



**Title: Synthesis and photocatalytic evaluation of
graphitic carbon nitride based ternary
heterostructure systems**

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DECLARATION

I hereby declare that the work presented in this research project entitled: “Synthesis and photocatalytic evaluation of graphitic carbon nitride based ternary heterostructure systems” submitted for the requirement of PhD degree (Chemistry) to the Department of Chemistry, North-West University, Mahikeng Campus is an original research work of my own under the supervision of Prof. D.C. Onwudiwe. This research work has not previously been submitted to any other University or by another student at the North-West University or other University.

Signature: 

Ms V.M. Nkwe

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LIST OF ABBREVIATIONS

AOPs	advanced oxidation processes
OH [•]	hydroxyl
O [•]	superoxide
CB	conduction band
VB	valence band
SPR	surface plasmon resonance
CuS	copper sulphide
NO	nitric oxide
NaOH	sodium hydroxide
DDT	dodecanethiol-1
OAm	oleylamine
HDA	hexadecylamine
OAc	oleic acid
EG	ethylene glycol
MB	methylene blue
CV	crystal violet
CR	congo red
AC	activated carbon
AO	acid orange
AR	acid red
MO	methyl orange
RhB	rhodamine B
MY	metanil yellow

NCs	nanocrystals
UV	ultraviolet
XRD	X-ray diffraction
TEM	transmission electron microscopy
HRTEM	high resolution transmission electron microscopy
SEM	scanning electron microscopy
EDX	energy dispersive X-ray
NMR	nuclear Magnetic Resonance
CC	chemical coagulation
EC	continuous electrocoagulation
PL	photoluminescence
GCN	graphitic carbon nitride
CBO	copper bismuth oxide
TBA	tert-butyl alcohol
ASC	ascorbic acid
SN	sodium nitrate
TEA	tri-ethanol amine

ABSTRACT

The problem of water pollution continues to be of significant global concern, which has made water availability one of the biggest humanitarian issues. The use of dyes by the textile industries is considered to be one of the major causes of water pollution, which significantly hamper the availability and the aesthetic of water resources. It is therefore imperative that wastewater treatment techniques be enhanced to deal with this problem. Photocatalysis based on semiconductor heterojunction systems has shown to be a promising technique for the removal of these dyes from wastewater. Therefore, in this thesis, different heterostructures based on graphitic carbon nitride (g-C₃N₄) were synthesized as visible light photocatalysts for dye degradation. The as-synthesized materials were assessed for their structural, morphological, and optical characteristics using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and ultraviolet (UV) techniques, and their photocatalytic potentials were evaluated against methyl orange.

Firstly, Bi₂S₃ nanostructures were prepared using bismuth(III) dithiocarbamate as a single-source precursor and in different solvents. Then, the effect of Cu doping on the structural and optical properties of Bi₂S₃ was explored, as this is very important in improving the photocatalytic activity of developed heterostructures. The formation of bismuth sulphide (Bi₂S₃) and copper-doped bismuth sulphide (Cu-Bi₂S₃) with different amounts of Cu²⁺ dopant was successfully achieved through the solvothermal method. Structural analysis of the nanorods, using the Scherrer equation and Williamson-Hall technique showed a direct correlation between dopant concentration and crystallite size, which was in the range of 23.49 to 34.16 nm (Scherrer's) and 27.19 to 35.92 nm (Williamson-Hall's). The dislocation density, however, showed an inverse correlation with the dopant's concentration. The Cu doping shifted the bandgap of Bi₂S₃ between 1.35-1.78 eV, which was confirmed by first principle calculations. Subsequently, the photocatalytic degradation of methyl orange dye was carried out with Bi₂S₃ and Cu-doped Bi₂S₃ nanorods under visible light irradiation. The Cu-doped Bi₂S₃ showed a photocatalytic efficiency of 98% compared to the 88% recorded for the pristine materials. Further investigation into the mechanism was conducted on the possible mechanism involved in the MO degradation and the possible active species involved. In the degradation process, the most active species appears to be the radical through radical scavenging experiments.

In order to improve charge transfer, it is essential to reduce electron-hole recombination by controlling the charge transfer process and light absorption property of developed

photocatalysts. Therefore, the reported copper-doped bismuth sulphide nanoparticles (Cu-Bi₂S₃) were further incorporated into graphitic carbon nitride nanosheet (g-C₃N₄) using the solvothermal method. By forming heterostructures between g-C₃N₄ and Cu-Bi₂S₃, the band gaps were narrowed compared to the pristine materials. The obtained S-scheme heterostructure showed a Cu-Bi₂S₃ concentration-dependent photocatalytic efficiency, with the highest efficiency of 94% achieved for MO degradation, showing the high synergy between the components. Studies on radical scavenging indicated that superoxide radicals and photogenerated holes had the greatest impact on the process. This study confirms that the heterostructure formed from g-C₃N₄ and semiconductor nanomaterials could enhance dye degradation in an efficient and facile manner.

Furthermore, g-C₃N₄-based ternary heterojunctions (g-C₃N₄/Bi₂S₃/CuS and g-C₃N₄/CuBi₂O₄) were developed and their photocatalytic performance was evaluated under visible light. A novel g-C₃N₄/Bi₂S₃/CuS ternary heterostructure material was successfully achieved by the solvothermal method, which comprises p-type CuS, n-type Bi₂S₃, and n-type g-C₃N₄. The produced g-C₃N₄/Bi₂S₃/CuS heterojunction system was able to minimize the recombination rate of the photogenerated charge carriers, enhancing charge carrier separation. Compared to pristine materials (g-C₃N₄, Bi₂S₃, CuS) and binary composite (g-C₃N₄/Bi₂S₃, g-C₃N₄/CuS), the g-C₃N₄/Bi₂S₃/CuS heterostructure showed an improved photocatalytic performance for MO degradation, attaining 98% degradation efficiency and a reaction rate constant of $8.10 \times 10^{-2} \text{ min}^{-1}$. The improved photocatalytic performance of the ternary structure was due to the effective separation of charge carriers and enhanced visible light absorption. The ternary composite provides effective electron separation and transportation, as well as efficient application of visible light, making it a good photocatalyst for MO dye degradation. Based on the effect of the radical scavengers, the photogenerated hydroxyl radicals ($\cdot\text{OH}$), electrons (e^-), and holes (h^+) were observed to play major roles during the MO degradation process. A charge transfer scheme and mechanism of reaction were proposed on this basis. The ternary composite could possibly present new perspectives for developing new, effective and stable g-C₃N₄ based photocatalysts for dye removal applications.

Finally, g-C₃N₄/CuBi₂O₄ p-n heterojunction was developed and evaluated for its photocatalytic activity. The TEM and SEM images showed that CuBi₂O₄ was successfully incorporated into g-C₃N₄ nanosheets. The ternary g-C₃N₄/CuBi₂O₄ heterojunction showed good photocatalytic performance in the visible light irradiation compared with pristine g-C₃N₄ and CuBi₂O₄. The pseudo first-order rate constant was also considerably improved by the nanocomposite during

the process. The highest photocatalytic performance was achieved by g-C₃N₄/CuBi₂O₄(20%) composite, which is due to improved visible light absorption, and enhanced charge carrier separation between CuBi₂O₄ and g-C₃N₄ during photocatalysis. Moreover, g-C₃N₄/CuBi₂O₄ heterostructure showed great activity across different pH, concentration, and catalyst dosage values indicating that the system may be applicable to a variety of wastewater sources. The photogenerated holes (h⁺) and superoxide radicals (O₂^{•-}), were observed to be the main active radical species involved in photocatalytic MO degradation by the g-C₃N₄/CuBi₂O₄ p-n heterojunction photocatalyst.

The results from this study show that g-C₃N₄ based heterostructured photocatalysts are effective for the photocatalytic degradation of dye pollutants in wastewater. Therefore, the use of these technologies can be extended to other organic pollutants.

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RESEARCH OUTPUT

1. Morphological variations in Bi₂S₃ nanoparticles synthesized by using a single source precursor. Heliyon vol. 4, (2020) pp. e04505. <https://doi.org/10.1016/j.heliyon.2020.e04505>.
2. Synthesis, characterization, computational studies, and photocatalytic properties of Cu doped Bi₂S₃ nanorods. Materials Today Communications vol. 34, (2023) pp. 105418. <https://doi.org/10.1016/j.mtcomm.2023.105418>.
3. Dual heterojunction g-C₃N₄/Bi₂S₃/CuS composite with enhanced photocatalytic activity for methyl orange degradation. Inorganic Chemistry Communications vol. 155, (2023) pp. 111075. <https://doi.org/10.1016/j.inoche.2023.111075>.
4. Graphitic carbon nitride functionalized with Cu-doped Bi₂S₃ as a heterostructure photocatalyst for the visible light degradation of methyl orange. Ceramics International vol. 49 (2023) pp. 19451- 19462. <https://doi.org/10.1016/j.ceramint.2023.03.077>Get rights and content.
5. Synthesis of p-n GCN/CuBi₂O₄ heterostructures for enhanced visible light photocatalysis. Submitted to Materials Today Communications (MTCOMM-D-23-03046R2).

CHAPTER ONE

1.0. INTRODUCTION

1.1. Problem statement

Water pollution by organic dyes has become one of the significant global environmental challenges. Dyes are recalcitrant in nature due to their stability, high molecular weight, complex aromatic structure, and resistance to degradation [1]. With the increase in various industrial activities, a higher volume of different dye solutions is discharged into the environment and find their way into the water ways without being treated, thereby causing water pollution. Examples of this discharge is presented in Figure 1.1, which shows images of dyes discharged into the industrial surrounding from different industrial process without prior-treatment. Industrial wastewater is one of the most significant sources of water pollution due to the quantity and composition of dyes used. In addition, the presence of these dyes in wastewater does not only result in a shortage of clean water, but also causes harm to human health and the environment. Their carcinogenic and mutagenic properties make it very important to remove all of these dye pollutants from wastewater before being discharged into the environment [2].



Figure 1. 1: Different industrial wastes by various dye pollutants [3].

Several treatment methods including chemical, biological, adsorption, coagulation, sedimentation, filtration, and reverse osmosis have been developed to remove dyes in wastewater [4]. Some of these remedial methods, however, are not very efficient enough, as they require further treatment for the effective removal of dyes pollutant. However, the

application of advanced oxidation processes (AOPs) have proven to be sufficiently effective method for the treatment of wastewaters containing dyes [5], [6]. The most commonly used AOPs include H_2O_2 with UV radiation ($\text{H}_2\text{O}_2/\text{UV}$), ozone and ozone-hybrid mechanism (O_3 , O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$), Fenton reactions (Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$), sono-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{US}$), photocatalysis (TiO_2/UV and $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$) [7]. Among them, photocatalytic technology has proven to be more efficient for the removal of dyes pollutant in wastewater. It is less expensive, effective, and environmentally friendly. This process involves the generation of radical species such as hydroxyl ($\text{OH}^\bullet$) and/or superoxide ($\text{O}^\bullet$) radicals, which are subsequently used to break down dyes into less toxic products such as water (H_2O) and carbon dioxide (CO_2). Furthermore, different semiconductor materials can act as photocatalyst for the photocatalysis process depending on the suitability of their bandgap energies. One of the commonly used semiconductor is titanium oxide (TiO_2) which was first discovered in 1972 for water splitting, and its photocatalytic activity is external surface area dependent [8]. Other explored materials include metal sulphides (CuS) [9], metal oxides (ZnO) [10], antimony sulphides (Sb_2S_3) [11], antimony sulfoiodide (SbSI) [12], perovskites, and carbon-based materials such as $\text{g-C}_3\text{N}_4$ and graphene oxide. It is, however, unfortunate that pristine semiconductors, suffer from limited light absorption, high electron-hole recombination, or lack of sufficient active surface sites. To resolve such issues, however, techniques such as the combination of semiconductors, doping, surface modification, and heterojunction formations have been considered as suitable approaches to improve the efficiency and stability of photocatalysts [13], [14].

1.2. Motivation and rationale

To further improve the photocatalytic efficiency, the construction of ternary heterojunction systems has been the most promising and sustainable strategy. Development of ternary heterojunction materials with highly efficient visible-light photocatalytic activity has a great potential for highly efficient removal of dyes. Graphitic carbon nitride (g-C₃N₄) based ternary heterostructure material has been the focus of great interest as a replacement for commercial photocatalyst because it can provide different properties and stoichiometries. g-C₃N₄ has attracted much attention for the photodegradation of dyes, due to its stable chemical structure and its photo-response in the visible region of the electromagnetic spectrum. The basic principle in developing g-C₃N₄ based ternary heterostructure materials is to overcome the electron-hole pair recombination issues in g-C₃N₄. Semiconductor materials such as the metal oxides and metal sulphides, have been found to form ternary heterojunctions with g-C₃N₄. This is due to their unique physical and chemical properties such as high optical absorption coefficients and suitable bandgap. Metal oxide materials are very useful in environmental applications due to their compatible chemical, physical, and electronic properties. In photocatalysis process, reducing the grain size of metal oxide to the nanoscale opens up new possibilities resulting in an increase in the active surface of metal oxide rather than their bulk counterparts, making them more effective [15]. However, metal sulphides have an advantage over metal oxides because of their smaller bandgaps and ability to absorb and use readily available visible light [15], [16]. Metal sulphides have better absorption ability than metal oxides. They respond very well to sunlight because of the higher conduction bands potential compared to those of metal oxides. Any material that must act as a photocatalyst should show efficient light absorption, possess compatible and stable structural morphology, be reusable, and have large surface area. Furthermore, ternary heterostructure materials offer a facile and effective route to improve the charge separation, light absorption and achieve the enhanced photocatalytic activity. Hence, it has been the most frequently used technique for the engineering of effective photocatalysts so far.

1.3. Aim and objectives

1.3.1. Aim

The aim of this research work is the development of environmentally friendly ternary photocatalysts for the efficient removal of dye pollutant in wastewater.

1.3.2. Objectives

The aim of this research would be accomplished through the following objectives:

- synthesis of copper and bismuth dithiocarbamate complexes as single source precursors and their characterization,
- synthesis of Bi_2S_3 , CuS , $\text{Cu-Bi}_2\text{S}_3$, CuBi_2O_4 , and $\text{g-C}_3\text{N}_4$ nanomaterials by hydrothermal/solvothermal methods and their characterization,
- synthesis of $\text{g-C}_3\text{N}_4$ incorporated with Bi_2S_3 ; CuS ; $\text{Cu-Bi}_2\text{S}_3$; CuBi_2O_4 ; and $\text{Bi}_2\text{S}_3/\text{CuS}$ heterostructure materials and their characterization,
- evaluation of the photocatalytic performance of the synthesized nanomaterials for the photodegradation of methyl orange (MO) dye in aqueous solution under visible light irradiation,
- evaluation of the effect of process variables such as pH, catalyst dosage, and concentration of dye pollutant on the photocatalytic process,
- determination of the main active species during the photocatalytic processes,
- study and proposition of the basic mechanisms during the photocatalytic degradation of dye contaminant.

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CHAPTER TWO

2.0. LITERATURE REVIEW

2.1. Introduction

Environmental pollution problems, especially those associated with wastewater and toxic pollutants, have become a global challenge. South Africa is one of the countries that are seriously faced with challenges of poor-quality safe water because of the increase in water pollution. This chapter is designed to highlight the different organic pollutants, with a special focus on dyes as a major contaminant. The sources of this contaminant to the environment, both health and environmental effects of dyes will be discussed. The existing water treatment technologies including adsorption, chemical precipitation, flocculation, reverse-osmosis, air stripping, ultra-filtration, and their limitation will be presented as well. Furthermore, the relatively new technique of photocatalysis will be discussed and a critical look at its merits over other conventional methods as well as the mechanism of the process will also be highlighted. Subsequently, properties of the desired individual components of the photocatalyst of interest in the current studies (graphitic carbon nitride-based ternary heterostructure) will be surveyed with the aim of highlighting their properties and merit as photocatalyst materials.

2.2. Classifications of water pollutants

The effects of water pollutants may differ depending on the types and their sources. Water pollutants can be grouped into several categories such as organic pollutants, inorganic pollutants, suspended solids, radioactive pollutants, and pathogens [1]. Each of these class of pollutants poses a significant threat to the availability and sustainability of water resources. Among these contaminants, organic and inorganic pollutants mainly from industrial effluents and sewages, are the most critical contaminants in wastewater. Organic compounds in wastewater may be natural organic matter (microbial secretions and animal waste) and synthetic organic compounds (agricultural, industrial, food processing wastes *etc.*). Furthermore, water pollutant sources can be categorized as either point sources or nonpoint sources [2]. The point sources are all dry weather pollutants that enter the environment through pipes or channels as shown in Figure 2.1 [2]. Non-point sources include agricultural runoff, construction sites, and land disturbances.



Figure 2. 1: Images showing different sources of water pollution; (a) effluent discharged pipe from the factory, (b) oil spillage, (c) disruption of sediment, (d) organic dyes, (e) agro-chemical wastes, (f) gas effluents.

Some of the organic pollutants include soluble organic solvents (e.g., alcohols, dyes *etc.*) and insoluble pollutants (e.g., oils, grease *etc.*) [3]. The presence of dyes in wastewater is considered the most important source of water pollution that has attracted much attention. These dyes are released from industrial processes such as food processing, clothing textile, paper printing, and metal-complex processing.

2.3. Dyes as pollutants

2.3.1. Classification of dyes

Dyes are the most important groups of pollutants detected in wastewater. This is due to their wide applications to various substrates including papers, leathers, plastics, *etc.* as well as their chemical structures [4]. Structurally, dyes are made up of two components: chromophores and auxochromes. Chromophores are the functional groups, which are typically electron receivers and are responsible for dye colour formation. They often contain heteroatoms such as N, O, and S with non-bonding electrons. However, collective's chromophores include carbonyl ($C=O$, $C=C$, $C-NH$, $-CH=N-$), nitroso ($-N=O$), nitro ($-NO_2$ or $NO-OH$) and sulphur ($C-S$). The auxochromes are electron donors that give extra support to the chromophores for colour by enhancing the solubility and adhesion of the colour to the fiber. Auxochromes include amine ($-NH_2$), carboxyl ($COOH$), sulfonate (SO_3H), and hydroxyl groups ($-OH$) [5], [6]. Their structural classification is divided into the subclasses. As shown in Figure 2.2, synthetic dyes

can be divided into three groups, the cellulose fiber dyes (reactive, direct, indigo, sulphur dye), protein fiber dyes (azo, anthraquinone, triarylmethane dye) and synthetic fibers dyes (disperse, basic dye) [7].

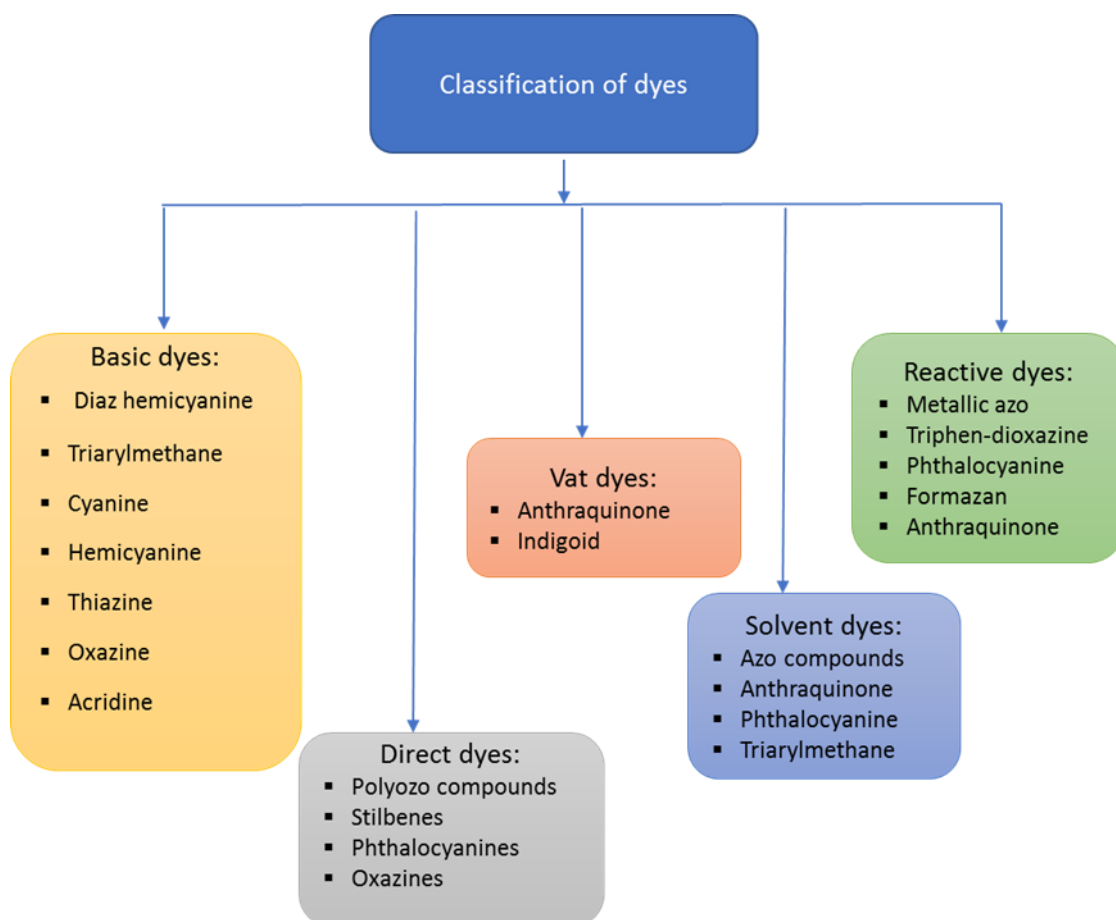


Figure 2. 2: Synthetic dyes and their subclasses.

Most common dyes that are applied in the textile industry include azo, dispersed, direct, acid, reactive, basic, vat, and mordant dyes. Among these dyes, azo dyes are the most important synthetic dyes since they account for almost 50% of dyes used in the industry [5]. They are widely used due to their well-known excellent chemical stability and versatility [8]. Most of these synthetic dyes are very toxic with serious threat to public health and environment [9].

2.3.2. Synthetic dyes

Azo dyes are regarded as the leading group of commercial dyes synthesized worldwide by Chang [10]. Some major examples of azo dyes that are commonly used in industries include, amido B, acid red 337, basic blue, acid, solvent red 1, congo red, methyl orange, naphthol blue black, acid yellow 17 dye etc. [11], [12]. They are being used as synthetic dyes in industrial processes such as pharmaceutical, printing, food processing, leather, rubber, gasoline, textile, cosmetic, papers, plastics, inks, and paints [13], [14]. Another group of synthetic dyes that have

been extensively employed are the nitro and nitroso dyes. They are important in plastics, polyester, nylon, acrylic fibers, and other colouring applications [12], [15]. They contain the nitro, triphenylmethane, nitroso, azo, anthraquinone chromophore groups. Figure 2.3 shows the different types of synthetic dyes, their sources and application in the textile industry.

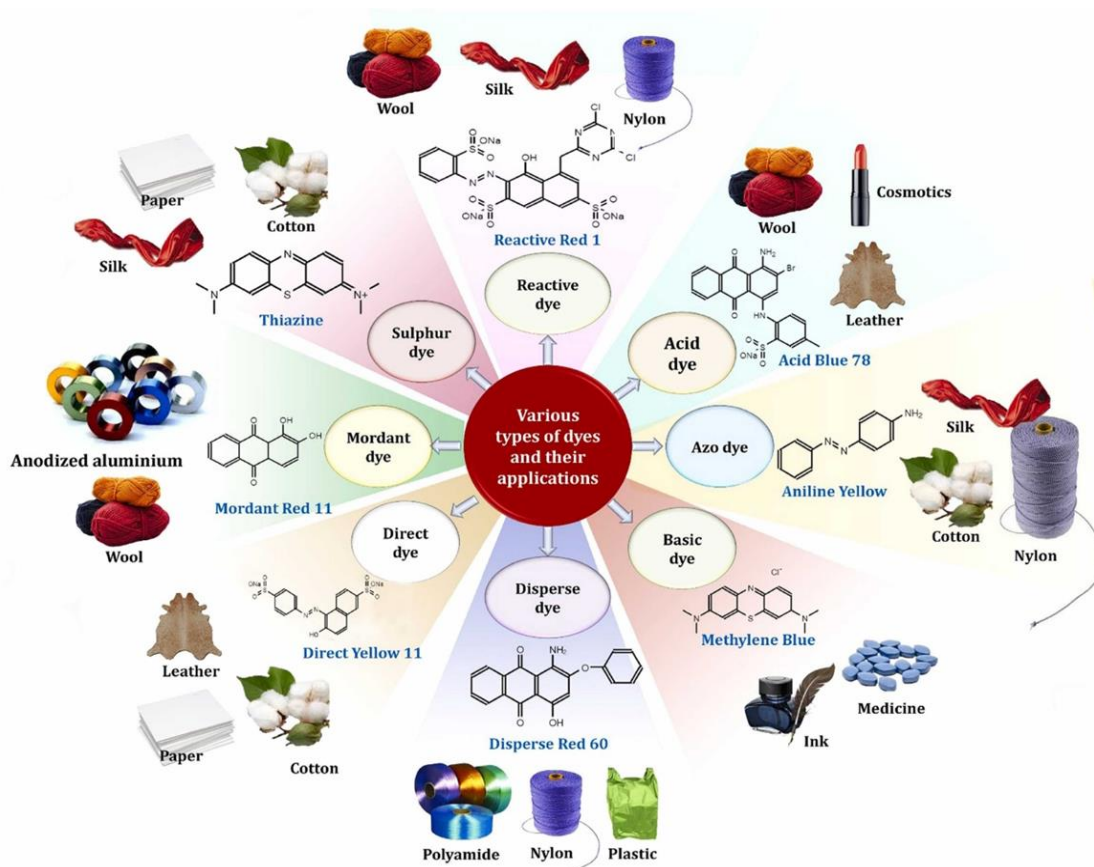


Figure 2. 3: Several kinds of synthetic dyes and their potential sources [16].

2.3.3. Decolouration of structurally different dyes

Dyes can be classified based on their decolouration of chemical structures and their particle charge when dissolves in an aqueous application medium [17]. They can be categorised as reactive, solvent, basic, direct, and sulphur dyes (see Figure 2.2). The photocatalytic decolouration of basic dyes is extensively used in dyeing processes and are very soluble in water. They are the brightest group of dyes that consist of an overall positive charge, hence are called cationic dyes [15]. Typically, examples of basic dyes are found in cyanine, triarylmethane, triphenylmethane, thiazine, oxazine, acridine and xanthenes dyes. Some of the

examples of cationic dyes are presented together with their molecular structures in Figure 2.4.

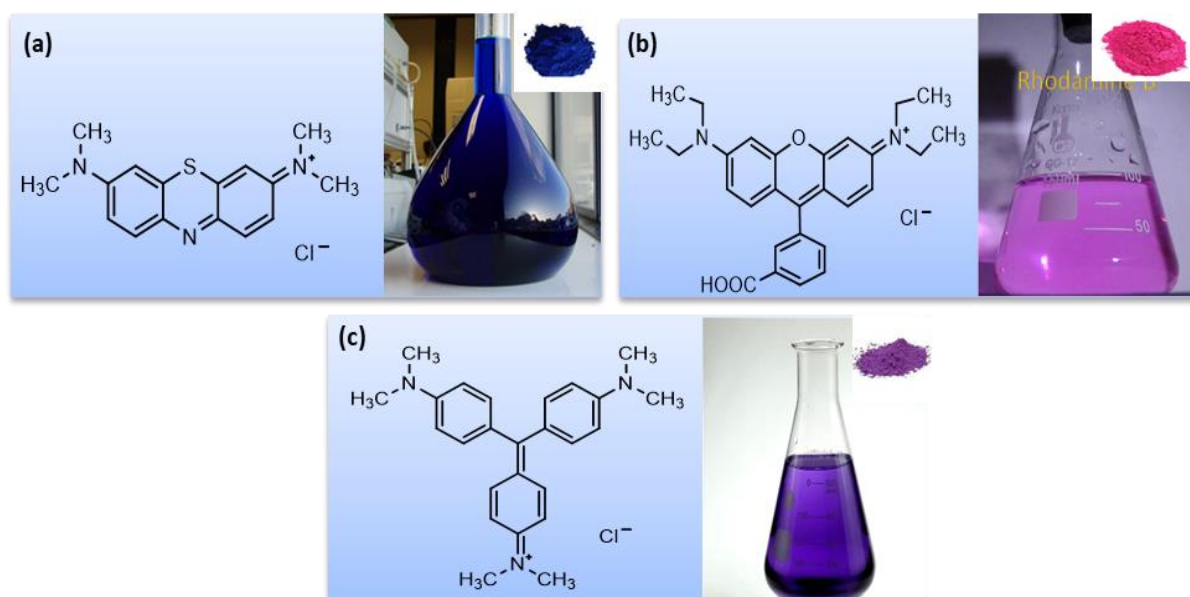


Figure 2. 4: The molecular structure of (a) methylene blue, (b) rhodamine B and (c) crystal violet dyes.

Other dyes such as acid, reactive, and direct dyes are classified as anionic dyes in nature and are negative in soluble form. They are also water-soluble. These anionic dyes are widely used for dyeing with various functional group such as triphenylmethane, anthroquinone, azo, azine, xanthene, nitro, and nitroso dyes. Figure 2.5 shows some examples of anionic dyes together with their molecular structures.

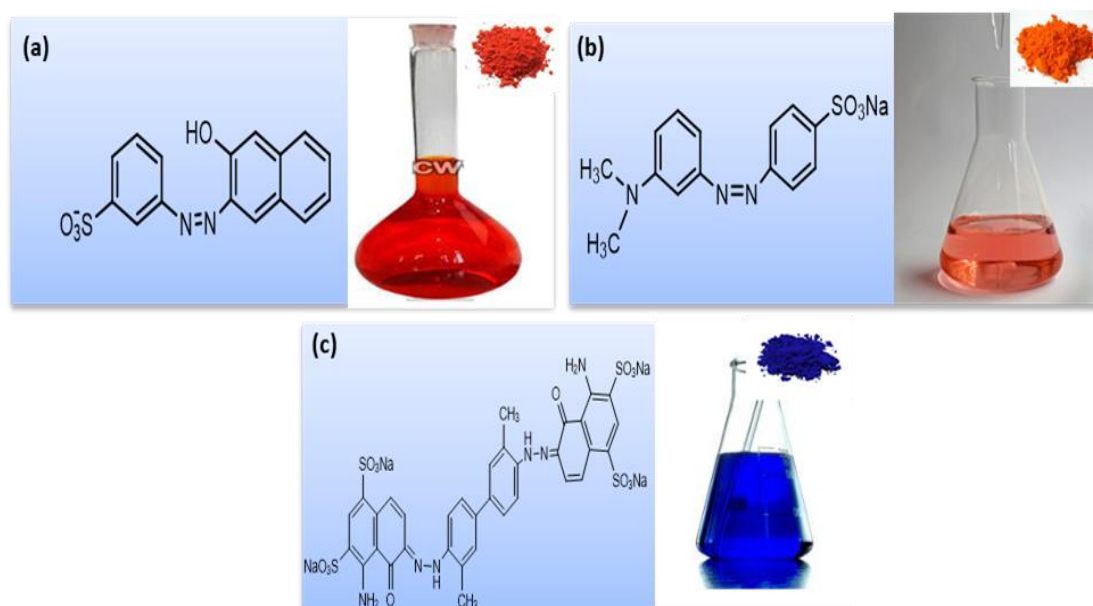


Figure 2. 5: The molecular structure of (a) acid orange, (b) methyl orange, and (c) direct blue dyes.

Furthermore, disperse dyes are another category of dyes which are considered as non-ionic organic colouring substances which are almost insoluble in water. They are widely used as azo dyes in textile industries and are only effective for dyeing of polyester fibers and some are used for dyeing of nylon, acetate, and cellulose. Majority of disperse dyes are found in the functional groups such as anthraquinone, styryl, azo, nitro, and benzodifuranone. Typical examples of the dispersed dyes are shown in Figure 2.6.

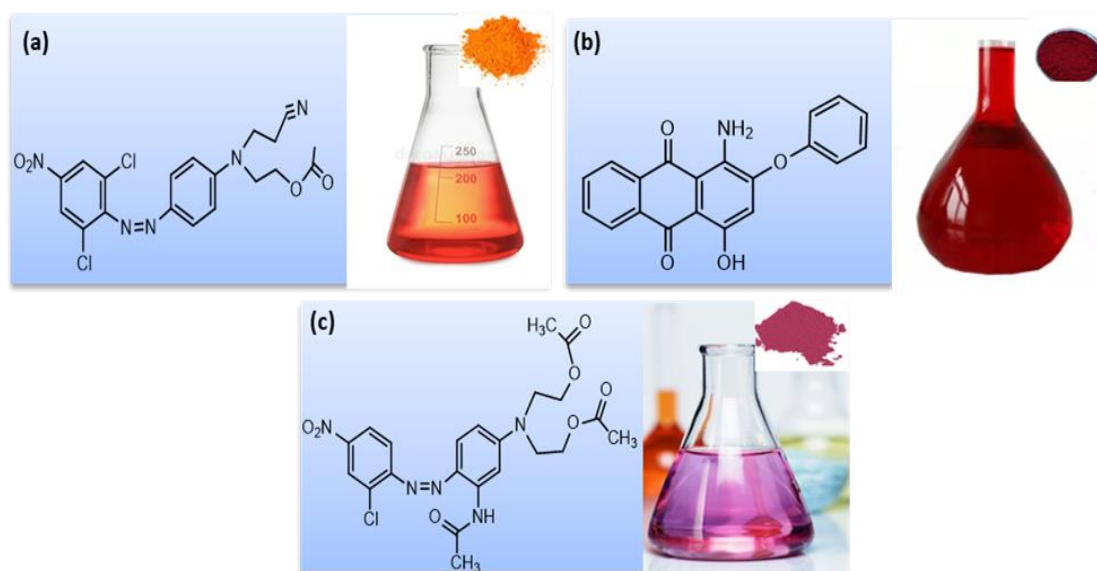


Figure 2. 6: Chemical structures of (a) disperse orange 30, (b) disperse red 3B and (c) disperse red 167 dyes.

2.4. Health and environmental effects of dyes

2.4.1. Health challenges caused by dyes

A lot of industrial processes make use of synthetic dyes for the colouring of products, and the waste from these industries is discharged into rivers, seas, sediments, soil, lakes, and streams, thereby causing serious health impact on humans, animals, and plants [17], [18]. Exposure to these toxic materials can occur by inhalation, food chain, soil, or when in contact with contaminated water [19], [20]. Most synthetic dyes are very poisonous, carcinogenic and can result in gene mutation in humans. Azo dyes from industrial effluents are very dangerous because they contain toxic amines, carcinogenic and volatile substances [21]. Acid yellow 17 dye has been confirmed to have negative effects on the gastrointestinal tract, skin, and lungs of humans [22]. It could also react with the haemoglobin to form adducts, which could interfere in the process of blood formation even in low concentrations. Other dyes such as crystal violet dye which is extensively used in a variety of textile industries, also causes eye burns, nausea, vomiting, and diarrhoea [9]. Also, anthraquinone dyes are highly resistant to degradation and

remain as colour in effluents for a long period [21]. Reactive water-soluble dyes are known to cause serious problems in the environment with their highly coloured effluent [23]. Different synthetic dyes can cause diseases to humans that could affect the skin, vital organs (brain, liver, heart *etc.*), systems (enzymatic, reproductive, nervous systems) and human chromosomes [24], [25].

Furthermore, the discharge of this toxic dye-containing wastewater could further affect the aquatic organisms such as fish, algae, and flora. Fish and other living organisms when exposed to these dyes, develop a variety of health problems like the disruption of normal architecture of gills, cells, gut, *etc.* [26]. Exposure of humans to fishes and other sea organisms (as they are the most important sources of protein), could cause cramps, fever, and hypertension to human [27]. It is, therefore, important to remove all these synthetic dyes from industrial wastewater before being discharged to water bodies due to their toxic effect. It has been reported that even a trace amount of dye present in water could possess a very high risk for human health [28], [29].

2.4.2. Environmental effects of dyes

Dyes are highly toxic to the environment, and they can even stay for a very long period due to their great thermal, and photo-stability toward biodegradation [30]. The presence of these dyes in water may affect the photosynthetic process in the aquatic environments because of the absence of oxygen circulation and light absorption [17]. When this poor light absorption decreases the photosynthesis rate of aquatic plants and organisms, their biological activities are upset. This could result in death of photosynthesis process of the aquatic environment, thus affecting the food source of aquatic organism/ecosystem and could result in oxygen depletion. High-level concentration of dyes in aquatic environment can also affect the growth of the aquatic organism and decrease the nutrients level of living things, thereby causing an ecological imbalance.

Dyes such as the methylene blue are commonly used in various industries, and can cause reduction in the growth level, pigment, and protein of the aquatic plants [31]. Other dyes such as crystal violet and congo red are the most harmful and widely employed dyes in different textile industries. The presence of these dyes in the aquatic environment, could cause low concentration, and high water turbidity, therefore making photosynthesis impossible for aquatic plants [32], [33]. It also decreases the volume of oxygen inside water, hence suffocating the aquatic plants. In humans, they can cause increased heart rate, permanent blindness, eye

irritation, respiratory disease, anorexia, kidney failure, mutation, lung and bladder cancer [34]–[37]. Therefore, the removal of synthetic dyes has grown to be a huge challenge that has encouraged the search for effective methods to reduce the environmental dye pollution caused by different textile industries.

2.5. Dye removal processes

Several techniques have been established for the removal of synthetic dyes from wastewater including biological, chemical, and physical treatment processes. The most recent methods include techniques, such as adsorption, flocculation/coagulation, advanced oxidation processes, precipitation, reverse osmosis, air stripping and ultra-filtration methods [38]–[40]. These methods are commonly used for dye removal; however, they are known to be non-destructive. They simply transfer the dyes into sludge, giving rise to secondary pollution, which then requires extra treatment [38]. Apart from the advantages of using these methods, they also have their own shortcomings; hence, it is very significant to adopt an appropriate method for the removal of dyes as pollutants.

2.5.1. Adsorption

Adsorption is one of the widely used physical methods because of its simplicity, flexibility, ease of operation and its higher efficiency for the removal of dissolved organic pollutants [41]. This method transfers pollutants from solution phase into a solid phase called adsorbent. The efficiency of this method is limited by some physicochemical properties of the adsorbent [41]. Activated carbon (AC) is one of the most explored adsorbent material for dye absorption because of its effectiveness and reliability [42]. It is also commercially available, with different physical and chemical properties, which are tailored for various applications. AC is, however, not often used because it is very costly. Researchers have therefore, explored different less costly adsorbent materials, such as clay minerals [43], fly ash [44], polymeric resins [45], wood [46], corn/maize cobs [47], wheat straw [48], as alternatives to AC for dye removal from wastewater. Figure 2.7 illustrates the adsorption process.

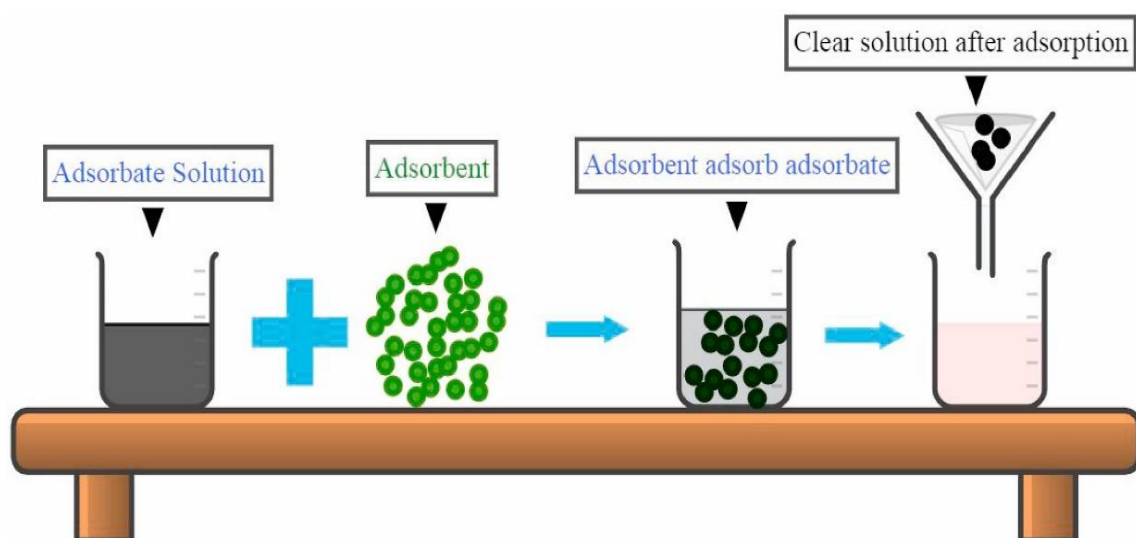


Figure 2. 7: The adsorption process [49].

The removal of Rhodamine B, Eriochrome black T, and Murexide dyes from aqueous solutions has been studied using calcined eggshell powder by Borhade, and Kale [50]. According to the findings of the study, the calcined eggshell powder can be a potential economical adsorbent for dye removal. Sun *et al.*, reported the use of carbon-based waste materials by fly ash to produce the inexpensive AC for the adsorption of various anionic dyes [51]. The study showed that AC from fly ash failed to boost dye removal effectiveness. The adsorption capacity of olive stone-based activated carbon was assessed for the removal of methylene blue from wastewater. Based on the results, olive stone-based activated carbon can be used to remove organic compounds from wastewater at a low cost [52]. Another report on mesoporous carbon compound derived from waste tire rubber was also used as a suitable adsorbent for the removal and toxic Acid Blue 113 dye [53]. Most of these adsorbents are however, limited by some challenges such as disposal or regeneration, high sludge production, high cost, inability to meet demand for treating the large volume of dye waste generated from industries. Furthermore, the choice of adsorbent is influenced by the adsorption capacity and affinity towards the target pollutant and the possibility of restoration of the adsorbent.

2.5.2. Chemical precipitation

Chemical precipitation is a conventional method used for wastewater treatment for many years. In addition to its simplicity, it is less expensive to operate and can be used for the removal of dyes from industrial wastewater. This method involves forming insoluble precipitates from organic and inorganic pollutants present in wastewater through the reaction of chemical reagent such as hydroxides (NaOH , $\text{Ca}(\text{OH})_2$), carbonates (Na_2CO_3 , CaCO_3), and sulphides (CaS , NaS), and the coagulant ($\text{KAl}(\text{SO})$, FeCl_2) [54]. When these chemicals react with dissolved

dye molecules, insoluble precipitates are formed, which can then be removed. Adding chemicals to wastewater treatment, forming a precipitate with the dye molecules, and then waiting for the insoluble particles to settle are typical measures. Then the wastewater can now be transferred to separate the sludge. The removal of dyes using chemical precipitation is most achieved by hydroxide precipitation. Bouyakoub *et al.*, investigated the two bivalent cation-based coagulants, magnesium chloride (MgCl_2) and manganese chloride (MnCl_2) to generate hydroxide precipitates for the removal of azo-dye pigment Levafix Brilliant Blue EBRA [55]. The reported study showed that the chemical dosage required for the removal of dyes is really increasing with most dyeing.

Another report on a white mud leaching solution from the soda production waste material for the removal of anionic dyes, such as acid orange II, reactive light-yellow K-6G, reactive bright red K-2BP was reported by Zhang *et al.* [56]. The leaching data proved that the treated water was harmless and was appropriate to treat the alkaline dye effluents. The report indicated the chemical precipitation's potential of the process for large-scale water purification with more than 94.6% removal of the dyes achieved due to the rapid kinetics of the process used. Furthermore, the removal of methylene blue and congo red using calcium derivatives (CaCO_3 and Ca(OH)_2), prepared from gastropod shells was also reported [57]. The precipitation of methylene blue and congo red reached 67 and 98% respectively. Chemical precipitation methods offer several advantages for treatment processes as it is an efficient, fast and easily monitored/implemented method. A major obstacle to industrial application of this technology is the generation of large amount of sludge and the chemical costs [38]. The adsorption process is inefficient in removing cationic dyes through charge neutralization process, because the most common adsorbent (AC) is positively charged [38], [58]. Although there is a lot of research being conducted for producing adsorbents capable of removing cationic dyes, however, the essential problem of adsorption still persists: it moves waste from one form to another without much degradation, which does not certainly solve the pollution problem [59]–[61].

2.5.3. Coagulation

Coagulation method is an effective and simple method for the removal of dyes from industrial wastewater. This method is used collectively with flocculation or sedimentation, with effectiveness depending on the sort of flocculants or coagulants and the pH level of the form used for wastewater treatment [62]. The process involves three stages: (1) the transportation processes, (2) the charge neutralization, and (3) the formation of smaller flocculants to agglomerate into larger flocculants. The sedimentation process to remove the large particles of

dyes formed often subsequently follows the coagulation-flocculation. Different types of low cost coagulants and flocculants have been reported by researchers to remove different dyes from wastewater [63]–[65]. This includes metal salts such as aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), ferric chloride (FeCl_3), polymeric aluminium sulphate, poly-aluminium chloride, calcium chloride (CaCl_2) sludge and some natural materials (alum, starch, iron materials, activated silica). Khayet *et al.*, reported the removal of acid red (119) dye using FeCl_3 as coagulants from aqueous solutions by the response surface methodology [66]. The result showed that low initial pH was advantageous for increasing the removal of dye and up to 96% of dye removal was achieved.

Another investigation of disperse red dye removal from wastewater by the chemical coagulation (CC) and continuous electrocoagulation (EC) using FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ (as coagulant) was reported by Merzouk *et al.* [67]. The study reported that $\text{Al}_2(\text{SO}_4)_3$ was much more efficient compared to FeCl_3 for dye removal using chemical coagulation, irrespective of operating conditions. In comparison with CC, it was concluded that EC offers the additional benefits of being more resistant to pH change while also reducing equipment costs. Furthermore, Patel and Vashi studied the effectiveness of chitosan, surjana and maize seed powders as coagulants for the removal of congo red dye [68]. Congo red removal for chitosan, surjana and maize seed powders reached 94, 98 and 89% respectively. Interestingly, the use of low cost surjana seed coagulants were found to be a better choice for congo red dye removal followed by chitosan and maize seed powder coagulants. Some flocculants are polymers including, the sodium poly-methacrylate, CHT-flocculant CV, cationic organic flocculant, epichlorohydrin-dimethylamine, and organic polyacrylamide polymer flocculants [63], [69], [70]. These compounds can simultaneously increase the flocculants aggregation forming larger particles for easy separation. In addition, the removal of dyes can also be a hybrid of the precipitation and adsorption processes involving the adsorption of dye molecules onto polynuclear coagulant species and hydrated flocs (see Figure 2.8).

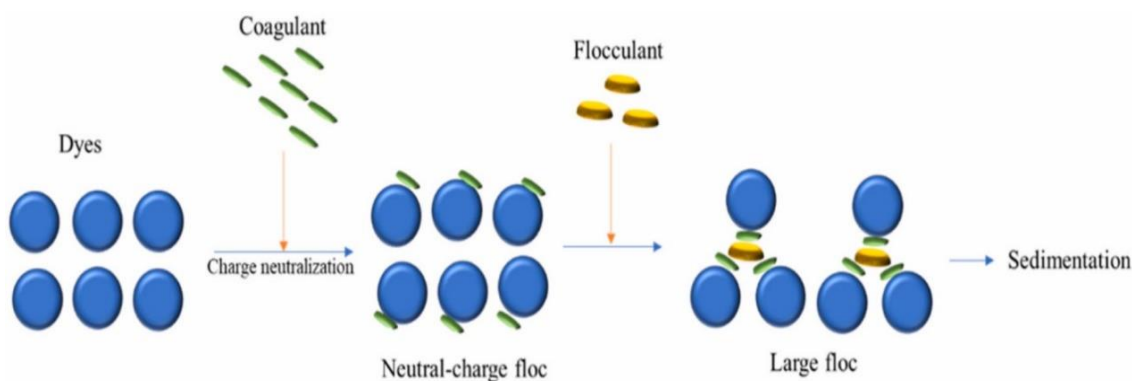


Figure 2. 8: Typical representative mechanism for the removal of dye through coagulation-flocculation process [38].

The mechanism in Figure 2.8, shows that the coagulation process is ineffective for the removal of cationic dyes due to the positively charged coagulants, by negating charge neutralization process [38], [58]. In addition, this method is often not efficient in removing the anionic dyes (acid, direct, reactive *etc.*). Even though they could coagulate, the floc produced does not settle well, resulting in poor results. It is also suitable for the removal of non-ionic dyes (e.g., disperse dyes). Low efficiency of dye removal in high concentration and high sludge generation is a major limitation of the process leading to a higher cost for water treatment [23].

2.5.4. Advanced oxidation processes (AOPs)

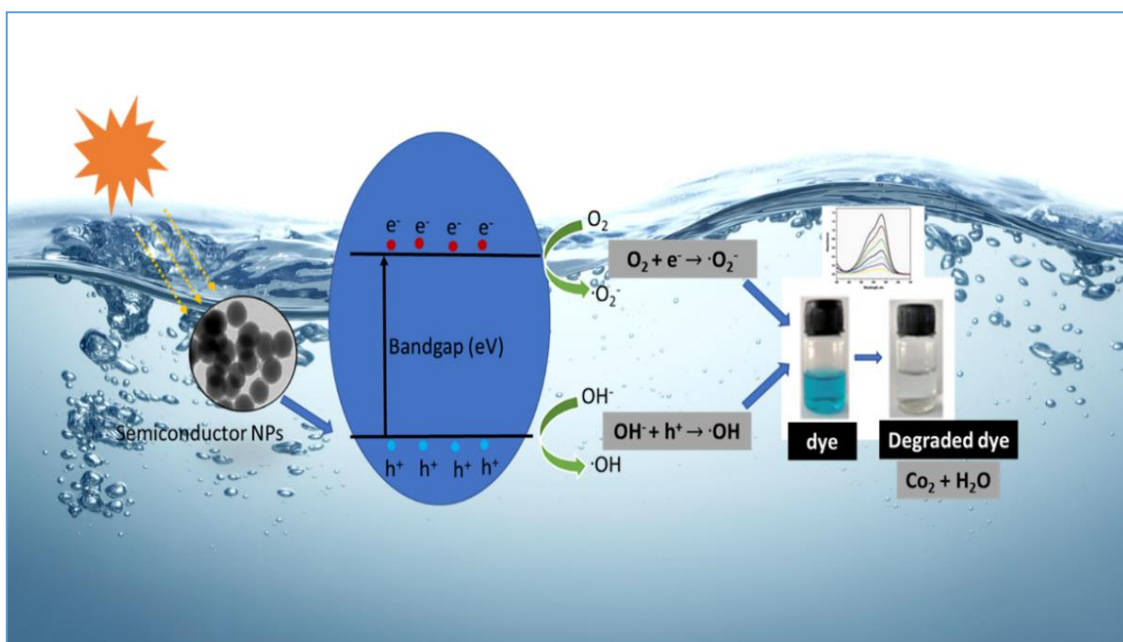
Advanced oxidation processes (AOPs) is an alternative method for the degradation of dye compounds. In this method, highly reactive species are produced, such as hydroxyl radicals ($\cdot\text{OH}$) and sulfate radical ($\text{SO}_4^{\cdot-}$), or superoxide ($\cdot\text{O}_2^-$). According to several studies, sulfate ($\text{SO}_4^{\cdot-}$) or hydroxyl ($\cdot\text{OH}$) radicals based AOPs are the most effective at removing dyes from the wastewater [71], [72]. AOPs include Fenton and electro-Fenton [73], Fenton-like processes [74], sono-electro-Fenton and photo-electro-Fenton [75], O_3 -derived AOPs (e.g., O_3/Fenton , $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV , $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$, $\text{O}_3/\text{photo-Fenton}$, $\text{O}_3/\text{UV}/\text{TiO}_2$ and $\text{O}_3/\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$) [75]–[82], catalytic ozonation [83], photocatalysis [84], ultrasound electrochemical [85], catalytic wet peroxide oxidation [86], and UV and $\text{UV}/\text{H}_2\text{O}_2$ process [87] for the removal or degradation of dyes. Recently, more attention has been focused on the photocatalysis process for the removal of dyes from wastewater due to its simplicity, cost effectiveness, flexibility, and eco-friendliness. As a result, this research study aims to investigate the photocatalytic removal of dye pollutant in water.

2.6. Photocatalysis

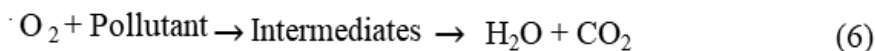
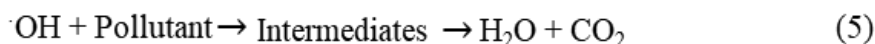
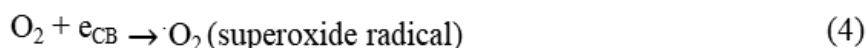
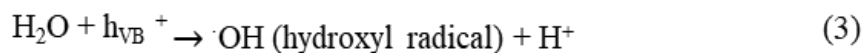
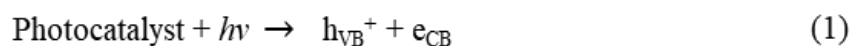
Photocatalysis is a process that involves the generation of reactive radical species by the absorption of light energy of appropriate wavelength by a semiconductor material [88]. The generated radical species are then used in initiating a variety of chemical reactions, which are explored in different processes such as water splitting, pollutant degradation and energy generation [89]. Photocatalysis has become an important process that has been studied widely for the removal of dyes from water. In recent years, a wide range of different photocatalysts for dye removal have been studied, including metals, metal oxides/sulfides, semiconductors, carbon-based nanostructures, quantum dots, and other materials [90]–[93]. Semiconductor photocatalysis can either be used solely or in combination with other technologies such as in photo-Fenton, photo-electrochemical and photon-enhanced chemical activation processes. Another advantage of the photocatalytic technique is that the potential for complete mineralization of the organic dyes is high, thus no secondary waste stream is generated by the process [94].

2.6.1. Mechanism of photocatalytic degradation of dye

The basic principle of semiconductor photocatalysis is already well-known and has been extensively reported [95], [96]. Semiconducting materials have proven to be excellent photocatalysts for the degradation of dyes in wastewater. This is due to their suitable bandgap energy and ability to absorb light radiation in a wide range of the electromagnetic radiation spectrum. Based on the bandgap theory, researchers have proposed several mechanisms for electron-hole formation, their transfer across the valence, conduction, and forbidden energy bands, and their recombination [97]. The photocatalytic mechanism process begins with the photocatalyst (e.g., semiconductor) absorbing photon energy higher than its bandgap energy from a light source [94]. The electrons in the semiconductor become excited in the valence band and get excited to the conduction band (e_{CB}^-) (see Scheme 2.1), leaving behind holes (h_{VB}^+) in the valence band. The photogenerated electron-hole pairs then migrate to the surface of the photocatalyst to initiate redox reactions with H_2O and O_2 on the catalyst surface to generate reactive radical species such as O_2^- and $\cdot OH$. These radical species then react with organic contaminants in water to form degradation by-products. Apart from the generation of reactive radical species, the photogenerated electron-hole pairs are also capable of inducing the pollutant degradation. The oxidation and reduction reactions, however, take place simultaneously in photocatalytic reactions and detailed as follows:



Scheme 2. 1: Basic mechanism of photocatalysis for the degradation of dyes.



