposite sample fall in the range from 9 nm to 10.5 nm. It must be noted that the XRD peaks of CCO are shifted towards the lower 2θ (see **Fig. 5.1(b)**) indicating presence of certain interaction between the components in the nanocomposite.

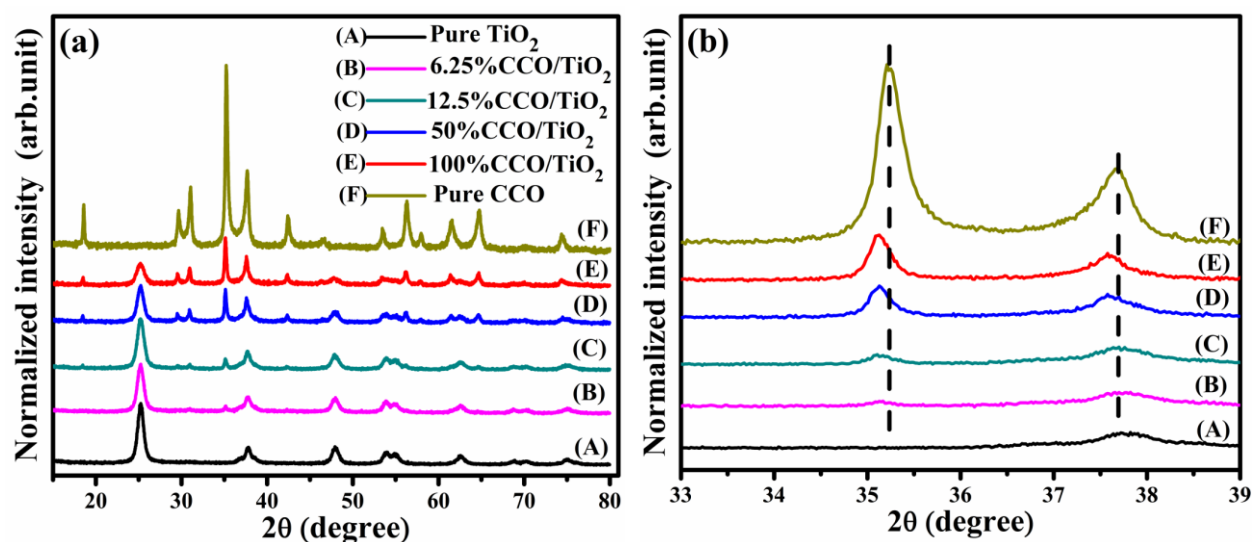


Fig. 5.1: Powder XRD patterns of CCO, TiO_2 and their nanocomposites: (a) for the whole 2θ range and (b) expanded view in the 2θ range 33° – 39° to visualize shift in peak positions subsequent to nanocomposite formation.

5.2.2. Morphology and microstructure analyses

Fig. 5.2(a-c) presents the TEM images of CCO, TiO_2 and 100%CCO/ TiO_2 . The low-resolution TEM of TiO_2 (see **Fig. 5.2(b)**) shows highly aggregated semi sphere like nanoparticles with a particle size nearly 6 nm to 10 nm. From the low-resolution TEM image, an irregular spherical shape of CCO in its pure form (particle size nearly 25 nm to 30 nm) (see **Fig. 5.2(a)**) and spherical type CCO when present in the nanocomposite system (see **Fig. 5.2(c)**) can be identified where TiO_2 nanoparticles are decorated on the large sized CCO surface. The HRTEM of 100%CCO/ TiO_2 nanocomposite (see **Fig. 5.2(d)**) confirmed the presence of two different lattice fringe patterns of which the fringe spacing of 0.30 nm corresponds to (220) lattice plane of CuCr_2O_4 and the other with spacing of 0.35 nm corresponds to (101) lattice plane of TiO_2 . The EDX analysis of 100%CCO/ TiO_2 catalyst (see **Fig. 5.2(e)**) indicates the presence of all the expected elements Cu, Cr, Ti and O in the nanocomposite with the atomic percentages of the various elements close to the nominal composition. The elemental mapping analysis of 100%CCO/ TiO_2 sample (see **Fig. 5.2(f-k)**) further confirmed the presence as well as uniform distribution of the elements Cu, Cr, Ti and O in the nanocomposite.

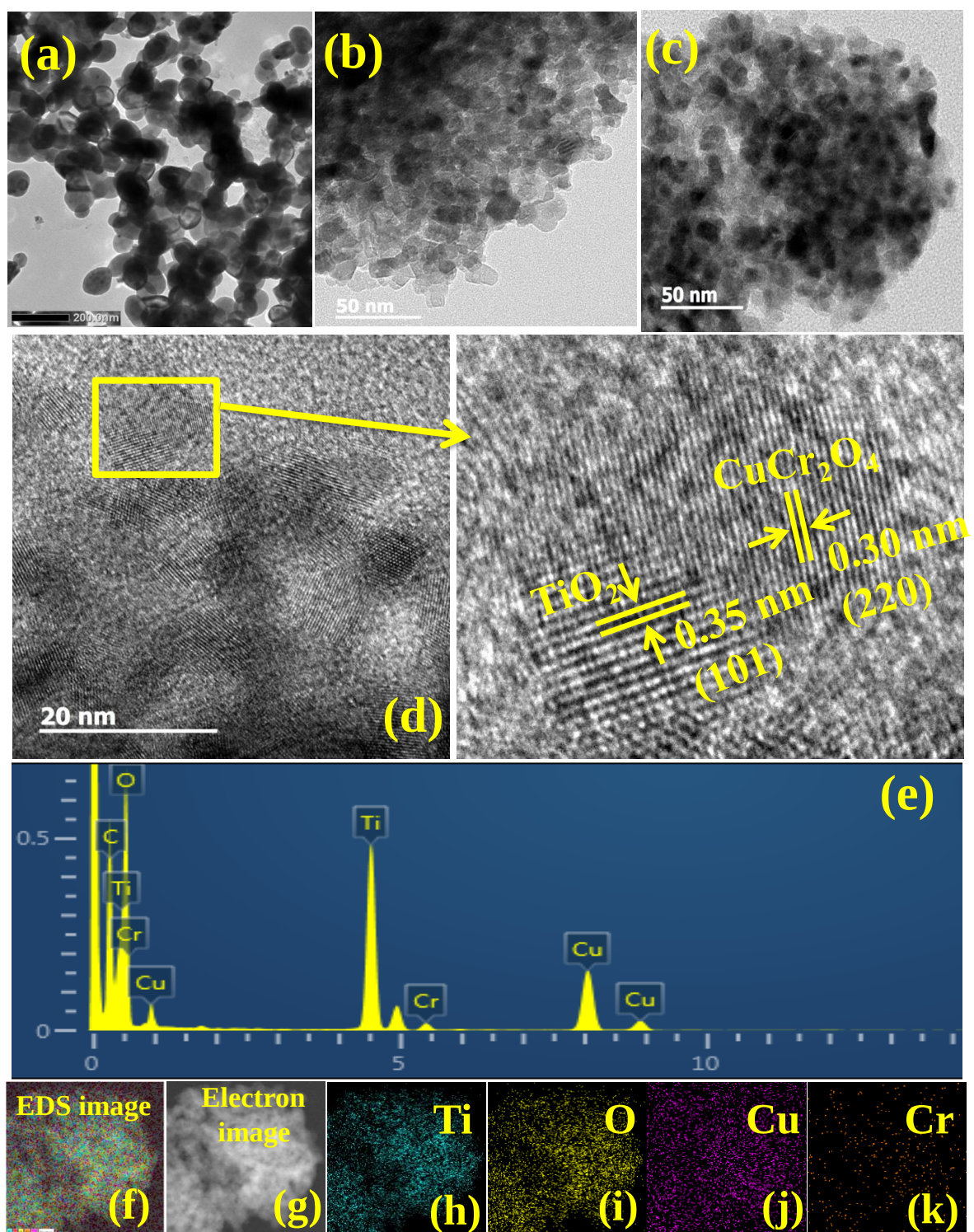


Fig. 5.2: Low-resolution TEM images of (a) pure CCO, (b) pure TiO_2 and (c) 100%CCO/ TiO_2 nanocomposite; (d) HRTEM and (e) EDX and (f-k) EDS elemental mapping analyses of 100%CCO/ TiO_2 nanocomposite.

5.2.3. BET analyses

The values of multipoint BET specific surface areas, pore volumes and pore sizes of CCO, TiO₂ and CCO/TiO₂ nanocomposites are listed in **Table 5.1**. The adsorption-desorption isotherms of the synthesized samples are displayed in **Fig. 5.3** and the respective pore size distribution curves are included in the inset. The nature of isotherms corresponds to type IV with a H3 type hysteresis loop. These findings confirm the mesoporous nature of the materials. From **Table 5.1** it is seen that the BET specific surface area is increased for the CCO/TiO₂ nanocomposites from 6.25% CCO-loading to 50% CCO-loading than that of the pure oxide components. The 12.5%CCO/TiO₂ sample exhibited the maximum BET surface area of 106.7 m² g⁻¹. A certain decrease of surface area is observed for 100–200% CCO-loaded samples probably due to blocking effect of high surface area TiO₂ by low surface area CCO.

Table 5.1: Textural properties of CCO, TiO₂ and CCO/TiO₂ nanocomposite material.

materials	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Scherrer size (nm)
CCO	12.3	0.026	1.45	30.1
TiO ₂	85.3	0.124	2.076	10.9
6.25%CCO/TiO ₂	96.7	0.168	2.271	10.5
12.5%CCO/TiO ₂	106.7	0.149	1.985	9.6
50%CCO/TiO ₂	99.6	0.145	2.076	9.4
100%CCO/TiO ₂	82.5	0.132	2.271	9.3
200%CCO/TiO ₂	57.8	0.110	2.271	9.1

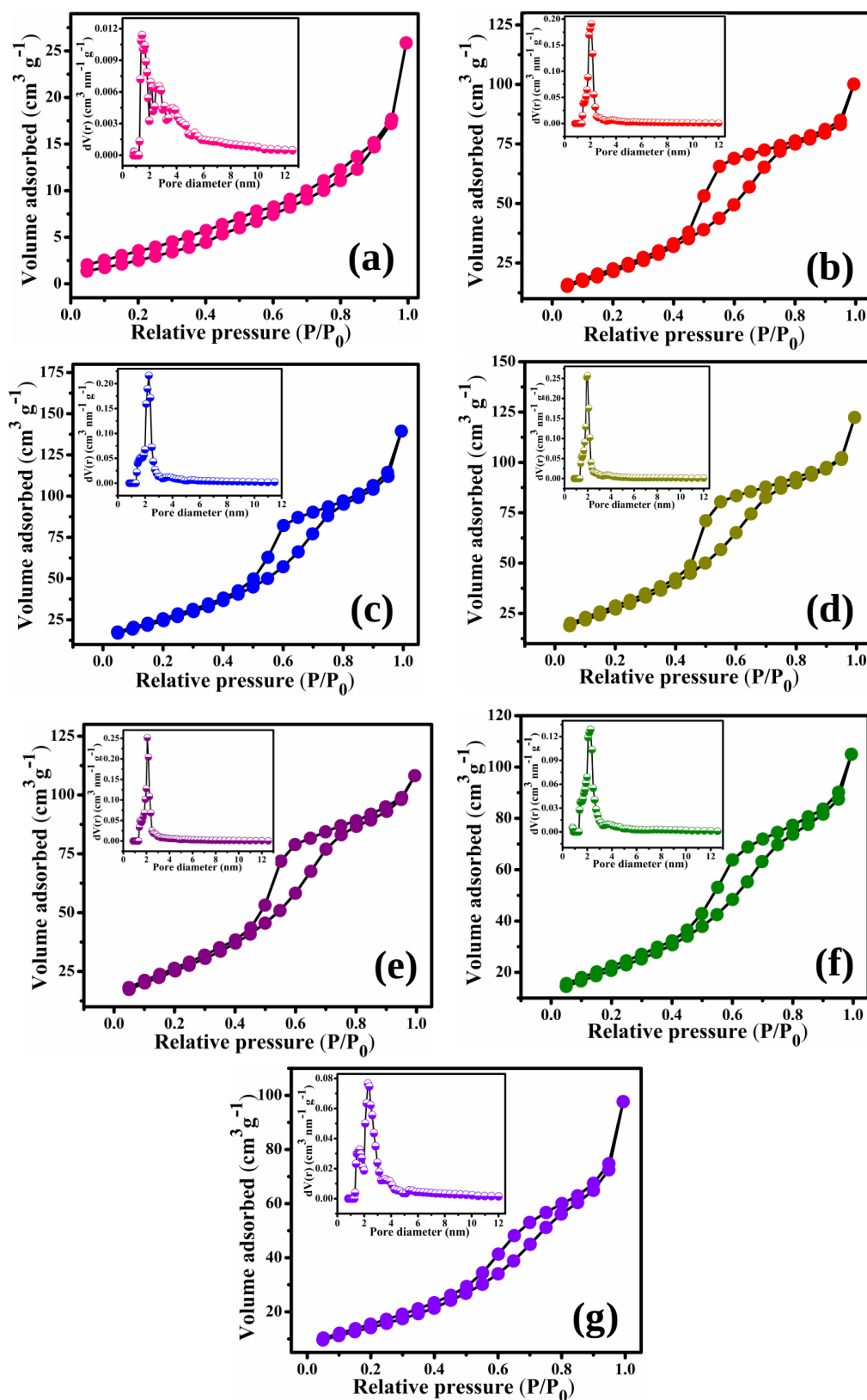


Fig. 5.3: Nitrogen adsorption-desorption isotherms and pore size distribution curves (in the inset) of (a) pure CCO, (b) pure TiO_2 , (c) 6.25%CCO/ TiO_2 , (d) 12.5%CCO/ TiO_2 , (e) 50%CCO/ TiO_2 , (f) 100%CCO/ TiO_2 and (g) 200%CCO/ TiO_2 nanocomposite.

5.2.4. XPS analyses

The preliminary XPS data of the finalized samples are shown in **Fig. 5.4**. The finer details of XPS data of pristine as well as the post treatment samples will be discussed in section 6.2.15. In the present study, broad envelope of Cu 2p core level spectrum of CCO/TiO₂ nanocomposite indicates the presence of different Cu species and is resolved by curve-fitting as displayed in **Fig. 5.4(a)**. Because of interference from Cr LMM Auger peak, Cu 2p_{3/2} core level spectral region is only curve-fitted for better understanding. Cu 2p_{3/2} peaks at 932.4 and 933.7 eV with characteristic satellite peaks are attributed to Cu⁺ and Cu²⁺ species. Weakly intense satellites indicate the presence of lower amount of Cu²⁺ species in CCO/TiO₂ nanocomposite. From the area under the corresponding peak it is estimated that 51.1% of total Cu is present in +1 oxidation state and rest amount is Cu²⁺ species. Asymmetric nature of Cr 2p core level spectrum of CCO/TiO₂ nanocomposite signifies variable nature of Cr in the nanocomposite and its deconvolution into component peaks by curve fitting is depicted in **Fig. 5.4(b)**. Intense Cr 2p_{3/2,1/2} peaks around 576.5 and 586.1 eV are attributed to Cr³⁺ species in octahedral environment [17]. However, weak component peaks at 576.0 and 585.1 eV is assigned to Cr⁴⁺ [19, 20]. Moderate intense peaks at higher binding energies of 579.8 and 589.3 eV are ascribed to the presence of certain fraction of Cr(OH)₃ surface species [21] formed in-situ from the hydroxylation of CCO during nanocomposite synthesis. Because the thermal decomposition of Cr(OH)₃ occurs usually in the range 430–1000 °C, the surface hydroxide species persists at the calcination temperature of 400 °C used for the nanocomposite formation [22]. Ti 2p core level spectra of pure TiO₂ and CCO/TiO₂ nanocomposite are compared in **Fig. 5.4(c)**. Ti 2p_{3/2,1/2} peaks at 458.5 and 464.3 eV observed in pure TiO₂ are assigned to Ti⁴⁺ species [23]. However, it is clear from the figure that Ti 2p core level spectral nature of TiO₂ in CCO/TiO₂ nanocomposite is also broad signifying the existence of different Ti species and is separated into component species by the process of curve-fitting. **Fig. 5.4(d)** represents the curve-fitted Ti 2p core level spectra of CCO/TiO₂ nanocomposite. Along with Ti 2p_{3/2,1/2} spin-orbit peaks at 458.7 and 464.5 eV, there are weak component peaks at 457.2 and 462.9 eV which stand for Ti³⁺ species in the composite. From the area under the corresponding peak it is estimated that 13.6% of total Ti is in +3 oxidation state. Thus, Ti is slightly reduced in the composite in relation to pure TiO₂ clearly suggesting the formation of oxygen vacancy in the composite. This is also corroborated by O 1s core level spectra as shown in **Fig. 5.4(e)**. Intense O 1s binding energy peak at 530.3 eV is associated with oxide peak in TiO₂. However, asymmetric spectral nature

of O 1s core level spectrum in CCO/TiO₂ nanocomposite indicates the presence of several oxygen species. The main peak at 530.3 eV is assigned to Ti⁴⁺ oxide species and the peak around 532.2 eV may be related to oxygen vacancy [24, 25].

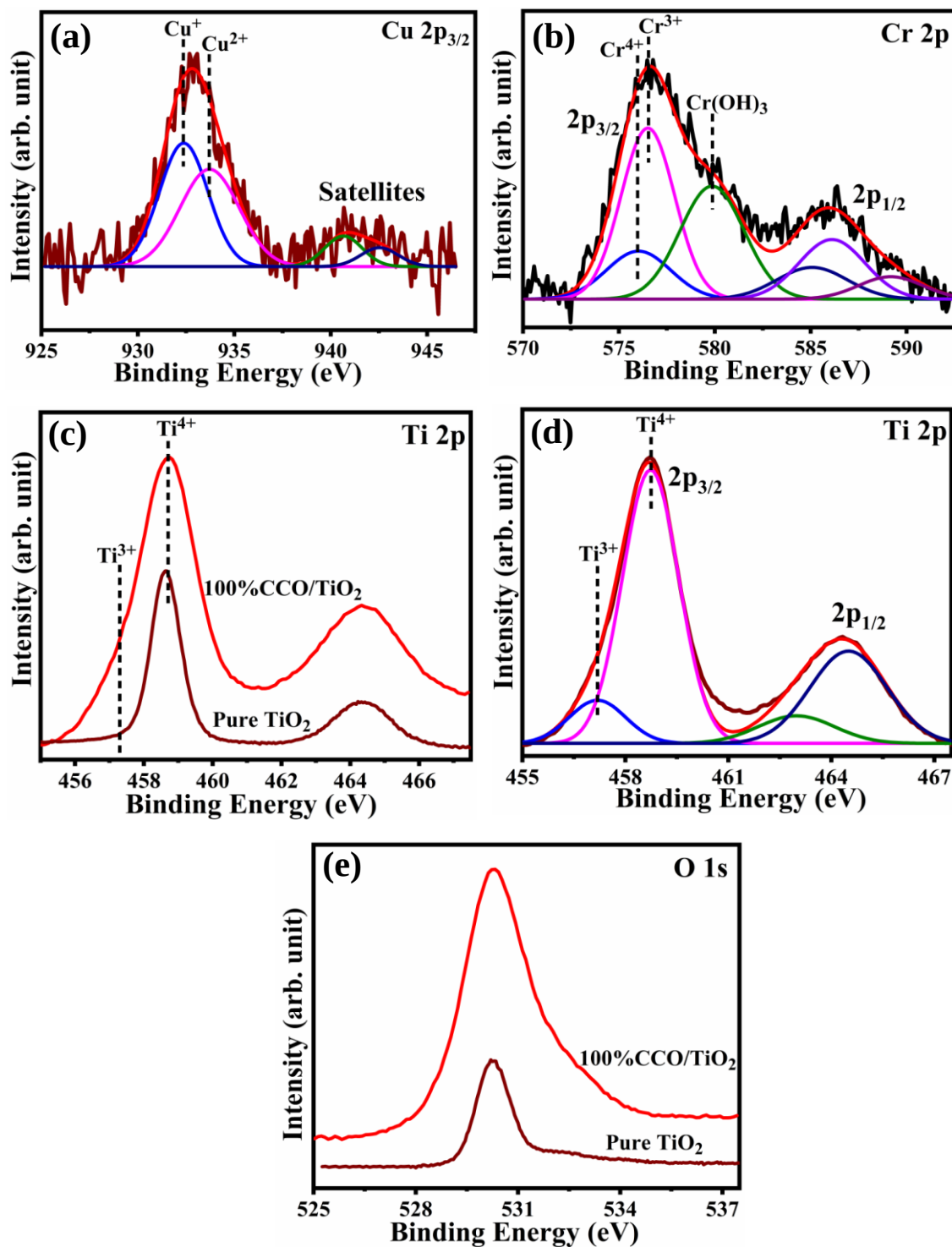


Fig. 5.4: XPS core-level peaks of (a) Cu 2p, (b) Cr 2p, (c) Ti 2p, (d) deconvoluted Ti 2p of the 100%CCO/TiO₂ nanocomposite and (e) O 1s regions.

5.2.5. UV-Vis DRS and band gap analyses

The absorption edge of pure TiO_2 is found to be near 402 nm, while pure CCO nanoparticles show very high absorption over the full visible range (see **Fig. 5.5(a)**). Generally, the absorption edge of pure TiO_2 falls at a wavelength below 400 nm, but in our case we have observed a red shift in the absorption edge that may be due to a comparatively higher temperature used for the synthesis of TiO_2 contributing to its higher crystallinity. Such a shift has also been reported in other works [26, 27]. It is clearly evident that all the CCO/ TiO_2 nanocomposite samples show an enhanced light absorption in the visible region compared with pure TiO_2 . It is thus obvious that the improved light absorption property of TiO_2 in CCO/ TiO_2 nanocomposite is mainly due to the presence of CCO nanoparticles. With the increase of CCO loading amounts, the light absorption of CCO/ TiO_2 nanocomposite follows an increasing trend in the visible region. When the CCO loading amount is reached to 50%, the light absorption profile curve in the UV-Vis DRS spectrum approaches close to that of pure CCO, which indicates that CCO introduction in the nanocomposite catalyst surface plays a crucial role for visible light absorption. After loading of CCO, the absorption edge of TiO_2 was red-shifted. Additionally, the CCO/ TiO_2 nanocomposite system with higher CCO loading such as 50%, 100% and 200% has a higher light absorption and catalytic activity than that of the CCO/ TiO_2 nanocomposite with lower CCO loading such as 6.5% and 12.6%. Therefore, it is suggested that the PFL activity of CCO/ TiO_2 nanocomposite sample with higher CCO loading is postulated to be much better than that of the nanocomposites with lower CCO loading. The band gap energies of CCO and TiO_2 obtained from Tauc plots (see **Fig. 5.5(b, c)**) are 3.11 eV and 1.40 eV, respectively. The estimated band gap energies of 6.25%CCO/ TiO_2 , 12.5%CCO/ TiO_2 , 50%CCO/ TiO_2 , 100%CCO/ TiO_2 and 200%CCO/ TiO_2 are 2.82, 2.58, 1.68, 1.52 and 1.28 eV, respectively and the corresponding Tauc plots are shown in **Fig. 5.6**.

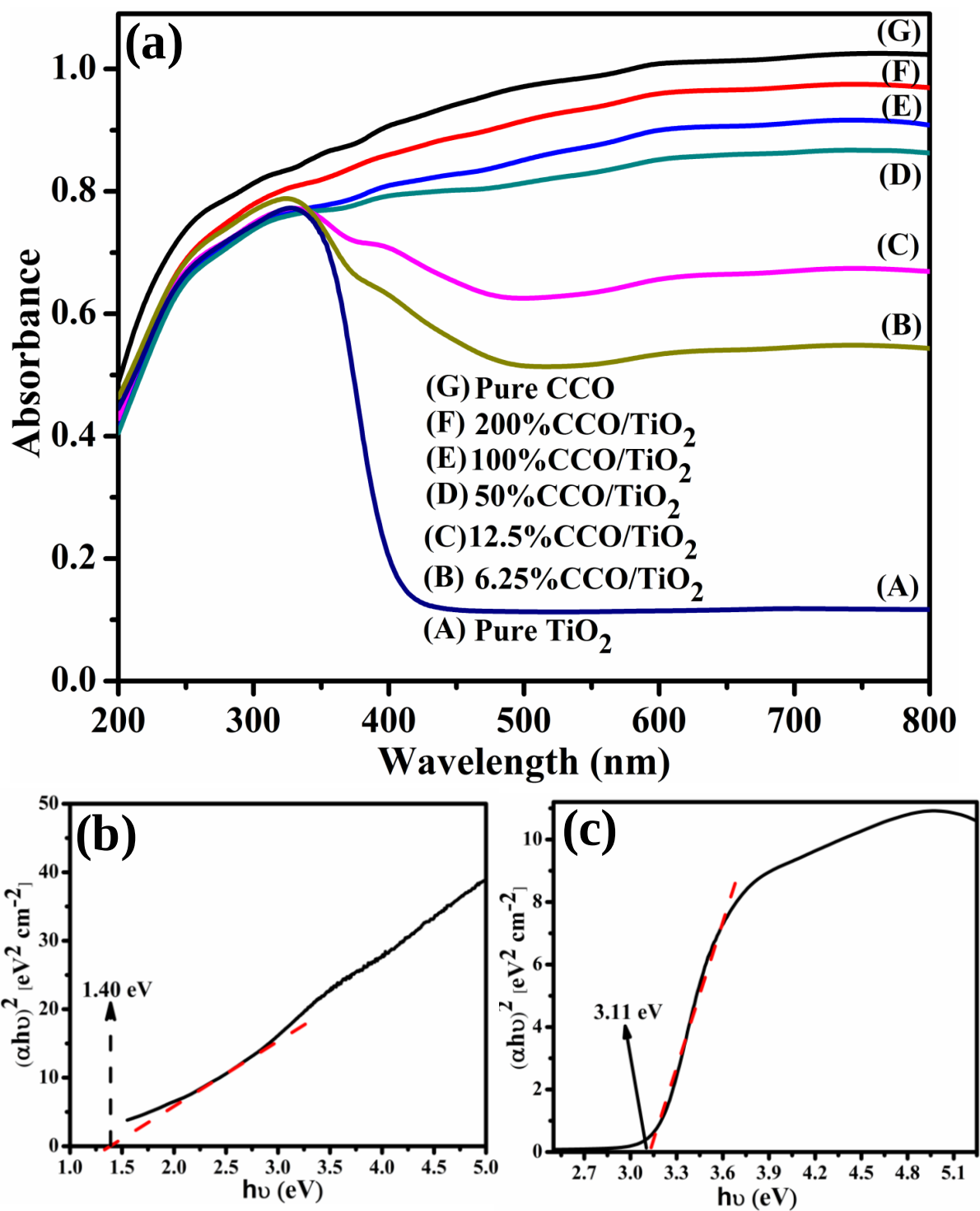


Fig. 5.5: (a) UV-Vis DRS spectra of pure as well as nanocomposite materials and Tauc plots of (b) pure CCO and (c) pure TiO_2 .

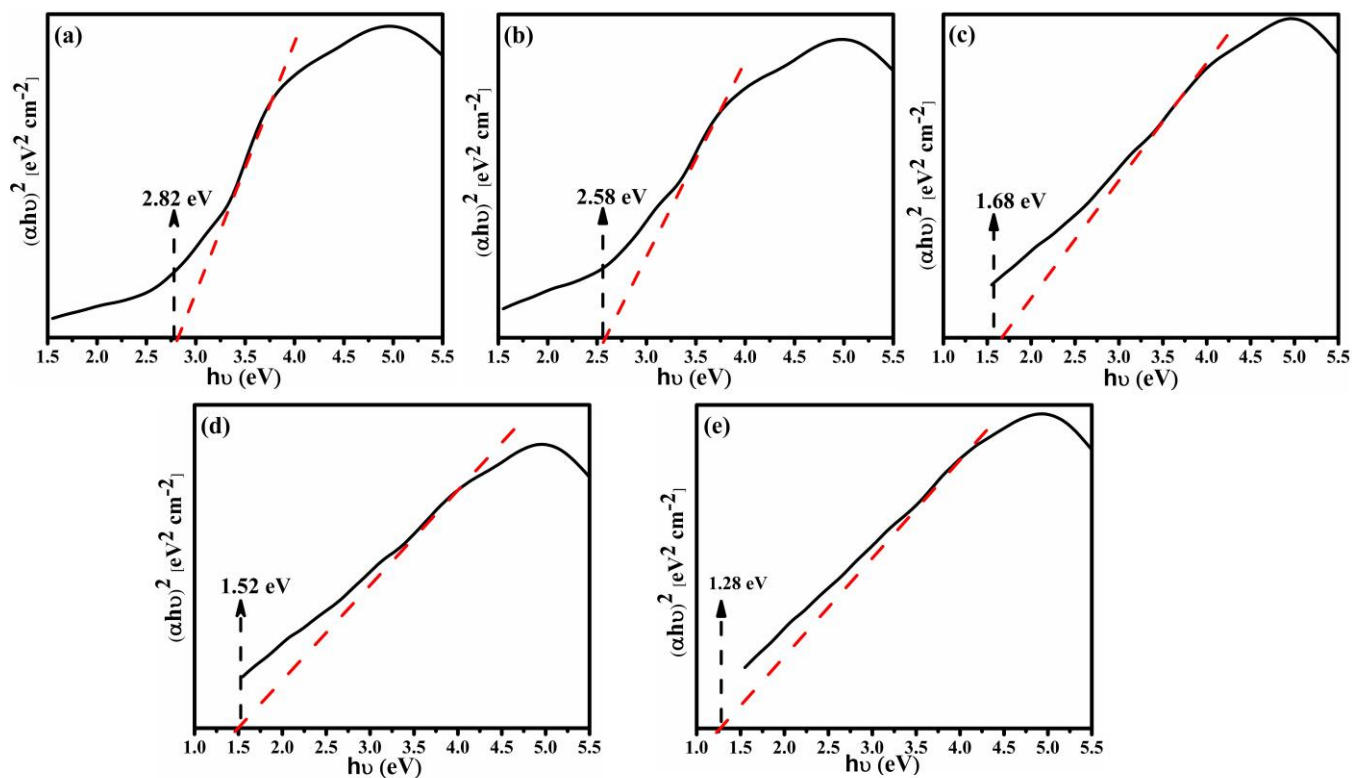


Fig. 5.6: Tauc plots of (a) 6.25%CCO/TiO₂, (b) 12.5%CCO/TiO₂, (c) 50%CCO/TiO₂, (d) 100%CCO/TiO₂ and (e) 200%CCO/TiO₂ nanocomposites.

5.2.6. PL spectral analyses

The improved electron-hole pair recombination of CCO/TiO₂ nanocomposite system compared with pure TiO₂ was investigated by PL spectroscopy at an excitation wavelength of 360 nm. The PL spectrum of pure TiO₂, 12.5%CCO/TiO₂ and 100%CCO/TiO₂ nanocomposite sample is displayed in **Fig. 5.7(a)**. With the increase of CCO loading amounts, the PL intensity was decreased and 100%CCO loaded nanocomposite sample (i.e., 100%CCO/TiO₂) shows the lowest PL intensity, which indicates the maximum charge separation. Therefore, the PL studies suggest that the charge separation is effectively improved in CCO/TiO₂ nanocomposite system consequent upon CCO loading.

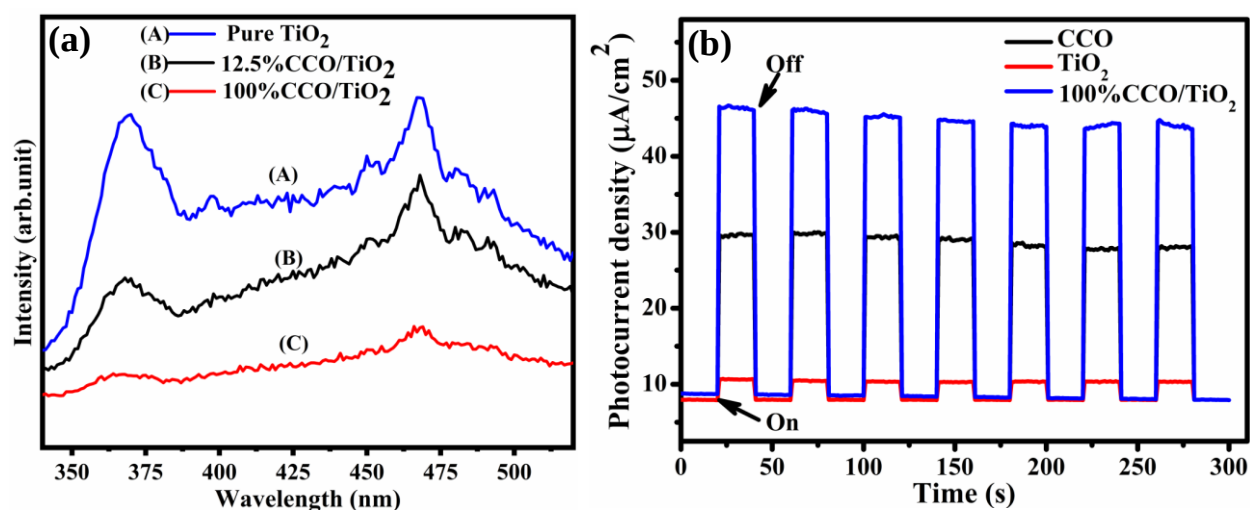


Fig. 5.7: (a) Photoluminescence spectra of pure TiO₂ and CCO/TiO₂ nanocomposite and (b) transient photocurrent response of CCO, TiO₂ and 100%CCO/TiO₂ nanocomposite.

5.2.7. Photocurrent response analyses

The photocurrent response of CCO, TiO₂ and CCO/TiO₂ nanocomposite were investigated by electrochemical chronoamperometric measurement. **Fig. 5.7(b)** shows the photocurrent densities of CCO, TiO₂ and 100%CCO/TiO₂. The photocurrent density of 100%CCO/TiO₂ is 46.71 $\mu\text{A cm}^{-2}$ which is respectively 1.5 and 4.3 times higher than that of pure CCO and pure TiO₂. A noticeably improved photocurrent density of the 100%CCO/TiO₂ nanocomposite than the pure phases is suggestive of high photocatalytic activity of the nanocomposite.

