

Visible light driven CuBi_2O_4 heterostructures and their enhanced photocatalytic activity for pollutant degradation: A review

Olalekan C. Olatunde^{a,b,*}, Lawrence Sawunyama^{a,b}, Tunde L. Yusuf^c, Damian C. Onwudiwe^{a,b,*}

^a Materials Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Natural and Agricultural Sciences, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa

^b Department of Chemistry, School of Physical and Chemical Sciences, Faculty of Natural and Agricultural Sciences, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa

^c Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Private Bag X20, Hatfield 0028, Pretoria, South Africa

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ABSTRACT

The existence of organic, inorganic, and microbiological contaminants in water bodies continues to pose a serious threat to public health worldwide. The photocatalytic elimination of these contaminants using copper bismuthate (CuBi_2O_4) heterostructures has been the subject of numerous studies. CuBi_2O_4 heterostructures have demonstrated their effectiveness as a photocatalyst because of their longer charge carrier lifespan, enhanced capacity to absorb solar light, and greater charge carrier separation. The various techniques for fabricating CuBi_2O_4 heterostructures such as hydrothermal, sol-gel, solid state, solvothermal, electrospinning, spray pyrolysis, and electrodeposition are extensively discussed in this review paper. A wide range of CuBi_2O_4 heterostructures and their different mechanisms of action are also covered. The photocatalytic degradation of pollutants by copper bismuthate (CuBi_2O_4) heterostructures is also presented in detail. Furthermore, a thorough critical discussion is included about the prospects and difficulties of using CuBi_2O_4 heterostructures for the photocatalytic purification of wastewater.

1. Introduction

Global population growth, prolonged droughts, and rapid industrialization have significantly increased the demand for and scarcity of clean water sources [1]. Many practical measures and solutions have been implemented to establish more sustainable water resources in response to this rising demand [2,3]. However, finding sustainable water supplies is increasingly difficult in arid regions with abundant sunshine, minimal precipitation, and extended droughts. Currently, an estimated 4 billion people worldwide lack or have limited access to clean, sanitized water, and millions die each year from severe water-borne illnesses. These statistics are expected to worsen due to rising water contamination caused by excessive contaminants and micro-pollutants entering the natural water cycle [4–6].

Freshwater resources, including lakes, rivers, and groundwater, are contaminated by various organic, inorganic, and microbiological substances such as agricultural chemicals, pharmaceuticals, and personal

care products [7–9]. For example, 20 % of dyes used in the textile industries are discharged as wastewater into the environment. With a medial lethal dose (LD_{50}) of $>2 \times 10^3$ mg/kg and being non-biodegradable, their acute toxicity could result in severe ailments in the human body [10,11]. Similarly, Pharmaceuticals, being non-biodegradable, pose environmental hazards even at low concentrations, contributing to antibiotic resistance and disrupting endocrine and immune systems. Persistent pharmaceutical waste threatens aquatic life by degrading water quality, which is particularly problematic in water-scarce areas where reuse is common [12]. Consequently, developing innovative, affordable, and highly effective wastewater treatment technologies is crucial to prevent the worsening clean water shortage.

Recycling treated municipal wastewater from treatment plants or on-site rural wastewater for industrial and agricultural purposes is a promising solution [13,14]. This approach can significantly contribute to clean water resources since they constitute one of the largest potential water sources [15]. However, recalcitrant organic and inorganic

* Corresponding authors at: Materials Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Natural and Agricultural Sciences, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa.

E-mail addresses: 32587139@mynwu.ac.za (O.C. Olatunde), Damian.Onwudiwe@nwu.ac.za (D.C. Onwudiwe).

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compounds, suspended solids, and health-threatening coliforms often hinder recycling, necessitating time-consuming and costly treatments [13,16–18]. Traditional wastewater treatment techniques like adsorption and coagulation typically transfer pollutants from one phase to another rather than eliminating them [19]. Other methods, such as chemical treatment, filtration, sedimentation, and membrane technologies, are expensive and can release harmful secondary pollutants into the environment. While chlorination is the most popular and extensively used disinfection method, its byproducts are carcinogenic and mutagenic to human health [20].

These challenges have driven research into advanced oxidation processes (AOPs) as novel water treatment technologies. AOPs generate highly reactive radical species such as H_2O_2 , $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$, O_3 , and $\text{SO}_4^{\cdot-}$ in situ to degrade inorganic and organic compounds, inactivate water pathogens, and degrade disinfection by-products [21,22]. AOPs include wet oxidation processes, heterogeneous and homogeneous photocatalysis, Fenton and Fenton-like processes, ozonation and electrochemical processes [20]. Heterogeneous photocatalysis, in particular, has proven effective in degrading refractory organics into more minor, biodegradable compounds that can be mineralized into carbon dioxide and water. Furthermore, its potential has been explored in other applications, such as water reduction and H_2O_2 production [23,24] and the synthesis of organic compounds [25].

When light irradiates, a photocatalyst generates numerous holes and electrons that can engage in redox reactions with organic and inorganic pollutants, thereby eliminating contaminants [26,27]. Additionally, the photogenerated holes and electrons can react with O_2 and $\text{H}_2\text{O}/\text{H}^+$ to generate active oxygen species, such as radicals ($\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$) and non-radicals ($^1\text{O}_2$) [28,29]. Key features of heterogeneous photocatalysis include low operating costs, ambient operating temperature and pressure, and the complete breakdown of target compounds and their intermediates without generating secondary pollutants.

To optimize photocatalytic wastewater treatment, ongoing research aims to identify photocatalysts with enhanced activity. Also, since a significant portion (approximately 43 %) of the solar spectrum comes from the visible light region, visible light-responsive semiconductors are being extensively studied for a wide array of photocatalytic applications [30]. Copper bismuthate (CuBi_2O_4) has recently gained attention as a visible-light responsive p-type semiconductor photocatalyst. Discovered by Arai *et al* [31], CuBi_2O_4 crystallizes in a tetragonal structure composed of staggered square planar $[\text{CuO}_4]^{6-}$ units stacked along the c-axis, with Bi^{3+} ions placed between the stacks and coupled to six O^{2-} ions with three distinct bond distances (Fig. 1a) [32]. This unique structure results in the formation of straight channels around Bi^{3+} ions (Fig. 1b) [33]. The isolated $[\text{CuO}_4]^{6-}$ stacks, distinct from the edge-sharing oxygen octahedra or tetrahedra in typical metal oxides, are crucial to CuBi_2O_4 's electronic properties [34]. The material is considered an excellent photocatalyst due to its favourable band position,

narrow band gap, visible light absorption, low cost, and high flat band potential [35]. However, CuBi_2O_4 suffers from a low absorption coefficient, high charge recombination rate, and poor charge transport, stemming from its electronic band structure. For a detailed explanation of CuBi_2O_4 's electronic structure, consult the comprehensive review by Gonzaga *et al* [36].

Mitigating the limitations of CuBi_2O_4 has received much attention recently to enhance its optoelectronic properties. This is usually achieved through doping [37] or heterostructure formation [38]. The development of semiconductor heterojunctions formed by direct contact between two semiconductors is an effective design to mitigate the limitations faced by single semiconductors [39]. In heterostructure design, extended charge carrier lifetime, increased charge carrier separation, and expanded solar light absorption are facilitated by the coupled semiconductors' appropriate band edge positions. The continual interest in CuBi_2O_4 heterostructures, as shown in the publication trend presented in Fig. 1c, attests to the potential of these materials as effective photocatalysts for wastewater treatment. Therefore, this review thoroughly explores copper bismuthate (CuBi_2O_4) heterostructures for photocatalytic wastewater treatment, highlighting various synthesis methods and their comparative advantages. The different mechanisms of action of these heterojunctions were explored in detail and the photocatalytic activity of other categories of CuBi_2O_4 heterojunctions was discussed. The suggested future research directions also offered valuable insights for developing more efficient and sustainable photocatalysts.

2. Synthesis of CuBi_2O_4 heterostructures

Due to its effective light absorption characteristic, copper bismuth oxide (CuBi_2O_4) has garnered significant attention in several applications, including photocatalytic degradation of pollutants. However, there have been reports of problems with this Cu-based ternary oxide material, including: (1) fast recombination of photogenerated electron-hole pairs; (2) reduced charge carrier mobility; (3) excessive photostability; and (4) insufficient charge carrier diffusion length. All of this can be addressed effectively by forming a heterojunction interface or other enhancing techniques, such as doping and forming composites [40]. Copper bismuth oxide (CuBi_2O_4) and its heterostructures can be fabricated using various methods. These methods include pulsed laser deposition, solid state, solvothermal, electrodeposition, hydrothermal, sol-gel, electrospinning, and spray pyrolysis. Table 1 shows some advantages and disadvantages of the different methods employed in synthesizing CuBi_2O_4 -based materials. These methods can be employed individually or in combination. Comprehending the chemistry and variables influencing each fabrication method is crucial since they impact the final Cu-based ternary oxide material's structure, morphology, and functionality [41]. Therefore, the application of these techniques to the synthesis of CuBi_2O_4 and its heterostructures will be covered in this section.

