Chapter 2

Bismuth-Based Nanoparticles as Photocatalytic Materials

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Additional information is available at the end of the chapter

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Abstract

Bismuth-based nanoparticles are a unique category of materials that possess interesting properties such as excellent chemical, electrical, optical and catalytic activities among others. The application of bismuth-based nanoparticles as photocatalytic materials has caught the interest of the scientific community in recent times due to these unique properties. Consequently, a number of data have been generated in relation to the photocatalytic application of these nanoparticles. This chapter intends to organise and provide the recently generated information on the use of bismuth-based nanoparticles in photocatalytic degradation processes. A detailed discussion is provided on bismuth-based nanoparticles including bismuth chalcogenides, bismuth vanadate, bismuth oxyhalides and other bismuth-related nanoparticles. Attention was also paid to the modification of these nanoparticles to improve their photocatalytic activities. The application of the modified nanoparticles in various photocatalytic processes with emphasis on water treatment, waste gas treatment, hydrogen production and air purification has also been thoroughly discussed.

Keywords: bismuth-based nanoparticles, photocatalytic degradation, hydrogen generation, carbon dioxide reduction, water treatment, pharmaceutical products, organic pollutants

1. Introduction

Photocatalysis is gradually becoming a dependable technological approach in many industries due to its cost-effective and environmentally friendly nature. This technique has the tendency to convert light energy into chemical energy under mild reaction conditions [1].

Subsequently, the technology has had successful application in many areas and is seen as a possible solution to the ever-increasing environmental and energy shortage issues.

Recent advancement in population growth coupled with the expansion of industrialisation has brought about serious environmental pollution and energy shortages. This has necessitated the rising demands for environmental remediation, the alternative supply of energy and novel methods for pollution eradication by researchers [2]. A lot of methods have been employed to degrade complex toxic pollutants to less toxic compounds. Among them are the convention ones (coagulation, oxidation, ion exchange, membrane filtration and flocculation) [2]. These methods are, however, considered ineffective by a lot of researchers due to their severe disadvantages including producing a large volume of sludge and operating at a very high cost [3]. Photocatalysis using semiconductors has been recommended as a potential method for environmental clean-up because it is economical and degrades pollutants by using artificial or natural sunlight which is cheap and abundant worldwide. Besides, there is no formation of sludge, and the catalyst can be reused after the process since it remains unchanged [4].

A number of semiconductors (TiO_2, ZnO, Fe_2O_3, CdS and ZnO) have been employed for varied photocatalytic activities due to their unique properties such as excellent electronic structure and light absorption, degradation of pollutants, thermal stability, less toxicity, low cost and inertness [5]. However, these semiconductors suffer two serious drawbacks. These drawbacks include large energy band gap which is too wide to absorbed visible light [6]. Thus, these semiconductors are only photoactive in UV range. The second limitation is the rate at which the photo-generated electrons and holes recombine; a phenomenon that reduces the effectiveness of photodegradation process [7]. Hence, for a semiconductor to attain its maximum potential as an efficient photocatalyst, some effective modifications that can enhance its photosensitivity in the visible light range and also retard the recombination of the electrons and holes [8] are required. Thus, the development of a novel photocatalyst that has potential to eliminate the environmental pollutants is an essential requirement for photocatalysis process.

Documented reports on bismuth-related nanoparticles including BiOCOOH, Bi_2WO_6, $(BiO)_2CO_3$, $BiVO_4$, $BiPO_4$, Bi_2O_3 and BiOCl [9], have been found to attract considerable attention because of their proficient photocatalytic performance, cost-effectiveness, low toxicity and high stability. Modification of bismuth-related nanoparticles with metals and non-metal, carbonaceous materials and biopolymers is reported to further endow these catalysts with exceptionally high visible light responsivity and efficient photocatalytic performances [10]. Modified bismuth-related nanoparticles have been efficaciously utilised in many photocatalytic processes including antifogging, self-cleaning, disinfection, carbon dioxide reduction, organic pollutant degradation in water, hydrogen generation, air purification and so on.

This chapter discusses bismuth as a metal and its related nanoparticles. It also dwells on the modification of bismuth-based nanoparticles for enhanced photocatalytic activity and finally elaborated on the various photocatalytic applications/processes that these nanoparticles have been successfully applied to.

1.1. Bismuth

Bismuth (Bi) occurs naturally as a diamagnetic element with atomic number 83. It is a pentavalent transition metal and its oxides and sulphides represent significant commercial ore. It has

low thermal conductivity, high Hall coefficient and high electrical resistivity [11]. Deposition of a thin layer of bismuth on the surfaces of materials causes it to behave as a semiconductor [12]. Again, bismuth is reported to be denser in its liquid phase than the solid phase and expands about 3% during solidification. This property enables it to be used as a component of alloys so that it can compensate for the contraction of other components of the alloy [12]. Bismuth is relatively non-toxic and has a relatively low melting point (271 C). Approximately, 63% bismuth is used to produce cosmetics, pigments and pharmaceuticals. 26% of it is also used in the field of metallurgy for galvanising and casting [13]. 7% is used in bismuth alloys, solders and ammunition and the 4% also are used in research fields [13].