5.2.8. Fenton like degradation activity

5.2.8.1. PFL activity and normal photocatalytic activity

To evaluate the photocatalytic activity of CCO/TiO₂ nanocomposite catalysts we have chosen methylene blue and rhodamine-B as cationic and methyl orange as an anionic model organic pollutant. The time-dependent PFL activity of all the CCO/TiO₂ nanocomposites and the parent oxides for the degradation of MB, RhB and MO under domestic visible LED irradiation are demonstrated in **Fig. 5.8**. The corresponding degradation percentages after 15 min of visible LED irradiation in presence of 50 mg catalyst and 4 mM of H₂O₂ (30% W/W) are listed in **Table 5.2**. From the results, it is clearly observed that all the CCO/TiO₂ nanocomposite catalysts show much higher PFL activity than the pristine oxides CCO and TiO₂. Results of blank tests, i.e., degradation in the absence of catalyst suggest about 4%

degradation of the azo dyes by H_2O_2 alone. The degradation is only significantly increased in the presence of catalyst, which facilitates H_2O_2 dissociation to form very active $\cdot\text{OH}$ radicals for enhanced degradation of the azo dyes as confirmed from the radical trapping analysis discussed later (see **Section 5.2.9**). Careful monitoring of PFL activity reveals that 100%CCO/ TiO_2 nanocomposite catalyst exhibits best PFL activity; the degradation percentage is approximately 4.5, 5.7 and 11.6 times higher than that of pure CCO and 3.6, 3.4 and 4.2 times higher than that of pure TiO_2 , respectively for MB, RhB and MO degradation. PFL activity of pure TiO_2 is a little higher than that of pure CCO due to higher $\cdot\text{OH}$ generation from H_2O_2 by the reaction with TiO_2 (see section 3.10). The Fenton like activity of pure TiO_2 involving reaction of $\text{Ti}^{4+}/\text{Ti}^{3+}$ with H_2O_2 is supported by the report of Liu et al. [28]. It is thus evident that although TiO_2 and CCO both show low activity towards PFL reaction, they can form a highly efficient PFL catalyst when a nanocomposite system is formed.

The experimental data can be fitted best by using the pseudo first-order kinetics model, which is justified from the very high values of regression co-efficient (R^2) that ranges from 0.96 to 0.99 (see **Table 5.2**). The values of rate constants estimated from the slope of the linearly fitted curve of $-\ln(C_t/C_0)$ vs. t are listed in **Table 5.2**. It is obvious that 100%CCO/ TiO_2 catalyst possesses maximum values of rate constants 0.30794, 0.24358 and 0.14943 min^{-1} , respectively for MB, RhB and MO degradation. These values are respectively 19 and 14.5 times higher for MB, 19.9 and 11.3 times higher for RhB and 27 and 9 times higher for MO than that of pure CCO and pure TiO_2 . Under identical conditions, the visible LED assisted PFL activity of the CCO/ TiO_2 nanocomposites towards the degradation of MB, RhB and MO follows the order, MB>RhB>MO. The degradation percentages and rate constant values of CCO/ TiO_2 clearly indicate that the catalyst shows a slightly lower PFL activity for the anionic dye (MO) in comparison with the cationic dyes (MB and RhB). The heterojunction of CCO/ TiO_2 is capable of generating long-lived photo-excited electrons to enhance the cycling of $\text{Ti}^{4+}/\text{Ti}^{3+}$ and $\text{Cu}^{2+}/\text{Cu}^+$ couple as will be discussed later. This highly efficient cycling may be at the root cause for the improved PFL activity of CCO/ TiO_2 nanocomposite in comparison with the pure oxides.

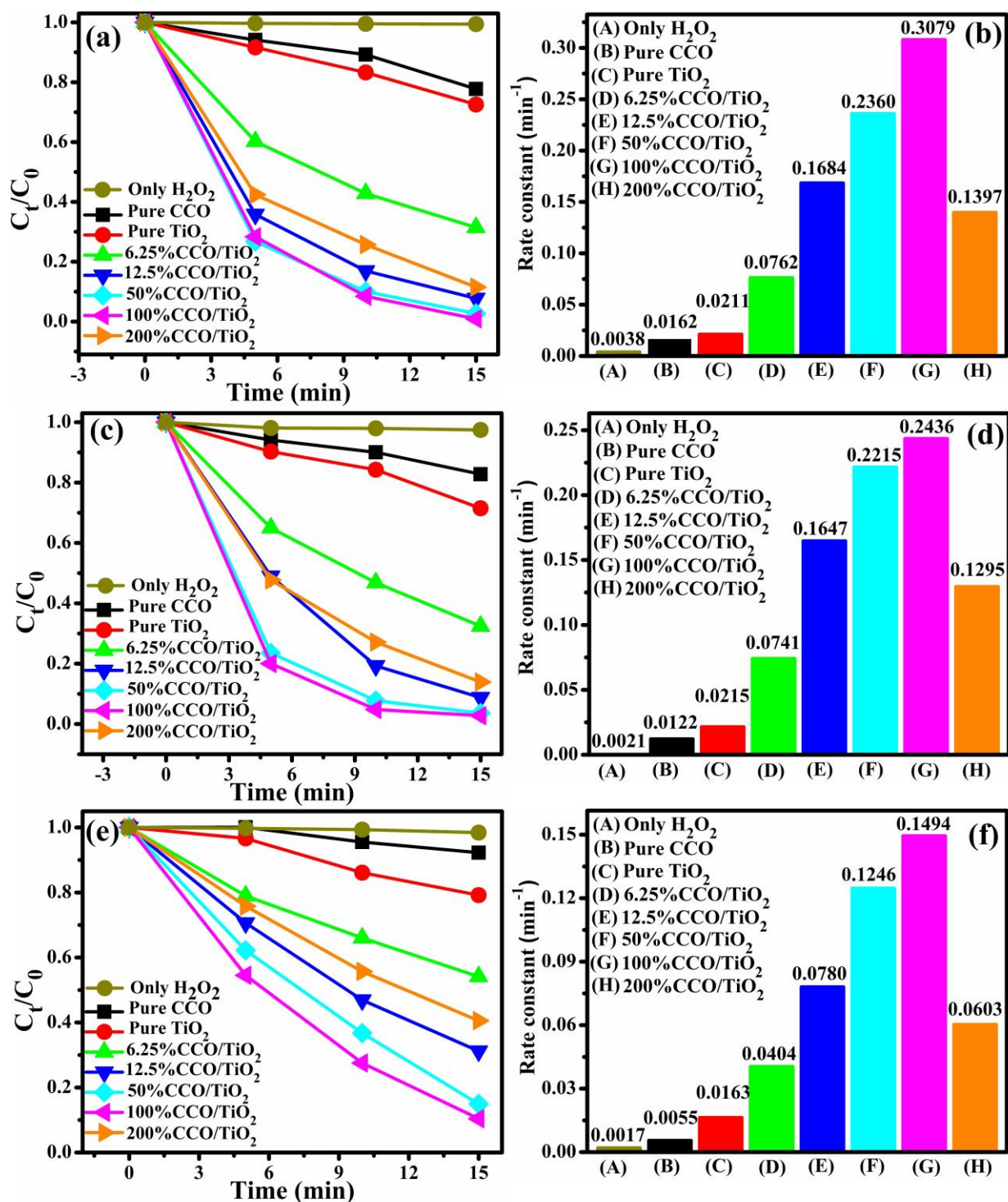


Fig. 5.8: PFL activity and rate constant values (in bar diagram) of (a, b) MB, (c, d) RhB and (e, f) MO in presence of pure CCO, pure TiO₂ and CCO/TiO₂ nanocomposite catalysts.

Besides the PFL activity of CCO/TiO₂ nanocomposite samples, the normal photocatalytic activity was also tested by using the optimum sample of the nanocomposite series, namely 100%CCO/TiO₂. The experimental condition of this test was the same as for

the PFL reaction with the exception that the degradation was performed in the absence of H_2O_2 . Normal photocatalytic activity of the nanocomposite was also compared with those of the pure components to understand the beneficial effect of nanocomposite formation. The results are displayed in **Fig. 5.9**. It is observed that the degradation percentages of MB, RhB and MO for the 100%CCO/ TiO_2 nanocomposite are respectively 29.6%, 35.6% and 21% after 15 min of LED irradiation, whereas the respective degradation percentages are 4.6%, 3% and 4% for pure CCO and 4%, 5% and 3% for pure TiO_2 . So it may be concluded that the photocatalytic activity of pure CCO as well as pure TiO_2 is very low and the activity is enhanced when they form nanocomposite. Therefore, the PFL activity and normal photocatalytic activity tests of 100%CCO/ TiO_2 nanocomposite indicate that the PFL activity is very much significant than the normal photocatalytic activity.

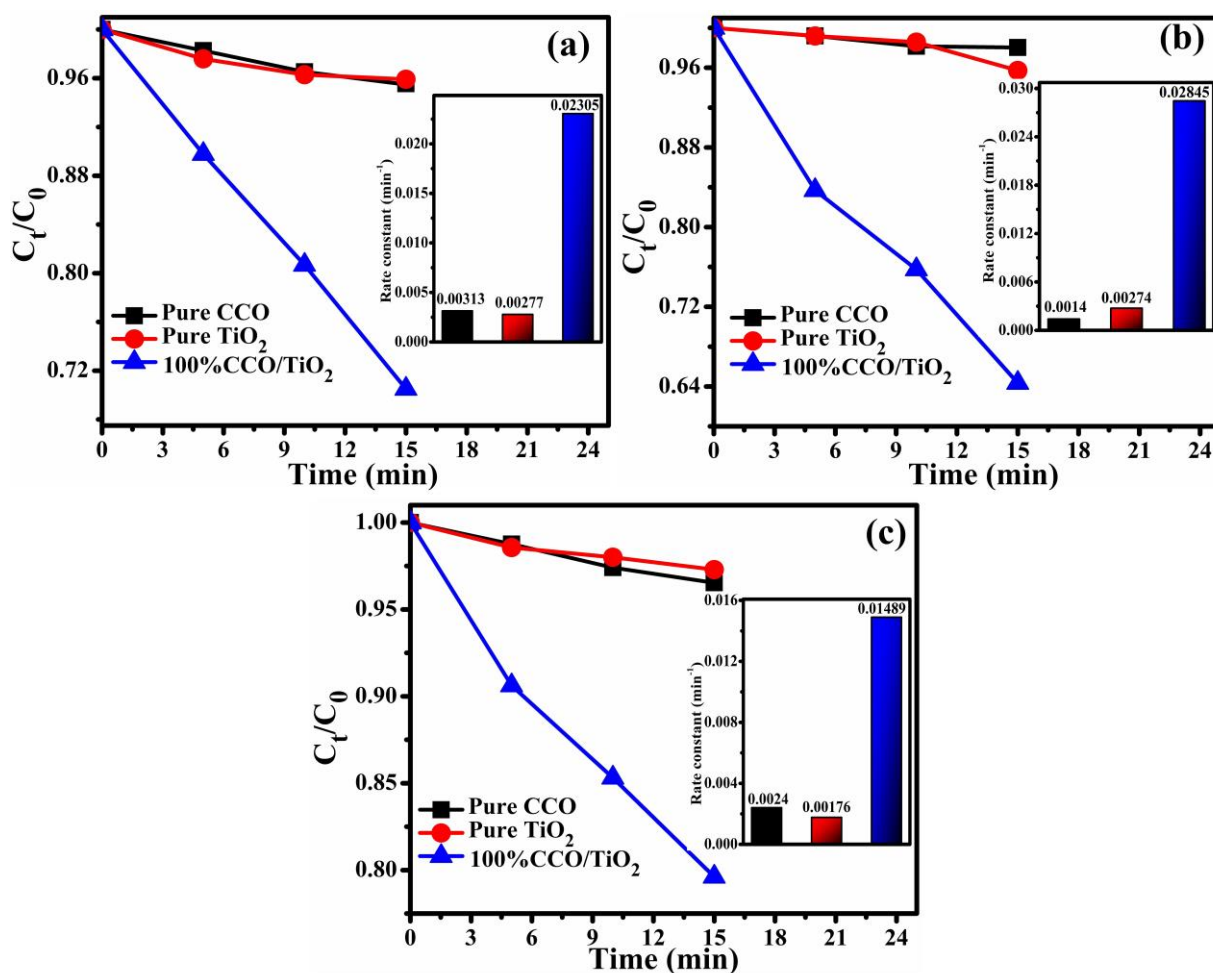


Fig. 5.9: Normal photocatalytic activity of pure CCO, pure TiO_2 and 100%CCO/ TiO_2 nanocomposite sample for the degradation of (a) MB, (b) RhB and (c) MO (the rate constants are shown in the inset of the corresponding plot).

Table 5.2: Degradation percentage (D%), rate constant (k) and regression co-efficient (R^2) for PFL reaction of pure CCO, pure TiO_2 and CCO/ TiO_2 nanocomposites.

Catalyst	MB			RhB			MO		
	D%	k (min^{-1})	R^2	D%	k (min^{-1})	R^2	D%	k (min^{-1})	R^2
Without catalyst (Only H_2O_2)	3.88	0.0038	0.9855	2.73	0.0021	0.9918	2.03	0.0017	0.9825
Pure CCO	22.24	0.01616	0.9170	17.2	0.01222	0.9772	7.7	0.00552	0.9331
Pure TiO_2	27.47	0.02119	0.9818	28.52	0.02152	0.9543	20.8	0.0163	0.9453
6.25%CCO/ TiO_2	68.57	0.07625	0.9781	67.56	0.07411	0.9955	45.9	0.04043	0.9953
12.5%CCO/ TiO_2	92.25	0.16845	0.9916	91.2	0.16474	0.9964	68.8	0.07806	0.9978
50%CCO/TiO_2	97.28	0.23603	0.9953	96.4	0.22154	0.9722	85	0.12468	0.9618
100%CCO/TiO_2	99.2	0.30794	0.9617	97.2	0.24358	0.9408	89.6	0.14943	0.9809
200%CCO/ TiO_2	88.5	0.13979	0.9863	86	0.12954	0.9962	59.4	0.06032	0.9985

5.2.8.2. Effect of catalyst amounts and H_2O_2 concentration on PFL activity of CCO/ TiO_2

The effect of catalyst dosage on the PFL activity for the degradation of MB, RhB and MO was investigated by using the most active 100%CCO/ TiO_2 catalyst for the degradation of 10 ppm of MB, RhB and MO dyes. The results are summarized as bar diagram in **Fig. 5.10(a)** from which it clear that the degradation of all the dyes is increased with the increase of catalyst loading from 25 mg to 50 mg, beyond which the activity follows a decreasing trend. Hence, we chose 50 mg of catalyst as the optimum catalyst amount for our investigation. Decrease of degradation with higher catalyst amounts is presumably due to too closeness of the active sites on the surface of the catalyst that suppresses the $\cdot\text{OH}$ formation.

The H_2O_2 concentration also plays an important role in the investigation of PFL activity and **Fig. 5.10(b)** displays the corresponding data for the degradation for 100%CCO/ TiO_2 nanocomposite. The variation followed the usually expected pattern. Initially, it is increased with an increase in H_2O_2 concentration from 2 mM to 4 mM. Specifically, after 15 min of PFL reaction, the degradation percentages of MB, RhB and MO were increased from 60%, 65% and 58% to 99%, 97% and 89.6%, respectively. Further

increase of H_2O_2 concentration greater than 4 mM, a decreasing trend of PFL activity was observed because some of the highly active $\cdot OH$ is scavenged by excess H_2O_2 ($\cdot OH + H_2O_2 \rightarrow \cdot OOH + H_2O$) to form less reactive $\cdot OOH$ which reduces the probability of attacking $\cdot OH$ towards the dye.

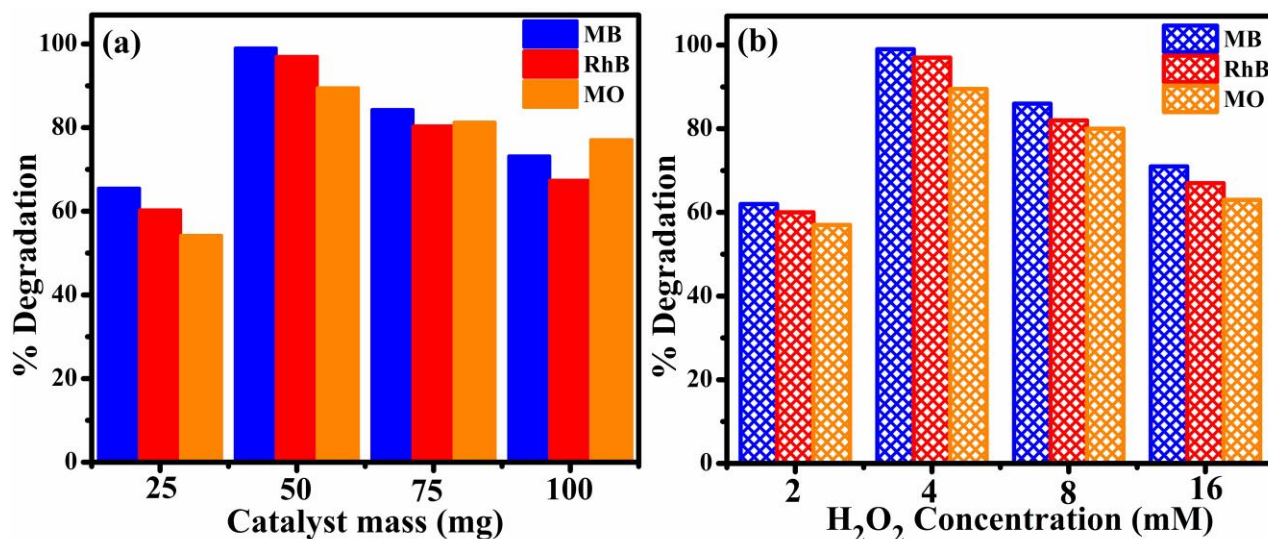


Fig. 5.10: Effects of (a) catalyst amounts and (b) H_2O_2 concentration on the PFL reaction for the degradation of MB, RhB and MO over 100%CCO/ TiO_2 .

5.2.8.3. Effect of sample synthesis temperature on PFL activity

The PFL activity was also carried out over variously calcined 100%CCO/ TiO_2 nanocomposite. The nanocomposite was synthesized by calcination at different temperatures such as 300 °C, 400 °C, 500 °C and 600 °C for 2 h and their effects on photodegradation of MB, RhB and MO are shown in **Fig. 5.11(a-c)**. It is clear that the PFL activity of 100%CCO/ TiO_2 nanocomposite is the highest for the catalyst obtained on calcination at 400 °C and follows the order: 400 °C > 500 °C > 600 °C > 300 °C. For understanding the underlying reasons of this dependency of PFL activity on catalyst calcination temperature, the cumarine based fluorescence probe experiments were conducted under identical reaction conditions to compare the $\cdot OH$ formation activity (discussed in details in **Section 5.2.10**) of the variously calcined nanocomposite catalysts (see **Fig. 5.11(d)**) because $\cdot OH$ is the main responsible species for the degradation of these dyes (discussed in details in **Section 5.2.9**). It is seen that $\cdot OH$ formation is highest for the 400 °C calcined catalyst and the order of $\cdot OH$ formation activity is the same as the order of PFL activity.

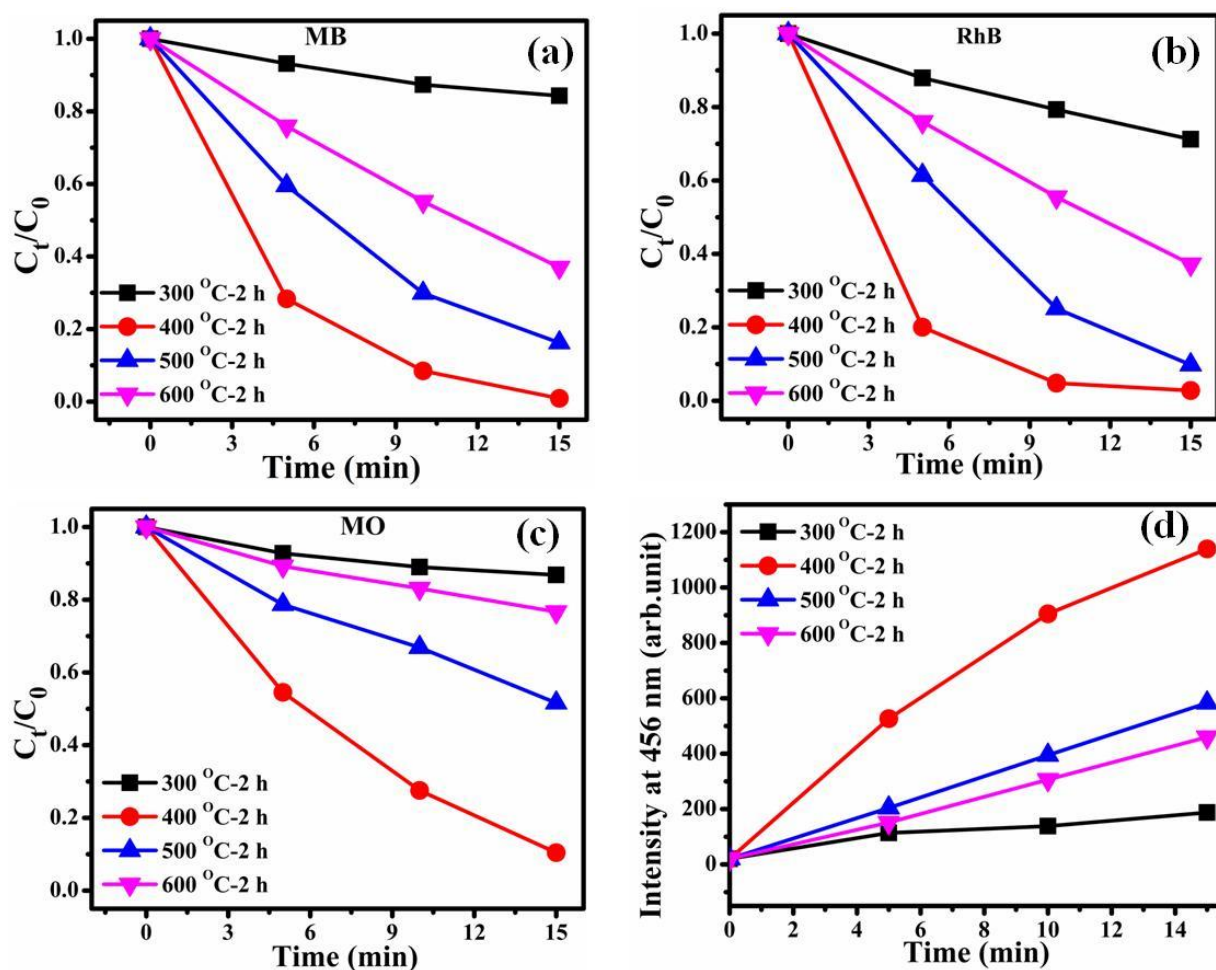


Fig. 5.11: The effect of calcination temperature of 100%CCO/TiO₂ nanocomposite on the PFL activity for the degradation of (a) MB, (b) RhB, (c) MO dyes and (d) generation activity of $\cdot\text{OH}$.

5.2.8.4. DFL activity

We have also investigated the DFL activity of the most active nanocomposite catalyst 100%CCO/TiO₂ for the degradation of MB, RhB and MO under identical conditions in the absence of LED i.e., under dark condition. The results of DFL activity are shown in **Fig. 5.12(a,b)**. Although the DFL activity is lower in comparison with its PFL activity, but a significant DFL activity of 100%CCO/TiO₂ sample was observed for the degradation of all these three dyes. In case of PFL reaction, the MB, RhB and MO degradation percentages after 15 min are respectively 99.2%, 97.2% and 89.6%, whereas the corresponding values for DFL reaction are 60%, 58% and 55%. The rate constants of MB, RhB and MO degradation for PFL reaction are 5.44, 3.37 and 4.23 times higher than that of DFL reaction. This expected higher PFL activity of the nanocomposite catalyst is mainly due to fact that the

decomposition rate of H_2O_2 is greatly accelerated by light energy and produces higher amounts of hydroxyl radicals (see **Fig. 5.12(c,d)**), the primary reactive species involved in the Fenton like degradation. The variations of photoluminescence intensities at different intervals of degradation for PFL and DFL reactions are shown in **Fig. 5.12(c,d)**. The results suggest formation of $\cdot\text{OH}$ in both the Fenton like reactions and this result also shows that the intensity of fluorescence peak at 456 nm (monitored up to 15 min) is higher in presence of visible LED irradiation than in its absence, which strongly suggests higher $\cdot\text{OH}$ generation in PFL reaction than in DFL reaction. The variations of absorbance of MB, RhB and MO at different time intervals in PFL and DFL reaction are shown in **Fig. 5.13**.

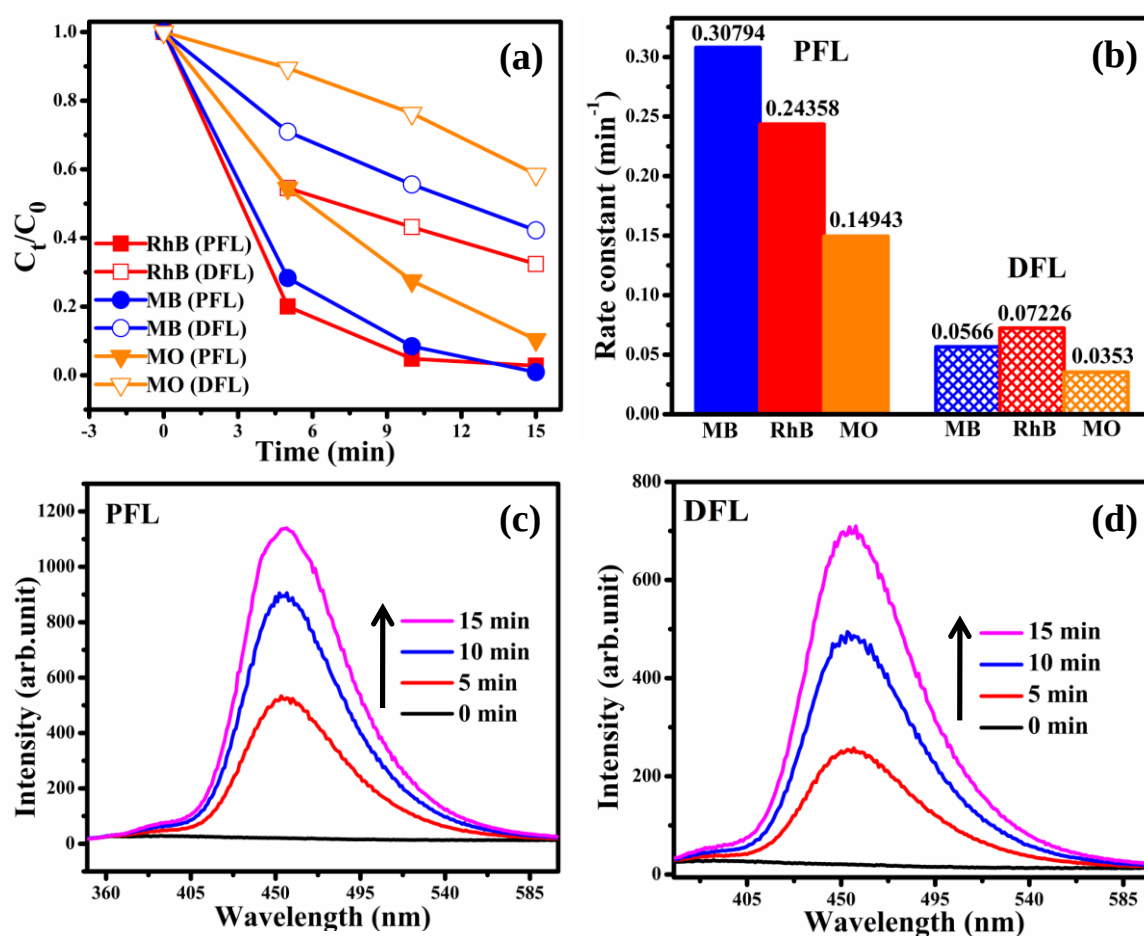


Fig. 5.12: (a) PFL and DFL activity, (b) rate constants, $\cdot\text{OH}$ generation activity in (c) PFL reaction and (d) DFL reaction of 100%CCO/TiO₂.

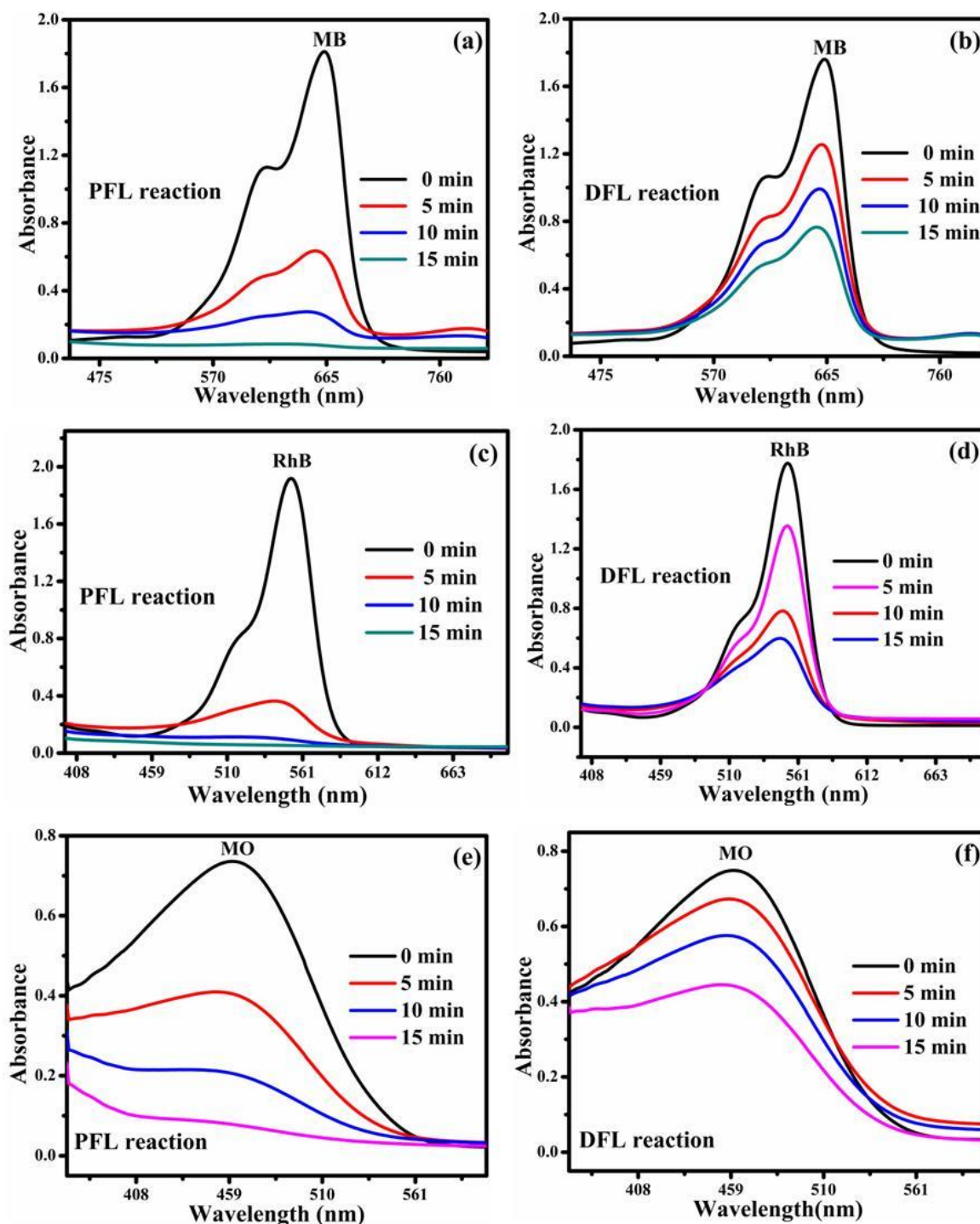


Fig. 5.13: Time resolved absorbance change during the degradation of (a, b) MB, (c, d) RhB and (e, f) MO in PFL and DFL reaction.

5.2.9. Radical trapping experiments

The results of radical trapping experiment of PFL reaction (see **Fig. 5.14(a)**) clearly indicate that MB, RhB and MO degradation activity is significantly decreased when IPA and AgNO_3 are used supporting the formation of $\cdot\text{OH}$ and excited electrons as the main

responsible species. The degradation activity decreased only a little due to addition of Na_2EDTA , which indicates that holes play a minor role in PFL reaction. The degradation activity remained nearly unchanged after BQ addition indicating hardly any role of super oxide species in PFL reaction. The results of radical trapping experiments for DFL reaction (see **Fig. 5.14(b)**) demonstrate that the degradation activity decreased remarkably in presence of IPA and the degradation process remain unaffected in presence of BQ, Na_2EDTA and AgNO_3 . So $\cdot\text{OH}$ is again the only formed reactive species in DFL reaction.

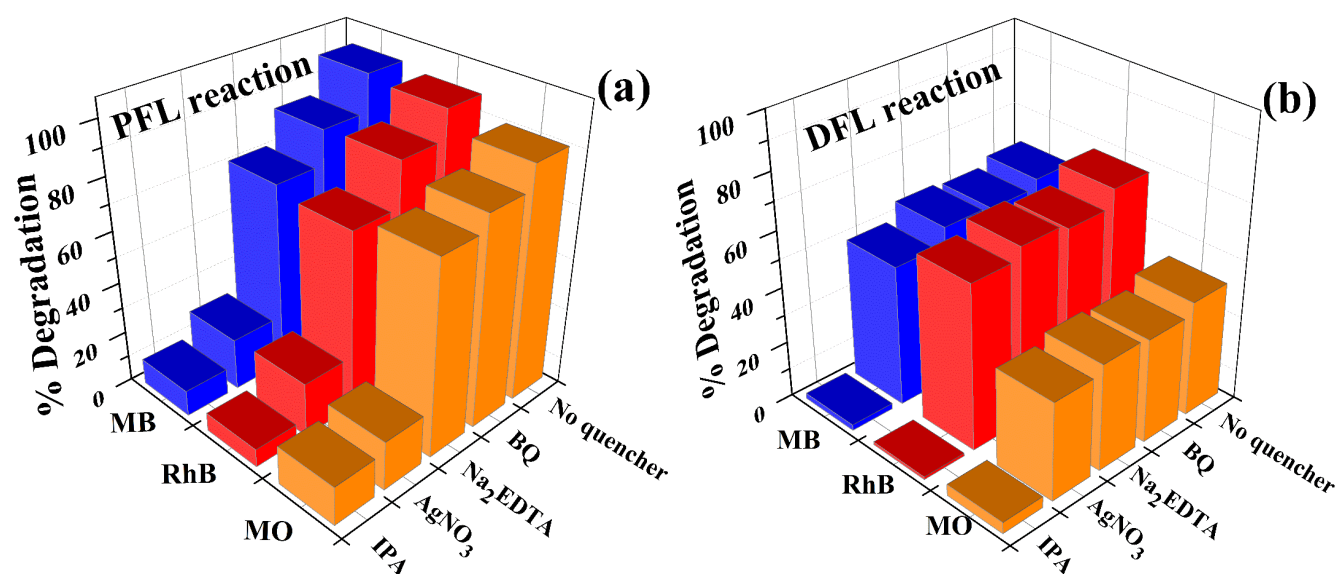


Fig. 5.14: Effect of different radical quenchers on PFL and DFL activity of 100%CCO/ TiO_2 nanocomposite for the degradation of MB, RhB and MO.