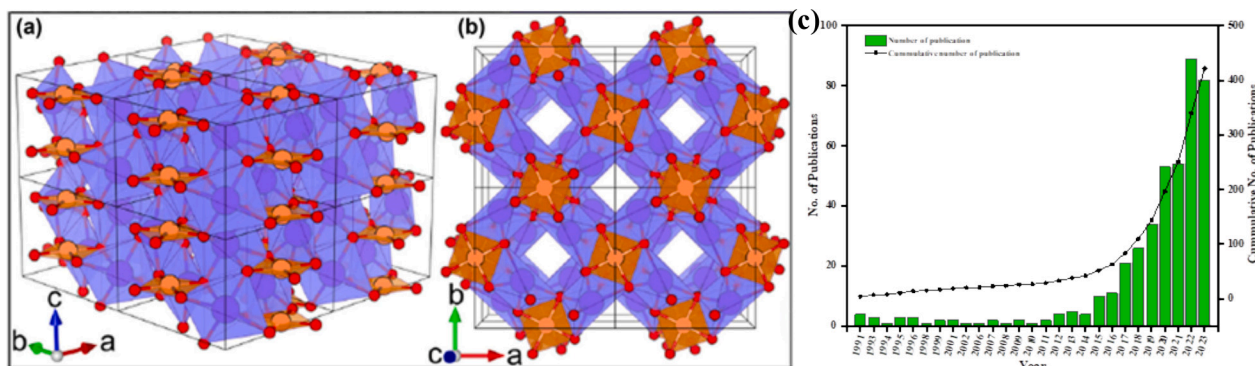


Fig. 1. Isomeric (a) and c-axis projection (b) of CuBi_2O_4 crystal structure. Reprinted with permission from ref. [22]. Copyright © 2022 De Gruyter, (c) Publication trend for copper bismuthate from 1991 to 2023.

Table 1Advantages and disadvantages of CuBi₂O₄ synthetic methods.

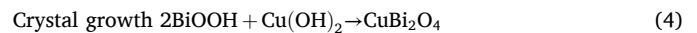
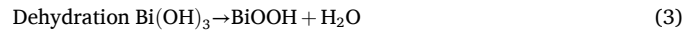
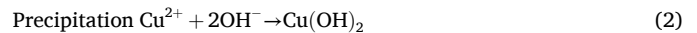
Fabrication	Advantages	Disadvantages	References
Spray pyrolysis	It can be used for the preparation of pure phases.	Affected by extreme temperatures.	[79,80,175,176]
	It's a low-cost preparation method that uses low temperature.	Chemical stability of the precursor solution is another great issue.	
	Film production cycle is short. Useful for large scale production.	Low deposition efficiency. The method uses solvents, molecular precursors, and stabilizers that can be costly and potentially toxic.	
	Operation of the apparatus is easier and simple.	The structure morphology has limited control.	
Electrospinning	Simple and effective synthesis route for one-dimensional materials.		[56,71]
Solvothermal method	An easy method with a comparatively low processing temperature.	The method requires high volumes of solvents which might be toxic.	[56,72,177]
	Great degree of repeatability.	High-cost equipment such as autoclaves are required.	
	Advantageous in large-scale manufacturing.	The issue of associated effluent pollution remains a challenging and inevitable issue.	
	Easier to regulate the material's size and shape.	The required equipment is expensive and the method has a higher percentage of impurities compared to other methods.	
Solid state method	Relatively easy usability.		[63,69]
	it's a solvent-free method.		
	Ability to produce large quantities of synthesized materials.		
Sol gel method	Simple and economical method that uses low sintering temperature.	It takes longer time. Organic solvent used may be toxic.	[43,178]
	Simple and cheap method that uses low temperature.	Safety issues during fabrication process.	
Hydrothermal method	No requirement of toxic precursors and solvents.	The industrial application of this method is restricted by its lengthy preparation time.	[179,180]
	Easier to modify material morphology and size.	High cost equipments such	

Table 1 (continued)

Fabrication	Advantages	Disadvantages	References
Pulsed laser deposition (PLD)	Quite simple to be carried out and doesn't require post-annealing process.	as autoclaves are required. The production of high-quality single-crystal thin films presents a significant challenge.	[86,88]
Electrodeposition	Depositing sharp interfaces between heterojunctions. Simple and low-cost technique for large area films.	Not ideal for large scale applications.	
	The morphology can be significantly manipulated by controlling the synthesis conditions.		[37,89,90,93,181]

2.1. Hydrothermal method

The hydrothermal approach is the most utilized and versatile technique for fabricating CuBi₂O₄ and its heterostructures because of its low temperature, simplicity of use, affordability, uses of low temperature and ability to modify particle size and shape when compared to alternative techniques. It also doesn't require any hazardous or organometallic precursors [42,43]. However, the lengthy preparation period, which might take up to 24 h, restricts the method's industrial applicability. In this synthetic method, the primary precursors utilized in the fabrication of CuBi₂O₄ are bismuth (III) nitrate pentahydrate Bi(NO₃)₃·5H₂O and Copper(II) nitrate trihydrate Cu(NO₃)₂·3H₂O. In a study illustrated in Fig. 2a, Zhang *et al* [44] used these precursors for the preparation of CuBi₂O₄/CdMoO₄ heterojunctions. A sequence of chemical reactions and reaction eqs. (1–4) resulted in the synthesis of CuBi₂O₄ nanoparticles [45]. Rapid hydrothermal synthesis can be facilitated by adding acids like acetic acid and HNO₃ to increase the solubility of Bi(NO₃)₃·5H₂O. The reaction is often conducted for 0.5–24 h at a temperature between 100 and 200 °C in a stainless steel autoclave lined with Teflon [46,47]. Additionally, alkaline conditions should be used for these reactions to aid in the dissolution-crystallization process, which is the process by which mineralizers attack the amorphous precipitates to form CuBi₂O₄ [48].



It is often necessary to optimize the Cu/Bi content and reaction time since they affect the final material's morphology, optical absorption properties, and photocatalytic capabilities. Abdulkarem *et al.* [46] reported the formation of CuBi₂O₄ with cubic rod morphology only at specific precursor concentrations and hydrothermal time. In another study, limited hydrothermal duration time resulted in incomplete crystal growth of CuBi₂O₄. Extended hydrothermal time eventually displays comparable XRD peaks except for peak intensity. Superior material morphology was achieved through extended hydrothermal duration [49].

Furthermore, the hydrothermal process can be combined with other fabrication techniques. For instance, Xiong *et al* [50] used *in-situ* chemical oxidative polymerization followed by a hydrothermal reaction

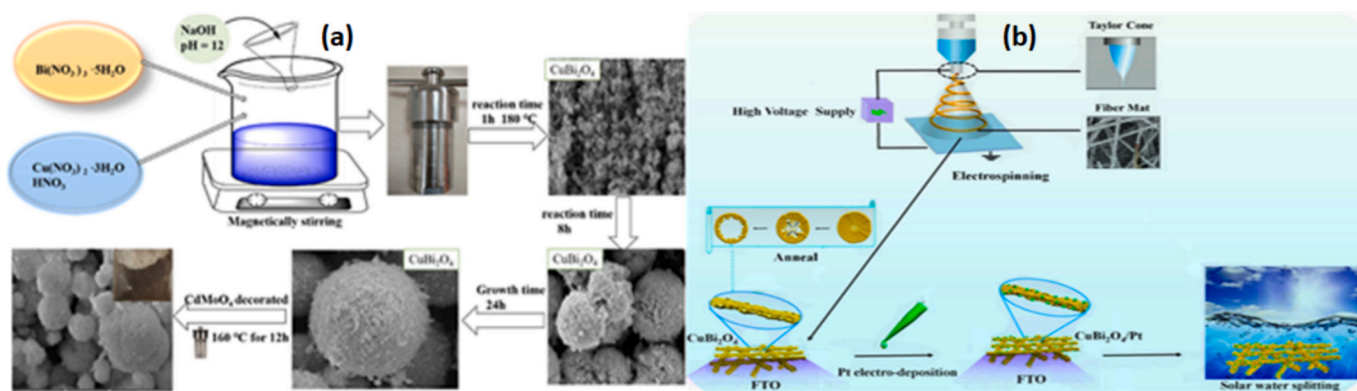


Fig. 2. (a) The preparation of $\text{CuBi}_2\text{O}_4/\text{CdMoO}_4$ heterojunction nanocomposites via the hydrothermal treatment. Reproduced from Zhang et al. [44], Copyright © 2021, Elsevier. (b) Synthesis of $\text{CuBi}_2\text{O}_4/\text{Pt}$ nanofiber using electrospinning method. Reproduced from Yuan et al. [54], Copyright © 2021 Elsevier.

pathway to fabricate a polyaniline/ CuBi_2O_4 p-p heterostructure. PANI microsphere was fabricated using *in-situ* chemical oxidative polymerization. Hydrothermal approach was used to fabricate the heterostructure. In another study, Yang *et al* [51] used the hydrothermal method and surface anion exchange method to prepare the Z-scheme $\text{CuBiOS}@\text{CuBi}_2\text{O}_4$ heterojunction.

2.2. Electrospinning

Electrospinning synthesis is an effective and simple synthesis route that is mainly used to fabricate one-dimensional CuBi_2O_4 heterostructures through an electrohydrodynamic process [52]. The method forms a jet of polymer solution using an electrified liquid droplet to fabricate the required material [53]. Yuan *et al* [54] reported the fabrication of $\text{CuBi}_2\text{O}_4/\text{Pt}$ nanofiber using the electrospinning method. The electrospinning setup contained a high-voltage system and plate collector, as shown in Fig. 2b. Annealing and electro-deposition of Pt completed the fabrication of the heterostructure. Electrospinning rendered the homogenous distribution of the various components on the heterojunction possible [55]. Sometimes, electrospinning can be used in conjunction with other methods to fabricate CuBi_2O_4 heterostructures with the precise characteristics that are needed. For example, one-dimensional $\text{CuBi}_2\text{O}_4\text{-Bi}_2\text{WO}_6$ was synthesized by electrospinning assisted by solvothermal method [56]. Viscosity and surface tension of the solution are important factors in determining the concentrations needed to achieve continuous post-electrospinning.