1.2. Bismuth-based nanoparticles

The use of bismuth-based nanoparticles instead of the traditional bismuth-containing bulk materials/compounds for application in various advanced technological areas has received greater attention recently. This widespread interest in bismuth-based nanoparticles is as a result of the fact that the nanoparticles possess peculiar properties that are absent in the bulk solid materials. These unique features which include high optical, electrical, thermal, photocatalytic and magnetic properties are mainly dependent on the nanoparticles' large specific surface area and small sizes [14]. Fortunately, opportunities exist, through colloidal chemistry, to synthesis bismuth-based nanoparticles. This process involves utilisation of bismuth salts as precursors with the addition of surface modifiers and reducing agents to produce size controllable and highly crystalline bismuth-based nanoparticles. Among the bismuth-based nanoparticles of interest are Bismuth chalcogenides, Bismuth vanadate, Bismuth oxyhalides and other bismuth-related nanoparticles.

1.2.1. Bismuth chalcogenides

Bismuth chalcogenides are a class of photoelectric compounds consisting of bismuth and group VI elements. These compounds are generally represented as Bi_2E_3 (E = O, S, Se, Te) and consist of bismuth oxide (Bi_2O_3), bismuth sulphide (Bi_2S_3), bismuth selenide (Bi_2Se_3) and bismuth telluride (Bi_2T_3). These class of compounds are technologically important semiconductors owing to their peculiar properties and have been applied in different industries. A recent study in bismuth chalcogenides' visible-light-responsive properties and enhanced photocatalytic activities has stimulated a great research interest in their nanomaterials.

Bi_2O_3 is a p-type semiconductor with six crystallographic polymorphs which are represented as α-, β-, γ-, ω-, ε-, and δ-Bi_2O_3. Monoclinic α-Bi_2O_3 is the phase present at room temperature. This phase can transition to the face-centred cubic δ-Bi_2O_3 phase when heated. The other phases of Bi_2O_3 include tetragonal β-Bi_2 phase, body-centred cubic γ- Bi_2O_3, orthorhombic ε-Bi_2O_3 and triclinic ω- Bi_2O_3 phases [15]. Bi_2O_3 has high refractive index, narrow energy band gap (2.40–2.80), dielectric permittivity and outstanding photoconductivity [16]. Bi_2O_3 is also considered as an amphoteric semiconductor as there are reports of the material exhibiting both p and n-type conductivity based on the methods of synthesis [16]. These properties enable Bi_2O_3 to be used as a sensor and electrochromic materials, optical coating and photocatalyst.

Bi_2S_3 possesses interesting optical and electronic properties and a direct band gap ranging from 1.3 to 1.7 eV. These qualities enable Bi_2S_3 to be applied in various fields including thermoelectric

transport for the fabrication of optoelectronic, photovoltaic and thermoelectric devices [17] and photocatalysis. Various morphologies of Bi_2S_3 have been fabricated through different routes of synthesis. These one-dimensional nanostructures which include nanowires, nanotubes, nanorods and nanoflowers are considered to be the most appropriate for the above-named applications of Bi_2S_3 because of quantum confinement effect which subsequently enhances the thermoelectric efficiencies of the materials [18].

Bi_2Se_3 has a stacked layered laminated structure. Each layer is about 0.96 nm thick and contains five atoms which are bonded covalently along the z-axis in the following order: Se-Bi-Se-Bi-Se [19] (**Figure 1**). As a result of the weak interlayer forces of attraction, exfoliation of Bi_2Se_3 into few-layer nanosheets is possible [19]. Being a narrow band gap semiconductor (0.3 eV) with a high charge carrier mobility, Bi_2Se_3 has high potential application in photoelectrochemical and thermoelectrical devices as well as optical recording systems and photocatalysis [20].

Bismuth telluride (Bi_2Te_3), is a semiconductor with a band gap of 0.15 eV. It has a trigonal structure and a high melting point of 585°C. When alloyed with antimony or selenium, Bi_2Te_3 becomes a highly efficient thermoelectric material at room temperature [21]. Because of these interesting properties, Bi_2Te_3 has been applied in thermoelectric power generation and refrigeration [22, 23].

1.2.2. Bismuth vanadate

Bismuth vanadate ($BiVO_4$) exists in three main phases. These phases include tetragonal scheelite, monoclinic scheelite and tetragonal zircon. The monoclinic phase has high visible light activity due to the narrow nature of its band gap (2.4 eV) [24]. This visible light absorption behaviour has stimulated a lot of research investigation into its application in environmental remediation through photocatalysis. Again, $BiVO_4$ has advantages over lots of its related semiconductors such as being environmentally friendly, highly resistant to photocorrosion, non-toxic and low cost [24].