5.2.10. Coumarin based fluorescence probe method of $\cdot\text{OH}$ detection

To further verify the evidence of $\cdot\text{OH}$ formation and to compare $\cdot\text{OH}$ formation activities of pure CCO, pure TiO_2 and CCO/ TiO_2 nanocomposites in PFL reaction, coumarin based fluorescence probe experiment was carried out under identical conditions. The experimental data are shown in **Fig. 5.15**. It is evident that the intensity of fluorescence peak at 456 nm that corresponds to highly fluorescent 7-hydroxy coumarin is enhanced considerably with time (up to 15 min) for 100%CCO/ TiO_2 in comparison with both pure CCO and pure TiO_2 (see **Fig. 5.15(a-c)**). The experimental findings also point to higher intensity of the fluorescence peak for 100%CCO/ TiO_2 among all other nanocomposites (see **Fig. 5.15(d)**), which suggests higher $\cdot\text{OH}$ generation and PFL activity for 100%CCO/ TiO_2 .

than the other samples. Note that the $\cdot\text{OH}$ generation ability of pure TiO_2 is little higher than that of pure CCO (see **Fig. 5.15(a,b)**).

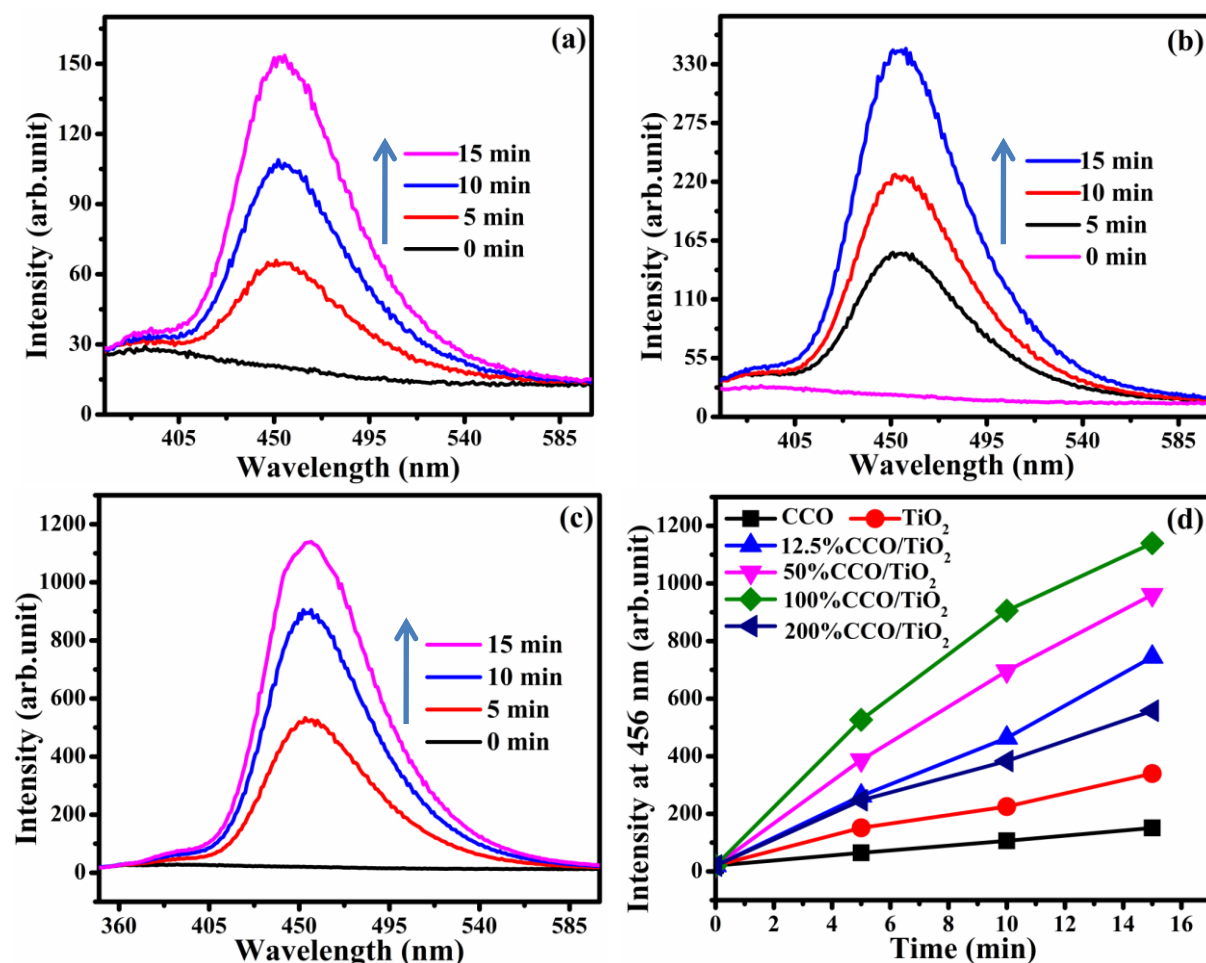


Fig. 5.15: Formation of 7-hydroxy coumarin in PFL for (a) pure CCO, (b) pure TiO_2 , (c) 100%CCO/ TiO_2 and (d) PL intensity at 456 nm of pure CCO, pure TiO_2 and all entire nanocomposite in PFL reaction.

5.2.11. PFL and DFL activity of CCO/ TiO_2 nanocomposite for antibiotics degradation

The activity of the most active nanocomposite 100%CCO/ TiO_2 for antibiotics degradation is also evaluated by the degradation of two antibiotics, namely TC-HCl and NORF. Furthermore, the degradation activities were examined for both PFL and DFL condition and the activity data were compared with those of the pure components. The findings on antibiotics degradation shown in **Fig. 5.16** demonstrate that the TC-HCl and NORF degradation activities of the nanocomposite are greater than the pristine materials for

both PFL and DFL reaction condition. In the absence of catalyst, H_2O_2 only can degrade TC-HCl and NORF up to the maximum of 4.1% and 5.2%, respectively whereas the degradation is increased significantly in the presence of both the catalyst and H_2O_2 . As expected, the activity under PFL reaction condition is significantly higher than that of DFL condition indicating light irradiation during the Fenton like reaction to be a dominating factor to initiate the activity of the nanocomposite. The degradation percentages of TC-HCl in PFL reaction are 99%, 45% and 24%, respectively for 100%CCO/ TiO_2 , CCO and TiO_2 after 15 min of reaction. These respective values are 58%, 33% and 8% for DFL reaction. On the other hand, the degradation percentages of NORF in PFL reaction are respectively 97%, 32% and 55% for 100%CCO/ TiO_2 , CCO and TiO_2 after 75 min, whereas these values for DFL reaction are 64%, 20% and 38%, respectively. The values of rate constants (see **Fig. 5.16(b)**) for TC-HCl degradation using 100%CCO/ TiO_2 are respectively 7.3 and 14.4 times greater for PFL reaction and 1.8 and 10.7 times greater for DFL reaction when compared with those of CCO and TiO_2 . No exception was noted for NORF degradation (see **Fig. 5.16(d)**) for which the rate constant obtained for the nanocomposite is respectively 8.5 and 4.3 times higher than that of CCO and TiO_2 for PFL reaction and 3.7 and 2.1 times higher for the DFL reaction. The normal photocatalytic activity of pure CCO, pure TiO_2 and 100%CCO/ TiO_2 nanocomposite for the degradation of TC-HCl and NORF are also investigated under the same reaction condition of PFL reaction in the absence of H_2O_2 and the results of activity test are given in **Fig. 5.17**. The results indicate that the percentages of TC-HCl degradation by pure CCO, pure TiO_2 and 100%CCO/ TiO_2 nanocomposite are respectively 6.3%, 4.8% and 21.4% after 15 min of LED irradiation and the respective percentages for NORF degradation are 4.7%, 2.3% and 22.3% after longer duration of 75 min. The findings thus point out the necessity of the presence of H_2O_2 in the reaction medium to manifest the maximum photodegradation activity of the nanocomposite catalysts.

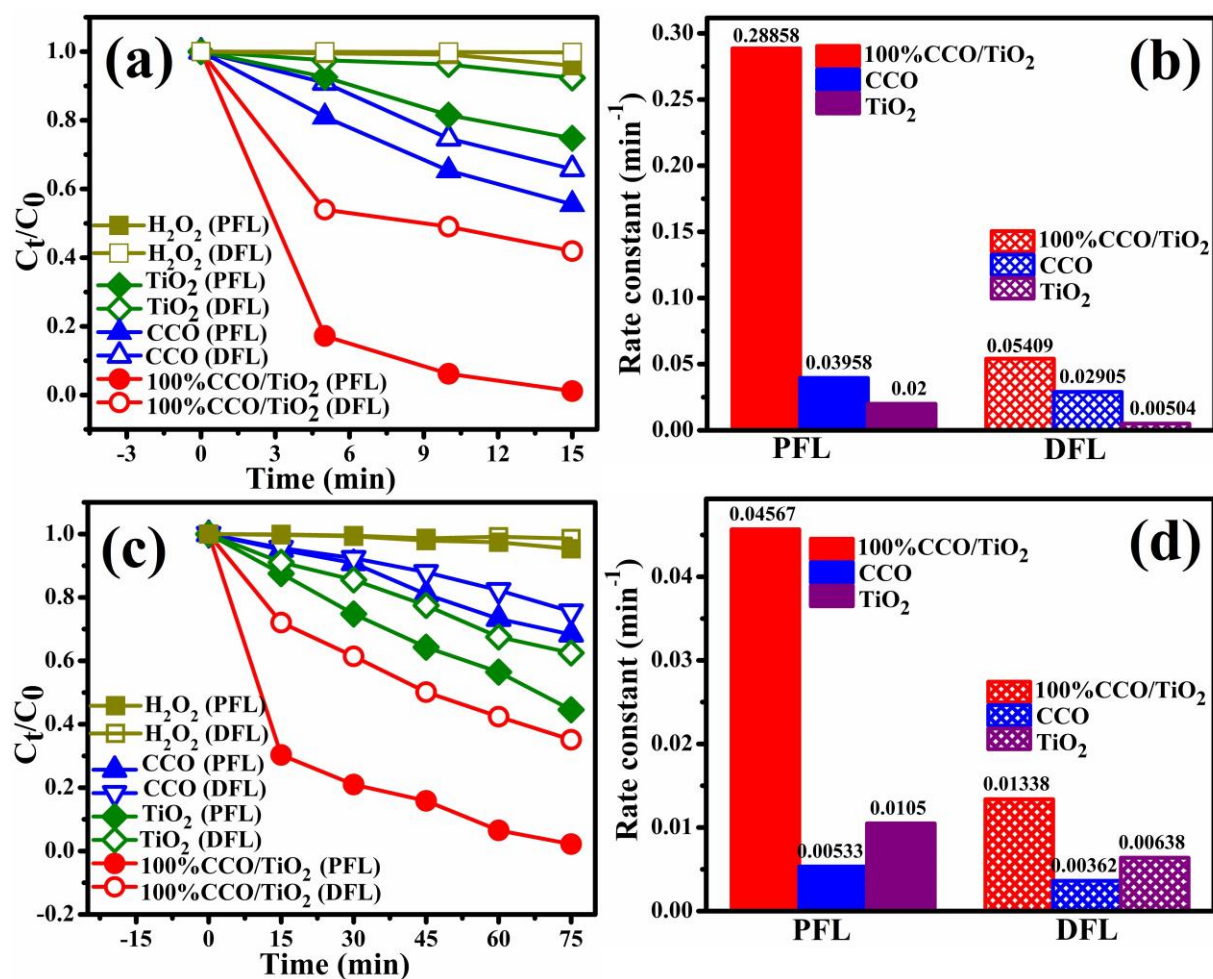


Fig. 5.16: Degradation activities and rate constants of (a, b) TC-HCl and (c, d) NORF for PFL and DFL reaction.

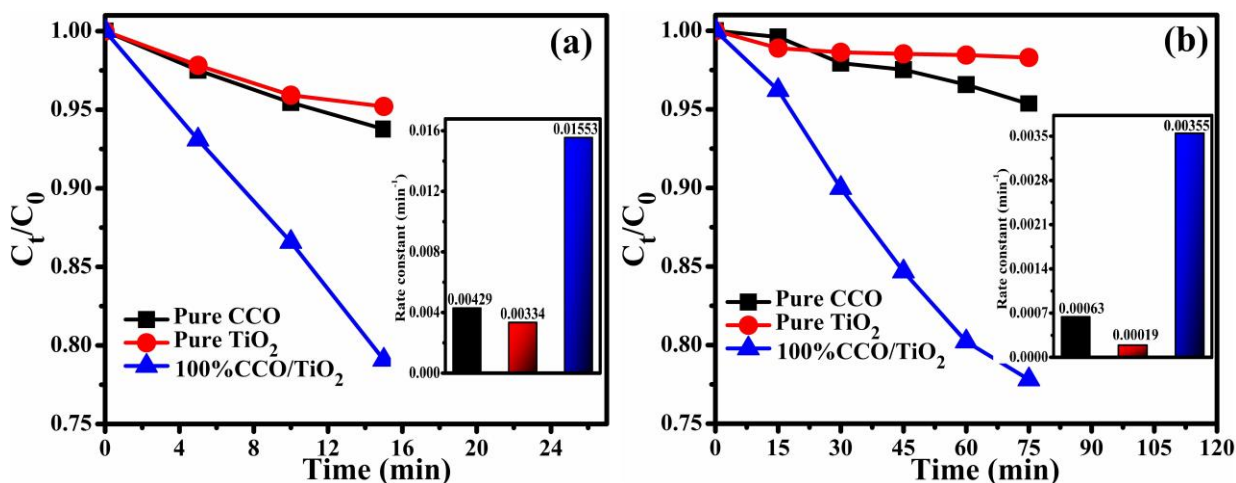


Fig. 5.17: Normal photocatalytic activity of pure CCO, pure TiO_2 and 100%CCO/ TiO_2 nanocomposite for the degradation of (a) TC-HCl and (b) NORF (corresponding values of rate constants are shown in the inset).

5.2.12. Photoelectrocatalytic oxygen evolution (OER) reaction activity of CCO/TiO₂

The OER activity of as synthesized CCO/TiO₂ nanocomposite was evaluated by using highly active sample of the nanocomposite series, namely, 100%CCO/TiO₂ sample and the obtained results were compared with the OER activity behavior of its pure phases. We performed Linear Sweep Voltammetry (LSV) measurement in 1 M NaOH to evaluate the photo-electrocatalytic activities of the electrodes towards OER (see **Fig. 5.18**). The applied potential when generating a current density of 5 mA cm⁻² was chosen arbitrarily for the comparison of different catalysts. The potential (E_j) at current density, $j = 5 \text{ mA cm}^{-2}$ for 100%CCO/TiO₂ in visible LED light irradiation is 0.71 V, which is lower than those obtained for other samples such as pure TiO₂ (0.79 V) and CCO (0.77 V). The onset potential of oxygen evolution is also lower for 100%CCO/TiO₂ (0.53 V) when compared to those of pure CCO (0.59 V) and pure TiO₂ (0.60 V) in presence of visible LED light irradiation. Furthermore, the 100%CCO/TiO₂ nanocomposite exhibits much higher current density (9.65 mA cm⁻²) than that of pure CCO (6.46 mA cm⁻²) and pure TiO₂ (5.6 mA cm⁻²) at 0.8 V versus Ag/AgCl electrode in presence of light. Moreover, current density exhibited in absence of light by 100%CCO/TiO₂ is 8.1 mA cm⁻² indicating improvement in current density by ~1.2 times under illuminated condition. Such an improvement in light condition is attributed to the formation of oxo-intermediates which facilitates the oxygen evolution by four distinct steps as reported by Ding et al. [29]. The lower onset potential and higher current density indicate that the 100%CCO/TiO₂ has the better OER activity under both the dark and the light conditions. The Tafel plots of oxygen evolution reaction were also used to evaluate the catalytic kinetics for OER (**Fig. 5.18(b,c)**). The Tafel plots were drawn from the quasi-steady-state curve obtained in 1 M NaOH solution with a fixed scan rate of 0.02 V s⁻¹. The 100%CCO/TiO₂ nanocomposite catalyst shows a lower Tafel slope of 194 mV dec⁻¹ in presence of visible light than in dark (226 mV dec⁻¹), which indicates greater transmission coefficient in visible LED light [30]. Moreover, the equilibrium exchange current density (i_0) is calculated using linear Tafel relation [31]. The equilibrium exchange current density of 100%CCO/TiO₂ nanocomposite sample is 1.513 mA cm⁻² which is respectively ~1.1 and ~1.7 times higher than that of pure CCO (1.40 mA cm⁻²) and pure TiO₂ (0.91 mA cm⁻²). The high Tafel slope and equilibrium exchange current density of 100%CCO/TiO₂ nanocomposite is an indication of a very high OER kinetics in presence of visible LED light irradiation.

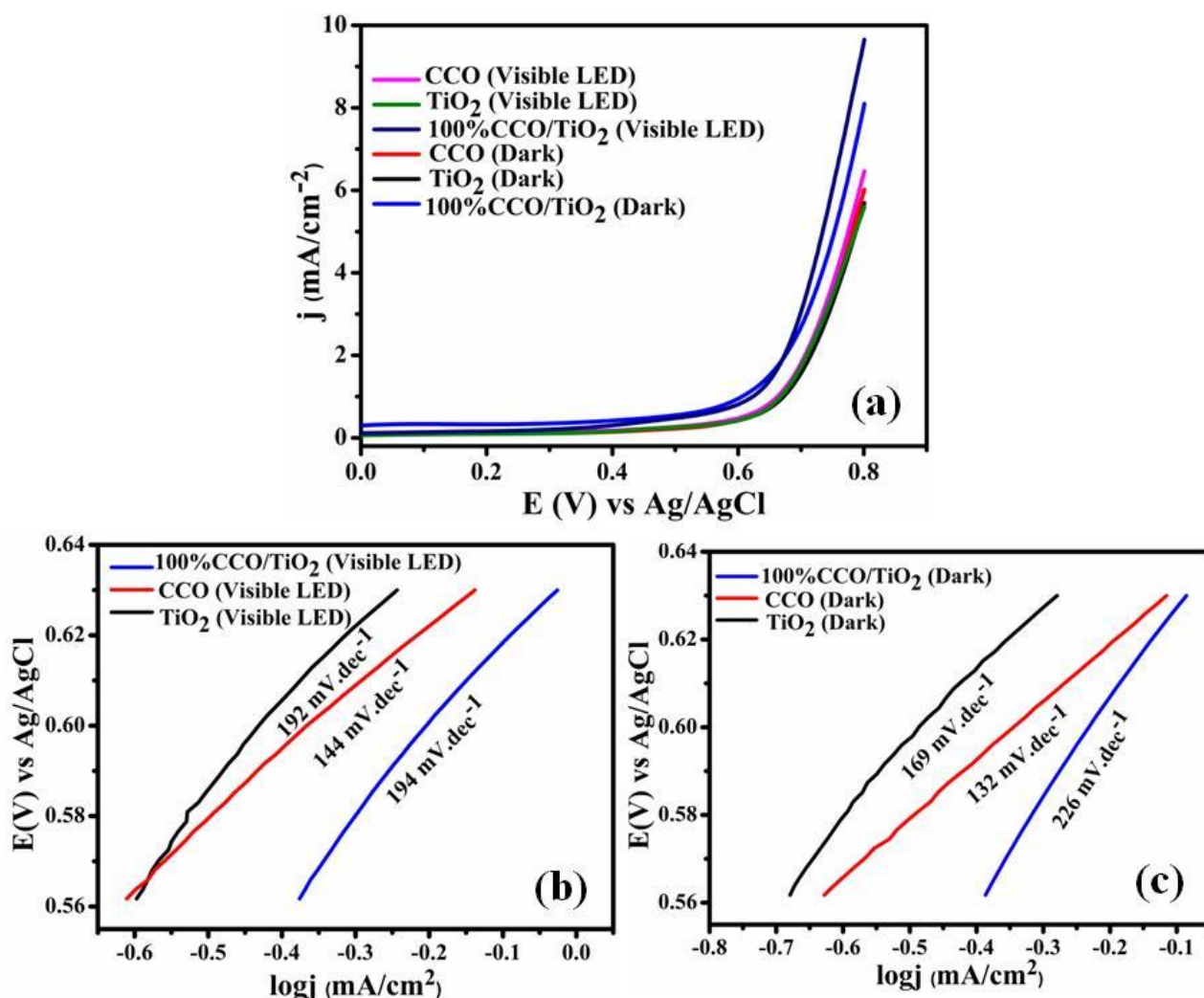


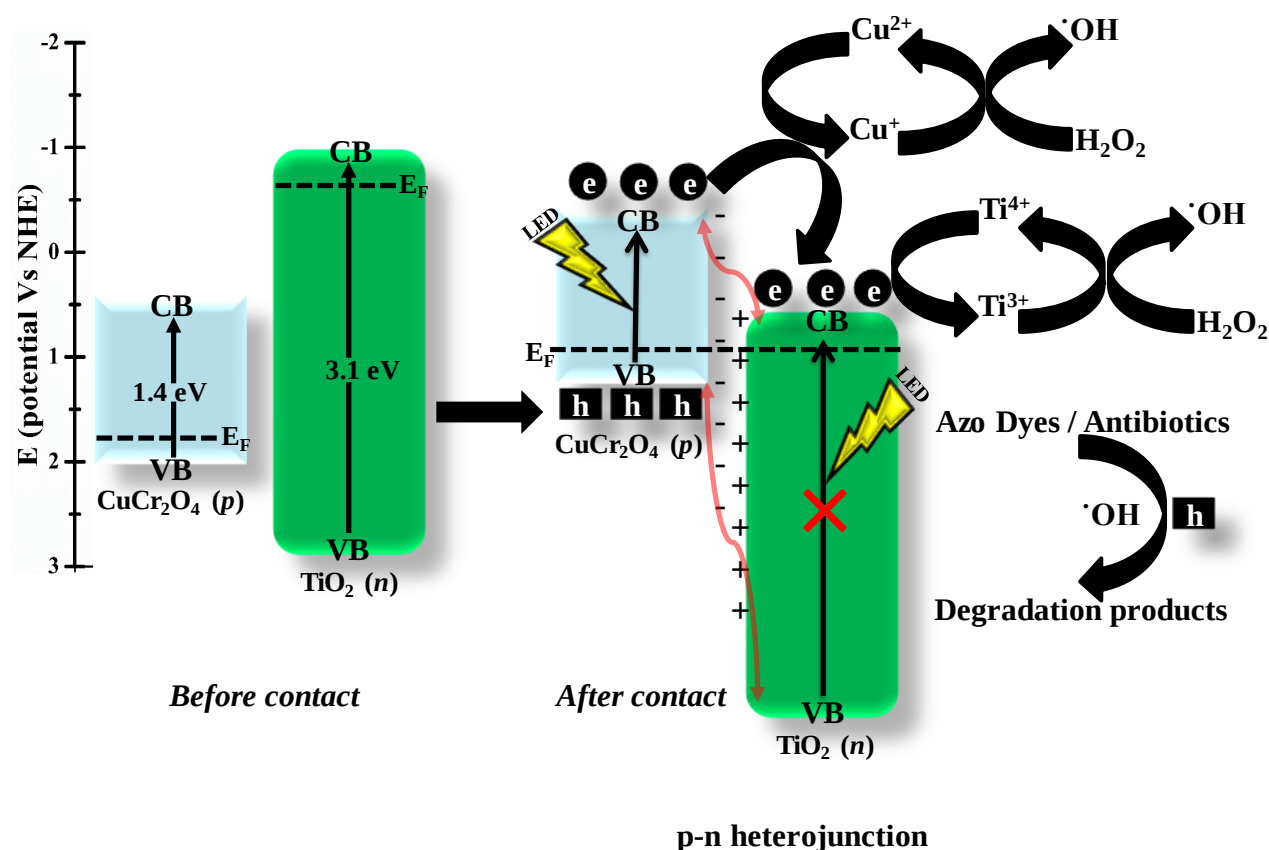
Fig. 5.18: (a) Oxygen evolution reaction under dark and LED light conditions, (b) Tafel plot in light and (c) Tafel plot in dark condition for CCO, TiO₂ and 100%CCO/TiO₂.

5.2.13. Mechanism of PFL reaction in CCO/TiO₂ nanocomposite

A possible mechanism of PFL reaction for pollutants degradation over CCO/TiO₂ nanocomposite under LED irradiation has been established below on the basis of the band potential energy positions of the VB and CB of CCO and TiO₂.

The electronegativity TiO₂ is 5.90 eV [32] and the estimated values of E_{VB} and E_{CB} are respectively to be 1.92 eV and 0.52 eV for CCO [33] and 2.955 eV and -0.155 eV for TiO₂ [32]. Based on band potential energy, radical trapping experiment and activity data, a possible mechanism of PFL reaction has been shown in **Scheme 5.1**. After Fermi level equilibrium is reached, an electric field is generated and the whole band positions of p-type CCO is lifted up while the whole band positions of n-type TiO₂ is shifted down. Thus after equilibrium, the renewed conduction band edge position of p-type CCO is higher than that of

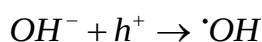
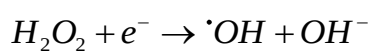
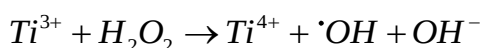
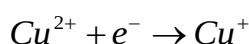
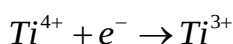
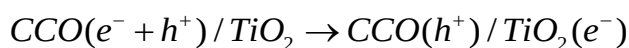
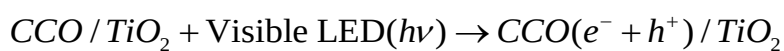
n-type TiO_2 [32]. Under visible light irradiation, only CCO can generate photoexcited electrons and holes, but TiO_2 cannot generate these due to very large band gap energy of nearly 3.11 eV, which is activated only under UV light irradiation. Due to the formation of inner electric field between CCO and TiO_2 , the photoexcited electrons on the CB of CCO get easily transferred to the CB of TiO_2 and the photoinduced holes are left on the valence band of CCO, which in turn reduces the electron-hole pair recombination in CCO/ TiO_2 . In this way photoexcited electrons of larger life time are produced on the nanocomposite surface which contributes to enhanced PFL activity of the CCO/ TiO_2 nanocomposite. The photoexcited



Scheme 5.1: Schematic representation of the PFL reaction mechanism over CCO/ TiO_2 nanocomposite.

electrons at the catalyst surface of CCO/ TiO_2 are captured by Ti^{4+} and Cu^{2+} to form Ti^{3+} and Cu^+ , respectively. The Ti^{3+} and Cu^+ ions then react rapidly with H_2O_2 to form $\cdot\text{OH}$ and in the process they are oxidized back to Ti^{4+} and Cu^{2+} . Thus in the presence of photoexcited electrons at the catalyst surface, the conversion cycles of Cu^{2+} to Cu^+ and Ti^{4+} to Ti^{3+} facilitate the formation of $\cdot\text{OH}$ from H_2O_2 . Hence in PFL reaction, the improved charge separation plays an important role in the enhancement of $\cdot\text{OH}$ formation. Moreover, the H_2O_2

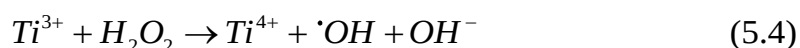
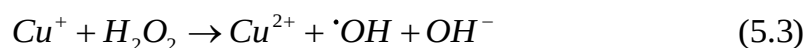
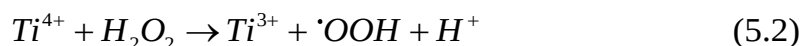
molecules on the catalyst surface can directly react with the photoexcited electrons to form $\cdot\text{OH}$ and OH^- and then the OH^- reacts with the holes to form $\cdot\text{OH}$. On the other hand, holes generated at the VB of CCO can also participate in this degradation process. Therefore, the enhanced cyclic turnover of $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ on CCO/ TiO_2 nanocomposite surface is the responsible factor for its high PFL activity. The $\cdot\text{OH}$ generation activity and degradation performance of pure TiO_2 in the presence of H_2O_2 indicate that TiO_2 participates in the Fenton like process. Furthermore, TiO_2 acts as an electron receiver from the CB of CCO which promotes better charge separation and the accumulated electrons enhance the transformation of Cu^{2+} to Cu^+ and Ti^{4+} to Ti^{3+} . The essential steps of photodegradation are summarized as follows:



5.2.14. Mechanism of DFL reaction

From the results of the DFL activity and radical trapping experiments, a possible mechanism of DFL performance over CCO/ TiO_2 nanocomposite system may be proposed. The DFL mechanism is quite different from the PFL mechanism since photoexcited electrons are not involved in this mechanism. So the DFL mechanism possibly involved the reaction between $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ metal ions in the CCO/ TiO_2 nanocomposite with H_2O_2 to form $\cdot\text{OH}$ and initiate the DFL reaction. It is well known that H_2O_2 can act as both oxidizing and reducing agent. To explain the DFL mechanism we considered both the advantages of this special chemical ability of H_2O_2 and variable oxidation states of Cu and Ti metal ions in the CCO/ TiO_2 nanocomposite system. Inspired from the Fe^{3+} based Fenton reaction [34], when the CCO/ TiO_2 nanocomposite system interacts with H_2O_2 molecules, the Cu^{2+} and Ti^{4+} on the nanocomposite surface can react with H_2O_2 to form $\cdot\text{OOH}$ and the metal ions get reduced to Cu^+ and Ti^{3+} (**equation 5.1 and 5.2**). The Cu^+ and Ti^{3+} ions produced so react readily with H_2O_2 to form $\cdot\text{OH}$ with the re-oxidation of Cu^+ and Ti^{3+} back to Cu^{2+} and Ti^{4+}

(equation 5.3 and 5.4). The $\cdot\text{OH}$ and $\cdot\text{OOH}$ generated in the process can act as oxidizer to degrade azo dye molecules in the aqueous solution. Thus in the presence of H_2O_2 , the consecutive oxidation-reduction reaction occurs to form $\cdot\text{OH}$ as well as degradation process.



5.2.15. Recycling test of the nanocomposite catalyst

Recycling of photocatalyst was performed only for the degradation MB, RhB and MO dyes. A major decrease of PFL activity of 100%CCO/TiO₂ nanocomposite sample was observed in the first cycle where the degradation of MB, RhB and MO decreased from 99.2%, 97.2% and 89.6% for the fresh catalyst (see **Fig. 5.8**) to respectively 25%, 35% and 15% for the catalyst after the first cycle of test, which is represented here as the activity of the catalyst ‘before heat treatment’ (see **Fig. 5.19(a)**, open symbols). Such a decrease in PFL activity is a common feature and is usually due to the deposition of carbon (C) and nitrogen (N) containing small organic compounds with low molecular weight on the catalyst surface during dye degradation [17, 35-36]. To ensure that the catalyst can be used continuously, the Fenton like catalyst was recovered after every run, washed at first with mille-Q water and then with 2-propanol for three times each followed by heating at 400 °C for 2 h in presence of static air and then it was used for the next cycle. As clear from **Fig. 5.19(a)** the PFL activity of 100%CCO/TiO₂ nanocomposite sample is recovered more or less completely subsequent to heat treatment (filled symbol that presents the activity of the catalyst ‘after heat treatment’). The bar diagrams in **Fig. 5.19(b)** show the activity behavior of the catalyst for four such consecutive cycles that suggest a minimal decrease in activity in the consecutive cycles of photodegradation. These findings are in line with the previous reports by our group [17] on CuCr₂O₄/CeO₂ catalyst (see chapter 4) and by Zhang et al. for iron-doped ceria catalyst [36]. It thus appears that the deposited organics can be removed by introducing an intermediate heat treatment step between two consecutive cycles of test and the nanocomposite catalyst can be used in a repeated manner in photodegradation. It should also be noted that the bulk phase of the catalyst remains unchanged before and after heat treatment (see **Fig. 5.19(c)**) suggesting the adsorption or deposition of degraded products on the catalyst surface as the prime cause of deactivation in dye degradation.

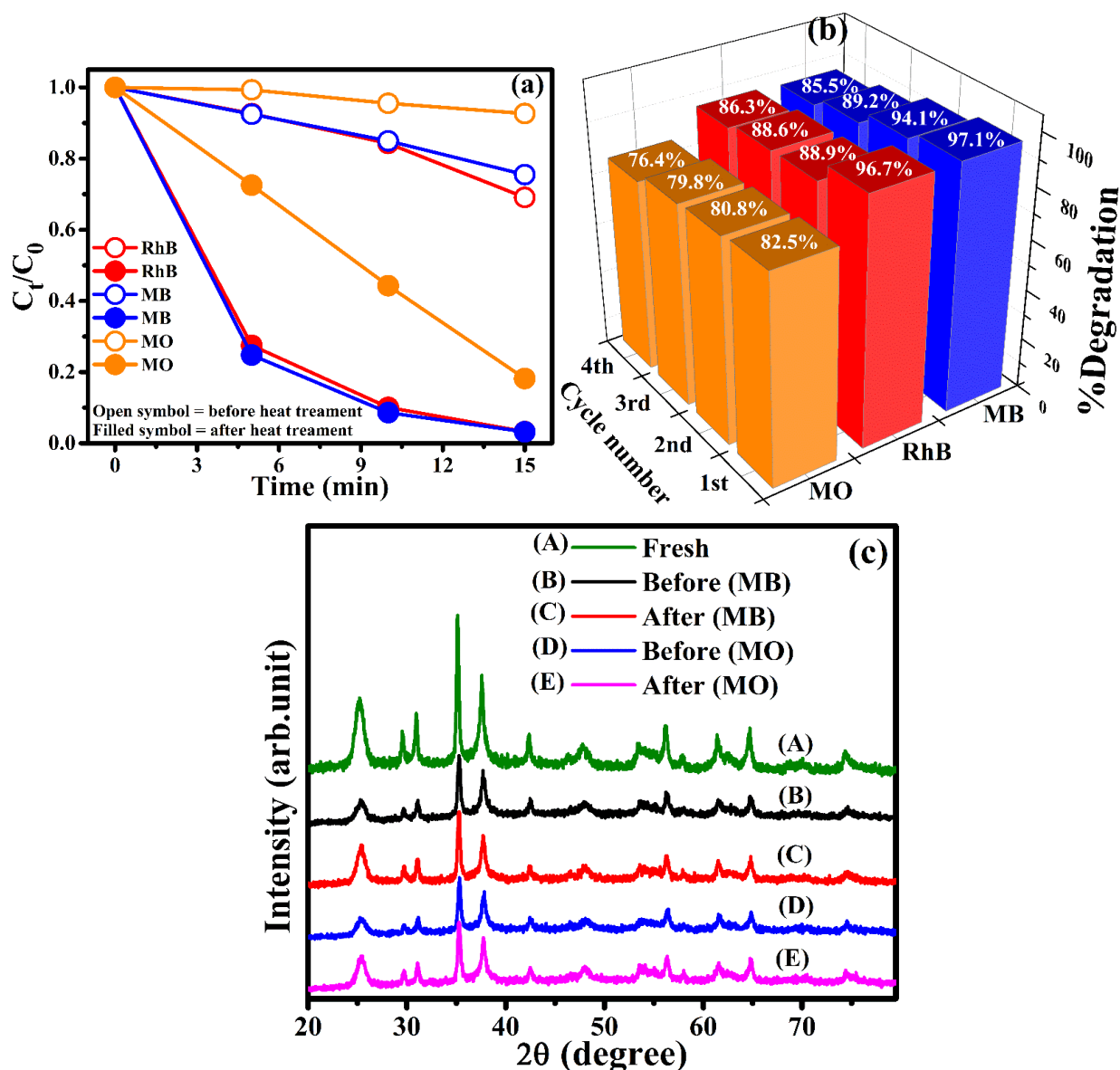


Fig. 5.19: (a) Activity behavior of 100%CCO/TiO₂ for MB, RhB and MO degradation before and after heat treatment of the catalyst sample collected after a cycle of degradation and (b) degradation activity of different cycles (each preceded by a heat treatment step) and (c) XRD patterns of the 100%CCO/TiO₂ nanocomposite catalyst before and after heat treatment.