2.3. Sol-gel method

The sol-gel method is a versatile technique for fabricating CuBi_2O_4 heterostructures. It starts by dissolving precursor molecules in a solvent like alcohol or water. The solution is then heated and stirred, promoting the formation of a gel-like network composed of interconnected nanostructures [57]. This method offers remarkable control over the morphology of CuBi_2O_4 heterostructure nanocomposites. By fine-tuning reaction conditions (temperature, stirring) and precursor composition, various morphologies can be achieved, including spheres, irregular shapes, plates, flower-like structures, and even flower-like structures with rod assemblies [58,59]. The sol-gel technique is significantly less complicated than hydrothermal methods. In most cases, the sol-gel method can be combined with other fabrication techniques. For instance, Zhang *et al* [60] used a solution process to fabricate CuBi_2O_4 . The as-prepared material was turned into $\text{CuBi}_2\text{O}_4/\text{TiO}_2$ p-n heterojunction using the *in-situ* sol-gel coating method. The crystal phase composition, morphology, and interfacial chemical characteristics of the $\text{CuBi}_2\text{O}_4/\text{TiO}_2$ heterojunction synthesized by the sol-gel technique have been reported to be influenced by changes in the precursors' molar ratio of Cu/Bi and the calcination temperature. The sol-gel method can be

modified to the Pechini method through complexing cations in an aqueous-organic medium [61]. Due to its homogenous ion distribution and utilization of inexpensive materials, the Pechini sol-gel technique has been investigated recently for the synthesis of CuBi_2O_4 heterojunctions. This technique also involves the addition of additives like gelling agents. In one instance, copper nitrate, bismuth nitrate, polybasic acids, and gelling agents were used to fabricate $\text{CuBi}_2\text{O}_4/\text{Bi}_3\text{ClO}_4$ nanocomposites using an improved Pechini sol-gel process [58].

2.4. Solid state method

The solid-state route preparation for CuBi_2O_4 heterostructures takes place via mechanical milling and mechanochemical synthesis from solid reagents [62]. Each of these methods has its advantages and shortcomings. Mechanical milling is the most widely utilized of these due to its ease of use, affordability, solvent-free environment, and capacity to generate substantial amounts of synthesized materials [63,64]. However, the method requires high monitoring and control against contaminations during mechanical milling. Merely using water as a dispersion and carrying out multiple annealing processes with different intermediate milling stages can enhance precursor mixture homogeneity and decrease powder particle size through mechanical milling [65]. Multiple annealing cycles can establish strong bonds between solid precursors, facilitating charge transfer across surfaces [66]. Chen *et al* [67] reported the fabrication of $\text{CuBi}_2\text{O}_4/\text{MWCNT}$ composites by mixing solid precursors, followed by a ball-milling reaction. The synthesis of CuBi_2O_4 heterostructures through a solid-state response involving mechanical milling of different ratios of CuBi_2O_4 and CeO_2 was also reported by Elaziouti *et al* [68]. This method is affected by the surface area, reactivity, and free energy change of the reactants.

2.5. Solvothermal method

The solvothermal method is a widely adopted traditional and robust route for fabricating CuBi_2O_4 and its heterostructures. The solvothermal method is a straightforward and efficient technique for fabricating nanostructured materials. Its benefits include large-scale production, low cost, high reproducibility, relatively low processing temperature, and the capability to control the material's size and morphology with the help of appropriate additives [69,70]. The method also uses both water and organic solvents. CuBi_2O_4 heterostructures have been prepared using ultrapure water, glycerol, ethylene glycol, and ethanol. These have been used to modify the coordination of solvated species, induce specific structures, and increase the mobility of the dissolved ions [71–73]. The Solvothermal method is carried out in a closed reaction vessel that is heated above the boiling point of the solvents being used, such as a sealed autoclave lined with Teflon. CuBi_2O_4 heterojunction materials can be synthesized in one or two steps using solvothermal methods. The

most common methods are the one-step ones [74]. Muthukrishnaraj *et al* [75] successfully fabricated a reduced graphene oxide/CuBi₂O₄ heterostructure using a single-step solvothermal process. A mixture of graphene oxide and CuBi₂O₄ precursor solutions was placed in a Teflon-lined autoclave and heated for 24 h at 180 °C during synthesis. Reactant chemical reactivity and the solvothermal reaction kinetics in the solvothermal method can be improved by combining it with other technologies like microwaves, electrospinning, mechanical mixing, sonochemistry, and others [76]. For instance, using a solvothermal-assisted electrospinning method, Teng, Li [56] fabricated a one-dimensional Bi₂WO₆/CuBi₂O₄ heterojunction. The solvothermal method was used to fabricate Bi₂WO₆, while CuBi₂O₄ heterojunction material was fabricated by the electrospinning method under a high voltage. Chemical parameters like the composition, characteristics, and pH of the solvent and precursor, as well as thermal parameters like pressure and temperature, can impact solvothermal reactions [77,78].

2.6. Spray pyrolysis

Fabrication of CuBi₂O₄ heterostructures by spray pyrolysis involves spraying precursor solution on a heated substrate. The sprayed droplets undergo thermal degradation due to the heat from the heated surface. The desired heterostructures are formed by sintered and crystallized constituent elements that have recombined because of heat breakdown. Spray pyrolysis has been used to deposit CuBi₂O₄ heterostructures on a variety of substrates, including metals, glass (Fluorine Tin oxide-coated glass substrate), and ceramics [79]. Water scavengers (such as trimethyl orthoacetate and triethyl orthoformate) and additives like polyethylene glycol can be added to the precursor solution to enhance sprayed droplet dispersal characteristics and avoid the quick hydrolysis and polycondensation of bismuth ions [80]. The structural and optical characteristics of the synthesized heterostructures are influenced by the spray drying temperature, the pace at which the droplets evaporate, the concentration of the solution, and the preparative conditions. Shi *et al* [81] examined the impact of temperature during spray-drying on the growth of Bi₂O₃ nanoparticles on CuBi₂O₄. Results showed increased spray-drying temperature increased the peak intensity of 020 facets in the composites. As the temperature of the spray-drying process rose, the precursor's crystallization also progressively improved. High temperatures can efficiently shorten the time needed for the segregation gradient to form, resulting in pure-phase films. However, high temperatures can cause the supporting substrate to melt and the deposited film to adhere to the substrate poorly [82]. As with other fabrication methods, spray pyrolysis can be combined with other methods. For example, Wang *et al* [83] used the diffusion-assisted spray pyrolysis procedure to manufacture self-doped CuBi₂O₄.

2.7. Pulsed laser deposition

Pulsed laser deposition (PLD) is another method that has been used to fabricate CuBi₂O₄ heterostructures. The method's fundamental component is the high-intensity pulsed laser beam that is used to deposit a layer on the target material. As opposed to previously discussed methods, this method is carried out at a very high vacuum with the presence of a background gas [84]. Woo *et al* [85] reported the synthesis of CuBi₂O₄ thin-film photocathodes by pulsed laser deposition using pure Bi₂O₃ and CuO. Different oxygen partial pressures were used to manipulate stoichiometry. Combining PLD and other techniques, such as rapid thermal processing, can also be used to control the Bi: Cu stoichiometry [86]. In another study, Lee *et al* [87] used the pulsed laser deposition method to fabricate CuBi₂O₄/NiO thin film photocathodes. The synthesized material was reported to have a dense, homogeneous, flat surface that removes pores and voids in heterostructures. However, CuBi₂O₄ heterostructure thin film formed by the PLD method was in a polycrystalline rather than a single crystalline state. Therefore, to fabricate single-crystal thin films of CuBi₂O₄, it is important to optimize

the lattice misfit strain between the target material and the substrate [88].

2.8. Electrodeposition

The electrodeposition method has also been used to prepare CuBi₂O₄ and its heterostructures with excellent photoelectrochemical properties [89–91]. In a study reported by Nakabayashi *et al* [92], CuO and Bi₂O₃ precursors were co-deposited by anodic electrolysis on a conductive fluorine tin oxide-coated glass substrate (FTO). After that, the formed CuBi₂O₄ films were heated for 4 h at 500 °C. Before electrodeposition, the conductive substrate's surface was cleansed using air plasma. During the electrodeposition procedure, the clean FTO serves as the anode. The electrolyte solution's composition, bath concentration, electrodeposition time, and PLD deposition potential pulse count should all be optimized for the fabrication of pure material [93,94] and regulation of the thickness of the obtained material [45]. Electrodeposition can be combined with other techniques in the preparation of CuBi₂O₄ and its heterostructures. For instance, Liu *et al* [95] fabricated CuBi₂O₄/BiVO₄ p-n heterojunction using a combination of pulsed laser and electrodeposition.

3. CuBi₂O₄ heterostructures and mechanism of action

The main idea behind creating a semiconductor-based photocatalytic heterostructure is to maximize overall photocatalytic performance by a logical arrangement of component materials to fully utilize the benefits of each component. The photocatalytic process comprises three basic complementary and indispensable steps [96]: (1) generation of electron-hole pairs by light irradiation when the energy of the incident photons is larger than the bandgap energy ($h\nu > E_g$), electron promotion to the conduction band occurs [97]. (2) separation of photogenerated charge carriers; under the coulombic forces of attraction; the timescale for photogenerated electron-hole pair recombination is $<10^{-9}$ femtoseconds [98] and the efficiency of the photocatalytic process is hampered by this reverse recombination of charge carriers; (3) charge transfer onto catalytic sites for redox reaction; the buildup of charge carriers on the photocatalytic surface may result in unintended semiconductor instability due to the presence of highly oxidative holes and reductive electrons. The valence band maximum and conduction band minimum positions determine the oxidation and reduction potential of photo-generated electrons and holes, respectively. A shallow valence band and high conduction band position are the preference for photocatalytic degradation processes.

Based on the aforementioned fundamental steps of photocatalysis, broad light absorption and strong redox ability are two important properties of the photocatalytic activity of a semiconductor. However, both properties are mutually exclusive since narrowing of E_g is essential for broad light absorption, while band gap widening (highly positive valence and negative conduction bands) results in strong redox ability [99]. Therefore, to mitigate this obstacle, the development of heterojunction has proven effective. In heterojunction formation, appropriate band edge positions are advantageous for longer charge carrier lifetime, broader light absorption, and improved charge carrier separation [100].

3.1. Charge transfer mechanism in CuBi₂O₄ heterostructures

Based on the material composited with CuBi₂O₄, enhanced charge carrier lifetime and properties are achieved through charge transfer mechanisms such as type II, Z-scheme, S-scheme, plasmonic effect, Schottky junction or carbon-based electron sinks. While type II, Z-scheme, and S-scheme charge transfer mechanisms are associated with CuBi₂O₄/semiconductor heterostructures, plasmonic effect and Schottky junction are observed in CuBi₂O₄/metal composites.