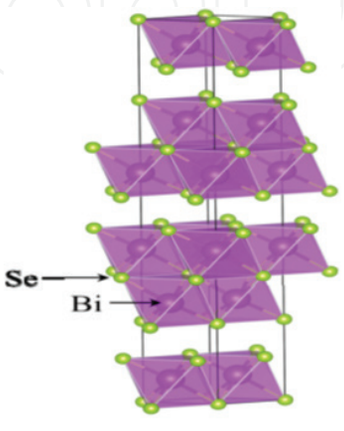

Figure 1. Structure of bismuth selenide [21].

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1.2.3. Bismuth oxyhalides (BiOX)

BiOX, with the X representing either Br, Cl or I, are layered semiconductor materials that are crystallised in a tetragonal matlockite form [25]. The layered structure is arranged in such a way that each bismuth atom is encircled by four oxygen and halogen atoms resulting in an asymmetric tetrahedral symmetry (X-Bi-O-Bi-X) [25]. This arrangement enables BiOX to possess remarkable optical, mechanical, electrical and catalytic properties. As a result, BiOX has been utilised in selective oxidation of alcohols, organic synthesis, water splitting, indoor-gas purification and photodegradation of organic pollutants in wastewater [26].

Bismuth oxychloride (BiOCl), a p-type semiconductor, exhibits excellent ionic conduction, optical, catalytic and electrical properties. It is made up of chlorine ions (Cl^-), bismuth ions (Bi^{3+}) and oxygen ions (O^{2-}) that pile up in tetragonal layered [Cl-Bi-O-Bi-Cl]n structure forming non-bonding attractions via the chlorine atoms (Cl) along C-axis. The four Bi-Cl and four Bi-O are arranged opposite to one another in a tetragonal pyramidal phase with the Bi in the centre of the structure (**Figure 2**). BiOCl is active in UV range with experimental band gap range of 3.1 to 3.5 eV while the theoretical values range from 2.8 to 2.9 eV [27].

Bismuth oxybromide (BiOBr) nanoparticle is also a p-type semiconductor and a promising photocatalyst due to its excellent optical properties, chemical stability and effective photocatalytic activity. Its layered tetragonal structure and appropriate indirect band gap bequeathed it with high visible light activity and the ability to efficiently separate electrons and hole leading to its pollutant degradation tendency [26].

Bismuth oxyiodide (BiOI) has a stacked tetragonal structure that contains alternate $[Bi_2O_2]^{2+}$ and I slabs. It is one of the attractive nanoparticles for visible light photocatalytic applications owing to its relatively narrow band gap (1.6 to 1.9 eV) which endowed it with high visible light activity. Photo-generated electrons and holes are also perfectly separated in BiOI as a result of the presence of strong intralayer and weak van der Waals interlayer

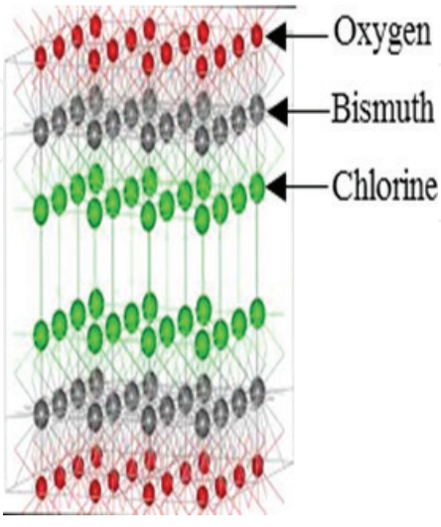

Figure 2. Structure of bismuth oxychloride [27].

bonding in its structure [28]. As a result, BiOI has been successfully applied in some photocatalytic processes including organic pollutant degradation, CO_2 conversion and hydrogen generation.

1.2.4. Other bismuth-related nanoparticles

1.2.4.1. Bismuth (III) phosphate ($BiPO_4$) and bismuth niobate (Bi_3NbO_7)

$BiPO_4$ is an intrinsic p-type semiconductor with two polymorphic phases. These phases include the stable monazite-type structure (known as low-temperature monoclinic phase (LBP)) and high-temperature monoclinic phase (HBP). The HBP polymorph is obtained by heating LBP at higher temperatures. $BiPO_4$ nanoparticles are known to be non-toxic and have low costs of production [29]. They possess high thermal and chemical stability, redox active species, and high photocatalytic activity [29]. Consequently, these materials have been used for Li-ion batteries, sensors and as photocatalysts for disinfection of water and photodegradation of organic pollutants in water [30].

Bi_3NbO_7 is noted for its favourable properties resulting in its use as electrochemical controllers, a catalyst for photolytic water splitting, selective oxidation of hydrocarbons and as oxygen sensors [31]. It exists in cubic and tetragonal phases and has the ability to undergo a reversible transition between tetragonal phase at 800°C to the cubic phases at 900°C and back to tetragonal phase. The cubic phase has defective fluorite-structure (Fm3m, a = 0.548), while the bismuth and niobium atoms are dispersed over similar crystallographic locations. [31].