2.6.2. Photocatalytic degradation of dyes

The photocatalytic degradation of dye as target pollutants in wastewater using semiconductor photocatalysts is a well-explored process. This method has an advantage because it is environmentally friendly and can effectively transform dyes into easily degradable products or completely mineralize them to CO_2 and H_2O . Most common dyes that are extensively utilized as a colouring agents in food, plastic, textile, and pharmaceutical industries include congo red (CR), acid orange (AO), acid red (AR), and methyl orange (MO). The other well-studied group

of dyes includes the thiazine (e.g., methylene blue (MB)); xanthenes and triarylmethane dyes such as rhodamine B (RhB) and crystal violet (CV). Dyes such as congo red (CR), methylene blue (MB), methyl violet (MV), methyl orange (MO), rhodamine B (RhB) and others have been studied and reported [98]–[102]. Several studies on semiconductor photocatalysts such as TiO_2 , CdS, ZnO, SnO_2 , WO_3 , and Bi_2O_3 using different dyes by the photocatalysis process have been reported [103]–[108].

Liu investigated the impact of shortcoming in the lattice of the semiconductor materials such as ZnO for the degradation of anionic dyes [109]. Methyl orange, acid red 27, and acid red 88 as anionic dyes and methylene blue and rhodamine 6G as cationic dyes, were degraded under light irradiation using ZnO nanoparticles. The obtained results for the degradation rates of dyes were found to follow the order: acid red 27 > acid red 88 > Methyl orange. ZnO photocatalysts had few higher defects exhibited in the dye adsorption but a low photocatalytic performance. However, it was found that the photodegradation of these dyes could result in decolourisation of the aqueous solution and eventually complete mineralization of the dyes solution. The pristine photocatalysts generally have poor light absorption, fast charge recombination, and few active sites, which seriously limit their practical applications. Therefore, developing an appropriate heterojunction system has been regarded as the most promising way for establishing effective charge transfer and separation to enhance the photocatalytic process. Table 2.1 presents different semiconductors and semiconductors-based heterojunctions as photocatalysts for photocatalytic degradation of dye [110].

Table 2. 1: Summary of different semiconductors and semiconductors-based heterojunction as photocatalysts for photocatalytic degradation of dye.

Photocatalyst	Method used	Dye pollutants	Light source	Degradation (%)	Ref
TiO ₂	One-pot	RhB	Solar/vis	86	[111]
ZnO	Precipitation	CR	UV/vis	90	[112]
BiOCl	Hydrolysis	RhB	UV/vis	98 - 100	[113]
Pd/TiO ₂	Sol-gel	MB	Vis	99	[114]
Ag/ZnO	Precipitation	MB	UV	98	[115]
SnS ₂ /g-C ₃ N ₄	Calcination	RhB	Vis	92	[116]
g-C ₃ N ₄ /Ag/MoS ₂	Hydrothermal/ Calcination	RhB	Vis	95	[117]
ZnFe ₂ O ₄	Combustion	RhB, CR	Solar	82 - 94	[118]
Bi ₂ O ₂ CO ₃ /Bi ₂ S ₃	Partial ion exchange	RhB	Vis	93	[119]
CdS/ZnO	SILAR	MB	Vis	91	[120]
ZnSnO ₃	Sol-gel	RhB	UV	98	[121]
g-C ₃ N ₄ /ZnS/SnS ₂	Hydrothermal	MB	Vis	95	[122]
g-C ₃ N ₄ /Ag ₂ WO ₄ /Ag	Hydrothermal	MB	Vis	90	[123]
MoS ₂ /Al ₂ O ₃ /g-C ₃ N ₄	Hydrothermal	CV	Vis	88 - 97	[124]

2.7. Bismuth-based chalcogenides heterostructures as photocatalysts

2.7.1. Bismuth sulphide

Bismuth sulphide (Bi₂S₃) is an important class of semiconductors with very rich and unique properties. It has been considered as an appropriate candidate in photocatalysis due to its good optical properties such as low band gap energy of 1.3 - 1.7 eV, high photo stability, and large absorption co-efficient [125]. Bi₂S₃ nanostructures have been synthesized by various methods such as microwave-assisted [126], photochemical synthesis [127], thermal decomposition of single-source precursor [128], simple wet chemistry [129], ionic liquid-assisted templating [130], and hydro/solvo thermal [128] processes. Diverse morphologies of Bi₂S₃ that have been

synthesized by different methods include nanostars [131], nanospheres [132], nanocrystals [133], nanoflowers [132], nanoflakes, nanorods [129], nanoplates [133] *etc.* nanostructures.

The photocatalytic properties of pristine Bi_2S_3 and ternary Bi_2S_3 nanoparticles as photocatalysts for the degradation of organic dyes have been explored. Bi_2S_3 nanostructures for removal of rhodamine B (RhB), Congo Red (CR), methylene blue (MB), under UV light conditions have been reported [131] [134]–[136]. Zhao *et al.*, reported Bi_2S_3 microsphere using one-pot urea assisted solvothermal method. The Bi_2S_3 microspheres were assessed for the photodegradation of methyl orange (MO) under visible light irradiation. The results showed that the Bi_2S_3 microsphere might be employed as a potential low-cost catalyst to remove MO from aqueous solutions, with a 91.07% degradation efficiency reported [137].

Doping of Bi_2S_3 nanoparticles with different atoms has been reported for the removal of various dyes. The introduction of impurity ions into the crystal of Bi_2S_3 semiconductor nanocrystals can increase the concentration of charge carriers by donating or accepting electrons. Song *et al.*, successfully reported the synthesis of selenium-doped bismuth sulphide (Se- Bi_2S_3) NPs using hydrothermal method for photodegradation of methylene blue (MB) dye under visible-light irradiation [138]. The results showed the photocatalytic degradation of 88, 92, and 96% for all the MB dyes. Different semiconducting binary heterojunction materials such as $\text{Bi}_2\text{S}_3/\text{TiO}_2$, $\text{Bi}_2\text{S}_3/\text{ZnO}$, $\text{Bi}_2\text{S}_3/\text{ZnS}$, $\text{Bi}_2\text{S}_3/\text{SnS}_2$, $\text{Bi}_2\text{S}_3/\text{MoS}_2$, and $\text{Bi}_2\text{S}_3/\text{BiVO}_4$, with controlled morphologies and properties, have also been investigated [139]–[144]. To further explore the photo-response and the photocatalytic performance, several reports on ternary heterojunctions have been investigated such as $\text{Bi}_2\text{S}_3/\text{BiOCl}/\text{g-C}_3\text{N}_4$, $\text{Bi}_2\text{S}_3/\text{MoS}_2/\text{TiO}_2$, $\text{BiOBr}/\text{Bi}_2\text{S}_3/\text{CdS}$, $\text{Bi}_2\text{S}_3/\text{TiO}_2/\text{Au}$ [145]–[148]. Because of this strategies, separating and transferring charge carriers is more efficient.

2.7.2. Bismuth oxide

Another attractive bismuth-based chalcogenide, bismuth oxide (Bi_2O_3), has received much attention in various photocatalytic applications. Bi_2O_3 semiconductor has a narrow band gap of 2.0 - 3.96 eV and in the visible light region, it exhibits good photocatalytic activity for the degradation of different dyes [146], [147]. The morphology of the Bi_2O_3 nanostructures can differ from nanoparticles [148], nanorods [146], nanotubes [149], nanobelts [150], nanowires [151], and flower-like hierarchical structures [151] depending on the synthesis method. Novel Bi_2O_3 -montmorillonite nanocomposite was successfully synthesized through sonochemical method. The photocatalytic degradation of the material was studied using the degradation of

congo red (CR) under visible light irradiation. The degradation efficiency percentage of CR dye was observed up to 86.4% [152]. The photocatalytic efficiency of $\text{Bi}_2\text{O}_3/\text{BiVO}_4$ heterojunction was assessed for the photodegradation of methyl orange (MO) under visible-light irradiation [153]. The results showed the degradation efficiency of 97% after 120 min of irradiation. The high surface area and unique porous structure of the p-n heterojunction semiconductors led to increased activity by promoting charge carrier transfer and reducing recombination of photogenerated hole-electron pairs.

Furthermore, $\text{Ag-CuBi}_2\text{O}_4/\text{Bi}_2\text{WO}_6$ heterostructure was reported for the removal of rhodamine B (RhB) dye under visible light irradiation [149]. The results showed enhanced photocatalytic activity when compared to pristine Bi_2WO_6 and Bi_2O_3 . The enhanced photocatalytic performance was due to high separation efficiency of the electron-hole pair, resulting from the Z-scheme heterojunction formation. Yu *et al.*, reported the synthesis of $\text{Bi}_2\text{S}_3/\text{SnS}_2/\text{Bi}_2\text{O}_3$ ternary heterojunction material through the solvothermal process for the efficient removal of dyes under the light assisted process [150]. The development of Z-scheme heterojunction photocatalytic system is crucial for efficiently tailoring the photoinduced charge separation. Sabri *et al.*, also investigated $\text{ZnO}/\text{CuBi}_2\text{O}_4$ heterostructure for photodegradation of methyl orange (MO), rhodamine (RhB), and congo red (CR) dyes [151]. The binary heterostructure showed good photocatalytic ability for removing of MO, RhB, and CR dyes from wastewater.

2.8. Copper sulphide heterostructures as photocatalyst

Copper sulphide (CuS) is an earth abundant and inexpensive material that has been extensively studied for its application in the visible light-driven photocatalysis for the removal of dyes [152]–[154]. It is an important p-type semiconductor with a direct bandgap of 2.0 eV material and is versatile, readily accessible, and less toxic. Several chemical techniques for the preparation of CuS nanoparticles including solvothermal, hydrothermal, hot-injection, heat-up, sol-gel, chemical co-precipitation, sonochemical, and solid-state reaction routes have been reported [155]–[162]. CuS nanoparticles consist of various crystalline phases, including chalcocite (Cu_2S), djurleite (Cu_{19}S), digenite (Cu_{18}S), anilite ($\text{Cu}_{17.5}\text{S}$), and covellite (CuS) from the copper-rich side (Cu_2S) to the copper-deficient side (CuS). Different morphologies have been reported for CuS nanomaterials such as nanoflakes [163], nanodisks [164], nanohollow spheres [165], urchin-like [166], nanorods [167], and flower-like structures [168]. High quality CuS and CuS/ZnS core/shell nanocrystals (NCs), by hydrothermal method, was studied for the photocatalytic removal of Rhodamine B (RhB) under visible light irradiation

[169]. The resulting morphology showed that with increase in time, the formation of rods from spherical particles was formed. The CuS/ZnS core/shell structures under visible light irradiation showed high photocatalytic than that of pristine CuS or ZnS NCs. This is due to the higher charge separation rates for the carriers in the core/shell structure. Another photocatalytic performance of pure CuS/ZnS nanostructures was investigated which displayed higher photocatalytic activity compared to pure CuS material. This could be attributed to more rapid charge separation rates between the photogenerated carriers. CuS as a photocatalysts suffer from the high rate of electron-hole recombination [152]. The use of different heterojunctions with other semiconductors and the decoration with graphene, carbon quantum dots and or metal nanomaterials have been developed to overcome such limitations.

Abdullah *et al.*, reported CuO/CuS/MnO₂ ternary heterostructure prepared by hydrothermal method for the photocatalytic degradation of methylene blue (MB) dye under visible light irradiation [170]. The photocatalytic performance of ternary heterostructure was showed to be greater than that of pristine material when exposed to visible light. Another ternary of NiS/CuS-CdS nanocomposite was investigated for the photodegradation of methyl orange (MO) and methylene (MB) under visible light region [171]. The results displayed an excellent photocatalytic activity due to the formation of efficient photocatalyst (NiS-CuS-CdS heterojunction) for the removal of MB and MO dyes in wastewater.

2.9. Graphitic carbon nitride

Graphitic carbon nitride (g-C₃N₄) is an economic and environmentally friendly semiconductor material that has received considerable attention due to its ability to absorb light in the visible light area. g-C₃N₄ has a reasonable bandgap of 2.7 eV, has unique properties such as, non-toxic, good chemical stability, and is inexpensive. The history of g-C₃N₄ was first developed in 1834 by Berzelius and Liebig as “melon” [172]. Its structure is similar to the unique structure of graphene as they both have two dimensions but differ in so many ways. The g-C₃N₄ is formed by connecting tri-s-triazines unit of tertiary amines (see Figure 2.15) [173]. Figure 2.9 shows the structure of tri-s-triazine ring bridged with the trigonal N atoms to the 2D layer structure constructed by the building blocks of g-C₃N₄.

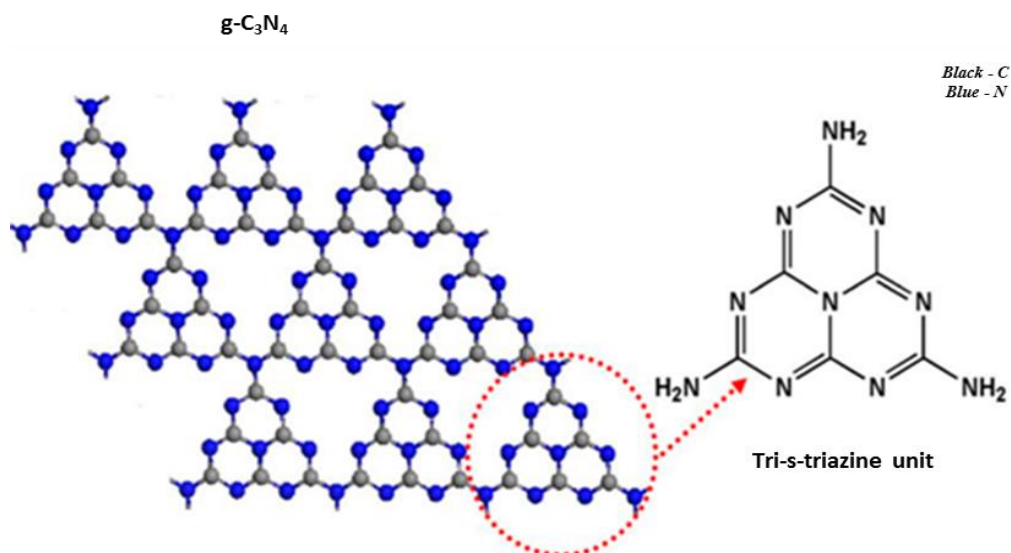


Figure 2. 9: The structure of $g\text{-C}_3\text{N}_4$ (tri-s-triazine units) [174].

$g\text{-C}_3\text{N}_4$ can be prepared from different nitrogen-rich organic precursors which include thiourea, melamine, urea, and dicyandiamide by thermal condensation under different temperature conditions (as shown in Table 2.2). These precursors easily form linear polymeric structure of $g\text{-C}_3\text{N}_4$. However, the choice of precursor, synthesis process, reaction temperature and the environment can significantly affect the surface of the material which can alter the chemical and physical properties of the prepared $g\text{-C}_3\text{N}_4$ [175]. $g\text{-C}_3\text{N}_4$ is thermally stable due to the Van der Waals forces holding the frameworks together, and it is also insoluble in most solvents like methanol, H_2O , diethyl ether, and tetrahydrofuran [176]. Different methods have been reported for preparing $g\text{-C}_3\text{N}_4$ such as solvothermal synthesis [177], hydrothermal synthesis [124], thermal polycondensation [178], plasma sputtering reaction deposition [179], microwave assisted [180], electrochemical deposition [181], physical and chemical vapour deposition [182].

Table 2. 2: Different methods for synthesizing of g-C₃N₄ nanocomposite using different precursors as starting materials.

No.	Precursors	Formula	Method	Calcination temp. (°C)	Ref.
1	Melamine	C ₃ H ₆ N ₆	Thermal condensation & polymerization	500 - 580	[174]
2	Cyanamide	CH ₂ N ₂	Thermal condensation & polymerization	550	
3	Dicyanamide	C ₂ H ₄ N ₄	Thermal condensation & polymerization	550	
4	Urea	CH ₂ N ₂ O	Poly-addition, thermal condensation & polymerization	520 - 550	
5	Thiourea	CH ₄ N ₄ S	Poly-addition, thermal condensation & polymerization	420 - 650	

2.9.1. Photocatalytic activity g-C₃N₄ based heterojunctions

Developing of g-C₃N₄ based heterojunction systems as photocatalysts has been extensively studied to improve the visible light irradiation, enhancing fast charge recombination and photostabilities [174], [183]–[185]. g-C₃N₄ like other semiconductor photocatalysts suffers from fast recombination rate of photoexcited electron-hole charges and small surface area that restrict its photocatalytic performance [186], [187]. Different materials such as the metal oxides-sulfides, chalcogenides and chalcogenides, have been studied to improve the photocatalytic activity. These materials have interesting electronic and optical properties, such as high optical absorption coefficients and suitable direct band gaps. For example, a heterojunction system of SnS₂/g-C₃N₄ composite for the photocatalytic degradation of rhodamine B (RhB) under visible light irradiation was reported. The photocatalytic activity was improved with degradation efficiency of 92% compared to pure SnS₂ and g-C₃N₄ materials [116]. Kim *et al.*, reported the photodegradation of methylene blue (MB) dye using ZnS/g-C₃N₄ Type II heterojunction for the improved photocatalytic performance [188]. The p-n type heterojunction photocatalyst is obtained by combining p-type and n-type semiconductor materials to increase photocatalytic activity by adding an extra electric field to speed up charge transfer.

The g-C₃N₄-based ternary heterostructured photocatalysts have much better photocatalytic efficiency than bare g-C₃N₄. Madhushree *et al.*, reported the Z-scheme MoS₂/g-C₃N₄/ZnO ternary heterostructure to improve photocatalytic performance [189]. Another, ternary composite of MoS₂/Al₂O₃/g-C₃N₄ heterostructured photocatalyst was reported by Vattikuti and Byon [124]. The ternary nanocomposites were effective for the photocatalytic degradation of crystal violet dye. The synthesis of g-C₃N₄/GO/MoS₂ ternary heterostructure was also reported for the degradation of organic dyes using visible light photocatalysts [190]. The flower-like structure obtained from the as-prepared nanocomposite effectively extended the lifespan of electrons-holes in MoS₂ and g-C₃N₄ by promoting the separation of photoexcited charge carriers. Furthermore, g-C₃N₄/Ce₂O₃/CuO ternary photocatalyst was successfully synthesized through a simple calcination and dynamic hydrothermal method for the degradation of metanil yellow (MY) with methylene blue (MB) dyes pollutants from wastewater [191]. It was found that the ternary nanocomposite degraded the aqueous solution to about 90.3% and 94.5% for MY and MB irrespectively [192]. Li *et al.*, synthesized g-C₃N₄/Ag/Ag₃PO₄ nanocomposite in such a way that elemental Ag acts as the charge-carrier bridge to study the photocatalytic degradation using RhB dye photocatalysis and kinetics pathway through tracing kinetics in real-time and thermodynamics [193].

2.10. References

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CHAPTER THREE

Morphological variations in Bi₂S₃ nanoparticles synthesized by using a single source precursor

3.1. Introduction

Metal sulphides are particularly attractive within the broad family of functional materials due to their wide applications in electronic, energy storage and conversion, optics and in biomedical fields [1-4]. They have unique optical and structural properties and have also found application in electrochemical detection and photocatalysis [5-7]. The synthesis of nanocrystalline materials and the manipulation of their synthesis conditions in order to obtain materials with different properties is one of the interesting research aspects that has been explored recently [8-10]. This is because morphology, dimensionality, crystallinity, and chemical composition of nanostructured materials profoundly influence their physicochemical properties and applications. Thus, the optical and structural properties of nanomaterials ultimately depend on the methods and conditions of preparation [11, 12]. Achieving a narrow size distribution in addition to a well-defined morphology are the two parameters that allow the modification of fundamental properties of nanoparticles; thereby enhancing the efficiency of their performance for applications in various areas [13, 14].

Different methods of wet chemical processes have been used to afford series of isotropic and anisotropic chalcopyrite nanocrystalline materials such as spherical, star-like, flower-like, nanorods/wires/tube, and nanofibers [15-20]. The solvothermal method has emerged as one of the wet chemical routes that offer better control on the preparation of different nanostructures in different kinds of media [17]. Solvents play an important role during reaction process and in nanoparticles preparation; the role may include temperature control, surface passivation, regulating the particle growth and coarsening, controlling NPs shape, size, aspect ratio and size distribution [21]. The solvent, thus, provides means to achieving control over the nanoparticles, which influences the different properties of nanomaterials for specific applications [22].

Among the different solvents used in the synthesis of nanoparticles, oleylamine (OAm), oleic acid (OAc) and hexadecylamine (HDA) are well-known for their extensive use as capping agents in synthesis. This is due to their high boiling point, good coordinating property, and high chemical and thermal stability even up to their boiling points (330 – 360 °C). Due to the good coordinating potential of their ligating atoms (O and N), they have high tendency to form

complexes with the metals at intermediate temperatures, which allows a controlled decomposition of the metal-OAm/OAc/HDA complex to produce nanoparticles.

Bismuth sulphide is an n-type semiconductor with multiple intrinsic properties, such as low direct energy band gap of 1.3 eV, high ionic conductivity, high absorption coefficient (10^4 – 10^5 cm^{-1}) and a good incident photon to electron conversion efficiency ($\sim 5\%$) [23, 24]. It is a unique material whose structure is made up of a lamellar arrangement of Bi^{3+} and S^{2-} in alternating infinite chains [24]; and it prefers the orthorhombic system when it crystallizes out [24-26]. These properties, in addition to its non-toxicity make it an attractive material in different fields of applications such as energy storage [27], photovoltaics [28] and in the removal of pigments from water [29]. Research on Bi_2S_3 has increased recently due to its structural flexibility, since the morphology of a semiconductor remains an important factor when considering their application.

Bismuth sulphide nanostructures of different morphologies have been fabricated by various approaches using different solvents as capping agents and also to direct the growth of the nanomaterials towards different anisotropic patterns. Sarkar *et al.*, [30] reported diverse morphologies of Bi_2S_3 including nanospheres, nanorods and hexagonal nanostructures, prepared by solvothermal decomposition of Bi(III) dithiocarboxylate complex in various solvents. Thioglycolic acid (TGA) has been used as a capping agent to prepare hierarchical nanostructures of Bi_2S_3 , with thioacetamide as the sulphur source [31]. Using TGA as both sulphur source and stability agent in a hydrothermal process, Salavati-Niasari *et al.*, [32] synthesized Bi_2S_3 nanostructures with different morphologies including nanoflower, nanorod and nanobelt. Polyol was used as passivating agent to prepare some flake-like and rod-like Bi_2S_3 nanostructures in a simple refluxing process [33]. Due to the ability of gelatine to complex to metal ions via their polar groups and influence the assembly and morphology of inorganic nanostructures, it has been used to prepare Bi_2S_3 nanorods under microwave irradiation [34]. The single source precursor route offers the benefits of a single step reaction with relatively easy to manipulate synthesis conditions. Compared to the multiple source precursors approach, it has the advantage of containing both elements that are required in the desired product. Therefore, a better control of stoichiometry is guaranteed and there is no need for pre reactions or the use of toxic gases such as H_2S [35]. The use dithiocarbamate as single-source precursors for the synthesis of nanoscale metal sulphides is well established [36]. This has been ascribed to their easy synthesis process and clean thermal decomposition [37-42]. In this research, bismuth(III) tris (*N*-methyl-*N*-phenyl dithiocarbamate) has been used as a single

source precursor to prepare different nanostructures of Bi_2S_3 using solvothermal method in oleylamine, oleic acid and hexadecylamine as capping molecules.

3.2. Experimental section

3.2.1. Chemicals

Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), *N*-methylaniline, hexadecylamine (HDA), oleic acid (OAc) and 1-oleylamine (OAm) were obtained from Merck chemicals. Analytical grade toluene, methanol, and ethanol were purchased from Alfa Chemical Co.

3.2.2. Synthesis of bismuth(III) tris(*N*-methyl-*N*-phenyldithiocarbamate)

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.30 g, 0.003 mol) was suspended in 50 mL water. To this, was added few drops of concentrated HCl until a clear solution was obtained and then followed by 12 mL aqueous solution of ammonium *N*-methyl-*N*-phenyldithiocarbamate (0.001 mol). The mixture was stirred for 1 h and the yellow solid obtained was filtered and rinsed thoroughly with ethanol/water. Pure product was obtained by dissolving in chloroform, filtering and then recrystallizing the product.

Yield: 64%, M.p. 203 - 206 °C. ^1H NMR (CDCl_3) δ = 7.41 – 7.28 (m, 10H, $-\text{C}_6\text{H}_5$), 3.67 (s, 6H, $\text{N}-\text{CH}_3$). ^{13}C NMR (CDCl_3) δ 145.82, 129.55, 128.23, 126.50 ($-\text{C}_6\text{H}_5$), 45.69 ($-\text{CH}_3$), 205.05 ($-\text{CS}_2$). Selected IR, $\nu(\text{cm}^{-1})$: 1489 ($\text{C}=\text{N}$), 1362 (C_2-N), 1002 ($\text{C}=\text{S}$), 3010 ($=\text{CH}$), 2923 ($-\text{CH}$). Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{S}_6\text{Bi}$ (755.84): C, 38.14; H, 3.20; N, 5.56; S, 25.45. Found: C, 38.60; H, 3.40; N, 5.10; S, 24.70.

3.2.3. Synthesis of Bi_2S_3 nanostructures

All experiments were carried out by heat-up method under N_2 atmosphere [43]. In a typical synthesis, 0.25 g of bismuth(III) tris(*N*-methyl-*N*-phenyldithiocarbamate) was added into a 10 mL oleylamine (OAm) in a round bottom flask with a condenser. After stirring at room temperature for 15 min, the mixture was then degassed for 10 min and then backfilled with nitrogen. This process was repeated twice, and then the mixture was heated steadily to 180 °C and maintained for 1 h. Afterwards, the dark solution was cooled down to room temperature, and the product was separated by the addition of methanol and centrifugation. Purification of the product was carried out by centrifugation using a mixture of toluene and ethanol (1:3 v/v) and repeating the process four times to ensure complete removal of the excess capping agent. The same process was repeated using oleic acid (OAc) and hexadecylamine (HDA) as solvent,

and in each case the final products were dispersed in 15 - 20 mL toluene to obtain stable solutions.

3.2.4. Characterization

The complex, bismuth(III) tris(*N*-methyl-*N*-phenyldithiocarbamate), was characterized using Alpha Bruker FTIR spectrophotometer for the identification of functional groups. Elementar, Vario EL Cube for the analysis of the percentage C, H, N, and S, and a Bruker Avance III NMR spectrophotometer (600 MHz) for the (^1H and ^{13}C) NMR measurement in chloroform. The as-synthesized nanostructures were characterized by X-ray diffraction using a Bruker AXS D₈ Discover XRD (Cu K_α = 1.5406Å) X-ray diffractometer operated at 40 KV and 40 mA. The UV-vis-NIR absorption spectra of the nanostructures solutions were measured in toluene using a Perkin Elmer Lambda 750S UV-vis-NIR spectrophotometer. A JEOL JEM 2100 High Resolution Transmission Electron Microscope (HRTEM) was used for TEM imaging and SAED patterns. This was done at an accelerating voltage of 200 kV. Spatula tips of samples were dispersed in Ethanol and sonicated for 30 min and allowed to dry for a few minutes prior to analysis. Scanning electron microscope (SEM) analysis was carried out using a FEI Quanta FEG 250 Environmental Scanning electron microscope (ESEM), and the elemental composition was determined using Oxford X-map 20 detector at 15 kV and using INCA software for energy dispersive X-ray analysis (EDAX).

3.3. Results and discussion

3.3.1. Spectral studies of the bismuth complex

The FTIR spectrum of the complex show $\nu(\text{C-N})$ (thioureide) peak at 1489 cm^{-1} . The position of this band, typical of dithiocarbamates, indicated a partial double bond character [44]. The bond energy falls between the single ($1350\text{--}1250\text{ cm}^{-1}$) and double ($1690\text{--}1650\text{ cm}^{-1}$) bond energies. Only one signal appeared around 1002 cm^{-1} due to the $\nu(\text{C-S})$, supporting a bidentate coordination fashion of the dithiocarbamate ligand [45]. ^1H and ^{13}C NMR spectra of the complex are shown in Figure 3.1. The ^1H NMR spectrum exhibits a signal around 3.67 ppm for the CH_3 protons attached to the nitrogen atom of the dithiocarbamate. A multiplet in the range 7.28–7.41 ppm is attributed to the protons on phenyl ring. Apart from these signals, the peak at 1.55 ppm is due to the residual water peak. The $^{13}\text{CS}_2$ chemical shifts reveal a weak signal, which is usually associated with the backbone carbon (N^{13}CS_2), at 205.0 ppm. The N^{13}CS_2 carbon signals for phenyl ring were observed at 145.82, 129.55, 128.23, 126.50 ppm. The carbon signals due to the methyl proton associated with the N-substituted groups of the

dithiocarbamate resonated at relatively low field around 45.69 ppm; and may be attributed to the electronegativity of the nitrogen atom and the presence of the aromatic ring.

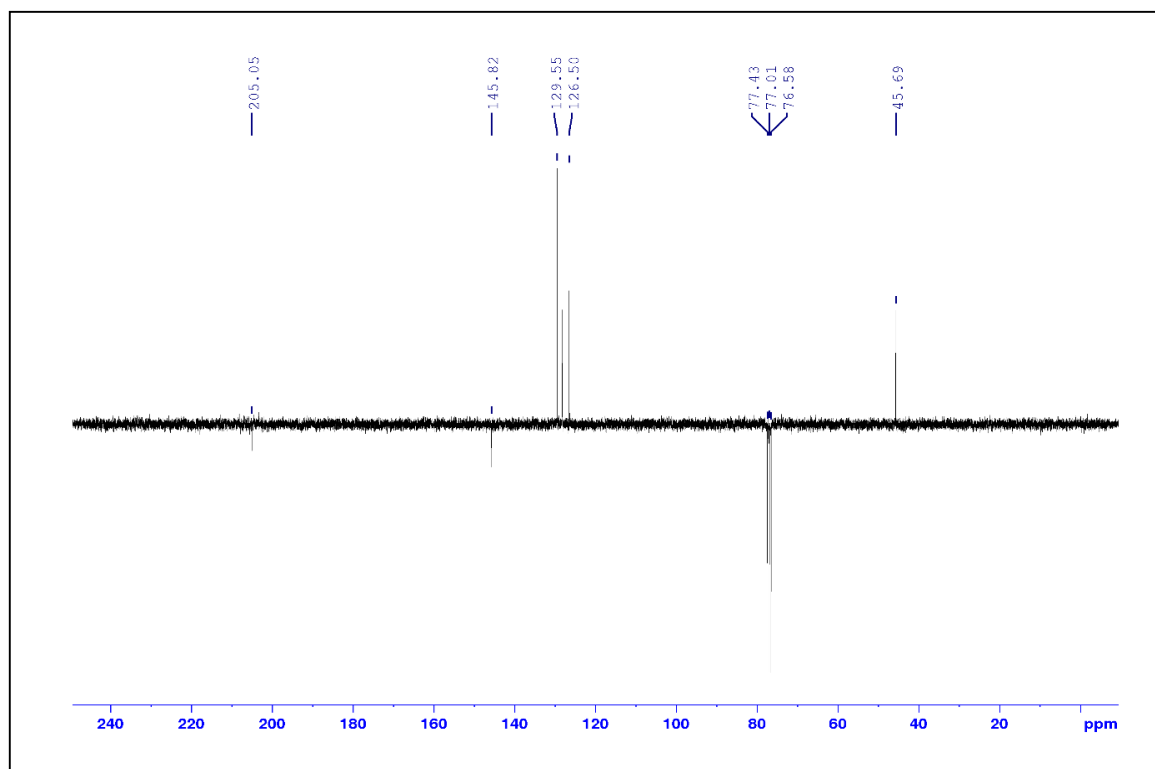


Figure 3. 1: (a) ^1H and (b) ^{13}C NMR spectra of the bismuth(III) tris(*N*-methyl-*N*-phenyl dithiocarbamate) complex.

3.3.2. Synthesis of bismuth sulphide

The nanostructured Bi_2S_3 were synthesized using OAm, OAc and HDA as capping ligand with bismuth(III) tris(*N*-methyl-*N*-phenyldithiocarbamate) as precursor complex. The nucleation of Bi_2S_3 occurred upon the decomposition of the metal complex and subsequent growth or assembly into nanostructures at the reaction temperature. At the optimum reaction temperature of 180 °C, the precursor complex completely decomposed and phase pure Bi_2S_3 nanostructures were formed. Crystal formation has been reported to be controlled by kinetic and thermodynamic growth factors, of which the type of precursor compounds, nature of capping agents and the reaction temperature predominantly govern the morphology and crystalline phase of the product [46, 47]. The effect of the solvent types on the crystal structure and morphology of the synthesized Bi_2S_3 samples were investigated using XRD, SEM, and TEM. In the formation mechanism of the different morphologies, the reaction commenced with the development of weak coordination by the capping ligand to the surface of the bismuth complex at elevated temperature. As the reaction progressed, with increase in temperature, the

decomposition of the complex was followed with nucleation which resulted in Bi_2S_3 nuclei. The growth pattern/rate of the nuclei and likely aggregation into different nanostructures was dependent on the type of capping agent used and the coordinating potency.

3.3.3. Structural analysis

Typical XRD diffraction patterns of the $\text{Bi}_2\text{S}_3(\text{OAm})$, $\text{Bi}_2\text{S}_3(\text{OAc})$, and $\text{Bi}_2\text{S}_3(\text{HDA})$ are presented in Figures 3.2(a) - (c) respectively. All the patterns showed peaks at 2θ values of 24.9° , 28.6° , 31.8° , 39.8° , and 46.5° , which were assigned to the diffraction line produced by (130), (211), (221), (141), and (431) planes; and were attributed to orthorhombic phase bismuthinite Bi_2S_3 (JCPDS 00-017-0320), with space group Pbnm. One of the most important aspects revealed from these patterns was the difference in the intensity of diffraction peaks based on the type of capping agents used. In $\text{Bi}_2\text{S}_3(\text{OAm})$, they seem to be a significant intensification of the (2 1 1) peak, compared with the characteristic (1 3 0) diffraction peak of Bi_2S_3 . This was an indication that there existed a bias of orientations of these crystallographic plane [32]. The ratio of the intensities of the (211) to the (130) diffraction peak, $I(211)/I(130)$, of $\text{Bi}_2\text{S}_3(\text{OAm})$, $\text{Bi}_2\text{S}_3(\text{OAc})$, and $\text{Bi}_2\text{S}_3(\text{HDA})$ were obtained as 1.02, 0.57 and 0.09 respectively. The smaller ratio values obtained for $\text{Bi}_2\text{S}_3(\text{OAc})$ and $\text{Bi}_2\text{S}_3(\text{HDA})$ compared to the value for standard Bi_2S_3 is suggestive of a (130) preferred orientation, contrary to the orientation of the $\text{Bi}_2\text{S}_3(\text{OAm})$ with a significantly higher value. This might be attributed to the growth of Bi_2S_3 nanorods, which usually show a preferential direction along the c-axis due to its intrinsic crystal structure [48]. Studies have shown that Bi_2S_3 possesses a lamellar structure in which the Bi_2S_3 units are linked in such a way that they form infinite chains that are parallel to the c-axis and are joined via weaker van der Waals interactions [49, 50]. The enhanced growth rate along the c-axis is facilitated by a stronger covalent bond between the planes which are perpendicular to the c-axis.

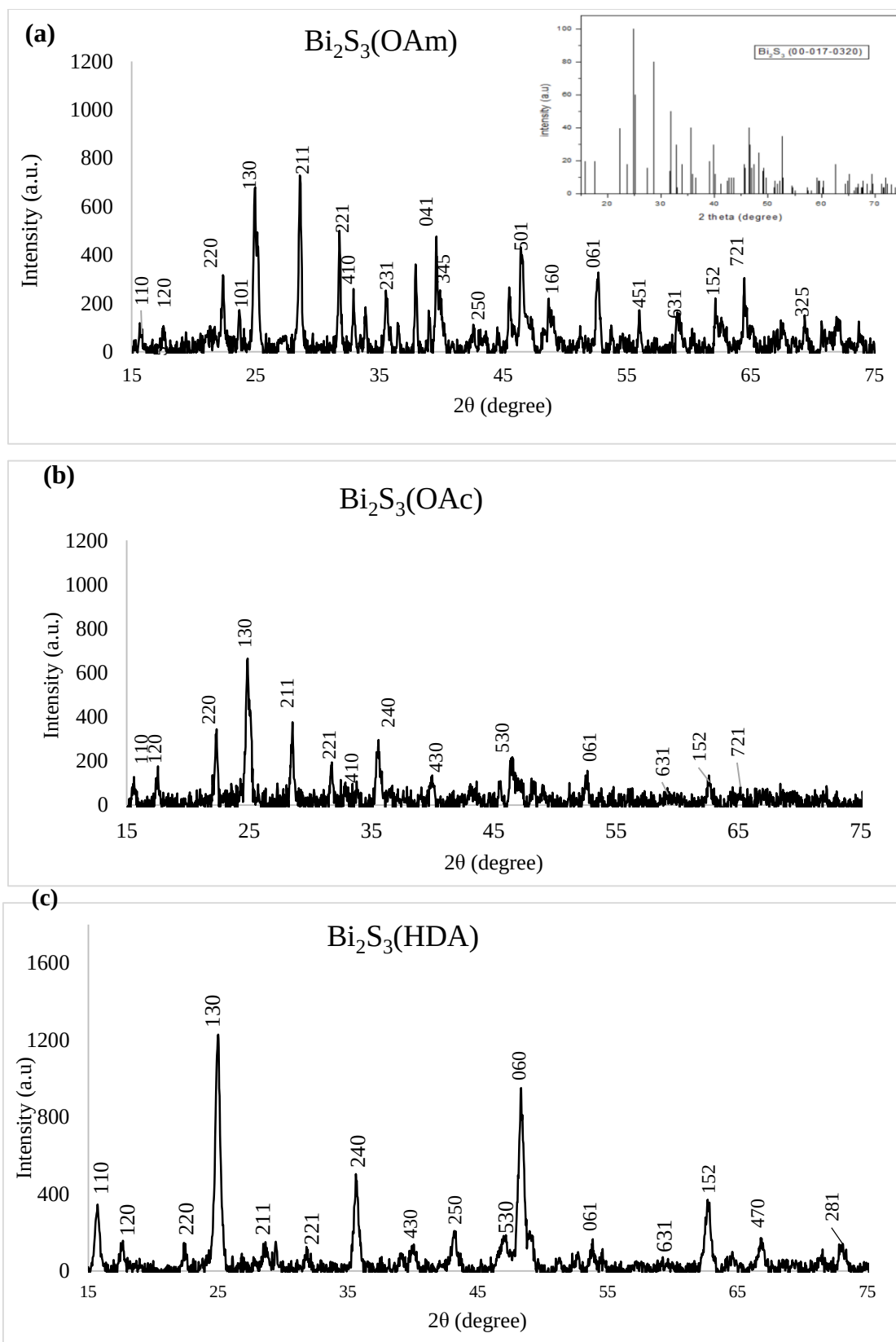


Figure 3. 2: XRD patterns of Bi_2S_3 synthesized by the thermal decomposition of bismuth(III) tris(N-methyl-N-phenyldithiocarbamate) in (a) oleylamine, (b) oleic acid, and (c) hexadecylamine.

3.3.4. Morphological studies

Figures 3.3, 3.4, and 3.5 demonstrate the SEM and TEM micrographs of the synthesized Bi_2S_3 nanoparticles in oleylamine, oleic acid and hexadecylamine respectively. The figures illustrate the effect of the different solvents on the morphology of the synthesized Bi_2S_3 . The SEM micrographs of $\text{Bi}_2\text{S}_3(\text{OAm})$ (Figure 3.3a) showed short rods embedded in interlocking sheets, while the TEM image showed distinct rods with an average diameter of 46 nm and length of 128 nm, shown in the particle size distribution histogram in the inset of Figures 3.3b. The SEM and TEM micrographs of $\text{Bi}_2\text{S}_3(\text{OAc})$ in Figures 3.4a and b respectively, show predominantly spherical shape of Bi_2S_3 . The particle size was calculated from the TEM image by considering a reasonable number of the particles and plotting their size histogram as shown in the inset of Figure 3.4b. An average size of 28 nm was obtained. A flower-like morphology was obtained for the $\text{Bi}_2\text{S}_3(\text{HDA})$ sample as shown in the SEM image of Figure 3.5a, which also appeared as agglomeration of interlocked ultrathin fine structures in the TEM micrograph (Figure 3.5b). The HRTEM images of the three samples, presented in Figures 3.3c, 3.4c and 3.5c, indicated that the particles were crystalline with $\text{Bi}_2\text{S}_3(\text{OAm})$ displaying the highest crystallinity.

The suitability and versatility of oleylamine as the reaction medium has been demonstrated for a broad range of nanomaterials in chemical synthesis [51]. OAm has been reported to work not only as a stabilizer for the oriented growth of nanoparticles, but also acts as a catalyst, thereby accelerates the thermal decomposition of precursors. Therefore, it controls both nucleation and growth kinetics processes [51]. It combines its roles as solvent and surfactant, with its suitability as reducing agent in materials synthesis. Unlike hexadecylamine which is solid at room temperature, OAm has advantage of existing in liquid state and is easily removed by centrifugation.

The variation in morphology of nanoparticles during the solvothermal process, could be attributed to their growth mechanisms. This is dependent on the capping agent, which acts by suppressing the growth of certain crystal facet via coordination to the metal cations [52]. The properties of the capping agents have been reported to play important role in controlling both the size and morphology of nanoparticles [53]. The growth of nanostructures is dependent on Ostwald ripening and oriented attachment. Capping agents can largely influence the oriented attachment processes since they directly modify the nanostructures surface [54]. The different capping agents used have different molecular weights, and this also influences the pattern of assembly of the capped nanoparticles. In the presence of the capping ligands, the mechanism by which the nanoparticles growth proceeds largely depends on the nature of the capping

ligands, the concentration of the monomer that is formed, in addition to the amount of the capping agent that is present to prompt nucleation. While the growth of the monomer attachment characteristically gives the best route for the formation of single crystalline materials, the coalescence growth typically leads to nanoparticles which have multiple twin structures including high-energy facets [55]. The functional groups of the capping agents are different from one other. For example, oleic acid has a carboxylic acid functional group, HDA and oleylamine possesses an ammine end, and in addition both of them have double bonds between C-9 and C-10. The capping agents form coordination bonds with Bi^{3+} ion and are able to modify the size and morphology of Bi_2S_3 nanoparticles during crystal growth in the solvothermal system. Due to the high electronegativity of the reacting sites of oleic acid, the molecules could orient and attach to the surface of the nanoparticles with their $-\text{OH}$ groups during the synthesis process. This is possible since the molecules are capable of approaching the Bi_2S_3 surface at all facets (along all axis and all planes); consequently, resulting in the formation of spherical nanoparticles. The oleylamine and hexadecylamine have nitrogen as ligating atom, thus the interaction of these ligands with bismuth cations in the solvothermal medium was relatively weaker compared to the oleic acid. This would allow growth of particles either via Ostwald ripening or oriented attachment. Thus, in $\text{Bi}_2\text{S}_3(\text{OAm})$ and $\text{Bi}_2\text{S}_3(\text{HDA})$, the possible preferential adsorption of ligands on certain facets of the nanoparticle surface might be one of the possible contributions to the anisotropic morphology of the nanostructures.

The thermal decomposition of single source precursor in HDA has been reported to yield anisotropic morphologies of nanocrystals [56]. The mechanism of the nanostructure pattern has been attributed to the crystalline phase formation during nucleation, in addition to the growth rate difference between the surfaces of the crystal. These processes finally determine the overall structure of the nanostructure. Hexadecylamine could act both as a shape controlling ligand and also a stabilizing solvent. In the present study, HDA seems to enhance the growth rate towards one direction which resulted in ultrathin Bi_2S_3 nanorods (Figure 3.5b). The elemental mapping images in the (e) and (d) of Figures 3.3 – 3.5 show that bismuth and sulphur were homogeneously distributed throughout the scan area of $\text{Bi}_2\text{S}_3(\text{OAm})$, $\text{Bi}_2\text{S}_3(\text{OAc})$, and $\text{Bi}_2\text{S}_3(\text{HDA})$, suggesting a good dispersion of the elemental composition of the nanostructures.

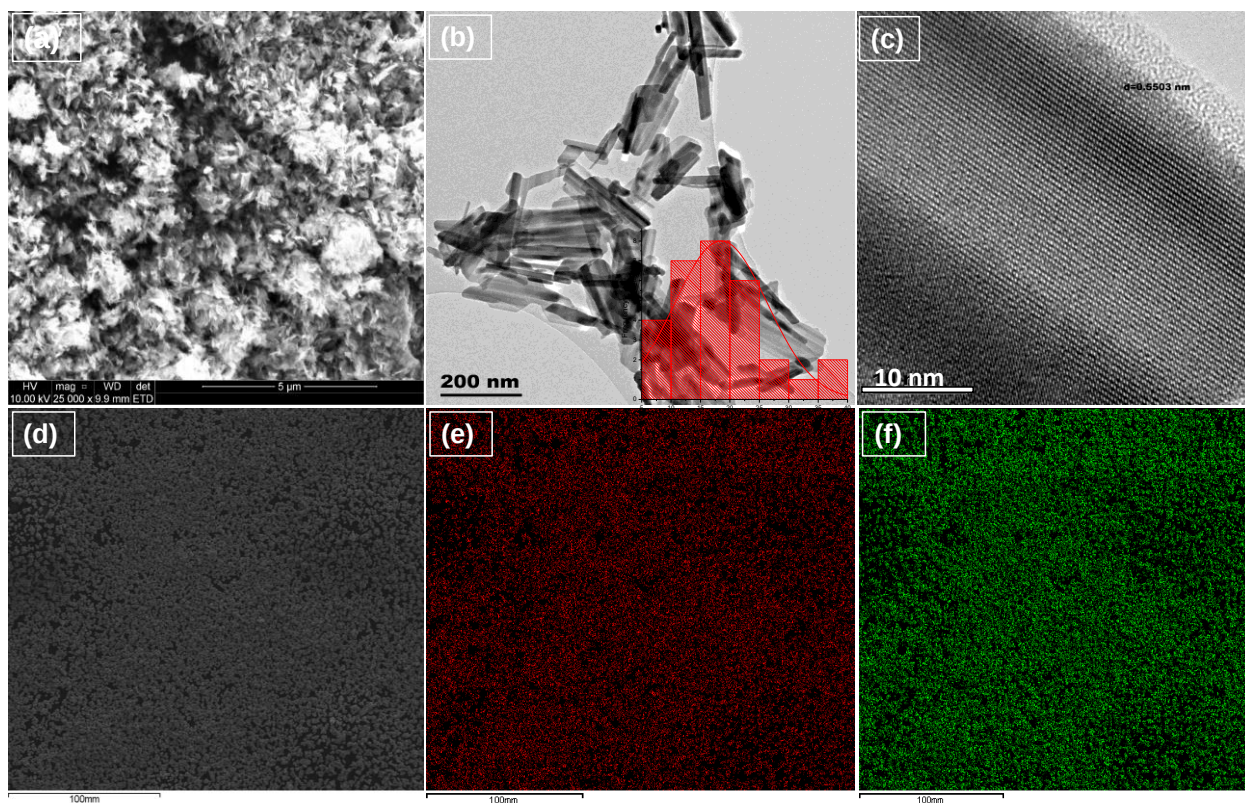


Figure 3. 3: (a) SEM, (b) TEM, (c) HRTEM, (d) elemental mapping of Bi_2S_3 (e) Bi, and (f) S elements of $\text{Bi}_2\text{S}_3(\text{OAm})$ obtained in oleylamine.

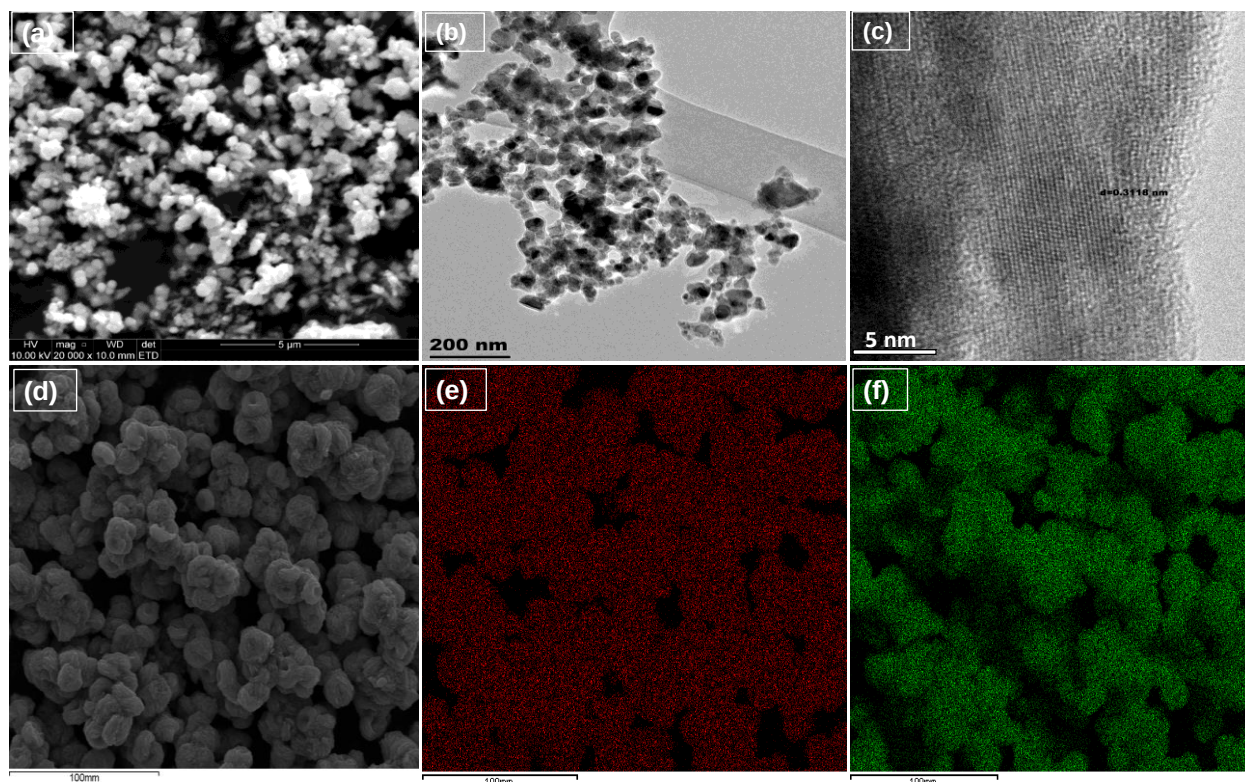


Figure 3. 4: (a) SEM, (b) TEM, (c) HRTEM, (d) elemental mapping of Bi_2S_3 (e) Bi, and (f) S elements of $\text{Bi}_2\text{S}_3(\text{OAc})$ obtained in oleic acid.

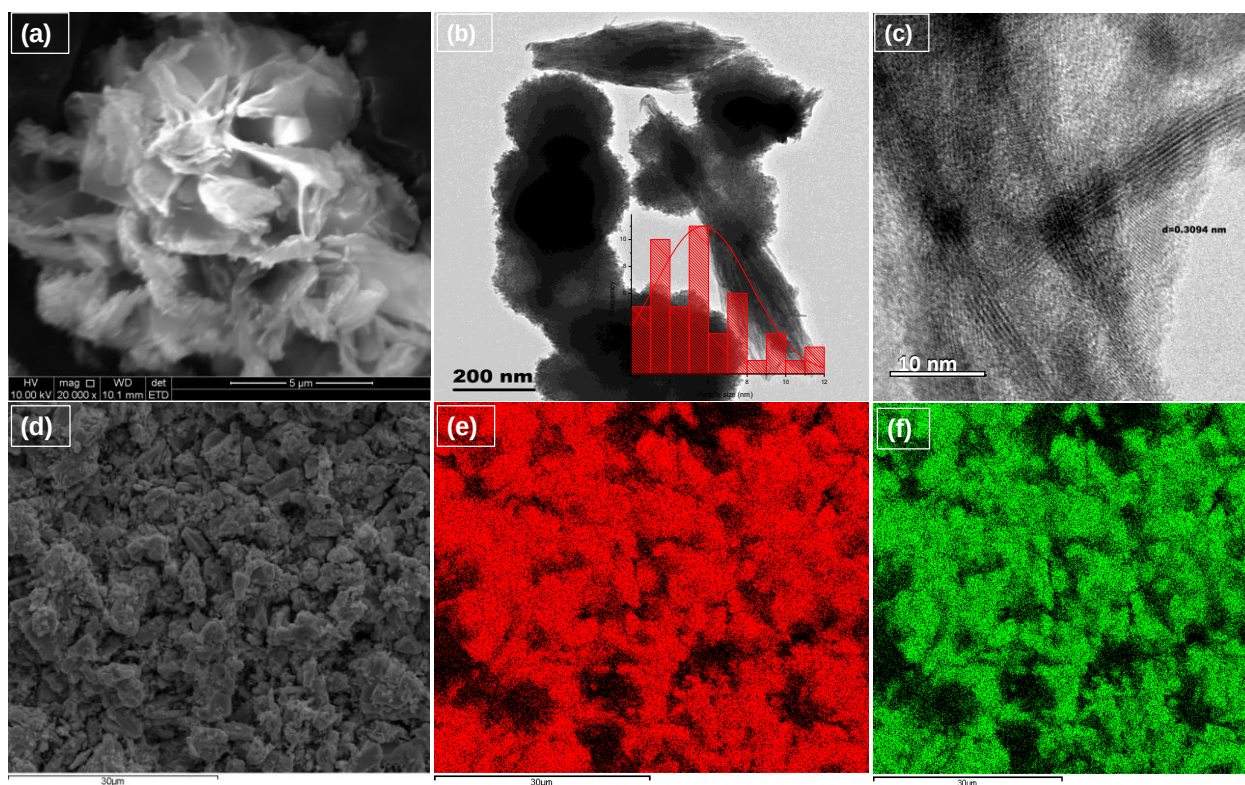


Figure 3. 5: (a) SEM, (b) TEM, (c) HRTEM, (d) elemental mapping of Bi₂S₃ (e) Bi, and (f) S elements of Bi₂S₃(HDA) obtained in hexadecylamine.