In CuBi₂O₄/semiconductor heterostructures, the disparity in band energy potential results in three different types of band alignment: (1)

straddling gap, (2) broken gap, and (3) staggered gap, as shown in Fig. 3a. However, in practice, only staggered heterojunctions can enhance charge transport [101]. A staggered gap heterojunction can be formed by combining semiconductors of the same or different types. Many studies reveal that the heterojunction formed by combining p-type and n-type semiconductors with staggered energy gaps is more efficient in improving photocatalytic activity [102–104]. This improvement is primarily attributed to the existence of a built-in electric field. Creating a built-in electric field arising from the majority carrier diffusion effect at the interface which interferes with the photogenerated charge carrier transport in p-n heterojunctions [105]. This has been explored in limiting charge carrier recombination and enhancing photocatalytic activity [106,107]. According to Che et al. [101], p-n heterojunction can be of two types. In the first type of p-n heterojunction, the Fermi level of the reduction p-type semiconductor is relatively large, while the n-type semiconductor has a relatively small Fermi energy. Local band bending occurs after the compounding of the semiconductors, leading to the flow of electrons from the oxidation n-type semiconductor to the p-type semiconductor until the equilibration of the Fermi levels. This establishes an internal electric field (IEF) directed from the n-type semiconductor to the p-type. The transfer mode of photogenerated charge carriers could follow the type II, Z-scheme, or S-scheme pathway based on the influence of IEC and band structure.

The other type of p-n heterostructure is formed from n-type semiconductors with small conduction bands (CB) and p-type semiconductors with large valence bands (VB). In this structure, IEF is developed similarly to what was described earlier. The charge transfer mechanism in this heterostructure is either by type II or Z-scheme mechanism. However, the Z-scheme is the most prevalent in this type of p-n heterojunction. The electrostatic force generated by the IEF due to p-n heterojunction can improve the transfer of photogenerated charge carriers. For CuBi_2O_4 heterostructures, this type of p-n heterojunction is prevalent in dual Z-scheme materials.

3.1.1. Type II CuBi_2O_4 /semiconductor heterostructures

In a typical type II heterojunction, photogenerated electrons migrate from the CB of the semiconductor with the higher potential to the CB of the semiconductor with a lower CB. In contrast, the flow of photogenerated holes follows the opposite direction [108]. The occurrence of this charge transfer remains debatable due to the role played by the IEF and the work function-induced interfacial band bending [109]. The major difference between the type II charge transfer mechanism and the other mechanisms is the direction of the generated IEF, as shown in Fig. 3b. While the direction of the IEF is from the reduction photocatalyst to the oxidation photocatalyst in S-Scheme and Z-scheme charge transfer, the IEF flows in the opposite direction in type II heterojunctions. Despite the ability of the type II charge transfer mechanism to suppress charge carrier recombination, this is usually at the expense of

the redox ability of the photocatalyst, which weakens the photocatalytic reaction's driving force.

In the study by Li et al. [110], *in-situ* mechanochemical fabrication of p-n $\text{Bi}_2\text{MoO}_6/\text{CuBi}_2\text{O}_4$ heterojunction with type-II charge transfer mechanism was reported. The CuBi_2O_4 CB experienced an upward shift, while the Bi_2MoO_6 VB underwent a downward shift, leading to Fermi level equilibration during the mechanochemical process. These shifts were accompanied by the creation of an IEF that formed in the direction of Bi_2MoO_6 to CuBi_2O_4 . Under visible light irradiation, the photogenerated electrons on the CB of CuBi_2O_4 were inclined to transfer to the CB of Bi_2MoO_6 due to the influence of the IEF. Similarly, the photogenerated holes on the VB of Bi_2MoO_6 transferred to the VB of CuBi_2O_4 . The effective movement of electron-hole pairs ultimately led to the exceptional photocatalytic ability of the $\text{Bi}_2\text{MoO}_6/\text{CuBi}_2\text{O}_4$ heterojunction. The Mott-Schottky plot confirmed the p-type in CuBi_2O_4 and p-n-type heterojunction in $\text{Bi}_2\text{MoO}_6/\text{CuBi}_2\text{O}_4$, while the photoluminescence spectra of the heterojunction showed increased charge carrier lifetime, compared to CuBi_2O_4 and Bi_2MoO_6 .

Other CuBi_2O_4 /semiconductor type II heterojunctions that have been proposed include $\text{CuBi}_2\text{O}_4/\text{ZnFe}_2\text{O}_4$ [111], $\text{CuBi}_2\text{O}_4/\text{CuO}$ [112], and $\text{AgI}/\text{CuBi}_2\text{O}_4$ [113]. Recently, type II heterojunctions have also been proposed for CuBi_2O_4 /metal heterostructures such as n-Si/ CuBi_2O_4 [114].

3.1.2. S-scheme CuBi_2O_4 /semiconductor heterostructures

Similar to the type II mechanism, the S-scheme mechanism also relies on establishing direct electrical contact between two semiconductors. When two semiconductors with dissimilar band structures are interfaced, Fermi level (E_f) equilibration occurs due to charge redistribution. Band bending must, therefore, occur in the space charge zone. This produces an internal electric field, which makes it easier for electrons and holes to separate in the region [116]. The holes flow to the more negative site, while electrons flow to the more positive region. The valence band and conduction band of both semiconductors determine the direction of band bending [117]. The upward band bending increases the oxidation ability by attracting holes, while the downward band bending promotes reduction reactions by concentrating electrons onto the surface. The S-scheme mechanism thus leads to effective charge separation, while preserving the semiconductors' redox ability [118]. The mechanistic scheme for S-scheme charge transfer is shown in Fig. 4 (a).

The S-scheme charge transfer mechanism was proposed for $\text{CuBi}_2\text{O}_4/\text{CoV}_2\text{O}_6$ with CuBi_2O_4 acting as the reduction photocatalyst while CoV_2O_6 was the oxidation photocatalyst [119]. The flow of electrons after contact between the two materials was from CuBi_2O_4 , which has the higher Fermi level, to CoV_2O_6 , with the lower Fermi level, until Fermi level equilibration is achieved. This led to the upward bending of the CuBi_2O_4 band edge due to electron loss and producing electron

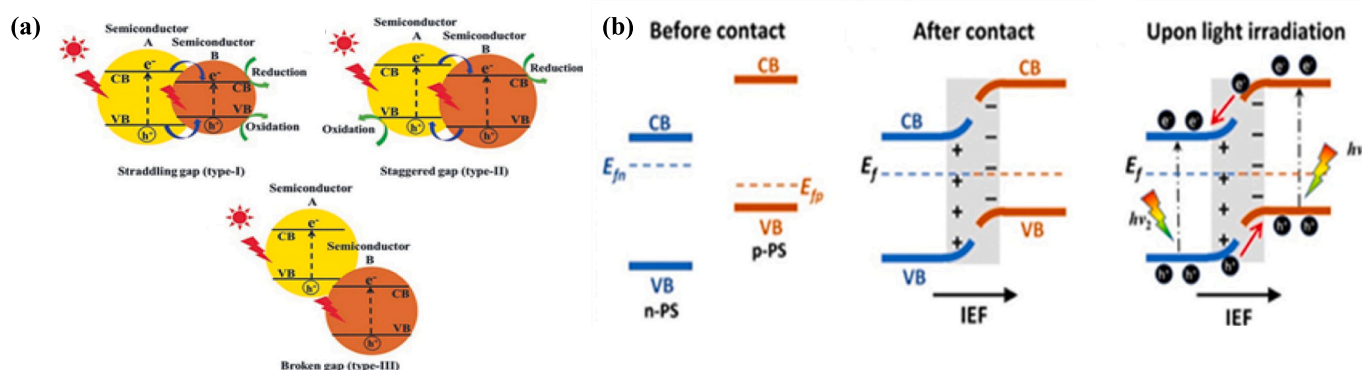


Fig. 3. (a) Band alignment in semiconductor-semiconductor heterojunctions. Reproduced from Che et al. [101]. Copyright ©, 2023 Elsevier. (b) Mechanistic scheme for type II charge transfer heterojunction. Reprinted with permission from Schumacher et al. [115].