2. Modified bismuth-based nanoparticles and their photocatalytic applications

2.1. Modified bismuth-based nanoparticles

Bismuth-based nanoparticles are receiving substantial consideration as promising photocatalysts as a result of their comparatively narrow band gaps. They are non-toxic and have the potential to resist corrosion. They are environmentally friendly and relatively cheap [32]. There are a number of available reports regarding the efficient visible light activities of these nanoparticles, and their use for water disinfection and organic pollutants degradation [33]. Their effectiveness as photocatalysts for production of hydrogen gas from water as well as carbon dioxide conversion to useful hydrocarbon products has also been studied. Notwithstanding all these advantages, bismuth-based nanoparticles have some disadvantages that limit their practical application as effective photocatalysts. For example, they have small specific surface areas which impair their photocatalytic activities. They also experience recombination of the photogenerated electrons and holes [34] and thus reduce their effectiveness as photocatalysts.

Attempts to overcome these problems and improve the efficiency of these nanoparticles have culminated in the use of different approaches/techniques to modify them. These approaches comprise the use of carbon-based materials and modification with biopolymers [35], doping

with metals and non-metal [36], and the use of heterostructures/mixed metal oxides [37]. The modified bismuth-based nanoparticles are reported to display higher photocatalytic activities compared to their bare/pure counterparts. Some of the photocatalytic processes to which these materials have been applied are discussed in the subsequent sections.

2.2. Photocatalytic applications of modified bismuth-based nanoparticles

2.2.1. Application in water treatment

A number of publications are available on the use of modified bismuth-based nanoparticle for water treatment through the degradation of organic pollutants and removal of bacteria. This section presents some of the research works that have been performed in this regard.

2.2.1.1. Degradation of organic pollutants

Harmful organic contaminants in water can be degraded or mineralised into innocuous/inoffensive products (CO_2 and H_2O) through a photocatalytic reaction involving photo-generated electrons and holes and reactive oxygen species. Photodegradation of organic contaminants through the use of bismuth-based nanoparticles occurs when the photocatalyst absorbs light of appropriate wavelength from sunlight or illuminated light source. This light energy excites and promotes electrons in the photocatalyst's valence band to its conduction band. This results in the creation of positive charges (holes) and negative charges (electrons) on the valence and conduction bands respectively leading to the creation of electron-hole pairs. The hole oxidise water molecule into hydrogen gas and hydroxyl radical while the electron reduces oxygen molecules into superoxide radicals. The hydroxyl and the superoxide radicals then attack the pollutants and degrade them into harmless products [38]. These hydroxyl ions and superoxide radicals are also responsible for inactivation of bacteria through degradation of their cell walls [38]. The mechanism of the photodegradation process is presented in **Figure 3**.

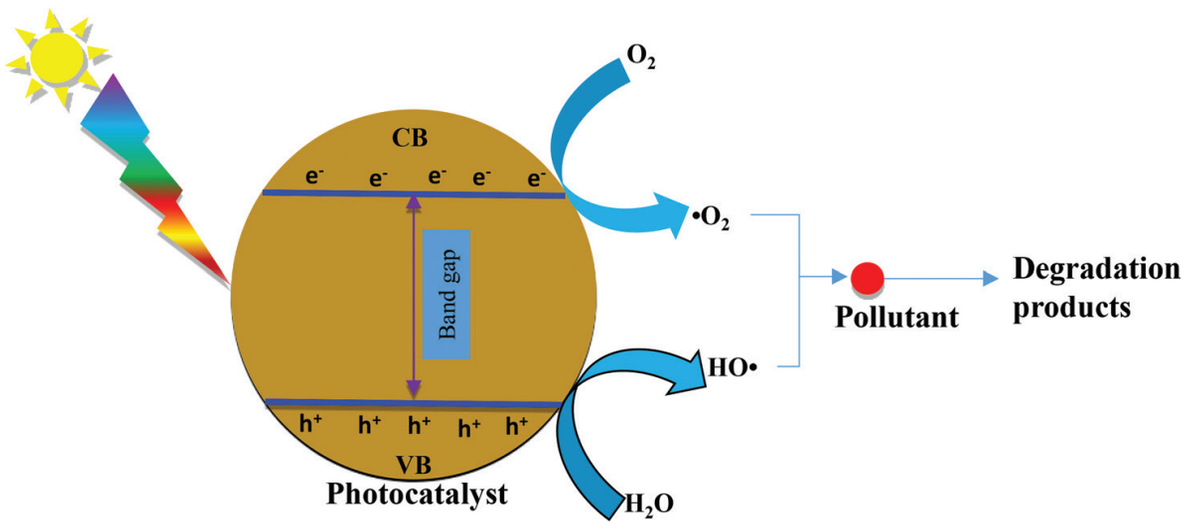

Figure 3. Mechanism of photocatalytic degradation of organic polluting.