XPS studies have also been carried out to understand the elemental nature on the catalyst surface after a cycle of the PFL reaction and subsequent heat treatment experiments. For this purpose, core level spectra of C 1s, Cu 2p, Cr 2p, Ti 2p, N 1s, and O 1s of the catalyst before and after the heat treatment have been recorded.

Cu 2p core level spectra in both conditions are broad and hence curve-fitted into component peaks which are presented in **Fig. 5.20(a,b)**. Cu 2p spectrum of the sample after the reaction may have slightly reduced Cu²⁺ species as evident from the main peak to satellites intensity ratio ($I_{\text{main peak}}/I_{\text{satellites}}$). However, after heat treatment concentration of Cu²⁺ species gets increased as noticed from the $I_{\text{main peak}}/I_{\text{satellites}}$ ratio. Similar observation has also been noticed in Cr 2p and Ti 2p core level spectra which are shown in **Fig. 5.20(c,d)** and **5.20(e,f)**, respectively. Cr 2p core level spectral comparison reveals more Cr³⁺ species in the heat-treated sample (**Fig. 5.20(d)**). In Ti 2p core level spectrum of before heat-treatment, a visible bulge around 457.3 eV indicates the presence of Ti³⁺ species whose concentration is evaluated to be 9.1% (**Fig. 5.20(e)**). Therefore, it can be inferred that the oxidation states of some Cu, Cr, and Ti species may get changed due to the 'OH formation on the catalyst surface as they participate in the Fenton like reaction. However, they are regenerated after the heat treatment which is the same as in the fresh CCO/TiO₂ nanocomposite sample. C 1s core level spectra of the samples before and after heat treatment are displayed in **Fig. 5.20(g)**. The carbon peak intensity of the sample before heat treatment is more due to the deposition of small carbon species in the CCO/TiO₂ nanocomposite surface. However, in the heat-treated sample, the carbon peak intensity is reduced because of the removal of deposited carbon species present on the surface of CCO/TiO₂ nanocomposite and hence, the composite is considered to be ready for the next cycle. N 1s core level spectra of the catalyst sample before and after heat treatment have also been recorded to assess the complete nature of the surface as displayed in **Fig. 5.20(h)**. The nitrogen peak intensity of the sample before heat treatment is more due to the deposition of small N-species on the CCO/TiO₂ nanocomposite surface and the observed binding energy at 398.6 eV is attributed to nitride species. However, for the sample after heat treatment, the nitrogen peak intensity is reduced because of the removal of the deposited N-species from the CCO/TiO₂ nanocomposite surface and the sample is meant for the next cycle. O 1s core level spectra of the samples are shown in **Fig. 5.20(i)**. The spectrum before the heat treatment is found to be broad containing the main O 1s peak around 530.3 eV related to oxide species. However, FWHM of the spectrum gets reduced in the catalyst sample after the heat treatment which indicates that the sample is regenerated after the heat treatment. This sample resembles the fresh nanocomposite sample that can be understood by comparing the O 1s core level spectra in **Fig. 5.20(i)** and **Fig. 5.4(e)**.

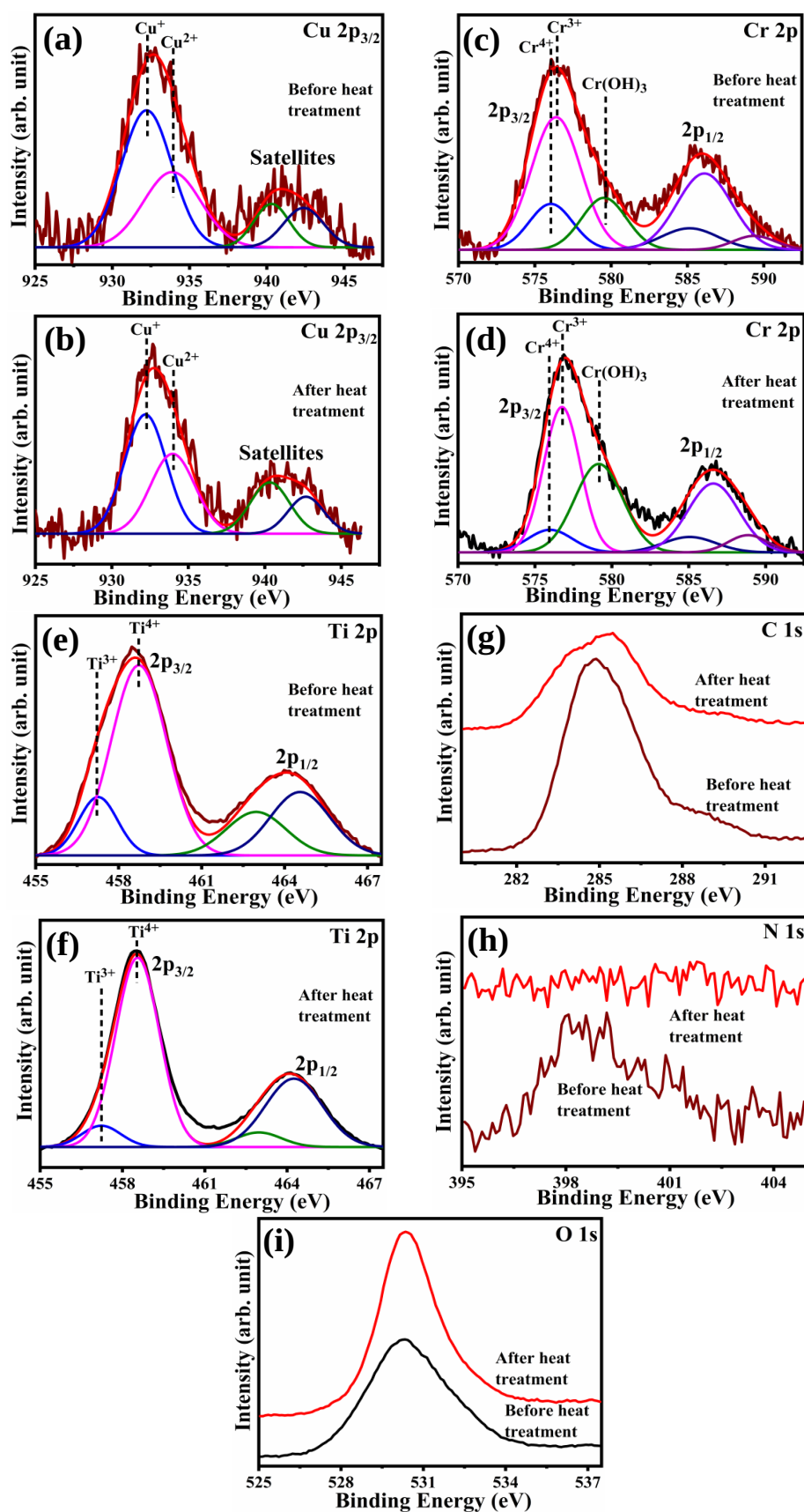


Fig. 5.20: XPS core-level regions of 100%CCO/TiO₂ nanocomposite catalyst before and after heat treatment: (a, b) Cu 2p, (c, d) Cr 2p, (e, f) Ti 2p, (g) C 1s, (h) N 1s and (i) O 1s.

5.3. Conclusions

A series of nanocomposites of CuCr_2O_4 and TiO_2 are synthesized by chemical deposition of CuCr_2O_4 into Ti precursor under sonochemical treatment and finally by thermal treatment. The synthesized catalysts are successfully characterized by various spectroscopic and microscopic techniques such as XRD, TEM, HRTEM, EDS, XPS, UV-DRS and PL spectroscopy. The synthesized CCO/ TiO_2 nanocomposite shows an excellent PFL activity for the degradation of MB, RhB and MO, antibiotics such as TC-HCl and NORF, as well as a promising candidate for OER under domestic visible LED irradiation. The Fenton like activity was improved considerably after nanocomposite formation with CCO and TiO_2 , showing optimal Fenton like performance for 100%CCO/ TiO_2 . The normal photocatalytic activity of CCO/ TiO_2 nanocomposite system is less significant compared to its PFL activity suggesting the necessity of both H_2O_2 and visible light in achieving the maximum photocatalytic activity. The XRD, TEM and XPS results support formation of nanocomposite and the DRS study indicates enhancement of visible light absorption of the nanocomposite system. The $\cdot\text{OH}$ is the responsible species for degradation and its primary role was confirmed by the IPA quenching method and the formation of $\cdot\text{OH}$ from the CCO/ TiO_2 - H_2O_2 system was confirmed by coumarin based fluorescence probe method. The formation of $\cdot\text{OH}$ in the CCO/ TiO_2 - H_2O_2 system was increased under domestic visible LED irradiation due to the generation of longer-lived photoexcited electrons which increased the efficiency of the cyclic reaction of $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ with H_2O_2 on the nanocomposite surface. The transfer of photoexcited electron from CB of CCO to CB of TiO_2 is suggested to be responsible for the delayed electron-hole recombination. The lower mass carbon compounds formed on degradation get strongly deposited on the active sites of the catalyst affecting its activity considerably and the catalyst can be made reusable only after a heat treatment at $400\text{ }^\circ\text{C}$ for 2 h in air to remove these deposited carbon species. In summary, this finding will certainly motivate the researchers to explore different class of oxide systems to combine with prototype photocatalysts in nanocomposite form to unravel the possibility of their multipurpose catalytic activities.

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Chapter 6

Studies on Z-scheme type $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ nanocomposite photocatalyst for pollutants degradation under natural sunlight irradiation

Chapter abstract

The major findings in this chapter are (i) development of nanocomposite photocatalyst working through Z-scheme charge transfer pathway across the heterojunction, (ii) utilization of direct sunlight as the photo-source, and (iii) prospect of ligand-hole in photocatalysis through enhanced sub-band gap absorption. The photocatalysts, namely LaNiO_3 , $\text{g-C}_3\text{N}_4$ and $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ nanocomposites were synthesized via solid state mixing method and were characterized by using several physicochemical techniques. The photocatalytic performance of the nanocomposite was tested through the degradation of hazardous azo dye pollutants, namely RB5 and MB as well as the colorless antibiotic-pollutant TC-HCl in presence of natural sunlight with excellent recycling activity. The enhanced photo-absorption of the nanocomposite can possibly be related to sub-bandgap absorption, which is associated to the midgap state originated from ligand-hole formation or defects in the structure. The photodegradation process is mediated through the formation of super oxide radical and hole as the main responsible species.

6.1. Introduction

As discussed in the preceding chapters, different types of photo sources have been used for photocatalysis. The ultimate provision of light source with no cost, ecofriendly and basically having unlimited lifetime is sunlight [1]. However, the practical utilization of sunlight in photocatalysis demands the band gap engineering. This puts a big challenge to design materials of right band gap for an efficient solar energy absorption as well as high catalytic performance.

Several semiconductors like WO_3 [2], CeO_2 [3], TiO_2 [4], Ag_3VO_4 [5], BiOBr [6], Bi_2O_3 [1], graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [7-14] and many more have been reported till date as photocatalyst for wastewater treatment. Among these materials, $\text{g-C}_3\text{N}_4$ has been demonstrated to be an active as well as a promising photocatalyst due to its several intriguing features like nontoxicity, good photochemical stability, photoelectricity, thermal property, low cost, metal free nature, ease of synthesis and narrow band structure [7-14]. Consequently, several attempts have been made to use $\text{g-C}_3\text{N}_4$ in photocatalysis purposes such as wastewater treatment [8-9], hydrogen production [10], water splitting [11], CO_2 reduction [12], oxygen evolution reaction [13], supercapacitor [14] etc. However, $\text{g-C}_3\text{N}_4$ exhibits

serious drawbacks like poor hydrophilicity, low surface area, poor electrochemical activity, high electron-hole pair recombination rate and non-persistent activity for a long run [15]. Consequently, it demands for modification of its electronic structure to restrain from electron-hole recombination without compromising with the absorption edge into the visible light region and its photocatalytic efficiency. An effective strategy to modify the electronic structure is the composite formation. There are a number of reports available in the open literature which demonstrate that composite of g-C₃N₄ with other semiconductor materials such as g-C₃N₄/TiO₂ [16], g-C₃N₄/CeO₂ [17], g-C₃N₄/ZnO [18], g-C₃N₄/CdSe [19], g-C₃N₄/Sn₂S₃ [20], g-C₃N₄/LaFeO₃ [21], g-C₃N₄/CaTiO₃ [22] etc. can effectively reduce the electron-hole recombination thereby leading to improved photocatalytic activity of the composite. Most of these composites are found to form Z-scheme band structural feature across the heterojunction which is considered as a smart choice of designing a photocatalyst for wastewater treatment.

The iono-covalent nature of the M–O bond in transition metal oxides has been attributed to remarkable functionalities like electronic, magnetic, magnetoelectric, catalytic and other properties [23]. The unique flexibility of AMO₃ perovskite family in accepting a large variety of cations at A- or M-sites provides wide range of functionalities which are of interest both from scientific and application points of views. Accordingly, perovskite oxides have recently attracted much attention of the researchers as an effective photocatalyst [24–26]. Furthermore, several perovskite-based oxide formulations are found to exhibit enhanced photocatalytic activity [27–28]. A greatly augmented (17–19 times) catalytic activity compared to the single phase materials is achieved for the visible light induced dye degradation in LaFeO₃/g-C₃N₄ composites [29–31]. Such an enhanced photocatalytic activity has been attributed to the improved absorption in the visible light region and low recombination rate of the electron-hole pairs. The efficient separation and transfer of photogenerated electron-hole pairs at the composite interface is facilitated through the Z-scheme electron transfer.

Perovskite nickelate such as LaNiO₃ has been demonstrated to perform excellent photocatalytic behavior by several researchers [32–34]. Li et al. have fabricated LaNiO₃/TiO₂ heterojunction with improved photocatalytic activity for the degradation of methyl orange and antibiotic ciprofloxacin under visible light irradiation [32]. Ding et al. have reported a direct Z-scheme photocatalyst, namely ZnIn₂S₄/LaNiO₃ with enhanced photocatalytic H₂ production [33]. Recently, Zhou et al. have reported the photocatalytic degradation of

tetracycline under visible light irradiation from a xenon lamp in the presence of LaNiO₃ in composite form with g-C₃N₄ [34]. Additionally, the photogenerated electrons and holes preserved the strong redox ability. Another noticeable feature of the nickelate structure is the availability of ligand-hole. Akin to several other TMOs, LaNiO₃ accommodates hole on ligand. The ground state of Ni³⁺O²⁻ is actually a strongly mixed 3d⁷2p⁶ (Ni³⁺O²⁻) and 3d⁸ $\bar{L}$ (Ni²⁺O⁻) configurations, where $\bar{L}$ denotes a hole in the ligand 2p band [35-36]. It has been reported that the electrocatalytic activity of LaNiO₃/g-C₃N₄ composite is enhanced with the change in Ni³⁺/Ni²⁺ ratio [37]. The oxygen reduction reaction is influenced by the composition strategy which changes with the Ni³⁺/Ni²⁺ ratio.

Bearing all these in mind, we have attempted to synthesize LaNiO₃/g-C₃N₄ (LNO/g-CN) nanocomposite for the degradation of azo dyes like reactive black 5 and methylene blue as well as colorless antibiotic-pollutant tetracycline hydrochloride under natural sunlight irradiation. The synthesized LNO/g-CN nanocomposite exhibits enhanced photocatalytic activities as well as excellent recycling capacity. Observation in this study has been described using Z-scheme type electron transfer mechanism across the nanocomposite interface for pollutants degradation. However, the role of ligand-hole in O 2p band of LaNiO₃ cannot be ignored for enhanced activity.

6.2. Results and discussion

6.2.1. PXRD studies

The normalized powder PXRD patterns of pure g-CN, pure LNO, and LNO/g-CN nanocomposites are displayed in **Fig. 6.1**. It is clear from the figure that LNO shows main diffraction peaks at 23.3°, 32.83°, 40.8°, 41.3°, 47.3°, 53.3°, 58.8°, 68.7°, and 69.8°, which are indexed to (101), (110), (021), (003), (202), (211), (122), (220) and (024) diffraction planes, respectively, corresponding to rhombohedral structure (JCPDS 34-1181). Pure g-CN formation is evident from the characteristic diffraction peaks at 27.5° and 13.0°. While, the peak at 13° corresponds to in plane packing of tri-s-triazine units, the intense peak at 27.5° corresponds to stacking of conjugated aromatic systems [20]. In LNO/g-CN nanocomposite system, both the characteristic peaks of LNO and g-CN are observed without any impurities confirming successful formation of the nanocomposite system. The intensity of diffraction peaks of g-CN is observed to become weaker upon increasing the mass of LNO nanoparticles in the nanocomposite, which clearly suggests that LNO was highly decorated on the surface

of g-CN layer. Importantly, the g-CN peak at 27.5° is shifted towards higher 2θ value in the nanocomposites with increased loading of LNO. With an increase in the loading of LNO in g-CN matrix, LNO grains are introduced into the interlayers of g-CN. As a result of this phenomenon, size of the unit cell of the resulting nanocomposite materials decrease, this naturally prefers to shift the XRD peaks towards higher angle in order to relax the micro-stress [38-40]. These facts indicate that the g-CN gets exfoliated after the formation of nanocomposite with LNO.

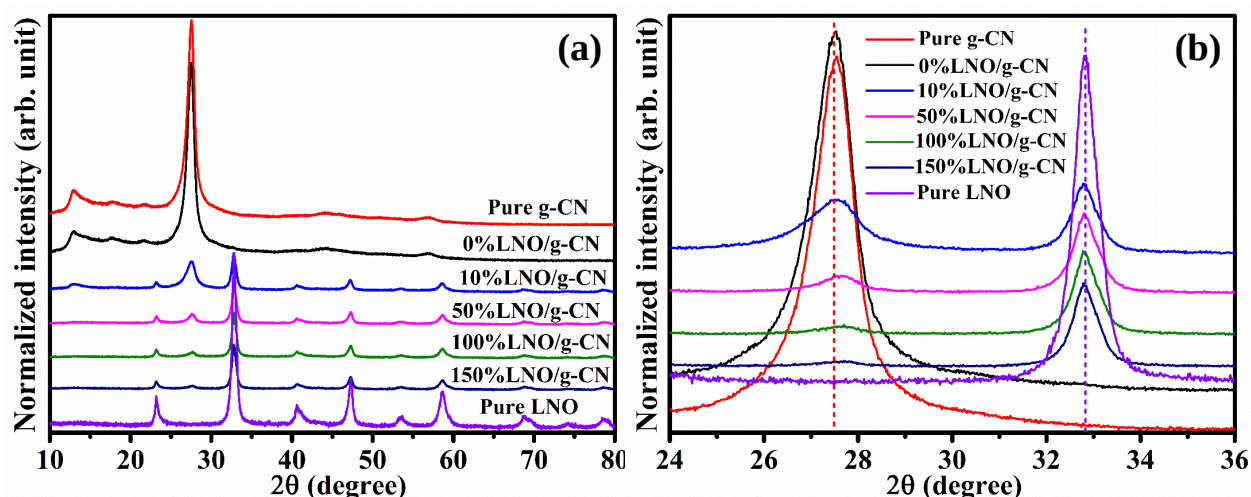


Fig. 6.1: Normalized PXRD patterns of (a) pure g-CN, LNO and LNO/g-CN nanocomposites and (b) magnified PXRD patterns in the 2θ range of $24\text{--}36^\circ$.

6.2.2. Morphology and microstructure analyses

The TEM images of pure LNO (see **Fig. 6.2 (a-d)**) show highly aggregated nanoparticles with the particle sizes of about 5–60 nm. The images indicate an irregular-shaped granular block-like morphology of LNO nanoparticles. The SAED pattern of LNO confirms that the sample is polycrystalline in nature (see inset in **Fig. 6.2 (a)**). The HRTEM of LNO (see **Fig. 6.2 (e)**) is resolved into a fringe pattern with a d -spacing value of 0.27 nm that corresponds to (110) plane of LNO nanoparticles consistent with the results of powder XRD. The EDS elemental mapping (see **Fig. 6.2 (f)**) of LNO indicates the presence of lanthanum (La), nickel (Ni) and oxygen (O). Furthermore, the elemental mapping analysis (see **Fig. 6.2 (g-k)**) also supports the formation of LNO and the presence of La, Ni, and O. The TEM images of pure g-CN show nanosheets with smooth surface and a layered like structures (see **Fig. 6.3 (a,b)**). From the TEM images of 10% LNO/g-CN nanocomposite (see **Fig. 6.3 (c,d)**), it is clearly seen that the LNO nanoparticles are fully encapsulated with

g-CN nanosheets resulting in the formation of a heterojunction structure with g-CN. The HRTEM of 10%LNO/g-CN (see **Fig. 6.3 (e)**) clearly identified the lattice fringe pattern of LNO nanoparticles with a d -spacing value of 0.27 nm which can be indexed to the (110)

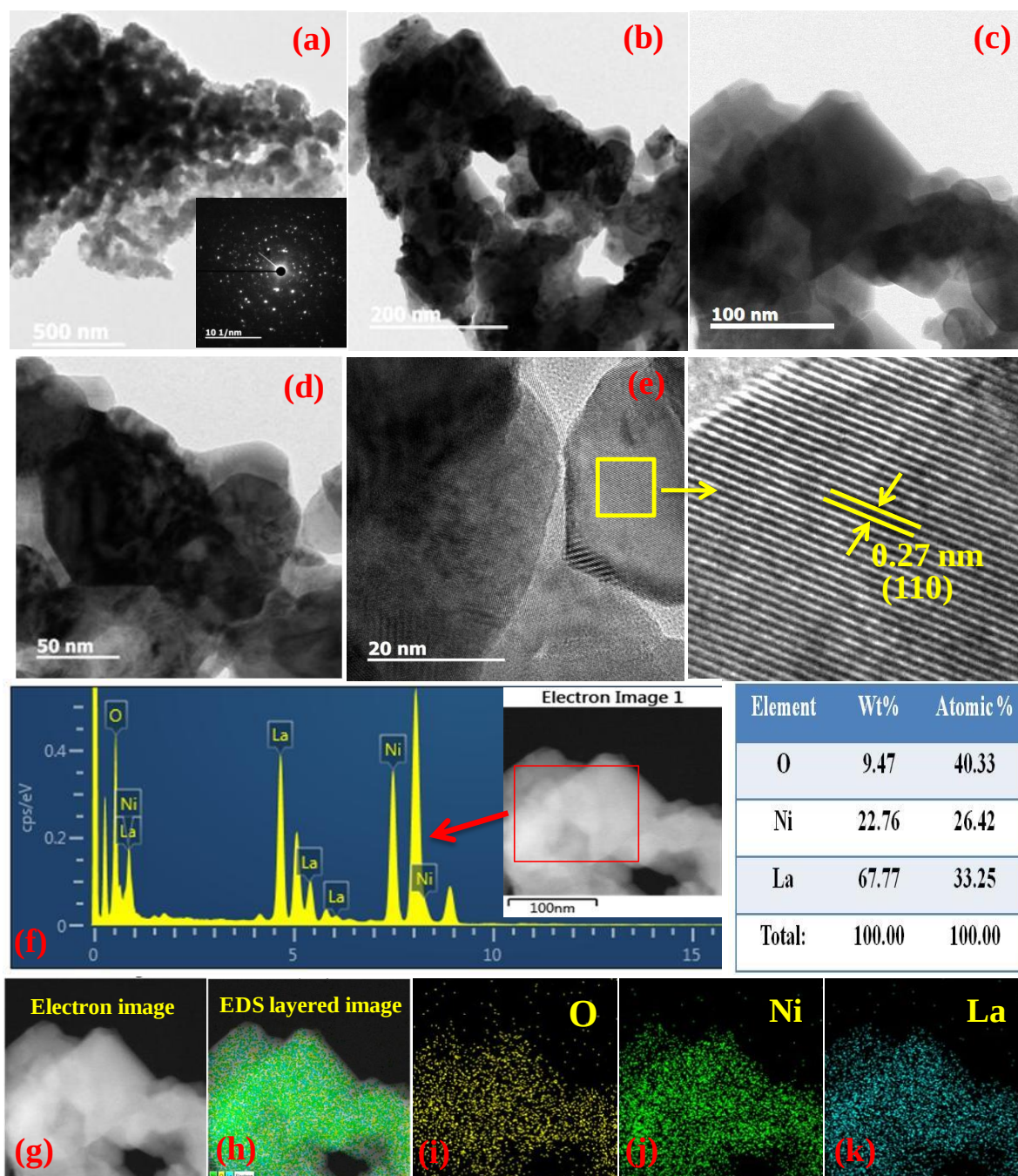


Fig. 6.2: TEM images (a–d), HRTEM (e), EDS (f), and elemental mapping (g–k) of pure LNO.

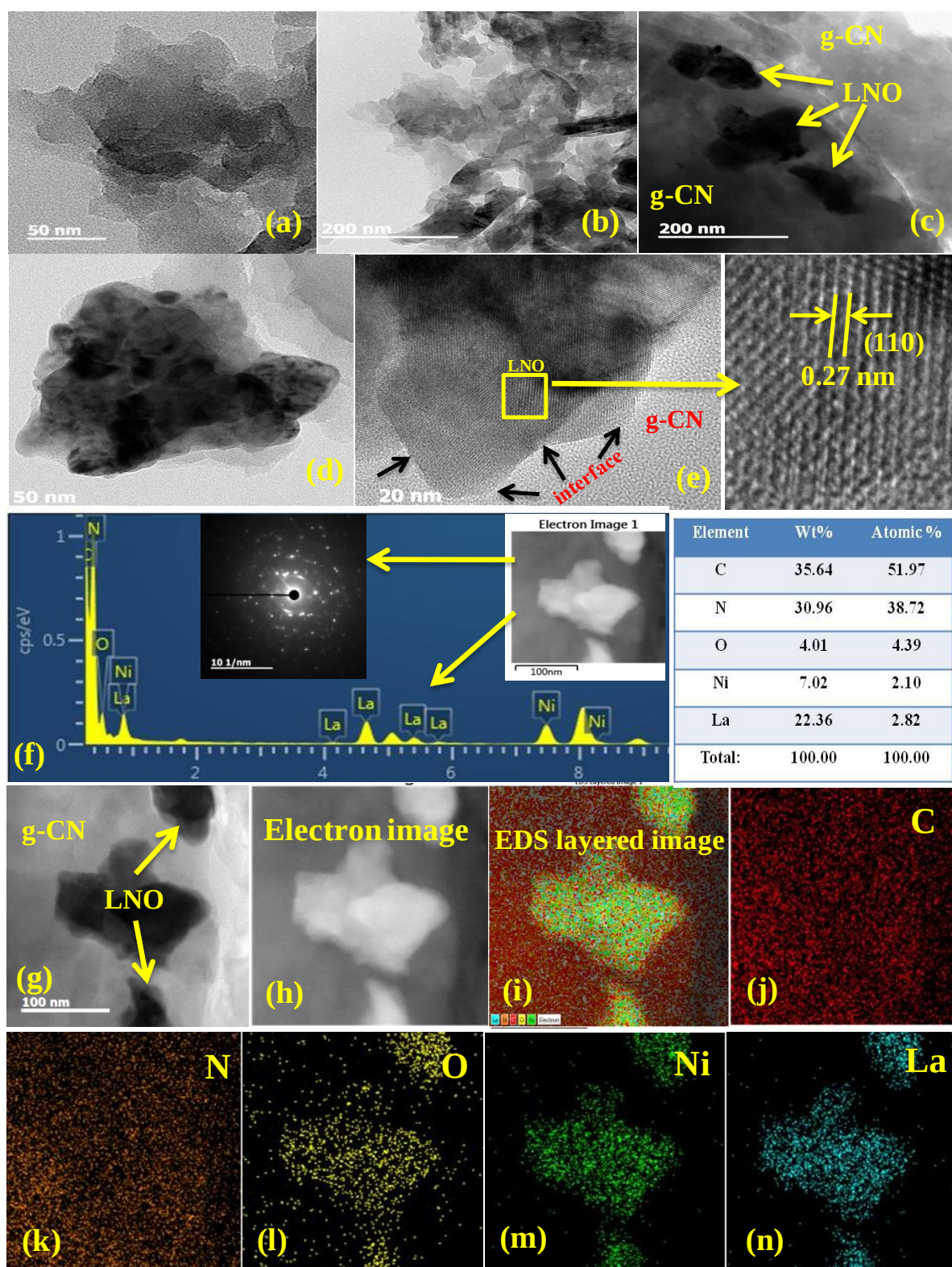


Fig. 6.3: TEM images of pure g-CN (a,b), TEM images (c,d), HRTEM (e), EDS (f), and elemental mapping (g–n) of 10%LNO/g-CN nanocomposite.

lattice plane. Therefore, in LNO/g-CN nanocomposite system, the LNO nanoparticles are tightly interacted with the g-CN surface resulting with the construction of binary heterojunction between LNO and g-CN. The EDS indicates the presence of La, Ni, O, C, and N in the nanocomposite system (see **Fig. 6.3 (f)**). Moreover, the elemental mapping analysis of 10%LNO/g-CN nanocomposite confirms the formation a nanocomposite of g-CN with LNO and also the existence of La, Ni, O, C, and N element in the nanocomposite (see **Fig. 6.3 (g-n)**).

6.2.3. BET surface area analyses

The specific BET surface areas, pore volumes and pore size distributions are listed in **Table 6.1**. The adsorption-desorption isotherms of the catalysts are displayed in **Fig. 6.4**, while the pore size distributions curves are given in the inset of **Fig. 6.4**. According to IUPAC classification, the nature of isotherm of all the photocatalysts are of type IV with a H3 type hysteresis loop which confirms that the materials belong to the family of mesoporous structure. From **Table 6.1**, it is clear that in case of nanocomposites, the specific surface area and pore volume are increased a little or remains similar (for the highest LNO-loaded nanocomposite) when these are compared to its pure components. Note that, the 0%LNO/g-CN is essentially pure g-CN but treated in the same way as the nanocomposites that has the effect of increasing the surface area marginally. This was done to make the comparison of activities of the nanocomposites with g-CN more realistic. The surface areas of LNO/g-CN nanocomposites are increased from 10%LNO-loading to 100%LNO-loading on g-CN. Further increase in LNO-loading (150%LNO/g-CN) has the effect of decreasing the surface area of the nanocomposite. The 10%LNO-loaded nanocomposite possesses the maximum surface area ($30.4 \text{ m}^2 \text{ g}^{-1}$) among the nanocomposite series. The values of pore size of the all the synthesized photocatalysts fall in the region of 1.4–2.3 nm indicating again their mesoporous nature. Here, it must be noted that there is no direct relationship between the pore size and the pore volume and so it is necessary to have data with very high accuracy for a detailed pore structure analyses.

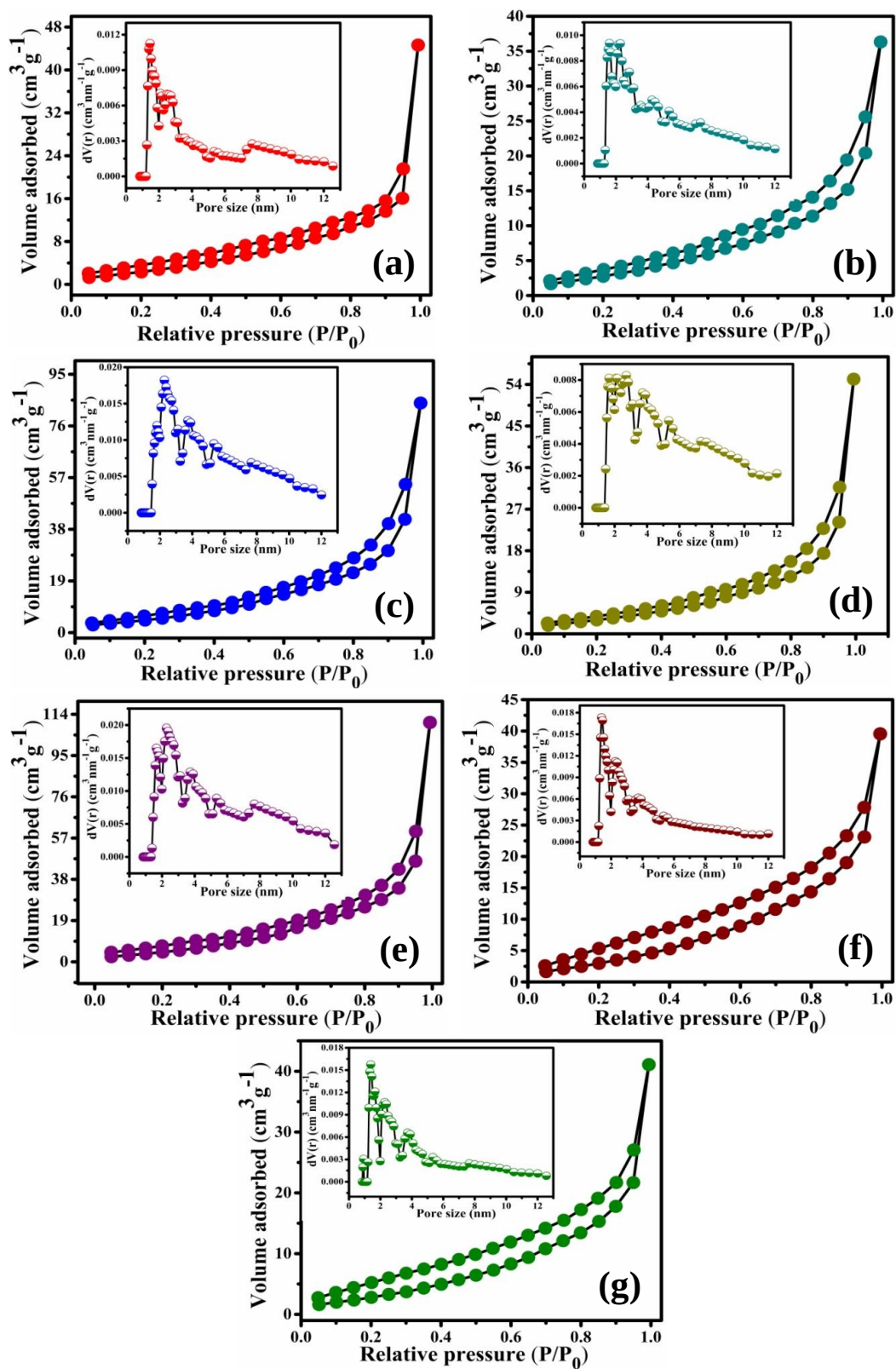


Fig. 6.4: Nitrogen adsorption-desorption isotherms and pore size distribution curves (in the inset) of (a) LNO, (b) g-CN, (c) 0%LNO/g-CN, (d) 10%LNO/g-CN, (e) 50%LNO/g-CN, (f) 100%LNO/g-CN, and (g) 150%LNO/g-CN.