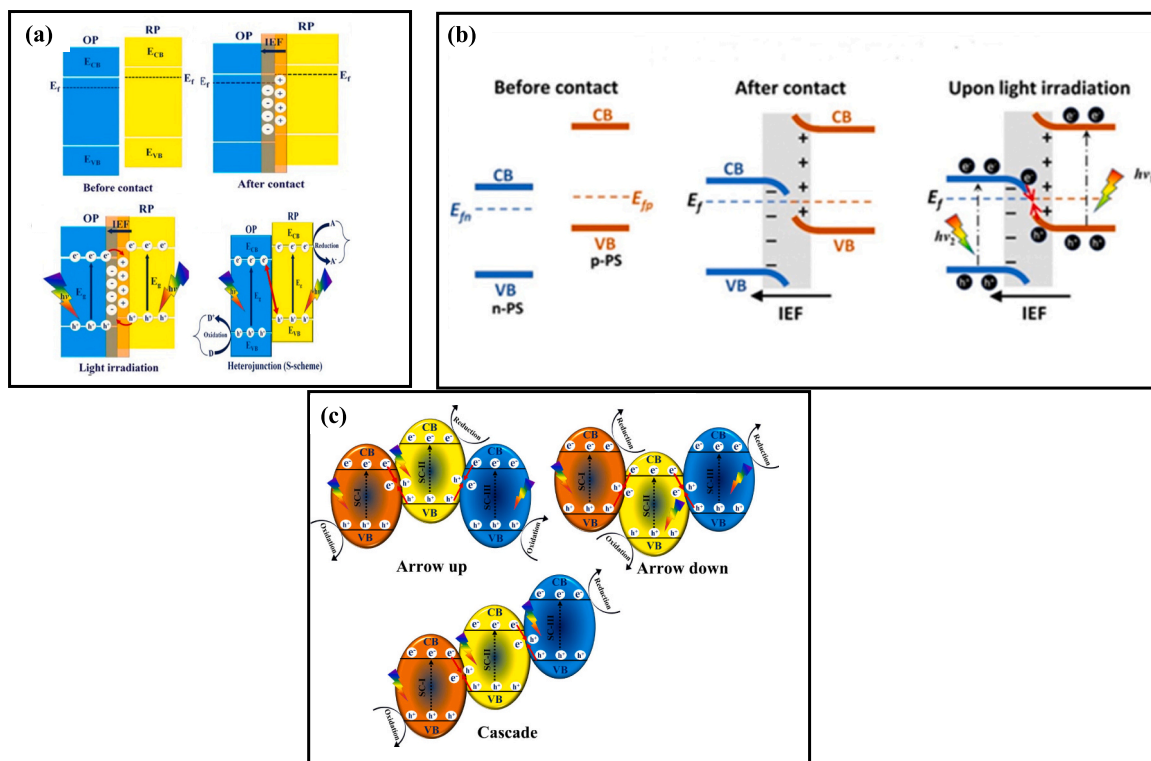


Fig. 4. (a) S-scheme charge transfer mechanism. Adapted from Hasija et al. [117], Copyright © 2021 Springer (b) Mechanistic scheme for Z-scheme charge transfer heterojunction. Reprinted with permission from Schumacher et al. [115], Copyright © 2022 Springer (c) Dual Z-scheme charge transfer configurations, adapted from Kumar et al. [132], Copyright © 2022, Elsevier.

depletion region. In contrast, the reception of electrons by CoV_2O_6 led to the downward bending of the band edge with the corresponding establishment of IEF from CuBi_2O_4 to CoV_2O_6 . Under light irradiation, photogenerated electrons in the CB of CoV_2O_6 combine with holes in the valence band of CuBi_2O_4 resulting in the preservation of the electrons in the CB of CuBi_2O_4 and holes in the VB of CoV_2O_6 .

The S-scheme mechanism has recently gained much attention in understanding the improved photocatalytic activity of CuBi_2O_4 heterostructures. Other S-scheme CuBi_2O_4 heterojunctions that have been reported include $\text{CuBi}_2\text{O}_4/\text{BiOBr}$ [120], $\text{Bi}_2\text{WO}_6/\text{CuBi}_2\text{O}_4$ [121], and $\alpha\text{-Fe}_2\text{O}_3/\text{CuBi}_2\text{O}_4$ [122].

3.1.3. Z-scheme CuBi_2O_4 /semiconductor heterostructures

The Z-scheme mechanism mimics the natural photosynthesis process. The traditional Z-scheme mechanism involves the transfer of electrons between the semiconductors through a shuttle redox mediator (electron acceptor/donor pair such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ or IO_3^-/I^-) [123–125]. In 2006, the all-solid-state Z-scheme was introduced in which noble metals, or conductive materials such as graphene and carbon nanotubes, acted as the electron mediator. The Z-scheme mechanism relies on forming low-contact resistant ohmic contact at the semiconductor interface arising from a conductor or large surface defects [126]. The photogenerated holes in the semiconductor with a higher valence band edge combine with photogenerated electrons in the semiconductor with a lower conduction band edge through the ohmic contact. Furthermore, the electrons located at the higher CB edge and the holes at the lower VB edge will be conserved for the reduction and oxidation reactions, respectively as shown in Fig. 4(b).

In their study on $\text{CoFe}_2\text{O}_4/\text{CuBi}_2\text{O}_4$ p-n heterostructure as nano-photocatalyst for C(OH)-H bond activation, Ghobadifard et al [127], reported a Z-scheme charge transfer mechanism. A shift in the VB and CB of CuBi_2O_4 to more negative values was observed compared to those of CoFe_2O_4 . The study confirmed the electron migration from the CB of

CoFe_2O_4 to combine with holes in the VB of CuBi_2O_4 , thus preserving photogenerated charge carriers with high redox potential for enhanced catalytic activity. The radical scavenging experiment significantly supported the proposed Z-scheme mechanism.

In real Z-scheme heterojunctions, the electron and hole transfer pathway may sometimes differ from the proposed mechanism, reducing its efficiency. This is, however, circumvented by developing multicomponent Z-scheme systems for improved photocatalytic performance, such as the dual Z-scheme systems. Charge carrier separation efficiency is further enhanced because of the multiple charge transfer routes in dual Z-scheme heterojunctions compared to traditional Z-scheme systems [128]. Three different charge transfer configurations have been identified for the dual Z-scheme heterojunctions: arrow up configuration, arrow down configuration, and cascade configuration (Fig. 4(c)). The difference among the configurations lies in the band alignment and the resulting enhancement in the redox ability of the heterojunction. In the arrow up configuration, the band edges of the semiconductor in the middle are higher than those of the other two.

In contrast, in the arrow-down configuration, the band edges of the middle semiconductor are lower than the other semiconductors [129,130]. In the cascading configuration, the band edges of the middle semiconductor lie between those of the other two semiconductors [131]. Furthermore, the arrow-up configuration leads to enhanced oxidative ability, while the arrow-down configuration results in more reductive ability. For the cascade configuration, the photocatalyst's oxidative and reductive ability are enhanced [132].

Mafa et al [133] designed a novel $\text{Co}_3\text{O}_4/\text{CuBi}_2\text{O}_4/\text{SmVO}_4$ dual Z-scheme heterostructure photocatalyst with enhanced charge transfer efficiency for improved degradation of carbamazepine under visible light irradiation. The improved catalytic activity of the heterojunction compared to the pristine materials was due to the enhanced charge separation in the heterojunction, which is significant for improving catalytic activity. The Z-scheme mechanism results in photogenerated

electrons in CuBi_2O_4 and SmVO_4 recombined with holes in Co_3O_4 , leading to the preservation of holes in the VB of CuBi_2O_4 and SmVO_4 and electrons in the CB of Co_3O_4 .

3.1.4. Schottky junction and plasmonic resonance CuBi_2O_4 heterostructures

Integrating semiconductors with noble metals is a widely employed strategy to exploit their charge kinetics. The metal may serve several roles in enhancing photocatalytic performance; however, in terms of charge transfer, two main mechanisms are involved in this heterostructure type: the plasmonic effect and the Schottky junction. While the plasmonic effect does not require direct contact between the metal and the semiconductor, direct contact is significant for the Schottky junction [134]. These two mechanisms depend on the photocatalytic system, such as the types of metal and semiconductor, as well as the wavelengths of incident light, and may operate either in conjunction or independently [116].

Schottky junctions are developed when a metal and a semiconductor make an interface and the metal's work function is higher than that of the semiconductor. In that case, electrons flow from the semiconductor to the metal, accompanied by a simultaneous formation of space-charge region. This leads to the semiconductor band's upward bending, and the space charge region facilitates charge separation and enhances electron and hole transport (Fig. 5a-c). Metal loading is an important factor to be considered in developing a Schottky junction, as more metal does not correlate to more Schottky barriers. High metal loading may lead to a larger number of electron trapping sites and may also reduce the semiconductor's exposure to light [135].

When plasmonic metals such as gold (Au), silver (Ag), and copper (Cu) are doped onto semiconductors, their surface plasmonic resonance (SPR) effect can be explored in photocatalysis since these surface plasmons resonate within UV-visible light [136,137]. Surface plasmon refers to the coordinated movement of conduction electrons at the boundary between a conductor and an insulator. It involves three primary mechanisms (Fig. 5(d)): 1) resonant photon scattering by metal, 2) creation of plasmon resonance energy transfer (PRET), which is an intense oscillating electric field around the metal, and 3) generation of hot electron-holes in the metal [138].

In the report by Shi *et al* [140], the visible-light-driven photocatalytic activity of Au/ CuBi_2O_4 heterostructure showed the involvement of both the plasmonic effect and Schottky junction in the enhancement of the photocatalytic activity of the composite. The plasmonic effect of Au was evident in the enhanced absorption of the composite in the UV and visible regions. Simultaneously, the hot electrons generated by Au through surface plasmon resonance (SPR) can be transferred to the conduction band of CuBi_2O_4 , resulting in increased charge carrier generation. While there are a few metal- CuBi_2O_4 heterostructures such as Pt/ CuBi_2O_4 [141], Pd@ CuBi_2O_4 [142], Ag- CuBi_2O_4 [143], not much

attention has been paid to the charge transfer mechanisms in these heterostructures. It is, therefore, imperative to understand these processes in metal- CuBi_2O_4 heterostructures for highly effective heterostructures of this class to be discovered.

4. CuBi_2O_4 -based heterojunctions in wastewater treatment

4.1. CuBi_2O_4 /transition metal oxide heterostructures

CuBi_2O_4 /transition metal oxide heterostructures are one of the most explored heterojunctions for photocatalytic degradation of pollutants. Recently, Zhang *et al* [144] reported the synthesis of a 0D/1D CuBi_2O_4 @ WO_3 heterojunction fabricated through the electrospinning method. The method achieved a uniform distribution of CuBi_2O_4 nanoparticles on WO_3 nanofibers while ensuring intimate contact between the nanoparticles and the nanofibers, which was significant for charge transfer and separation enhancement. Energy level difference calculation showed that while CuBi_2O_4 was the reduction photocatalyst, WO_3 was the oxidation photocatalyst, implying electron migration from CuBi_2O_4 to WO_3 to achieve Fermi level equilibration. This establishes a built-in electric field at the composite interface, which is consistent with the S-scheme charge transfer mechanism. The successful establishment of the charge transfer scheme resulted in efficient charge transfer across the heterostructure interface, reducing the recombination of photo-generated charge carriers while also enhancing the light-absorbing ability of the composite. The enhanced charge carrier property of the heterostructure was evidenced in the improved photocatalytic activity, achieving 70 % degradation efficiency for tetracycline, compared to 31 % and 16 % achieved by CuBi_2O_4 and WO_3 , respectively.