2.2.1.2. Degradation of textile dyes

A modified bismuth-based nanocomposite consisting of α-$BiO_{3,}$ silver (Ag) and graphene oxide (GO) (Ag/GO/α-Bi_2O_3), has been synthesised by [39] and deployed in photodegradation of crystal violet and rhodamine 6G dyes by visible light illumination. The Ag/GO/α-Bi_2O_3 exhibited six times photocatalytic activity compared to Degussa-P25. It degraded both dyes at a higher efficiency than the bare α-BiO_3 and achieved about 90% degradation of the crystal violet and rhodamine 6G dyes in 40 minutes and 150 minutes respectively. Nickel doped Bi_2S_3 has also been applied in the degradation of congo red and rose bengal dyes by visible light illumination with successful results [40]. A nanocomposite consisting of $BiVO_4$, Ag and reduced graphene oxide (rGO) was also synthesised and used to degrade rhodamine B dye [41]. They identified the composite to possess more photocatalytic reaction sites because of enhanced charge carriers separation ability of the $BiVO_4$, electron transfer property of the silver nanoparticles and surface plasmon effect. The composite showed enhanced visible light activity and exhibited higher degradation efficiency of the dye compared to the bare $BiVO_4$ and the $BiVO_4$-rGO composite.

Qu and Huanyan [42] synthesised a $BiOCl_xBr_{1-x}$ photocatalysts consisting of BiOCl, BiOBr, $BiOCl_{0.5}Br_{0.5}$, $BiOCl_{0.75}Br_{0.25}$ and $BiOCl_{0.25}Br_{0.75}$. The photocatalytic degradation abilities of the catalysts were assessed by applying them to degrade methyl orange under ultraviolet light. $BiOCl_{0.5}Br_{0.5}$ was identified to be the best photocatalyst for the degradation of 5 mg/L of the dye at pH 7 with 90% degradation efficiency within 90 min. In addition, BiOI-graphene nanocomposite's photodegradation ability was tested on methyl orange. The BiOI-graphene was found to degrade the dye at a faster rate than BiOI. The enhanced photodegradation efficiency of the BiOI-graphene composite was credited to its ability to effectively separate and transport the generated electrons and holes owing to the bonding between graphene and BiOI, the increase light adsorption and the high dye adsorption [43]. Studies on the photocatalytic degradation ability of Bi_2WO_6-rGO nanocomposite was performed by Rajagopal et al. [44] with impressive results. The improved performance of the catalyst against the degradation of rhodamine B was assigned to the fact that the catalyst possessed a large surface area, as well as the capability to reduce the rate at which the electrons and holes recombined as a result of the inclusion of rGO. Similarly, $Bi_2O_2CO_3/ZnWO_4$ nanocomposite was synthesised and used to degrade methylene blue [45]. Compared to the individual $ZnWO_4$ and $Bi_2O_2CO_3$, the $Bi_2O_2CO_3/ZnWO_4$ demonstrated excellent ability to photocatalytically degrades the dye [45]. This was as a result of the existence of a heterojunction in the composite. The presence of the heterojunction favoured the separation of the holes and electrons [45].

2.2.1.3. Degradation of pharmaceutical products (antibiotics)

The occurrence and accumulation of pharmaceutical products in water bodies can be injurious to humans as well as aquatic organisms. Hence the need for an appropriate technology for the removal of this pollutants becomes paramount. Scientists have been studying photocatalysis as a suitable means to remove these pollutants. As a result, a number of photocatalytic degradation studies using bismuth-based nanoparticles have been carried out. Some of these research works have been discussed here.

In their study, [46] synthesised a Bi_2WO_6/Fe_3O_4 heterojunction through the hydrothermal process and supported it over graphene sand composite by in situ wet impregnation method. The tendency of the composite (Bi_2WO_6/Fe_3O_4/GSC) to photocatalytically degrade pharmaceutical waste was tested by its application in the degradation of oxytetracycline and ampicillin. They obtained a high degradation efficiency of the antibiotics into CO_2, H_2O and NO_3^- under solar light irradiation due to high adsorption property of the composite. The magnetic nature of the catalyst ensured its easy separation and recyclability [46]. Tetracycline degradation with $BiFeO_3$ prepared through hydrothermal method was also undertaken with successful results [47]. BiOBr modified with chelating agents (citric acid and ethylenediaminetetraacetic acid) was reported to have been used in the degradation of norfloxacin with high photocatalytic efficiency [48]. The chelating agents modified BiOBr was noted to be more photoactive and displayed higher degradation efficiency compared to the bare BiOBr. Again, a successfully prepared BiOBr-activated peroxymonosulfate system (BiOBr/PMS) demonstrated exceptional visible-light-responsive activities for photodegradation of Ciprofloxacin [49] and carbamazepine [50] respectively. A mesoporous Bi_2WO_6 prepared by hydrothermal technique was used to degrade tetracycline in water, further endorsing the visible-light-driven photodegradation of pharmaceutical wastes using bismuth-based nanoparticles [51]. About 97% of the pollutant (20 mg/L) was degraded after 120 minutes of simulated solar light irradiation.