Table 6.1: Textural property of LNO, g-CN and LNO/g-CN nanocomposite materials.

Sample name	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Adsorption capability (%)	
				MB	RB5
LNO	13.2	0.032	1.45	3.4	16.3
g-CN	22.1	0.068	2.27	15.7	7.3
0%LNO/g-CN	23.9	0.079	2.27	17.1	7.1
10%LNO/g-CN	30.4	0.074	1.65	17.9	13.3
50%LNO/g-CN	28.0	0.081	2.27	22.4	14.7
100%LNO/g-CN	26.7	0.067	1.58	24.4	14.6
150%LNO/g-CN	20.6	0.079	2.27	24.1	17.0

6.2.4. XPS studies

XPS of La 3d, Ni 2p, N 1s, and O 1s core levels of g-CN and 10%LNO/g-CN nanocomposite were carried out to investigate the elemental oxidation states in the material and shown in **Fig. 6.5**. Survey spectra of both materials show the presence of C, N, and O in g-C₃N₄ and La, Ni, C, N, and O in LNO/g-CN as presented in **Fig. 6.5(a)**. La 3d and Ni 2p core levels were recorded simultaneously because of overlapping of La 3d and Ni 2p_{3/2} core level regions. The broad nature of the spectrum in the higher binding energy region indicates the presence of La and Ni species in the nanocomposite. Hence, careful curve fitting of the spectrum in this region has been carried out keeping in mind all the possible component peaks of Ni along with La 3d_{3/2} peaks. The curve-fitted La 3d and Ni 2p core level spectrum of LNO/g-CN is displayed in **Fig. 6.5(b)**. In the curve-fitted spectrum, two doublets with 16.8 eV spin-orbit separation correspond to La 3d_{5/2,3/2} peaks. The doublet peaks observed at 834.2, 851.0 and 837.8, 855.0 are attributed to La³⁺ species in these type of materials [41-43]. These doublet peaks are result of contributions from several initial and final states of La related to 3d⁹4f¹ (lower binding energy) and 3d⁹4f⁰ (higher binding energy). Observed Ni 2p_{3/2,1/2} component peaks at 854.3 and 872.8 eV with weak intensities are assigned to Ni²⁺ species present in the nanocomposite. Intense decomposed peaks at 856.1 and 874.3 eV confirm the presence of Ni³⁺ species in the LNO/g-CN nanocomposite. Therefore, Ni is present in +2 and +3 oxidation states in the nanocomposite. [42, 44, 45]. Concentrations of Ni species in the nanocomposite is estimated from the respective area under the peak and it is

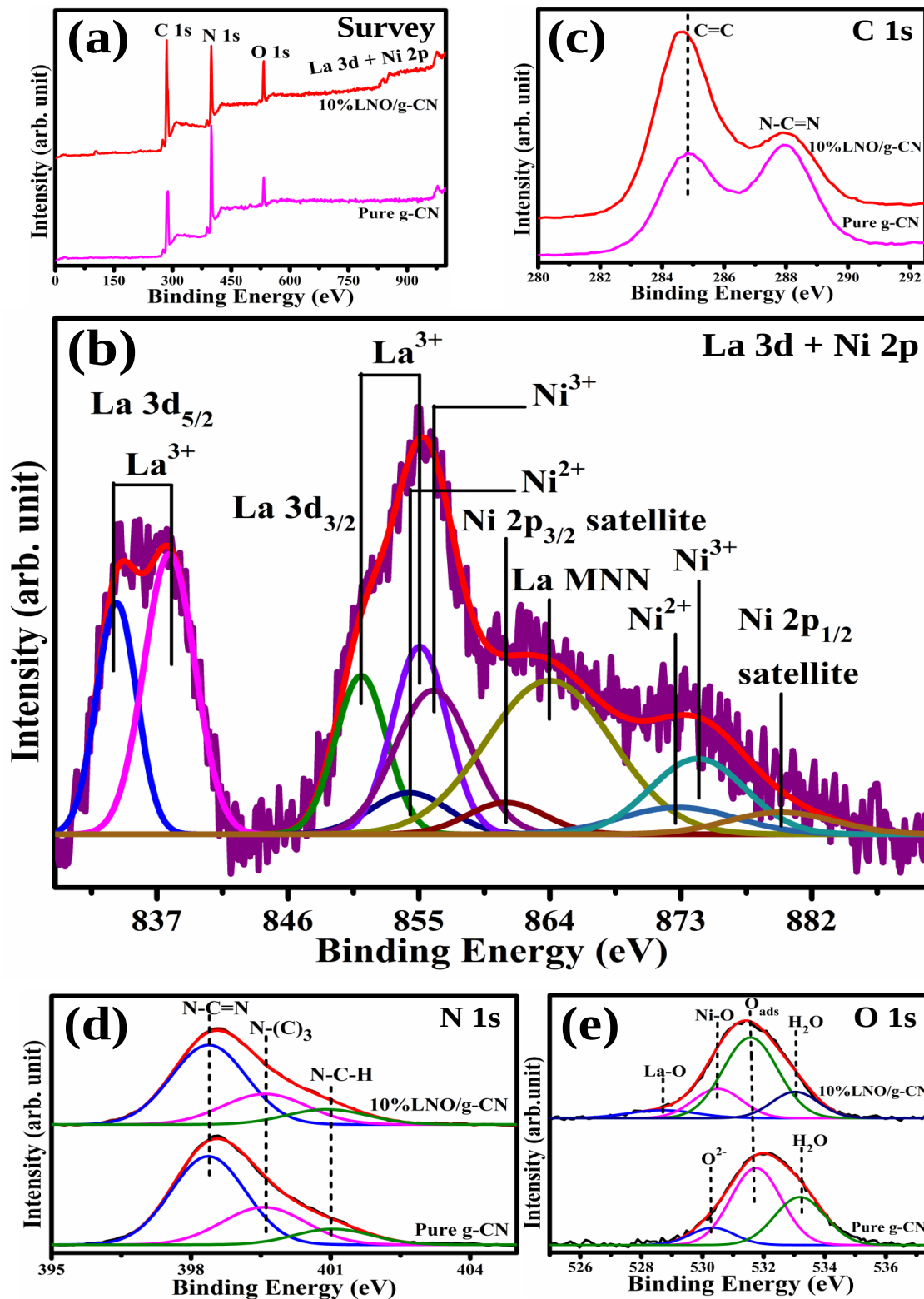


Fig. 6.5: (a) Survey spectra and (b) La 3d+Ni 2p (only for the 10%LNO/g-CN nanocomposite sample), (c) C 1s, (d) N 1s and (e) O 1s core level spectra of pure g-CN and 10% LNO/g-CN nanocomposite.

observed that 75% of Ni species is present in +3 oxidation state and 25% is Ni^{2+} species. Considering the fully stoichiometric phase of LaNiO_3 , the oxidation state of Ni is expected to be +3. However, our XPS analyses suggest the presence of Ni^{2+} in significant amount. Such deviation cannot be accounted for by invoking only the under-stoichiometry of oxygen suggesting the formula $\text{LaNiO}_{2.875}$. The other possibility to explain the occurrence of Ni^{2+} is the ligand-hole where the charge from oxygen ligand is transferred to Ni^{3+} resulting in $3d^8\bar{L}$ (Ni^{2+}O^-) configuration, where $\bar{L}$ denotes a hole on the ligand [35, 36]. C 1s core level spectra of g-CN and LNO/g-CN are given in **Fig. 6.5(c)**. Peaks at 284.6 and 288.0 eV are associated with C=C and N–C=N bonds, respectively [34]. N 1s core level spectra of g-CN and LNO/g-CN are broad in nature indicating the presence of different component species. In **Fig. 6.5(d)**, curve-fitted spectra are shown. In both materials, observed peaks at 398.4, 399.5, and 401.0 eV are attributed to N–C=N, N–(C)₃, and N–C–H, respectively, that agrees well with these types of materials reported in the literature [34]. O 1s core level spectra of g-CN and LNO/g-CN are asymmetric in nature and are resolved into different component species by curve-fitting as displayed in **Fig. 6.5(e)**. Observed low intense peak at 530.3 eV in O 1s core level spectrum of g-CN is related to oxide species, whereas intense peaks at 531.7 and 533.2 eV are assigned for adsorbed oxygen and H_2O , respectively. In the curve-fitted O 1s core level spectrum (see **Fig. 6.5(e)**), observed two low binding energy peaks at 528.6 and 530.5 eV in the O 1s core level spectrum of LNO/g-CN are attributed to lattice oxygen associated with La and Ni, respectively [37]. Higher binding energy peaks at 531.5 and 533.0 eV are ascribed for adsorbed oxygen and H_2O [46].

6.2.5. UV-Vis DRS and band gap studies

The light absorption property of pure g-CN, pure LNO, and the LNO/g-CN nanocomposite samples were investigated by UV–Vis DRS in the wavelength range from 200 nm to 800 nm. The UV–DRS spectral results are displayed in **Fig. 6.6**. It is clear that the light absorption property of LNO/g-CN nanocomposite is higher than that of pure g-CN. This suggests the enhanced absorption efficiency of the nanocomposite. Pure g-CN shows strong absorption edge at 480 nm indicating its visible light absorption ability, while pure LNO has the ability to absorb light over the whole visible range. In the nanocomposite system, the absorption edge of g-CN is shifted towards the visible region and there occurs an increase in its light absorption ability. This enhancement of visible light absorption activity of LNO/g-CN nanocomposite could effectively produce more photogenerated electron-hole pair than

that of pure g-CN and as a result of improved photocatalytic activity of g-CN in the nanocomposite system with LNO nanoparticles. The band gap energy of pure g-CN, pure LNO and the all the LNO/g-CN nanocomposites have been estimated from the Tauc's plot analysis (see **Fig. 6.7**). According to the published literature the value of n is 0.5 for both LNO and g-CN [47, 48]. The calculated band gap energies are 2.73, 1.81, 2.72, 2.62, 2.35, 2.13 and 1.87 eV for pure g-CN, pure LNO, 0%LNO/g-CN, 10%LNO/g-CN, 50%LNO/g-CN, 100%LNO/g-CN and 150%LNO/g-CN, respectively. Thus, an increase in LNO loading causes a decrease in the band gap energy value of g-CN in the nanocomposite system and this may be the key factor for improved photocatalytic activity of g-CN in nanocomposite form with LNO nanoparticles. A closer look at **Fig. 6.6(c) & 6.6(d)** reveals that there is an extended absorption tail which can contribute significantly to the absorption of photons with energies lower than the optical gap. There are different ways for the generation of these tail states [49, 50]. For example, weak absorption tails may be due to small optical transitions from one tail state to another tail state. The localized tail states mainly occur in amorphous/lower crystalline semiconductors generated through defect levels/ structural disorder in the material. Secondly, it can appear in the region where optical transition occurs from the localized tail states above the VB to the extended states in the CB and/or from the extended states in the VB to the localized states below the CB, called Urbach tail state. The tail state can also appear when the optical transition occurs from one extended state to another extended state, where we usually fit Tauc's relation to calculate the band gap energy. There can as well be contribution from enhanced sub-band gap absorption [51, 52]. This feature arises due to the formation of localized states extended in the band gap i.e. the so-called mid gap states related to the existence of disorders/defects in the structure [53-55]. The prevalence of ligand-hole in LaNiO_3 can be regarded as localized states and possibly contribute to the absorption. The formation of ligand-hole is supported from the presence of Ni^{2+} contribution in the XPS spectra as discussed above.

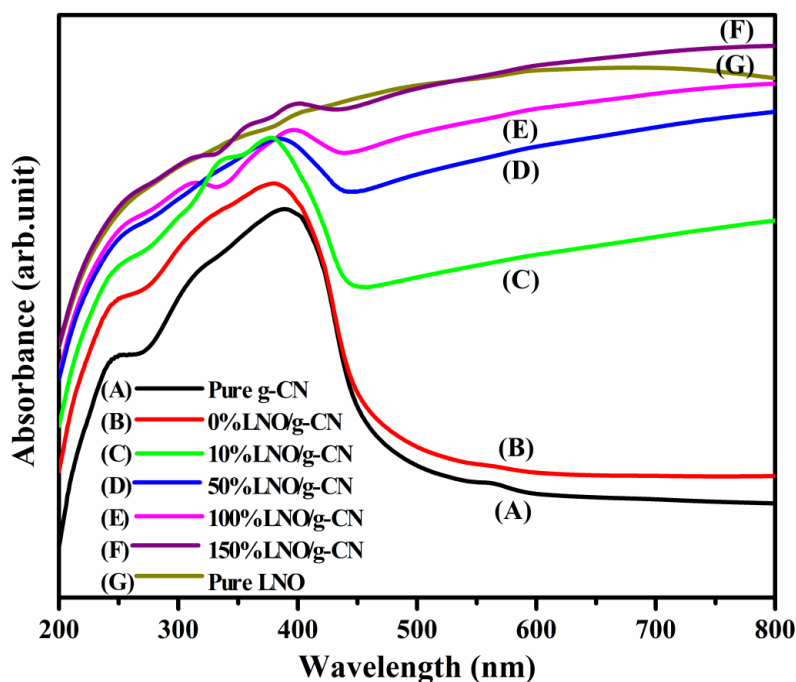


Fig. 6.6: UV-Vis DRS spectra of pure g-CN, LNO, and LNO/g-CN nanocomposite materials.

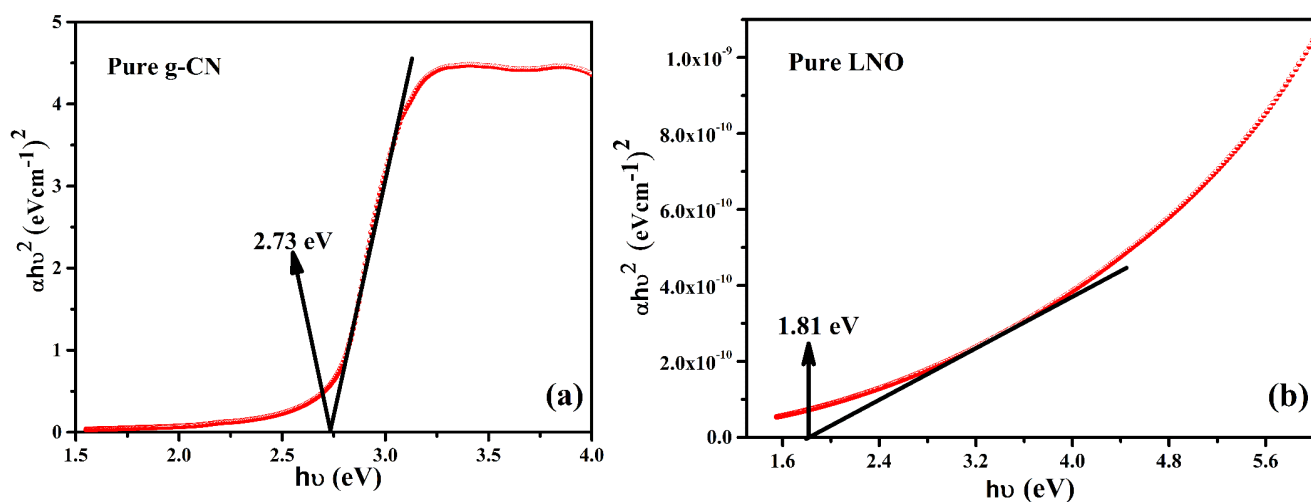


Fig. 6.7: Tauc's plot for band gap values of (a) pure g-CN and (b) pure LNO.

6.2.6. Electrochemical studies for band gap measurement

Detail procedure of electrochemical studies for band gap energy measurement including electrode fabrication, and result analysis procedure is discussed in chapter 2. **Fig. 6.8** represents the half-wave potential of Fc/Fc^+ redox couple related to the Ag/AgCl reference electrode which found to be +0.49 V.

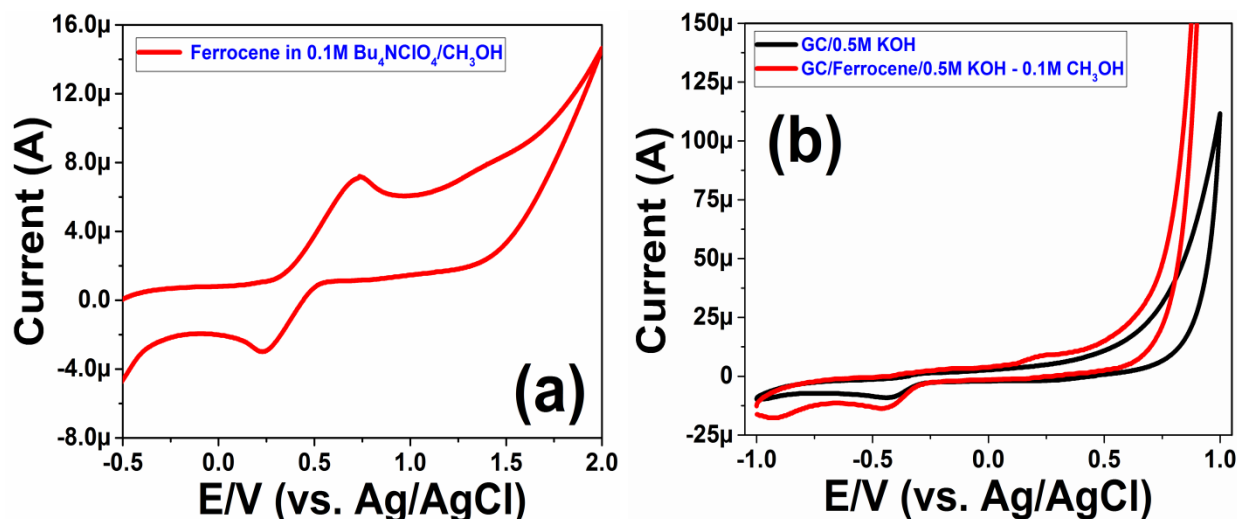


Fig. 6.8: Cyclic voltammograms of (a) ferrocene in $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{OH}$ and (b) in 0.5 M KOH and in 0.5 M KOH - 0.1 M CH_3OH with GC as working electrode, Pt-wire as counter electrode and Ag/AgCl as reference electrode at a scan rate 50 mVs^{-1} .

Cyclic voltammograms of dispersed solutions of LNO, g-CN and 10%LNO/g-CN represent the reproducibility of anodic and cathodic peak potentials in the absence and in the presence of ferrocene (see **Fig. 6.9**).

The composite materials show slight changes in the oxidation and reduction potentials at a certain condition. HOMO levels were found to be at -5.16 eV, -5.24 eV and -5.52 eV for LNO, g-CN and 10%LNO/g-CN, respectively and the corresponding LUMO levels were situated at -3.74 eV, -3.45 eV and -3.42 eV, respectively. The evaluated band gap energy of the three materials is tabulated in **Table 6.2**. The obtained band gap energies of LNO, g-CN and 10%LNO/g-CN from the optical and electrochemical studies are close to each other. The comparative differences have been attributed to the fact that during the optical studies, solid-solid interfaces of samples with light have been performed whereas in the electrochemical studies, solid-liquid interfaces of samples with respective electrolytes in an electrolytic bath have been done.

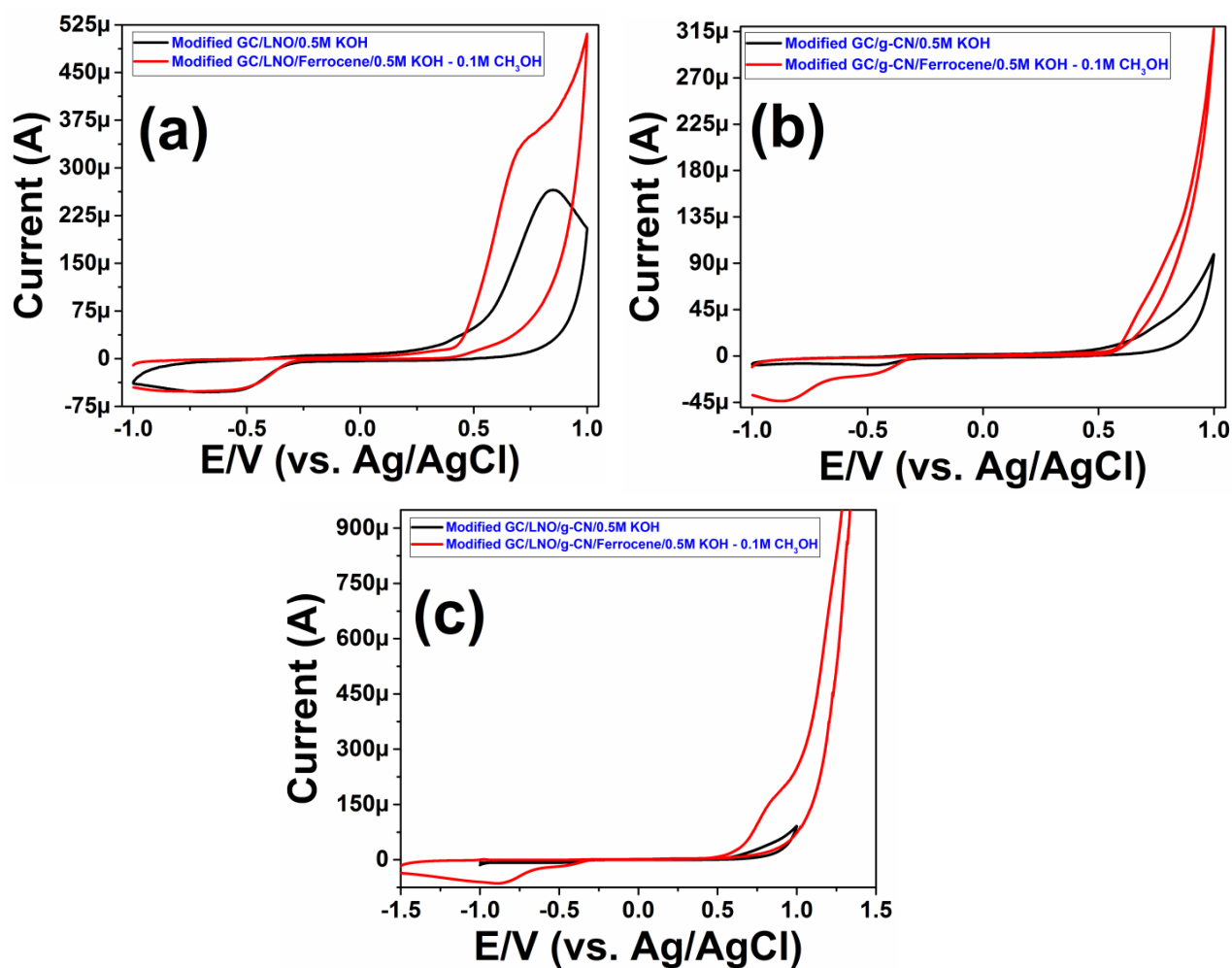


Fig. 6.9: Cyclic voltammograms of (a) LNO (b) g-CN and (c) 10%LNO/g-CN in 0.5 M KOH-0.1 M CH₃OH with the modified GC as working electrode, Pt-wire as counter electrode and Ag/AgCl as reference electrode at a scan rate 50 mVs⁻¹.

Table 6.2. Assessed band gap energy values of LNO, g-CN and 10%LNO/g-CN material.

Materials	Optical studies (eV)	Electrochemical studies (eV)	Reported (eV)	Ref.
LNO	1.81	1.42	1.89	[34]
g-CN	2.73	1.79	2.68	[34]
10%LNO/g-CN	2.62	2.10	This work	

6.2.7. Photoluminescence spectroscopic analysis

PL studies of all the materials were performed at an excitation wavelength of 340 nm. The PL spectra in **Fig. 6.10** show a peak with maximum emission intensity located at nearly 440 nm for all the samples. The intensities of this peak are greatly reduced for all the LNO/g-CN nanocomposites that are suggestive of reduction in electron-hole pair recombination ability via a Z-scheme charge transfer pathway in the nanocomposite system. The 10%LNO/g-CN nanocomposite exhibits the lowest PL intensity among all the photocatalyst samples, indicating faster charge separation as well as lower electron-hole pair recombination efficiency of this nanocomposite and hence, it is expected to act as the most active sample.

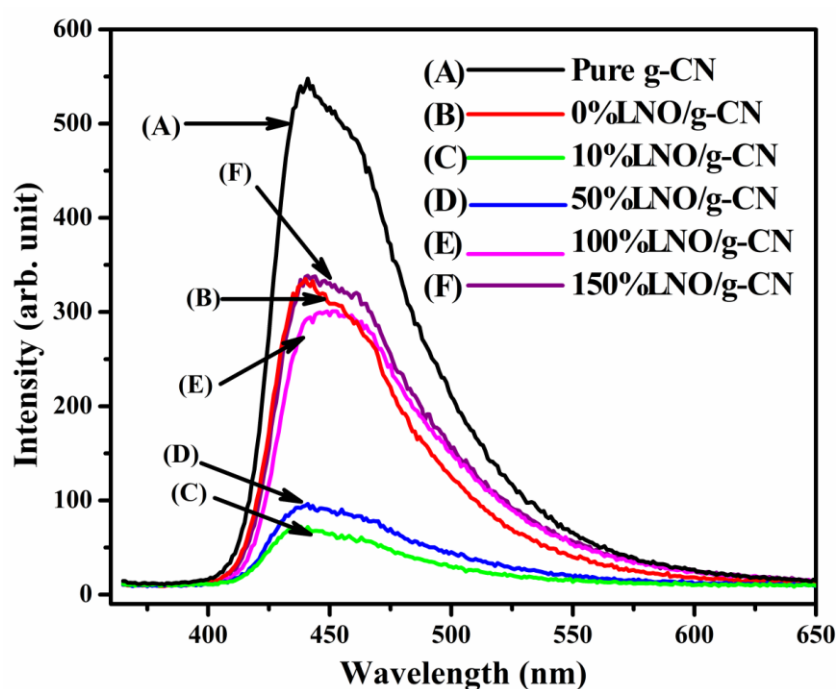


Fig. 6.10: PL spectra of pure g-CN, LNO and their nanocomposites.

6.2.8. Photocurrent response

Fig. 6.11 presents the photocurrent densities of LNO, g-CN and 10%LNO/g-CN nanocomposite. The photocurrent density of 10%LNO/g-CN is $50.63 \mu\text{A cm}^{-2}$ that is about 2 and 3 times higher than g-CN and LNO, respectively. A significantly enhanced photocurrent density of the 10%LNO/g-CN nanocomposite than the pure phases is suggestive of high photocatalytic activity of the nanocomposite. Such activity behavior may be due to the formation of direct Z-scheme heterojunction between g-CN and LNO as elaborated in mechanistic studies.

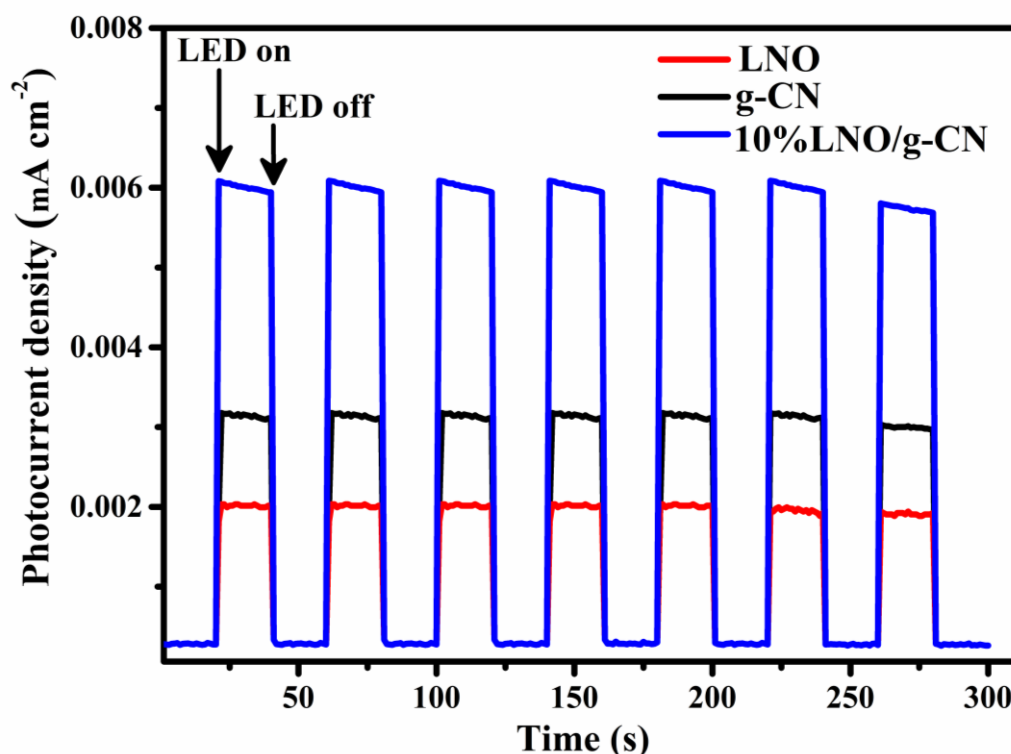


Fig. 6.11: Transient (I-t) photocurrent response of LNO, g-CN and 10%LNO/g-CN nanocomposite.

6.2.9. Photocatalytic activity studies

6.2.9.1. Degradation behaviors of RB5 and MB

The photocatalytic activities of as-synthesized photocatalysts are evaluated by the degradation of RB5 and MB under natural sunlight irradiation and the results are shown in **Fig. 6.12(a,b)**. The data of adsorption capabilities of all the samples are listed in **Table 6.1** and the adsorption curves of RB5 and MB over different photocatalysts are provided in **Fig. 6.12(c,d)** to reveal their adsorption capability differences. In respect of the pure samples, pure g-CN has a higher capability of adsorbing MB than LNO, while a reverse trend is observed for RB5 adsorption. The adsorption capability increases a little in the nanocomposite from the value obtained for pure g-CN when LNO-loading is increased, RB5 being less adsorbed than MB. Representative changes in temporal absorbance of dye pollutants during the sunlight assisted photocatalytic degradation are shown in **Fig. 6.13**. The degradation activities of all the LNO/g-CN nanocomposite samples are much higher than the pure components. Specifically, pure LNO, pure g-CN, 0%LNO/g-CN, 5%LNO/g-CN, 10%LNO/g-CN, 50%LNO/g-CN, 100%LNO/g-CN, and 150%LNO/g-CN nanocomposite degrade,

respectively, 13.3%, 37.5%, 48.5%, 84.5%, 94%, 90%, 82.7%, and 75.6 % of RB5 in 60 min, while the corresponding values for MB degradation are, respectively, 10%, 33.8%, 44%, 58%, 72%, 67%, 64%, and 57.5%. The degradation activities of MB over these series of catalyst samples are improved to 33.4%, 57.9%, 68.7%, 91%, 98.6%, 92.5%, 89%, and 85%, respectively, after 180 min. From these results it is evident that 10%LNO/g-CN nanocomposite exhibits the maximum photocatalytic performance that is more towards RB5 than MB. The photocatalytic degradation results also indicate that pure g-CN is not a suitable candidate for sunlight assisted photocatalytic degradation of RB5 and MB dyes. This is presumably due to its very high electron-hole pair recombination tendency. When this apparently inactive semiconductor with lower band gap is allowed to form a nanocomposite with LNO nanoparticles, the photocatalytic activity of g-CN is improved considerably owing to the formation of Z-scheme type heterojunction which helps suppressing the recombination tendency of g-CN. With the higher addition of LNO (from 5% to 150%) to g-CN matrix, the defect density level in 10%LNO-loaded nanocomposite seems to have the optimum level and its lower recombination tendency of photogenerated carriers (e^- - h^+) in turn increases the photocatalytic activity. PL studies also resembles the fact that 10%LNO containing nanocomposite sample possesses lower intensity among all other samples indicating excitons are residing at higher energy states with life span.

The structural and morphological studies of LaNiO_3 decorated $\text{g-C}_3\text{N}_4$ (**Section 6.2.2**) put impacts on the enhanced photocatalytic actives towards organic hazardous dyes. Moreover, from the BET analysis it is clear that the hetero phase of LaNiO_3 with $\text{g-C}_3\text{N}_4$ increases the mesoporosity throughout the structure. The findings of the electrochemical studies on 10% $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ in a suitable redox couple with the fabricated electrode also resembles much more current densities in comparison to that of individual matrix of the pure materials. All these in effect play a dominant role for the observed catalytic performances of the materials.

Photo degradation reactions follow pseudo first order reaction kinetics and $-\ln(C_t/C_0)$ Vs t plot can be fitted with very high correlation coefficient (R^2). The estimated rate constants from these plots are illustrated as bar diagram in **Fig. 6.12(e,f)**. All the LNO/g-CN nanocomposite samples have higher rate constant values of both RB5 and MB photodegradation reaction than its parent components, LNO and g-CN. Noticeably, the 10%LNO/g-CN nanocomposite shows highest photocatalytic activity with the values of rate

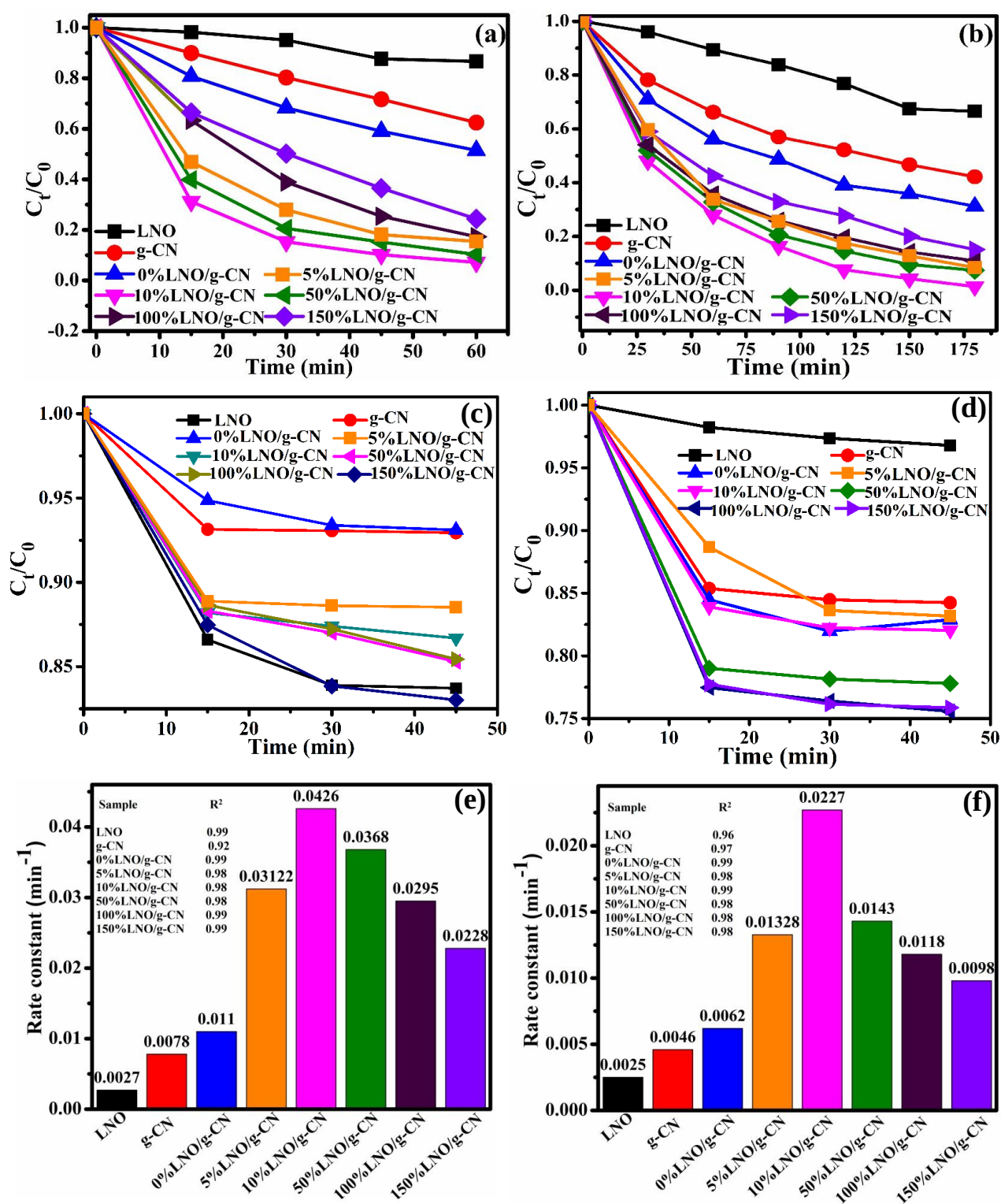


Fig. 6.12: Results of sunlight assisted photocatalytic activity, adsorption curves and values of rate constants of pure g-CN, pure LNO, and the entire nanocomposite series for the degradation of RB5 (a,c,e) and MB (b,d,f).

constant which are respectively 16 and 5.5 times higher for RB5 degradation and 9.1 and 4.9 times higher for MB degradation when compared with pure LNO and pure g-CN.