Zinc oxide (ZnO) is another well explored metal oxide photocatalyst because of its non-toxicity, high chemical and thermal stability, strong oxidation ability and low-cost [145]. Its applicability is, however, limited by its wide band gap energy, fast charge carrier recombination and low visible light utilization [146]. Sabri *et al* [147], however, showed in their study that the formation of ZnO/ CuBi_2O_4 heterostructure could benefit from improved visible light absorption, large surface area and p-n heterojunction formation at the interface of the semiconductors to achieve improved photocatalytic activity for different dyes. The charge transfer mechanism reportedly followed the type II mechanism, which significantly enhanced charge transfer and separation as supported by the photoluminescence spectra, electrochemical impedance spectroscopy, and transient photocurrent response of the material. In the presence of persulfate anion, the photocatalytic activity of the ZnO/ CuBi_2O_4 catalyst was significantly enhanced due to the reaction of photogenerated electrons with $\text{S}_2\text{O}_8^{2-}$ to produce $\text{SO}_4^{\cdot -}$ radical. Therefore, in addition to the generation of a highly powerful radical species, the separation of the photogenerated charge carrier was simultaneously enhanced.

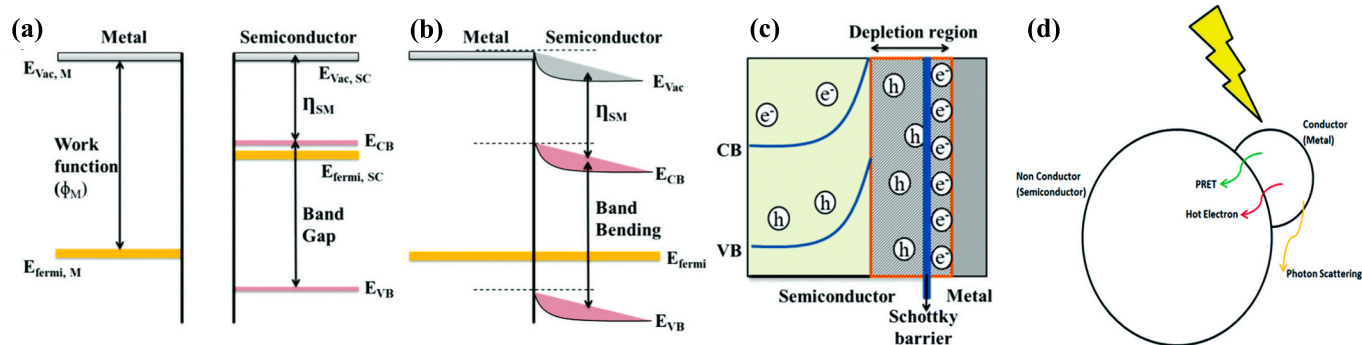


Fig. 5. Mechanistic scheme for Schottky heterostructures (a) metal and semiconductor band structure before contact, (b) band structure of metal and semiconductor after contact (c) charge carrier flow and depletion region formation at the metal-semiconductor interface and (d) Surface plasmon resonance mechanism. Reprinted with permission from [139]. Copyright Royal Society of Chemistry.

Other reported CuBi₂O₄/metal oxide heterostructures with improved photocatalytic activity for wastewater treatment include CuBi₂O₄/TiO₂ [71,148], Co₃O₄/CuBi₂O₄ [149], CuBi₂O₄/SrO [150] and α -Fe₂O₃/CuBi₂O₄ [151]. Table 2 presents a summary of the photocatalytic activity of some CuBi₂O₄ heterostructures. These heterostructures generally leverage the enhancement of charge carrier separation and increased surface area to achieve increased efficiency in the photocatalytic degradation of wastewater.

4.2. CuBi₂O₄/oxyhalide heterostructure

Bismuth-based ternary oxyhalides such as BiOBr, BiOI and BiOCl have recently been considered potential photocatalysts for wastewater purification [152]. Due to their layered structure and indirect band gap, BiOX allows for the generation of the intrinsic internal electric field, which aids charge carrier separation [153]. The formation of CuBi₂O₄/BiOX heterostructure has a high prospect of exhibiting improved photocatalytic activity as shown in literature such as CuBi₂O₄/BiOBr/Biochar [154], CuBi₂O₄/Bi/BiOBr [155] and N-BiOBr/CuBi₂O₄ [72]. The amplification of reactive oxygen species generation by 5%Bi₃O₄Br/CuBi₂O₄ was demonstrated by Tian *et al* [156], while exploring the heterojunction in a PS/Vis light system for tetracycline degradation. Electron paramagnetic resonance (EPR) analysis confirmed the generation of a high level of $\cdot$ OH and ^{1} O₂ species, which accounted for the high activity of the catalysts. The type II charge transfer mechanism was observed to be responsible for increasing photogenerated charge carrier separation and transient photocurrent with the subsequent generation of radical species.

The improved photocatalytic activity of CuBi₂O₄/BiOCl was reported by Qiu *et al* [157] for the photocatalytic degradation of tetracycline hydrochloride. The 20 % CuBi₂O₄ weight composition was reported to show enhanced activity, which is 58.2 and 4.1 times those of CuBi₂O₄ and BiOCl, respectively. The enhanced visible light absorption and the improved separation of photogenerated charge carriers due to the built-in electric field accounted for the improved activity. The type II charge transfer mechanism was observed to be prevalent in the p-n

heterojunction (Fig. 6(a)), with a charge transfer from the n-type BiOCl to the p-type CuBi₂O₄ confirmed from the X-ray photoelectron spectroscopy analysis (Fig. 6(b)). The improved charge carrier property of the heterostructure was also confirmed by the smaller radius of the EIS spectra and the reduced intensity of the PL compared to the individual compounds (Fig. 6(c&d)).

4.3. CuBi₂O₄/ternary metal oxide heterostructure

Ternary metal oxides with multiple oxidation states have demonstrated superior photocatalytic activity compared to binary metal oxides. This is due to their ability to undergo multiple redox reactions during electrochemical processes [158]. Typically, the valence band of ternary metal oxide semiconductors combines the O 2p orbital with a d0 or d10 orbital of a metal cation [159]. The additional metal cation in the ternary metal oxide contributes an orbital that plays a part in forming its conduction band. The hybridization of the O 2p orbital with the metal orbital results in the elevation of the valence bands of ternary metal oxides, leading to a slight reduction in their band gaps compared to binary metal oxides. This reduction in band gap energy makes ternary metal oxides suitable materials for heterojunction formation. Some reported CuBi₂O₄/ternary metal oxide include CuBi₂O₄/ZnFe₂O₄ [111], Bi₂WO₆/CuBi₂O₄ [160], BiFeO₃@CuBi₂O₄ [161] and CoTiO₃/CuBi₂O₄ [162].

Ternary metal oxides with piezoelectric effect, such as AgNbO₃, could play an essential role in achieving charge carrier separation due to the depolarization electric field arising from the spontaneous polarization of ferroelectrics and the piezoelectric potential generated under stress. This phenomenon was demonstrated by Huang *et al* [163] in their study on the piezo-photocatalytic performance of CuBi₂O₄/AgNbO₃ heterojunction for degrading rhodamine B dye. The study affirmed that the piezo-phototronic coupling effect in the polarized catalyst greatly improved the separation of charge carriers, leading to enhanced activity for organic dye degradation.

A novel Bi₂SiO₅/CuBi₂O₄ heterojunction with high oxygen vacancies was explored for the photocatalytic inactivation of *E. coli* and the

Table 2
Summary of the photocatalytic activity of some CuBi₂O₄ heterojunction photocatalysts.

Heterojunction	Pollutant	Process Parameters	Charge transfer mechanism	Efficiency %	Kinetic rate (min ⁻¹)	Ref
CuBi ₂ O ₄ /CuO	Methylene blue	Visible light, 50 mg, 30 mg/L, 25 mL	Type II	100	11 × 10 ⁻⁴	[182]
Ag@Bi ₂ O ₃ /CuBi ₂ O ₄	Metronidazole	Visible light (250 W, Xe lamp), 40 mg, 10 mg/L, 100 mL	S-Scheme	36	36 × 10 ⁻⁴	[183]
	17 α -ethinylestradiol			94.6	1.8 × 10 ⁻²	
	Cr(VI)			96.9	1.1 × 10 ⁻²	
CuBi ₂ O ₄ /In ₂ O ₃	Methylene blue	Visible light (300 W, Xe lamp), 50 mg, 10 mg/L, 50 mL	Z-Scheme	97	3.2 × 10 ⁻²	[184]
Sb ₂ O ₃ /CuBi ₂ O ₄	Methylene blue	Visible light (400 W, metal halide lamp), 10 mg, 10 mg/L, 20 mL	Z-Scheme	90	–	[185]
	Acid Blue			83		
CuBi ₂ O ₄ /TiO ₂	Cr(VI)	Visible light, 100 mg, 30 mg/L, 100 mL	–	98	1.4 × 10 ⁻²	[186]
CuBi ₂ O ₄ /WO ₃	Tetracycline	Visible light (500 W, Xenon lamp), 50 mg, 20 mg/L, 50 mL	Z-Scheme	90	1.7 × 10 ⁻²	[187]
CuBi ₂ O ₄ /MoS ₂	Tetracycline	Visible light (300 W, Xenon lamp), 50 mg, 10 mg/L, 100 mL	Type II	76	9.5 × 10 ⁻³	[188]
BiFeO ₃ /CuBi ₂ O ₄ /BaTiO ₃	Norfloxacin	Visible light (500 W, Xenon lamp), 20 mg, 10 mg/L, 20 mL	Z-scheme	93	1.1 × 10 ⁻¹	[189]
CuBi ₂ O ₄ /Bi ₂ Sn ₂ O ₇ /Sn ₃ O ₄	Tetracycline	Visible light (300 W, Xenon lamp), 100 mg, 20 mg/L, 100 mL	Z-Scheme	85	3.9 × 10 ⁻¹	[190]
CuBi ₂ O ₄ /Bi/BiOBr	Methylene blue (MB)	Visible light (500 W, Xenon lamp), 50 mg, 5 mg/L, 100 mL	Z-scheme	73	5.2 × 10 ⁻³	[155]
NaNbO ₃ /CuBi ₂ O ₄	Rhodamine B	Visible light (250 W, Xe lamp), 40 mg, 10 mg/L, 100 mL	Polarized electron transfer	75	1.1 × 10 ⁻²	[191]
Bi ₂ MoO ₆ /CuBi ₂ O ₄	Ciprofloxacin	Visible light (500 W, Xe lamp), 200 mg, 10 mg/L, 200 mL	Type II	90.2	1.2 × 10 ⁻²	[110]
CuBi ₂ O ₄ /Bi ₂ WO ₆	Tetracycline	Visible light (300 W, Xenon lamp), 50 mg, 20 mg/L, 50 mL	Z-Scheme	93	2.8 × 10 ⁻²	[179]
CuBi ₂ O ₄ /ZnFe ₂ O ₄	Tetracycline	Visible light (300 W, Xe lamp), 100 mg, 20 mg/L, 100 mL	Type II	80.1	1.2 × 10 ⁻²	[192]
Bi ₂ WO ₆ /CuBi ₂ O ₄	Tetracycline	Visible light (300 W, Xe lamp), 50 mg, 15 mg/L, 100 mL	Z-Scheme	91	2.7 × 10 ⁻²	[77]