2.2.1.4. Water disinfection (removal of bacteria)

The need for cost-effective and non-toxic antibacterial agents for an effective water treatment has become urgent due to the life-threatening consequences of water pollution with various species of bacteria. The use of nanoparticles as disinfection systems for water treatment is gaining recognition due to its effectiveness. Bismuth-based nanoparticles are among the category of nanoparticles that are being tested for water disinfection. Some of the progress that has been made so far with respect to the use of bismuth-based nanoparticle for bacterial inactivation in water is discussed below:

Inactivation of *Escherichia coli* was determined through the use of Z-scheme photocatalyst of $AgI/BiVO_4$ synthesised through chemical deposition precipitation [52]. The catalyst could inactivate 7.0 × 107 CFU/mL of the bacteria species within 50 minutes under visible light. Superoxide radical ($\bullet O_2$) and holes (h^+) were identified to be responsible for the photocatalytic disinfection process. In much the same manner, *Escherichia coli* inactivation under visible light was performed by using $Ag/BiVO_4$ nanocomposite with impressive results [53]. There was a total inactivation of the bacterial cell (107 CFU mL^{-1}) within 120 minutes. They assigned the effectiveness of the composite for the bacterial inactivation to the presence of the metallic silver nanoparticle in the composite. The silver nanoparticle trapped the generated electrons and hence promoted charge carriers separation for the creation of the necessary reactive oxygen species. Zhang et al. [54] reported the application of AgBr−Ag − Bi_2WO_6 nanocomposite in photodisinfection of *Escherichia coli* K-12 by visible light illumination. The AgBr−Ag − Bi_2WO_6 was more effective than the other catalysts i.e. Bi_2WO_6 superstructure, Ag-Bi2WO_6 and AgBr-Ag-TiO_2 used in this experiment. The AgBr−Ag − Bi_2WO_6 nanocomposite was able to completely disinfect 5 x 107 cfu mL^{-1} of the *Escherichia coli* K-12 under 15 minutes through the influence of hydroxyl radicals (•OH).

A Bi_2O_3 and $NiFe_2O_4/Bi_2O_3$ photocatalysts with different concentration of $NiFe_2O_4$ were fabricated and applied in a comparative photocatalytic degradation of tetracycline in water [55]. The $NiFe_2O_4/Bi_2O_3$ was more efficient that Bi_2O_3 in the visible light degradation process with $NiFe_2O_4/Bi_2O_3$ (50%$NiFe_2O_4$) being the most efficient catalyst. This catalyst demonstrated a high degradation efficiency of 90.78 within 90 minutes. The catalyst was easily recovered and recycled due to its magnetic nature [55]. The destruction of bacteria cells (*Escherichia coli* K-12) using Bi_2MoO_6 –rGO was also noted to achieve high efficiency [56]. In all these cases, large surface area for enhanced pollutant adsorption, improved electron-hole reparation and the subsequent generation of sufficient oxygen reactive species were identified to be responsible for the impressive photocatalytic performance of the composites.

2.2.2. Application in waste gas treatment (reduction of carbon dioxide)

The release of carbon dioxide (CO_2) into the atmosphere resulting mainly from fossil fuels combustion is contributing significantly to the global climate change. This phenomenon necessitates the need for appropriate strategies to abate the increasing level of CO_2 in the atmosphere. An appropriate approach to reducing the level of atmospheric CO_2 is its conversion into useful chemicals. Photocatalytic reduction of CO_2 to useful chemicals as a way of recycling it to a fuel feedstock is receiving attention as an appropriate substitute for fossil fuels combustion [57].

The mechanism of CO_2 photoreduction to hydrocarbon fuels is similar to that of organic pollutants degradation. This process also involves illumination of the semiconductor photocatalyst with a photon of appropriate energy resulting in the creation of electron and hole pairs on the conduction and valence bands respectively. The generated electrons must have greater energy than the reduction potential of CO_2 i.e. the conduction band potential of the catalyst should have higher negative value than the reduction potential of CO_2. At the same time, the valence band potential of the catalyst must have higher positive value than water oxidation potential. In other words, the hole must have the potential to oxidise water to produce hydrogen ion (H^+) [58]. The notable thing about this process is that the type of hydrocarbon produced depends on the number of protons present in the reaction system. The possible reactions involved in the reduction/conversion of CO_2 to various hydrocarbon products are presented in Eqs. 1 to 4 [59]:

The presence of two protons (H^+) in the system leads to the conversion of CO_2 to Carbon monoxide (CO) i.e.:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (1)$$

Methanol (CH_3OH) is produced when six protons are available in the reaction system:

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad (2)$$

The availability of eight and twelfth protons results in the production of methane and ethanol respectively:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O \quad (3)$$

$$2CO_2 + 12\,H^+ + 12\,e^- \rightarrow C_2H_5OH + H_2O \quad (4)$$

In this section, we discuss some of the achievement made so far as the use of bismuth-based nanocomposites in CO_2 photoconversion to useful hydrocarbon products is concerned.