The representative EDX spectrum presented in Figure 3.6 shows the distinct peaks corresponding to bismuth (Bi) and sulphur (S) and no impurity or extra peaks were detected which confirmed the high purity of the samples. The weight % of Bi and S present in Bi₂S₃(OAm), Bi₂S₃(OAc), and Bi₂S₃(HDA) are given as: 83.39, 16.61; 83.06, 16.94; and 84.25, 15.75 respectively. The weight % of Bi and S in Bi₂S₃ is ideally expected to be 81.29 and 18.71% respectively. The obtained values are quite close to this, which revealed that the stoichiometric ratio of Bi to S was approximately 3:2. Although, the percentage Bi appeared slightly higher than the expected value, the slight percentage excess of Bi might be due to the absorption of excessive bismuth ions on the surface of nanomaterials [57]. Figure 3.7 demonstrates the fabrication of Bi₂S₃(OAm), Bi₂S₃(OAc), and Bi₂S₃(HDA) and their morphological variations. Significant differences in morphology are obvious for different capping materials used.

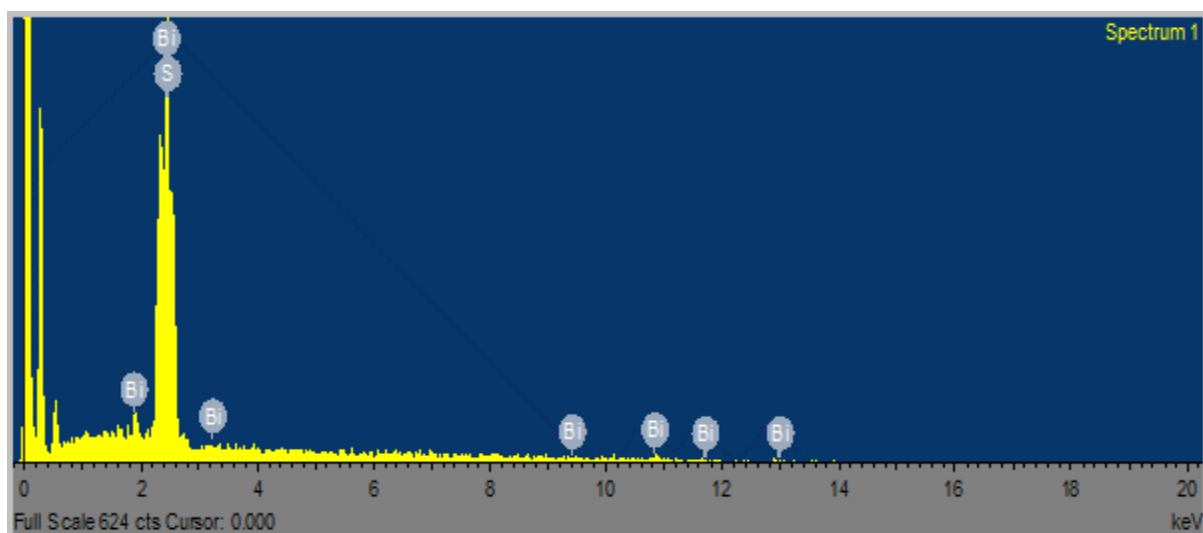


Figure 3. 6: EDX spectrum of the as-prepared Bi_2S_3 using bismuth(III) tris(N-methyl-N-phenyldithiocarbamate) as single source precursor compound.

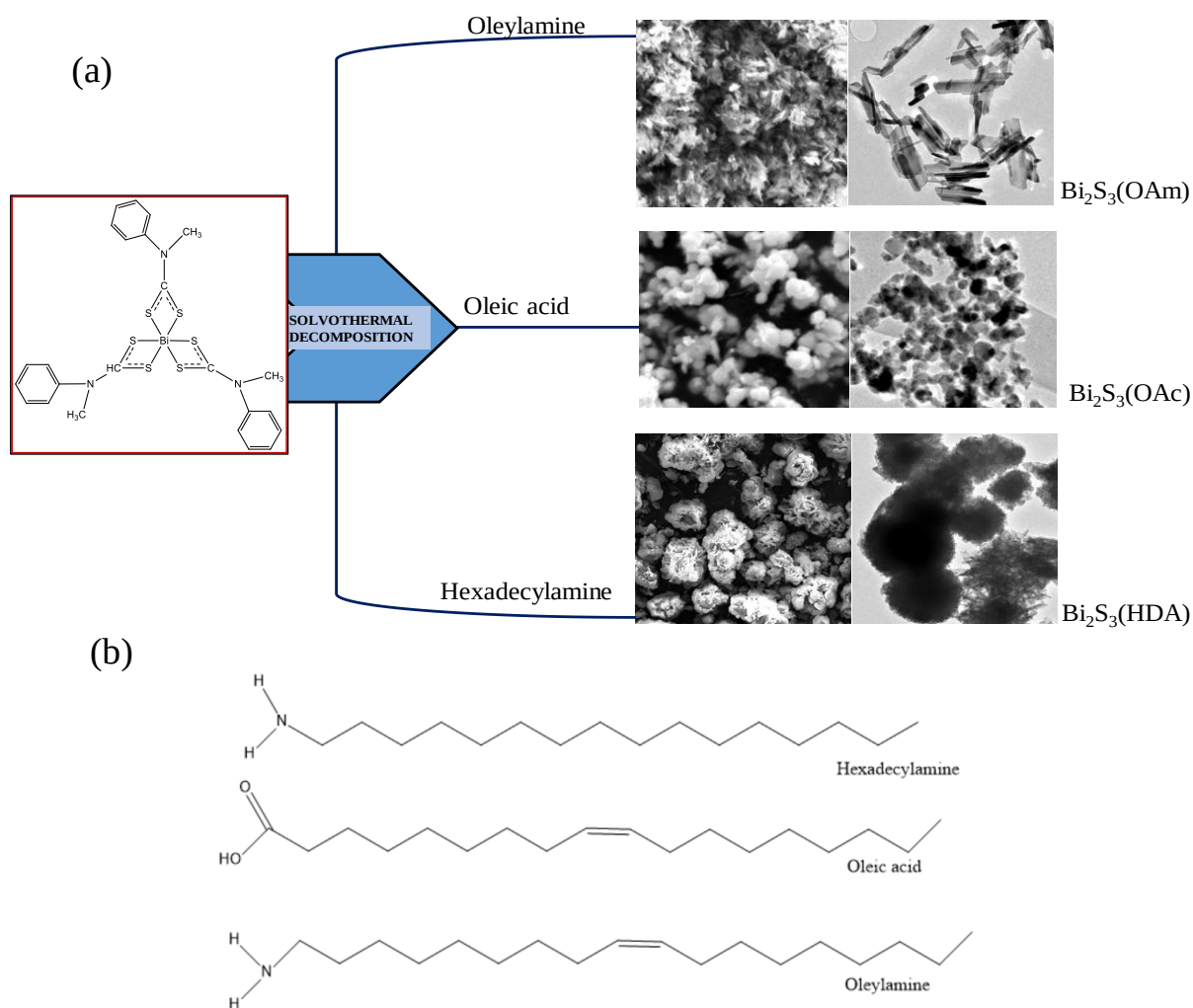
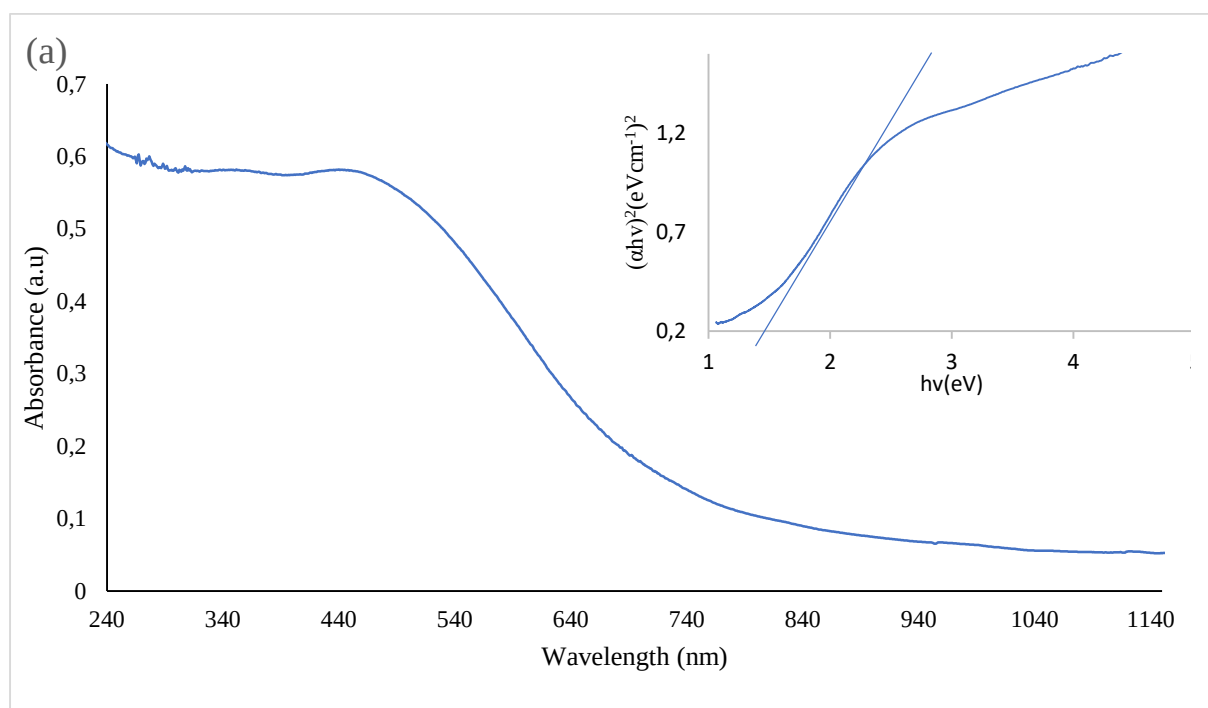


Figure 3. 7: (a) Fabrication of $\text{Bi}_2\text{S}_3(\text{OAm})$, $\text{Bi}_2\text{S}_3(\text{OAc})$, and $\text{Bi}_2\text{S}_3(\text{HDA})$ and their shape variations with change in capping materials, (b) structures of the different capping ligands.

3.3.5. Optical studies

The UV–vis–NIR absorption and the corresponding photoluminescence spectra of the as-prepared $\text{Bi}_2\text{S}_3(\text{OAm})$, $\text{Bi}_2\text{S}_3(\text{OAc})$, and $\text{Bi}_2\text{S}_3(\text{HDA})$ samples are presented in Figure 3.8. As shown in Figure 3.8a, $\text{Bi}_2\text{S}_3(\text{OAm})$ has a maximum absorption around 565 nm, while the spectrum of $\text{Bi}_2\text{S}_3(\text{OAc})$ clearly show a broad band absorption, with peak around 300 nm (Figure 3.8b). The $\text{Bi}_2\text{S}_3(\text{HDA})$ exhibited a broad but low absorption which ranged from UV to visible region [58]. The energy band gap calculated from the Tauc plot of the respective $(\alpha h\nu)^2$ vs. $h\nu$ (where α is the absorbance, h is Planck constant and ν is the frequency) gave the values 1.46, 1.50 and 1.72 eV for the $\text{Bi}_2\text{S}_3(\text{OAm})$, $\text{Bi}_2\text{S}_3(\text{OAc})$ and $\text{Bi}_2\text{S}_3(\text{HDA})$ respectively. These showed an increase in the energy band gap value of 1.3 eV reported of for bulk bismuth sulphide [59].



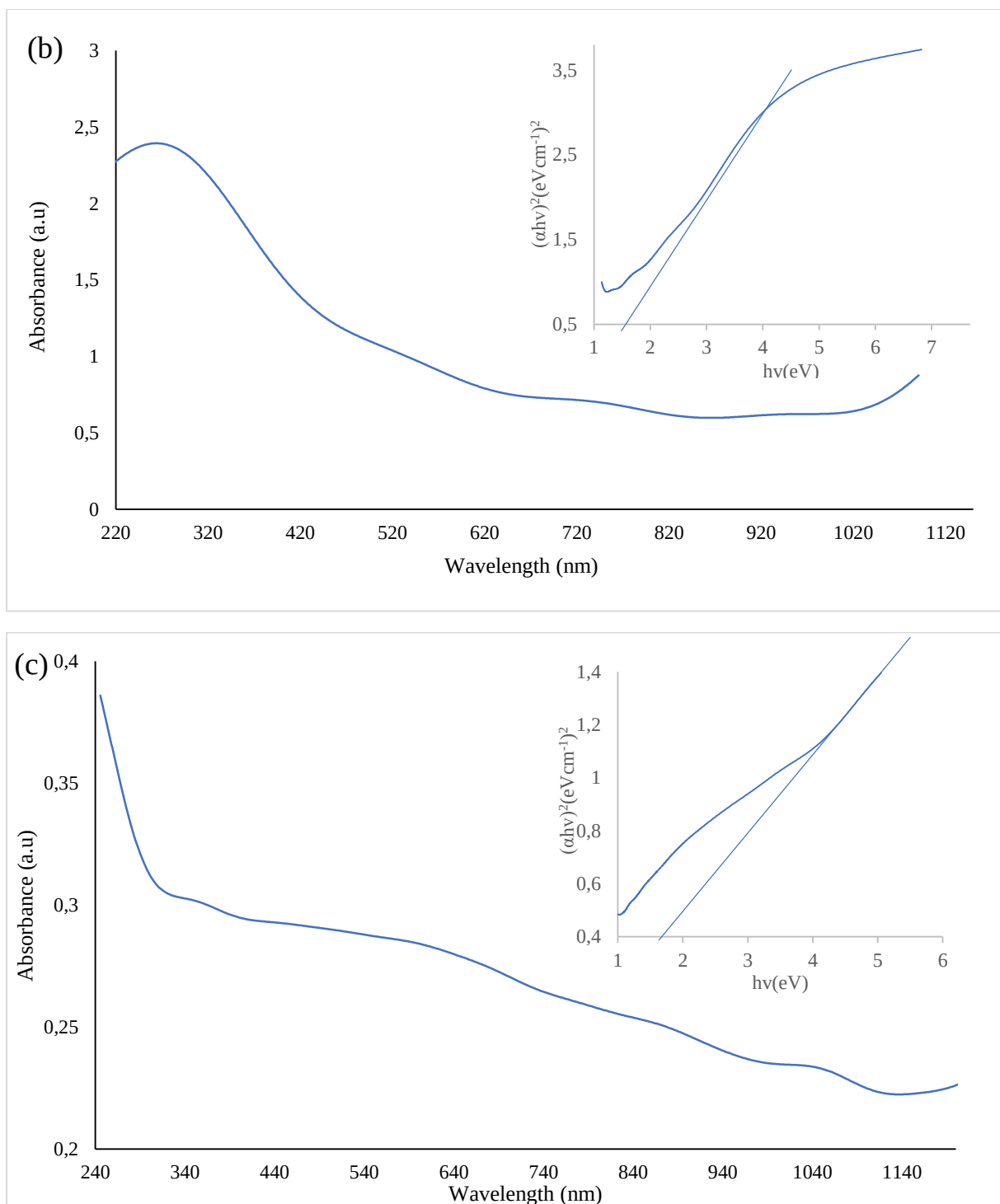


Figure 3. 8: UV-vis-NIR and their respective Tauc plot of Bi_2S_3 synthesized using bismuth(III) tris(N-methyl-N-phenyldithiocarbamate) in (a) oleylamine- $\text{Bi}_2\text{S}_3(\text{OAm})$, (b) oleic acid- $\text{Bi}_2\text{S}_3(\text{OAc})$, and (c) hexadecylamine- $\text{Bi}_2\text{S}_3(\text{HDA})$.

The photoluminescence (PL) spectra of the nanostructures at an excitation wavelength of 350 nm are presented in Figure 3.9, and they showed slight variation in intensity, broadness and positions of maximum peak. The photoluminescence spectra of the $\text{Bi}_2\text{S}_3(\text{OAm})$ exhibited a narrow peak at 615 nm with a weak broad shoulder at 665 nm, whereas $\text{Bi}_2\text{S}_3(\text{OAc})$ and $\text{Bi}_2\text{S}_3(\text{HDA})$ nanostructures displayed only a peak at 646 and 648 nm respectively corresponding to band edge emission. In the spectra of $\text{Bi}_2\text{S}_3(\text{OAm})$ and $\text{Bi}_2\text{S}_3(\text{HDA})$ nanostructures, the narrow peak widths were indicative of narrow size distribution of the Bi_2S_3 . In contrast, $\text{Bi}_2\text{S}_3(\text{OAc})$ showed a broad emission in the range 620 – 675 nm, with maximum at 646 nm. The accompanying broad shoulder in the spectrum of $\text{Bi}_2\text{S}_3(\text{OAm})$ may be indicative that a small portion of rods with different size distributions could also be present in addition to the nanorods that exhibited emission at 615 nm while the broadness of the peak could be attributed to a large distribution of the nanostructure [60, 61].

The optical properties of nanoparticles could be affected by factors which are inherent in the materials' properties such as the morphology, size, and concentration of the nanoparticles in solvent. In addition to this, external factors including the type of capping agents and dielectric constant of the solvent also play significant roles. In a solution of the nanoparticles, a charge transfer from the attached ligand molecules to nanoparticles could affect the optical and also the magnetic properties of the nanoparticles, and could cause a spectral shift [62]. Therefore, nanoparticles whose capping ligands contain functional groups such as amine, carbonyl and hydroxyl that act as electron donor or electron acceptor groups could form internal charge transfer states. Hence, with excitation there are possibilities of increase in charge separation within the nanoparticles. Furthermore, when there is an increase in the dielectric constant of the surrounding medium or solvent, the emission wavelength could shift to red or blue or even remain unaffected. The possibility of this shift or its extent is dependent on surface defects and therefore on the nature of the capping agent [63, 64]. Other factors that could affect the spectral shifts are the polarity and viscosity of the solvent, as well as changes in decay rates of radiative and non-radiative transitions [62]. The presence of some or all of these factors could make emission behaviour a complex phenomenon.

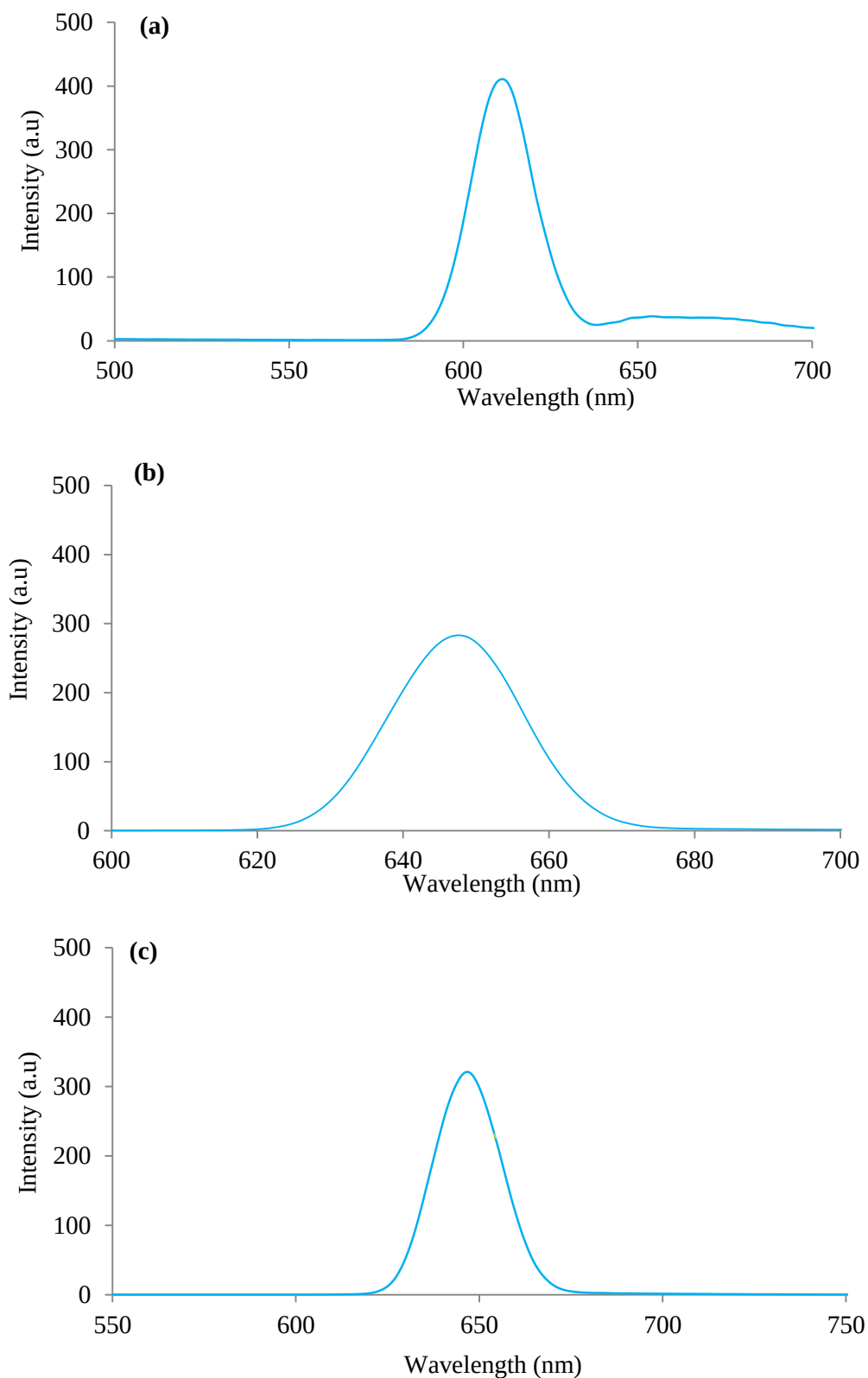


Figure 3. 9: Photoluminescence spectra of Bi_2S_3 synthesized using bismuth(III) tris(N-methyl-N-phenyldithiocarbamate) in (a) oleylamine- $\text{Bi}_2\text{S}_3(\text{OAm})$, (b) oleic acid- $\text{Bi}_2\text{S}_3(\text{OAc})$, and (c) hexadecylamine- $\text{Bi}_2\text{S}_3(\text{HDA})$.

3.4. Sub-Conclusion

A variation in the morphology and size of bismuth sulphide nanoparticles was successfully achieved by using different solvents including oleylamine, oleic acid and hexadecylamine at 180 °C. XRD pattern showed that the crystallinity of the Bi₂S₃ was influenced by the solvent media, and a bias of orientations existed in the (2 1 1) crystallographic plane of the samples obtained using oleylamine. The TEM measurements showed that a significant difference occurred in the growth pattern and overall shape of nanoparticles due to the variation of solvents at uniform temperature and time of reaction. Since, the optical and electronic properties, which dictates the areas of application of different nanomaterials, is influenced by their morphology and structural properties, it implies that the synthesis of bismuth sulphide in oleylamine, oleic acid and hexadecylamine could be used to direct their growth patterns and areas of applications.

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CHAPTER FOUR

Synthesis, characterization, computational studies, and photocatalytic properties of Cu doped Bi_2S_3 nanorods

4.1. Introduction

Environmental pollution is one of the major global challenges facing humanity in the present century. With the ever-increasing quest for urbanization and industrialization, the increase in environmental pollution continues to possess a serious health hazard for the entire world [1]. Both chemical and other allied industries continue to release toxic waste into the environment at an alarming rate. An estimated 300 - 400 million tons of hazardous substances are released into the environment every year [2].

In order to deal with the problem of environmental pollution, numerous technologies have been developed such as the use of conventional activated sludge or activated carbon, membrane filtration and chemical treatment processes including chlorination, ozonation, UV irradiation, and potassium permanganate oxidation. The success of these technologies has been impeded by their inability to achieve pollutant removal to the standard levels required for wastewater reuse [3, 4]. In addition, in some instances, the energy demand puts a further strain on the already stretched available energy.

Photocatalytic degradation of organic pollutants using semiconductor nanomaterials has attracted much attention recently because it is environmentally friendly and inexpensive. Despite its merits, there is still an ongoing search for photocatalytic materials, which allows for the optimal use of solar energy for photocatalytic degradation of pollutants. The desired material must, thus, possess a narrow band gap and show a high absorption of light in the visible range of the solar radiation. Although, there are several factors that may influence the activity of a semiconductor photocatalyst such as structure and morphology, temperature, pH, and corrosion resistance, the selection of photocatalytic materials is strongly influenced by the band gap of the material as this determines the absorption and efficient utilization of light energy [5].

Bismuth sulfide (Bi_2S_3) is a semiconductor with a relatively narrow band gap in the range 1.3-1.7 eV and absorbs both visible and near-infrared lights. This makes it an excellent candidate for several optoelectronic devices such as gas sensing, photovoltaics, X-ray computed imaging and visible-wavelength photodetectors. Despite the strong absorbance and ideal n-type electron acceptor behavior of Bi_2S_3 , its performance as a photocatalyst is still limited, which makes the

modification of Bi_2S_3 an important approach for improving its optoelectronic performance [6]. The photocatalytic performance of Bi_2S_3 can be controlled by facilitating the generation of electron-hole pairs and minimizing the rate of charge carrier recombination. This could be achieved by different approaches such as developing various heterostructures including $\text{Bi}_2\text{S}_3/\text{SnS}_2$ [7], $\text{Bi}_2\text{S}_3/\text{BiPO}_4$ [8], $\text{Bi}_2\text{S}_3/\text{MoS}_2$ [9], and $\text{Bi}_2\text{S}_3/\text{ZnS}_2$ [10], and metal and non-metal doping in order to enhance the photocatalytic activity of Bi_2S_3 . Doping has been reported to have immense effect on the charge transport behavior of semiconductors by increasing the concentration and lifetime of charge carriers [11, 12]. Supplementary energy levels created by the dopant ions can act as charge traps, thus reducing the recombination of photogenerated charge carries. Some reported non-metals/metals ions that have been used as dopant for Bi_2S_3 include Se [13], Eu^{3+} [14], Sn^{2+} [15] and Co^{2+} [16]. Addition of transition elements as dopants in semiconductors can enhance their photostability and their crystalline lattice. In addition, the use of two dopants (co-doping) has been used to lower the defect formation energy via Coulombic interaction or covalent coupling between co-dopants and decreases the transition energy level of the emergent semiconductor through level repulsion. This is also accompanied by reticular distortions, thereby resulting into defects that could also lead to higher efficiency in the separation of electron-hole charges [17, 18].

Copper-doping has been reported to induce band gap reduction and also reduce the charge carrier recombination [19]. Cu^{2+} ion is also a notable luminescence activator, which by the generation of confined impurity concentration can alter the luminescence of the material. In this present work, an investigation of the effect of copper doping on the the structural, morphological and optical properties of Bi_2S_3 has been studied. The photocatalytic activity of the $\text{Cu-Bi}_2\text{S}_3$ was further explored for the degradation of methyl orange.

4.2. Experimental and Materials

4.2.1. Materials

All chemicals used in this study were of analytical grade with 99% purity (Merck chemicals) and were used without further purification. They include Bismuth(III) nitrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], and Copper(II) nitrate hemi-pentahydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$], ethylene glycol (EG), dodecanethiol-1 (DDT), oleylamine (OAm), chloroform, N-alkyl aniline, ammonia solution (NH_4OH), carbon disulphide (CS_2), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and deionized water (H_2O) were also used.

4.2.2. Preparation of bismuth(III) dithiocarbamate complexes

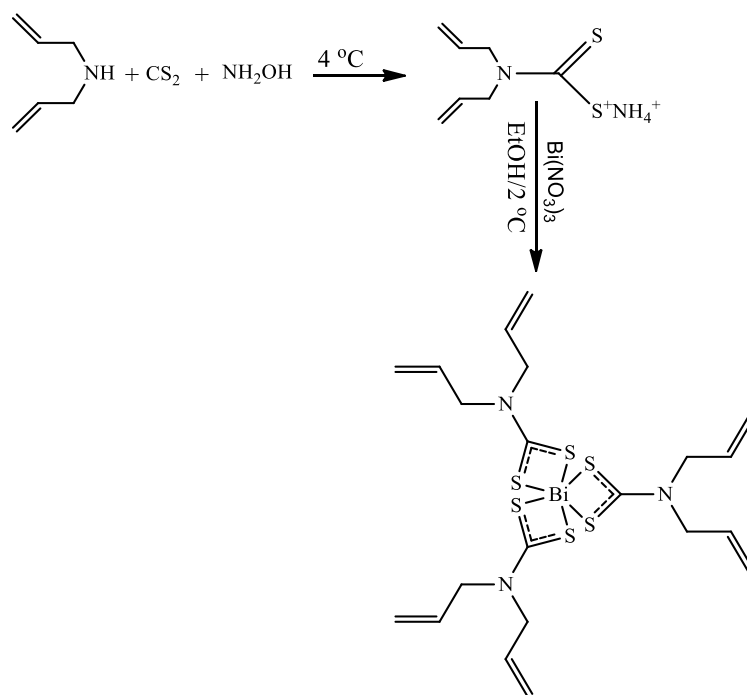
4.2.2.1. Synthesis of diallyldithiocarbamate ligand

The dithiocarbamate ligand was prepared by modifying an earlier method reported by Adeyemi, Onwudiwe [20]. In a typical synthesis allyl amine (2.72 mL, 0.01 mol) and aqueous ammonia (1.50 mL, 0.01 mol) were added into a round bottomed flask and cooled to 4 °C using ice bath. After 15 min, carbon disulphide (0.60 mL, 0.01 mol) was slowly added to the mixture, stirred for about 4 - 6 h, and then filtered by suction. The product obtained was then washed with cold ethanol and kept for further use.

4.2.2.2. Synthesis of bismuth(III) tris(diallyldithiocarbamate) complex

The bismuth complex was prepared by reacting an aqueous solution of diallyldithiocarbamate ligand with $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$, in 3:1 mol ratio (ligand to metal ion). Then, the precipitate formed was stirred for 1 h, filtered, and then washed thoroughly using a mixture of ethanol (50 mL) and water (150 mL). The pure complex was obtained by dissolving the crude product in chloroform, filtering to remove the by-product and subjecting the filtrate to slow evaporation. The reaction scheme for the formation of the metal complex is as shown in scheme 4.1.

Yield: 64%, M.P. 259 °C. ^1H NMR (CDCl_3) δ = 7.29 (s, 3H, $-\text{CH}$), 5.78-5.89 (m, 6H, $=\text{CH}$), 5.19-5.81 (s, 6H, $\text{H}_2\text{C}=\text{}$), 4.33-4.47 (d, 12H, CH_2). ^{13}C NMR (CDCl_3) δ 131.42, 119.00 ($-\text{CH}_2=\text{CH}_2$), 45.69 ($-\text{CH}_3$), 203.62 ($-\text{CS}_2$). Selected IR, FTIR, ν (cm^{-1}): 1458 ($\text{C}=\text{N}$), 1215 (C_2-N), 920 ($\text{C}=\text{S}$), 2984 ($-\text{CH}$), 3087 ($=\text{CH}$), 544 ($\text{S}-\text{C}$), 640 ($\text{Bi}-\text{S}$)



Scheme 4. 1: Synthesis route of Bi(III) tris (diallyldithiocarbamate) complex.

4.2.2.3. Characterization of the complex

The infrared spectral study of the complex was done using Fourier-transform infrared (FTIR) spectrometer (Nicolet 560), in the wavenumber range of $4000 - 3000 \text{ cm}^{-1}$ at room temperature. The Nuclear Magnetic Resonance (NMR) spectra were recorded using a 600 MHz Bruker Avance III NMR spectrometer for ^1H and ^{13}C NMR analysis. The melting point measurement was done using a Gallenkamp melting point instrument.

4.2.3. Preparation of Bi_2S_3 , and Cu- Bi_2S_3 nanoparticles

Bi_2S_3 nanorods were prepared following an earlier reported solvothermal method [21]. In a typical synthesis, 0.25 g of the complex was dispersed in 25 mL of ethylene glycol (EG) and sonicated for 1 h. The mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180°C for 4 h. Afterwards, the autoclave was cooled to room temperature, the obtained black precipitate was washed several times with ethanol to remove unreacted precursor and dried for further characterization. For the synthesis of Cu-doped Bi_2S_3 , the same preparation procedure was employed, with $\text{Cu}(\text{NO}_3)_2$ introduced into the system. The samples were designated as Cu-BiS(x), where “x” represents the concentration of $\text{Cu}(\text{NO}_3)_2$ with respect to the precursor complex. The concentration, x was set at 0.2, 0.4, 0.6, 0.8, and 1.0 mol.

4.2.3.1. Characterization of the Bi₂S₃ and Cu-doped Bi₂S₃ nanorods

The absorption spectra of all the samples were obtained using a variant UV-vis spectrophotometer, measured in the wavelength range of 400 - 1200 nm. The photoluminescence (PL) spectra were measured using Perkin Elmer LS 45 Fluorimeter. Powder X-ray diffractogram (XRD) of the nanoparticles were recorded on a Bruker D8 Advanced XRD machine, equipped with a proportional counter using Cu K α radiation ($\lambda=1.5405$ Å, nickel filter). Samples were added on a flat steel sample holder and scanned from 10 to 80 °C. The diffraction peaks were matched with recorded standards in JCPDS database. The surface morphology of the nanoparticles was studied using scanning electron microscopy-SEM. Energy dispersive X-ray- EDX, was used to determine the elemental composition of the nanoparticles.

4.2.4. Computational method

First principle calculations were carried out based on the density functional theory (DFT) method, by employing the pseudopotential plane wave as implemented in CASTEP code [22, 23]. The structural model of Bi₂S₃ (ICSD 201066) was used as starting sets. The electronic exchange-correlation energy (XC) was treated using the generalized gradient approximation (GGA) together with Perdew–Burke–Ernzerhof parameterization (PBE) [24, 25]. The PBE-GGA+U [26] scheme (where U is the Hubbard Coulomb energy term, U=2.5 eV) was employed for the computation of the electronic and magnetic properties of Cu-doped Bi₂S₃. The norm-conserving pseudopotential was used to describe the ionic core and valence electron interactions. An energy cutoff of 400 eV for the plane wave basis set and a 4×13×4 special Monkhorst-Pack [27, 28] k-point mesh for the Brillouin zone (BZ) were adopted for the two structure. The BFGS (Broyden-Fletcher-Goldfarb-Shannon) algorithm [29] was used to determine the minimum energy of the crystal structure. The atomic force, maximum displacement, and total energy convergence criteria were 0.05 eV Å⁻¹, 0.002 Å, and 10⁻⁶ eV, respectively.

4.2.5. Photocatalytic Study

The photocatalytic activity of the prepared Bi₂S₃ nanorods was evaluated for methyl orange (MO) degradation using a photocatalytic reactor. In a typical process, 10 mg of the catalyst was measured into the reaction chamber, followed by the addition of 50 mL of 10 mg/L MO. The solution was allowed to stir in the dark for 30 min to achieve adsorption-desorption equilibrium. During the process, aliquots were taken from the test solution at 10 min intervals and filtered to remove the catalyst particles. The concentration of the MO was monitored by

measuring the absorbance of the solution over the wavelength range of 200 - 800 nm. The percentage degradation with time was calculated using Eq. 1:

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

where C_t and C_o are the concentration of MO at time t and initial concentration respectively. The degradation data was further fitted into the linear form of the pseudo first order kinetic (Eq. 2) to determine rate constant of the reaction. Where k is the reaction rate constant of the process and t is the time.

$$\ln \frac{(C_t)}{(C_o)} = -kt \quad (2)$$

4.3. Results and discussion

4.3.1. X-ray diffraction (XRD) studies of Bi_2S_3 and Cu-doped Bi_2S_3

The synthesized pristine and Cu-doped Bi_2S_3 with different concentrations of Cu^{2+} were characterized by XRD to determine the purity and crystallinity of the samples. Figure 4.1 presents the overlaid diffraction patterns for all the samples which showed pattern that was consistent with the orthorhombic Bi_2S_3 phase (JCPDS no. 00-017-0320) with lattice constants of $a = 11.149 \text{ \AA}$, $b = 11.304 \text{ \AA}$, and $c = 3.981 \text{ \AA}$ [30, 31]. No diffraction peaks of Cu^{2+} species could be seen, indicating the Cu^{2+} (73 pm) only occupied substitutional positions or voids in the crystals due to its smaller ionic radii compared to Bi^{3+} (103 pm). Figure 4.2 presents an enlarged view of the 2θ range of $23 - 30^\circ$ for the pure and Cu^{2+} doped Bi_2S_3 . A slight shift of the (130) diffraction plane was observed, which was more pronounced at higher dopant concentration, resulting from the non-uniform stress/strain generated within the Bi_2S_3 lattices due to the incorporation of Cu^{2+} . A decrease in intensity of the diffraction peaks for all the Cu-doped Bi_2S_3 compared to the pristine Bi_2S_3 was also observed, indicating a reduction in crystallinity. This could be as a result of defects induced in the crystal of Bi_2S_3 by the incorporation of Cu^{2+} [32].

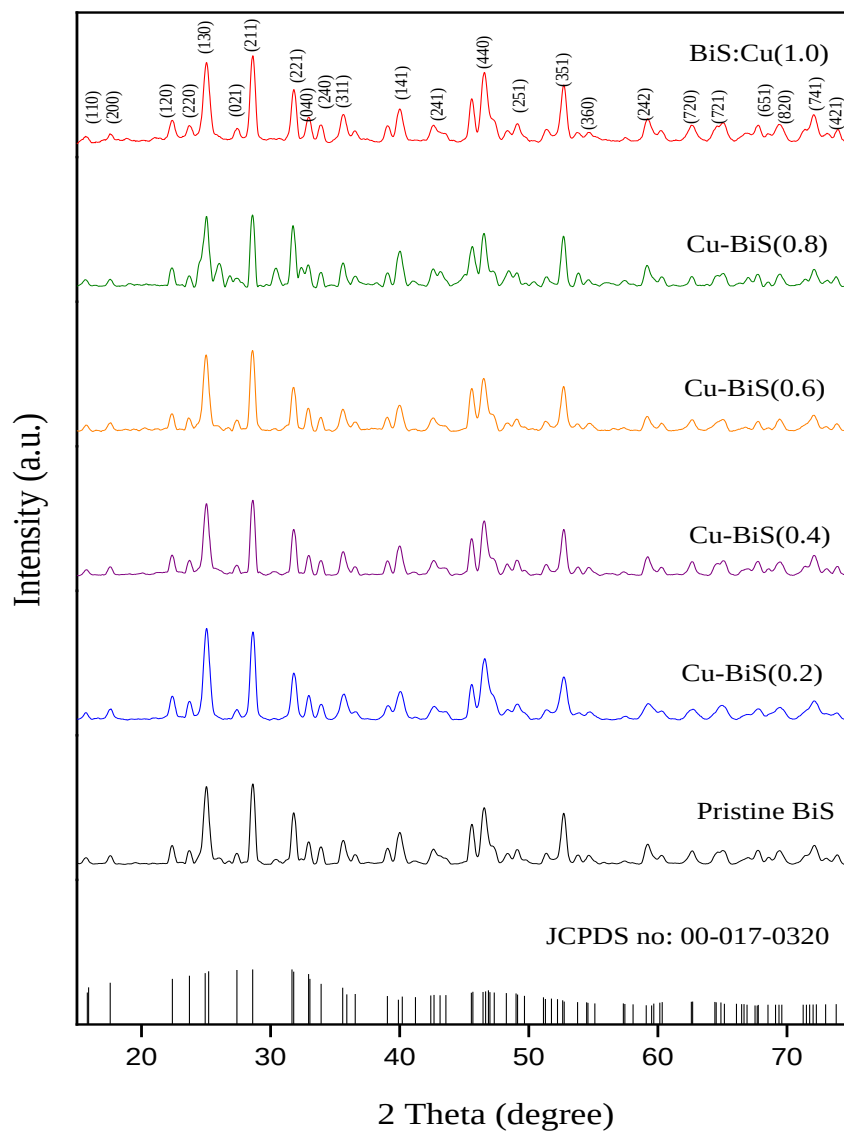


Figure 4. 1: XRD patterns of pristine Bi_2S_3 and Cu-doped Bi_2S_3 nanoparticles at different dopant concentration (0.2, 0.4, 0.6, 0.8, and 1.0 mol).

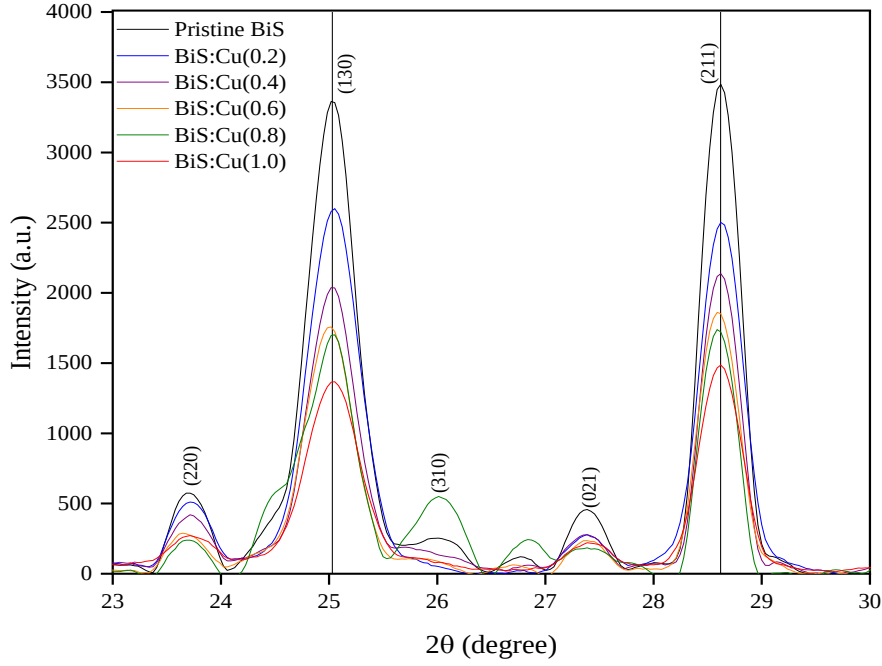


Figure 4. 2: Enlarged view of the X-ray diffraction pattern of pristine and Cu-doped Bi₂S₃ nanoparticles in 2θ range 23.00°- 30.00 ° peaks.

The XRD peak broadening analysis of the samples was carried out using Scherrer equation, Williamson–Hall (W-H) models that is uniform deformation model (UDM), to calculate the average crystallite size and lattice strain.

4.3.2. Scherrer method

The particle size of the undoped Bi₂S₃ and Cu-doped Bi₂S₃ nanomaterials was calculated from the Scherrer equation (Eq. 3) [33]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where K is the Scherrer's constant (0.9),

λ is the wavelength of the X-ray (1.5406 Å),

β and θ are the full-width-at-half maximum (FWHM) and the diffraction angle, respectively.

The calculated crystallite size for undoped Bi₂S₃ was found to be 23.42 nm, and 25.10, 28.31, 31.11, 33.60, and 36.44 nm for Cu-doped Bi₂S₃ nanocomposite at 0.2, 0.4, 0.6, 0.8, and 1.0 mol concentrations respectively. This shows the crystallite size of the material increased with increase in Cu²⁺ doping concentration.

4.3.3. Williamson–Hall (W-H) method

According to the Williamson–Hall method, peak broadening is made up of two contributions: size-dependent broadening and lattice strain (ϵ) broadening [34]. Therefore, the peak broadening (β) could be written as: $\beta = \beta_{\text{size}} + \beta_{\text{strain}}$ and β_{strain} could be expressed by Eq. 4. By considering the total broadening by the crystal size (D) and lattice strain (ϵ), the linear fitting equations based on Uniform deformation model (UDM) could be expressed by Eq. (5) & (6) [16]:

$$\beta_{\text{strain}} = 4\epsilon \tan\theta \quad (4)$$

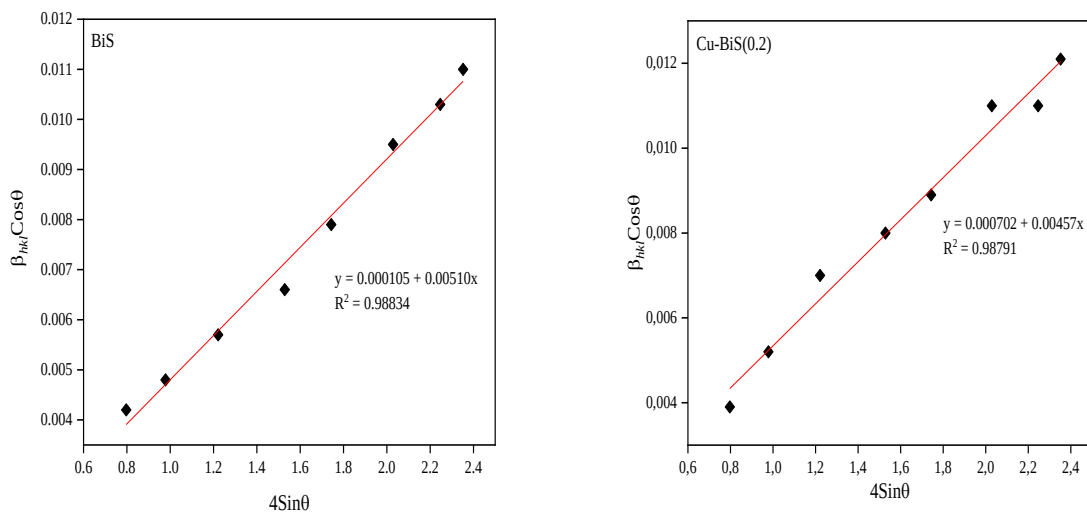
$$\beta_{hkl} = \frac{K\lambda}{D} \cdot \frac{1}{\cos\theta} + 4\epsilon \tan\theta \quad (5)$$

$$\text{or,} \quad \beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4\epsilon \sin\theta \quad (6)$$

where ϵ = is the average lattice strain.

Figure 4.3 shows the plot of $\beta_{hkl} \cos\theta$ against $4\sin\theta$, and the crystal size (D) and micro strain (ϵ) was obtained from the y-intercept and the slope respectively using the linear fitting in Eq. (6). The dislocation density (δ) which is the length of dislocation lines per unit volume of the crystal was calculated using the average crystallite size (D) from the Williamson and Smallman's formula (Eq. 7) [35].

$$\delta = \frac{1}{D^2} \quad (7)$$



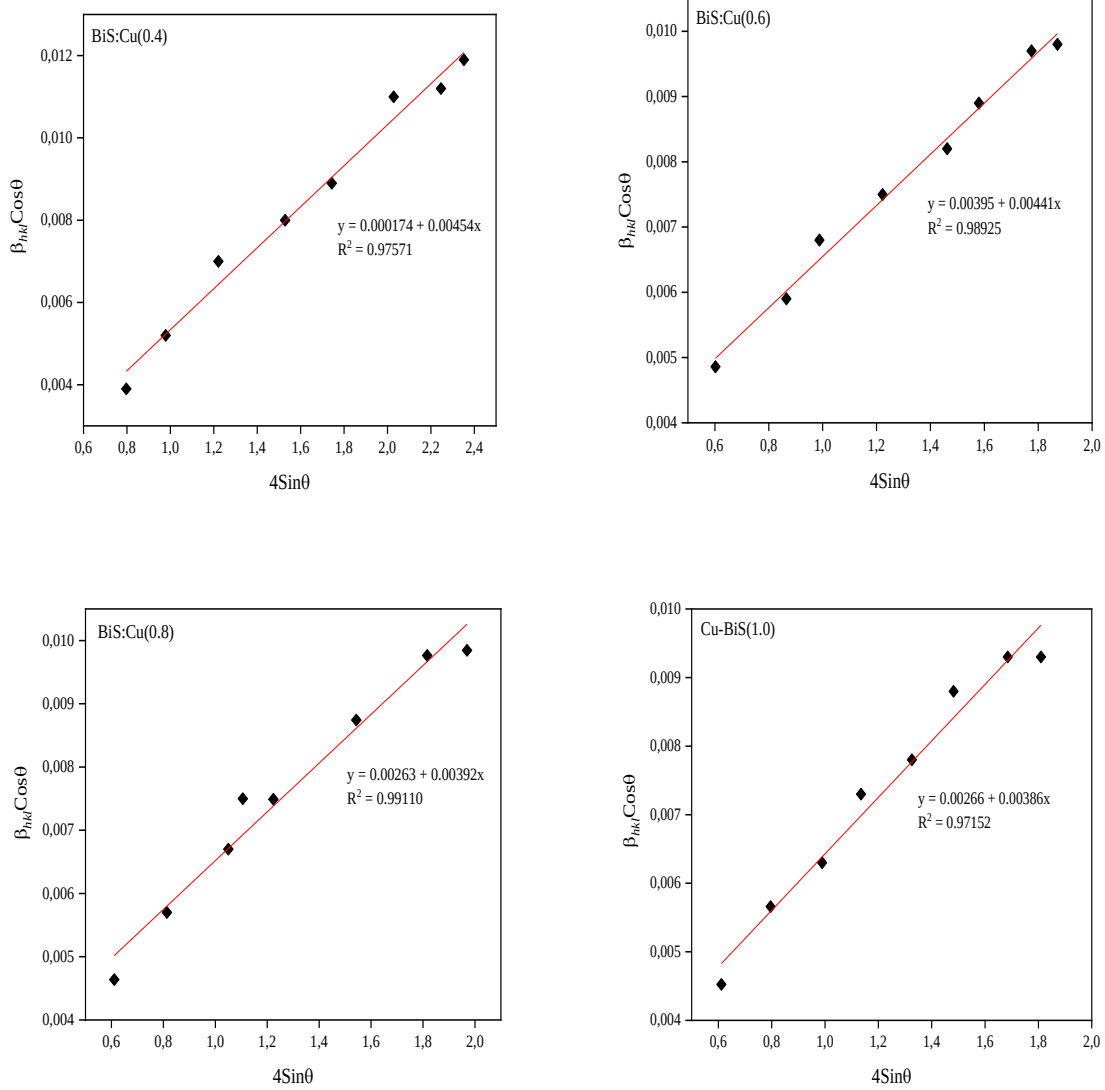


Figure 4. 3: Uniform deformation model (UDM) plot of Cu-Bi₂S₃ (0.2, 0.4, 0.6, 0.8, and 1.0).

The values of the crystallite size and strain as determined from Williamson–Hall (W-H) and Scherrer plot are given in Table 4.1.

Table 4. 1: Comparison between the Scherrer and Williamson–Hall methods.

Samples (mol)	Scherrer method			Williamson–Hall method		
	2θ (°)	FWHM ($\times 10^{-3}$ rad)	Crystallite size (nm)	Microstrain ($\epsilon \times 10^{-3}$)	Dislocation density (δ $\times 10^{-3} \text{ nm}^{-2}$)	Crystallite size (nm)
BiS	28.62	3.49	23.49	0.11	1.35	27.19
Cu-BiS(0.2)	26.65	3.40	24.13	0.70	1.09	30.34
Cu-BiS(0.4)	28.63	2.80	29.26	1.74	1.07	30.54
Cu-BiS(0.6)	28.60	2.56	32.01	3.95	1.01	31.44
Cu-BiS(0.8)	28.62	2.50	32.82	2.63	0.80	35.37
Cu-BiS(1.0)	28.61	2.40	34.16	2.66	0.78	35.92

The average crystallite size of Cu-doped Bi_2S_3 nanoparticles calculated from the Williamson–Hall method was found to be higher (35.92 nm) than the size estimation from the Debye–Scherrer’s method (34.16 nm). However, the values followed a similar trend confirming the increase in crystallite size with dopant ion concentration. Similar trend was observed for dislocation density, which is thought to be due to decrease in grain boundary because of an increase in crystallite size for all the doped Bi_2S_3 .

Wurtzite structural parameters like lattice distances d_{hkl} , lattice constants (a , b , and c), interplanar angle and unit cell volumes (V) were calculated from the lattice geometry equation using the Bragg’s law expression (Eq. 8) [16].

$$2d_{hkl}\sin\theta = n\lambda, \quad (8)$$

where d_{hkl} is the lattice spacing distance with the corresponding Miller indices of h , k , and l .

The lattice parameters (a , b , and c ,) for the orthorhombic structure were calculated from the most intensive peaks using the linear algebraic expressions in Eq. (11) derived from Eq. (9) & (10).

$$a^2 = \frac{n^2 \lambda^2}{4 \sin^2 \theta} (h^2 + k^2 + l^2) \quad (9)$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \quad (10)$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 \sin^2 \gamma} + \left(\frac{k^2}{b^2 \sin^2 \gamma} \right) - \frac{2hk \cos \gamma}{ab \sin^2 \gamma} + \frac{l^2}{c^2} \quad (11)$$

where the lattice parameters a , b , and c indicate the unit cell parameters,

θ is the Bragg's angle,

γ is the Bragg's angle between the a and b axis ($\gamma = 90^\circ$).

The values of the unit cell lattice parameters (a , b , c ,) and unit cell volume (V) of the undoped and Cu-doped Bi_2S_3 calculated from the Bragg's expression are given in Table 4.2.

Table 4. 2: Structural parameters of the undoped and Cu-doped Bi_2S_3 .

Sample (mol)	2θ ($^\circ$)	hkl	d_{hkl}	Lattice constants ($\text{\AA}$)			V ($\text{\AA}^3$)
				a	b	c	
BiS	28.656	211	3.113	11.625	10.735	2.495	311.362
Cu-BiS(0.2)	28.656	211	3.113	11.625	10.735	2.495	311.362
Cu-BiS(0.4)	28.621	211	3.116	11.633	10.739	2.492	311.318
Cu-BiS(0.6)	28.621	211	3.116	11.633	10.739	2.492	311.318
Cu-BiS(0.8)	28.587	211	3.120	11.643	10.746	2.487	310.693
Cu-BiS(1.0)	28.553	211	3.124	11.643	10.746	2.487	310.693

The calculated values of the lattice parameters (a , b and c) showed a good matching with the literature data presented in JCPDS card no 000-017-320 [35]. The miller indices (hkl) were selected from the strongest peak observed at 28.62° (211). Calculation of the interplanar distance (d_{211}) values showed that a is greater than the standard value (11.149 $\text{\AA}$), while b is comparable to the standard value (11.304 $\text{\AA}$), and c is smaller than the standard value (3.981 $\text{\AA}$), which is acceptable due to the ionic radius of Cu^{2+} that is less than Bi^{3+} . A steady decrease in volume was observed from Cu-BiS(0.4) and Cu-BiS(1.0) with a slight increase of the lattice a and b values respectively due to the smaller ionic radii of Cu^{2+} atoms replacing larger ionic radii of Bi atoms in the lattice of Bi_2S_3 (Figure 4.4).