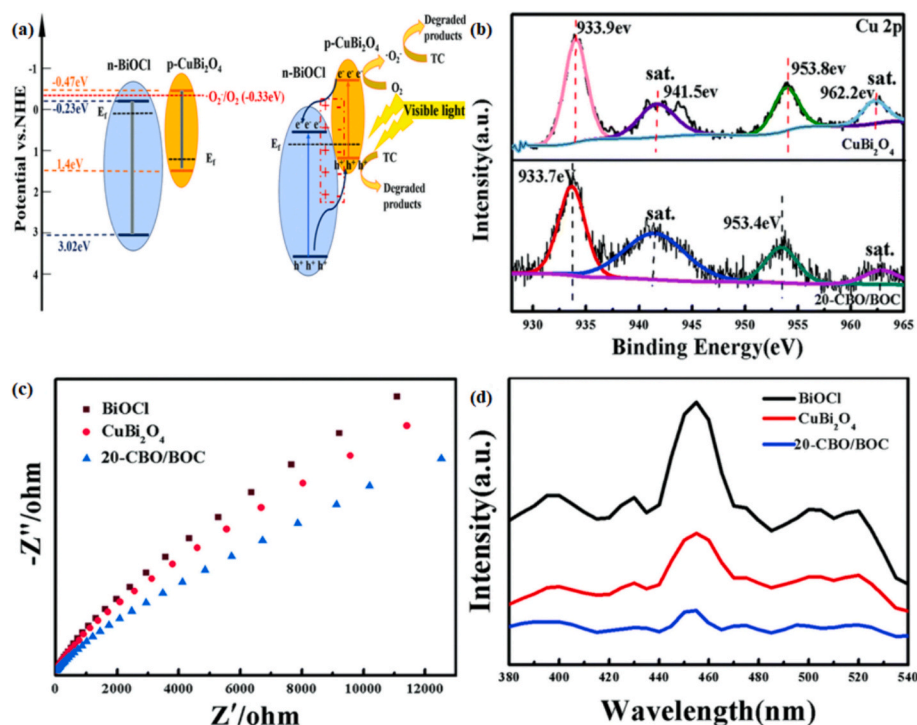


Fig. 6. (a) Proposed charge transfer mechanism for CuBi₂O₄/BiOCl (b) XPS spectra of the Cu 2p orbital of CuBi₂O₄ and CuBi₂O₄/BiOCl-the shift in the binding level of the energy confirms the charge transfer from BiOCl to CuBi₂O₄ (c) EIS spectra of BiOCl, CuBi₂O₄ and CuBi₂O₄/BiOCl and (d) Photoluminescence spectra of BiOCl, CuBi₂O₄ and CuBi₂O₄/BiOCl. Adapted from ref. [140]. Copyright © 2022 RSC.

photocatalytic degradation of tetracycline by Yu *et al* [164]. Bi₂SiO₅ is considered a suitable material for heterostructure due to its strong stability and non-toxicity. Its layered structure facilitates photogenerated charge carrier migration and oxidation reactions [165,166]. Improved light absorption properties and charge carrier separation efficiency were observed in the heterostructure due to the formation of oxygen vacancies and the Z-scheme charge transfer mechanism. The heterojunction attained 83.3 % degradation of tetracycline after 2 h while completely inactivating the *E. coli* in 2.5 h. Fig. 6 shows the characterization of the photogenerated charge carriers of the Bi₂SiO₅/CuBi₂O₄. The heterojunction showed a higher photocurrent response (Fig. 7(a)) compared to CuBi₂O₄ and Bi₂SiO₅, signifying improved charge carrier separation and migration. Fig. 7(b) shows the EIS measurement of the catalysts, showing the heterojunction had a smaller charge transfer resistance and high separation efficiency. Furthermore, the improved charge carrier separation was confirmed by the significant reduction in the intensity of the PL spectra of the heterojunction (Fig. 7(c)), while

Fig. 7(d) shows the higher absorption capacity of the heterojunction and the extension of the band edge into the visible region. From Fig. 7(e), the inverted V-shape of the Mott-Schottky plot showed the formation of a p-n heterojunction, with the Z-scheme charge transfer mechanism shown in Fig. 7(f).

Table 2 summarises the photocatalytic activity of some CuBi₂O₄/ternary oxides heterostructures. These materials' photocatalytic activity benefited from the redox activity of the ternary metal oxides, resulting in enhanced pollutant degradation.

4.4. CuBi₂O₄/carbon nanostructure heterostructure

Carbon-based materials such as graphene, graphene oxide, reduced graphene oxide, and carbon nanotubes possess good electrical conductivity and can thus act as an electron sink for semiconductor materials [167–170]. Also, the high surface area of these materials enhances the adsorption properties of the composites, which is a crucial factor in applications such as photocatalysis. In explaining the improved photocatalytic activity of MWCNT/CuBi₂O₄, Chen *et al.* [67] proposed the transfer of photogenerated electrons from CuBi₂O₄ into MWCNT, which resulted in enhanced charge separation and a subsequent improvement in photocatalytic activity. A simultaneous improvement in visible light absorption was also observed in the MWCNT/CuBi₂O₄ heterostructure. A similar charge transfer mechanism was reported for CuBi₂O₄/rGO by Annamalai *et al* [171]. Carbon-based materials could also act as electron transfer bridges between two semiconductors as reported by Dutta *et al.* [143] and Zhou *et al.* [154]. According to the report by Dutta *et al* [172], CNTs could act as an electron transfer bridge between AgBiO₃ and CuBi₂O₄ in a Z-scheme CNTs@CuBi₂O₄/AgBiO₃ leading to improved light absorption and improved charge separation and transport.

The purpose of forming a CuBi₂O₄/carbon heterostructure photocatalyst is to enhance electron-hole pair separation and use photocatalysis's redox potential. It has been observed that this CuBi₂O₄ heterostructure exhibits superior efficiency in pollutant degradation [173]. Muthukrishnaraj *et al.* [75] fabricated reduced graphene oxide/

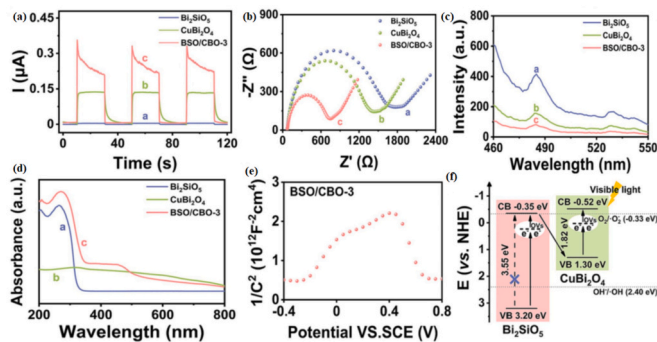


Fig. 7. (a) photocurrent response (b) Nyquist plot, (c) PL spectra (d) UV-vis Drs of Bi₂SiO₅, CuBi₂O₄ and BSO/CBO, (e) Mott-Schottky and (f) charge transfer mechanism of BSO/CBO heterostructure. Adapted from Yu *et al.* [164]. Copyright © 2023 Elsevier.

CuBi₂O₄ heterojunction through a solvothermal technique. The incorporation of graphene oxide resulted in strong absorption in the visible region. This resulted in outstanding degradation for methylene blue and methyl orange, with 87 % and 95 % degradation efficiencies, respectively. The elevated catalytic effectiveness of the heterostructure may be ascribed to effective separation of photo-induced hole-electron pairs, enhanced surface area, enhanced adsorption capability, and π - π interaction with graphene, hence promoting rapid degradation. In another study, and Shi [174] reported the fabrication of CuBi₂O₄/g-C₃N₄ p-n heterojunction, which was thereafter used to remove tetracycline from wastewater. In comparison with pristine CuBi₂O₄ and g-C₃N₄, the CuBi₂O₄/g-C₃N₄ heterojunctions demonstrated enhanced photocatalytic activity in the degradation of TC. The increased photocatalytic activity was also attributed to three factors: (1) stronger visible light absorption, (2) larger hierarchical surface area; and (3) promoted charge carrier separation and transfer.

4.5. CuBi₂O₄/inorganic polymer hybrid heterostructure

The hybrid heterostructure of CuBi₂O₄ and inorganic polymer is one of the least explored CuBi₂O₄ heterostructures in the photocatalytic degradation of pollutants. Xiong et al. [50] reported the fabrication of polyaniline/CuBi₂O₄ composite for photocatalytic reduction of Cr(VI). The enhanced photo-reduction performance of the synthesized photocatalyst on Cr(VI) was ascribed to increased specific surface area for pollutants adsorption and desorption, the reduced recombination of charges, and the effective transfer of charges across the interface.