A comparative study on CO_2 photocatalytic conversion using titanium oxide (TiO_2) nanotubes and palladium decorated bismuth titanate was conducted by Raja et al. [60]. The experiment was executed through light illumination of the catalyst in a CO_2 saturated sulphuric acid solution. Formic acid (HCOOH) was the resultant product. According to their result, the palladium decorated bismuth titanate nanocomposite was the better of the two catalysts as it produced about two times formic acid than that produced by the TiO_2 nanotubes composite. They attributed the effectiveness of the palladium decorated bismuth titanate to effective charge carriers' separation. In addition, a $Bi_4O_5Br_xI_{2-x}$, $Bi_4O_5Br_2$ and $Bi_4O_5I_2$ composite solutions which were prepared by the molecular precursor method were applied in CO_2 photocatalytic reduction experiment [61]. The results showed that the $Bi_4O_5Br_xI_{2-x}$ composite exhibited the highest photocatalytic activity with the Bi_4O_5BrI (x = 1) being the best catalyst. This catalyst (Bi_4O_5BrI) was able to convert CO_2 to carbon monoxide (CO) at the rate of 22.85 μmol $h^{-1}g^{-1}$CO generation. High CO_2 adsorption tendency and excellent electron-hole separation were identified to be the reason for the effectiveness of this catalyst for the reduction of CO_2 to CO.

Again, different structures of Bi_2S_3 (nanoparticles and microsphere hierarchical nanostructure) prepared by Chen et al. [62] through facile and template-free solvothermal route were used to convert CO_2. The microsphere composite exhibits a better visible light photocatalytic CO_2 conversion activity than the Bi_2S_3 nanoparticle. The CO_2 was reduced to formate in methanol. Excellent light harvesting ability, profound permeability and the unique hierarchical structure are the factors that accounted for the effectiveness of the Bi_2S_3 microsphere hierarchical nanostructure. Palanichamy et al. [63] also showed the trend in the photocatalytic performance of $BiVO_4$, and Cu_2BiVO_4 in the CO_2 conversion to methanol. The percentage CO_2 conversion efficiencies of the $BiVO_4$ and Cu_2BiVO_4 were 2.78% and 2.50% respectively within 80 minutes under the same conditions.

2.2.3. Application in hydrogen production (reduction of water)

The ever-increasing air pollution as a result of fossil fuels combustion has heightened the need to develop alternative fuel sources. One of the alternative sources is hydrogen gas production through photocatalytic splitting of water [64]. In order to achieve an economically feasible hydrogen generation through photocatalysis, the photocatalyst must be visible light active so as to effectively utilise the limitless and readily available visible light [64]. Bismuth-based nanocomposites are highly active under visible light owing to their narrow band gaps. Consequently, generation of hydrogen gas using bismuth-based nanoparticles/composites with visible light is regarded as one of the promising approaches. The mechanism of this process is discussed as follows [59]:

Similar to the mechanism of photodegradation of organic compounds, electron and hole are produced on the conduction and valence bands of the photocatalyst when it is exposed to light with energy greater than or equal its band gap. Modification of the catalyst enhances its ability to minimise the recombination of the holes and the electrons upon generation.

The holes in the valence band directly oxidise the chemisorbed water molecule on the catalyst's surface resulting in the generation of four hydrogen ions (H^+) and oxygen molecules (O_2):

$$2H_2O \rightarrow 4H^+ + O_2 \quad (5)$$

The conduction band electrons then reduce the hydrogen ions to produce hydrogen gas:

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (6)$$

A number of experimental results on the utilisation of visible light active bismuth-based nanocomposite for production of hydrogen through water splitting have been published. Some of these published results are discussed in this section.

The ability of a bismuth-based catalyst, $Cr_2O_3/Pt/RuO_2$:Bi_2O_3, to photocatalytically split water into hydrogen gas was studied in the presence of a sacrificial hole scavenger (oxalic acid) by Hsieh et al. [65]. According to their result, the photocatalyst showed a high ability to generate hydrogen gas from water at a rate of 17.2 μmol g^{-1} h^{-1}. In their experiment, Adhikari et al. [66] carried out the synthesis and characterisation of visible light active bismuth-based photocatalysts (Ta_2O_5/Bi_2O_3, $TaON/Bi_2O_3$, and Ta_3N_5/Bi_2O_3). They then evaluate their tendency to generate hydrogen from water under visible light using water-methanol solution. The result showed enhanced hydrogen generation potential of the catalysts. The composites showed significant hydrogen production in comparison to the individual component (Ta_2O_5, Bi_2O_3, TaON and Ta_3N_5) as a result of the existence of heterojunction in the composites. The heterojunction enhanced separation of the electrons and holes. In addition, the synthesis, characterisation and the photocatalytic hydrogen gas production tendency of Pt-Bi_2O_3/RuO_2 under visible light was also assessed [67]. The experiment was performed by adding 0.3 M Na_2SO_3 and 0.03 M $H_2C_2O_4$ as sacrificial agents. The presence of Na_2SO_3 and $H_2C_2O_4$ assisted the catalyst to increase hydrogen production at the rates of 11.6 mol g^{-1} h^{-1} (Na_2SO_3) and 14. 5 mol g^{-1} h^{-1} ($H_2C_2O_4$) [67].