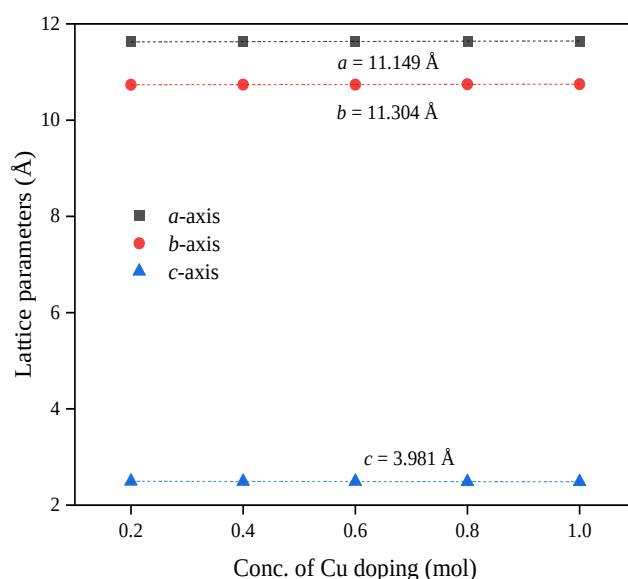


Figure 4. 4: Lattice parameters a, b, and c of Bi_2S_3 and Cu-doped Bi_2S_3 .

4.3.4. Morphological studies

The surface morphology of Bi_2S_3 and Cu-doped Bi_2S_3 was studied using SEM and TEM. The TEM and SEM images, EDX spectrum and particle size histogram from Bi_2S_3 and Cu-BiS(0.4) and Cu-BiS(1.0) are shown in Figure 4.5, Figure 4.6, Figure 4.7 as representative for the prepared materials. Figure 4.S1 – 4.S3, shows the morphological studies for the other doped materials. The SEM images of the materials showed highly aggregated nanoparticles, while the TEM images showed the shape of the material as being rod-like for the pristine Bi_2S_3 and Cu-doped Bi_2S_3 at all concentrations. The doped- Bi_2S_3 showed larger particle size and a narrow size distribution compare to pristine Bi_2S_3 , substantiating the calculations from XRD analysis. This suggests an influence of Cu^{2+} ion on the growth and nucleation phase of the nanoparticle synthesis [36] . A gradual increase in the width of the nanoparticles was observed in the range of 17.7 - 23 nm, which agrees significantly with the values obtained from the Scherrer equation, although, a significant dispersity in the length of the nanorods was observed with increase in dopant concentration. The aspect ratio for the nanorods was in the range of 2.95 - 7.70 reaching the maximum at Cu doping concentration of 0.6%. The presence of Cu^{2+} was confirmed in the EDX spectra of the Cu-doped Bi_2S_3 .

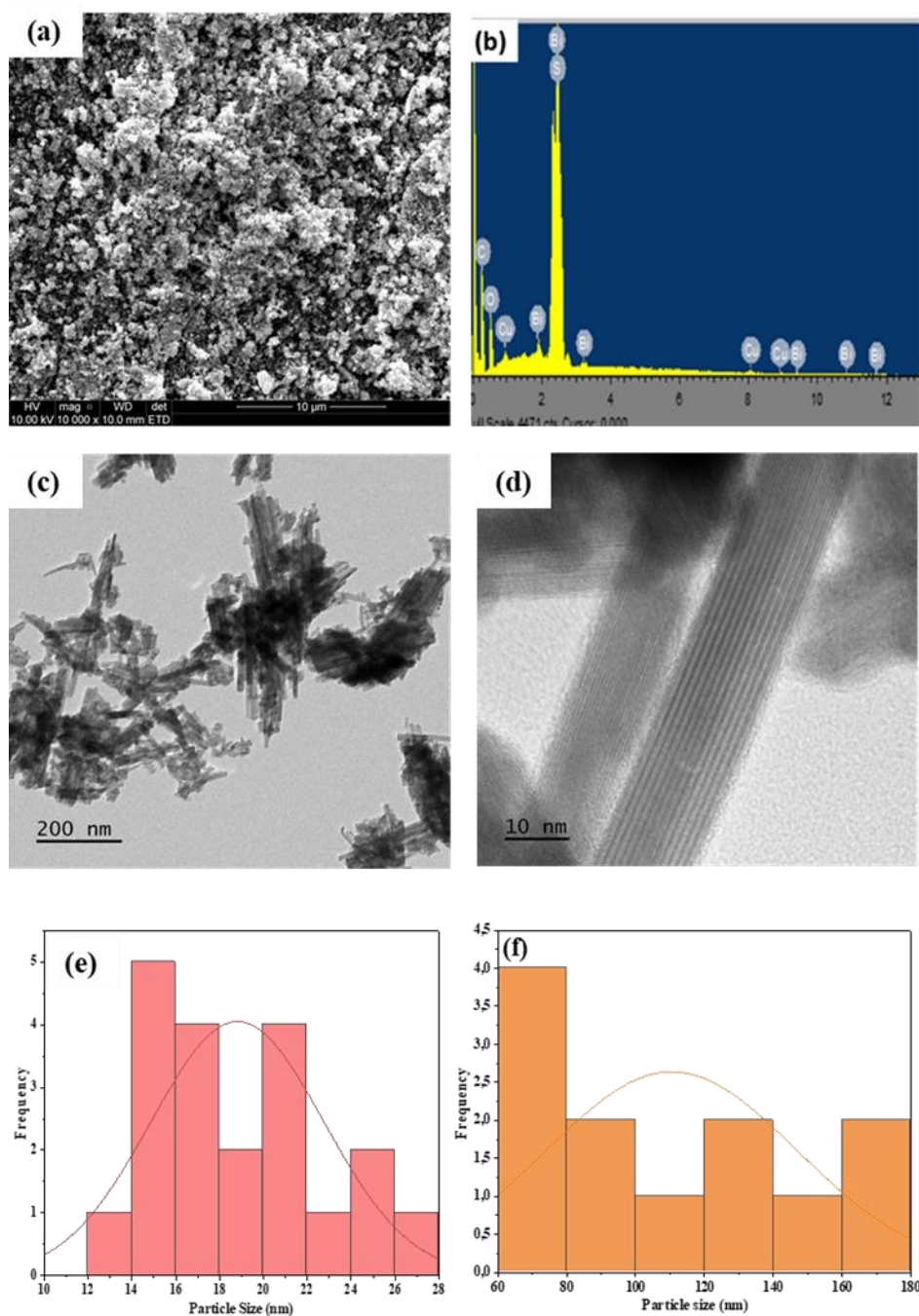


Figure 4. 5: (a) SEM image (b) EDX spectrum (c) TEM image (d) HRTEM image showing lattice fringes; with corresponding particle size histogram showing (e) width and (f) length of the BiS nanorods.

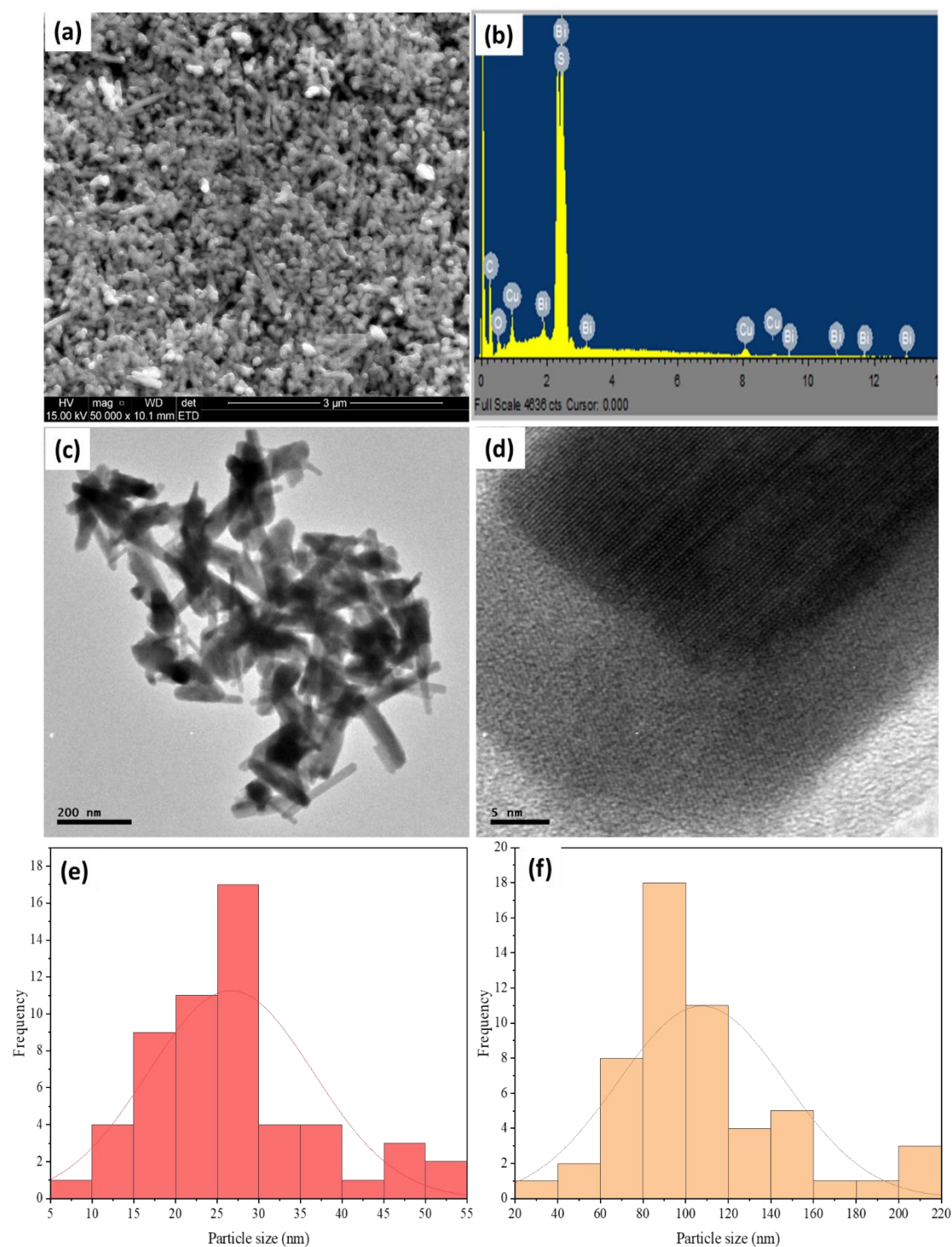


Figure 4. 6: (a) SEM image (b) EDX spectrum (c) TEM image (d) HRTEM image showing lattice fringes; with corresponding particle size histogram showing (e) width and (f) length of the Cu-BiS(0.4) nanorods.

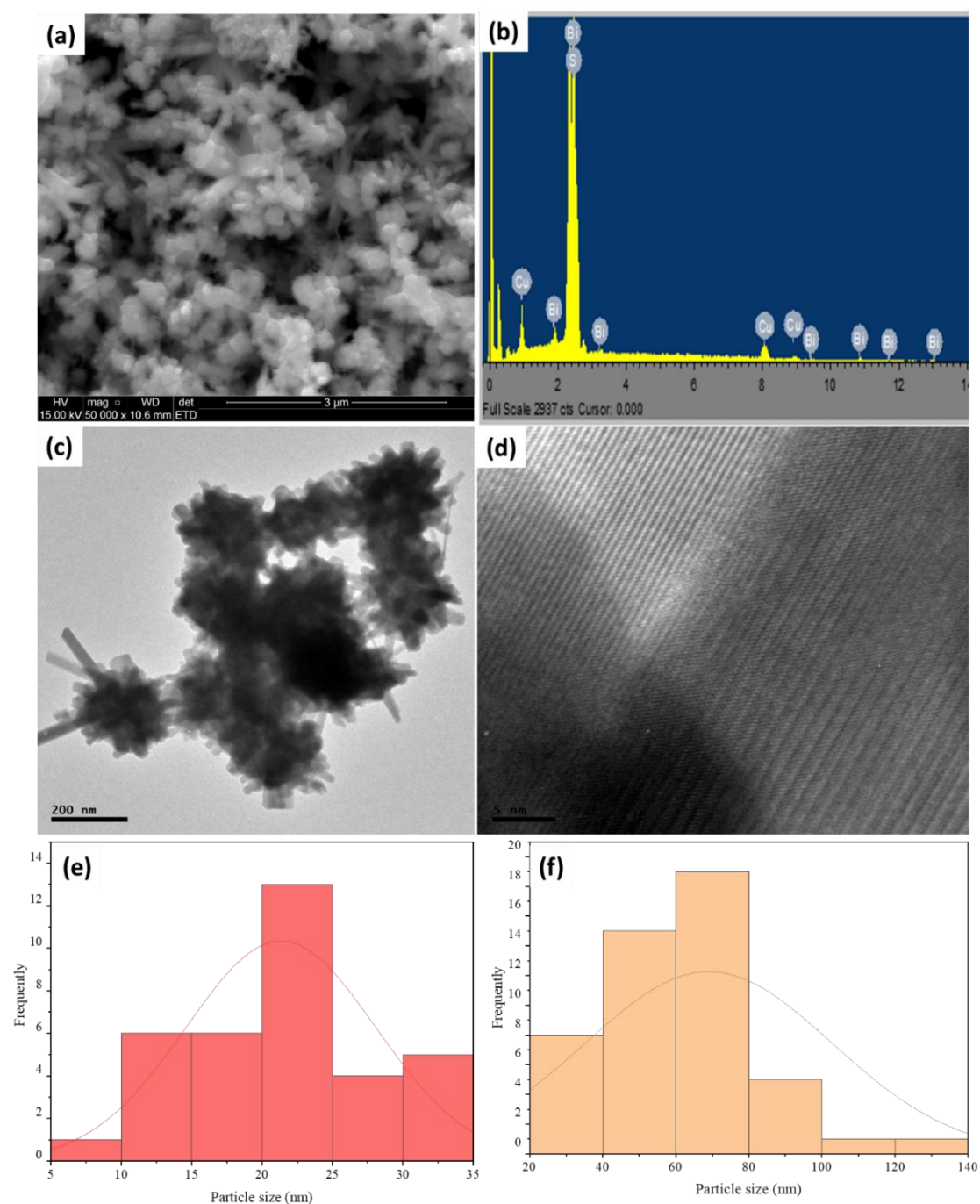


Figure 4. 7: (a) SEM image (b) EDX spectrum (c) TEM image (d) HRTEM image showing lattice fringes; with corresponding particle size histogram showing (e) width and (f) length of the Cu-BiS(1.0) nanorods.

4.3.5. Optical properties

To investigate the optical properties of the pristine Bi_2S_3 and Cu-doped Bi_2S_3 nanorods, the UV–vis–NIR absorption spectra were measured and the results are presented in Figure 4.8. The absorption spectra of nanomaterials provide information about the optical bandgap of the semiconducting materials. The optical excitation of electrons across the bandgap is permitted from the semiconductor material, resulting in a sharp increase in the absorptivity at which the wavelength corresponds to the bandgap energy. This feature of the optical spectrum is recognised as the optical absorption edge [37, 38]. However, some features, such as size, size distribution and shape of the nanomaterials can influence the position of the band edge and the shape of the absorption edge. As shown in Figure 4.8(a), both the pristine and Cu-doped Bi_2S_3 nanoparticles showed very broad absorption in the visible region of the spectrum with a maximum peak around 915 nm. A slight blue shift in the peak of absorption was observed with an increase in Cu^{2+} content and the position of the absorption edge. This blue shift is attributed to the quantum confinement effect on nanomaterials that significantly decrease the bandgap with increasing particle size [39–41]. This is also consistent with the trend of the particle size variation of the Bi_2S_3 materials. Fazal *et al.*, also reported a blue shift upon the introduction of Cu^{2+} into Bi_2S_3 thin films, which was attributed to the effect of the substitution of the Cu^{2+} into the Bi_2S_3 crystal lattice [42]. It was also noticed that the absorption peak increases with an increase in Cu^{2+} content, which may be due to the sp-d exchange interaction between the transition phase of Cu^{2+} and Bi_2S_3 material [43, 44].

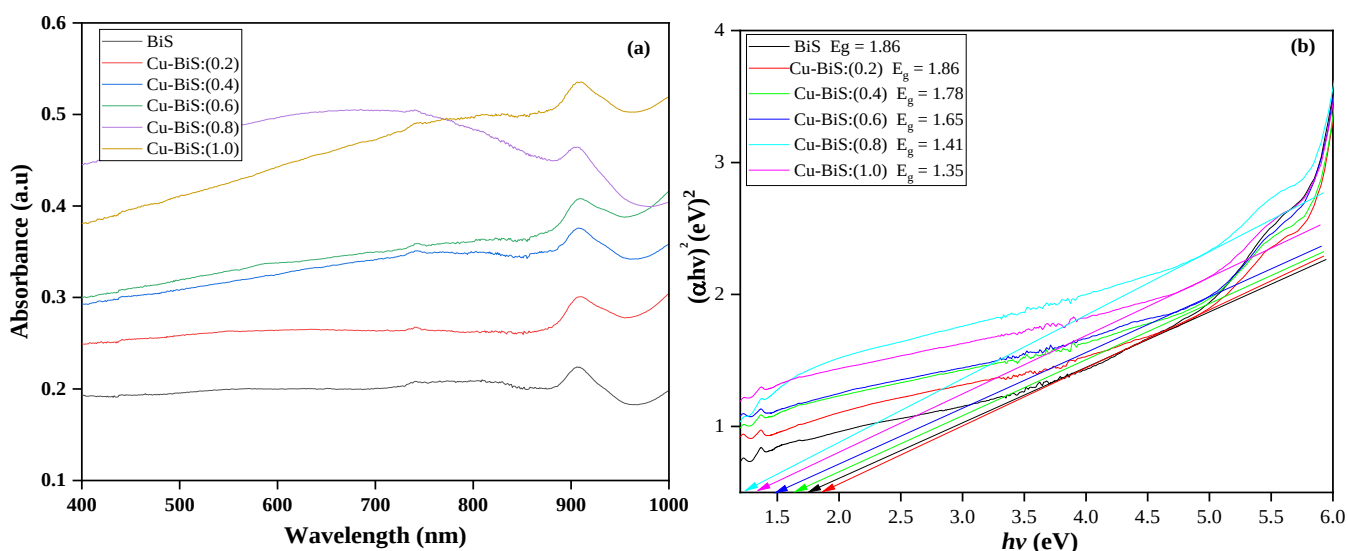


Figure 4. 8: UV–Vis–NIR absorption spectra of (a) pure Bi_2S_3 and doped Bi_2S_3 nanoparticles with different dopant concentration (0.2, 0.4, 0.6, 0.8 and 10 mol), and (b) respective Tauc plot (inset Table are the band gap energies).

From the Tauc plot (Figure 4.8b), obtained from Eq. (12) [45], the direct bandgap energy of the pristine and Cu-doped Bi₂S₃ nanomaterials was estimated from the absorption plot of the $(\alpha h\nu)^2$ against the photon energy curve ($h\nu$).

$$(\alpha h\nu)^n = B (h\nu - E_g) \quad (12)$$

Where α = the absorption coefficient,

h = Planck's constant,

ν = the frequency,

E_g = optical bandgap energy,

B = constant to the content,

n = value of 2 for the direct bandgap of Bi₂S₃.

The bandgap energy (E_g) was estimated by extrapolating the linear portion of the plot to the x-axis. The estimated bandgap energy of Cu-BiS(0.2), Cu-BiS(0.4), Cu-BiS(0.6), Cu-BiS(0.8), and Cu-BiS(1.0) samples was found to be 1.78, 1.65, 1.53, 1.41, and 1.35 eV respectively. These values were similar to the optical bandgap energy (E_g) of Bi₂S₃ reported in previous studies, which was in the range 1.38–2.17 eV [42, 46]. The increase in the concentration of the Cu²⁺, resulted in reduction of the bandgap energy from 1.78 to 1.35 eV. This is because metal ion doping can alter the bandgap structure of the semiconducting host material, having a significant impact on the optical properties of the material. The band edge position of Bi₂S₃ and Cu-Bi₂S₃ were theoretically calculated from the bandgap energy. The band edge potential of valence band (VB) and the conduction band (CB) were calculated by using Mulliken electronegativity equations (Eqs. 13 & 14) [45]:

$$E_{VB} = X - E_e + 1/2E_g \quad (13)$$

$$E_{CB} = E_{VB} - E_g \quad (14)$$

where E_{VB} and E_{CB} are the potential edge of valence band and conduction band, respectively. E_e is the energy of free electrons on the hydrogen scale (4.5 eV) and E_g is the optical energy bandgap of Bi₂S₃. X is the absolute electron electronegativity of the semiconductor and was calculated from Eq. (15) [47].

$$X = [x(A)^a x(B)^b x(C)^c]^{1/a+b+c} \quad (15)$$

where a , b , and c are the number of atoms in the compounds.

The calculated X value for Bi_2S_3 and $\text{Cu-Bi}_2\text{S}_3$ was found to be 5.27 and 5.13 eV respectively. A pictorial representation of the band structure is shown in Figure 4.S4 and the band edge values are presented in Table 4.3.

Table 4. 3: The summary of the calculated value of the bandgap.

Semiconductor	Estimated bandgap energy (Eg)	Calculated valence bandgap edge (E_{VB})	Calculated conduction bandgap edge (E_{CB})
BiS	1.86	1.56	-0.05
Cu-BiS(0.2)	1.78	1.52	-0.08
Cu-BiS(0.4)	1.65	1.46	-0.14
Cu-BiS(0.6)	1.53	1.40	-0.20
Cu-BiS(0.8)	1.41	1.34	-0.26
Cu-BiS(1.0)	1.35	1.31	-0.30

The calculated values of E_{VB} of the pristine Bi_2S_3 and Cu-doped Bi_2S_3 (0.2), (0.4), (0.6), (0.8), and (1.0) samples were found to vary from 1.56, 1.52, 1.46, 1.40, 1.34 and 1.31 eV respectively. The corresponding E_{CB} positions were calculated by subtracting the respective bandgaps and were found as -0.30, -0.26, -0.20, -0.14, -0.08, and -0.05 eV, respectively. A linear relationship exists between the value of the bandgap energy and the concentration of Cu^{2+} dopant. There is a consistent decrease in the value of E_{VB} with an increase in the value of E_{CB} , which may be due to the localized surface plasmon resonance (SPR) effect of electrons after doping with Cu^{2+} . The introduction of Cu ion into the host of Bi_2S_3 , promotes the separation of photo-excited electron-hole pairs, thereby suppressing the recombination of the electron-hole. Generally, it has been reported that different doping metal ion exhibit different effects on the absorption spectra of the nanomaterials of interest. The smaller ionic radius of the Cu^{2+} with respect to the Bi^{3+} makes it easier to fill the vacancies in the Bi_2S_3 orthorhombic phase [48, 49].

First principle calculations were used to evaluate the effect of Cu^{2+} doping into the crystalline structure of the Bi_2S_3 on its electronic structure. This was carried out by investigating the band structure and the density of states of the compounds. It should be noted that the structure of Bi_2S_3 used in the calculation was the Pmcn (ICSD 201066) as shown in Figure 4.9a. The other two structures (Pnma and Pbnm) gave calculated optical gap close to the studied structure.

To study the effect of the incorporation of the copper in the Bi_2S_3 , one of the eight bismuth atoms in the unit cell was replaced with one copper atom, thereby resulting to $\text{Bi}_{15}\text{CuS}_{24}$ as the molecular formula of the new material, which implies $\text{Bi}_{1.875}\text{Cu}_{0.125}\text{S}_3$ (Figure 4.9b). The Bi_2S_3 structure has two bismuth positions. The choice of substitution is arbitrary and, in both cases, gives similar results. The use of only one-unit cell of Bi_2S_3 in the calculation allows the change of the space group when the copper is introduced (full occupancy), thus the space group becomes Pm. Since the electronic structure depends on the symmetry of the materials, the space group of Bi_2S_3 structure has been changed to Pm, and this is what will allow us to compare the two structures.

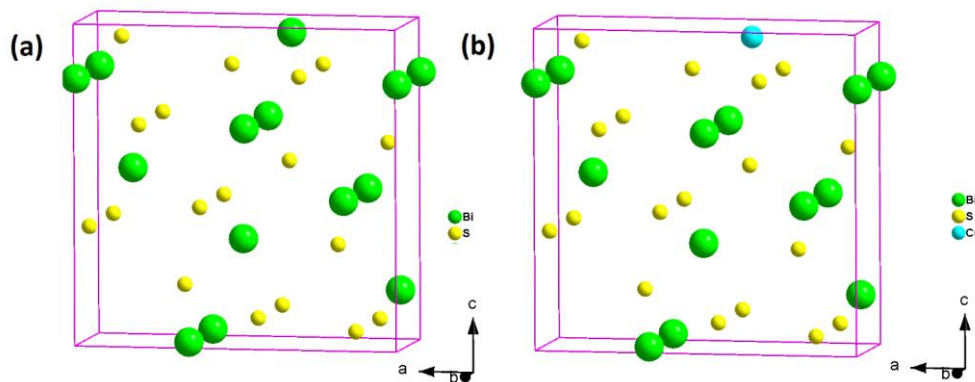


Figure 4. 9: Projection of the unit cell of (a) Bi_2S_3 and (b) $\text{Bi}_{1.875}\text{Cu}_{0.125}\text{S}_3$ in the Pm space group.

Figure 4.10a and b show the band structure of pure Bi_2S_3 in Pm space group. The valence band maximum (VBM) and the conduction band minimum (CBM) appear at different points in the Brouillon zone, which implies that the pristine Bi_2S_3 is an indirect semiconductor with a calculated band gap energy of 1.505 eV [50]. The calculated energy gap of Bi_2S_3 reported in previous studies ranged between 1.3 and 1.7 eV [50-54] which is also dependent on the approximation used, crystal system and calculation conditions. On the other hand, some previous workers reported that Bi_2S_3 is an n-type direct semiconductor [52-54]. However, Zahedi [50] showed that Bi_2S_3 is a p-type indirect semiconductor. Also, Zhan, Wan [54] reported an indirect semiconductor from a DFT calculation on Bi_2S_3 in P1 space group. The nature of the band gap may be altered by the application of pressure, or the presence of vacancy defect [50, 54]. Moreover, to the best of our knowledge, there are only few theoretical studies on the electronic structure of metal-doped (Fe, Co, Cr) Bi_2S_3 [16, 48, 55].

Figure 4.10c-f show the band structure of Cu-doped Bi_2S_3 . In general, the two band structures (spin up and spin down) are very similar. However, the incorporation of copper in Bi_2S_3 generates the intercalation of the Cu 3d band and S 3p in the forbidden band (Figure 4.10e-f). By comparing the electronic structure of pure Bi_2S_3 and Cu-doped Bi_2S_3 , we observed a great similarity with decrease in the level of the conduction band. Hence, the band gap energy decreases from 1.505 to 1.407 eV for pure Bi_2S_3 and Cu-doped Bi_2S_3 respectively. Another very important observation was the change of semiconductor type from indirect band to direct band type. In fact, Figure 10d shows that the valence band maximum (VBM) and the conduction band minimum (CBM) of the Cu-doped Bi_2S_3 appear at different D point of Brillouin zone. This effect of Cu^{2+} incorporation into the electronic structure of Bi_2S_3 has been reported previously in similar studies involving other semiconductor nanomaterials such as the case of Cu-doped ZnO [56]. A decrease in the band gap energy and the change of semiconductor type from direct to indirect has been observed in Ni-doped Bi_2Se_3 [57], which has the same structure and close properties as Bi_2S_3 .

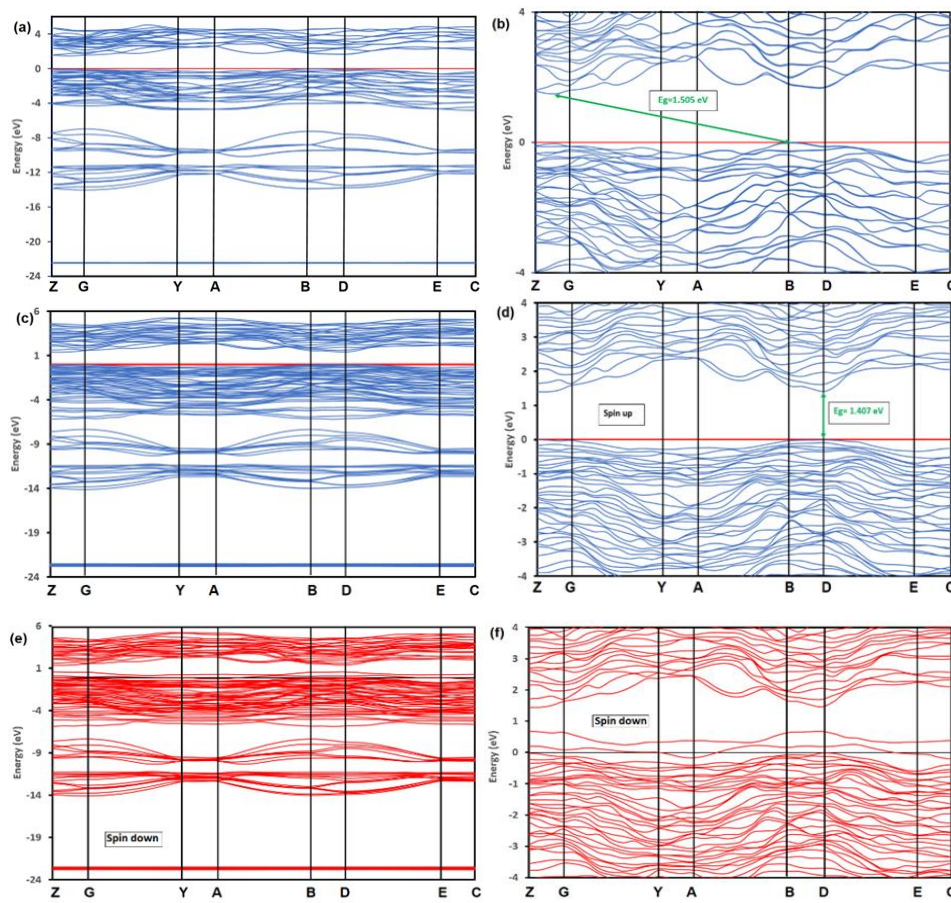


Figure 4. 10: Bond structure of Bi_2S_3 ((a) overall view and (b) enlarged view) and Cu-doped Bi_2S_3 spin up ((c) overall view and (d) enlarged view) and spin down ((e) overall view and (f) enlarged view).

The total and partial density of states of the pristine Bi_2S_3 and Cu-doped Bi_2S_3 are shown in S5. For the pristine Bi_2S_3 (Figure 4.S5a), the sub band valence is formed mainly by p-states of S and p-states of Bi atom. On the other hand, the conduction band consists of the p-states of S and p-states of Bi. Thus, the first transition with the lowest energy is p-p type. For the Cu-doped Bi_2S_3 (Figure 4.S5b), the total and partial density of states for the spin up is similar to the pure Bi_2S_3 with the same intensity and profile of the peaks and the contribution of s-states of Cu is not very outstanding. However, for the spin down, the presence of the d-states of Cu and p-states of S in the forbidden band was observed.

4.3.6. Photoluminescence spectroscopic studies

Figure 4.11 shows the PL spectra of pristine Bi_2S_3 and Cu-doped Bi_2S_3 nanorods excited at 350 nm. Two emission peaks were observed at 358 nm and 705 nm. The intense narrow peak at 358 nm could be ascribed to the recombination of trapped electron-hole pairs at sulphur vacancy sites in the vacancy band, while the small intensity peak at 705 nm could be attributed to stoichiometric variations in the nanoparticles [58]. The PL spectra of the doped samples showed a reduction in the intensity of Cu-BiS(0.4), Cu-BiS(0.6) and Cu-BiS(1.0) compared to pristine BiS. The reduction in PL intensity could be attributed to the creation of shallow traps created by the introduction of lattice defects and new defect levels after Cu^{2+} doping, and trapped photogenerated charge carriers. This enhances the non-radiative recombination of electron-hole pairs and consequently reduces the PL intensity. The incorporation of Cu^{2+} could also induce lattice distortions in the Bi_2S_3 crystals, resulting in the generation of negative charges [6]. These electrons could react with hole energy levels in the matrix, which acts as luminescence centres and ultimately lead to PL reduction.

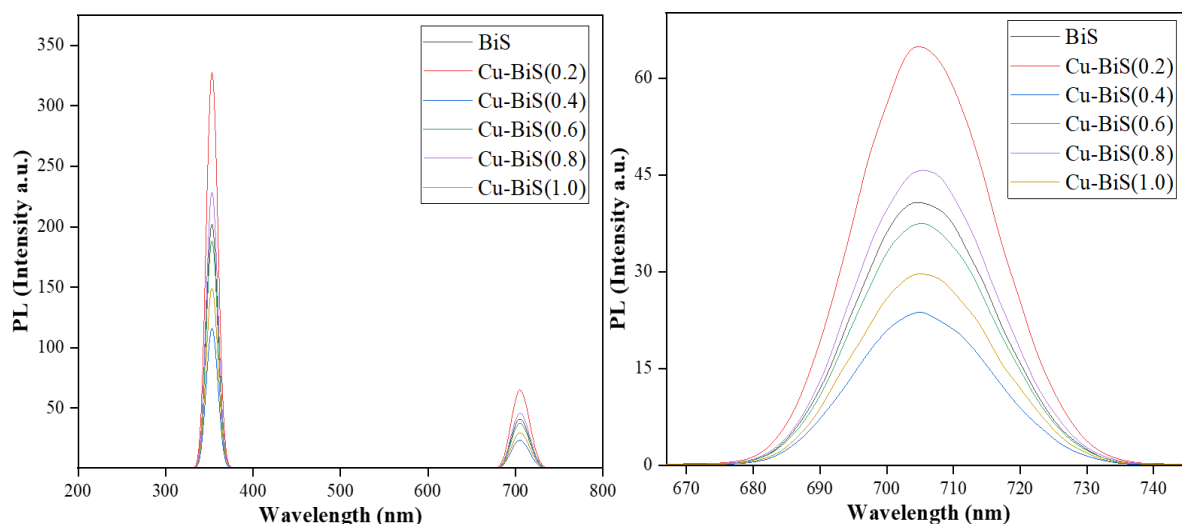


Figure 4. 11: Photoluminescence spectra of BiS, Cu-BiS(0.2), Cu-BiS(0.4) Cu-BiS(0.6) Cu-BiS(0.8) and Cu-BiS(1.0).

4.3.7. Photocatalytic activity of Bi₂S₃ and Cu-doped Bi₂S₃

For the evaluation of the photocatalytic activity, the Cu-BiS(0.4) and Cu-BiS(1.0) were chosen to evaluate the effect of Cu²⁺ doping on the photocatalytic degradation of MO dye because of their enhanced charge carrier separation as confirmed by the PL analysis. The photocatalytic efficiency of pristine and doped Bi₂S₃ on the degradation of methyl orange (MO) after 120 min are shown in Figure 4.12. The degradation of methyl orange reached ~88% for pristine BiS, while Cu-BiS(0.4) and Cu-BiS(1.0) achieved ~95% and 98% efficiency respectively. The reaction rate constant for the degradation process was 0.0153, 0.0186 and 0.02285 min⁻¹ for BiS, Cu-BiS(0.4) and Cu-BiS(1.0) respectively. The improvement in the activities of the doped Bi₂S₃ could be attributed to the enhancement in the adsorption capacity and improved light absorption of the doped Bi₂S₃. In addition, the decrease in the band gap energy of the doped-Bi₂S₃ could also improve the quantity of photogenerated charge carriers. The higher activity of Cu-BiS(1.0) compared to Cu-BiS(0.4) could be due to the reduction in the charge carrier recombination as a result of the creation of trap states by Cu²⁺ ions.

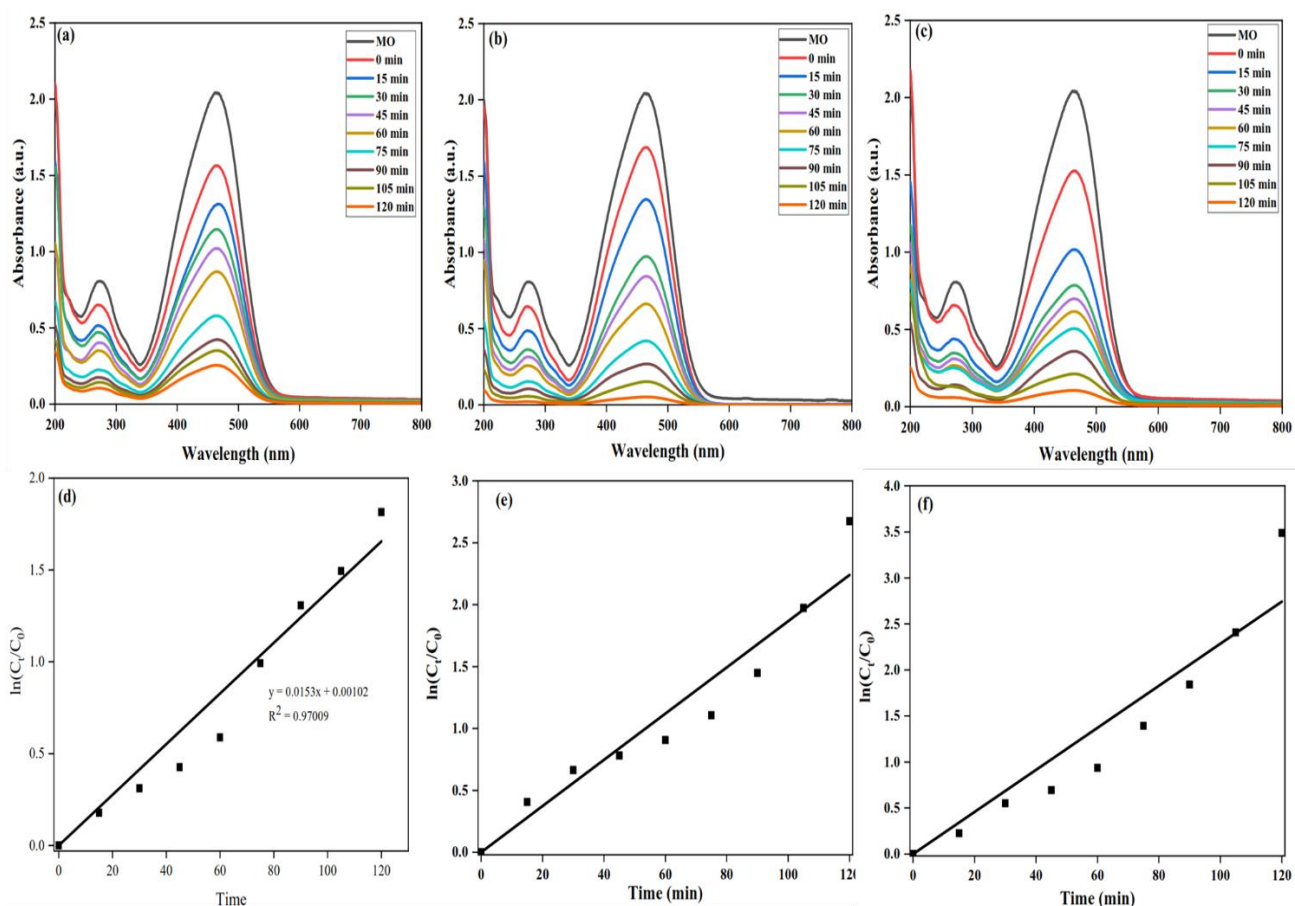


Figure 4. 12: Photocatalytic degradation of MO and first-order kinetic plots of: (a&d) BiS (b&e) Cu-BiS(0.4) and (c&f) Cu-BiS(1.0).

3.7.1. Effect of process parameters on photocatalytic activity of Cu-BiS(1.0)

The effects of catalyst dosage, MO concentration and pH on the degradation efficiency of the process was evaluated by varying these parameters at different levels. Figure 4.13, shows the effect of catalyst dosage on the degradation process. The degradation efficiency was observed to increase with increase in catalyst dosage and this was due to an increase in the quantity of charge carrier generated. In addition, an increase in the adsorption of the methyl orange dye on the surface of the catalyst, which facilitates the contact between the dye molecule and the charge carriers also plays significant role. Figure 4.14, presents the effect of dye concentration on the degradation efficiency. The degradation efficiency was observed to reduce with increase in dye concentration. As the dye concentration increases, more radical species would be required to effectively degrade the dye molecule. At a fixed catalyst dosage, the charge carriers produced would be quickly used up, thus reducing the efficiency of the process at increased dye concentration. The effect of solution pH on the degradation efficiency of the photocatalytic process is shown in Figure 4.15. The catalytic activity of the photocatalyst remained high under

acidic, neutral, and basic conditions. The higher degradation efficiency at high pH may be attributed to increased adsorption of MO on the catalyst surface due to the negative surface charge of Cu-BiS(1.0). The surface charge on the catalyst also influences its dispersity in solution. At pH values close to the neutral value of the catalyst, no surface charge will exist on the catalyst surface, reducing the conglomeration between the particles and thus enhance the photocatalytic process. This might account for the high degradation reported for the process at neutral pH [59].

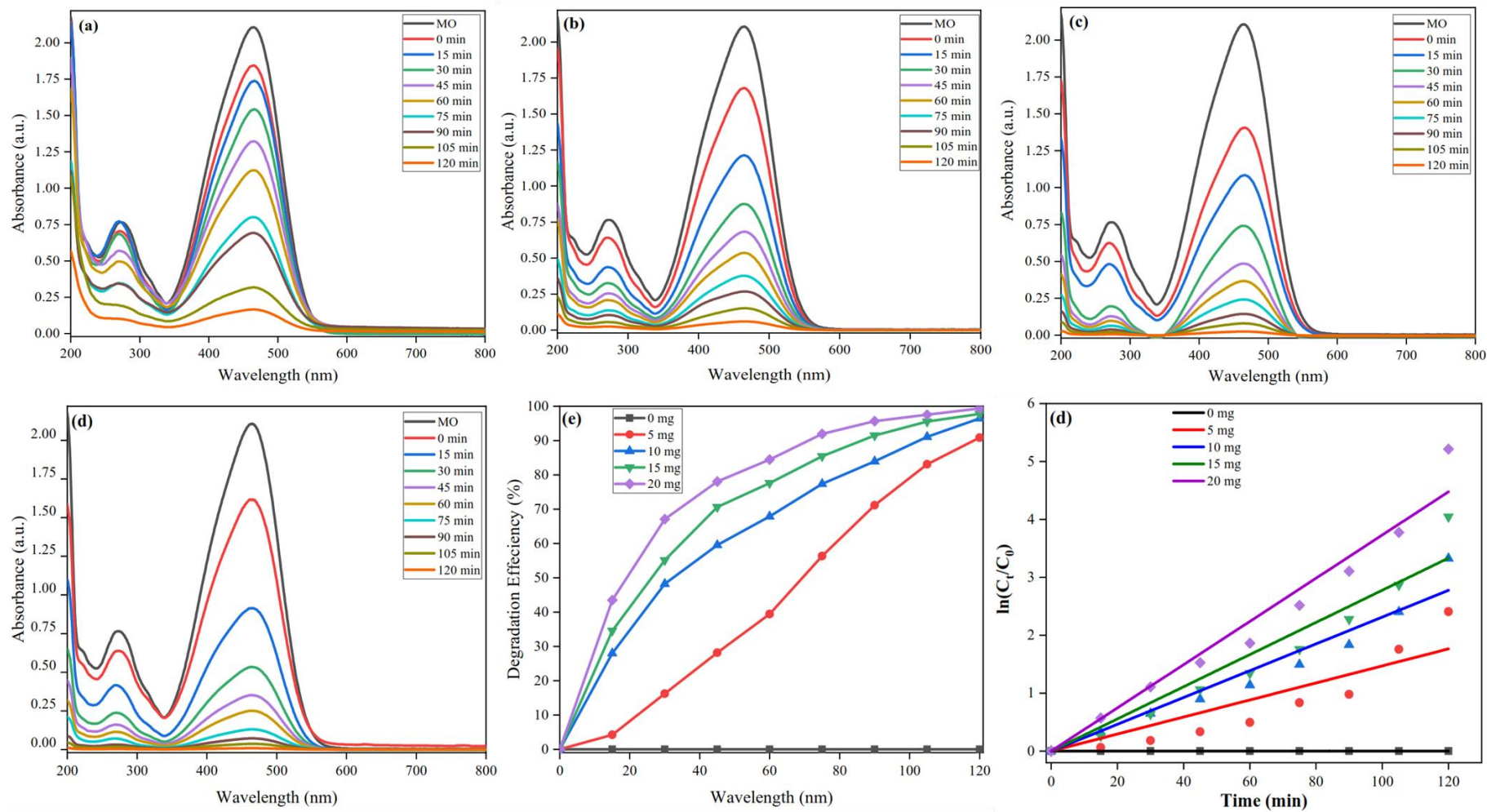


Figure 4. 13: Effect of catalyst dosage on the degradation efficiency of MO by Cu-BiS(1.0).

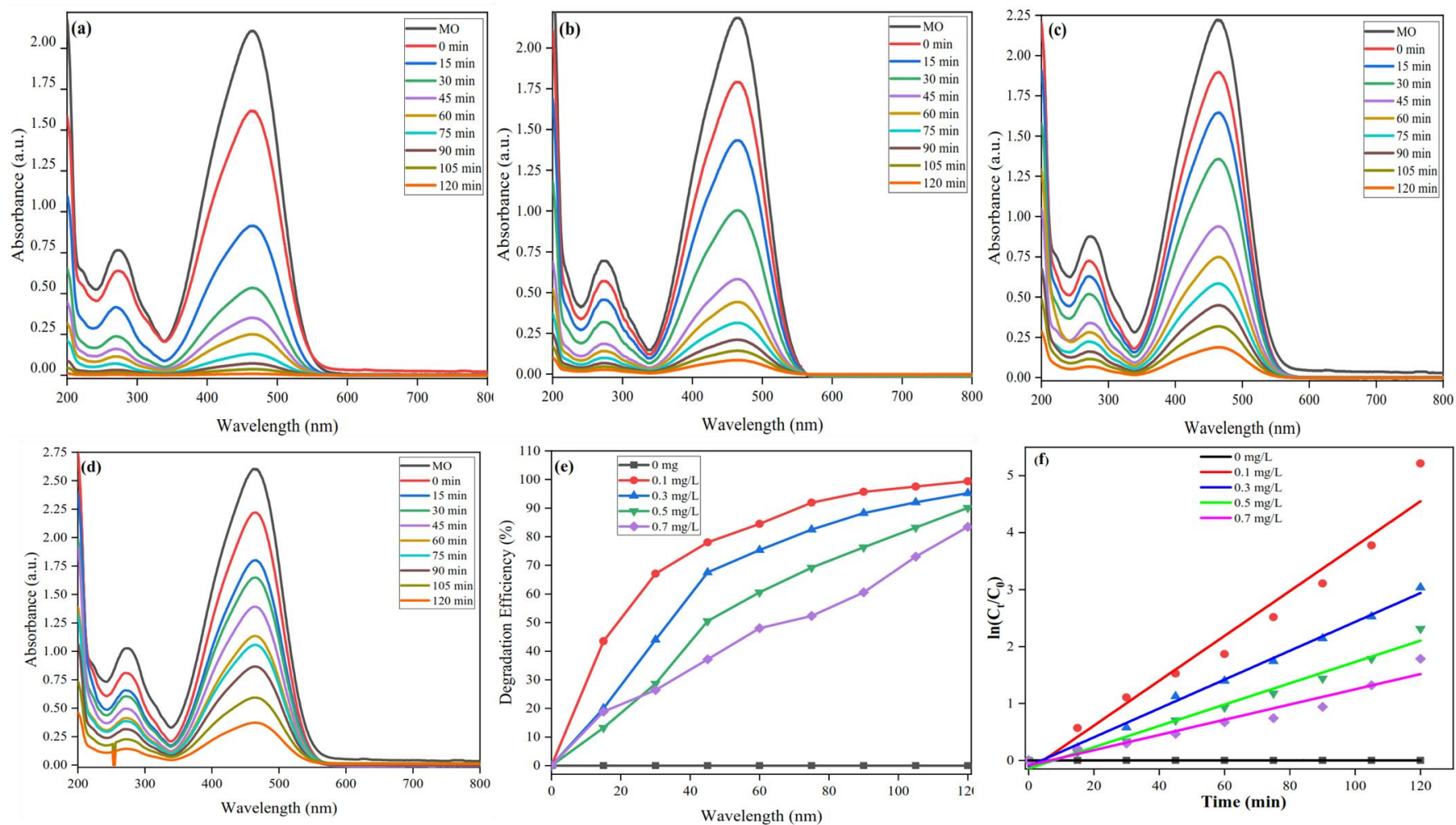


Figure 4. 14: Effect of concentration of MO on the degradation efficiency of Cu-BiS(1.0).

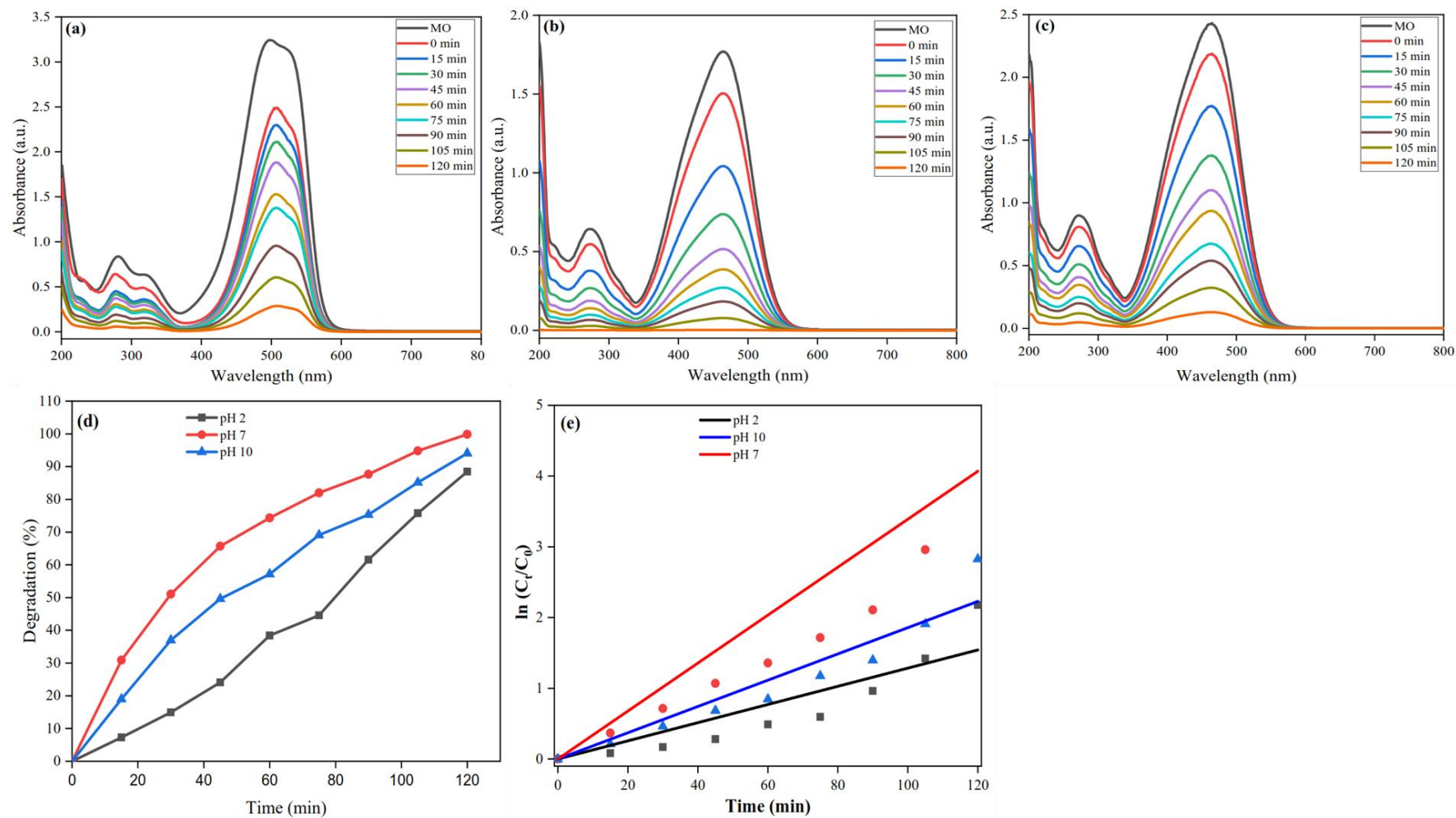


Figure 4. 15: Effect of pH on the degradation efficiency of MO by Cu-BiS(1.0).

3.7.2. Effect of radical scavengers

To determine the most influential specie in the photocatalytic process, radical scavenging compounds were introduced into the system and their effects measured. Tert-butyl alcohol (TBA), Ascorbic acid (ASC), Sodium nitrate (SN), and Tri-ethanol amine (TEA) were used each for hydroxyl $[OH^\cdot]$, superoxide $[O_2^\cdot]$, electron $[e^-]$, and hole $[h^+]$ radical scavengers. The study showed the influence of radicals on the degradation process was in the order $OH^\cdot > e^- > O_2^\cdot > h^+$ as shown in Figure 4.16.

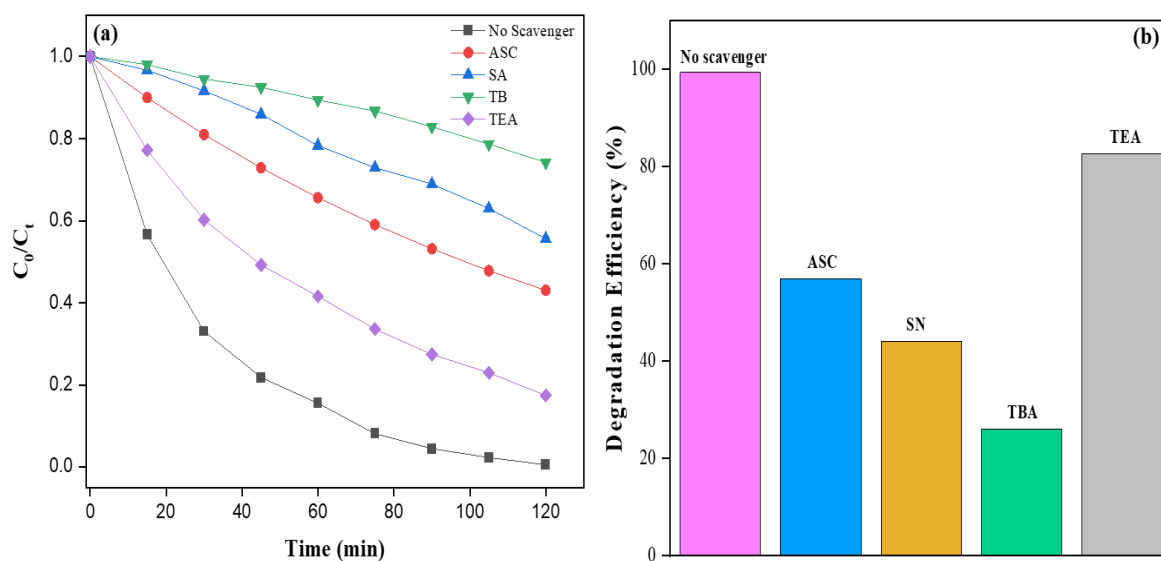


Figure 4. 16: UV-visible absorption spectra of (a) degradation percentage of MO with change in time; and (b) the corresponding photodegradation efficiency (ASC, SA, TB, and TEA).