Similarly, Ahmad et al [174] reported the degradation of ammonia by CuBi₂O₄/polyaniline composite fabricated via *in situ* polymerization of aniline with pre-synthesized CuBi₂O₄ composites. The study showed that 96 %, 78 % and 70 % of ammonia was degraded in 180 mins under visible light by CuBi₂O₄/polyaniline composite PANI and CuBi₂O₄, respectively. The strong absorption intensity in the visible range and the effective charge transfer of photogenerated electrons and holes are responsible for the heterostructure composite material's increased ammonia degradation. In comparison to pure materials, the composite material also demonstrated remarkable stability.

4.6. CuBi₂O₄ ternary heterojunctions

Several CuBi₂O₄ ternary heterojunctions have been studied as potential photocatalysts for the degradation of different pollutants. In contrast to pure CuBi₂O₄, CuBi₂O₄ ternary heterojunctions effectively separate photogenerated electrons and holes and broaden the light absorption range [44,58]. A dual Z-scheme heterojunction photocatalyst, Co₃O₄/CuBi₂O₄/SmVO₄, with effective activity for tetracycline degradation was reported by Mafa et al. [133]. The ternary material showed higher activity than the binary compositions of the explored materials. This showed a high synergy within the ternary material, which accounted for the improved charge carrier transport and separation. In another study, Hou et al. [78] studied the degradation of rhodamine B and methylene blue using a ternary Bi₂O₃-CuO-CuBi₂O₄ photocatalyst. The photoluminescence (PL) experiment was used to establish the ideal material composition for the composite material. It revealed a decreased

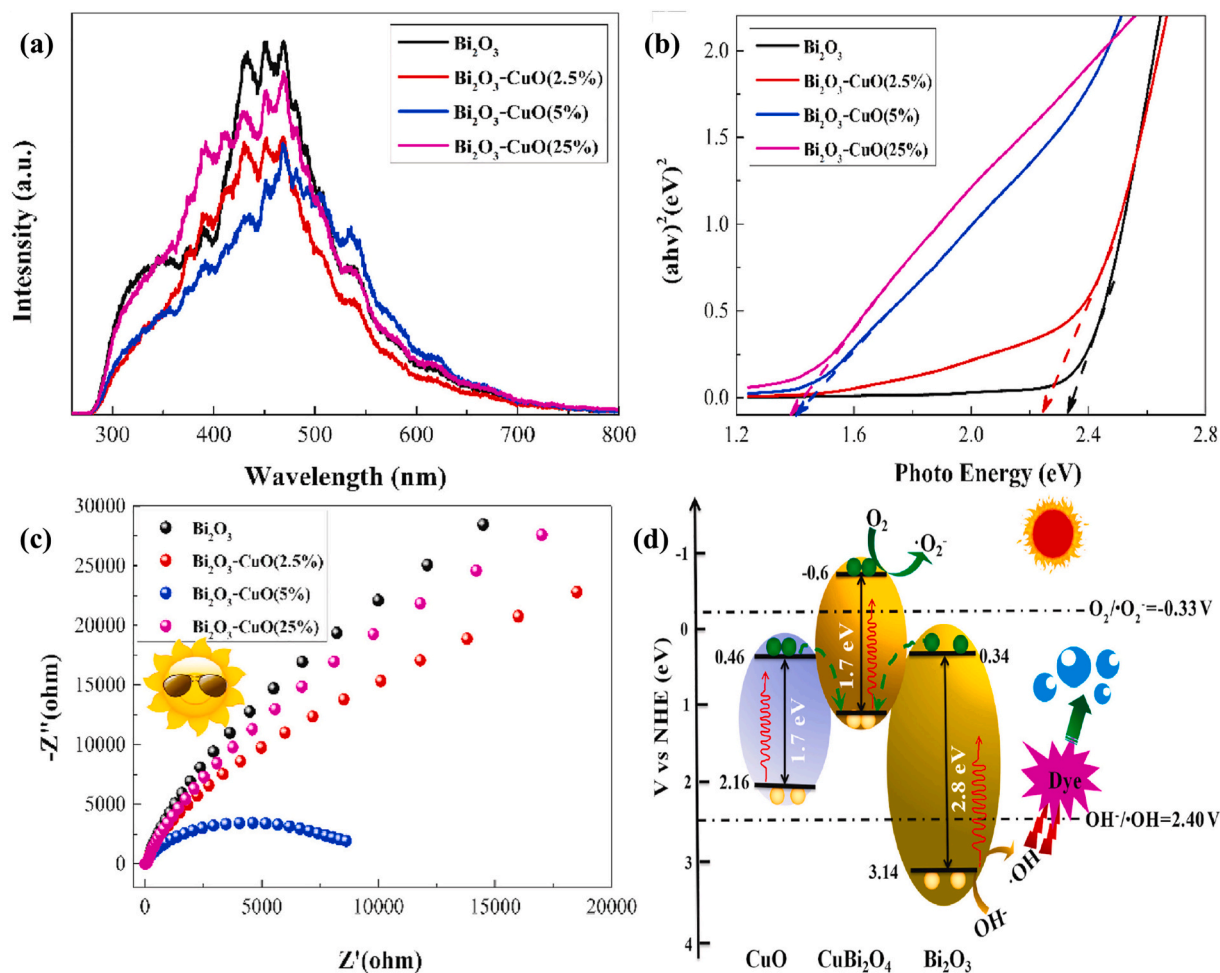


Fig. 8. a) PL spectra of photocatalytic materials (b) Kubelka-Munk plots, (c) EIS and (d) Charge transfer scheme for Bi₂O₃-CuO-CuBi₂O₄. Adapted from ref. [78]. Copyright © 2022, Elsevier.

PL peak intensity (Fig. 8(a)) in the composite with $\text{Bi}_2\text{O}_3\text{-CuO}$ (5 %) with the 5 % Cu/Bi concentration ratio, indicating reduced electron-hole recombination. Furthermore, as demonstrated by the band gap energies in Fig. 8(b), it was found that a small amount of CuO added to the heterostructure might increase the absorption intensity throughout the visible spectrum. The EIS measurement of the photocatalysts in Fig. 8(c) demonstrates that $\text{Bi}_2\text{O}_3\text{-CuO}$ (5 %) heterojunction had the greatest separation efficiency and lowest charge transfer resistance. The photocatalytic study demonstrated that the ternary catalyst was able to achieve 100 % solar-driven photocatalytic degradation efficiency in 140 min for RhB and 60 min for MB, respectively, through the utilization of hydroxyl radicals ($\cdot\text{OH}$) and superoxide anions ($\text{O}_2^{\cdot-}$) as illustrated in Fig. 8d. The photocatalytic performance of pristine materials was much lower than that of ternary catalysts.

5. Future challenges and prospects

Photocatalytic degradation of pollutants is one of the most potent options for improving the quality and availability of potable water for human consumption. Therefore, developing semiconductor materials with suitable optical properties has become a significant endeavour. Recently, CuBi_2O_4 has gained much attention because of its environmental friendliness and unique optical properties. However, like most semiconductors, it also suffers from inadequate light absorption and high charge carrier recombination, which has led to the exploration of its heterojunctions.

The applicability of CuBi_2O_4 -heterojunction in wastewater treatment is constrained by several key issues that need to be investigated further. Firstly, a proper understanding of the interfacial properties of the heterojunction and how it influences the photocatalytic properties. To optimize the potential of these heterojunctions fully, a clear understanding of interfacial interaction and charge transfer at this interface needs to be clearly understood. This enables the understanding of the intrinsic mechanism of the enhanced photocatalytic activity of these heterojunctions. As demonstrated in the review, understanding the mechanisms behind the longer charge carrier lifespan and greater charge carrier separation in CuBi_2O_4 heterostructures is vital for their practical application.

Secondly, there is a need to investigate the built-in electric field generated in CuBi_2O_4 -based heterojunctions. Due to the lack of appropriate characterization techniques, providing evidence for this phenomenon is difficult. Attempts at using *in-situ* XPS and advanced microscopic techniques may offer an indirect route to studying this effect.

Finally, there is a need to explore data-driven investigations of CuBi_2O_4 -based heterojunctions, as this may provide a shorter route to identifying highly effective CuBi_2O_4 -heterojunctions. Integrating machine learning and high-throughput screening in materials science could accelerate the discovery of optimal heterojunction configurations and processing conditions.

As environmental protection continues to gain more attention, identifying semiconductor photocatalysts with enhanced activity will become necessary. The potential of CuBi_2O_4 -based heterojunctions makes them promising for further exploration in obtaining highly effective photocatalytic materials. Continuous research and development, mainly focusing on these heterojunctions' synthesis methods and interfacial properties, will be critical in overcoming the current challenges and realizing their full potential in environmental remediation applications.

6. Conclusion

The review highlights the significant potential of CuBi_2O_4 heterostructures in the photocatalytic degradation of water pollutants. CuBi_2O_4 heterostructures exhibit remarkable photocatalytic properties due to their enhanced solar light absorption, extended charge carrier

lifespan, and efficient charge carrier separation. Various synthesis methods provide a versatile toolkit for optimizing performance. The advancements in this field hold great promise for developing sustainable and effective solutions for water purification, contributing to public health and environmental protection. Future research should address challenges such as stability, scalability, exploring novel synthesis techniques, and conducting real-world application trials. The promising results and future advancements in CuBi_2O_4 heterostructures are crucial for achieving efficient water purification.

CRediT authorship contribution statement

Olalekan C. Olatunde: Writing – original draft, Conceptualization. **Lawrence Sawunyama:** Writing – original draft, Conceptualization. **Tunde L. Yusuf:** Conceptualization, Writing – review & editing. **Damian C. Onwudiwe:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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