2.2.4. Application in air purification

The desire to purify urban or indoor air by removing nitrogen oxide pollutants (NO_X) and volatile organic compounds (VOCs) from it particularly in public places including schools, churches, shopping mall and so on, has become an issue of high necessity. This is due to the health consequences associated with these groups of pollutants which are mostly released into the air through vehicular emissions, building materials, personal care products, office equipment, cleaning agents etc. [68]. Photocatalysis has been identified as an appropriate technology for the removal of these pollutants from the air because of the technique's tendency to completely mineralise these pollutants [68].

The principle behind the photocatalytic degradation of the NO_X and VOCs in the air is similar to that described in the previous sections: The holes generated after excitation of electrons from the valence band to the conduction band due to illumination of the catalyst oxidise water molecules in the air to for •OH. The •OH then attach the organic pollutants in air and mineralise them through the destruction of their molecular bonds.

Bismuth-based photocatalysts are among the catalysts that have been tested for effective air purification experiments. Some results of these experiments are discussed here:

The successful application of Bi nanoparticles modified TiO_2 (Degussa P25) with mixed anatase and rutile phase in the photocatalytic removal of NO from the air at ppb level was undertaken by Zhao et al. [69]. The Bi-TiO_2 was noted to outperform the pure TiO_2 in the NO photocatalytic removal process. Among the catalysts used, Bi-TiO_2 with Bi nanoparticles diameters ranging from 5 to 8 demonstrated excellent photocatalytic activity as this diameter range acted as an excellent visible light active site with improved charge separation [69]. The improved performance of this catalyst was assigned to the movement of the electrons, which were generated through plasmonic activation of the Bi nanoparticles, between the conduction band of the anatase and rutile phases of TiO_2; thus reducing their rate of recombination with the holes. In their experiment, Ai et al. [70] compared the ability of a hierarchial BiOBr microsphere, BiOBr bulk, Degussa TiO_2 and C doped TiO_2 to photocatalytically remove NO from indoor air (400 ppb level). According to their result, the BiOBr microsphere performed extremely well compared to the other catalysts as a result of its unique hierarchical structure which enhanced the diffusion of intermediates and NO oxidation final product leading to the efficient removal of the NO. NO removal from air at ppb levels through visible light photocatalysis has also been studied by [71, 72] using N-$Bi_2O_2CO_3$-graphene quantum dot and Br-BiOCOOH respectively with excellent results.

Photocatalytic decomposition experiment was also performed to remove toluene from air. The experiment was conducted comparatively using V_2O_5/$BiVO_4$/TiO_2, V_2O_5/$BiVO_4$ and TiO_2 photocatalysts through illumination with visible light. The V_2O_5/$BiVO_4$/TiO_2 was identified to be the best catalyst for the decomposition of toluene due to enhanced charge carriers separation across the multiple interfaces of the ternary nanojunctions [73]. Similarly, toluene removal from air through photocatalysis using BiOI/TiO_2, pure TiO_2 and Degussa P25 was carried out by Boonprakob et al. [74]. They observed that the highest toluene photodecomposition activity (*ca*. 68%) was exhibited by BiOI/TiO_2 as a result of its excellent visible light activity and efficient charge carriers separation. In their study, Xu et al. [75] synthesised Bi_2O_3/TiO_2 nanocomposite and tested its ability to photocatalytically decompose 4-chlorophenol in air. They noted that the Bi_2O_3/TiO_2 catalyst effectively removed the pollutant from air compared to the pure TiO_2 and Degussa P25 owing to the narrow band gap of α- Bi_2O_3 which improved on the visible light activity of the composite.

3. Conclusion

The necessity to develop more efficient photocatalysts for effective water treatment, carbon dioxide conversion, hydrogen reduction and air purification so as to alleviate the increasing energy crisis, air pollution, and to make clean and potable water readily available cannot be overemphasised. The use of bismuth-based nanoparticles/nanocomposite in this regard has been organised in this chapter. The chapter also provided recently generated information on the use of bismuth-based nanoparticles in various photocatalytic degradation processes. A detailed discussion was provided on bismuth as an element/metal, and bismuth-based

nanoparticles including bismuth chalcogenides, bismuth vanadate, bismuth oxyhalides and other bismuth-related nanoparticles. Attention was also paid to the modification of these nanoparticles to improve their photocatalytic activities. The application of the modified nanoparticles in various photocatalytic processes with emphasis on water treatment, waste gas treatment, hydrogen production and air purification has also been thoroughly discussed.

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