4.4. Sub-Conclusion

The effect of copper doping on the microstructural, morphological, optical and photocatalytic activity of Bi_2S_3 was explored in this study. XRD profile broadening analysis using Scherrer equation and Williamson–hall analysis showed a direct correlation between the crystallite size and the dopant concentration. The strain induced in the nanoparticle also followed a direct trend with dopant concentration. Morphological studies confirmed significant agglomeration of the nanoparticles and confirmed the shape to be nanorods. Aggregation of the particles was observed to peak at dopant concentration of 8%, confirming the influence of the dopant on the crystalline nature of Bi_2S_3 . The absorption of Bi_2S_3 was significantly red shifted by Cu-doping with the band gap also increasing with dopant concentration. The influence of Cu-doping was also observed in the photocatalytic activity of Bi_2S_3 . The photocatalytic activity for methyl

orange (MO) degradation was enhanced from 88% to 98%, which shows the positive impact of Cu-doping on Bi_2S_3 . The outcome of the study showed that the use of Cu-doped Bi_2S_3 nanorods in water treatment may guide the development of future semiconductor photocatalysts in environmental remediation.

4.5. References

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CHAPTER FIVE

Graphitic carbon nitride functionalized with Cu-doped Bi₂S₃ as a heterostructure photocatalyst for the visible light degradation of methyl orange

5.1. Introduction

The visible light-based photocatalytic process for the degradation of contaminants in water is a well-studied technique. This is because of its effectiveness and environmental friendliness. Despite the huge potential of this technology, it has yet to achieve the expected impact due to several challenges, such as low photocatalytic efficiencies and high costs of photocatalysis in large-scale applications [1]. If the challenge of low photocatalytic efficiency of the process is effectively addressed, it makes the process an easily accessible and highly efficient technique compared to other wastewater treatment technologies such as adsorption, membrane technology, and photolysis. This has led to an intensification of the need for the development of functional materials with suitable properties.

Hybridization of semiconductors to form heterostructures is a technique that has been widely explored to enhance the effectiveness of photocatalysts. This is due to their ability to enhance the functionality of semiconductors, thereby making them of widespread interest in energy storage, environmental remediation, materials science, catalysis, and biomedicine [2]. Interest in semiconductor heterostructures is based on their ability to explore the synergy between two materials to improve their effectiveness while mitigating their deficiencies. Semiconductor heterostructures have proven to be important in the research for effective photocatalysts for environmental remediation, therefore, a wide range of heterostructures has been reported.

Since the discovery of graphene, a lot of attention has been focused on 2D materials because of their unique structural and optical properties, such as high surface area, great stability, and unique electronic properties. Recently, other carbonaceous 2D materials such as graphene oxide and graphitic carbon nitride have attracted much interest because of their semiconductor properties. Graphitic carbon nitride (g-C₃N₄) has gained much attention because of its attractive band gap of 2.7 eV, which makes it suitable for application under visible light [3]. The desirability of visible light for photocatalytic processes stems from the high portion of the electromagnetic radiation of the sun lying in this region, and thus photocatalytic processes could be carried out under direct sunlight. Therefore, researchers are exploring the development of visible light to satisfy the essential requirements of practical viability. However, despite this huge potential, g-C₃N₄ suffers from high charge carrier recombination,

which significantly limits its photocatalytic efficiency [4]. This limitation is often addressed by doping it with non-metals, metals, and the formation of heterostructures [5]. Therefore, g-C₃N₄ is often used in building heterostructures for photocatalytic processes. Several g-C₃N₄ heterostructures have been reported for the removal of organic pollutants including Ti₃C₂/g-C₃N₄ [6]/ Bi₂O₃-V₂O₃/gCN [7], TiO₂QD/g-C₃N₄ [8], g-C₃N₄/ZnO [9], CaSnO₃/g-C₃N₄ [10], MoS₂/g-C₃N₄ [4], SrTiO₃/g-C₃N₄ [11], Bi₂MoO₆/g-C₃N₄ [12], SnO₂/g-C₃N₄ [13] and g-C₃N₄/BiOI [14].

Heterostructures of g-C₃N₄ with bismuth sulphide (Bi₂S₃) have shown high effectiveness as catalysts in a variety of processes. The bandgap energy of Bi₂S₃, which is around 1.3 - 1.7 eV, makes it a suitable semiconductor for visible light-based photocatalytic processes [15]. Due to its low band edges, Bi₂S₃ suffers significantly from charge carrier recombination, resulting in reduced photocatalytic activity [16]. Elemental doping and the formation of heterostructures are well explored techniques for enhancing the activity of Bi₂S₃. Some reported doped Bi₂S₃ include Sn-doped Bi₂S₃ [17], Mn-doped Bi₂S₃ [18], Cu-doped Bi₂S₃ [19], Eu-doped Bi₂S₃ [20], and Fe-doped Bi₂S₃ [21]. More significantly, heterostructures of Bi₂S₃ with other semiconductor nanoparticles have been reported. Liao *et al.*, [22] reported the synthesis of MoS₂/Bi₂S₃ heterojunction, which showed 76.2% degradation efficiency for methylene blue degradation. A 3D/2D Bi₂S₃/SnS₂ heterostructure with high charge separation was reported by Paul *et al.*, [23]. Theoretical calculations showed that the material exhibited a typical type-II band alignment, which accounted for the enhancement in methylene blue (MB) degradation [23]. In another study, Bi₂S₃-In₂S₃ Z-scheme heterostructure was successfully reported for the efficient reduction of Cr⁶⁺. The intimate contact at the heterojunction created a robust interface for electron transfer and improved charge carrier separation efficiency [24].

There are only a few examples of improved photocatalytic activity of g-C₃N₄/Bi₂S₃ heterostructure in literature. Ganesamurthi *et al.*, (2022) [25] reported the synthesis of Bi₂S₃ and Zn-doped g-C₃N₄ heterostructure via thermal and ultrasonication process with enhanced electrochemical sensing of nitric oxide (NO). Similarly, a Bi₂S₃@g-C₃N₄ heterostructure with enhanced degradation of NO under solar irradiation was obtained by Hussain *et al.*, (2022) [5]. However, there is no report on the photocatalytic efficiency of metal-doped Bi₂S₃ heterostructure with g-C₃N₄. This material, which will benefit from the advantage of metal doping and the interface created at the heterojunction with g-C₃N₄, is expected to show enhanced photocatalytic activity for organic pollutant degradation.

Dyes are important raw materials in the textile, leather, pharmaceuticals, and printing industries. However, they are one of the major causes of environmental pollution, when released into the environment [26]. Methyl orange (MO) is a synthetic, anionic azo dyes that contains aromatic and -N=N- groups in its molecule. It is highly toxic, teratogenic, carcinogenic, and harmful to the environment and organisms [27-29]. Several composites of g-C₃N₄ heterostructures have been reported for MO degradation; however, only a few studies on g-C₃N₄ and Bi₂S₃ composites have been reported [30, 31]. Therefore, in this study, metal-doping and heterostructure formation have been synergistically employed in enhancing the photocatalytic activity of g-C₃N₄ for the degradation of methyl orange.

Graphitic carbon nitride was prepared through the polycondensation of melamine, and Cu-Bi₂S₃ was obtained from the thermal decomposition of bismuth dithiocarbamate metal complex as a single source precursor. The two materials were employed in the synthesis of gC₃N₄/Cu-Bi₂S₃ heterostructures through the solvothermal technique using ethylene glycol. The gC₃N₄/Cu-Bi₂S₃ heterostructure was then employed as photocatalyst for the degradation of methyl orange. The heterostructure obtained showed improved absorption in the visible region with a reduction in band gap energy, which accounted for the improved photocatalytic activity of g-C₃N₄/Cu-Bi₂S₃.

5.2. Methodology

5.2.1. Chemicals and materials

Copper(II) nitrate hemi-pentahydrate [Cu(NO₃)₂•2.5H₂O], bismuth nitrate(III) pentahydrate [Bi(NO₃)₃•5H₂O], melamine (C₃H₆N₆), ethylene glycol (EG), *N*-alkyl aniline, dodecanethiol-1 (DDT), oleylamine (OAm), carbon disulphide (CS₂), chloroform (CHCl₃), ammonia (NH₃), and ethanol (C₂H₅OH), used in this study were obtained from Sigma Aldrich and were used without further purification.

5.2.2. Synthesis of ammonium *N*-methyl-*N*-phenyldithiocarbamate ligand [NH₄L]

The dithiocarbamate ligand was prepared by following an already reported method [32, 33]. In a typical synthesis, *N*-methyl aniline (2.72 mL, 0.01 mol) and aqueous ammonia (1.50 mL, 0.01 mol) were added to a round bottom flask and cooled to 4 °C using an ice bath. Afterwards, 0.60 mL of carbon disulphide (0.01 mol) was slowly added to the mixture, stirred for about 6 h, and then filtered by suction. The bright yellow product obtained was washed with cold ethanol and stored below 4 °C for subsequent use.

5.2.3. Synthesis of bismuth(III) tris(*N*-phenyldithiocarbamate) complex [BiL]

The bismuth complex was prepared by reacting an aqueous solution of the ligand with an aqueous solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in mole ratio of 3:1 (ligand to bismuth salt). The precipitate that formed was filtered, washed thoroughly using a mixture of ethanol (50 mL) and water (150 mL), and dried under vacuum. The pure complex was obtained by dissolving the crude product in chloroform, followed by filtering to remove the unwanted materials, and subjecting the filtrate to slow evaporation. Copper(II) bis(*N*-phenyldithiocarbamate) complex was synthesized using the same procedure, but with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and a mole ratio of 2:1 (ligand to copper salt).

5.2.4. Synthesis of Bi_2S_3 and Cu- Bi_2S_3 nanoparticles

The solvothermal method was used for the synthesis of Bi_2S_3 , and copper doped Bi_2S_3 (Cu- Bi_2S_3) [32, 34]. In a typical synthesis, 0.25 g of BiL was dispersed in 25 mL of ethylene glycol (EG) and sonicated for 1 h. The mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 4 h. Thereafter, the autoclave was allowed to cool to room temperature, and the obtained black precipitate was washed several times with ethanol to remove impurities and then dried under vacuum. To synthesize Cu- Bi_2S_3 , 1.0 mol of copper(II) nitrate hemi-pentahydrate $[\text{Cu}(\text{NO}_3)_2] \cdot 2.5\text{H}_2\text{O}$ was added to the system and the procedure described above was followed.

5.2.5. Synthesis of g- C_3N_4 nanosheets

The g- C_3N_4 was prepared through a polycondensation process using melamine as a precursor [35]. Melamine powder (5 g) was weighed into an alumina crucible with a cover, then heated at 550 °C for 4 h under nitrogen gas using the muffle furnace method. Afterwards, the muffle furnace was allowed to cool down naturally to room temperature. Then, the yellow product (bulk g- C_3N_4) was ground in an agate mortar and stored.

5.2.6. Synthesis of g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{S}_3$, and g- $\text{C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ composite

The nanocomposites were synthesized through the *ex-situ* solvothermal method [36]. Typically, 0.15 g of g- C_3N_4 powder and a certain amount of Bi_2S_3 were added into a beaker and dispersed in 60 mL ethylene glycol (EG) by ultrasonication for 1 h. The mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. Subsequently, the autoclave was cooled to room temperature, and the obtained product was washed three times with ethanol and dried for further characterization. The g- $\text{C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$

product was also synthesized by the same process. The amount of Cu-Bi₂S₃ was varied to achieve a 5, 10, and 20% composition.

5.2.7. Characterization of nanocomposite

The absorption spectra of all the samples were obtained using a variant UV–vis spectrophotometer. The UV–vis absorption spectra were measured in the wavelength range of 400–1000 nm using the UV–vis spectrophotometer. The photoluminescence (PL) spectra were measured using a Perkin Elmer LS 45 fluorimeter. Powder X-ray diffractogram (XRD) of the nanoparticles were recorded on a Bruker D8 Advanced XRD machine, equipped with a proportional counter using Cu K α radiation ($\lambda = 1.5405$ Å, nickel filter). The diffraction pattern was matched with standards in the JCPDS database. The morphology of the nanoparticles was studied using transmission electron microscopy (TEM) (Hitachi HF–2000 TEM at 200 kV) and scanning electron microscopy (SEM) (FEI Tecnai G2 Twin at 20 kV). Energy dispersive X-ray (EDX), was also used to determine the elemental composition of the nanoparticles.

5.2.8. Photocatalytic evaluation

The photocatalytic activities of the synthesized materials (g-C₃N₄, Bi₂S₃, g-C₃N₄/Bi₂S₃, g-C₃N₄/Cu-Bi₂S₃) were evaluated for the degradation of methyl orange (MO) dye (100 mL, 0.1 mg/L) under visible light irradiation. In a typical process, 10 mg of the catalyst and dye solution were mixed in a Pyrex glass vessel. Then, the suspensions were magnetically stirred in the dark cupboard for about 30 min to ensure an adsorption-desorption equilibrium between the dye and the catalyst. After 30 min, the solutions were exposed to the halogen lamp for 1-2 h with constant stirring in the photocatalytic reaction compartment. The degradation efficiency of the process was monitored using a UV-vis spectrometer by measuring the absorbance of aliquots taken from the system at regular intervals. The percentage degradation for the process was determined using Eq. 1.

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

For the kinetic study, the absorption data for the photocatalytic process was fitted into the pseudo first order kinetics as shown in Eq. 2.

$$\frac{\ln(C_t)}{\ln(C_0)} = -kt \quad (2)$$

where C_t and C_0 represent the initial and final concentrations, respectively, k is the reaction rate constant, and t is the time.

5.3. Results and discussion

5.3.1. Characterization of nanomaterials

Figure 5.1 presents the XRD pattern of g-C₃N₄, Bi₂S₃ and gC₃N₄/Cu-Bi₂S₃ composites. In the pattern of g-C₃N₄, two peaks at 13.1° and 27.3° correspond to the (100) and (002) planes of hexagonal g-C₃N₄. This is in accord with the typical feature of the polymeric carbon nitride reported in literatures [37] and confirms the presence of repeated units of triazine rings as well as the interlayer reflection of the graphitic structure. The pattern for Bi₂S₃ matched well with the standard diffraction data of pure primitive orthorhombic phase of Bi₂S₃ (JCPDS No. 170320) with lattice parameters $A = 11.17$, $b = 11.319$, $c = 3.992$ and space group Pbnm [38]. Both the g-C₃N₄/Bi₂S₃ and g-C₃N₄/Cu-Bi₂S₃ composites showed peaks that were consistent with both gC₃N₄ and Bi₂S₃. This is in agreement with the observation reported by Hussain *et al.*, [5] for the Bi₂S₃/g-C₃N₄ composite obtained by the calcination method. An expanded view of the 002 peak of the pristine g-C₃N₄ and composite materials is presented in Figure 5.2, which shows a slight shift in the position of the peak and suggests a strong interaction between the g-C₃N₄ and Cu-Bi₂S₃. In addition, the intensity of the Bi₂S₃ peaks increased with the addition of g-C₃N₄ and Cu(II)ions, indicating an increase in crystallinity. This improvement in crystallinity is vital for Cu-Bi₂S₃ because most reports on metal-doped Bi₂S₃ revealed a reduction in crystallinity due to the distortion of the material's crystal lattice. Also, the 211 peak from Bi₂S₃ was also observed to have shifted in the composites compared to the pristine Bi₂S₃. This indicates a strong interaction between g-C₃N₄ and Cu-Bi₂S₃. The doping of Bi₂S₃ with Cu could also induce a higher charge carrier separation. The XRD pattern of Cu-Bi₂S₃ is shown in Figure 5.S1.

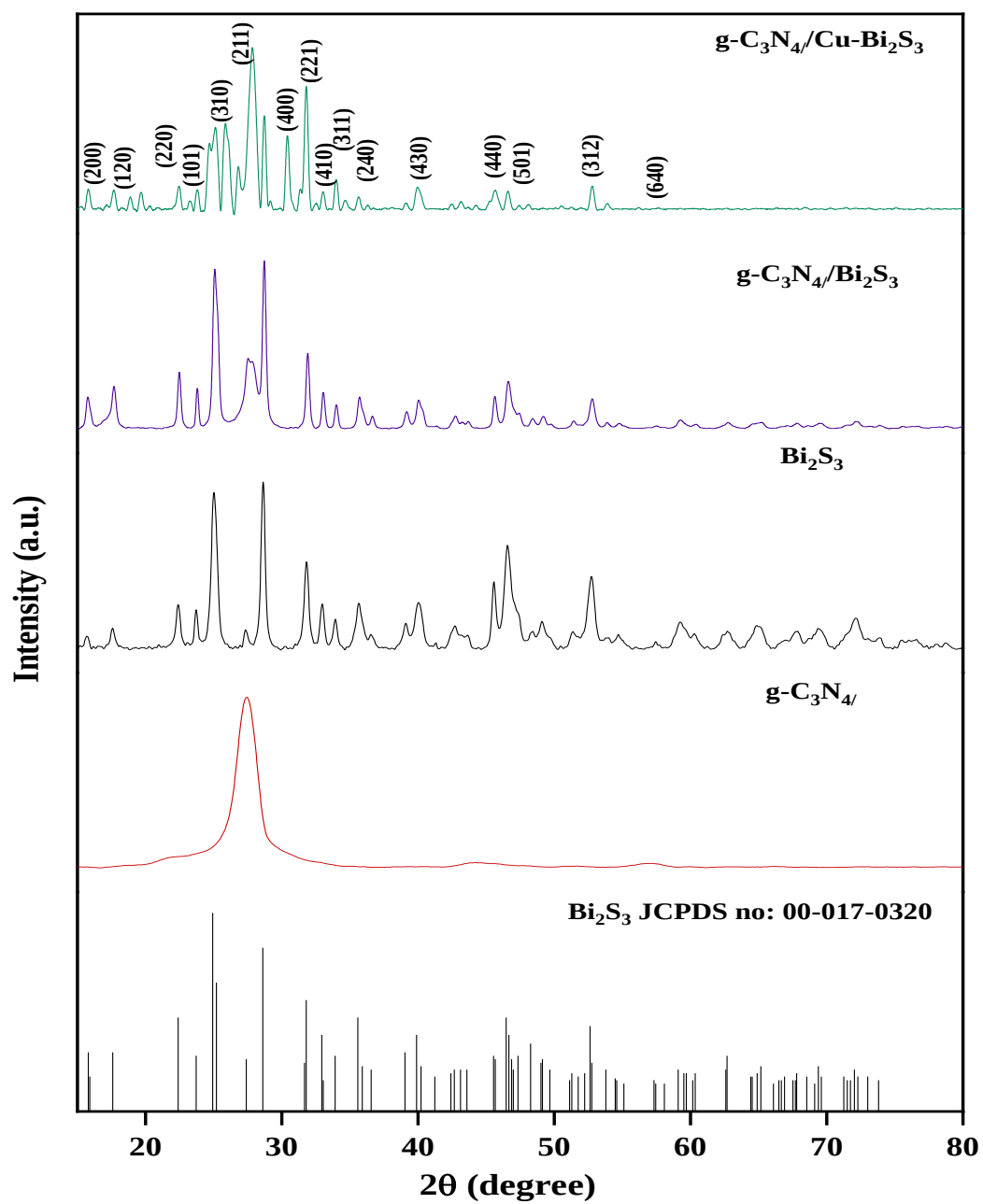


Figure 5. 1: XRD patterns of the $g\text{-C}_3\text{N}_4$, Bi_2S_3 , $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ and $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$.

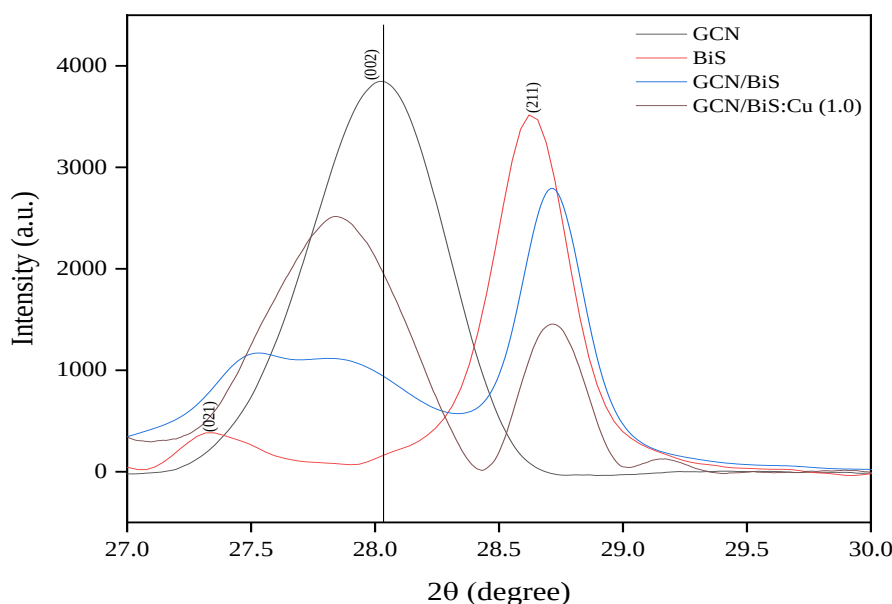


Figure 5. 2: Enlarged view of the X-ray diffraction pattern of the g-C₃N₄, Bi₂S₃, g-C₃N₄/Bi₂S₃, and g-C₃N₄/Cu-Bi₂S₃ in 2θ range of 27.00° - 30.00 °.

Figures 5.3 and 5.4 show the TEM, HRTEM and SAED images of g-C₃N₄/Bi₂S₃ and g-C₃N₄/Cu-Bi₂S₃ heterostructures, respectively. The SEM and TEM images of Bi₂S₃ (Figure 5.S2) show highly aggregated nanoparticles, while the TEM images at different magnifications in Figures 5.3a and 5.3b confirm the shape of the materials to be rods. The presence of diffused and bright spots in the SAED pattern of Figure 5.3c indicates the presence of polycrystalline and amorphous constituents in the heterostructures. Hence, it confirms the formation of heterojunction between g-C₃N₄ and Bi₂S₃ [39], while the d-interplanar spacing of Bi₂S₃ in g-C₃N₄/Bi₂S₃ was 0.3696 (Figure 5.3d). This could also affirm the difference in interaction between the two composites. The size histogram for the length and width of the rods in Figures 5.3e and f, respectively, gave 110 and 19 nm. Majority of reported literature shows a preference for Bi₂S₃ for the rod-shape morphology [40, 41], but there are few reports of other morphologies [42, 43]. In the SEM and TEM micrographs of the g-C₃N₄, the lamellar shape of the sheets could be observed. The sheets are also non-uniform in shape and aggregated (Figure 5.S3). Bi₂S₃ could be observed in the g-C₃N₄/Bi₂S₃ composite to be well distributed on the g-C₃N₄ surface. However, in the TEM image of the g-C₃N₄/Cu-Bi₂S₃, at low and higher magnification in Figures 5.4a and 5.4b respectively, a denser coverage on the g-C₃N₄ could be observed, indicating a stronger interaction in the g-C₃N₄/Cu-Bi₂S₃ heterostructure. Similar to Figure 5.3c, the SAED pattern depicts the presence of diffused and bright spots, indicating the

presence of polycrystalline and amorphous constituents in the $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ composite heterostructures. Also, the interplanar d-spacing of Bi_2S_3 in $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ and $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ was 0.3243 nm (Figure 5.4d). The observed strong interaction in these composites is very significant for enhancing and promoting charge carrier transfer and separation, which improves photocatalytic activities [19].

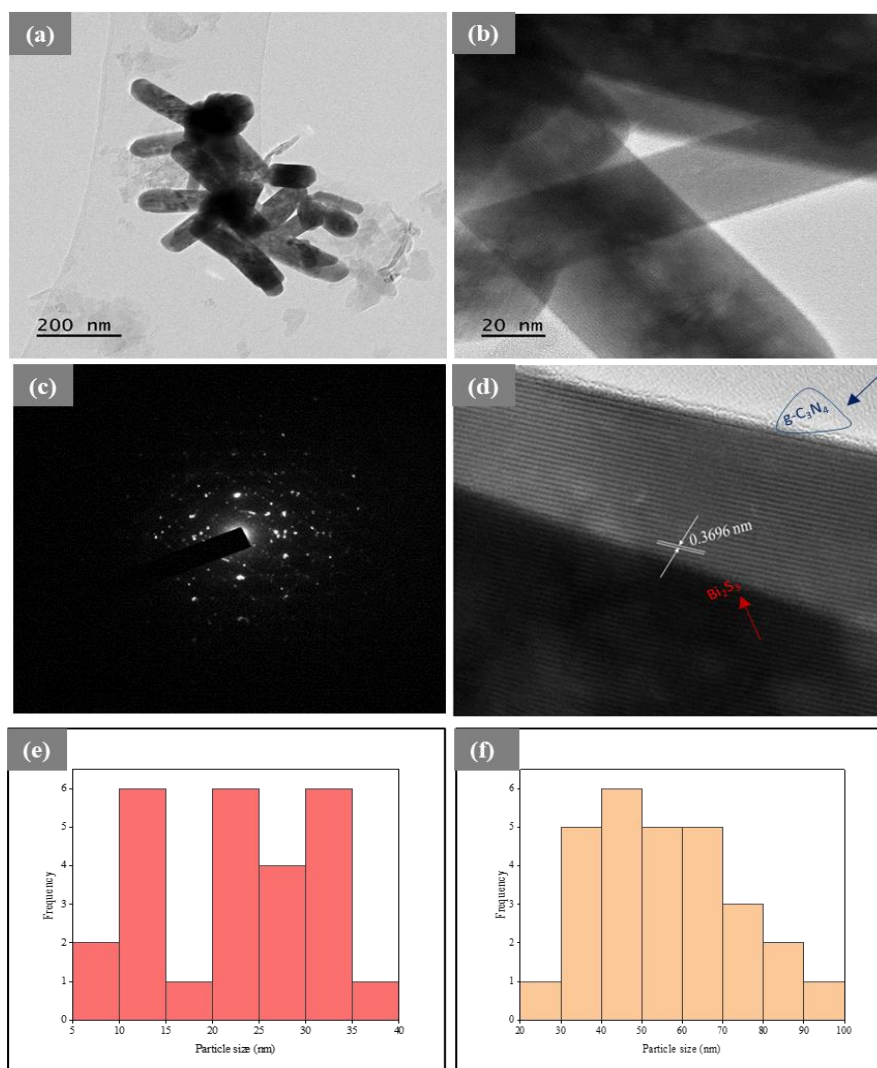


Figure 5. 3: TEM (a) Low mag. (b) High mag. (c) SAED (d) HRTEM; with corresponding particle size distribution histogram showing (e) Width and (f) Length of the $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ nanorods.

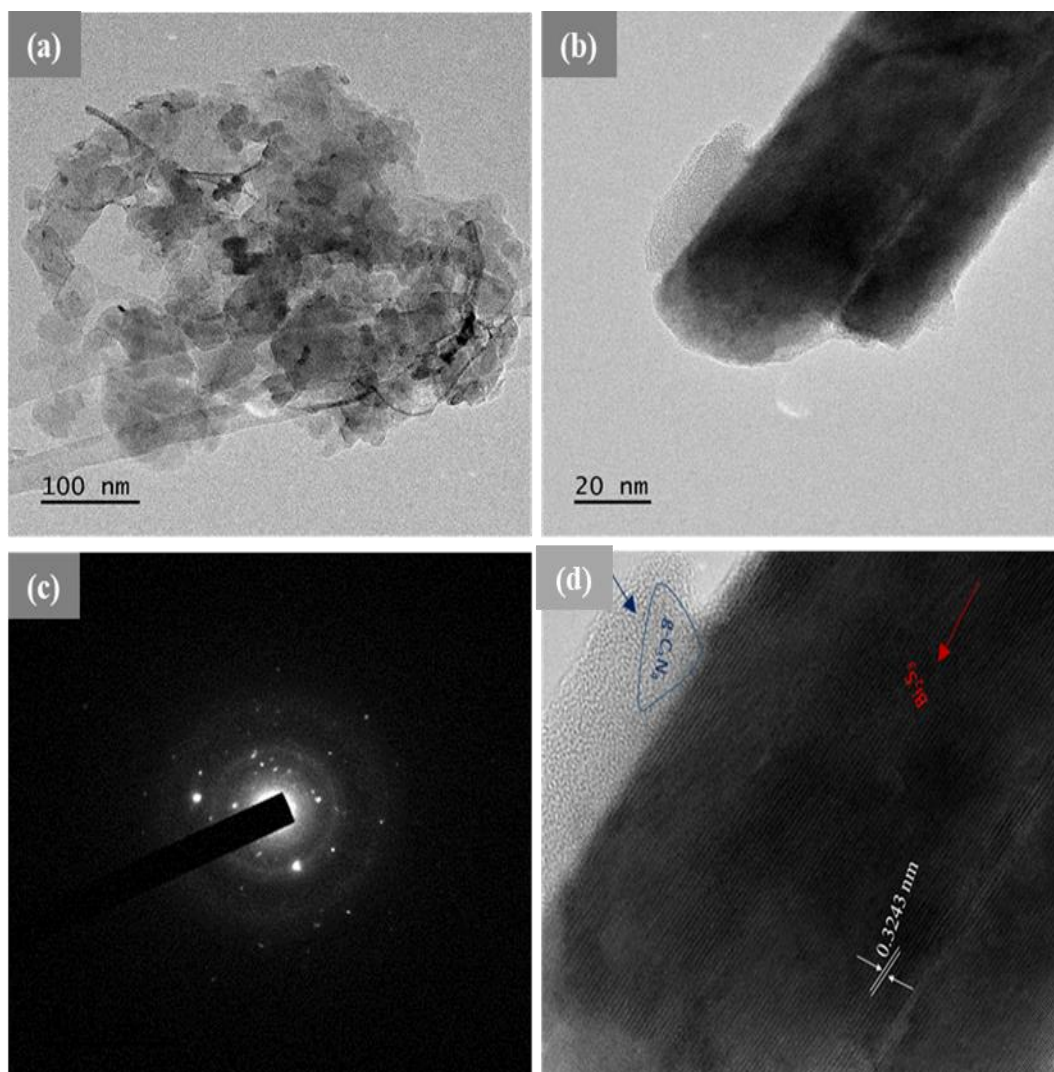


Figure 5. 4: TEM (a) Low mag., (b) High mag., (c) SAED, and (d) HRTEM of the g-C₃N₄/Cu-Bi₂S₃.

Figure 5.5 shows the UV-vis spectra of g-C₃N₄, Bi₂S₃, g-C₃N₄/Bi₂S₃, and g-C₃N₄/Cu-Bi₂S₃ heterostructures. The absorption spectra of g-C₃N₄ (Figure 5.5a) show a strong, broad absorption that peaked at around 400 nm and tailed over the UV-vis range. This is due to the overlap of N 2p orbitals, which lengthens the π -conjugated aromatic systems [44]. The absorption spectra of Bi₂S₃ showed a strong and broad absorption, which tailed significantly into the visible region. This shows the high absorption potential of Bi₂S₃ in the visible range of the electromagnetic spectrum. Similar observation has been previously reported [45]. The g-C₃N₄/Bi₂S₃ and g-C₃N₄/Cu-Bi₂S₃ showed higher absorption intensities compared to pristine g-C₃N₄ and Bi₂S₃. The materials show similar absorption trend, with absorption maximum observed at about 950 nm. Figure 5.5b shows the Tauc plots for the materials from which the optical bandgap energy for the materials was extrapolated. The optical bandgap energy of g-

C_3N_4 , Bi_2S_3 , $\text{Cu-Bi}_2\text{S}_3$, $\text{g-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ were 2.7 eV, 1.86 eV, 1.35 eV and 1.26 eV respectively. The optical bandgap energy became narrowed with the compositing of $\text{Cu-Bi}_2\text{S}_3$ with $\text{g-C}_3\text{N}_4$. This confirms a significant interaction at the electronic level between the two materials and shows a potential for the generation of higher amount of photogenerated charge carriers for the initiation of photocatalytic degradation of pollutants. This can be attributed to the creation of sub-orbital levels within the band edge of the materials. The decrease in the bandgap energy is positive for photocatalytic activity as it signifies an increase in charge carrier generation upon irradiation with light energy of appropriate energy.

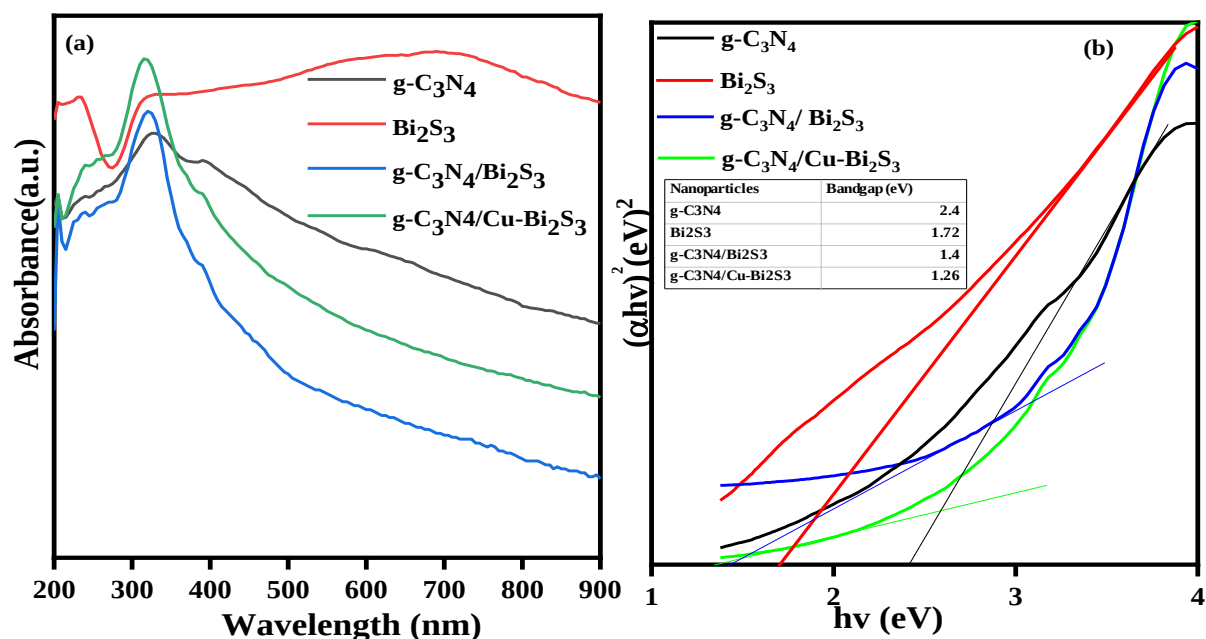


Figure 5. 5: UV–Vis-NIR absorption spectra of (a) $\text{g-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ and $\text{g-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ s with different dopant concentration, and (b) respective Tauc plot (inset Table are the band gap energies).

5.3.2. Photocatalytic activity

The photocatalytic activity of $\text{g-C}_3\text{N}_4$, Bi_2S_3 , and $\text{g-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ heterostructures was tested for the degradation of methyl orange (MO) under visible light irradiation for 2 h. The degradation efficiencies of the $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$, and $\text{g-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ were 85, 87, and 94%, respectively, as shown in the graph in Figures 5.6 (a, b, and c). The improved catalytic activity of the $\text{g-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ composite relative to the others could be attributed to the lowering of the bandgap energy of the heterostructure, which resulted in increased photogenerated charge carriers [7]. Also, the photoluminescence spectra of the materials showed improved charge carrier separation, which could also enhance the photocatalytic activity. This shows that metal doping of Bi_2S_3 had a positive influence on the photocatalytic

activity of the heterostructure formed with g-C₃N₄, and it is a technique that should be explored for enhancing the photocatalytic activity of g-C₃N₄ composites. The photocatalytic degradation data were fitted using the pseudo-first-order reaction kinetics model as shown in Figure 5.6 (d, e, and f). The degradation rate constants (k) for g-C₃N₄, g-C₃N₄/Bi₂S₃, and g-C₃N₄/Bi₂S₃ were 0.00718, 0.0143, and 0.0256 min⁻¹, respectively. This shows the doping of Bi₂S₃ with Cu²⁺ leads to a doubling of the reaction rate constant of g-C₃N₄/Cu-Bi₂S₃ for methyl orange degradation compared to g-C₃N₄/Bi₂S₃. Also, the g-C₃N₄/Cu-Bi₂S₃ heterostructures showed comparable activity compared to the other heterostructures as shown in Table 5.1.

Table 5. 1: Comparison of g-C₃N₄/Cu-Bi₂S₃ with other reported heterostructures for the degradation of MO.

Heterostructure	Parameters	Efficiency	k (min ⁻¹)	Time	Ref
g-C ₃ N ₄ /Cu-Bi ₂ S ₃	MO = 0.1 mg/L CAT = 10 mg Light source = sodium vapour lamp.	94%	0.0256	90 min	This study
Ag ₂ CrO ₄ -g-C ₃ N ₄	MO = 15 mg/L CAT = 25 mg Light source = 300 W xenon lamp.	90%	0.10136	20 min	[46]
BiOI-g-C ₃ N ₄	MO = 10 mg/L CAT = 30 mg Light source = 300 W xenon lamp.	92.1	0.0309	60	[14]
Ag@AgBr/g-C ₃ N ₄	MO = 10 mg/L CAT = 100 mg Light source = 300 W xenon lamp.	94%	-	10 min	[47]

MO = methyl orange

CAT = catalyst

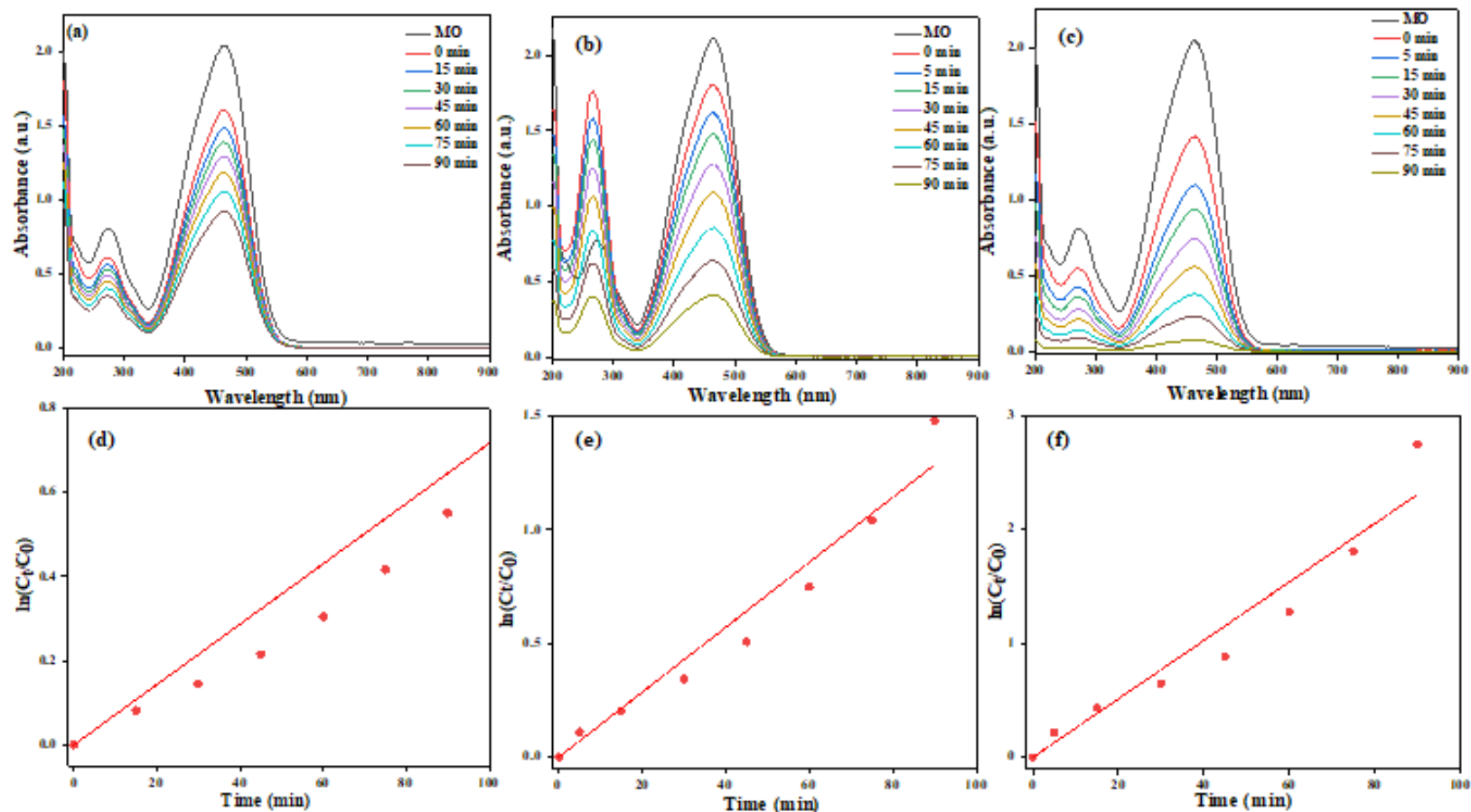


Figure 5. 6: Degradation profiles of MO using 10 mg of (a) g-C₃N₄, (b) g-C₃N₄/Bi₂S₃, (c) g-C₃N₄/Cu-Bi₂S₃, and the kinetics plots given in d, e, and f respectively.

5.3.2.1. Effect of process parameters on catalytic activity

The effect of process parameters, such as the composition of Cu-Bi₂S₃, pH, dye concentration, and catalyst concentration, on the degradation process was studied. Figure 5.7 shows the effect of the composition of Cu-Bi₂S₃ on the degradation efficiency of the process. The degradation efficiency reached 100% by increasing the composition of Cu-Bi₂S₃ in the heterostructure from 5 to 10% in 90 min. This could be attributed to an increase in charge carrier generation due to an increase in the number of active species on the system. Increasing the composition of Cu-Bi₂S₃ to 20% also achieved complete degradation of methyl orange. The rate of MO degradation increased as the percentage composition of Cu-Bi₂S₃ increased. The pseudo first order reaction rate kinetics for the process were 0.0276, 0.0324, and 0.0496 min⁻¹ for 5, 10, and 20% wt of Cu-Bi₂S₃, respectively. The reaction rate was therefore almost doubled by increasing the composition of Cu-Bi₂S₃ from 5 to 20%. This shows that increasing the composition of Cu-Bi₂S₃ did not negatively influence the penetration of light or the photogenerated charge carriers. Excess dopants have been reported to sometimes mask the active sites or act as recombination centres for photogenerated charge carriers, as reported for NiO/g-C₃N₄ composites [48-50]. This implies that the reaction rate for the degradation process could be increased while the time taken for degradation could be significantly reduced by increasing the percentage composition of Cu-Bi₂S₃ in the composite.

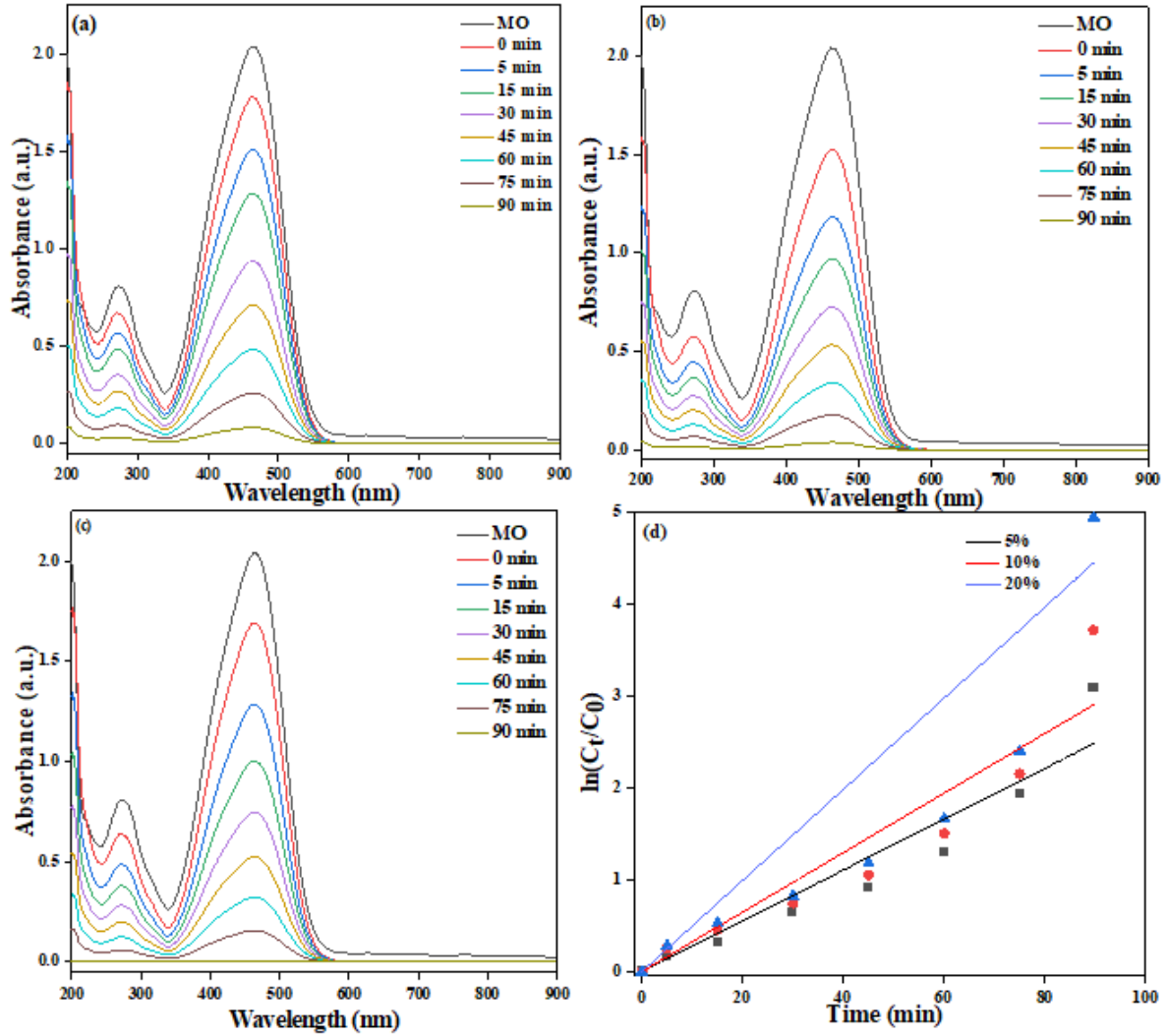


Figure 5. 7: (a) UV-visible absorption spectra of g-C₃N₄/Cu-Bi₂S₃ using (a) 5%, (b) 10%, and (c) 20% nanocomposite using MO dye.

The effect of dye concentration on the photocatalytic process is shown in Figure 5.8. The dye concentration was varied between 0.1 and 0.5 mg/L. At 0.1 mg, the photocatalysts achieved complete degradation of the dye in 90 min, while 97.2% and 93.5% degradation efficiencies were achieved for 0.3 and 0.5 mg/L, respectively. The reaction rate constants for the process were 0.0499, 0.0276 and 0.00275 for 0.1, 0.3, and 0.5 mg/L of MO, respectively. This further affirms the high photocatalytic potential of the g-C₃N₄/Cu-Bi₂S₃ heterostructure for methyl orange degradation. Most studies have reported a reduction in photocatalytic activity with an increase in pollutant concentration. This is attributed to the saturation of the catalyst's surface by the pollutant, leading to a diminishing of the photonic efficiency of the catalyst. Also, a competition between the pollutant and the degradation products for the catalyst surface could also impact the degradation efficiency of the process [51].

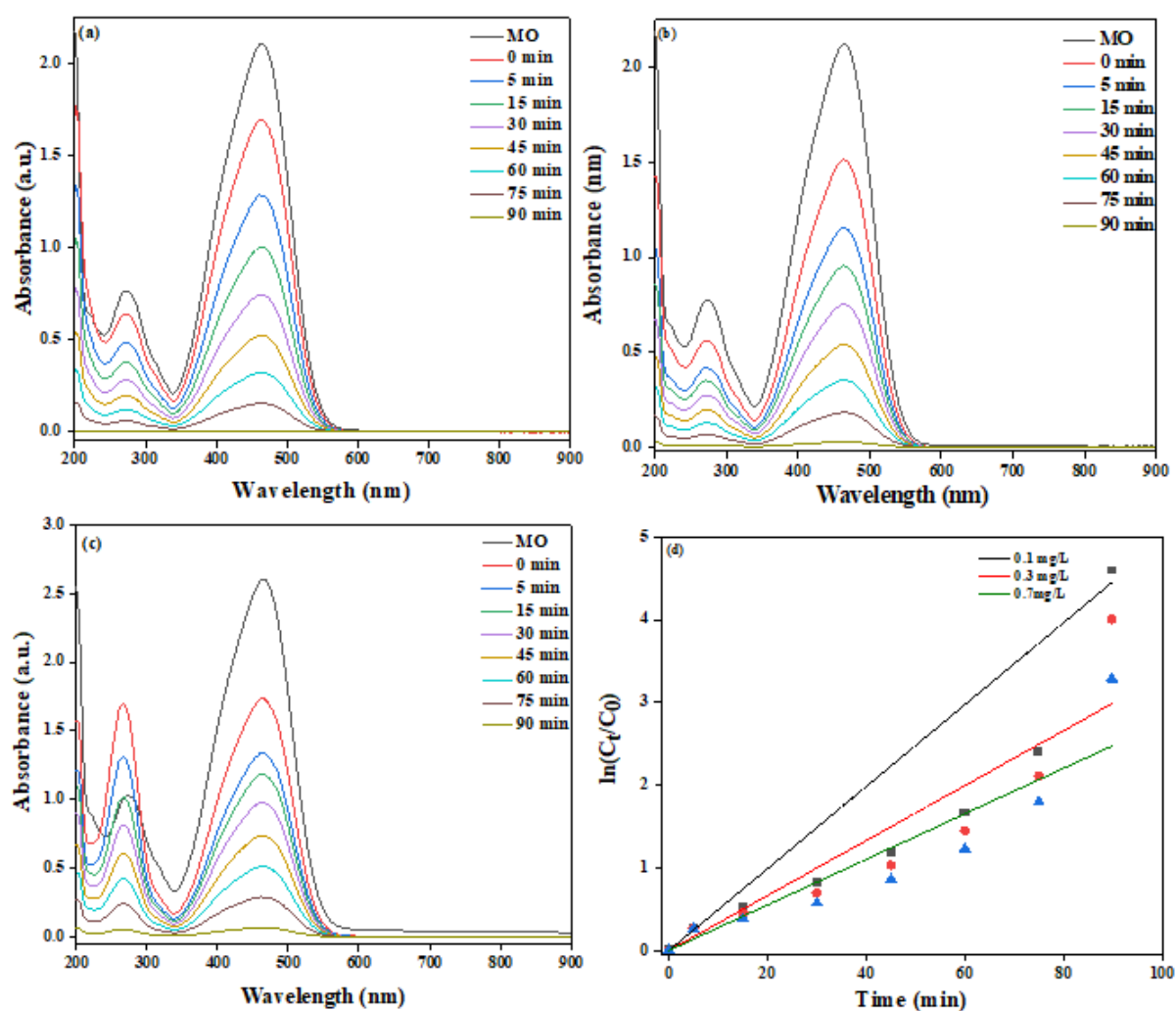


Figure 5. 8: UV–visible spectra of 0.1 mg/L MO dye showing its photodegradation by g- $C_3N_4/Cu-Bi_2S_3$ (20%), catalyst loading (a) 0.1 mg/L, (b) 0.3 mg/L, and (c) 0.5 mg/L.

The photocatalytic removal of dyes is influenced by pH because pH significantly affects the diffusion process, surface adsorption, and surface charge of pollutants [52]. Figure 5.9 shows the effect of solution pH on the photocatalytic activity of g- $C_3N_4/Cu-Bi_2S_3$. The photocatalytic process was carried out at pH 2, 7 and 10 to evaluate the activity of the photocatalyst under acidic, neutral, and basic conditions. The material showed good activity under all conditions, with only a slight reduction in activity observed under acidic conditions. The degradation efficiencies were 95, 100, and 98%, and the reaction rate constants were 0.0122, 0.050, and 0.03 min^{-1} at pH values of 2, 7, and 10, respectively.