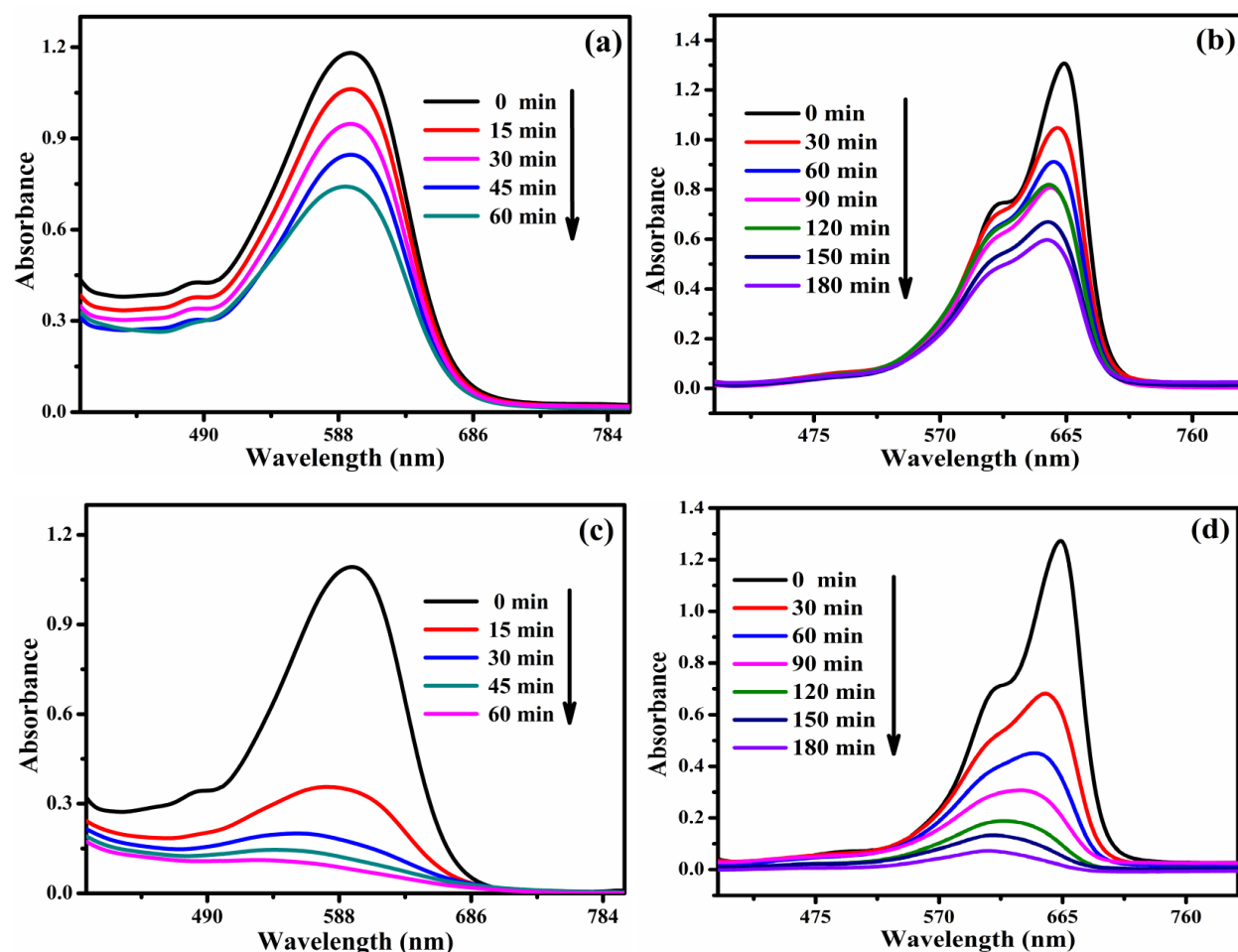


Fig. 6.13: Temporal absorbance change during the sunlight assisted photocatalytic degradation of respectively RB5 and MB in presence of (a,b) pure g-CN, and 10%LNO/g-CN (c,d).

6.2.9.2. Effects of catalyst mass on RB5 and MB degradation

The influence of catalyst loading on sunlight assisted photocatalytic degradation of RB5 and MB has been evaluated by using the most active 10%LNO/g-CN nanocomposite sample and the results are displayed in **Fig. 6.14(a,b)**. The degradation efficiencies of RB5 and MB are increased with the catalyst loading amounts from 25 mg to 100 mg and the maximum degradation efficiency is reached at 100 mg and then decreases at 125 mg. Here, it may be mentioned that one cannot avoid (a) loss of some sunlight due to reflection and (b) agglomeration of some nanoparticles causing lesser availability of active site for adsorption

of dye and hence, the radical production. Both these effects are attributed to the lowering of degradation beyond 100 mg of catalyst loading.

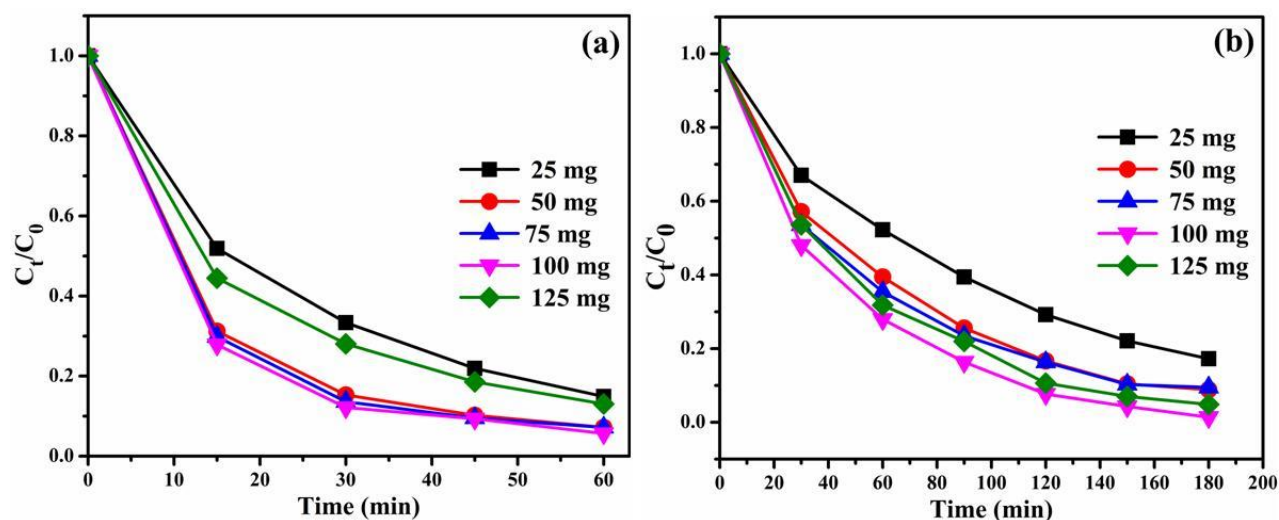


Fig. 6.14: Results of optimizing catalyst mass for (a) RB5 and (b) MB degradation by using the most active 10% LNO/g-CN nanocomposite photocatalyst sample under sunlight irradiation.

6.2.9.3. Determining the reactive species through radical trapping experiments

The experimental results of radical trapping are illustrated in **Fig. 6.15(a,b)**. When BQ, Na₂EDTA, IPA, and AgNO₃ are used as radical quencher, the degradation percentages of RB5 are, respectively, 8.8%, 64%, 91%, and 91.8%, while the degradation percentages of MB are, respectively, 16%, 67%, 95%, and 97.2%. These observations confirmed that the free radical was generated during the photocatalytic degradation of RB5 and MB under sunlight irradiation. The activity data suggest that degradation of RB5 and MB is highly reduced on addition of BQ and Na₂EDTA and remain unchanged on addition of IPA and AgNO₃ solution. So it may reasonably be concluded that $\cdot\text{O}_2^-$ and h^+ are formed as the major reactive species in the photocatalytic degradation process, while $\cdot\text{OH}$ and free electrons have no noticeable role in the degradation process. Since addition of BQ, a superoxide radical quencher, to the photocatalytic reaction solution causes considerable decrease in degradation (from 94% to 8.8% for RB5 and 99% to 16% for MB), it may be concluded that $\cdot\text{O}_2^-$ is the main (primary) species, while h^+ is the secondary reactive species in this photocatalytic degradation process.

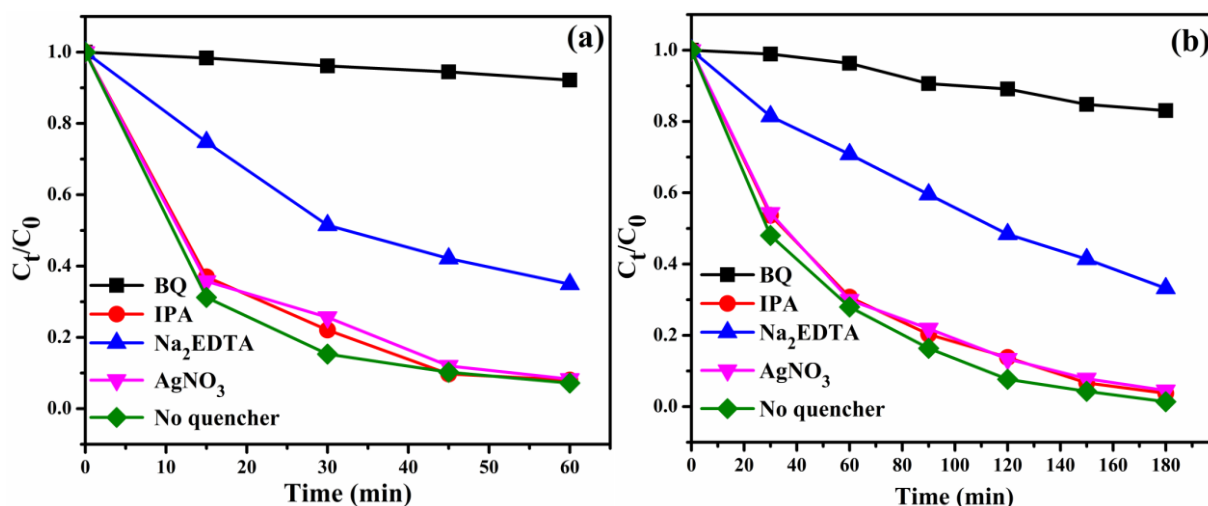


Fig. 6.15: Results of radical trapping experiments in the sunlight assisted degradation of (a) RB5 and (b) MB by using 10%LNO/g-CN nanocomposite sample.

6.2.9.4. Sunlight assisted photocatalytic degradation activity of 10%LNO/g-CN for a colorless antibiotic-pollutant

Further evaluation of sunlight assisted photocatalytic activity of the LNO/g-CN nanocomposites for the degradation of a colorless pollutant, TC-HCl was performed using the highly active 10%LNO/g-CN nanocomposite sample. The photocatalytic degradation experiment process was maintained similar to RB5 and MB degradation. In a typical experiment, 60 mL of 20 ppm TC-HCl solution and 100 mg of the photocatalyst sample were used and the degradation percentage is calculated by measuring the absorption at the wavelength of 357 nm using the same UV-Vis spectrophotometer. The findings of sunlight assisted photocatalytic degradation experiment are displayed in **Fig. 6.16**. The calculated degradation % of TC-HCl is 28.2%, 27.5% and 88.1% for pure LNO, pure g-CN and 10%LNO/g-CN nanocomposite, respectively. The respective values of rate constant (see **Fig. 6.16(b)**) are 0.00278, 0.00258 and 0.01803 min⁻¹. These data clearly indicate that the rate constant of 10%LNO/g-CN nanocomposite sample is respectively 6.4 times and 6.9 times higher than that of pure LNO and pure g-CN. The representative temporal absorbance change during photodegradation is displayed in **Fig. 6.16(c,d)**. So, the reported nanocomposite catalyst also performs quite well for the degradation of colorless pollutant TC-HCl making it as a truly general catalyst for the degradation of colored azo dyes like RB5 and MB as well as colorless antibiotic pollutant like TC-HCl under natural sunlight.

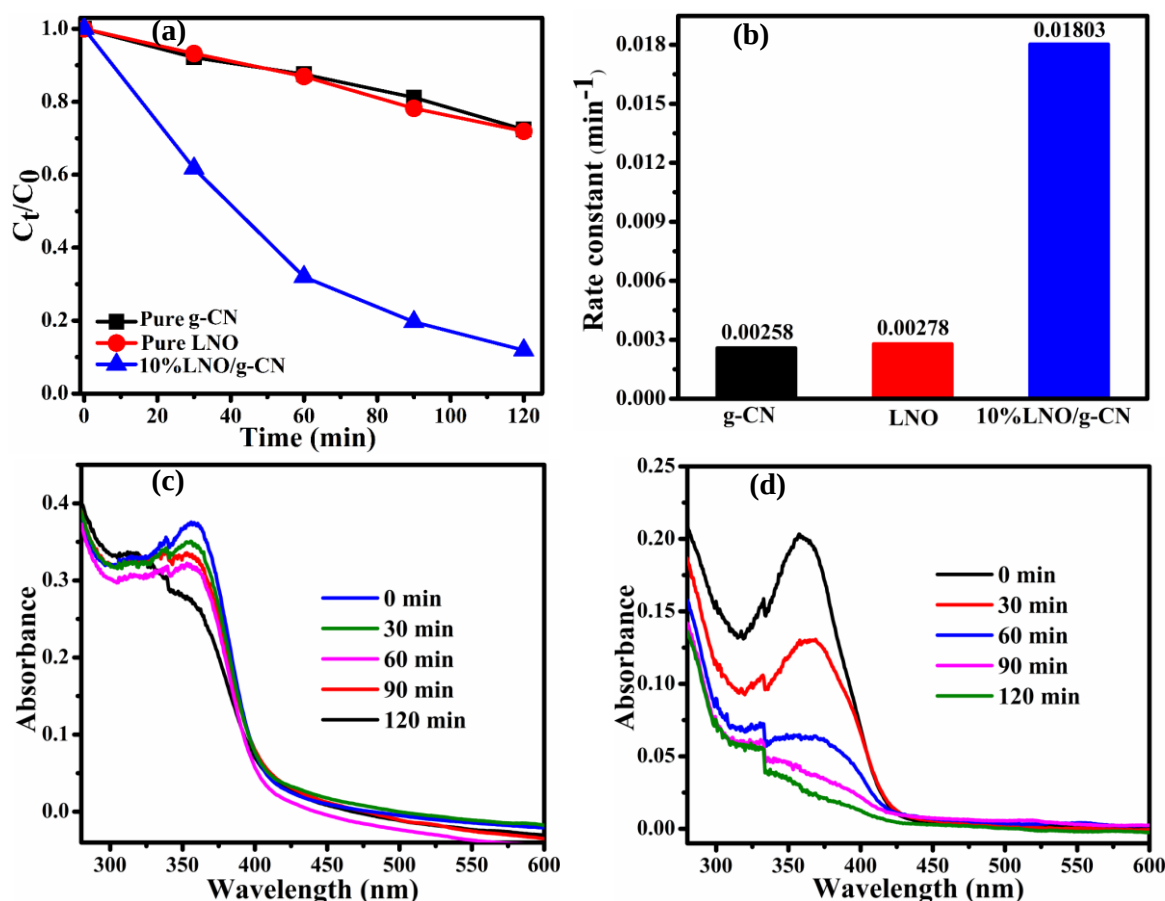


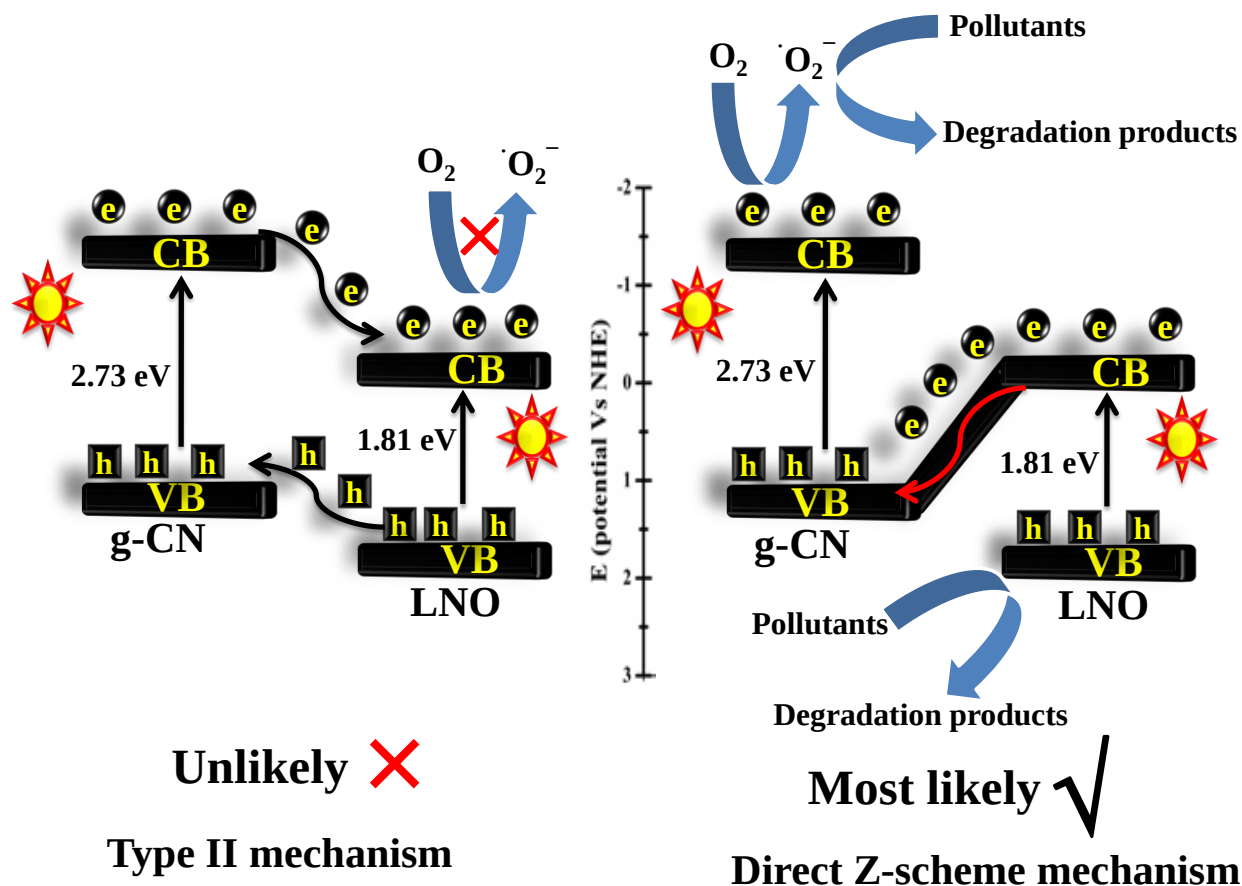
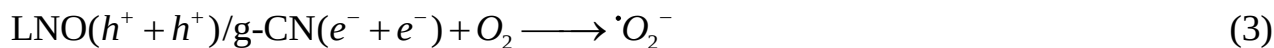
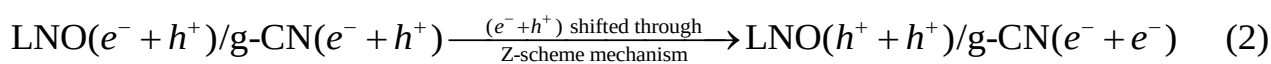
Fig. 6.16: (a, b) Results of sunlight assisted photocatalytic activity and values of rate constants of pure g-CN, pure LNO and 10%LNO/g-CN nanocomposite sample for the degradation of TC-HCl and temporal absorbance change during photodegradation of TC-HCl using (c) pure g-CN and (d) 10%LNO/g-CN nanocomposite.

6.2.9.5. Mechanism of photocatalytic degradation

To realize the mechanism of photo-degradation over LNO/g-CN nanocomposite system, it is essential to estimate the respective VB and CB energy values of both LNO and g-CN. According to the literature the χ value of LNO and g-CN are 5.67 and 4.72 eV, respectively [48, 30]. Based on the empirical equations (discussed in chapter 2), the E_{VB} and E_{CB} potential energy values of g-CN are estimated to be 1.135 eV and -1.595 eV, respectively, whereas the estimated values of E_{VB} and E_{CB} for LNO are 2.075 eV and 0.265 eV, respectively.

When the band edge potential energies of LNO and g-CN are closely considered, two photocatalytic mechanisms can possibly operate. Firstly, conventional type II heterojunction mechanism and secondly, direct Z-scheme type mechanism. Both these photodegradation

mechanisms are shown in **Scheme 6.1**. Initially, both LNO and g-CN generates photoexcited electrons on their CB upon natural sunlight irradiation and leave the holes on their VB. According to the conventional type II heterojunction mechanism, the photo-excited electrons on the CB of g-CN could easily be transferred to the CB of LNO and the holes of LNO on VB could be transferred to the VB of g-CN. As a result of these two processes electrons and holes get accumulated on the CB of LNO and VB of g-CN, respectively and eventually there results a reduction of electron-hole pair recombination efficiency. According to the radical trapping experiments, $\cdot\text{O}_2^-$ is the predominantly formed reactive species during the photodegradation process. But the conventional type II heterojunction mechanism cannot lead to the formation of $\cdot\text{O}_2^-$ radical because accumulated electrons on the CB of LNO cannot convert dissolved O_2 to form $\cdot\text{O}_2^-$ radical owing to more negative potential of $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV Vs. NHE) than the CB potential value of LNO (0.215 eV). So, the possibility of type II heterojunction mechanism can be ruled out. The VB and CB band edge potential values of g-CN and LNO are also suggestive of a Z-scheme band structure between the two components that we considered as the second possible mechanistic route. In this mechanism, the photoexcited electrons on the CB of LNO is shifted easily to the VB of g-CN and in the process excited electrons and holes get accumulated on the CB of g-CN and VB of LNO, respectively. The excited electron on the CB of g-CN can easily be transferred to dissolved oxygen of the reaction solution to form $\cdot\text{O}_2^-$ because the CB potential energy of g-CN is lower than that of the $\text{O}_2/\cdot\text{O}_2^-$ potential. The $\cdot\text{O}_2^-$ radical is strong enough to degrade RB5 and MB into smaller fragmented products. Additionally, the holes on the VB of LNO can also participate with ease in the degradation process. Therefore, the direct Z-scheme type photocatalytic mechanism is consistent with the findings of radical trapping experiments that suggest formation of $\cdot\text{O}_2^-$ and hole as the key players in this photocatalytic degradation process. The Z-scheme heterojunction type of band structure can effectively delay the electron-hole pair recombination efficiency that in turn attributes to improved photocatalytic activity of the nanocomposite compared with pure g-CN and pure LNO. Based on the above analysis, the important photocatalytic reaction steps are shown below followed by the schematic representations of the plausible mechanisms of dye degradation.



Scheme 6.1: Schematic representation of plausible mechanism for the photocatalytic degradation of RB5 and MB over LNO/g-CN nanocomposite.

In the degradation activities of the pollutants, we have used the Z-scheme mechanistic pathway that can be attributed to the proper band-bending and appropriate band-matching parameters of involved components. This is crucial for the selective electronic pathways of favorable oxidation and reduction reactions during the photocatalysis of respective pollutants under natural sunlight.

In addition to the primary Z-scheme charge transfer pathway across the heterojunction of the nanocomposite catalyst, the ligand-hole can facilitate further the redox process. The ligand-hole, expected to be positioned at the mid-gap, can act as a defect-center which should

trap the excited electron. These trapped electrons in the mid-gap states can serve as the charge carrier to reduce the dissolved O_2 in the reaction medium to form oxidized species which eventually leads to degradation of the dyes. Even the possibility of oxidation of Ni^{2+} by dissolved oxygen cannot be completely ignored. Onset of these additional boosting phenomena in the LNO/g-CN catalyst system enhances the photoactivity of the nanocomposite under direct sunlight.

6.2.9.6. Recycling activity of photocatalyst

In order to study the recycling behavior, the most active photocatalyst 10%LNO/g-CN was used. Before every recycling test the photocatalyst sample was collected through centrifugation and then washed with ultra pure water and ethanol for three times each followed by drying at 60 °C for 2 h. The 10%LNO/g-CN sample was used for consecutive four cycles in the degradation of RB5 and MB under identical conditions. The results of recycling test are shown in **Fig. 6.17(a)**. The degradation percentages of RB5 and MB are respectively 81.5% and 56% in 60 min and for MB the conversion increased further to 89.4% in 180 min after the 4th cycle of test. The bulk phase of the photocatalyst remains unchanged in both the cases of degradation as confirmed from the powder XRD patterns of 10%LNO/g-CN sample shown in **Fig. 6.17(b)**.

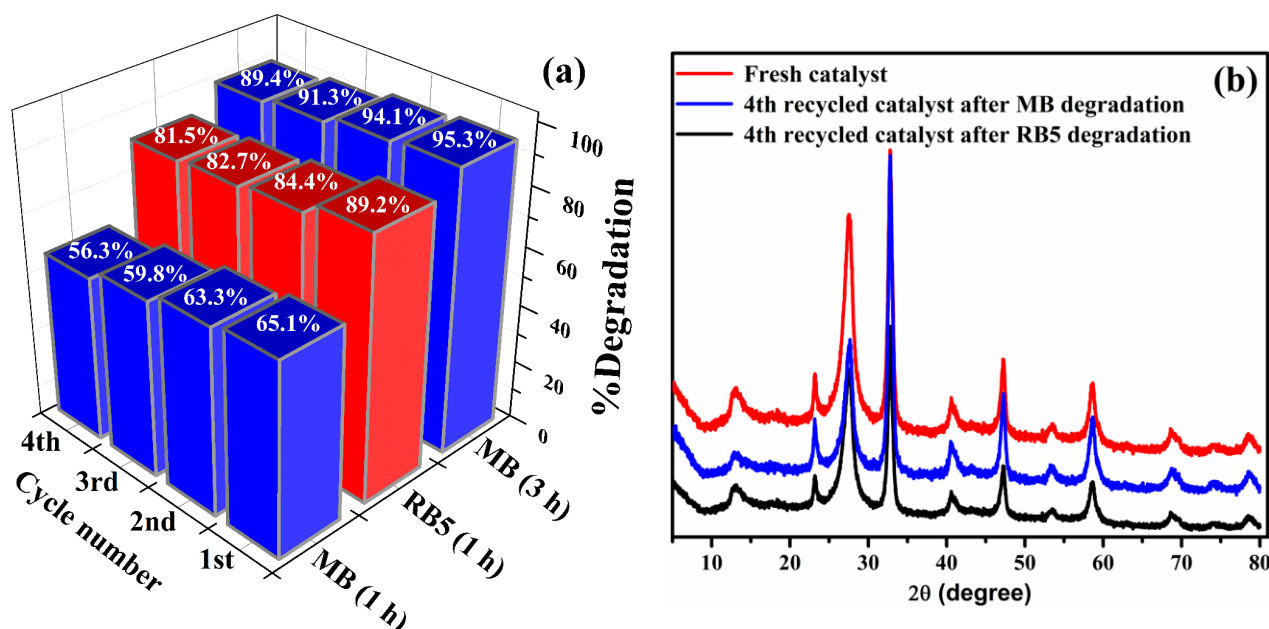


Fig. 6.17: (a) Recycling activity of 10%LNO/g-CN photocatalyst and its (b) XRD patterns before and after recycling test for RB5 and MB degradation.

A closer look at the powder XRD patterns before and after cycling reveals that there is a little change in the crystallinity of $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ nanocomposite, which may be due to the agglomeration or associative nature of the grains of the materials. As a whole FWHM value goes down indicating slight modifications of the crystal matrix. This can be attributed to blocking of some active sites of the nanocomposite matrix owing to its high surface energy.

6.3. Conclusions

In conclusion, a facile Z-scheme like $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ heterojunction nanocomposite photocatalyst has been prepared by simple mixing of the pristine samples with IPA dehydration followed by heat treatment method. Natural sunlight assisted photocatalytic activities of the photocatalyst samples have successfully been performed for the degradation of industrially hazardous azo dyes, RB5 and MB. Beside this the fabricated $\text{LaNiO}_3/\text{g-C}_3\text{N}_4$ nanocomposite photocatalyst is also shown to be active for the degradation of the colorless antibiotic-pollutant tetracycline hydrochloride. The degradation activities of both the azo dyes follow the order: 10%LNO/g-CN > 50%LNO/g-CN > 100%LNO/g-CN > 150%LNO/g-CN > 0%LNO/g-CN > pure g-CN > pure LNO. Thus, all the LNO/g-CN nanocomposites are highly active photocatalysts up to 150%LNO (wt.% of LNO) loading when compared with pure g-CN, among which 10%LNO/g-CN nanocomposite is the most active catalyst. Presence of the LNO nanoparticles effectively improved the photocatalytic activity of g-CN via formation of direct Z-scheme heterojunction which has the effect of delaying the electron-hole pair recombination of g-CN. In the photodegradation mechanism, O_2^- and h^+ are formed as main reactive species. The nanocomposite is reported to show good stability and recycling activity tested up to fourth cycle of degradation. Our findings thus disclose the fact that the virtually inactive LNO nanoparticles for sunlight assisted photodegradation can considerably enhance the photocatalytic activity of g-CN in nanocomposite form. We believe that the perovskite-type Z-scheme photocatalyst with the feasibility of ligand-hole formation should open new opportunities for more efficient removal of pollutants from wastewater in presence of direct sunlight.

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Chapter 7

Investigations on $\text{CuCr}_2\text{O}_4/\text{BiVO}_4$ nanocomposite catalyst for electrochemical oxygen evolution reaction (OER)

Chapter abstract

This chapter is based on the studies on $\text{CuCr}_2\text{O}_4/\text{BiVO}_4$ (CCO/BVO) nanocomposite system as an active electrocatalyst for oxygen evolution reaction (OER). A series of CCO/BVO nanocomposite materials is prepared by hydrothermal reaction at $\sim 180^\circ\text{C}$ for ~ 12 h. 10 mole percent CCO loaded BVO nanocomposite sample shows the highest OER activity which is much higher than that of the parent components. Various characterization techniques were used to explore its structural features in order to correlate with its activity. The OER activities of all the samples have been checked under visible LED light as well as under dark condition and the results indicate that OER activity is significantly improved in presence of visible light.

7.1. Introduction

Hydrogen is a substitute fuel for the generation of efficient energy as well as its storage. Hydrogen energy is the sustainable energy source that can fulfill the excess energy demands of our modern society. Among the various routes of hydrogen energy generation, water splitting is an eco-friendly, sustainable and short approach to produce high purity hydrogen energy [1-2]. The oxygen evolution reaction (OER) is a semi-process in water splitting and plays a key role to determine the overall efficiency of water splitting reaction. The oxides of Ru, Ir, Pd and Pt/C are most efficient and well known conventional electrocatalyst for OER but its insufficiency, high cost and moderate stability hinder their large scale applications [3-6]. Extensive research works are going on to search for high performance and cost effective alternative electrocatalyst materials for OER with a special attention towards alloys [7], doped metal oxide [8] and metal oxide based nanocomposite materials [9-10]. Literature survey indicates that recent research trend is shifted towards the fabrication of metal oxide based nanocomposite system as an efficient OER catalyst in both dark and light condition due to its noticeable electrochemical activity, low cost, high stability and high charge transfer rate in the heterojunction of nanocomposite system which can improve the electrocatalytic activity [11].

BiVO_4 (BVO) is a well known electrocatalyst for water splitting, CO_2 reduction, OER, alcohol oxidation and others but its moderate electrocatalytic efficiency restrict its

versatility [12]. Various attempts have been made to improve its electrocatalytic efficiency by doping of cation/ anion [13], combination with alloys [14], formation of oxygen vacancy [15], and composite formation with metal oxides [16]. Among all the modifications, the composite materials of BVO are beneficial because these materials meet all the criteria of an efficient electrocatalyst. Recently, Z. yang et al. have developed ferroelectric enhanced BiVO₄/BiFeO₃ nanocomposite system with Co₃O₄ as cocatalyst and reported it to be an extra efficient and highly stable photoelectrocatalyst for large current density OER activity (1280 mA cm⁻² at 1.86 V vs RHE) [17]. Here all the components of nanocomposite play a specific role to enhance the OER activity that is Co₃O₄ provided active sites for OER and BiVO₄/BiFeO₃ nanocomposite heterojunction encouraged charge transfer. Due to high charge separation, the OER performance is far better in the light than in dark condition. W. Wang et al. have reported that Z-scheme photoelectrocatalyst BiVO₄/Bi₆O₆(OH)₃(NO₃)₃ nanocomposite material with an improved OER activity is due to high charge transfer via Z-scheme mechanistic route [18]. Y. peng et al. have constructed BiVO₄/NiOOH nanocomposite photoelectrocatalyst for an improved water oxidation with high rate of O₂ generation by suppressing photoinduced electron-hole recombination through the creation of oxygen vacancy in the NiOOH layer [19]. Therefore, charge transfer is a crucial factor for improved electrocatalytic activity. Beyond this, M-BiVO₄/T-BiVO₄ [20], Bi₂O₃/BiVO₄@graphene oxide [21], 2D/3D WO₃/BiVO₄ [22], BiVO₄/FeVO₄/Cu₂O [23], etc. have been reported as highly active photoelectrocatalyst for OER. Unfortunately reports on metal based spinel oxide related nanocomposite material with BVO for electrochemical and photoelectrochemical OER is very limited. This motivated us to fabricate the nanocomposite system of BVO with metal based spinel oxide, especially Cu-based spinel oxides because it has a great contribution for the improvement of charge separation in the nanocomposite system due to its favorable electronic and band structure. We have already explored various types of catalytic applications of CCO and its related nanocomposite materials in the previous chapters. We choose CCO as spinel oxide because in our early reports we have already seen that nanocomposite materials of CCO have a greater charge transfer ability due to its lower band gap (~ 1.4 eV) and high visible light absorption activity [24-25]. Based on these beneficial effects of CCO-based materials, a series of CCO/BVO nanocomposite samples have been synthesized by a hydrothermal route and subsequently tested for their OER activity under light and dark conditions that forms the basis of this chapter.