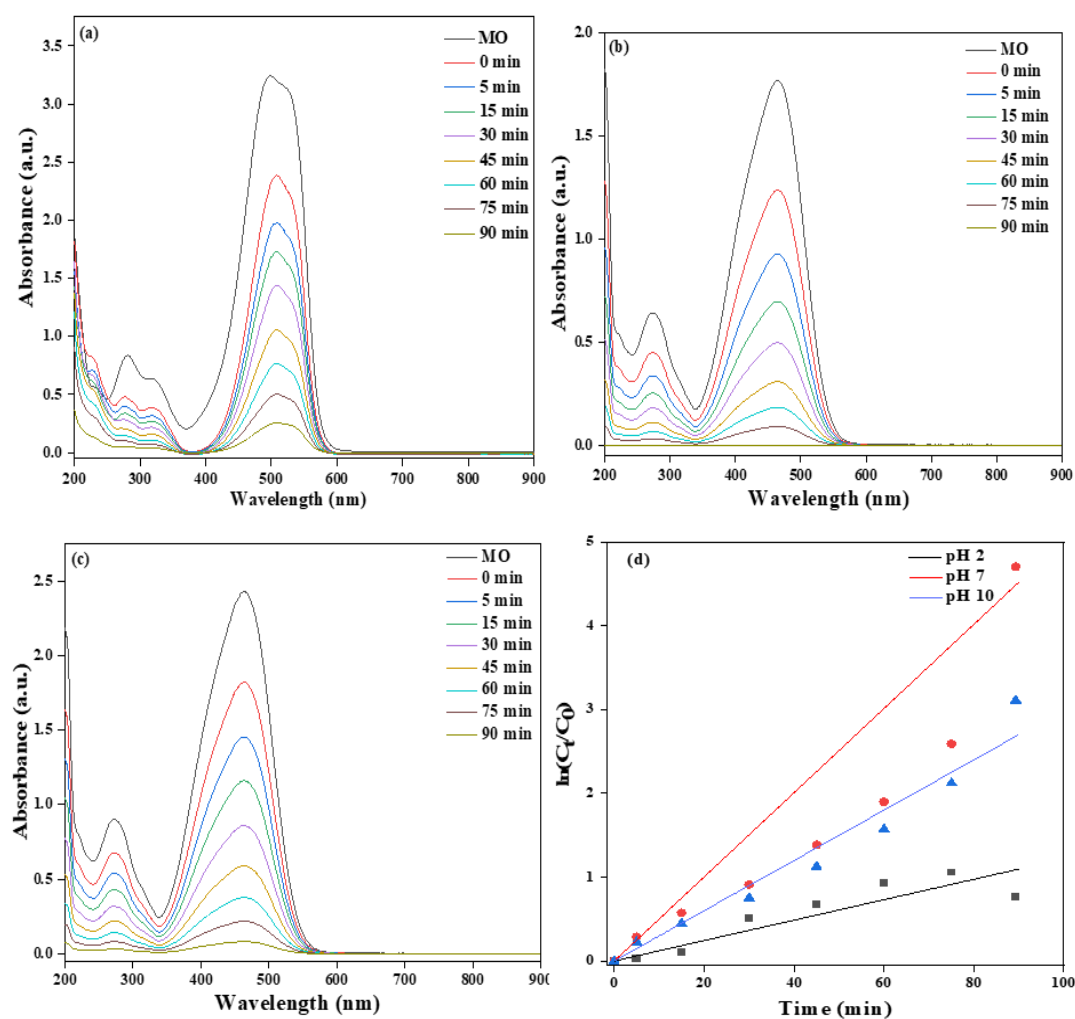


Figure 5. 9: (a) UV-visible spectra of 0.1 mg/L MO dye at different time using g-C₃N₄/Cu-Bi₂S₃ (20%) nanocomposite at pH values of (a) pH 2, (b) pH 7 and (c) pH 10.

5.3.2.2. Radical scavenging study and mechanism

To investigate the effect of radical species on the photocatalytic process, ascorbic acid (ASC), tert-butanol (TBA), triethyl amine (TEA) and silver nitrate (SN) were used as $O_2^{\cdot-}$, $\cdot OH$, h^+ and e^- scavengers. As shown in Figure 5.10, the photocatalytic efficiency of the process was significantly reduced by the addition of SN and TBA. This showed that $\cdot OH$ and e^- played a significant role in the high efficiency of the photocatalyst. The introduction of ASC, TBA, TEA, and SN led to about 40, 70, 20, and 50% reduction in the efficiency of the degradation process, respectively.

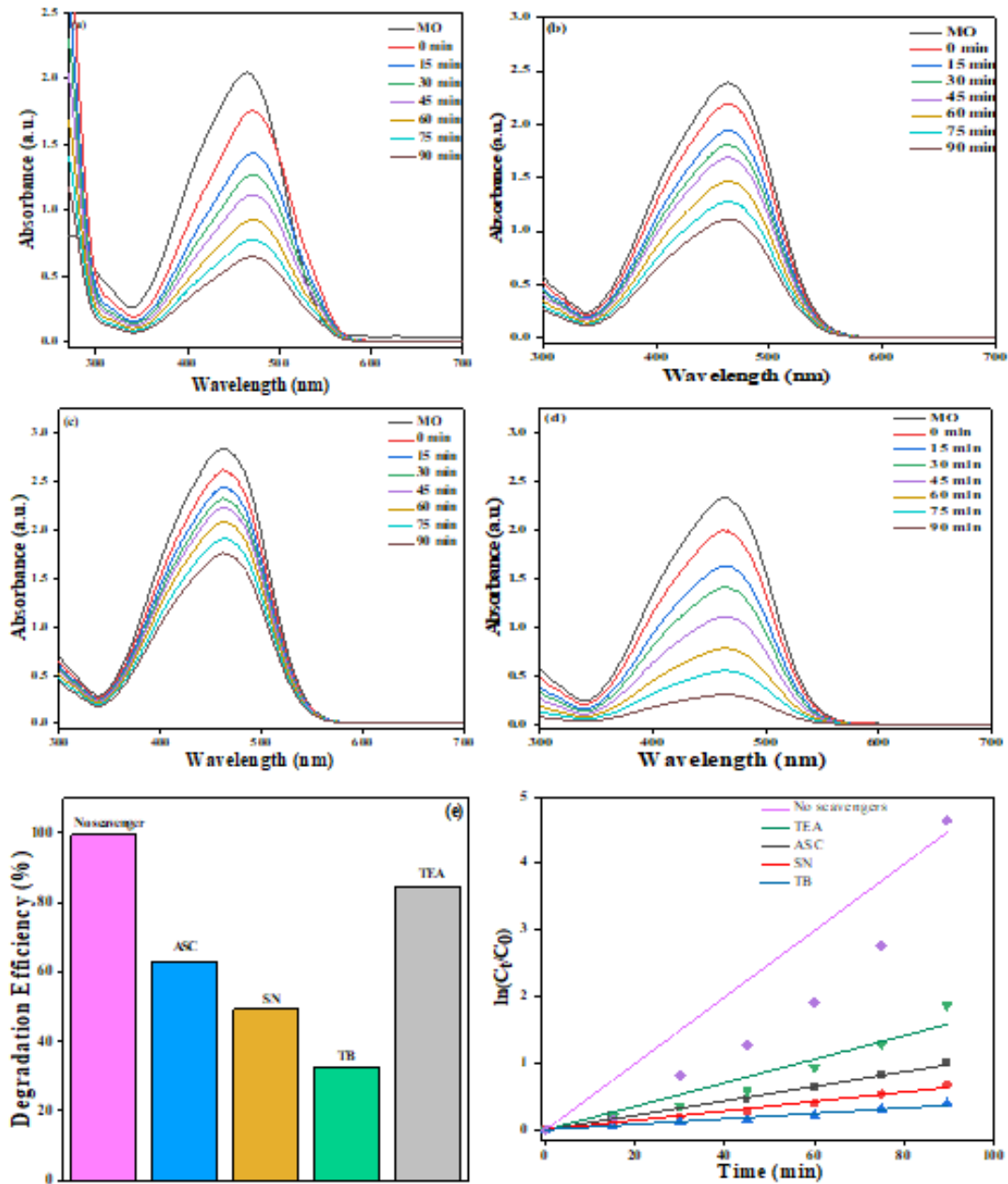


Figure 5. 10: The control experiment tests of the photodegradation study using MO dye with the addition of some radical scavengers: (a) ASC [$O_2^{\bullet -}$], (b) SN [e^-], (c) TBA [$\cdot OH$], and (d) TEA [h^+] under visible light irradiation.

To determine the energy band structures of g- C_3N_4 and Cu- Bi_2S_3 , conduction band (E_{CB}) and valence band (E_{VB}) potentials were estimated using Eqs. 3 and 4:

$$E_{CB} = X - E_e - 0.5E_g \quad (3)$$

$$E_{VB} = E_{CB} + E_g \quad (4)$$

Where X is the Mulliken's electronegativity,

E_e is the energy of free electrons on the hydrogen scale,

And E_g is the band gap energy.

The value of E_e is 4.5 eV, while the value of X for $g\text{-C}_3\text{N}_4$ and Bi_2S_3 is 4.64 and 5.27 eV respectively [53, 54]. From the calculations, the E_{CB} and E_{VB} of $g\text{-C}_3\text{N}_4$ were -1.1 and 1.3 eV, while the values in $\text{Cu-Bi}_2\text{S}_3$ were 0.095 and 1.45 eV for the E_{CB} and E_{VB} , respectively. Based on these values the band alignment of $g\text{-C}_3\text{N}_4$ and $\text{Cu-Bi}_2\text{S}_3$ was constructed as shown in Figure 5.11(a). The band alignment is obviously staggered, which could form traditional type-II or S-scheme heterojunction between $g\text{-C}_3\text{N}_4$ and $\text{Cu-Bi}_2\text{S}_3$. However, the $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ heterostructure seems more suitable for the S-scheme charge migration mechanism compared to the type-II heterostructure. This is because, if $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ followed the type-II charge migration mechanism, photogenerated electrons from the CB of $g\text{-C}_3\text{N}_4$ will migrate to the CB of $\text{Cu-Bi}_2\text{S}_3$, while photogenerated holes move in the opposite direction. Consequently, the photogenerated electrons are unable to generate $\text{O}_2^{\bullet-}$, because the E_{CB} value (0.095 eV vs NHE) of $\text{Cu-Bi}_2\text{S}_3$ is higher than that of $\text{O}_2/\text{O}_2^{\bullet-}$ (-0.33 eV vs NHE). This is, however, contradictory to the result obtained for the quenching experiments of the reactive species. Therefore, the S-scheme charge migration mechanism in which photogenerated e^- and h^+ from $\text{Cu-Bi}_2\text{S}_3$ and $g\text{-C}_3\text{N}_4$ respectively combine due to coulomb attraction and inner electric field created at the interface of the material, results in the accumulation of e^- on the CB of $g\text{-C}_3\text{N}_4$, which has a large reducing capacity for the generation of $\text{O}_2^{\bullet-}$. The formation of $\cdot\text{OH}$ radical could also not be accounted for by the $\text{Cu-Bi}_2\text{S}_3$ VB potential because its value is less positive to the $\text{OH}^-/\cdot\text{OH}$ potential (1.99 eV). Hence, a different mechanism, which involves the Cu(II) induced photo-Fenton like reaction is proposed to account for $\cdot\text{OH}$ formation [55].

The PL spectra of $g\text{-C}_3\text{N}_4$, Bi_2S_3 , $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$, and $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ were studied to evaluate the level of charge carrier separation. The intensity of the PL spectra indicates the rate of charge carrier recombination in the material, with higher spectra intensity indicating higher charge carrier recombination. As shown in Figure 5.11b, the PL intensity of $g\text{-C}_3\text{N}_4/\text{Cu-Bi}_2\text{S}_3$ and $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ were intermediate between that of $g\text{-C}_3\text{N}_4$ and Bi_2S_3 . The closeness of the PL intensity of $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ to $g\text{-C}_3\text{N}_4$ is a result of the main component of the heterostructure being $g\text{-C}_3\text{N}_4$. However, with the doping of Cu ion into Bi_2S_3 , a higher reduction in the charge carrier recombination of the heterostructure was achieved. This confirms the important role of Cu ion doping on the effectiveness of the heterostructure for photocatalytic activity.

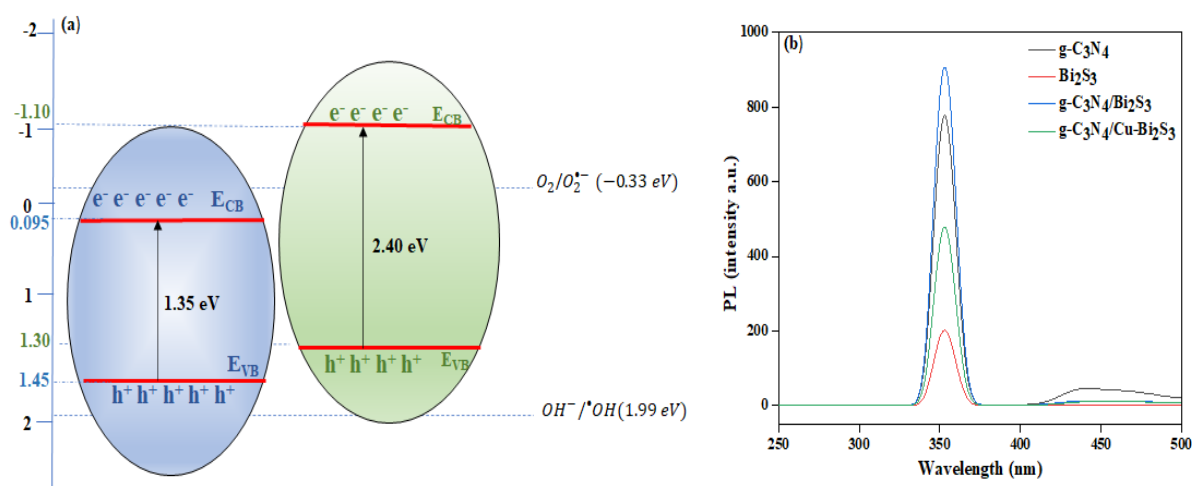


Figure 5. 11: Band structure diagram for g-C₃N₄/Cu-Bi₂S₃, (b) Photoluminescence (PL) spectra of g-C₃N₄, Bi₂S₃, g-C₃N₄/Bi₂S₃ and g-C₃N₄/Cu-Bi₂S₃ nanocomposite excited at a wavelength of 350 nm.

5.4. Sub-Conclusion

In this study, the photocatalytic activity of g-C₃N₄/Cu-Bi₂S₃ heterostructure for the degradation of methyl orange has been reported. By exploring the synergy between the elemental doping of Bi₂S₃ and the formation of heterostructure with g-C₃N₄, an enhancement in the activity of the composite was achieved. A significant interaction between g-C₃N₄ and Cu-Bi₂S₃ was observed, which suggested the formation of heterojunction at the interface, and was significant for enhanced charge carrier separation. The heterostructure was able to achieve 94% degradation in methyl orange, and the study confirmed that the time and efficiency of the process could be enhanced by increasing the percentage weight of Cu-Bi₂S₃ in the heterostructure, due to the strong synergy between the components. The materials showed great activity over the range of pH explored in this study. The radical scavenging experiment confirmed that the most prominent radical species in the degradation process were [•]OH and e⁻. This confirms the effectiveness of doping as well as the formation of a heterojunction system in the photocatalytic removal of organic pollutants from water.

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CHAPTER SIX

Dual heterojunction g-C₃N₄/Bi₂S₃/CuS composite with enhanced photocatalytic activity for methyl orange degradation

6.1. Introduction

Environmental pollution arising from the textile industry has been a serious global problem for many years despite the various environmental regulatory acts [1]. Wastewater from the textile industry contains ~30-40% residual dye, which is discharged into the environment without prior treatment. This waste stream comprises inorganic and organic salts, corrosive acids and metals which are potential carcinogens and mutagens [2, 3]. Methyl orange is a widely used monoazo dye in the textile, chemical and paint industries. It is associated with several harmful effects such as eye irritation and skin problems [4]. It, therefore, becomes important for these compounds to be removed from industrial waste streams before they are discharged into the environment.

Several technologies such as coagulation, adsorption, flocculation, photocatalysis, and ion exchange have been explored for the removal of MO from waste streams. However, most of these techniques suffer from various drawbacks such as high energy consumption, high cost, and production of toxic by-products [5]. Photocatalysis, which is one of the advanced oxidation processes, is a widely used technique for wastewater treatment because of its potential for the degradation of pollutants into harmless final products such as CO₂, H₂O and inorganic salts [6]. It has proven to be effective in the degradation of several dyes such as Sudan 1 [7], Rhodamine B [8], Bromophenol blue, Eosin Yellow [9], methyl orange [10] and methylene blue [11].

Different classes of semiconductor materials such as metal oxides [12], metal sulphides [13], Mxenes [14], metal-organic frameworks have been explored as photocatalysts in wastewater treatment [15]. Recently, carbon-based materials such as graphene oxide and graphitic carbon nitrides have also been explored [16]. However, the use of single photocatalytic semiconductor materials is often limited by the band alignment, which results in high recombination of photogenerated charge carriers [17]. Consequently, research focus has shifted to the development of heterostructure photocatalysts, which have proven to be able to mitigate the problem of rapid charge carrier recombination. In addition, heterostructure system can provide channels for charge carrier transport, which can enhance the photocatalytic performance [18].

Metal sulphides such as CuS and Bi₂S₃ have been utilized as photocatalysts in wastewater treatment due to their small band gap energy, non-toxicity, and low cost [19-22]. However, they suffer high charge carrier recombination that limits their application in photocatalytic processes. Similarly, graphitic carbon nitride (g-C₃N₄), which is a visible light active carbon material has enjoyed much attention in recent years [23, 24]. Its photocatalytic activity is also limited by high charge carrier recombination. Therefore, in this study g-C₃N₄/Bi₂S₃/CuS heterostructures have been synthesized through a facile solvothermal process to study the potential synergy among the materials in photocatalytic degradation of MO. The degradation experiment revealed a significant increase in the photocatalytic activity of the heterostructures compared to the pristine CuS, Bi₂S₃ and g-C₃N₄. This study shows the potential of achieving increased photocatalytic activity by creating heterostructures with semiconductor materials, which mitigates their limitations.

6.2. Experimental

6.2.1. Materials and methods

Bismuth nitrate(III) pentahydrate [Bi(NO₃)₃•5H₂O], copper(II) nitrate hemi-pentahydrate [Cu(NO₃)₂•2.5H₂O], melamine (C₃H₆N₆), ethylene glycol (EG), dodecanethiol-1 (DDT), N-alkyl aniline, ammonia (NH₃), carbon disulphide (CS₂), and ethanol (C₂H₅OH) were supplied by Merck Pty South Africa.

6.2.2. Characterization of g-C₃N₄/Bi₂S₃/CuS

Structural properties of the nanomaterials were studied using powder X-ray diffraction (XRD), which was recorded on a Bruker D8 Advanced machine equipped with a proportional counter using Cu K α radiation ($\lambda=1.5405$ Å, nickel filter). The morphology of the nanoparticles was studied using scanning electron microscopy and transmission electron microscopy (Hitachi HF-2000 TEM at 200 kV and FEI Tecnai G2 Twin at 20 kV). The optical properties of the materials were studied using absorption and emission spectroscopy. Absorption spectroscopy was measured using a variant UV-vis spectrophotometer. For emission spectroscopy, a Perkin Elmer LS 45 Fluorimeter was employed.

6.2.3. Synthesis of g-C₃N₄, CuS and Bi₂S₃

The method employed for the synthesis of g-C₃N₄ and Bi₂S₃ was earlier reported by Onwudiwe, *et al.* [25]. For the synthesis of CuS, the single source precursor method using copper(II) dithiocarbamate complex as precursor was employed. Full details of the synthesis procedures are discussed in supplementary file, 6.S1.

6.2.4. Synthesis of g-C₃N₄/Bi₂S₃/CuS

Solvothermal technique was employed for the synthesis of the ternary heterostructure. In a typical synthesis, g-C₃N₄ and Bi₂S₃ were dispersed in ethylene glycol in ratio 1:1, and the mixture was transferred into an autoclave, and heated at 180 °C for 24 h. The obtained g-C₃N₄/Bi₂S₃ was washed several times with ethanol and dried under vacuum. For the synthesis of g-C₃N₄/Bi₂S₃/CuS, the obtained g-C₃N₄/Bi₂S₃ was dispersed in ethylene glycol with varied ratio of CuS, to obtain weight percentage of 5, 10 and 20% of CuS. The mixture was transferred into an autoclave and heated for 24 h at 180 °C. The obtained ternary heterostructure was washed several times with ethanol and then dried under vacuum.

6.2.5. Photocatalytic degradation studies

The photocatalytic activity of the photocatalysts was evaluated using methyl orange as the test pollutant under visible light irradiation. In a typical process, 100 mL of 0.1 mg/L MO was measured into a beaker. Afterwards, 10 mg of the catalyst was added into the solution, which was then stirred for 30 min to achieve adsorption and desorption equilibrium. Subsequently, the mixture was irradiated under visible light and aliquots were taken from the sample at regular intervals. The percentage degradation of MO after 60 min was calculated using equation 1,

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

where C_0 and C_t are the initial and final absorbance of the solution respectively. The degradation data for the process was fitted into the linear form of the pseudo first order kinetics to evaluate the reaction rate constant for the process using equation 2,

$$\ln(C_t) = \ln(C_0) - Kt \quad (2)$$

where C_0 and C_t represent the initial and final concentrations of the solution after time t respectively, and K represents the reaction rate constant.

6.3. Results and discussion

6.3.1. Structural and morphological studies

The XRD patterns of GCN, CuS, Bi_2S_3 and GCN/ Bi_2S_3 /CuS heterostructures are shown in Figure 6.1. The diffraction pattern of GCN showed a distinct peak at 28° , which is ascribed to the 002 planes arising from the interlayer stacking of the graphitic-like structure [26]. In the CuS sample, the pattern could be indexed to the hexagonal phase of CuS (JCPDS No. 78-0876) [27], while the diffraction pattern of Bi_2S_3 showed peaks that matched the primitive orthorhombic phase of Bi_2S_3 (JCPDS No. 170320) with Pbnm space group [28]. The diffraction pattern for GCN/ Bi_2S_3 exhibited diffraction peaks due to both GCN and Bi_2S_3 , indicating that the structures of both materials were maintained after compositing. However, a slight reduction in the intensity of the peaks of Bi_2S_3 is noticeable, which indicates a reduction in the crystallinity of the Bi_2S_3 . The ternary GCN/ Bi_2S_3 /CuS composites showed a gradual increase in the CuS peak at 49° , which confirms an increase in the amount of CuS in the composite.

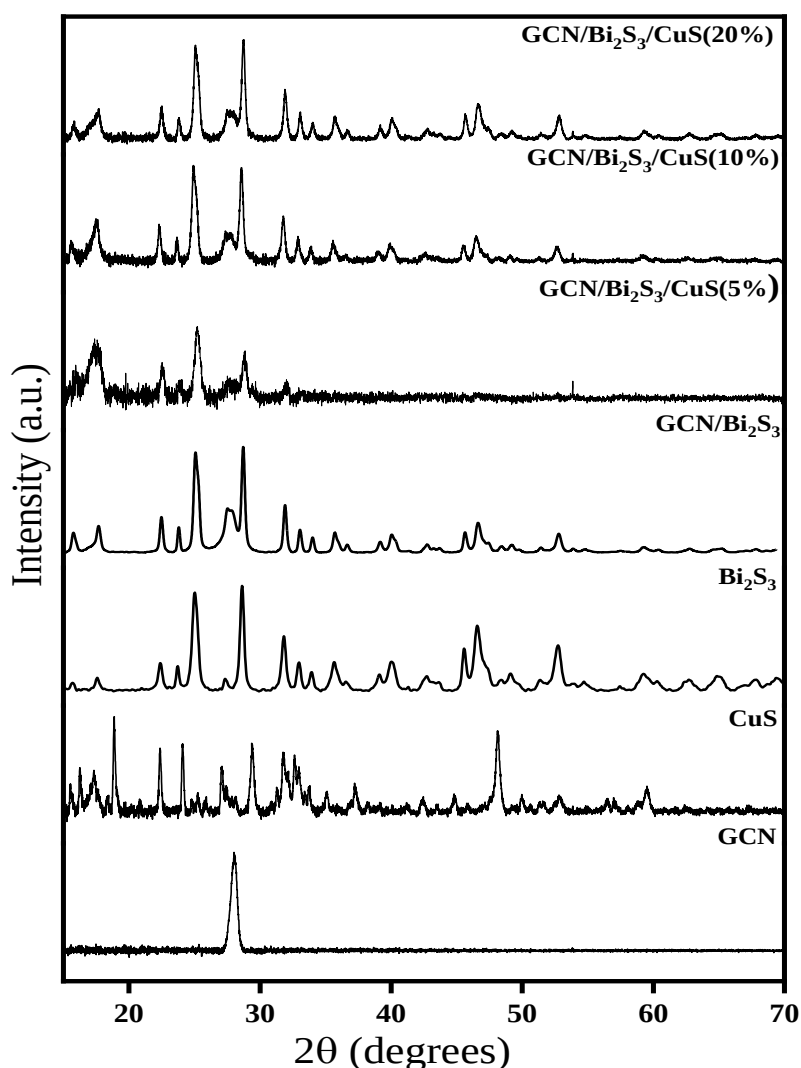


Figure 6. 1: XRD patterns of GCN, CuS, Bi₂S₃, GCN/Bi₂S₃/CuS (5%), GCN/Bi₂S₃/CuS (10%), and GCN/Bi₂S₃/CuS (20%).

The SEM and TEM images of GCN, CuS, and Bi₂S₃, are presented in Figures 6.S1 – 6.S3 of the supplementary document, which show that they are composed of rod-shaped particles. Figures 6.2a, b and c are the TEM micrographs of GCN/Bi₂S₃/CuS(5%), GCN/Bi₂S₃/CuS(10%), and GCN/Bi₂S₃/CuS(20%) respectively. The layered structures of GCN sheets are noticeable at the different concentration of the CuS. SEM measurement presents a better image of GCN because of its advantage in scanning the surface morphology and detecting the layers, folds, and discontinuities within the structure of the 2D material. The SEM images of the GCN/Bi₂S₃/CuS composites (Figures 6.2d -f) also showed the deposition of the nanoparticles on the g-C₃N₄ surface. With increase in the percentage composition of CuS, the images became darker, showing the presence of higher amount of the nanoparticles. The EDX spectra of the composites (Figures 6.2g - i) also confirmed the successful formation

of the GCN/Bi₂S₃/CuS composite, and the percentage of the elemental composition (in the inset) showed proportional increase in the percentage of Cu and S that conforms with the increase in the amount of CuS loading in the nanocomposite.

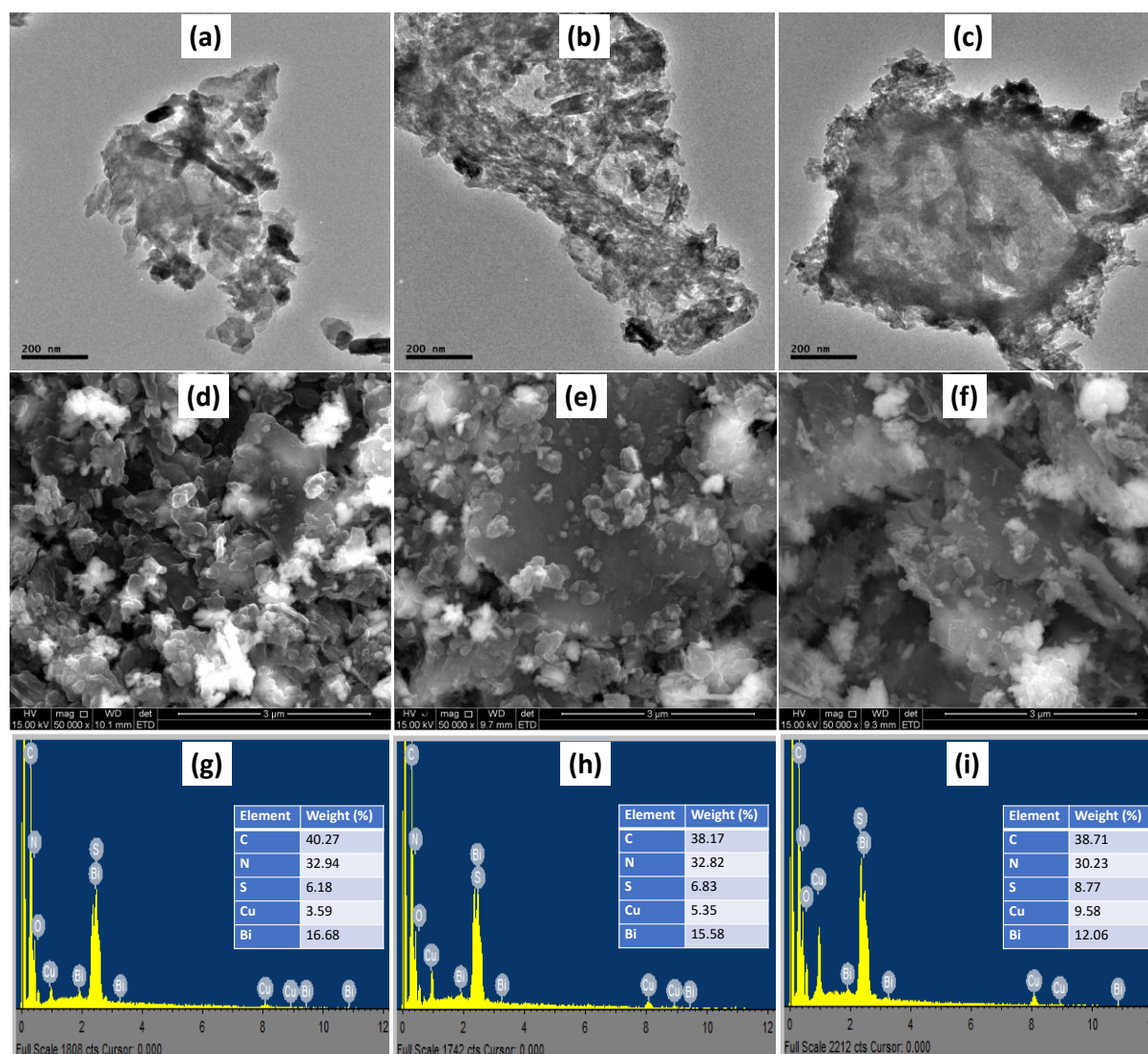


Figure 6. 2: TEM (a-c), SEM (d-f), and EDX (g-i) of GCN-BiS/CuS at 5, 10, and 20% of CuS loading respectively.

6.3.2. Optical properties studies

The absorption spectra of GCN, Bi₂S₃, CuS and GCN /Bi₂S₃/CuS composites are in Figure 6.3. GCN showed a relatively strong absorption in the visible range of the spectrum which tails into the near-infrared region with an absorption edge around 550 nm. The CuS nanoparticles exhibited the highest absorption intensity in the visible region and showed increasing absorption into the near infrared. Moreover, the absorption edge of the CuS was around 380 nm. In the spectrum of the GCN/Bi₂S₃/CuS composites, the absorption intensity was observed

to increase with the percentage composition of CuS, showing improved light absorption. Also, the band edge of the composite was red shift with increase in CuS composition. The calculated band gap energy for GCN, Bi₂S₃ and CuS was 2.25, 1.47 and 1.95 eV respectively, which agrees with literature reports [29-31]. A narrowing of the bandgap energy occurred in the GCN/Bi₂S₃/CuS composites as the percentage of CuS increased. The band gap was 1.79, 1.73 and 1.60 eV for GCN/Bi₂S₃/CuS(5%), GCN/Bi₂S₃/CuS(10%) and GCN/Bi₂S₃/CuS(20%) respectively. This reduction in bandgap energy could be ascribed to the formation of heterostructures between GCN, Bi₂S₃, and CuS. The narrowing of the band gap could be significant for enhancing the photocatalytic activity of the composites, as it could potentially improve charge carrier generation of the material [32].

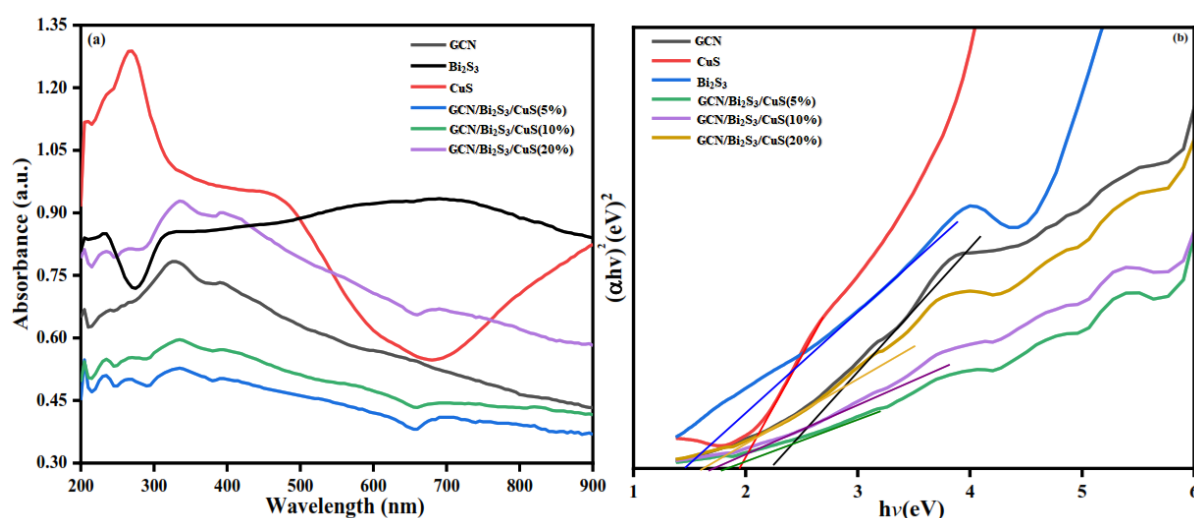


Figure 6. 3: UV-visible spectra of (a) g-C₃N₄, Bi₂S₃, CuS, GCN/Bi₂S₃/CuS(5%), GCN/Bi₂S₃/CuS(10%) and GCN/Bi₂S₃/CuS(20%) and (b) Tauc plot obtained from absorption spectra.

6.3.3. Photodegradation studies of the binary nanomaterials and composites

The degradation profile of GCN, CuS, Bi₂S₃, GCN/Bi₂S₃ and GCN/Bi₂S₃/CuS(5%) for methyl orange is presented in Figure 6.4. GCN, CuS and Bi₂S₃ showed 40, 55 and 57% degradation efficiency, Figures 6.4a, b and c, respectively. The compositing of GCN with Bi₂S₃ to form GCN/Bi₂S₃ composite resulted in an increase of the degradation efficiency to 75% (Figure 6.4d) indicating an enhancement of charge carrier generation and separation. After the introduction of CuS into the composite to form GCN/Bi₂S₃/CuS(5%), the photocatalytic degradation of methyl orange reached 98% (Figure 6.4e). The improved photocatalytic activity of the ternary composite could be attributed to the formation of heterostructure at the interface

of the materials. This could result in improved charge separation compared to the other materials. A pseudo-first rate constant for the degradation was 5.0×10^{-3} , 1.1×10^{-2} , 1.2×10^{-2} , 1.5×10^{-2} , $4.4 \times 10^{-2} \text{ min}^{-1}$ for GCN, CuS, Bi₂S₃, GCN/Bi₂S₃ and GCN/Bi₂S₃/CuS(5%) respectively (Figure 6.4f).

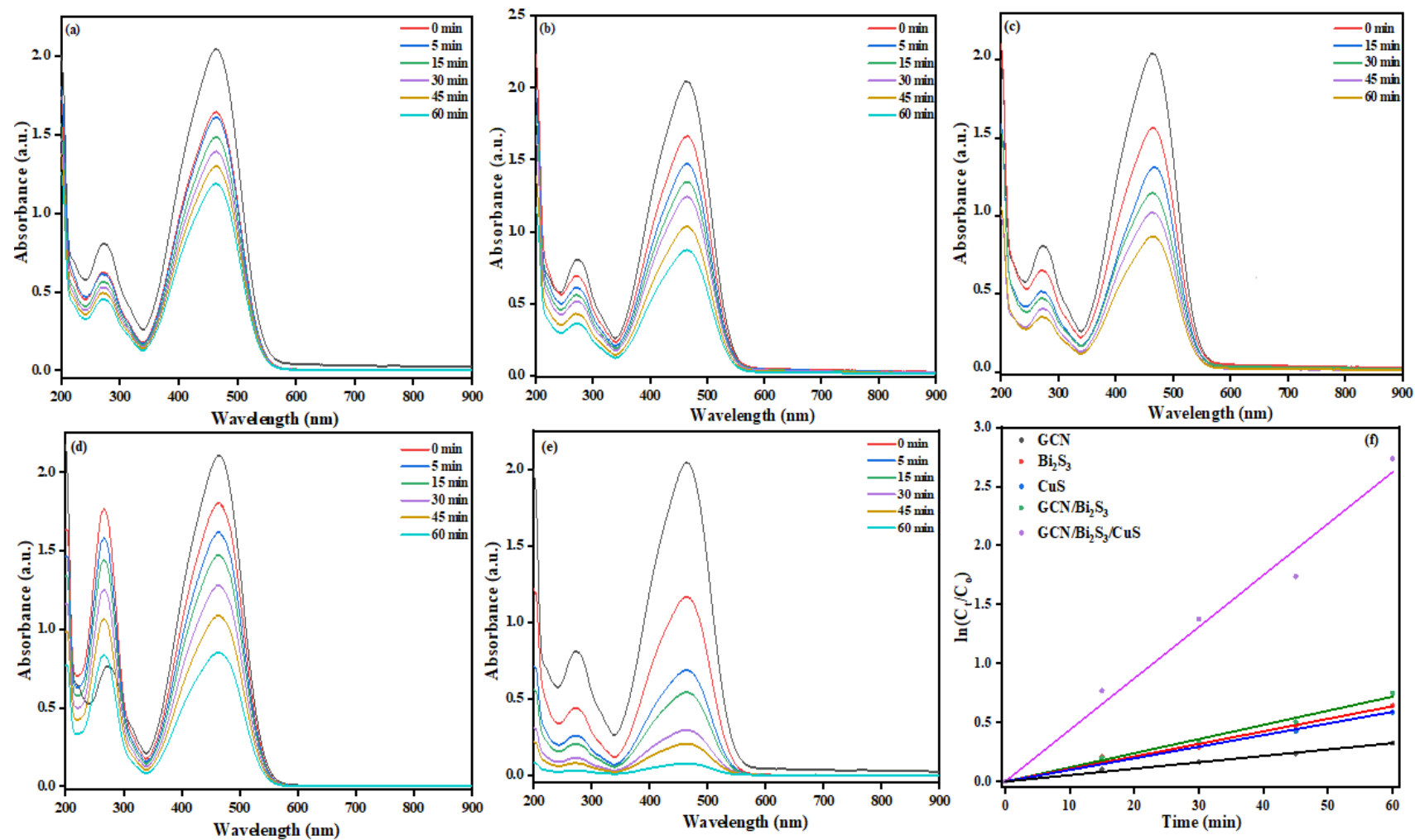


Figure 6. 4: Degradation profile of (a) GCN, (b) CuS, (c) Bi₂S₃, (d) GCN/Bi₂S₃ and (e) GCN/Bi₂S₃/CuS composite for methyl orange and (f) pseudo first order kinetic plot for the degradation profile of methyl orange by GCN, CuS, Bi₂S₃, GCN/Bi₂S₃ and GCN/Bi₂S₃/CuS.

6.3.4. Effect of process parameters

The effect of percentage composition of CuS on the photocatalytic activity of the catalyst is shown in Figure 6.5. An increase in the degradation efficiency of the catalyst was observed with increase in the ratio of CuS in the composite. GCN/Bi₂S₃/CuS(5%), GCN/Bi₂S₃/CuS(10%) and GCN/Bi₂S₃/CuS(20%) achieved 98, 100 and 100% degradation efficiency (Figures 6.5a, b and c respectively) with a corresponding k values of 4.40×10^{-2} , 5.30×10^{-2} , and $8.10 \times 10^{-2} \text{ min}^{-1}$ respectively (Figure 6.5d). The increase in k at higher percentage composition of CuS, is indicative of a faster reaction rate, due to higher active sites on the heterostructure and improved charge carrier generation due to lowered band gap energy. This ability of CuS to enhance degradation process was similarly reported when it was incorporated into ZnO for photocatalytic degradation of methylene blue dye [33].

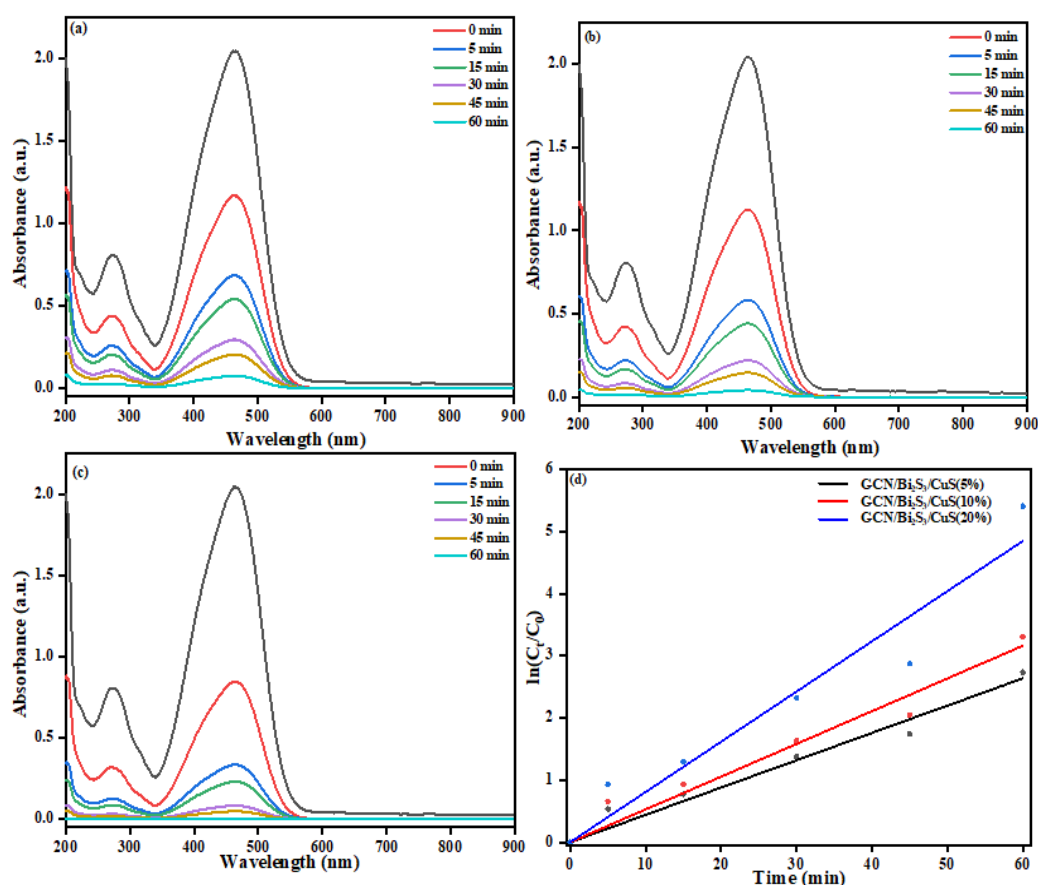


Figure 6. 5: Effect of percentage composition of CuS on the photocatalytic activity of GCN/BiS/CuS(5%), GCN/BiS/CuS(10%) and GCN/BiS/CuS(20%).

The ternary GCN/Bi₂S₃/CuS catalyst showed efficient photocatalytic activity for the dye degradation in the concentration range of 0.1 – 0.5 mg/L as shown in Figure 6.6. The degradation efficiency of MO reached 100, 100 and 98% at 0.1, 0.3 and 0.5 mg/L in Figures

6.6a, b and c respectively. The sustenance of the high catalytic activity of the catalyst even at increased dye concentration confirmed the effectiveness of the ternary heterostructure for MO degradation. The pseudo first order rate constant for the degradation was 9.90×10^{-2} , 5.90×10^{-2} , and $4.60 \times 10^{-2} \text{ min}^{-1}$ respectively (Figure 6.6d).

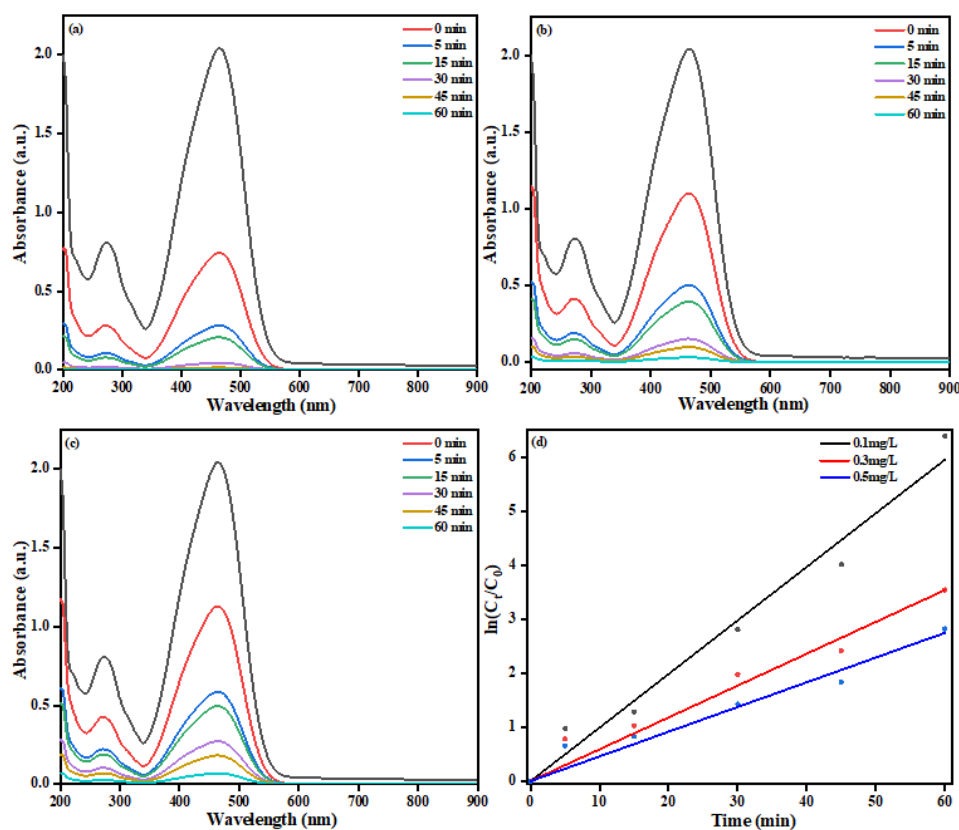


Figure 6. 6: Effect of dye concentration at (a) 0.1 mg/L, (b) 0.3 mg/L and (c) 0.5 mg/L on the photocatalytic degradation of methylene blue and (d) the kinetic plots for the effect of dye concentration on the photocatalytic degradation of methyl orange.

As shown in Figure 6.7, the ternary heterostructure exhibited high catalytic efficiency across the evaluated pH range of 3-10. No significant reduction in the activity of the catalyst was observed under acidic, neutral, and basic conditions. The solution pH often influences the ionic state of a specie in solution and, the nature of charge on the surface of a material [34]. Therefore, it could significantly influence the interaction between the MO molecule and the catalytic material. The effectiveness of the catalyst across the pH range, showed its potential for application in a wide range wastewater matrix.

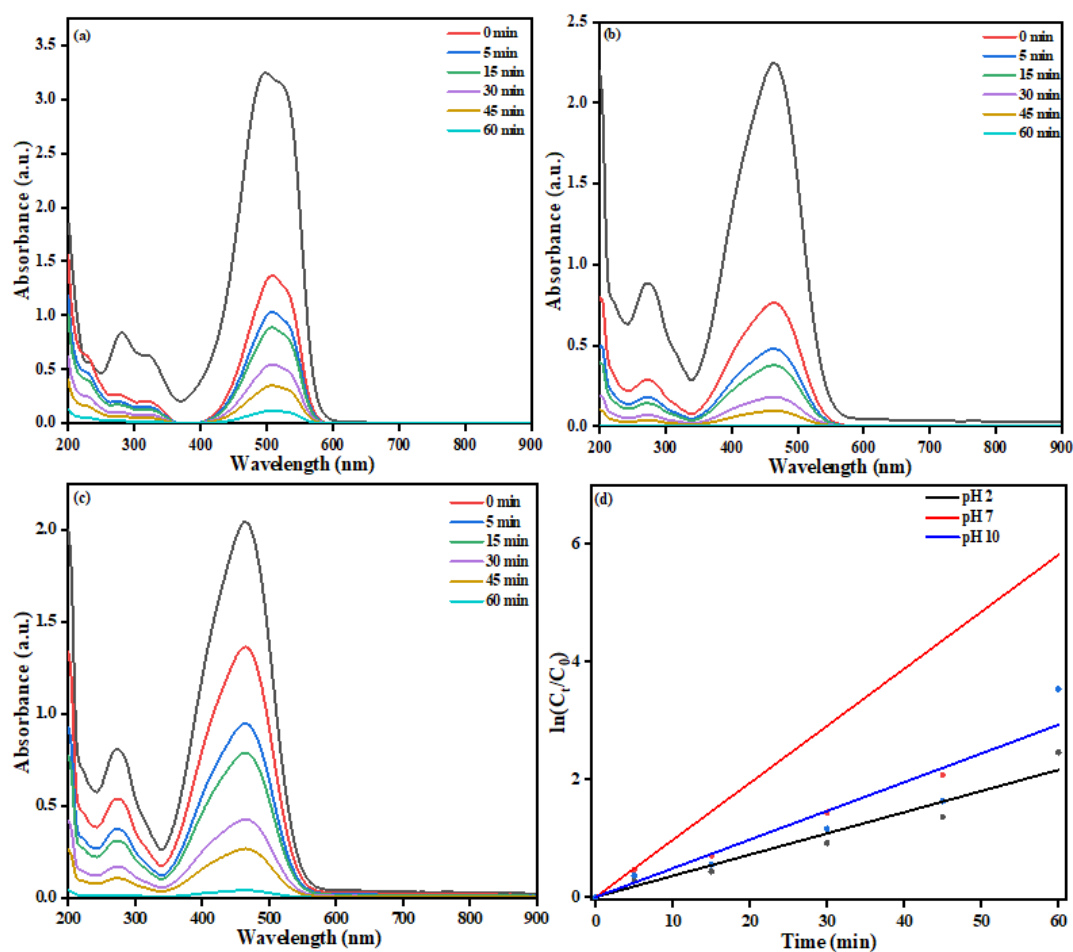


Figure 6. 7: Photocatalytic degradation profile of MO at pH of (a) 2, (b) 7, (c) 10 and (d) pseudo first order kinetics for the degradation of MO at pH 2, 7 and 10.

6.3.5. Radical scavenging studies

To understand the mechanism of action of the ternary heterostructure, radical scavenging experiments were carried out by introducing radical scavengers into the system. Ascorbic acid (ASC), silver nitrate (SN), tert-butanol (TBA) and triethylamine (TEA) were added as $O_2^{\bullet-}$, e^- , $\bullet OH$, and h^+ scavengers. Figure 6.8a shows that TBA had the most significant effect on the degradation efficiency of the process resulting in 50% reduction. TEA and SN both resulted in about 35 and 30% reduction, respectively. This implies that $\bullet OH$ radical had the most influence on the degradation process. The kinetics of the radial scavenging process followed a Pseudo first order kinetics as shown in Figure 6.8b.

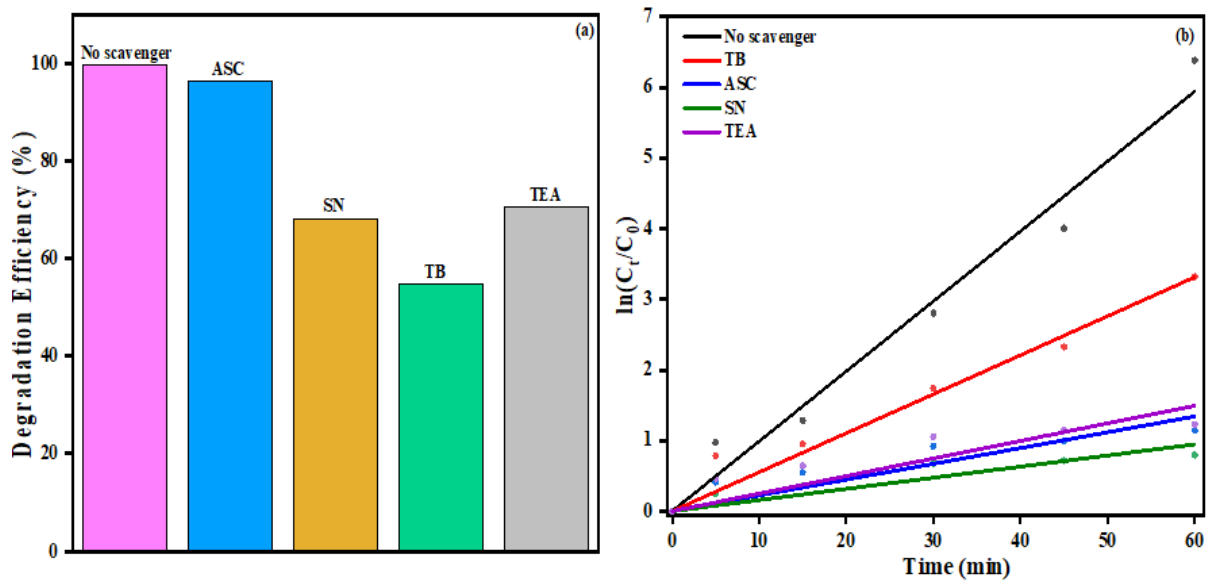


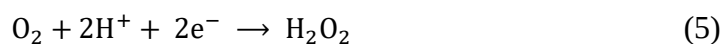
Figure 6. 8: Radical scavenging studies for methyl orange (a) in the presence of TB, TEA, SN, ASC and (b) Pseudo first order kinetics for the radial scavenging experiments.

The mechanism of radical generation in the ternary heterostructure was explored by studying the band alignment through the calculations involving the empirical data and equations 3 and 4:

$$E_{CB} = X - E_e - \frac{1}{2} E_g \quad (3)$$

$$E_{VB} = E_{CB} + E_g \quad (4)$$

where X is the Mulliken's electronegativity, E_e is the energy of free electrons on the hydrogen scale, E_{CB} is the conduction band potential, E_{VB} is the valence band potential, and E_g is the band gap energy. The value of E_e is 4.5 eV, while X for GCN, Bi_2S_3 and CuS are 4.64, 5.27 and 5.29 eV respectively. The calculated band alignments are shown in Table 6.1 and the E_{VB} of the semiconductors were less positive compared to the $OH^-/\cdot OH$ and are not capable of generating $\cdot OH$. The radical scavenging experiment confirmed $\cdot OH$ as the most significant radical in the degradation process, which suggests its formation through a different route in the reaction process. Since the E_{CB} of Bi_2S_3 is less positive than the O_2/H_2O_2 potential, the adsorbed O_2 may react directly with photogenerated electrons to produce H_2O_2 , which further reacts with electrons to produce $\cdot OH$ as shown in equations 5 and 6,



The overall mechanism of the MO degradation is presented in Figure 6.9(a). It shows that within the GCN/Bi₂S₃ structure, the photogenerated electrons by GCN are captured by Bi₂S₃ and these electrons could then react with adsorbed O₂ on the catalyst surface. After the incorporation of CuS, under visible light, GCN and CuS could form a heterostructure with staggered band structure to produce electron-hole pairs. The reported workfunction for CuS and GCN are 4.95 and 4.00 eV respectively [35, 36], so the Fermi energy (E_F) of CuS is lower than that of GCN. When GCN and CuS are in contact, a flow of electrons from the semiconductor with a high E_F to that with a low E_F is observed, leading to the generation of a built-in electric field (IEF) from GCN to CuS at the GCN/CuS interface. This IEF leads to the recombination of the oxidizing holes in GCN with electrons in the conduction band of CuS, resulting in an enhancement of photogenerated charge carriers in GCN/Bi₂S₃/CuS photocatalyst. This shows a S-scheme heterojunction path for charge transport and separation in the GCN/Bi₂S₃/CuS heterostructure [37, 38]. The holes in the E_{VB} of CuS could also migrate to the surface to induce direct oxidation of MO [39]. Figure 6.9(b) shows the PL spectra of GCN/Bi₂S₃/CuS and GCN, which confirms the enhanced charge carrier separation in the heterostructure compared to pristine GCN.

Table 6. 1: Calculated band alignment for GCN, Bi₂S₃, and CuS.

Semiconductor	E _{CB}	E _{VB}
GCN	-0.98	1.27
Bi ₂ S ₃	0.035	1.51
CuS	-0.185	1.77

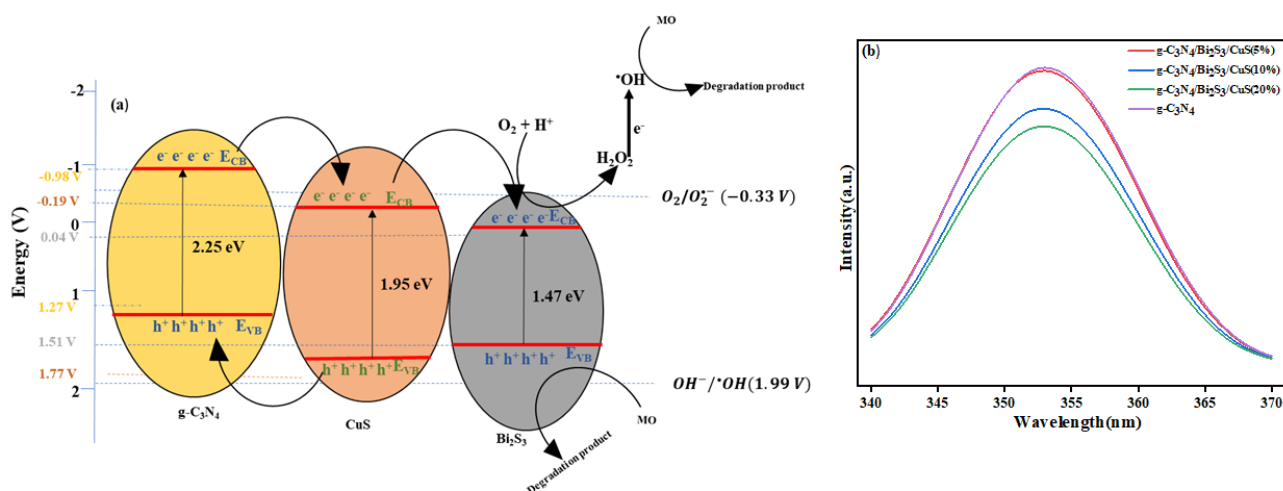


Figure 6. 9: (a) Mechanism of radical generation by GCN/Bi₂S₃/CuS and (b) PL spectra of GCN, GCN/Bi₂S₃/CuS(5%), GCN/Bi₂S₃/CuS(10%) and GCN/Bi₂S₃/CuS(20%).

6.4. Sub-Conclusion

The synthesis of a photocatalytically active dual heterostructure semiconductor was successfully achieved through a facile solvothermal process. The constructed heterostructure obtained from g-C₃N₄, CuS and Bi₂S₃ promises effective light absorption property which could be modified by varying the composition of the material. Compared to g-C₃N₄, the g-C₃N₄/Bi₂S₃/CuS heterostructure showed significant fluorescence quenching, which is indicative of improved charge separation. The ternary nanocomposite showed high photocatalytic performance for methyl orange degradation, achieving 98% degradation and a reaction rate constant of $8.10 \times 10^{-2} \text{ min}^{-1}$. The enhanced photocatalytic activity of the heterostructure could be ascribed to the band alignment of the semiconductors, which allows for the transfer of photogenerated electrons into the Bi₂S₃ CB, while photogenerated holes are accumulated in the VB of g-C₃N₄. This minimizes the chances of charge carrier recombination and the subsequent degradation of MO molecules. These results show the potential of this heterostructure to be explored in practical application for wastewater treatment.

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CHAPTER SEVEN

Synthesis of p-n GCN/CuBi₂O₄ heterostructures for enhanced visible light photocatalysis

7.1. Introduction

The availability of potable water is a global challenge despite several wastewater treatment techniques [1]. Several issues such as cost, energy demand, and waste disposal approach continue to be major problems in wastewater treatment [2, 3]. Also, the continual increase in demand for potable water and the current drive in chemical allied industries such as textile, agriculture, and pharmaceutical translate to a constant strain on water availability and preservation. This makes the sustainability of water resources a global issue as stated in the sustainable development goals of the United Nations [4].

Different wastewater treatment technologies such as adsorption, membrane filtration, thermal technologies, biological processes and advanced oxidation processes are some of the available process for the mitigation of inorganic, organic, and microbial contaminants in wastewater [5]. Among these, photocatalysis, which is one of the advanced oxidation technologies has received much attention in recent time due to its efficiency, cost, durability, and environmental friendliness. In a typical photocatalytic process, radical species such as $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, h^+ are generated by semiconductor materials after absorbing light of appropriate energy [6]. Thus, the semiconducting properties of photocatalytic materials and the light source are important criteria for photocatalytic processes. While the development of materials capable of absorbing within the entire solar spectrum is critical in photocatalysis, factors such as cost effectiveness, environmentally friendliness and suitable physicochemical and optical properties are also very important. These factors have dominated the criteria for the development of semiconductor photocatalysts in recent time.

A large class of materials including oxides [7], sulphides [8], oxychlorides [9], and nitrides [10] have been reported as photocatalysts in wastewater treatment. Also, the combination of two or more photocatalytic materials to form heterostructures have been explored as one of the effective routes for mitigating the weaknesses of semiconductor photocatalysts such as poor charge carrier generation and high charge carrier recombination [11]. Copper bismuth oxide (CBO) is a promising semiconductor material with an optical band gap energy of 1.5 – 1.8 eV, making it a good photocatalytic material for wastewater purification [12, 13]. It is a p-type oxide with a tetragonal crystal structure. The electronic property is significantly influenced by

the presence of isolated $[\text{CuO}_4]^{6-}$ stacks, which differs from the oxygen sharing octahedra or tetrahedra found commonly in metal oxides. However, despite the interesting properties of CBO and potential as photocatalyst, its efficiency in photocatalytic processes is low compared to other similar oxides such as CuFe_2O_4 . This is due to the high charge carrier recombination process within its electronic structure that arises from the electron band states [14].

The formation of heterostructures of CBO with other semiconductor materials is one of the most explored techniques for enhancing its photocatalytic ability. Several heterostructures of CBO have been reported for wastewater treatment such as $\text{NaNbO}_3/\text{CuBi}_2\text{O}_4$ [15], $\text{BiFeO}_3/\text{CuBi}_2\text{O}_4/\text{BaTiO}_3$ [16], $\text{CuBi}_2\text{O}_4/\alpha\text{-Fe}_2\text{O}_3$ [17], $\text{Bi}_2\text{WO}_6/\text{Ag-CuBi}_2\text{O}_4/\text{CNT}$ [18], $\text{Bi}_2\text{O}_3\text{-CuBi}_2\text{O}_4\text{-CuO}$ [19], $\text{Ag}_2\text{S/CQDs/CuBi}_2\text{O}_4$ [20], $\text{Ag-CuBi}_2\text{O}_4$ [21] and $\text{CuBi}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ [22]. These materials exhibited enhanced photocatalytic activity towards the removal of pollutants in water, due to heterostructure formation. Improved photocatalytic activity of $\text{BiFeO}_3/\text{CuBi}_2\text{O}_4/\text{BaTiO}_3$ composite was attributed to the extension of its light absorption range, enhanced charge carrier separation and improved oxidation-reduction ability [16]. The material showed improved solar light driven photocatalytic ability for norfloxacin degradation. Also, combining piezoelectric effect with the high-photo absorbing property of CBO was reported to induce enhanced photocatalytic activity in $\text{NaNbO}_3/\text{CuBi}_2\text{O}_4$ heterostructure. The composite showed enhanced photodegradation efficiency for Rhodamine B [15].

Graphitic carbon nitride (GCN) is one of the semiconductor materials that has gained much attention because of its optical, electrical, and structural properties. Its bandgap energy of 2.7 eV makes it a visible light-induced semiconductor material [23]. However, its applicability is often limited by its high recombination of charge carriers, poor visible light absorption, and low surface area [24-26]. Despite this disadvantage, GCN is a good material for the formation of heterostructures because of its layered structure and surface properties [27, 28]. Therefore, several heterostructures of GCN have been explored as photocatalysts for the degradation of pollutants in water [29-31]. The potential synergy between the morphological and optical properties of CBO and GCN implies that they could form suitable heterostructure for photocatalytic wastewater treatment. Only a few studies reported the use of CBO/GCN composite as photocatalyst. Flower-like $\text{GCN/CuBi}_2\text{O}_4/\text{Bi}_2\text{MoO}_6$ with high photocatalytic activity towards tetracycline hydrochloride and chlortetracycline under visible light irradiation was reported Yu *et al.*, [32]. Guo, Shi *et al.*, also reported the synthesis of $\text{-GCN/CuBi}_2\text{O}_4$ p-n heterojunction via a simple calcination method. The heterojunction showed a CuBi_2O_4 content dependent catalytic efficiency for tetracycline.

In this study, the photocatalytic activity of graphitic carbon nitride composited with copper bismuth oxide for methyl orange degradation is reported. The effect of process parameters on the photocatalytic process was further evaluated. Improved photocatalytic activity of the composite was attributed to the formation of heterostructures with enhanced charge carrier generation and separation.

7.2. Experimental

7.2.1. Materials and Physical Measurements

All the reagents and solvents used were commercially available and were utilized without further purification. The UV–vis absorption spectra were measured in the wavelength range of 400 - 900 nm using the variant UV–vis spectrophotometer, while the photoluminescence (PL) spectra were measured using Perkin Elmer LS 45 Fluorimeter. Powder X–ray diffractogram (XRD) of the nanoparticles were recorded on a Bruker D8 Advanced XRD machine, with a proportional counter using Cu K α radiation ($\lambda=1.5405$ Å, nickel filter). Samples were added on a flat steel sample holder and scanned from 10 to 80 °C. The morphology of the nanoparticles was studied using transmission electron microscopy-TEM (Hitachi HF–2000 TEM at 200 kV and FEI Tecnai G2 Twin at 20 kV) and scanning electron microscopy-SEM. Energy dispersive X-ray-EDX, was also used to determine the elemental composition of the nanoparticles.

7.2.2. Synthesis of GCN sheets

The GCN was prepared following a reported literature method with a slight modification[34]. Melamine powder (5.0 g), as a precursor, was added into an alumina crucible with a cover; then heated at 550 °C for 4 h under nitrogen gas using a muffle furnace. After that, the sample was cooled down naturally to room temperature. The resulting yellow product (bulk GCN) was then collected and grinded in agate mortar and stored for further use.

7.2.3. Synthesis of copper bismuth oxide

The hydrothermal method was employed for the synthesis of CBO. In a typical synthesis, Bi(NO₃)₃·5H₂O (0.97 g, 2 mmol), Cu(NO₃)₂·2.5H₂O (0.25 g, 1 mmol), and NaOH (6 g, 7 mmol) were stirred together in 100 mL distilled water for 3 h. After obtaining a homogeneous solution, the mixture was transferred into a 100 mL Teflon-lined autoclave and heated in the furnace at 180 °C for 6 h. Afterwards, the system was cooled to room temperature and the dark-brown

product obtained was recovered by vacuum filtration. Washing was done thrice with water and ethanol and the product was dried in the oven at 80 °C overnight.

7.2.4. Synthesis of GCN/CuBi₂O₃

Solvothermal technique was used for the synthesis of GCN/CuBi₂O₃ heterostructure. In a typical synthesis, GCN was weighed into 50 mL ethylene glycol and then stirred to form a uniform solution. Varying amount of the synthesized CuBi₂O₃ was then added to obtain 5, 10 and 20% weight composition, which were labelled as GCN/CBO(5%), GCN/CBO(10%) and GCN/CBO(20%). The product obtained was recovered and washed by centrifugation.

7.2.5. Photocatalytic evaluation of the composite

The photocatalytic activity of GCN, CBO and GCN/CBO heterostructures was measured using methyl orange as the test pollutant under visible light irradiation. For a typical measurement, 100 ml of 0.1 mg/L MB solution and 10 mg of the catalyst were weighed into a Pyrex glass vessel. Then, the suspensions were magnetically stirred in the dark cupboard to ensure adsorption-desorption equilibrium between the dye and the catalyst. After 30 min, the halogen lamp was switched on for the photocatalytic reaction. For time-dependent measurement of MO concentration, 2 mL of solution were sequentially drawn out of the solution at a 15 min time interval and the absorption of the solution was measured using UV-vis spectrophotometer at 462 nm. The percentage degradation of MO by the photocatalyst was calculated using Eq. 1

$$\% \text{ degradation} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where C_o and C_t represent the initial absorbance of the MO solution and the absorbance of the solution after time t . For the reaction rate kinetics calculation, the linear form of the pseudo-first order kinetics equation (Eq. 2) was employed.

$$\frac{\ln(C_t)}{\ln(C_o)} = -kt \quad (2)$$

where C_o and C_t are the initial and final concentration of MO, k is the reaction rate constant, and t is the reaction time.

7.3. Results and discussion

7.3.1. Structural properties

The XRD patterns of the prepared samples are shown in Figure 7.1. The XRD pattern for GCN, exhibited two distinct peaks around 12.8° (100) and 28.1° (002), ascribed to the tri-s-triazine rings and interlayer stacking of graphitic-like structure, respectively [23, 35]. The diffraction pattern of pure CBO was in good agreement with the reported tetragonal phase (JCPDS No.72-0493) [36]. The sharp and distinct diffraction peaks of CBO indicated their good crystallinity. After incorporating 5% of CBO into GCN, there was a slight change in the graphite-like layered structure of GCN due to the analogous diffraction peak positions. However, the intensity of the (002) peak was decreased, indicating the exfoliation of the GCN sheet [37]. The diffraction pattern of CBO was still clearly observable, indicating that GCN had no effect on the crystal structure of CBO. The intensity of these peaks gradually increased with the increasing mass ratio of CBO in the GCN/CBO nanocomposites.

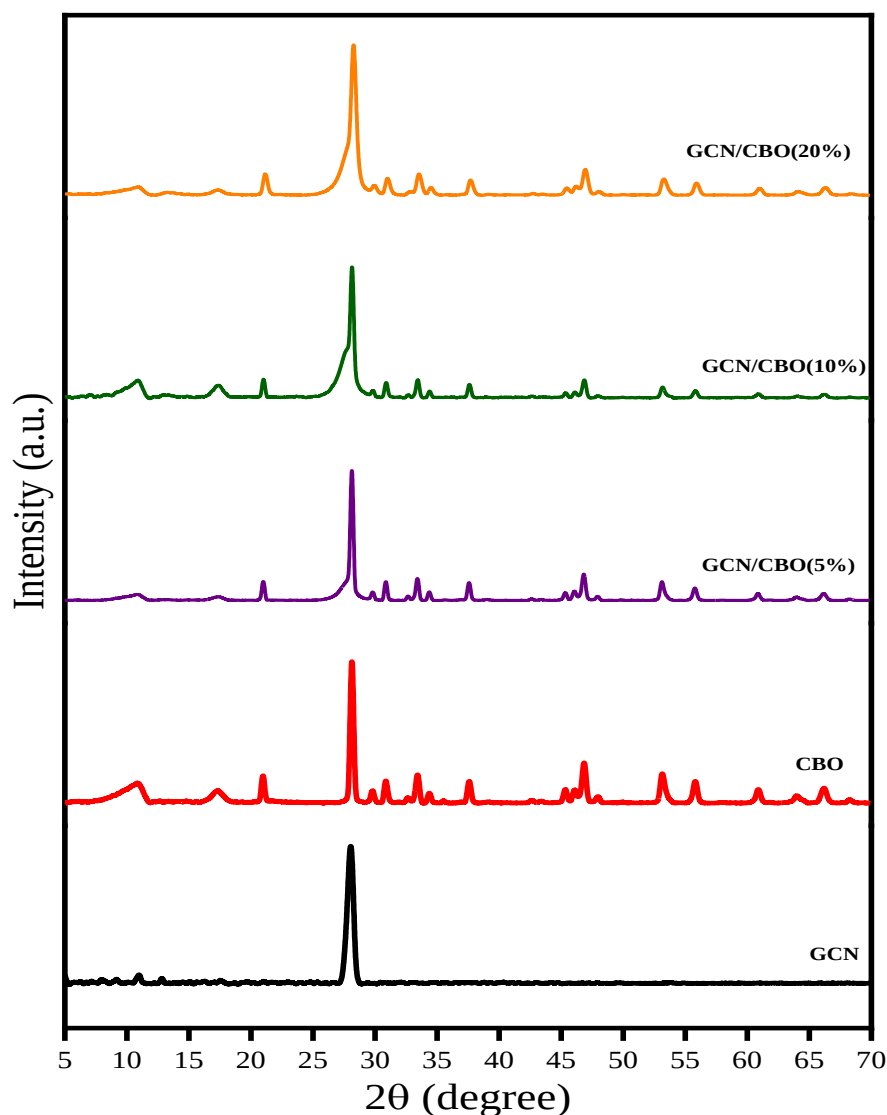


Figure 7. 1: XRD patterns of GCN, CBO, and GCN/CBO (5%, 10%, and 20%).

7.3.2. Morphological studies

The morphology of GCN, CBO and GCN/CBO was studied using SEM and TEM. Figure 7.2 – 7.6 shows the SEM, TEM, EDX and size distribution histogram of the prepared materials. GCN presents agglomerated layered structure, and the thickness of the edges shows that the material consists of several layers of GCN sheets. The SEM image of CBO (Figure 7.3) consists of highly aggregated short rods, while the TEM image confirmed the rod-like shape of the CBO. The average width and length of the nanoparticle measured using the Image J software was 97.12 ± 13.69 by 220.57 ± 47.09 nm. The EDX spectra of the sample, showed the presence of copper, bismuth and oxygen (without the presence of other peaks) confirming the purity of the materials. Atomic weight calculation of the composition of each element, showed a ratio composition of 1:1.5:3.5 for copper, bismuth and oxygen, which was close to stoichiometric

value of 1:2:4. Both SEM and TEM images of GCN/CBO nanocomposites (Figure 7.4-7.6) reveal a uniform distribution of CuBi_2O_4 across the matrices of GCN. This confirms the formation of heterojunctions between GCN and CBO which is advantageous for electron transfer. As the percentage composition of CBO was increased from 5 to 20%, the SEM image appears darker confirming an increase in the CBO concentration on the GCN surface. This was also confirmed by the EDX spectra as the atomic composition of Cu, Bi and O in the composite increased with an increase in CBO weight percent.

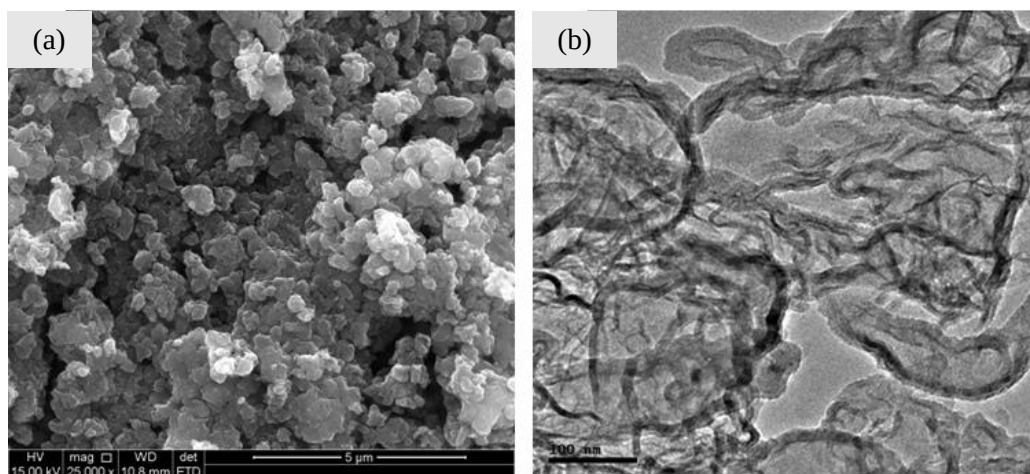


Figure 7. 2: (a) SEM and (b) TEM images of GCN.

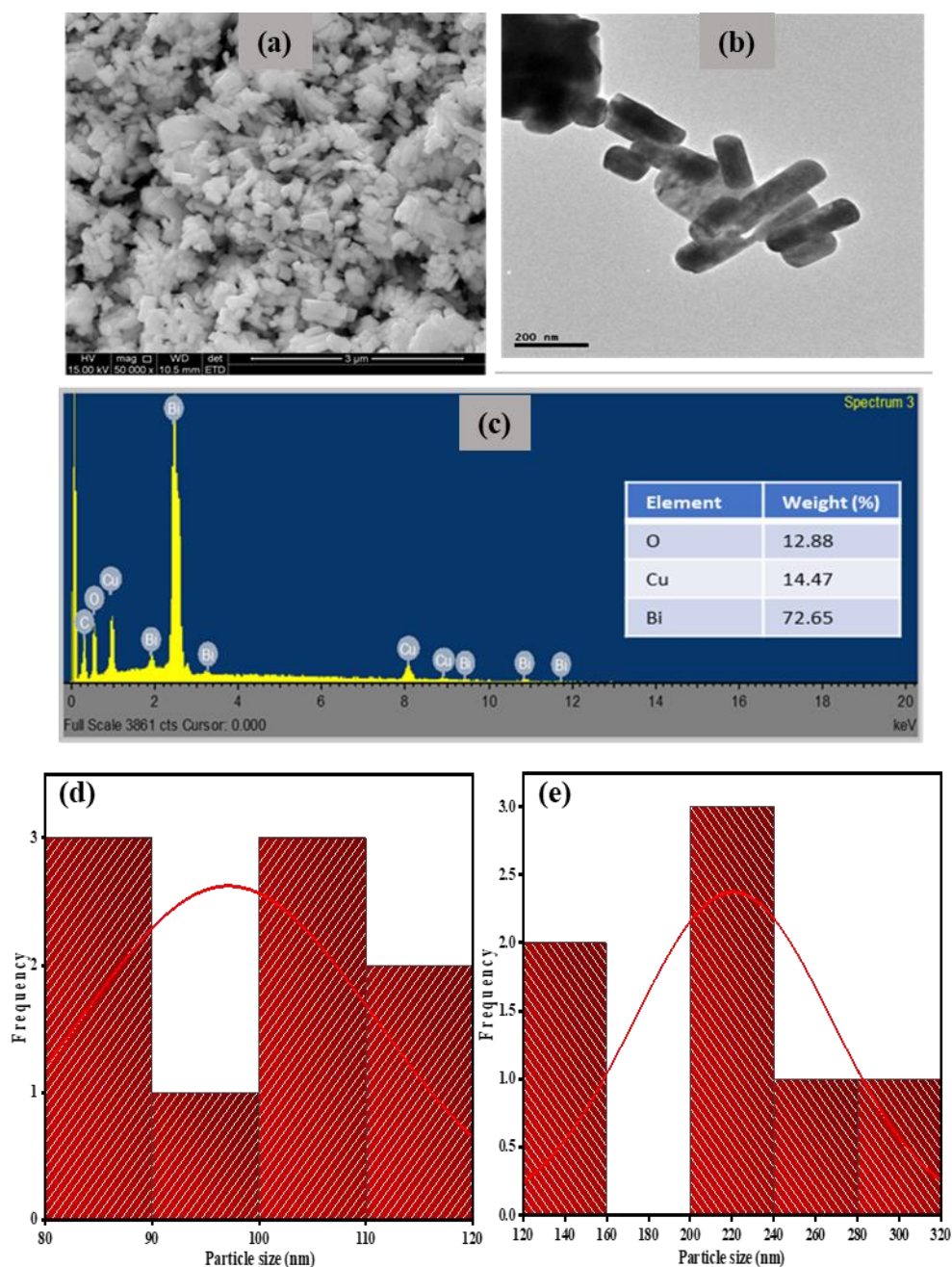


Figure 7. 3: (a) TEM (b) SEM (c) EDX images; and the corresponding particle size distribution histogram showing (d) width and (e) length of the CBO nanorods.

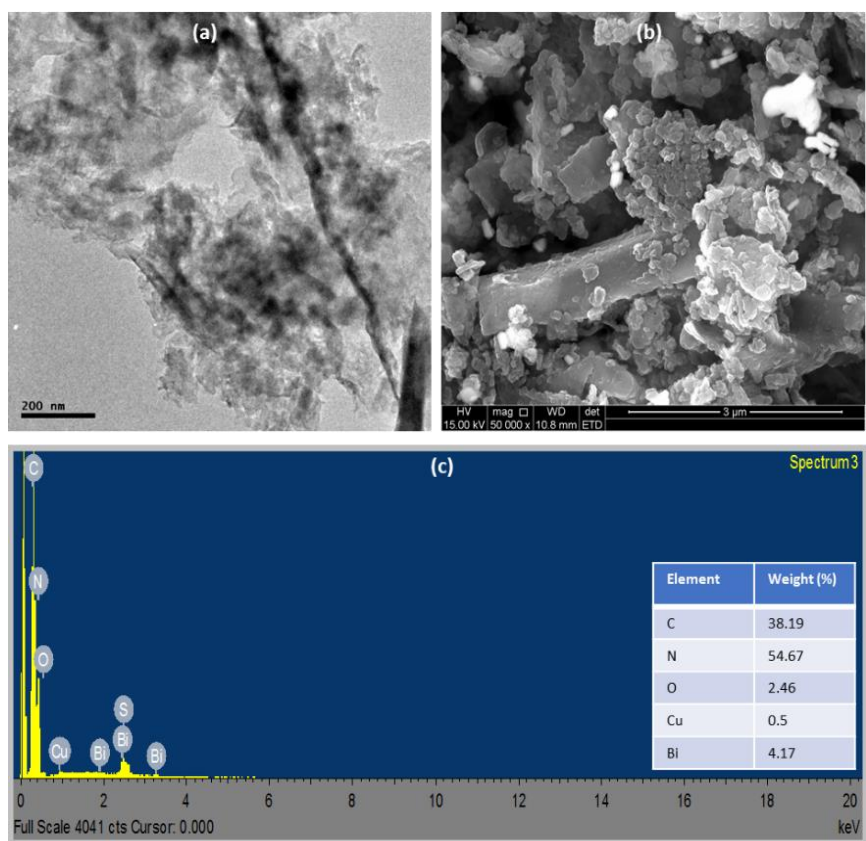


Figure 7. 4: (a) TEM, (b) SEM, and (c) EDX results of GCN/CBO(5%).

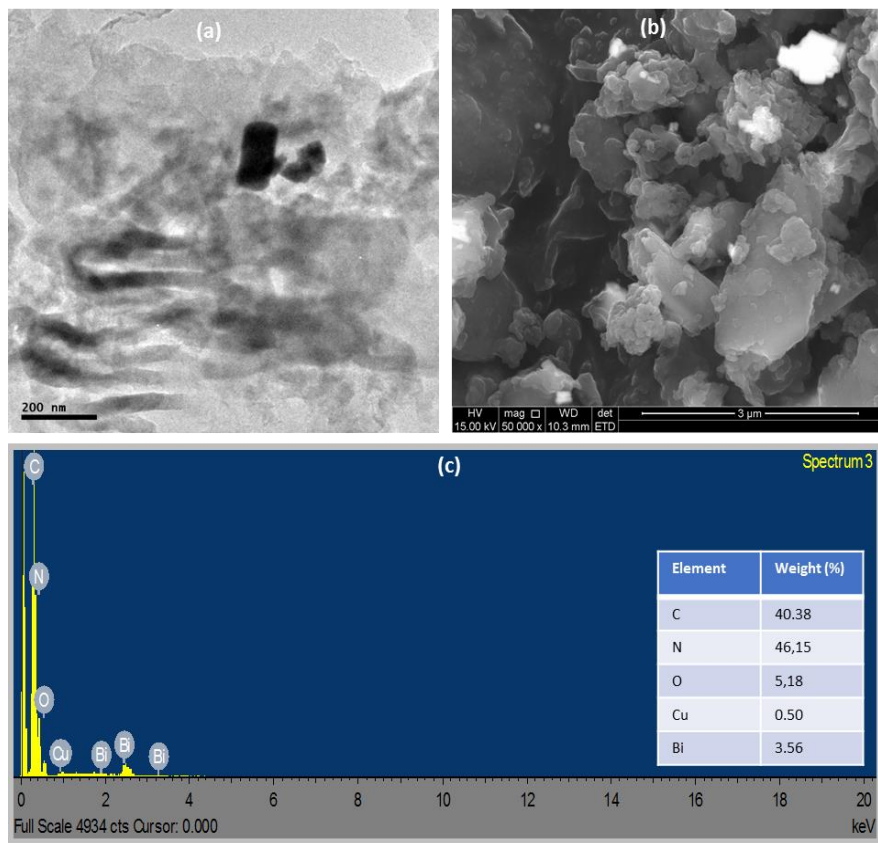


Figure 7. 5: (a) TEM, (b) SEM, and (c) EDX results of GCN/CBO(10%).

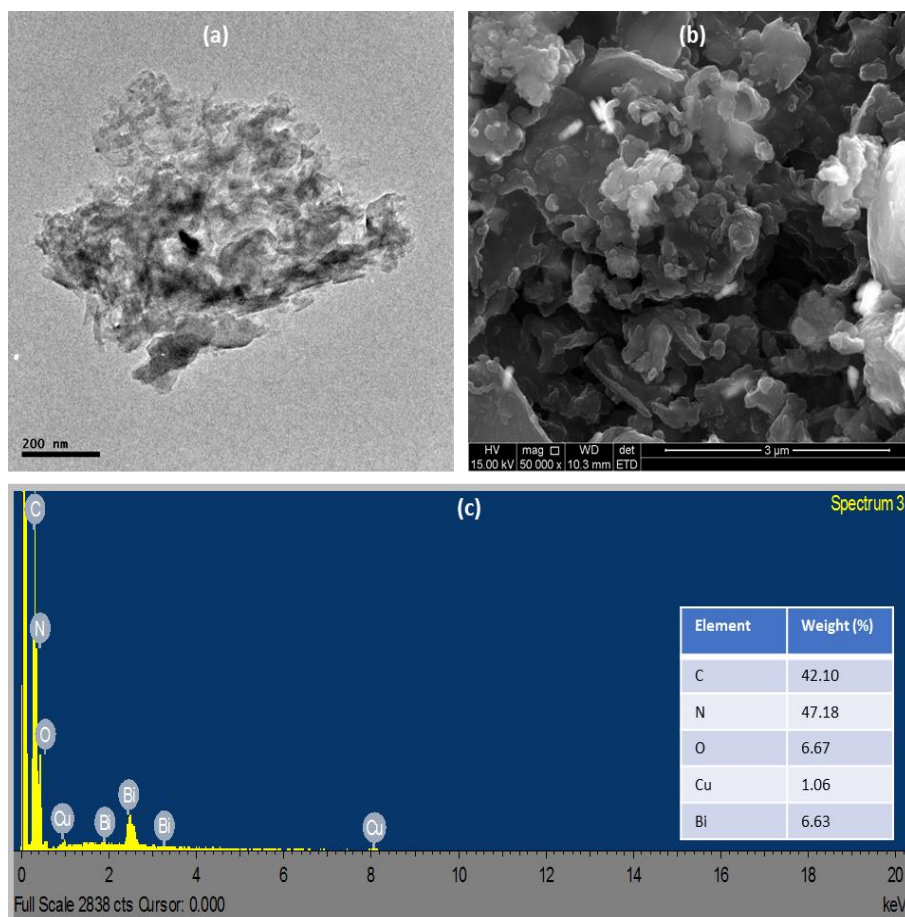


Figure 7. 6: (a) TEM, (b) SEM, and (c) EDX results of GCN/CBO(20%).

7.3.3. Absorption studies

Figure 7.7 shows the UV-vis spectra of GCN, CBO, GCN-CBO(5%), GCN-CBO(10%), and GCN-CBO(20%). GCN has an absorption maximum at around 300 nm, which is characteristic of the material [38], but the absorption tailed lower as the spectra moved towards the visible region of the spectrum. CBO showed a lower absorption in the UV region compared to GCN; however, its absorption intensity increased moving into the visible region showing higher absorption in the visible region of the spectrum. All the GCN-CBO composites showed reduced absorption intensity in the UV-vis region compared to the pristine GCN and CBO. However, the intensity of light absorption increased as the ratio of CBO in the composite increased. Also, the band edge of the composite shifted to higher wavelength with increase in CBO ratio showing a strong interfacial interaction between CBO and GCN and suggesting the formation of a heterojunction [39]. The bandgap energy of GCN, CBO, GCN/CBO(5%), GCN/CBO(10%) and GCN/CBO(20%) was 2.27, 1.40, 1.65, 1.62 and 1.55 eV respectively. The values obtained for pristine GCN and CBO were in agreement with values reported in literature [39, 40]. For the GCN/CBO composites a gradual reduction in the bandgap energy

was observed as the percentage ratio of CBO in the composite was increased. This shows the potential of the materials as a photocatalyst improved as the CBO content increased, because reduction in band gap energy is indicative of increased photogeneration of charge carriers.

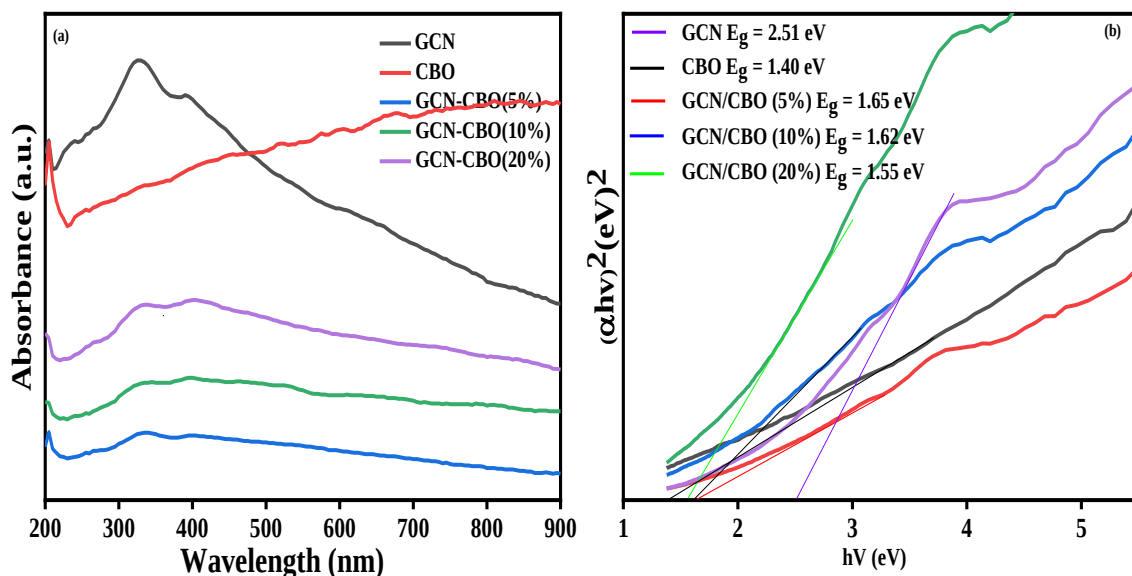


Figure 7. 7: (a) UV–Vis-NIR absorption spectra of GCN, CBO, GCN/CBO(5%),GCN/CBO(10%), and GCN/CBO(20%), (b) respective Tauc plot of $(\alpha h\nu)^2$ versus photo energy ($h\nu$).

7.3.4. Photoluminescence (PL) studies

The PL spectra of the materials was recorded in order to evaluate the level of charge carrier recombination. Fast charge carrier recombination is often detrimental to the efficiency of the photocatalytic process. This is because the quantity of reactive oxygen species (ROS) generated by the reaction of photogenerated charge carriers with oxygen and water at the surface of the catalyst is reduced [41]. Figure 7.8 shows that GCN and CBO had the highest and lowest PL intensity, while the composites showed intermediate intensity. Also, the intensity of the composite was observed to reduce with increase in CBO content, therefore showing improved charge carrier separation.

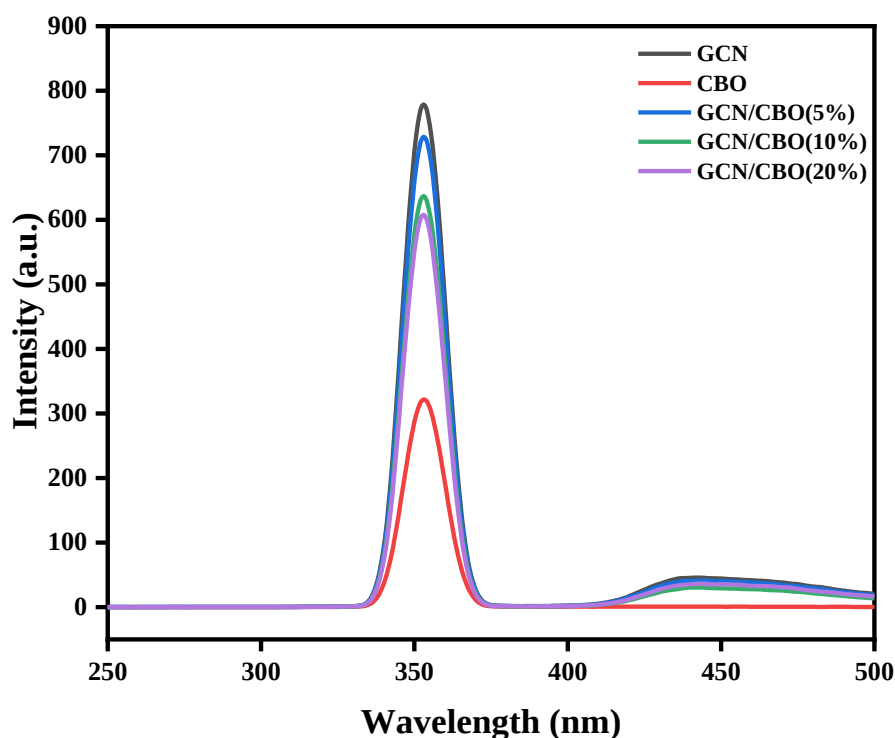


Figure 7. 8: Photoluminescence spectra of GCN, CBO, GCN/CBO(5%), GCN/CBO(10%) and GCN/CBO(20%).

7.3.5. Photocatalytic degradation study

The photocatalytic activity of GCN, CBO and GCN/CBO composites was evaluated for the degradation of methyl orange under visible light irradiation. The photocatalytic efficiency of GCN, CBO, GCN/CBO(5%), GCN/CBO(10%) and GCN/CBO(20%) was 50, 75, 86, 98 and 100% respectively as shown in Figure 7.9(a-e). The photocatalytic activity of the composites was higher than that of GCN and CBO, which showed the formation of GCN/CBO heterojunction resulted in improved charge carrier generation and separation. The GCN/CBO(20%), showed higher activity for methyl orange degradation compared to rGO/CBO heterostructures, reported by Muthukrishnaraj, Vadivel, Joni and Balasubramanian [42] which showed 87% efficiency. The degradation efficiency of the composite also showed a positive correlation with increase in the percentage composition of CBO in the composite, this shows the interaction between the surface of the materials resulted in enhanced charge carrier separation and thus improved photocatalytic activity. The higher band gap energy of GCN/CBO composites compared to that of pristine CBO, signifies a potential enhancement in charge carrier separation, while its lower value compared to GCN, implies a higher utilization of the visible light source. This shows the consequence of great synergy in compositing CBO and GCN. Figure 7.9(f) presents the pseudo first order kinetics plot for the degradation process.

The reaction kinetics rate constant for the heterostructures: 0.034, 0.042, and 0.065 min⁻¹ for GCN/CBO(5%), GCN/CBO(10%) and GCN/CBO(20%) respectively were higher compared to pristine GCN and CBO (0.0068 and 0.019 min⁻¹ respectively). The reaction rate constant for the heterostructures also increased as the composition of CBO in the material increased. This confirms the formation of the heterostructure lead to an increase in the photocatalytic activity of the composites.

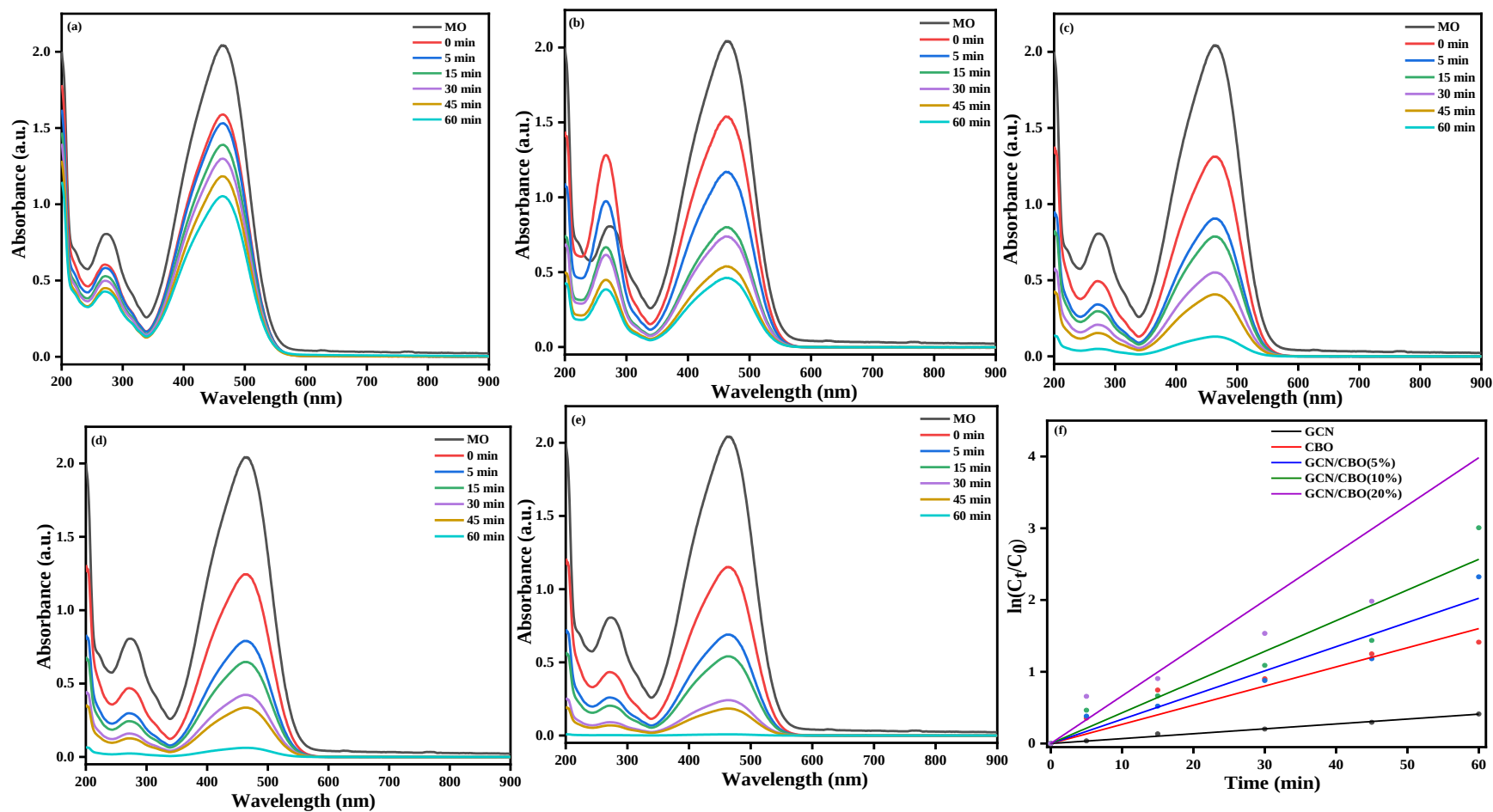


Figure 7. 9: Photocatalytic activity of (a) GCN (b)CBO (c) CBO/GCN(5%) (d) CBO/GCN(10%) (e) CBO/GCN(20%) and (f) kinetic plots for the degradation of methyl orange.

7.3.6. Effect of process parameters on the photocatalytic process

For optimization of the photocatalytic process, the effect of process parameters such catalyst dosage, methyl orange concentration, and pH on the photocatalytic activity are very important. The effect of GCN/CBO(20%) dosage on the photocatalytic process at 5-20 mg is presented in Figure 7.10. The optimal dosage of GCN/CBO(20%) was at 20 mg with 100% degradation of MO achieved. This could be attributed to increased generation of reactive radicals with high amount of active sites and also increased collision between the dye molecule and catalyst specie in the system [43]. The reaction rate constant value was 0.038, 0.065 and 0.077 min^{-1} at 5, 10 and 20 mg of GCN/CBO(20%) respectively.

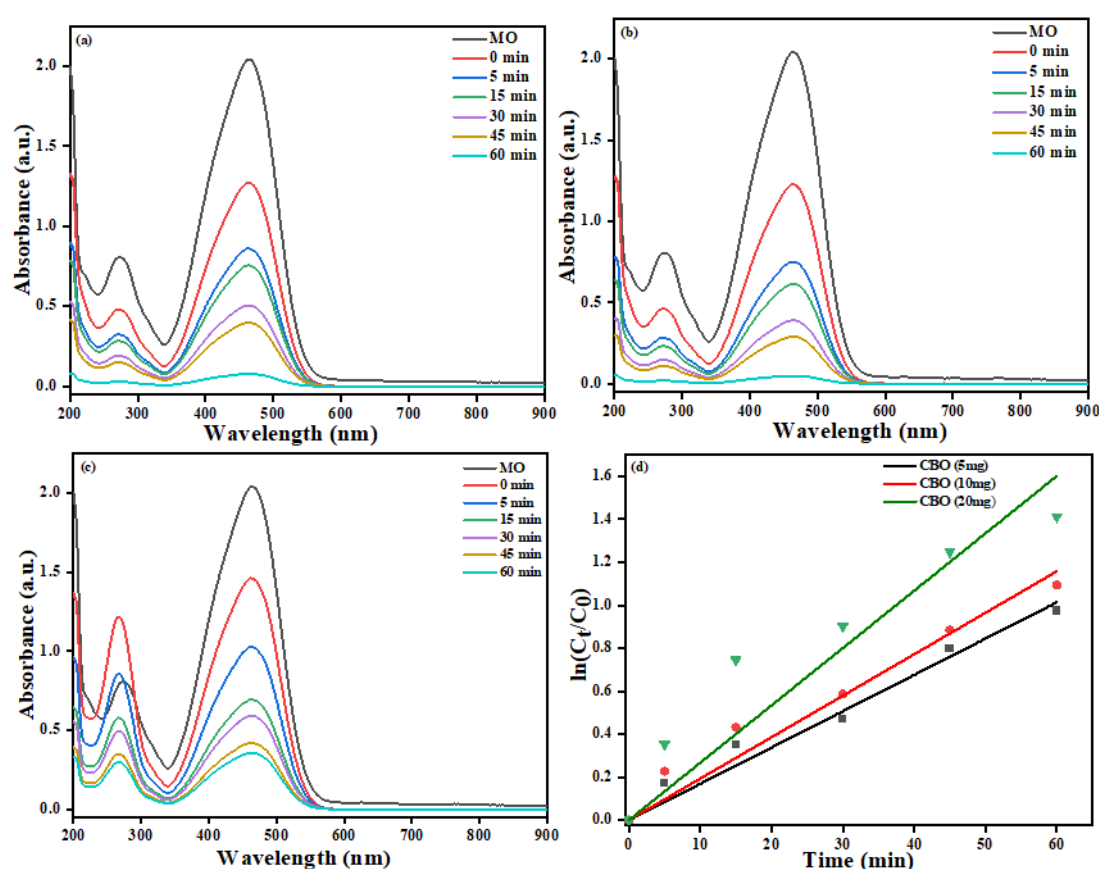


Figure 7. 10: Effect of catalyst dosage on the photocatalytic activity of GCN/CBO at catalyst dosage of (a) 5 mg (b) 10 mg (c) 20 mg and (d) kinetic plot for the degradation of MO at catalyst dosage of 5, 10 and 20 mg.

In Figure 7.11, shows the effect of MO concentration on the degradation efficiency of the process. The catalyst showed good efficiency for the degradation of MO at all the concentration range of this study. The degradation efficiency at 0.1, 0.3 and 0.5 mg/L was 100, 100 and 98% respectively; and the reaction rate constant at different MO concentration was 0.077, 0.049 and

0.040 min⁻¹ at 0.1, 0.3 and 0.5 mg/L respectively. The slight reduction in efficiency at higher concentration could be attributed to the covering of the surface of the catalyst by the dye molecule, thus reducing level of light penetration and subsequently the quantity of charge carrier generated [44].

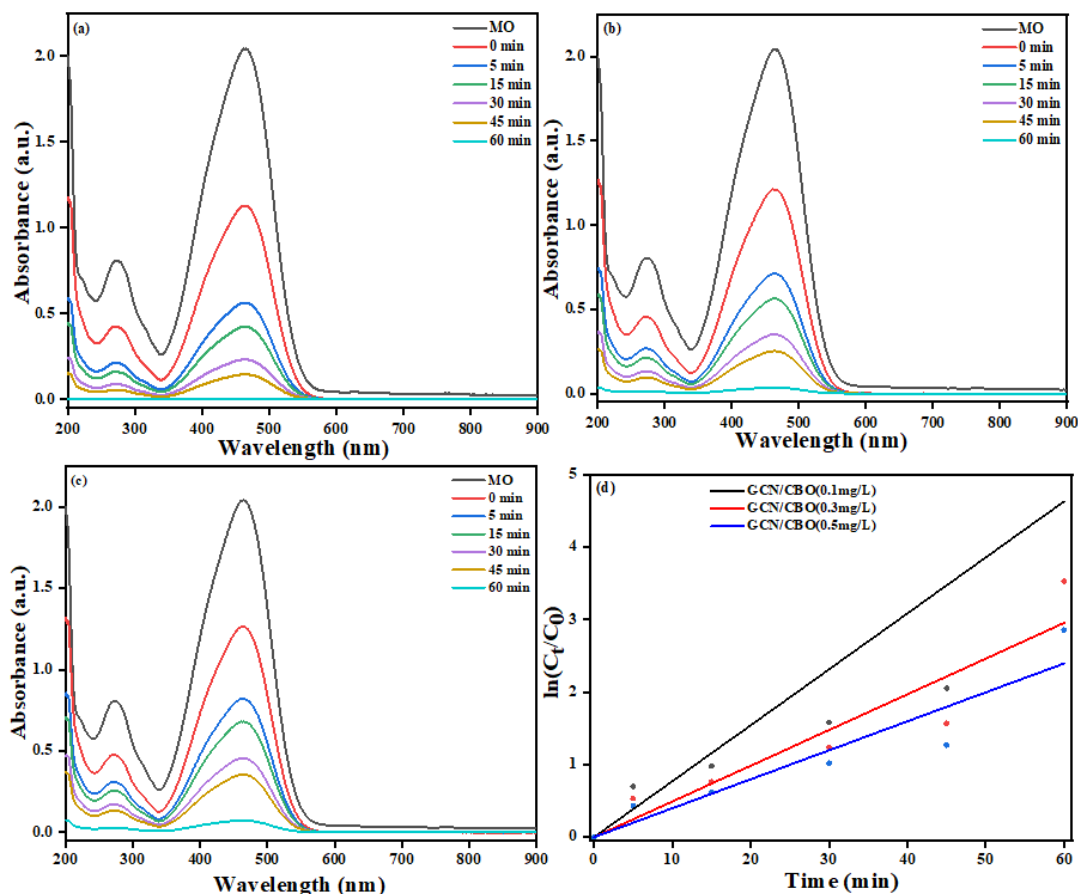


Figure 7. 11: Effect of MO concentration on the photocatalytic activity of GCN/CBO at concentration of (a) 0.1 mg/L (b) 0.3 mg/L (c) 0.5 mg/L and (d) kinetic plot for the degradation of MO at concentration of 0.1, 0.3 and 0.5 mg/L.

The effect of solution pH on the photocatalytic process was studied by adjusting the pH of the MO solution to 2, 7 and 10. Solution pH is an important parameter in evaluating the effectiveness of catalytic material as it influences the surface property of the material and also alters the ionic state of organic pollutants [45]. This significantly influences the nature of interaction between the catalyst and the pollutants solution and subsequently the photocatalytic efficiency. Figure 7.12 shows that the GCN/CBO exhibited high photocatalytic activity over a wide range of pH, with only a slight reduction in efficiency observed under acidic condition. This confirms the potential of GCN/CBO for practical application in a wide range of contaminated water sources. At neutral and alkaline conditions complete degradation of MO

was achieved, while under acidic condition about 96% degradation was achieved. This could be attributed to a reduction in the interaction between the catalyst surface and MO, which could impact on the adsorption of MO onto the catalyst's surface. The reaction rate constant for the process at pH values of 2, 7 and 10 was 0.032, 0.086 and 0.045 min⁻¹ respectively.

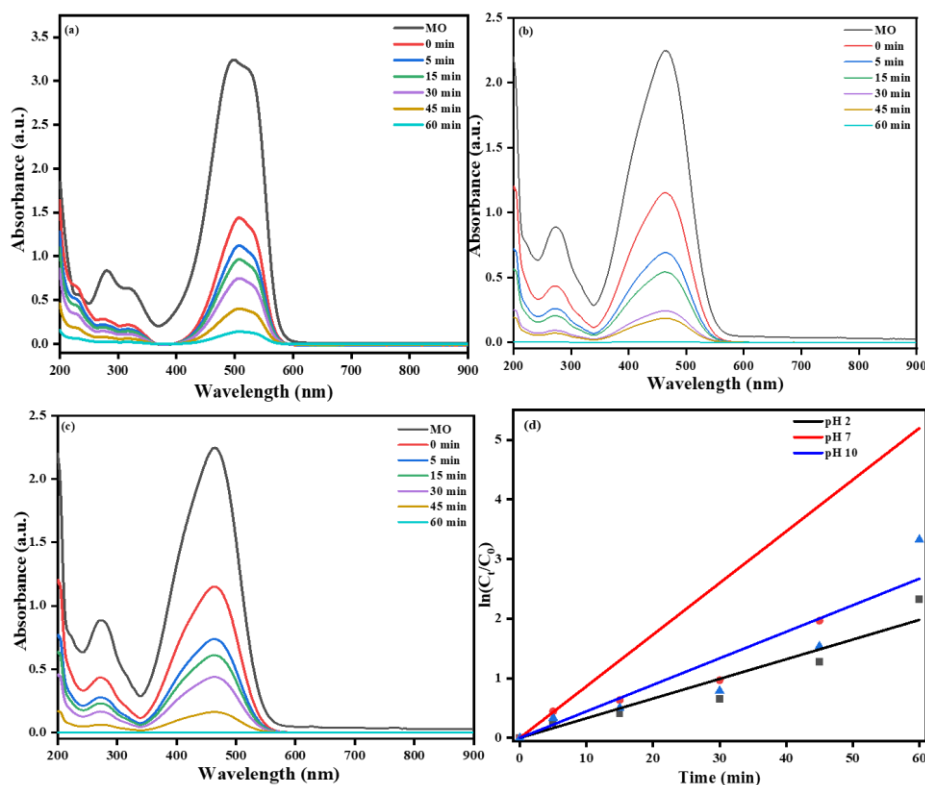


Figure 7. 12: (a) Effect of pH on the photocatalytic activity of CN/CBO(20%) nanocomposite,(a) pH 2, (b) pH 7, and (c) pH 10.