7.2. Results and discussion

7.2.1. PXRD analyses

Powder XRD patterns of BVO, CCO, 5%CCO/BVO, 10%CCO/BVO and 20%CCO/BVO are displayed in **Fig. 7.1**. The 2θ values 15.1° , 18.6° , 18.9° , 28.5° , 28.8° , 30.5° , 34.4° , and 35.2° correspond to the diffraction planes of (002), (101), (011), (103), (013), (004), (200), and (020), respectively for pure BVO which match perfectly with JCPDS file no. 83-1699. Pure CCO has a spinel oxide phase which is already discussed in chapter 3 (**Section 3.2**). The diffraction pattern of CCO/BVO nanocomposite contains peaks for both the phases of BVO and CCO. No additional peak appears in the composite phase suggesting their physical mixing without any chemical reaction. The intensity of CCO related peaks is very low as compared to BVO due to the presence of lower amount of CCO loading.

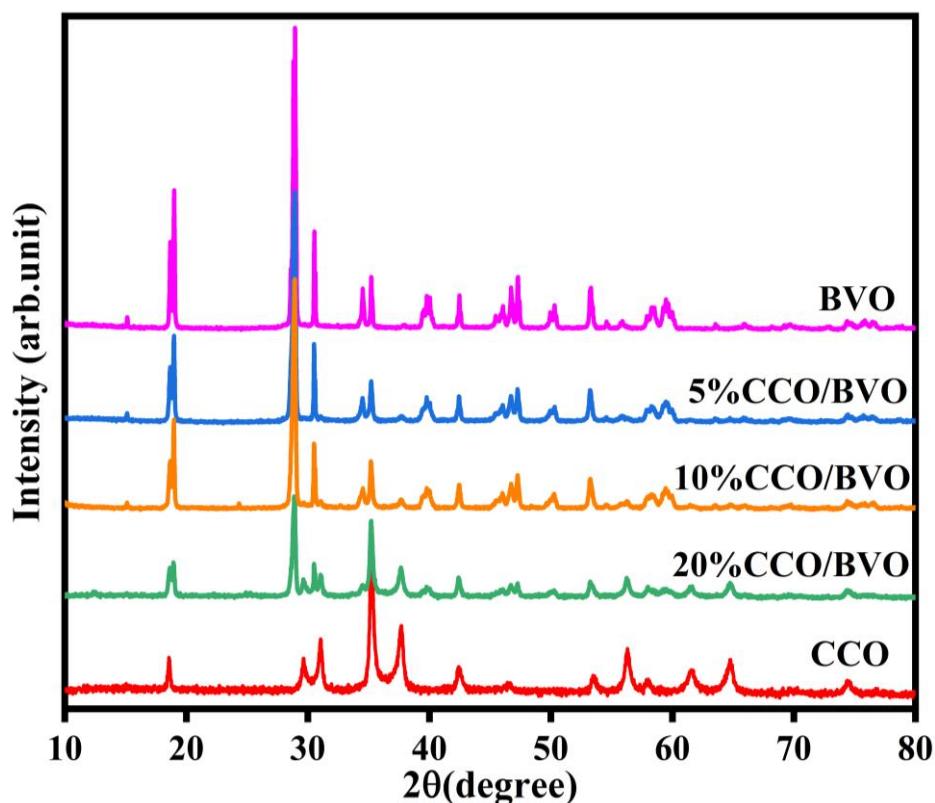


Fig. 7.1. Powder XRD patterns of (a) BVO, (b) CCO, (c) 5%CCO/BVO, (d) 10%CCO/BVO, and (e) 20%CCO/BVO.

7.2.2. Microstructure analyses

The low resolution TEM images of BVO and 10%CCO/BVO nanocomposite are shown in **Fig. 7.2 (a-b)**. The BVO nanoparticles consist of highly aggregated sphere like morphology. We have already explored the morphology and microstructure of CCO in the

previous chapters (**Chapter 3, 4 and 5**). The average particle size of BVO falls in the range from ~ 30 nm to 90 nm. In the nanocomposite system both the morphologies of CCO and BVO were observed. The HRTEM of 10%CCO/BVO nanocomposite (see **Fig. 7.2 (c)**) displays two different lattice fringe patterns of 0.34 nm and 0.30 nm which correspond to (113) lattice plane of BVO and (220) lattice plane of CCO, respectively. The elemental mapping and EDX (see **Fig. 7.3 (a-g)**) analysis confirmed the presence of homogeneously distributed Bi, V, Cu, Cr and O in the nanocomposite system.

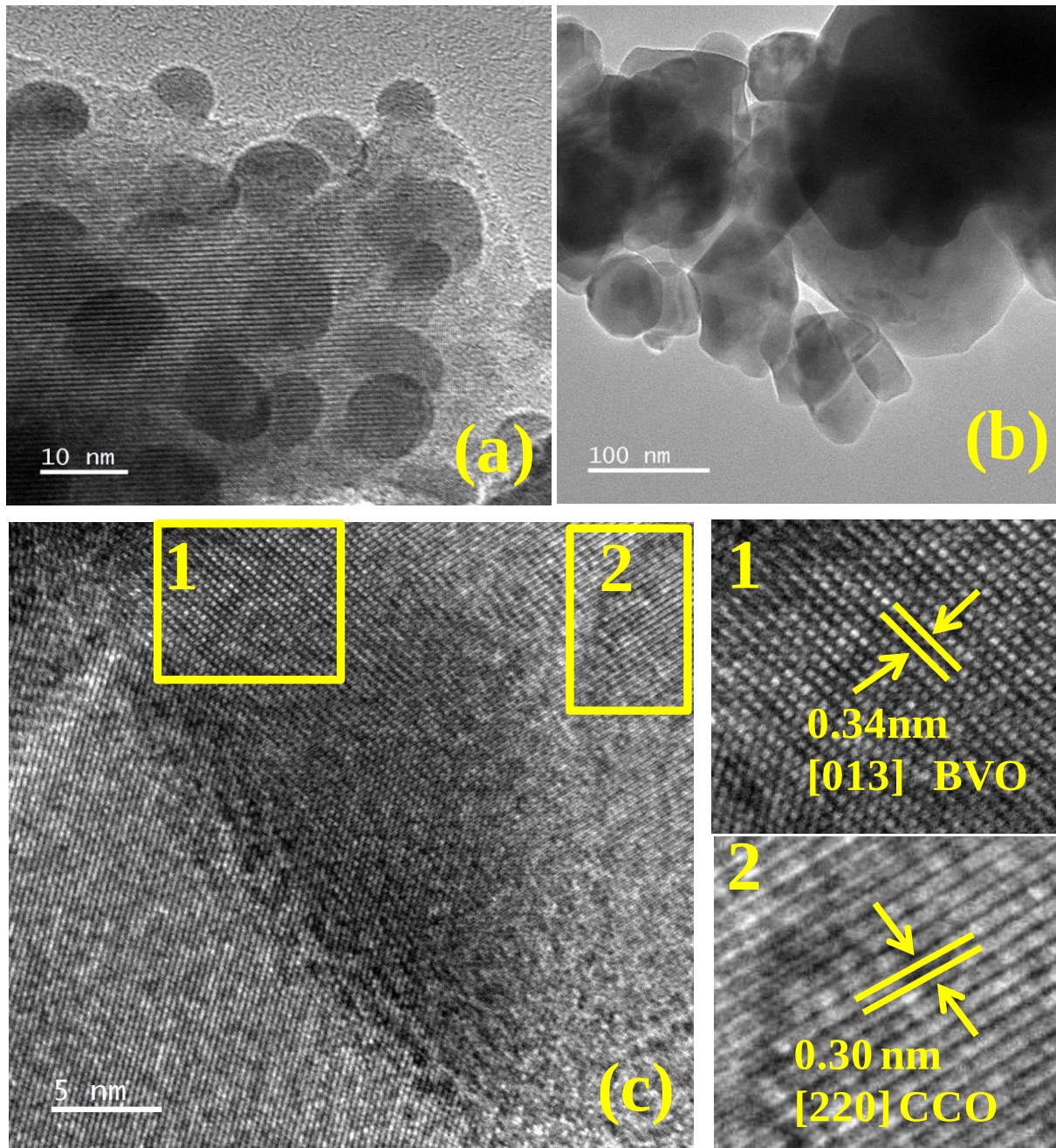


Fig. 7.2: The low resolution TEM image of (a) BVO and (b) 10%CCO/BVO nanocomposite and (c) HRTEM of 10%CCO/BVO nanocomposite.

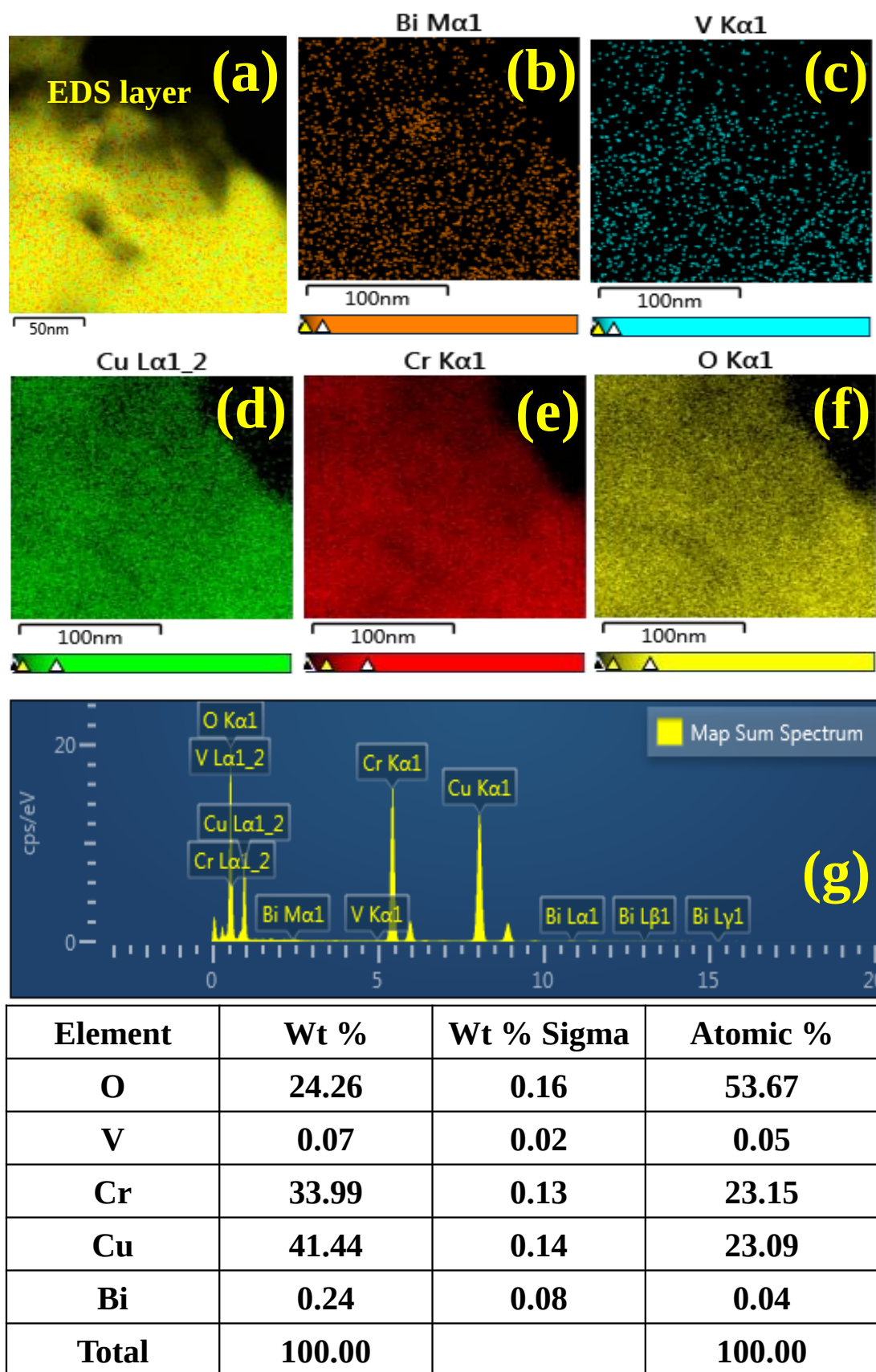


Fig. 7.3: (a-g) Elemental mapping and (j) EDX along with composition table of 10%CCO/BVO nanocomposite.

7.2.3. BET surface area analyses

BET surface area, pore volume and pore size of BVO, CCO and the CCO/BVO nanocomposite materials are tabulated in **Table 7.1** and their related adsorption-desorption isotherms are depicted in **Fig. 7.4** where respective pore size distribution curves are shown in the inset of corresponding isotherm plots. By the convention of IUPAC classification, the isotherms belong to Type IV with a H3 hysteresis loop which is a clear sign of mesoporous material. The surface area of pure BVO is $14.7 \text{ m}^2 \text{ g}^{-1}$, whereas it is $18.2 \text{ m}^2 \text{ g}^{-1}$ for pure CCO which is a clear indication of low surface area of the pure components. On the other hand, surface area is improved in the CCO/BVO nanocomposite material. A gradual increase in the surface area of nanocomposite from 27.3 to $37.8 \text{ m}^2 \text{ g}^{-1}$ is observed with an increase of CCO-loading from 5 to 20 mol%. Therefore, the surface areas of all the CCO/BVO nanocomposite are higher than that of pure CCO or pure BVO indicating that the surface area is improved in the nanocomposite systems. Among all the materials, 20%CCO/BVO possess the highest surface area ($37.8 \text{ m}^2 \text{ g}^{-1}$).

Table 7.1: Parameters of textural properties of CCO, BVO and their nanocomposites.

Sample	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore size (nm)
CCO	18.2	0.0626	1.5846
BVO	14.7	0.3420	1.5846
5%CCO/BVO	27.3	0.0420	1.5846
10%CCO/BVO	30.6	0.0353	1.5846
20%CCO/BVO	37.8	0.1046	1.5846

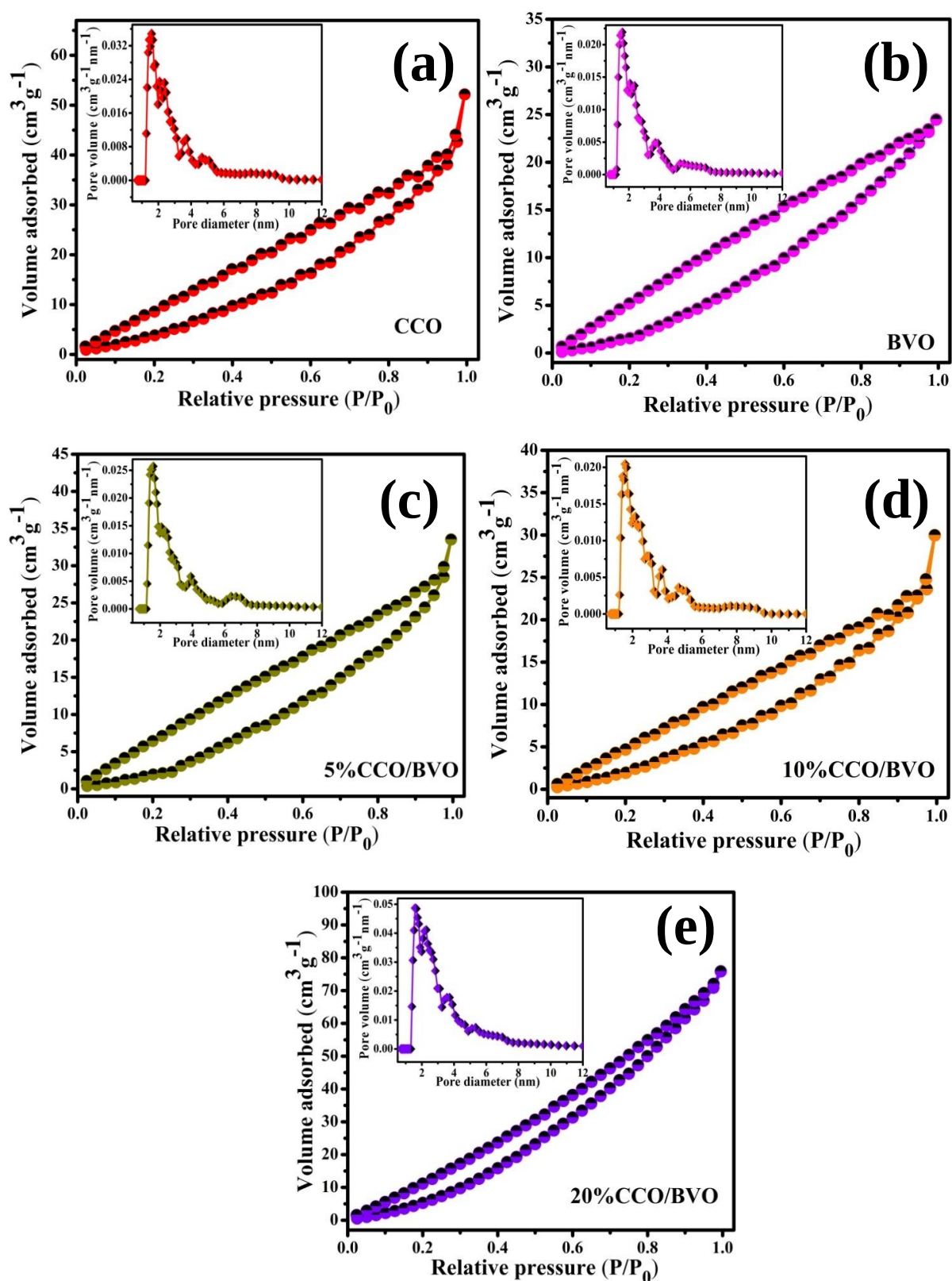


Fig. 7.4. Adsorption-desorption isotherm and pore size distribution (corresponding inset) of (a) pure CCO, (b) pure BVO, (c) 5%CCO/BVO, (d) 10%CCO/BVO, and (e) 20%CCO/BVO nanocomposite samples.

7.2.4. XPS analyses

XPS measurements have been carried out in order to determine the elemental composition, chemical environment and the oxidation state of elements present in the catalyst material. **Fig. 7.5 (a-f)** depicts the survey spectra and core level scan of respective elemental species. **Fig. 7.5 (a)** indicates the XPS survey spectra of pure BVO, pure CCO and 10%CCO/BVO in which the peaks of Bi 4f, V 2p, O 1s, Cr 2p and Cu 2p can be clearly identified. The Bi 4f core level XPS scan of pure BVO and 10%CCO/BVO nanocomposite are shown in **Fig. 7.5(b)**. The $4f_{7/2}$ and $4f_{5/2}$ peaks at 159.7 and 165.0 eV, respectively are assigned to Bi^{3+} species in pure BVO [26] whereas those peaks of Bi^{3+} for 10%CCO/BVO nanocomposite are observed at 158.4 eV and 163.7 eV, respectively. In 10%CCO/BVO nanocomposite material, there occurs a clear shifting of binding energy of Bi^{3+} -related peaks to the lower binding energy side with respect to pure BVO. The V $2p_{3/2}$ and $2p_{1/2}$ signals at 516.8 and 524.3 eV are attributed to V^{5+} species in pure BVO [27] and on the other hand, those signals for 10%CCO/BVO nanocomposite are found at 515.8 and 523.4 eV, respectively (see **Fig. 7.5(c)**). All the observed shifting of binding energies of V and Bi in the nanocomposite system towards lower binding energy region are attributed to change in the electron density around V and Bi, indicating a strong chemical interaction with CCO which favors the formation of composite system [28, 29]. The core level spectra of O 1s for pure BVO (see **Fig. 7.5(d)**) indicates the signature peak at 530 eV, which is responsible for lattice oxygen whereas the O 1s peak for nanocomposite is found at 529 and 530 eV which indicate existence of lattice oxygen as well as adsorbed oxygen [30, 31]. The core level XPS profile of Cu 2p for pure CCO (see **Fig. 7.5 (e)**) is characterized by the presence of two components peaks such as Cu $2p_{3/2}$ and Cu $2p_{1/2}$ and two satellite peaks. The peaks at 932 eV and 934 eV are assigned to Cu $2p_{3/2}$ component and attributed to the presence of Cu^{2+} species in the octahedral sites which is characterized by the appearance of satellite peaks at high binding energy. On the other hand, higher binding energy peaks at 951.5 eV and 954.1 eV are assigned to Cu $2p_{1/2}$ which indicated the presence of Cu^{2+} in tetrahedral sites of CCO spinel. A little shift of Cu 2p peaks in the nanocomposite system is identified because of electronic interaction between two different oxides [32]. The Cr 2p binding energy peaks (see **Fig. 7.5 (g)**) at 575.8 eV and 585.4 eV are assigned to Cr $2p_{3/2}$ and Cr $2p_{1/2}$, respectively which indicate the existence of Cr^{3+} in pure CCO. On the other side, the Cr 2p peaks in the nanocomposite is shifted slightly to the lower binding energy side which indicates the formation of binary mixture phase.

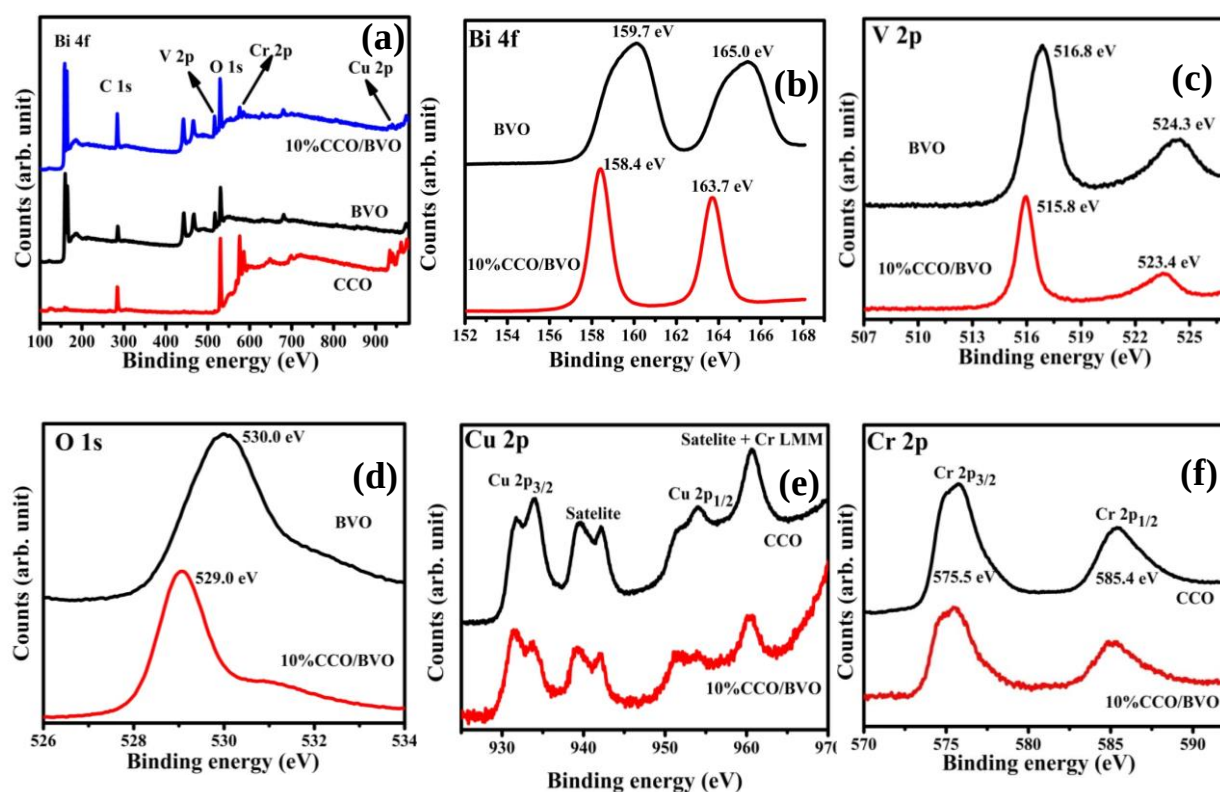


Fig. 7.5. XPS of BVO, CCO and 10%CCO/BVO nanocomposite: (a) survey spectra and core level spectra of (b) Bi 4f, (c) V 2p, (d) O 1s, (e) Cu 2p and (f) Cr 2p.

6.2.5. Electrochemical oxygen evolution activity

The electrocatalytic activity of CCO/BVO nanocomposite materials is tested for oxygen evolution reaction under dark and visible light condition and the obtained OER activity result were compared with pure CCO and BVO. Linear Sweep Voltammetric (LSV) measurement in 1 M NaOH is carried out to evaluate the OER activities of electrodes fabricated using the entire nanocomposite electrocatalyst samples that are shown in **Fig. 7.6 (a,b)**. In this experiment, the applied potential that generates a current density of $5 \text{ mA} \cdot \text{cm}^{-2}$ was setup as an arbitrary potential for the comparison of OER activity of different samples. The potential (E_j) at current density $j = 5 \text{ mA cm}^{-2}$ for 5%CCO/BVO, 10%CCO/BVO and 20%CCO/BVO electrode samples are 8.33, 36.86, and 17.64 mA cm^{-2} , respectively under irradiation of visible LED light, whereas these values under dark condition are 7.82, 22.48, and 14.13 mA cm^{-2} , respectively. On the other hand, these potential values under light and dark condition obtained for pure samples such as CCO (6.51 mA cm^{-2} and 6.07 mA cm^{-2}) and BVO (12.38 and 9.80 mA cm^{-2}) is lower compared to 10%CCO/BVO and 20%CCO/BVO nanocomposite samples under both the conditions. Whereas, 5%CCO/BVO nanocomposite

sample shows lower OER activity compared to pure BVO which indicate that OER activity is not up to the mark at lower CCO loading, but it is improved significantly at higher CCO loading. The onset potential values of OER of all the samples under light and dark condition are listed in **Table 7.2** and from the overall data it is confirmed that 10%CCO/BVO nanocomposite sample is highly active for OER among the whole series. The current density of 10%CCO/BVO nanocomposite sample is 36.86 mA cm^{-2} which is respectively 5.66 times and 2.98 times higher than that of pure CCO (6.51 mA cm^{-2}) and pure BVO (12.38 mA cm^{-2}) at 0.8 V versus Ag/AgCl electrode under LED light irradiation. Furthermore, the current density of 10%CCO/BVO under dark condition is 22.48 mA cm^{-2} which indicates an improvement of current density by nearly 1.64 times in light condition and this improvement in light condition is explained on the basis of formation of oxo-intermediates which facilitates the oxygen evolution by four distinct steps as reported by Ding. et al. [33]. The higher current density and lower onset potential indicate that the 10%CCO/BVO has the better OER activity under both the conditions. Moreover, the OER reaction kinetics under both the light and dark condition was evaluated with the help of Tafel plots which are displayed in Fig. 7.6 (c,d). The Tafel slope values of all the samples were measured from the quasi-steady-state curve obtained in 1 M NaOH solution with a setup scan rate of 0.02 V s^{-1} and all the estimated values of Tafel slope are listed in **Table 7.2**. The 10%CCO/BVO nanocomposite sample shows a lower Tafel slope of $222.4 \text{ mV dec}^{-1}$ in presence of light than in dark ($268.6 \text{ mV dec}^{-1}$), which indicates greater transmission coefficient in visible LED light [25].

Table 7.2: Different Parameters related to OER activities of CCO, BVO and CCO/BVO nanocomposite sample series.

Sample	Onset potential (V)		Tafel slope (mV dec^{-1})		Current density (mA cm^{-2})	
	Light	Dark	Light	Dark	Light	Dark
Pure CCO	0.618	0.630	144	132	6.51	6.07
Pure BVO	0.590	0.598	294.2	446.5	12.38	9.80
5%CCO/BVO	0.604	0.616	340.4	1180	8.66	7.82
10%CCO/BVO	0.497	0.515	222.4	268.6	36.86	22.48
20%CCO/BVO	0.566	0.575	264.3	524.4	17.64	14.13

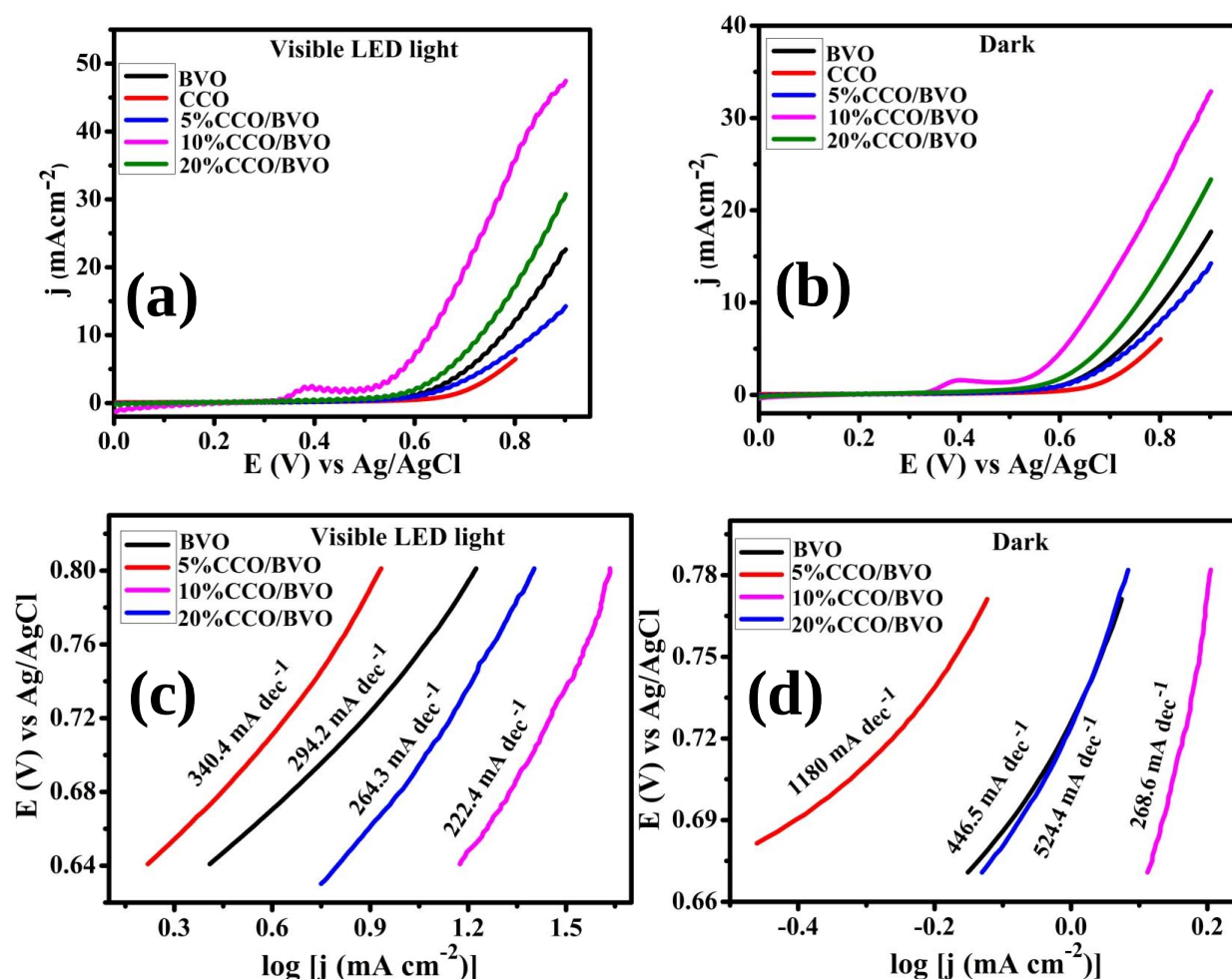


Fig. 7.6. Linear sweep voltammetric data and Tafel plot for OER activities of CCO, BVO and CCO/BVO nanocomposite series under (a,c) visible LED light and (b,d) dark condition.

7.3. Conclusions

We have successfully synthesized a series of CCO/BVO nanocomposite electrocatalysts via a hydrothermal reaction for oxygen generation reaction. All the electrocatalyst are thoroughly characterized by XRD, BET, HRTEM, EDS mapping and XPS. The particles are of spherical shape and they are agglomerated in nature. BET surface area is significantly increased due to composite formation though the pore size remains the same in both the pure and composite phases. Elemental mapping and EDX confirms the chemical homogeneity and nominal cationic ratio of the respective composite phases as well as for the parent compounds. The XPS analysis confirms the desired chemical environment and oxidation states of the respective cations, both in the parent and composite phases. This nanocomposite electrocatalyst shows remarkable oxygen evolution activity under both dark and light condition. The oxygen generation activity is greatly enhanced when electrochemical

experiment is carried out in presence of visible LED light compared to dark condition. Among the whole nanocomposite series, 10%CCO/BVO shows highest electrocatalytic activity in dark and light condition.

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Chapter 8

Concluding remarks

Chapter abstract

On the basis of the doctoral research work embedded in the present thesis, general concluding remarks on the nanocomposite photocatalyst materials are presented here.

Visible light active photocatalyst materials are very important one to deal with the various environmental and industrial issues. In this regard, transition metal oxides and their composites play a primordial role. In the view of recent research progress, transition metal oxide based nanocomposite materials are considered as chief visible light active photocatalyst material to address different types of challenges because of its synthetic simplicity, thermodynamic stability, high visible light absorption activity, great structural flexibility and photocatalytic performance. The work included in various chapters of this thesis is dedicated towards the synthesis and development of some high performance nanocomposite photocatalyst materials for photocatalytic applications. The nanocomposite materials are binary systems of two different transition metal oxides in which either CCO spinel or LNO perovskite is one of the components. Several reports on CCO and its doped materials for application in various areas like organic transformations, reforming and photocatalytic dye degradation had already been available in the literature when this research work was initiated, but the photocatalytic performance of these materials were not good enough with respect to similar types of catalysts. This poor performance is essentially due to high electron hole pair recombination of CCO. The trends in research on photocatalysis was thus subsequently moved from doped materials to nanocomposite systems with the expectation of promising photocatalytic performance because nanocomposite materials show high charge transfer tendency. Several researchers had reported nanocomposite systems of other materials with the desired photocatalytic outcome, but work on CCO related nanocomposite materials were not investigated much till that time. Thus, we were motivated to work on nanocomposite systems where CCO is used as the base material. The choice of CCO related nanocomposite materials relies upon four main key factors: (1) nanocomposite materials generally show very high photocatalytic activity as per modern research expectation which is less likely for the doped materials, (2) lower band gap energy of CCO can form a potential nanocomposite with

other oxide materials of high band gap energy (greater than 2 eV), (3) it has good visible light absorption activity and hence acts as good electron donor or good hole creator contributing to lowering of electron-hole pair recombination, and (4) the number of publications on CCO based nanocomposite photocatalyst is very limited so that it can be reported as a new photocatalyst material. Same scenario is observed for LNO based nanocomposites towards photocatalytic applications.