7.3.7. Radical scavenging study

The generation of radical species is a very important process in the photocatalytic activity because they attack organic molecules in water leading to their degradation. To understand the roles played by the generated radicals, radical scavenging study was carried out by the introduction of h^+ , $\cdot OH$, $O_2^{\cdot -}$, and e^- scavengers in the photocatalytic process. Figure 7.13 shows the photocatalytic efficiency of the process in the presence of radical scavengers. The efficiency of the process in the presence of these scavengers shows the effectiveness of the catalyst was significantly in the presence of $O_2^{\cdot -}$ and h^+ showing they are the most influential radicals in the degradation process. Dutta, Sonu, Raizada, Thakur, Ahamad, Thakur, Verma, Quang, Nguyen and Singh [18] similarly reported the significant role played by $O_2^{\cdot -}$ and h^+ in the photocatalytic activity of Ag-CuBi₂O₄/CNTs/Bi₂WO₆ in the degradation of Rhodamine B dye. In the presence of e^- and $\cdot OH$ the degradation process was only slightly impacted, showing

their contribution to the efficiency of the process was negligible. The reaction rate constant for the degradation process was 0.004, 0.035 and 0.019 min^{-1} in the presence of ascorbic acid, silver nitrate and tert-butanol respectively, while in the absence of any radical the reaction rate constant was 0.065 min^{-1} .

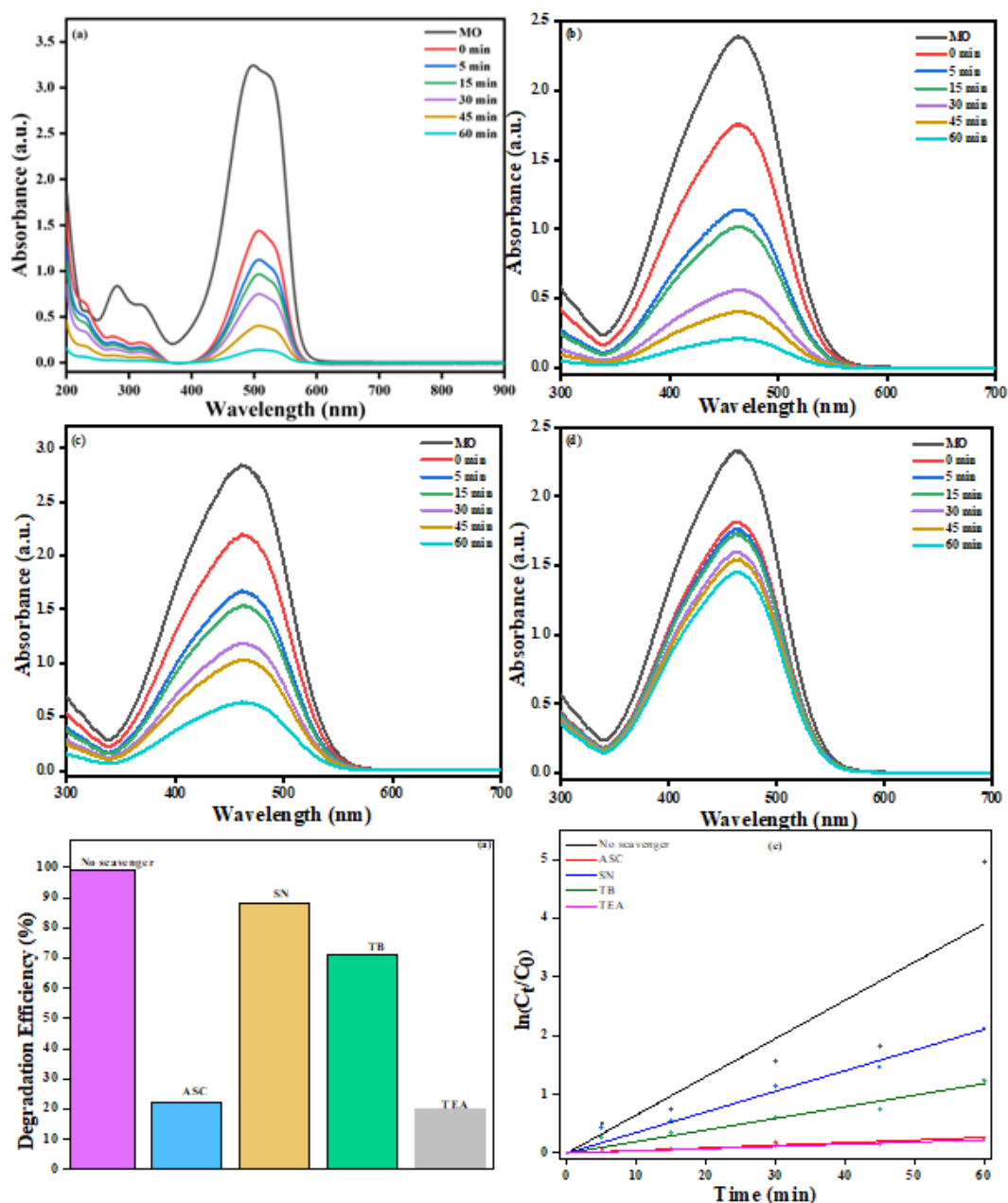


Figure 7. 13: Radical scavenging experiment in the presence of radical scavengers (a) ASC [O_2^-], (b) SN [e^-], (c) TB [$\text{OH}^\cdot$], and (d) TEA [h^+] (d) kinetic plots for radical scavenging experiment.

In order to understand the process of radical generation and the nature of heterostructure formed between CBO and GCN the CB and VB potential of the semiconductor materials were evaluated using the empirical equations 3 and 4:

$$E_{CB} = X - E_e - \frac{1}{2}E_g \quad (3)$$

$$E_{VB} = E_{CB} + E_g \quad (4)$$

Where X is the Mulliken's electronegativity, E_e is the energy of free electrons on the hydrogen scale, and E_g is the band gap energy. The value of E_e is 4.5 eV, while the value of X for CBO and GCN is 4.75 and 4.64 eV respectively [46, 47]. The E_{CB} and E_{VB} of CBO were evaluated to be -0.53 and 1.03 eV, while for GCN E_{CB} and E_{VB} were evaluated to be -1.12 and 1.40 eV respectively. The band alignment of GCN and CBO were constructed from the calculated band edge potentials, and it can be observed that the CB and VB of CBO were straddle by those of GCN (Figure 7.14a). Because GCN and CBO are n-type and p-type semiconductor respectively, the Fermi levels (E_F) of GCN lie close to the CB, while it lies close to the VB in CBO [33]. The formation of p-n heterojunction between GCN and CBO, therefore leads to an upshift in the energy levels of CBO, while there is a downshift in the energy levels of GCN until the E_F levels equilibrate between CBO and GCN as shown in Figure 7.14b [33]. This results in the CB of CBO being higher than that of GCN, which results in the generation of an inner electric field between the CBO negatively charged region and the positively charged GCN region. Therefore, photogenerated electrons in the CB of CBO can easily diffuse into GCN CB, which has a lower potential than $O_2/O_2^{\bullet-}$ (-0.33 eV vs NHE). The holes generated in the VB of GCN simultaneously migrate into the VB of CBO, which can directly oxidize MO. This agrees with the radical scavenging experiment, which showed that $O_2^{\bullet-}$ and h^+ had the major significant effect in the degradation process.

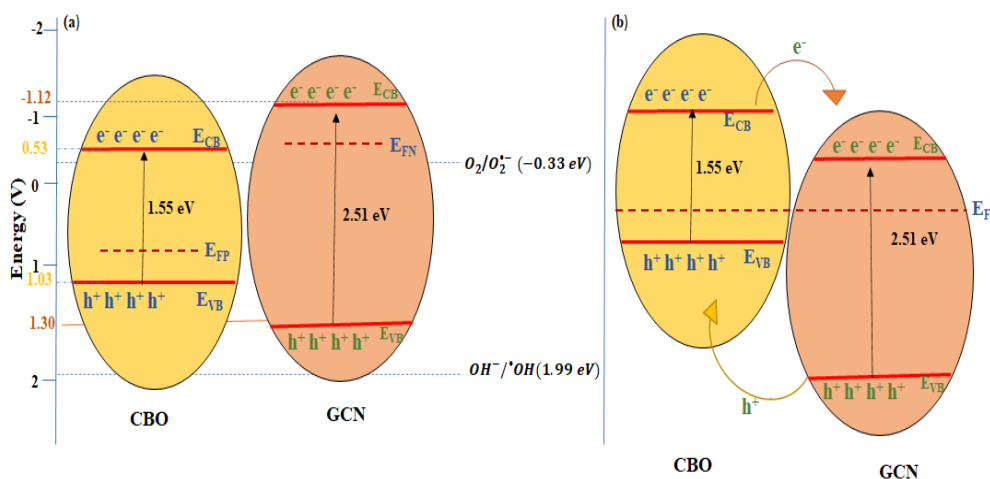


Figure 7. 14: (a) Band alignment of CBO and GCN before contact, and (b) band alignment of p-n GCN/CBO heterostructure.

7.4. Sub-Conclusion

Efficient photocatalytic degradation of MO was achieved by g-C₃N₄/CuBi₂O₄ heterostructure. Complete degradation of MO was achieved using GCN/CBO(20%) composite and the pseudo first order rate constant for the process was also significantly enhanced by the composite, compared to the pristine g-C₃N₄ and CuBi₂O₄. The improved activity of the heterostructure could be attributed to the formation of p-n heterojunction at the interface between the materials, which resulted in enhanced charge carrier migration and separation. The good activity of GCN/CBO heterostructure activity across different ranging values of pH, concentration, and catalyst dosage, shows the potential applicability for a wide range of wastewater source. The degradation efficiency of the process was accounted for mainly by $O_2^{\bullet -}$ and h^+ , which indicates the high activity of the radicals generated by GCN/CBO. This study shows that the formation of GCN/CBO heterostructure is a facile route to obtaining efficient and economical photocatalytic material for wastewater treatment.

7.5. References

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CHAPTER EIGHT

8.1. Conclusion and recommendations

8.1.1. Conclusion

This research study presents findings on g-C₃N₄ based ternary heterostructured materials for the enhanced photocatalytic degradation of methyl orange dye under visible light irradiation. The photocatalytic performance of the ternary structures was evaluated against g-C₃N₄/Bi₂S₃/CuS and g-C₃N₄/CuBi₂O₄. The study explored the individual semiconductors in separate chapters and studied the optical, structural, and morphological properties, before compositing them together in a band structural engineering for enhanced efficiency.

In chapter three, a solvothermal decomposition of bismuth dithiocarbamate complex in oleylamine, oleic acid, and hexadecylamine at 180 C, was carried out which yielded bismuth sulphide of different morphologies. This process established the potential of the dithiocarbamate complex to act as a single source precursor for the synthesis of Bi₂S₃ nanoparticles. It further lays the basis for the synthesis of the heterojunction system. The variation in the morphology and size of the synthesized bismuth sulphide nanoparticles was attributed to the difference in the coordination capability of the solvent.

Chapter four presented the synthesis, characterization, computational studies, and photocatalytic properties pristine of Bi₂S₃ as well as Cu doped Bi₂S₃ nanorods. The effect of the Cu ions on the structural, microstructural, optical, and photocatalytic properties of Bi₂S₃ nanorods was evaluated. Scherrer equation and Williamson-Hall analysis were used to carry out the structural analysis of the nanorods, and a direct correlation between the dopant concentration and crystallite size was established. The crystalline strain was also found to correlate directly with the dopant's concentration, while the dislocation density varied inversely with the dopant's concentration. Computational studies, using 89first principle calculation, and absorption studies showed that Cu-doping impacted a red shift on the bandgap of the Bi₂S₃. The materials showed efficient photocatalytic degradation of methyl orange.

Graphitic carbon nitride functionalized with Cu-doped Bi₂S₃ was prepared in chapter five and its efficiency as a heterostructure photocatalyst for the visible light degradation of methyl orange was evaluated. The results showed that the combination of graphitic carbon nitride with the Cu-doped Bi₂S₃ semiconductor of different structures promoted the unique properties that arise from the construction of heterojunctions. Furthermore, it confirms that the formation of the heterostructure of g-C₃N₄ with semiconductor nanomaterials offers a unique and facile

route to enhancing the catalytic degradation of dyes. This was attributed to improved charge separation, reduced recombination, and enhanced light absorption and steadiness of the composite.

In chapter six, a dual heterojunction g-C₃N₄/Bi₂S₃/CuS composite system was prepared and the photocatalytic activity for methyl orange degradation was evaluated. The band alignment of the synthesized heterostructure exhibited a synergistic effect, which significantly enhanced the charge carrier separation and mitigating their recombination. The g-C₃N₄/Bi₂S₃/CuS composite exhibited enhanced photocatalytic efficiency compared to the pristine g-C₃N₄, Bi₂S₃ and CuS. Furthermore, the activity of the heterostructure was observed to increase as the ratio of CuS in the photocatalyst was increased. The highest photocatalytic efficiency was recorded for the composite with the highest concentration of CuS with about 98% methyl orange degradation. Radical scavenging experiments showed that •OH, e⁻, and h⁺ all played significant roles in the degradation process. A charge transfer scheme and mechanism of reaction were proposed on this basis.

In chapter seven, a series of g-C₃N₄/CuBi₂O₄ heterostructure photocatalysts were synthesized through a solvothermal process. Compared with pristine g-C₃N₄ and CuBi₂O₄, the g-C₃N₄/CuBi₂O₄ heterojunctions showed improved activity in the photocatalytic degradation of methylene orange. This was attributed to the formation of p-n junction, which resulted in improved charge carrier migration and separation. Furthermore, photogenerated O₂^{•-} and h⁺ was found to account for the effective degradation of MO by the photocatalyst. The g-C₃N₄/CuBi₂O₄ heterojunction is therefore a promising photocatalyst for the effective degradation of MO.

In general, good photocatalytic degradation efficiency was obtained from all the prepared heterojunction systems compared to their pristine nanomaterials. The results confirmed the high improvement in the efficiency of materials by the engineering of the band structure to delay recombination process. Furthermore, the results showed that the photocatalyst derived from g-C₃N₄ based ternary heterostructure materials has the potential to be explored in practical applications for wastewater treatment as well as eco-friendly environmental applications.

8.1.2. Recommendations and future perspective

The photocatalytic application of g-C₃N₄ based ternary heterostructured materials has been established in this research work. Based on the results, g-C₃N₄ has presented itself as a material that needs further investigation because of its environmental friendliness and unique ability to absorb light in the visible spectrum. Some recommendations are highlighted below for future work:

1. This research work could provide a direction for developing novel efficient photocatalysts for the enhanced photocatalytic degradation of dye pollutants.
2. The possibility of developing heterojunction systems between g-C₃N₄ and other semiconductor materials should be explored as this would provide versatility for the application of g-C₃N₄.
3. The possibility of developing several p-n heterojunction systems with other semiconductors can be further explored by exploiting the versatility of p-n semiconductors with improved solar, ultraviolet and visible light absorption solving environmental problems.
4. To explore the use of doped g-C₃N₄ in the formation of the tertiary composite.
5. Explore the electronic properties of the composite materials experimentally and compare the results from the theoretical results.
6. Further applications of g-C₃N₄ can be extended to other organic dye pollutants, heavy metals, pharmaceutical and other contaminants of emerging concern.
7. The photocatalytic application of g-C₃N₄ heterostructured materials was only limited to simulated wastewater, further research works should be conducted on real industrial effluents.
8. Furthermore, the photoelectrochemical application of g-C₃N₄ heterostructured materials should also be considered.

SUPPLEMENTARY FILES

CHAPTER FOUR

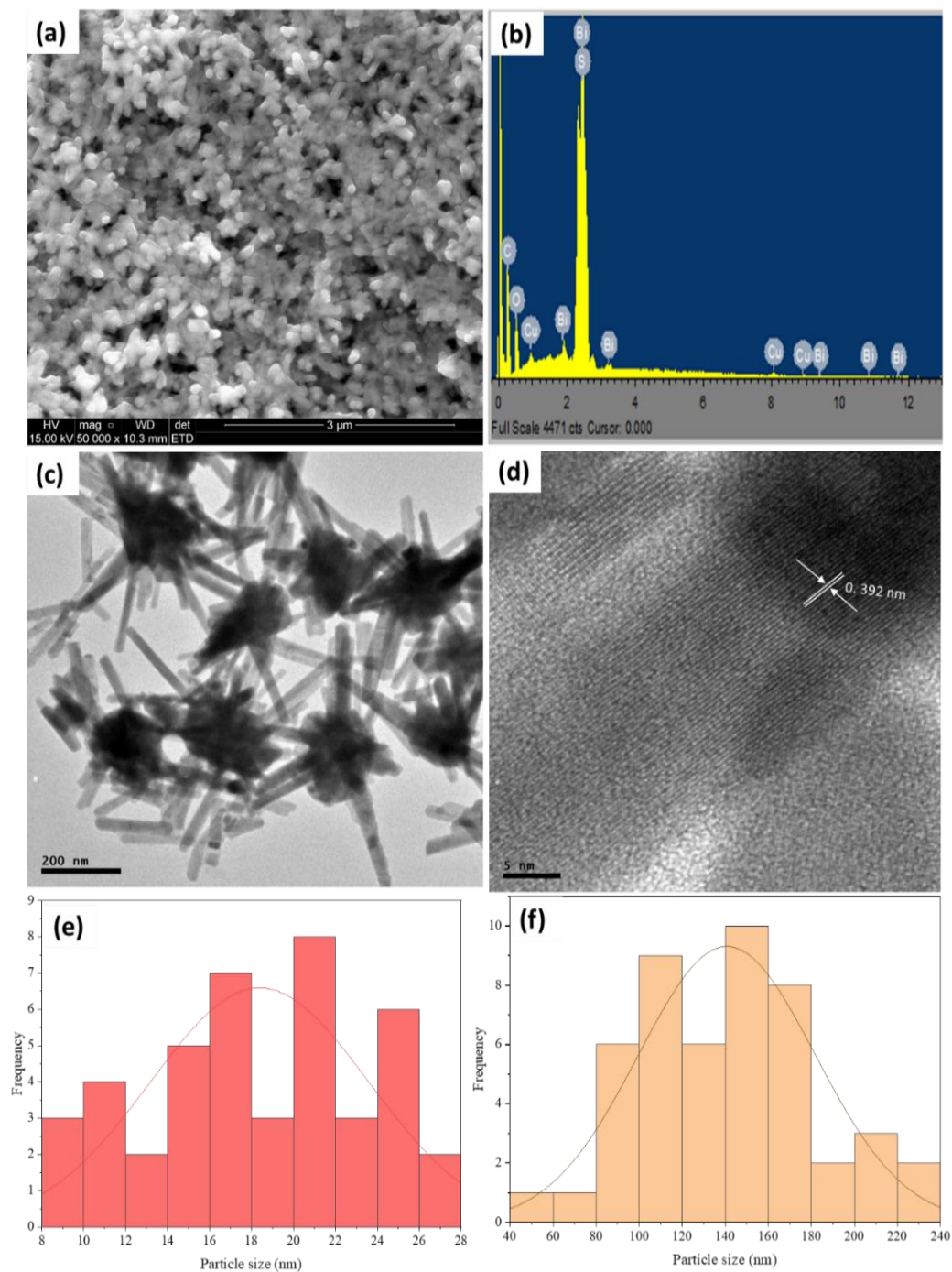


Figure 4.S1: (a) SEM image (b) EDX spectrum (c) TEM image (d) HRTEM image showing lattice fringes; with corresponding particle size histogram showing (e) width and (f) length of the Cu-BiS(0.2) nanorods.

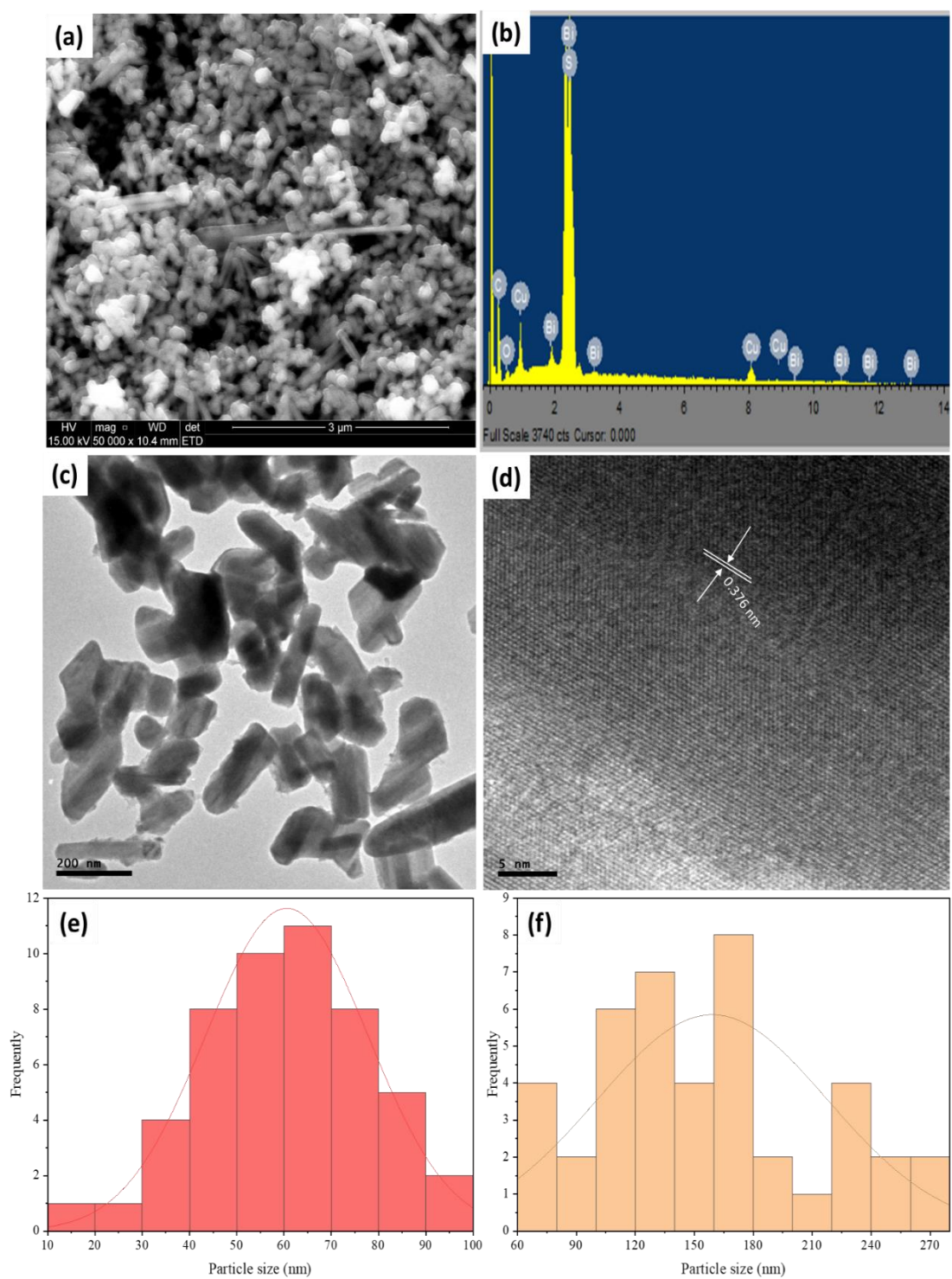


Figure 4.S2: (a) SEM image (b) EDX spectrum (c) TEM image (d) HRTEM image showing lattice fringes; with corresponding particle size histogram showing (e) width and (f) length of the Cu-BiS(0.6) nanorods.

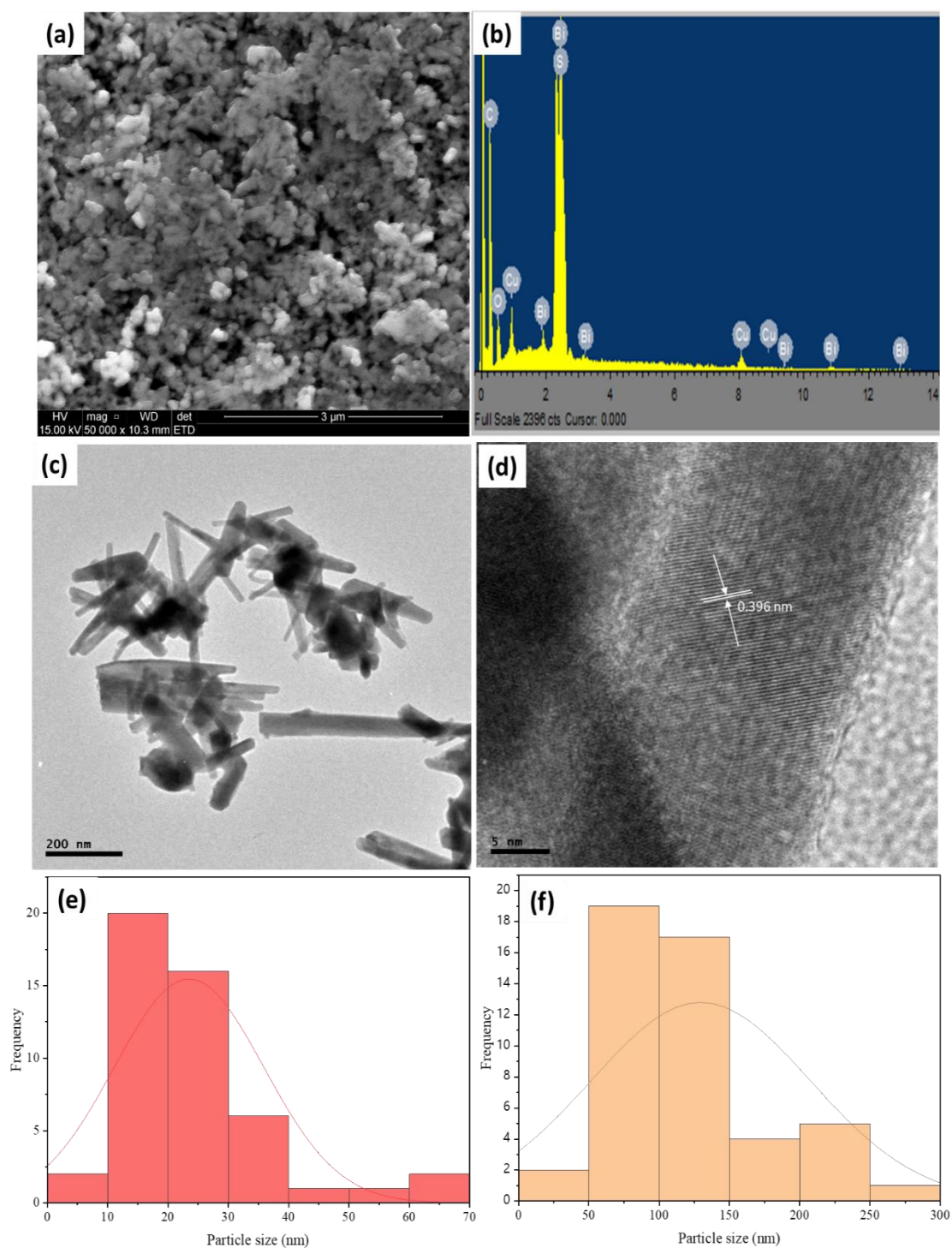


Figure 4.S3: (a) SEM image (b) EDX spectrum (c) TEM image (d) HRTEM image showing lattice fringes; with corresponding particle size histogram showing (e) width and (f) length of the Cu-BiS(0.8) nanorods.

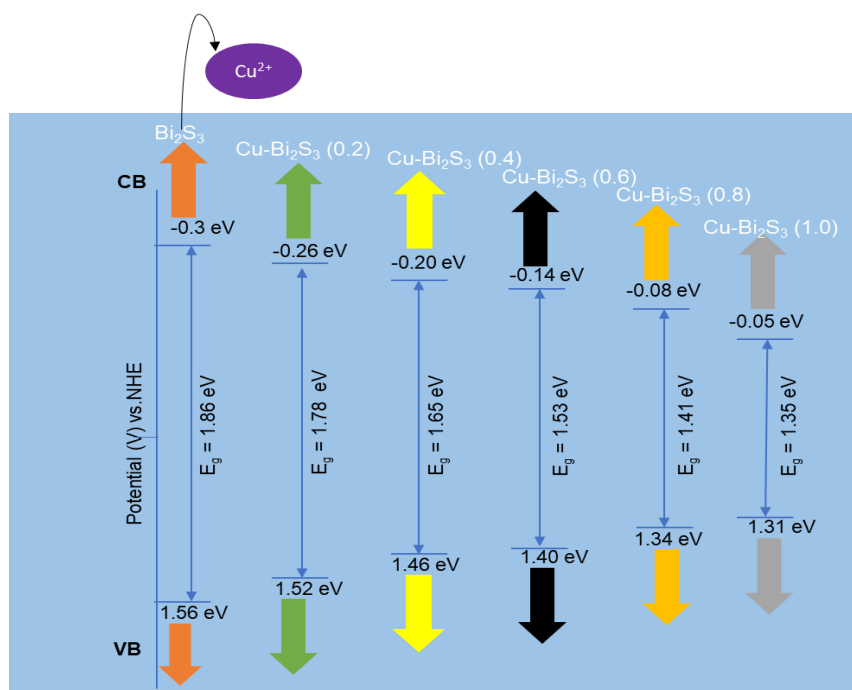


Figure 4.S4: Energy diagram showing the variation in the band gap energy, calculated valence bandgap edge (E_{VB}) and conduction bandgap edge (E_{CB}) with change in the concentration of the dopant ion.

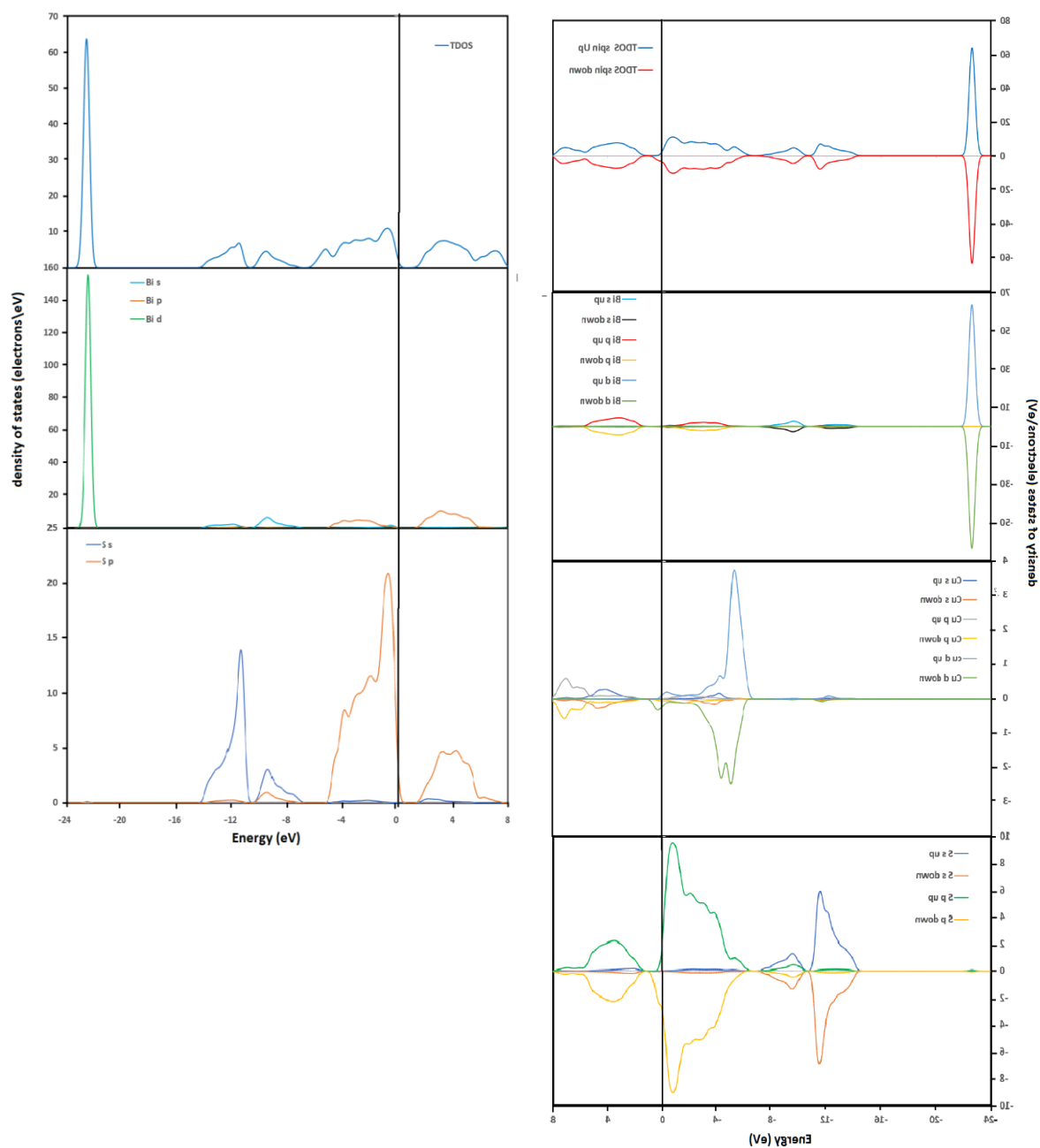


Figure 4.S5: Total and partial density of states of (a) Bi_2S_3 and (b) Cu-doped Bi_2S_3 .

CHAPTER FIVE

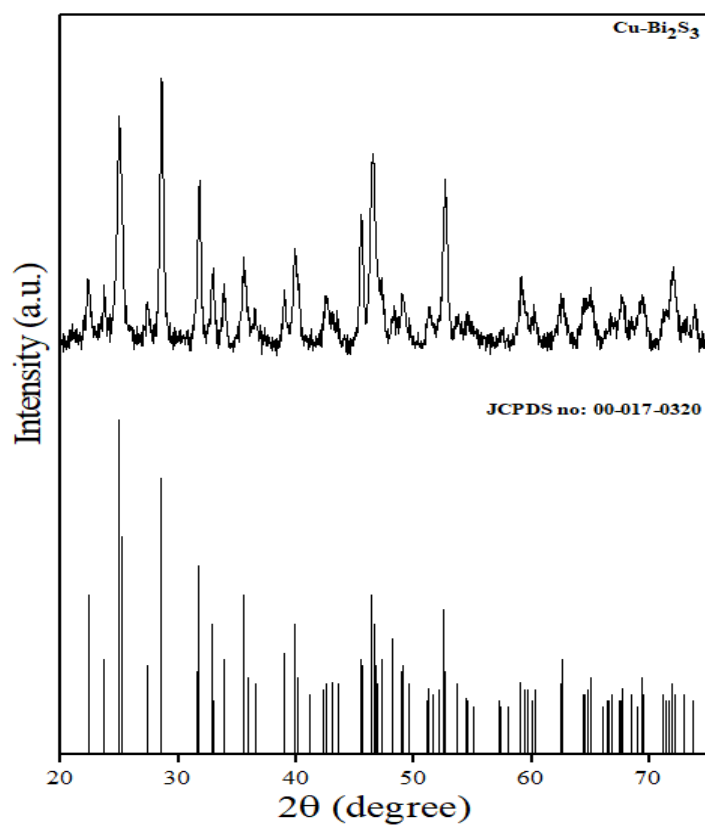


Figure 5.S1: XRD pattern of $\text{Cu-Bi}_2\text{S}_3$ with the JCPDS standard.

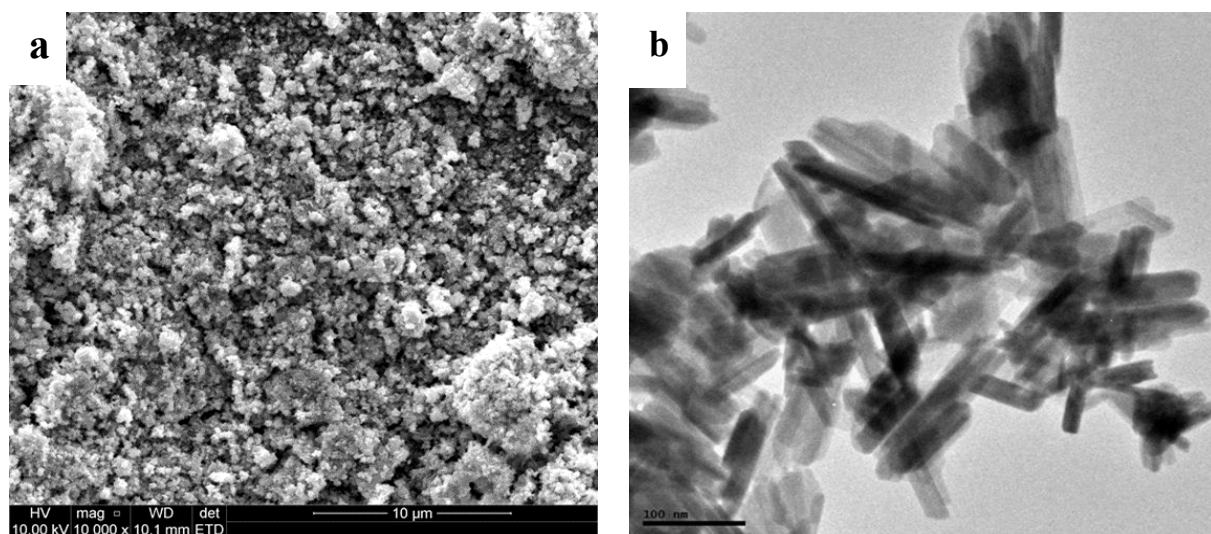


Figure 5.S2: (a) SEM and (b) TEM images of Bi_2S_3

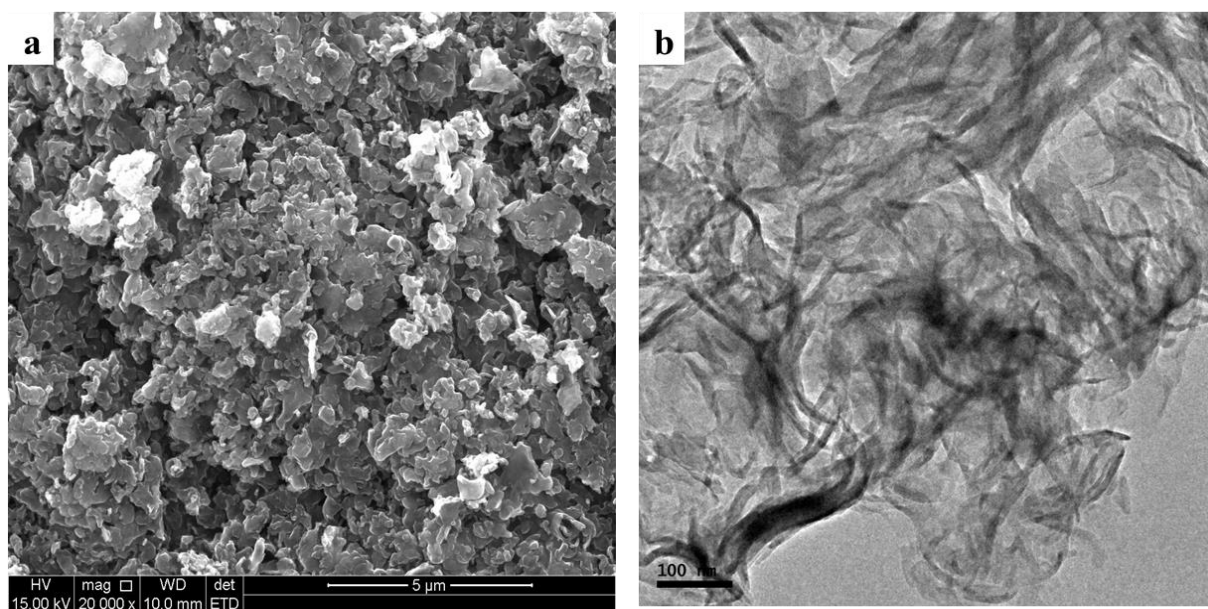


Figure 5.S3: (a) SEM and (b) TEM images of $\text{g-C}_3\text{N}_4$

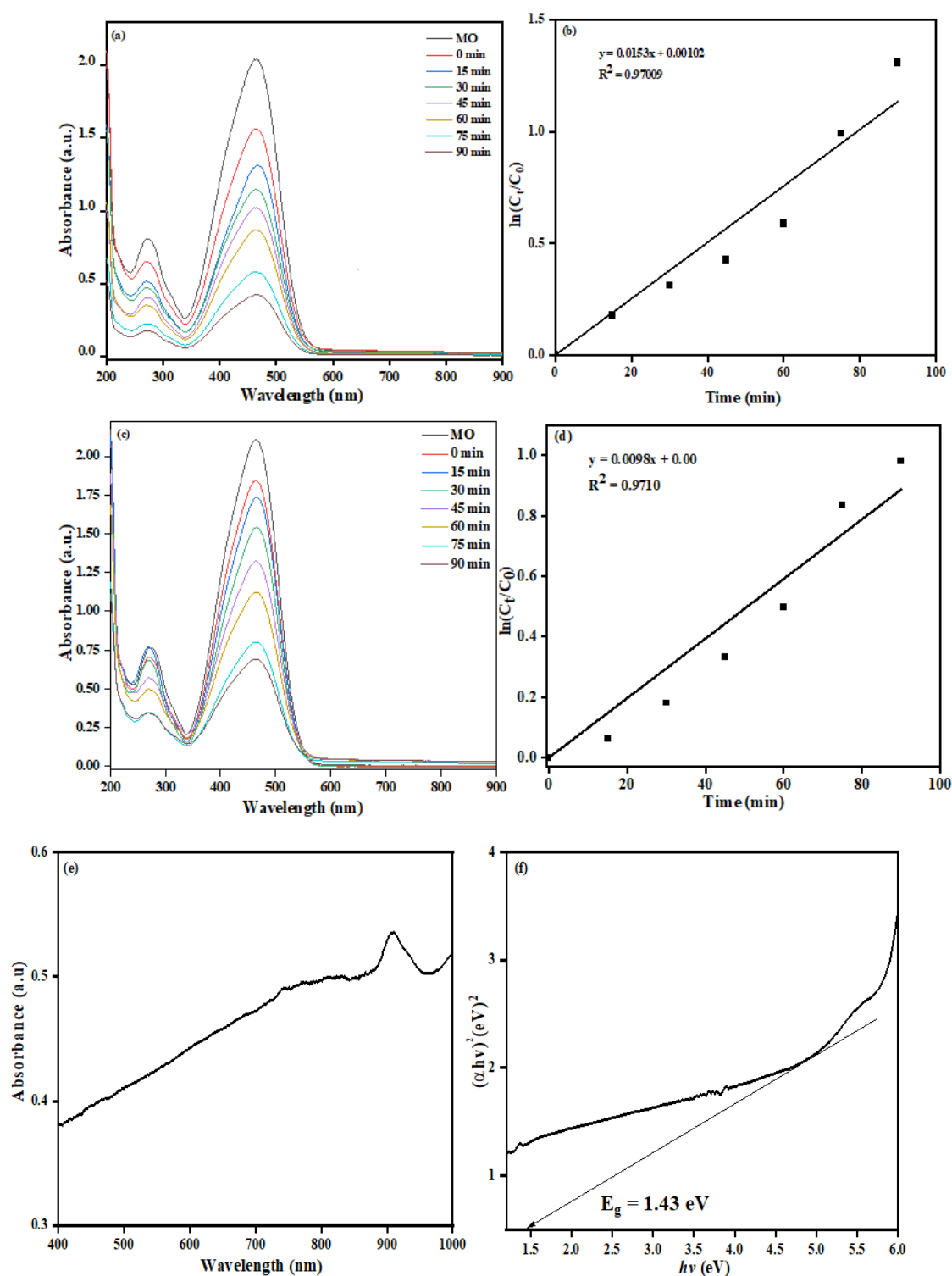


Figure 5.S4:(a,b) Degradation profile and kinetic plot of Cu-Bi₂S₃ for methyl orange degradation, (c,d) Degradation profile and kinetic plot of Bi₂S₃ for methyl orange degradation, and (e,f) absorption spectra and Tauc plot for Cu-Bi₂S₃.

CHAPTER SIX

6.S1: Synthesis of Bi_2S_3 , CuS and GCN

6.S1.1: Synthesis of N-methyl-N-phenyldithiocarbamate ligand

The single-source precursor method is used in the synthesis of the metal sulphides. In a typical synthesis, dithiocarbamate metal complexes of bismuth and copper were prepared. Firstly, N-methyl-N-phenyl dithiocarbamate ligand was prepared by mixing N-methyl aniline (2.72 mL, 0.01 mol) and aqueous ammonia (1.50 mL, 0.01 mol) in a round-bottomed flask and cooled to 4 °C in an ice bath. After 15 min, carbon disulphide (0.60 mL, 0.01 mol) was slowly added to the mixture, stirred for about 4 - 6 h, and then filtered by suction. Afterwards, metal complexes were prepared by mixing stoichiometric amounts of metal salt and ligand in solution and stirring for 1h. The obtained metal complex was recovered by centrifugation and then dried under a vacuum.

6.S1.2 Synthesis of Bi_2S_3 nanorods

The solvothermal heat-up method was used in the synthesis of Bi_2S_3 from the dithiocarbamate metal complex. Bi_2S_3 nanoparticle was obtained by dispersing the bismuth dithiocarbamate metal complex in ethylene glycol, after which the mixture is transferred into a stainless-steel autoclave. The mixture was heated at 180 °C for 24 h and the product was recovered by washing with ethanol and drying under a vacuum.

6.S1.3 Synthesis of CuS nanorods

CuS was synthesized by thermolyzing in dodecanthiol in a heat-up process under an inert atmosphere to achieve pure phase selectivity. In a typical synthesis, 0.05 mol of the copper dithiocarbamate complex was dispersed in 10 mL of dodecanethiol in a three-necked round bottom flask. The flask was fitted with a condenser and heated to 120 °C on a heating mantle. The set-up was held at this temperature for 1 h and the product obtained was washed by centrifugation using ethanol. The product was finally dried under a vacuum to obtain the CuS powder.

6.S1.4 Synthesis of graphitic carbon nitride (GCN)

GCN was synthesized by the polycondensation of melamine. In a typical synthesis, 10 g of melamine was weighed into a ceramic crucible with a lid. The crucible was then heated to 550 °C in a furnace for 4 h. The obtained solid mass was crushed and then stored for further use.

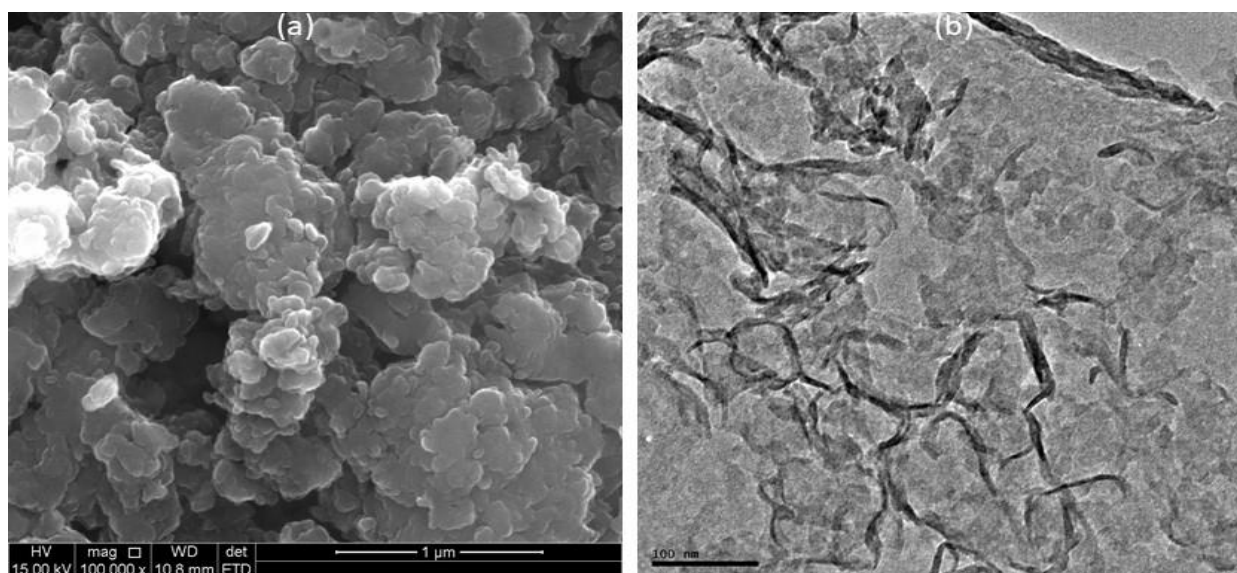


Figure 6.S1: (a) SEM and (b) TEM micrographs of GCN.

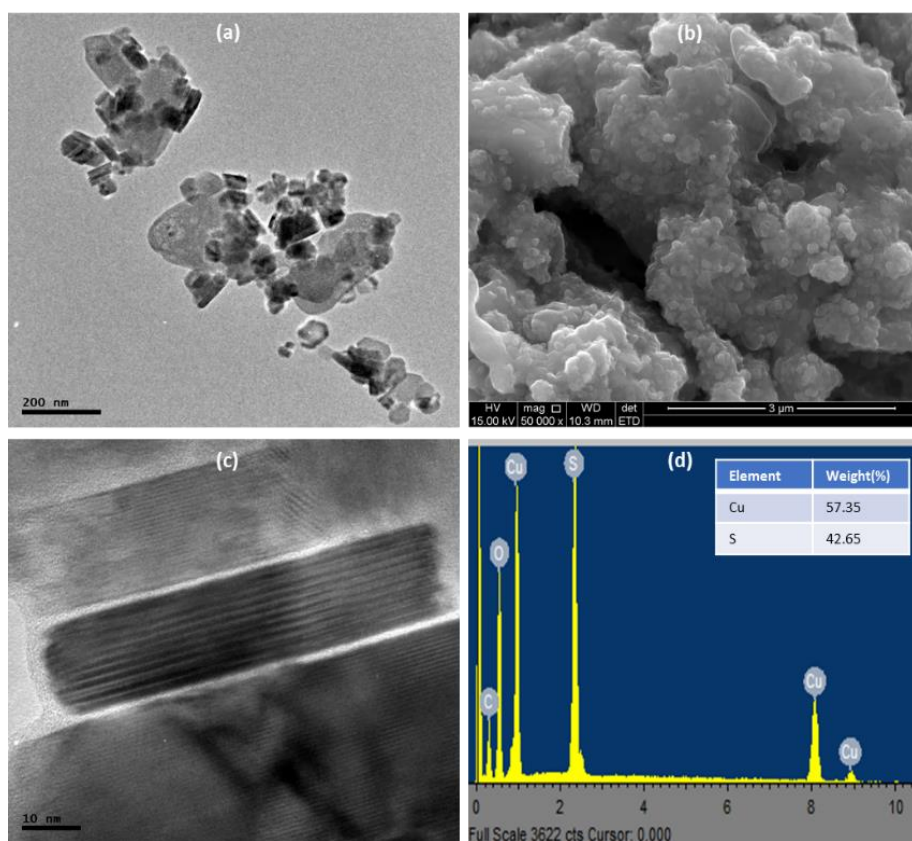


Figure 6.S2: (a) TEM, (b) SEM, (c) HRTEM and (d) EDX spectrum of CuS nanorods.

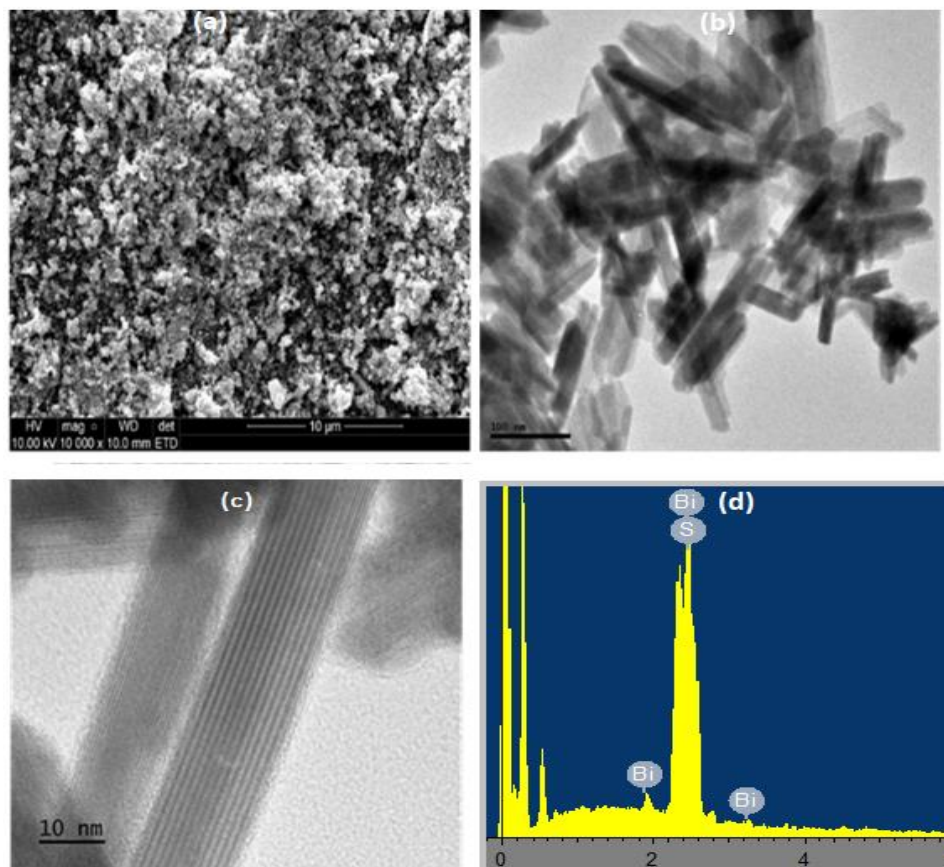


Figure 6.S3: (a) TEM, (b) SEM, (c) HRTEM and (d) EDX spectrum of Bi₂S₃ nanorods.