To synthesize the nanocomposite materials, we have explored various synthetic routes like solution combustion method with different fuel, sol-gel method with different chelating agent, coprecipitation method by changing precipitating agent and pH and finally hydrothermal method with varied reaction time and temperature. Unfortunately, all these one-step synthetic routes for nanocomposite materials synthesis were unsuccessful because during heat treatment all the metal precursors are easily converted into their stable individual oxide phases as impurity. Therefore, we used combination of methods like sol-gel with coprecipitation, sol-gel with sonochemical method, thermal polymerization with solid state mixing and finally sol-gel with hydrothermal method. This was followed by heat treatment of resulting crude in each case for the successful synthesis of our targeted nanocomposite materials. Our chosen synthetic protocols are beneficial because nanocomposite samples are formed without any other impurity and also the process is simple and time saving.

All the synthesized materials have been thoroughly characterized by use of extensive modern instrumentation techniques. Besides the routine study of structural and morphological investigation, the applicability of these nanocomposites in photocatalytic and electrochemical purposes have also been investigated in a systematic way and found to be interesting. Among all the synthetic routes adopted here, the combination of sol-gel with coprecipitation is found to be the best approach to synthesize the nanocomposite due to its simplicity and better performance in photocatalytic test.

We have investigated the phase analysis of all the synthesized nanocomposite materials as well as their pure counterparts by PXRD analyses using Bruker D8 Advance diffractometer fitted with Lynxeye fast detector with a reasonably slow scan rate of 1s per step. We have found that the diffraction pattern of nanocomposite sample is characterized by the presence of both the individual components which is an indication of nanocomposite phase formation without any noticeable impurities. In some cases, we have also observed that the few of the main diffraction peaks in the nanocomposite system are slightly shifted towards higher or lower 2θ values which indicate a tight binding of the different counterparts.

PXRD has also been used to understand any structural change of the recycled sample that helped us to explain the observed recycling behavior of materials.

The microscopic investigation by FESEM, TEM and HRTEM are found to be beneficial to understand the morphology and microstructure of nanocomposites as well as their pure counterparts. Different types of morphology are found to be observed for different types of materials. Expected lattice fringe pattern of individual components in the nanocomposite sample is detected. The elemental mapping technique has been shown to be very helpful to detect the elements present as well as homogeneous distributions of these in the nanocomposite materials. EDX analysis is also found to be useful to confirm the presence of elements and the nominal composition in the nanocomposite system.

The adsorption of pollutants on the catalyst surface being the primary step in photocatalytic degradation, BET surface area characterization shed light on the textural properties of the synthesized materials. Nature of porosity and surface area are the prominent issues. The nanocomposite materials of this work show mesoporous nature and exhibited high surface area as per our expectation that could explain the high activity of the nanocomposite catalyst.

The optical studies have shown very high light absorption activity of pure CCO and LNO over the whole visible region. The nanocomposite of these materials shows an improved light absorption activity in the visible region. On the other hand, as per our expectation from light absorption activity, a higher charge separation trend is observed in the nanocomposite system which is confirmed by PL spectroscopy and transient photocurrent density analysis. Band gap energy of all the materials is measured from the DRS data by Tauc plot analysis. Furthermore, electrochemical measurements have been carried out for better understanding of band gap energy values in the cases of CCO/BiOBr and LNO/g-CN nanocomposite materials which is in good agreement with the band gap energies calculated from Tauc plot analysis. Due limited accessibility we could not investigate the band gap measurement through electrochemical technique for the rest nanocomposite samples.

Raman spectroscopic analysis is beneficial in exploring some important aspects like surface properties and oxygen vacancy in the nanocomposite materials. In case of CCO/CeO₂ nanocomposite, the formation of oxygen vacancy is confirmed by analyzing the ratio of some stretching frequencies at a particular wavenumber. The decrease of stretching frequencies indicates the formation of nanocomposite system (CCO/BiOBr and CCO/CeO₂). It could

have been better if we could carry out this analysis for other samples, but due to limited facility we were unable to do this study.

The XPS analysis of nanocomposite as well as their pure components helped us to correlate the structure and catalytic activities which is a very important issue for studies in catalysis. With the help of XPS we can find out the metal ion concentration, oxidation state and oxygen vacancy which is very much helpful and convincing to explain the improved photocatalytic performance of CCO/CeO₂ and CCO/TiO₂ nanocomposite materials. In CCO/CeO₂ nanocomposite, Cu is present in +2 state and Ce exists in +3 and +4 oxidation states. The higher Ce³⁺ concentration in the nanocomposite compared to pure CeO₂ is attributed to formation of oxygen vacancy in the nanocomposite. XPS analysis was also advantageous to explain the decreased activity of CCO/TiO₂ nanocomposite on recycling and the subsequent regeneration behavior. We have noted variation in the oxidation state mainly for CCO, especially for Cu in the nanocomposite. For CCO/BiOBr nanocomposite, Cu exists in +2 oxidation state in both the octahedral and tetrahedral sites of CuCr₂O₄ spinel, the other metal being present in its normal oxidation state. On the hand, in the case of CCO/TiO₂ nanocomposite, Cu exists in two different oxidation states, +2 and +1 in which +2 state is the predominant one. Ti exists in +3 and +4 oxidation states, but the proportion of Ti³⁺ in the nanocomposite is higher than in pure TiO₂, which indicates the presence of oxygen vacancy in the nanocomposite. In LNO/g-CN nanocomposite, Ni exists in +3 and +2 oxidation states and similar type of oxygen vacancy is expected to be present in the nanocomposite.

We have performed photocatalytic degradation of various carcinogenic, stable and very harmful pollutants like MB, MO, RhB, RB5 as colored dyes and colorless antibiotics like TC-HCl and NORF under normal household visible LED light irradiation. In general, synthesized nanocomposite materials are very much effective to degrade such types of high molecular weight azo dyes as well as antibiotic pollutants into small fragmented species in both light and dark condition within a very short span of time. Furthermore, we have tried our best to carry out systematic and comprehensive work on the variations of catalyst mass, H₂O₂ concentration, reaction time, pollutants, CCO mass percentage and synthesis temperature to find the best catalyst and optimized reaction conditions. The optimized synthesis temperature falls in the range from 400°C to 500°C, whereas the best mass percentage of CCO ranges from 10% to 20%. The optimized catalyst mass and H₂O₂ concentration are 50 mg and 4 mM, respectively, while the reaction time is in the range 15 min to 300 min.

Besides the studies of photocatalytic pollutants degradation, photoelectrocatalytic activity of the synthesized nanocomposites is yet another important as well as emerging area of electrocatalysis. The results of photoelectrocatalytic OER activity tested for CCO/TiO₂ and CCO/BVO nanocomposite systems are in line with our expectation. We could not perform these tests for the other systems owing to limited availability of the facility. The OER activity of these materials under light and dark condition is significant of which the activity under light condition can compete with the conventional Pt based catalysts suggesting potential future of these nanocomposite catalysts in OER.

Recycling activity of all the catalysts is remarkable. But in certain cases, CCO/CeO₂ and CCO/TiO₂ nanocomposite, normal washing process is ineffective to clean the photocatalyst surface during the recycling test. We are able to overcome this issue through the intermediate heat treatment of materials to clean the catalyst surface from adsorbed degradation-products. In this case, XRD and XPS techniques were helpful to understand the phase, oxidation state as well as proportion of the elements with variable oxidation states, and surface composition of different species that play a crucial role in deciding the activity behavior.

All the photocatalysts follow Type II mechanistic pathway to improve the charge transfer rate, except the LNO/g-CN nanocomposite system, which follows Z-scheme mechanism. Type of charge transfer mechanism depends on band edge potential and the radical that is formed in the degradation process.

We have explored all the available tools to interpret the structure of these nanocomposites and understand the relationship of catalytic activity with catalyst structure. **Table 8.1** summarizes the most important details about the nanocomposites catalyst systems included in this thesis. Thus, we believe that the present nanocomposite photocatalyst systems have the potential to compete with the conventional photocatalysts.

The photocatalytic study of the research work covering different classes of pollutants is fully based on the degradation of these pollutants by the synthesized photocatalysts and forms the main goal, but toxicity of the degradation products, if any, is a big concern. This is a different yet pertinent arena in photocatalysis that demands analysis of the degradation products after the completion of photocatalytic reaction. Just by degrading the colored pollutants does not ensure that the formed products are acceptable from environmental consideration. We were, however, unable to investigate the degradation products due to limited facility of mass spectroscopy (LC MS) or HPLC that are the generally used analytical

Table 8.1: Details about the photocatalyst materials of this thesis work in a nutshell.

Nanocomposite (Type)	Synthetic method	Application	Catalyst mass, concentration (Mechanism)	Pollutant		Optimized photocatalyst
				Dye	Antibiotic	
CCO/BiOBr (Photocatalyst)	Sol-gel followed by surfactant assisted coprecipitation	Pollutant degradation	25 mg, 10 ppm (Type II)	RhB (97% in 15 min)	TC-HCl (96% in 300 min)	20%CCO/BiOBr
CCO/CeO ₂ (Fenton like photocatalyst)	Sol-gel followed by coprecipitation	Pollutant degradation	50 mg, 10 ppm (Type II)	RhB, MB, & MO (99% in 15 min, 98% in 20 min & 96% in 30 min)	–	10%CCO/CeO ₂
CCO/TiO ₂ (Fenton like photocatalyst & photo- electrocatalyst)	Sol-gel followed by sonochemical mixing	Pollutant degradation & OER	50 mg, 10 ppm (Type II)	RhB, MB, & MO (97%, 99% & 90% in 15 min)	TC-HCl & NORF (99% in 15 min & 97% in 75 min)	100%CCO/TiO ₂
LNO/g-CN (Z-scheme photocatalyst)	Thermal polymerization followed by solid state mixing	Pollutant degradation	50 mg, 50 & 10 ppm (Z-scheme)	RB5 & MB (94% in 60 min & 98% in 180 min)	TC-HCl (96% in 300 min)	100%LNO/g-CN
CCO/BVO (Photo-electrocatalyst)	Sol-gel followed by hydrothermal method	OER	Aqueous 1 M NaOH	–	–	10%CCO/BVO

techniques. Analysis of the fragmented products formed on degradation by such techniques also help to establish the mechanism on firm footing as well as deciding the suitability of its application in industry. From the knowledge of more than thousands of previously published reports it is found that most of the degradation products are friendly like CO_2 , H_2O , N_2 or other small fragmented species which is less toxic and hence relatively more environment friendly in nature in regard to the parent pollutant. Nevertheless, it is to be noted that the existence of only pollutant peaks along with a slightly red or blue shifting of the pollutant peaks at the end of photocatalytic degradation reaction and absence of any other peaks in the UV spectra of the reacting solution in our studies indicate formation of harmless or at the most less harmful small fragmented species. Treatment of industrial wastewater leading to the formation of less harmful products vis-à-vis harmless products will thus remain as one of the main challenges in photocatalysis!



Facile synthesis of $\text{CuCr}_2\text{O}_4/\text{CeO}_2$ nanocomposite: A new Fenton like catalyst with domestic LED light assisted improved photocatalytic activity for the degradation of RhB, MB and MO dyes

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ABSTRACT

Here, we report the findings on $\text{CuCr}_2\text{O}_4/\text{CeO}_2$ (CCO/ CeO_2) nanocomposite as a new heterogeneous Fenton like catalyst for the degradation of rhodamine B (RhB), methylene blue (MB) and methyl orange (MO) under domestic LED light irradiation. An extensive characterization of the samples were performed using several physicochemical techniques. A careful monitoring of photo-activities reveals the best performance of 10%CCO/ CeO_2 showing complete degradation of 10 ppm RhB, MB and MO dyes within 15, 20 and 30 min, respectively, in presence of 4 mM of H_2O_2 . The visible light absorption of CeO_2 is enhanced by CCO. The radical trapping and coumarin fluorescence probe methods suggest the generation of $\cdot\text{OH}$ in the catalytic pathways. A comprehensive analysis of $\cdot\text{OH}$ generation in presence and in absence of LED irradiation is presented to underscore both the Fenton like reactions of the nanocomposite system. Importantly, the nanocomposite catalyst shows encouraging recycling behavior through an intermediate heat treatment. The Fenton like catalytic behavior of marginally active CeO_2 is dramatically enhanced in presence of CCO in the nanocomposite due to larger creation of oxygen vacancy. Finally, a plausible explanation of this novel catalytic behavior based on band bending across the junction of the two semiconducting oxides has been presented.

1. Introduction

Plentiful inorganic compounds from different classes of materials have been investigated by the materials researchers till date for their suitability in varieties of catalytic applications including photocatalysis. Apart from their plethora of different properties, the transition metal oxides are one of those promising materials exhibiting potential photocatalytic application as well. Furthermore, the driving force of vast amount of research on transition metal oxides arises from their abundance, chemical as well as thermal stability under the operating conditions and ease of synthesis due to plenty of available synthetic methods. The spinel type $[\text{A}]_t[\text{B}_2]_o\text{O}_4$ oxides are of special significance in this regard and are extensively investigated. The spinel structure can accommodate a wide range of metal ions in their variable oxidation states (+1 to + 6) in both the tetrahedral and the octahedral

coordination. This structural feature provides an excellent opportunity to bring different metal ions of catalytically active binary oxides into a single structural network. They exhibit attractive photocatalytic activities due to their narrow optical band gap causing efficient absorption of light in the visible region. In the past few decades, transition metal-based spinel oxide materials have received major attention of many researchers because of their potential to solve the major problems of environmental water pollution [1-4], energy storage [5,6], liquid phase organic transformation [7,8] and hydrogen production [9,10]. Among the transition metal-based spinel oxides, CuCr_2O_4 is regarded as a prominent candidate for its wide range of applications in photocatalytic dye degradation for wastewater treatment [11-13], photocatalytic H_2 production [14,15], supercapacitor [16], organic transformation [17-19] and glycerol hydrogenolysis [20]. However, recombination rate of the photogenerated electron-hole pair is high for CuCr_2O_4 [12]

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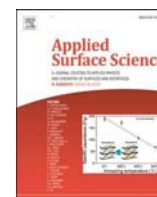
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Anatase TiO₂ decorated CuCr₂O₄ nanocomposite: A versatile photocatalyst under domestic LED light irradiation

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Photoelectrocatalytic oxygen evolution

ABSTRACT

The rutile and anatase polymorphs of TiO₂ are the most extensively studied photocatalyst materials with the efficient absorption in the violet to near ultra violet region of the electromagnetic spectrum, which boost tremendous research endeavors in increasing the photocatalytic activity of TiO₂ under visible light sources through rational modifications. Here, we report the astonishing performance of CuCr₂O₄(CCO)/anatase-TiO₂ nanocomposite as a Fenton like catalyst with potential impact for sustainable design and environmental protection. All the materials were thoroughly characterized by several physico chemical techniques. CCO/TiO₂ nanocomposite obtained by heat-treatment at 400 °C is found to exhibit high performance towards degradation of azo dyes like methylene blue (MB), rhodamine B (RhB) and methyl orange (MO), antibiotics like tetracycline hydrochloride and norfloxacin, and a promising Pt-free candidate for photoelectrocatalytic oxygen evolution reaction under domestic light emitting diode (LED) light irradiation. CCO/TiO₂ shows high recycling activity and chemical stability. Under domestic visible LED light irradiation, the electrons are photoexcited from the conduction band of CCO to that of TiO₂ resulting in enhanced charge separation eventually facilitating the catalytic performance of the nanocomposite. TiO₂ plays two primordial roles, firstly, it acts as an electron receiver to improve the charge separation in the nanocomposite and secondly, it participates in the Fenton like reaction.

1. Introduction

The contamination of surface water due to rapid industrial expansion poses a serious threat to ensuring that drinking water resources will be available for future generations as the world's population has crossed seven billion. The chemical pollutants such as cleaning agents, insecticides, herbicides, as well as pollutants derived from the coal, petroleum and pharmaceutical industries are quite challenging to remove from water resources due to their very persistent nature in the environment. Additionally, the most important sources of environmental pollution are the tannery and textile wastewaters. This has attracted much attention for the treatment of textile and dyeing wastewaters for sustainable design and environmental protection. There are many “state of the art technologies” for wastewater treatment including membrane separation, electrical, ultrasonic, magnetic, optical and thermal methods

[1–7]. The treatment of wastewater requires energy, production of which requires water that leads to the water/energy nexus. Thus, development and fabrication of photocatalysts with a high degradation rate of the pollutants under sustainable conditions such as visible or sunlight irradiation is highly desirable. In this regard, advanced oxidation processes (AOPs) attracted significant attention in recent times. AOPs such as ozone or hydrogen peroxide eventually produce highly reactive strongest oxidant, the hydroxyl radicals which effectively and non-selectively clean the dissolved organic micropollutants by mineralizing the organic molecules to water, carbon dioxide and harmless species [8,9]. Generally, AOPs involve several techniques such as Fenton oxidation [10], wet air oxidation [11], photoelectrocatalytic oxidation [12], electrochemical oxidation [13] and photocatalytic oxidation [14], etc. There are several reports on visible light assisted photo Fenton reaction where the photoexcited electrons on the catalyst surface help to

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Facile synthesis of $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ nanocomposite and its photocatalytic activity towards RhB and tetracycline hydrochloride degradation under household visible LED light irradiation



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ABSTRACT

Here we report the development of $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ nanocomposite photocatalysts for the first time to serve the purpose of rhodamine B (RhB) and tetracycline hydrochloride (TC-HCl) degradation using household visible light emitting diode (LED) light. In this nanocomposite, sol-gel combustion made spherical shaped CuCr_2O_4 nanoparticles are decorated on BiOBr plates in single pot via precipitation method using cetyltrimethylammonium bromide (CTAB) as the Br source as well as the template. The present investigation highlights a significant advancement to tackle the challenge of visible light induced photocatalytic degradation of harmful organic dye RhB and antibiotic-pollutant TC-HCl. The 20% $\text{CuCr}_2\text{O}_4/\text{BiOBr}$ nanocomposite exhibits high degradation activity for both RhB (96.0% in 15 min) and TC-HCl (96.7% in 300 min) in presence of LED light with good recycling characteristics. Detailed structural and optical characterization using XRD, BET, FESEM, TEM, HRTEM, EDX, XPS, UV-Vis DRS, PL spectroscopy and Raman spectroscopy have been carried out prior performing photocatalytic activity tests. The structural as well as optical data have revealed a significant improvement in visible light absorption of BiOBr in presence of CuCr_2O_4 . Based on energy band modification at the heterojunction of nanocomposite materials and their radical trapping ability, a plausible mechanistic path of photocatalytic degradation is presented.

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1. Introduction

The identification and control on variety of potentially hazardous chemical substances are big concerns to human health and environmental safety in present days. In this regard, the removal of high molecular mass dyes from wastewater is an important issue

for environmental safety [1–3]. These dyes have harmful effect to human health and aquatic life [4]. The major sources of hazardous dyes are tannery, cosmetics and textile industries [5,6]. Different techniques have been developed for the removal of such dyes like adsorption, chemical oxidation, biodegradation, photocatalytic degradation, coagulation, electrochemical and sonochemical degradation [7–12]. Photocatalytic degradation is one of the most viable and common method for dye removal from wastewater [1–3,7,10,13–18]. In most of the reports on photocatalysis, high power xenon lamp [1,2,6,14,15], halogen lamp [13], UV lamp [7,8] and high pressure mercury vapor lamp [19] are used as light sources, which are having certain benefits, but are hazardous, costly and difficult to handle. However, it would be convenient to

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LaNiO₃/g-C₃N₄ nanocomposite: An efficient Z-scheme photocatalyst for wastewater treatment using direct sunlight[☆]

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ABSTRACT

The major findings in this report are (i) development of nanocomposite photocatalyst working through Z-scheme charge transfer pathway across the heterojunction, (ii) utilization of direct sunlight as the photo-source, and (iii) prospect of ligand-hole in photocatalysis through enhanced sub-band gap absorption. The photocatalysts, namely LaNiO₃, g-C₃N₄ and LaNiO₃/g-C₃N₄ nanocomposites were synthesized via facile route and were characterized for their structure, morphology, microstructure, texture, elemental mapping and surface oxidation states by using several physicochemical techniques. The photocatalytic performance of the nanocomposite was tested through the degradation of hazardous azo dye pollutants, namely reactive black 5 and methylene blue as well as the colorless antibiotic-pollutant tetracycline hydrochloride in aqueous solution in presence of natural sunlight with excellent recycling activity. The 10%LaNiO₃/g-C₃N₄ nanocomposite sample shows the best catalytic activity, degrading respectively 94%, 98.6% and 88.1% of reactive black 5, methylene blue and tetracycline hydrochloride in 60, 180 and 120 min. The photocatalytic activity of the nanocomposite phase is several times superior to that of the pure phases. The improvements of photocatalytic activity of g-C₃N₄ in the nanocomposite have been rationalized through the construction of direct Z-scheme heterojunction and suppression of electron–hole pair recombination efficiency. The enhanced photo-absorption of the nanocomposite can possibly be related to sub-bandgap absorption, which is associated to the midgap state originating from ligand-hole formation or defects in the structure. The photodegradation process is mediated through the formation of super oxide radical (O₂^{•−}) and hole (h⁺) as the main responsible species.

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1. Introduction

The treatment of wastewater has become a serious challenge to human society due to the rapid expansion in textile and

pharmaceuticals industries. Apart from the domestic and agricultural water pollution, sewage from these industries containing harmful molecules largely contribute to water contamination. Such wastewater bodies pose a big threat to the aquatic ecosystem and of course to the human society. Several scientific techniques are already in use for wastewater treatment such as wet air oxidation,¹ Fenton technique,² sonocatalysis³ and photocatalysis.^{4,5} However, photocatalysis can be regarded as the most beneficial one because of its simple, cost-effective and eco-friendly nature.⁴ Consequently, photocatalysis has become a topic of intense research activity recently, where the photogenerated electron–hole pairs catalyze the reactions on semiconductor or metal oxide surfaces. Different types of

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Remarkable Ti-promotion in vanadium doped anatase titania for methylene blue adsorption in aqueous medium

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ABSTRACT

We report here the synthesis of vanadium (5–20 at.%) doped titania and the pristine oxides via surfactant assisted coprecipitation method using cetyltrimethylammonium bromide as the surfactant and investigated their adsorption behavior towards hazardous methylene blue dye. The formation of anatase phase in all the doped materials is confirmed by the powder x-ray diffraction (P-XRD) analysis as corroborated by the Fourier transform-infrared (FT-IR) analysis, with particle sizes in the range 8–11 nm. Pure titania doesn't show any adsorption property, but its presence enhances the adsorption property of vanadia considerably suggesting a promoting role of titania in the doped materials. The 10 at.% V-doped material, V_{0.1}Ti_{0.9}O₂ is found to exhibit the best adsorption behaviour. The low resolution transmission electron microscopy studies reveal homogeneous nature, while ring type electron diffraction pattern suggests polycrystalline nature of the material. The high resolution transmission electron microscopy analysis suggests formation of single phase oxide. Kinetic and equilibrium studies have revealed the pseudo-second-order kinetics and Langmuir isotherm nature for this physisorption process. The pH dependency and recycling ability of this material have been discussed. Finally, X-ray photoelectron spectroscopy, FT-IR and P-XRD studies have been applied to understand the mechanism of regeneration of the material.

1. Introduction

The presence of dyes in industrial wastewater is a major concern due to their adverse effects to many forms of life. Industries like textile, leather, paper, plastics, etc., use dyes in order to introduce colorful products. They consume a large amount of water during colorization technique and thus they also generate a considerable amount of colored wastewater [1]. Thus, dye wastewater needs to be treated for the protection of human health and environmental safety. The discharge of dyes in the environment is a dramatic source of aesthetic pollution, eutrophication and perturbation degradation [2]. It is well-known that public awareness regarding water quality is greatly influenced by the color because color is the first contaminant to be identified in wastewater. Even a very small amount of dyes in water (less than 1 mg L⁻¹ for some dyes) is highly visible and undesirable [3,4].

Methylene blue (MB; C₁₆H₁₈N₃SCl), a familiar basic dye is usually used for dyeing cotton, wood and silk. It can cause permanent injury to the eyes of human and animals. Several other injuries like burning

sensation of mouth, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia may also be caused by this dye [5–7]. MB remains very stable in the environment due to its synthetic origin and complex aromatic molecular structure. Therefore, the treatment of effluent containing such a dye is an important issue for researchers and environmentalists.

Several treatment processes have been reported for the removal of these kinds of dyes from wastewater, such as: photocatalytic degradation [8,9], electrochemical degradation [20], sonochemical degradation [10], integrated chemical–biological degradation [11], photo-assisted-biological treatment [12], Fenton-biological treatment scheme [13], cation exchange membranes [14] and adsorption processes [15–18]. Among the several separation techniques adsorption is a very effective process for the removal of such dyes because of its low initial cost, insensitivity to the toxic substances, flexibility in design and simplicity in operation [19,20]. Adsorption does not result in the formation of harmful substances and thus it is a well known equilibrium separation technique and an effective method for water

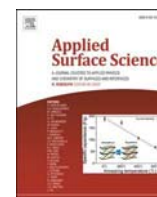
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Full Length Article

Visible light assisted photo-electrocatalytic oxidation of methanol using low Pt content NiO-rutile TiO₂ ternary heterojunction

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ABSTRACT

Platinum decorated binary hetero-junctions of NiO and TiO₂ of various mole-ratios have been synthesized for use of these as anode catalysts in the oxidation of methanol in alkali. The as synthesized composites are characterized by X-ray diffraction, spectroscopic and microscopic investigations. The ternary composite having 25.3 mass% of Pt deposited on the binary composite containing 34.36 mass% NiO and 40.34% TiO₂ is found to be the best catalyst both in dark and illuminated condition. The peak current density in cyclic voltammetry, the charge transfer conductance, and the steady chronoamperometric current density are increased by about 1.8, 4, and 1.5 times respectively, on the illumination of anode, in comparison to these in the dark. The electrochemical impedance spectroscopy (EIS) and photo responsive current measurements indicate that mixing of NiO with TiO₂ demonstrates a superior photo-electro catalytic performance for methanol oxidation plausibly due to enhancement of the electron-hole separation efficiency. Product analysis by HPLC reveals that the formation of formaldehyde, sodium formate, and methyl formate is facilitated on illumination while additional carbonate is formed in the dark.

1. Introduction

Direct methanol fuel cell (DMFC) is considered as a promising power source for application in cars and portable electronic devices because of high energy density [6.09 kWh Kg⁻¹], low volume occupancy, low cost, advantage in handling, transport, and storage [1–7] of fuel, methanol. The smart application of DMFC at a marketable price remains still an issue due to its limitations like sluggish anode kinetics, instability of catalyst, etc. [8–13]. To date, the most frequently used catalyst material is based on Pt in DMFC but it is less abundant and very costly. In addition, Pt catalyst tends to get poisoned by strongly adsorbed CO like intermediates. This leads to the rapid deactivation of Pt catalyst during electro-chemical methanol oxidation reaction (MOR). To mitigate the above poisoning and cost effect, many efforts have been committed in developing generation of Pt-based binary and ternary catalysts. A common strategy is allowing Pt to combine with other relatively oxophilic metals such as Ni, Sn, Ir, Ru, Au, etc. [14–18]. The utilization of the second metal in such alloys can generate oxygen-containing species such as M–OH (adsorbed OH⁻) which promotes the oxidation of strongly

adsorbed intermediates like CO_{ad} to CO₂ [19–20]. Another strategy is to prepare composite catalysts by coupling Pt with different oxides (Such as CeO₂, SnO₂, MnO₂, TiO₂, ZnO, Bi₂O₃, etc.) which can be employed both as support carrier and rescuer from poisoning to improve electro-catalytic activity and stability [21–23]. TiO₂ being a semiconductor has low electric conductivity which can be overcome by making a thin film and using high conductivity carbon materials as inert support [24]. As one of the most studied oxides, TiO₂ has also found wide applications especially in photo-catalytic activity like water splitting, dye decomposition reaction, etc. assisted by visible-UV light [25–30]. When irradiated with sunlight, TiO₂ nanoparticles can only absorb in the UV part of light, a small portion of solar spectrum (5% in the sunlight) [31,32]. To increase absorption capability and co-catalytic activity and stability, several composites of TiO₂ with carbon materials, polymers have been used along with Pt [33–35]. Since the catalytic performance of semiconductor oxides can be improved by exposing the electrode to UV–visible light, a recent trend has been developed to oxidize the fuels in presence of light and thus photo-assisted fuel cells are constructed [33,34]. Recently, it is reported that coupling TiO₂ with NiO (E_g = 3.4

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Photo-electrocatalytic methanol oxidation on Pd decorated BiOI nanoparticles in alkali

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ABSTRACT

Palladium–bismuth oxiodide nanocomposites of various molar ratios of Pd and BiOI have been synthesized by the facile solvothermal method following the chemical reduction technique. The as-synthesized particles have been characterized by X-ray diffraction, spectrophotometric and microscopic studies. All the electrodes made of different Pd–BiOI nanocomposites show improved catalytic performance with synergistic effects for the oxidation of methanol in comparison with the pure components, Pd and BiOI. The modified graphite electrode containing a thin layer of Pd–BiOI composite having 10 mol% of Pd, designated as PB10, has shown the best electrocatalytic performance in comparison with other electrodes for methanol oxidation. The current density using PB10 is increased by 5.4 times with respect to Pd which is further improved by 6.4 times in the presence of visible light for methanol oxidation reaction. The retention of peak current at the 200th cycle of voltammetric operation is found to be 99.5% indicating significant stability of the electrodes. The study essentially suggests PB10 can be used as an efficient anode catalyst for oxidation of methanol in alkali.

Introduction

A fuel cell is an elegant device that can convert chemical energy directly to electrical energy with high energy conversion efficiency and nominal pollutant emission. Among the different types of fuel cells, direct methanol fuel cells (DMFC) are

considered as attractive power sources for portable devices and electric vehicle applications, because of several reasons including the absence of hardship of C–C bond breaking, almost complete conversion, low emission, convenient fuel feeding, cost-effectiveness, etc. [1]. Pt is the traditional catalyst for methanol oxidation reaction (MOR), but it is costly metal and easily poisoned by oxidation

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Research articles

Synthesis, structure and magnetic properties of $\text{La}_{1-x}\text{Ln}_x\text{Cr}_{0.5}\text{Co}_{0.5}\text{O}_3$ ($x = 0$ and 0.2 & $\text{Ln} = \text{Pr}, \text{Sm}$ and Gd) perovskitesDebamalya Ghosh^{a,b}, Radhamadhab Das^a, Ariful Haque^a, Kalyan Ghorai^b, Arup Gayen^b, Partha Mahata^b, Asish K. Kundu^c, Md. Motin Seikh^{a,*}^a Department of Chemistry, Visva-Bharati, Santiniketan 731235, West Bengal, India^b Department of Chemistry, Jadavpur University, Kolkata 700032, India^c Discipline of Physics, Indian Institute of Information Technology, Design & Manufacturing Jabalpur, Dumna Airport Road, Madhya Pradesh 482005, India

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ABSTRACT

We report the sol-gel synthesis of $\text{La}_{1-x}\text{Ln}_x\text{Cr}_{0.5}\text{Co}_{0.5}\text{O}_3$ ($x = 0$ and 0.2 & $\text{Ln} = \text{Pr}, \text{Sm}$ and Gd) perovskites. The samples were characterized using powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX) and magnetization measurements. It is worth mentioning that all the samples in this study are found to be monophasic as attested from the PXRD patterns in sharp comparison with the previously reported work on $\text{LaCr}_{0.5}\text{Co}_{0.5}\text{O}_3$ [Solanki et al. *J. Magn. Magn. Mater.* 469 (2019) 95–99.]. This could be related to the slight modifications in synthesis condition like the metal to citric acid ratio, drying as well decomposition temperature of gel, final calcination temperature and time. The parent phase ($x = 0$) crystallizes in rhombohedral, $R\bar{3}c$, structure whereas the Ln -doped samples are orthorhombic, $Pbnm$. FE-SEM imaging revealed the irregular shape and large variation in particle size. The particles are highly agglomerated but show faceted surface irrespective of shape and size. The EDX analysis confirms the nominal cationic composition of the samples. The magnetic measurements suggest the onset of antiferromagnetic ordering in all the samples with T_N ranging from 130 K to 124 K depending on the size of the Ln -dopant ion. The high temperature effective paramagnetic moments obtained from Curie-Weiss law for all the samples suggest that the most likely spin-state of cobalt is intermediate-spin state. The low temperature magnetic behaviour of the substituted samples could be related to the rare earth-transition metal interaction. The magnetic ground states can be attributed to the $\text{Cr}^{3+}\text{--O--Co}^{3+}$, $\text{Cr}^{3+}\text{--O--Cr}^{3+}$ and $\text{Co}^{3+}\text{--O--Co}^{3+}$ antiferromagnetic superexchange interactions between the randomly distributed Cr^{3+} and Co^{3+} ions.

1. Introduction

Perovskites with the general formula ABX_3 form a large family of compounds. They encompass a huge range of crystal structures from simple cubic to ordered structures, modular phases like high- T_C superconducting cuprates and hexagonal perovskites related to BaNiO_3 . These perovskites exhibit intriguing physical properties of technological importance such as magnetic ordering, multiferroicity, superconductivity, magnetoresistance, magnetodielectric coupling, catalytic and optical properties [1–3]. However, the rapid technological advancement demands alternative functional materials. The methods of chemical substitution have enabled the researchers to address this issue since the early 1900s [4]. Accordingly, the physical properties of any member of these structural family can be tuned over wide ranges by chemical

substitution into all or some of the A-, B- and X-sites.

The simple perovskite oxides built of extended three-dimensional network of corner shared BO_6 octahedra are expected to show hybrid property with different B cations. It is also anticipated that the property of $\text{AB}_{0.5}\text{B}'_{0.5}\text{O}_3$ will be intermediate of ABO_3 and $\text{AB}'\text{O}_3$ terminal parent phases. However, generally it does not happen so. LaMnO_3 and LaFeO_3 are both antiferromagnetic with ordering temperatures 140 K [5–6] and 740 K [7–8], respectively. However, $\text{LaFe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ exhibits very complex magnetic features without any effective ordering of spins [9]. On the other hand, both LaNiO_3 [10–12] and LaCoO_3 lack of any kind of magnetic ordering whereas the latter one shows spin crossover for wide temperature range [1]. However, $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ and $\text{LaFe}_{0.5}\text{Ni}_{0.5}\text{O}_3$ are both canted antiferromagnet with the magnetic transition at 370 K and 100 K, respectively [13]. Furthermore, $\text{LaFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ exhibits

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