Solvothermal synthesis of pure and Sn-doped Bi$_2$S$_3$ and the evaluation of their photocatalytic activity on the degradation of methylene blue

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Abstract

Background: A large volume of dye molecules finds its way into the environment, accumulates in water bodies, and makes the aquatic system unsafe to human health. Due to the complex nature of these dye materials, most of the conventional techniques are not effective for their removal. Semiconductor photocatalysis has emerged as a promising technique for the destruction of organic pollutants under UV or visible light irradiation. Among the semiconductors, Bi$_2$S$_3$ is widely employed in photocatalysis due to its non-toxicity and chemical stability. However, one of its problems is the high recombination rate of the charge, and various methods have been employed to enhance the photo-reactivity. One of these methods is the incorporation of transition elements.

Results: Herein, a facile solvothermal method was used to prepare Bi$_2$S$_3$ nanorods and needle-shaped Sn doped Bi$_2$S$_3$, using bismuth(III) tris(N-phenyldithiocarbamate) as a single-source precursor. The prepared nanomaterials were characterized, and used as efficient photocatalyst for the photo enhanced degradation of methylene blue (MB) dye under visible light irradiation. The nanomaterials exhibited very good photocatalytic activity towards the photo degradation of MB, showing a degradation rate of up to 83% and 94% within 150 min for the pristine and Sn doped Bi$_2$S$_3$, respectively.

Conclusion: The enhancement in the photocatalytic activity of the Sn doped Bi$_2$S$_3$ was attributed to the suppression in the recombination rate of the electron-hole pairs, due to the formation of new energy level below the CB, that was capable of altering the equilibrium concentration of the carrier. This confirmed that Sn doped Bi$_2$S$_3$ could be utilized as valuable cost-efficient catalysts for eliminating methyl blue from aqueous solutions and also possible candidates in environmental pollution treatment.

Keywords: Bismuth sulphide, Sn-doped, Nanorods, Photocatalysis, Methylene blue

Introduction

Dyes are one of the harmful organic pollutants. They are released into the environment mainly from the textiles, foodstuffs, and leather industries [1, 2]. Their presence in effluents generally reduce sunlight transmission; thus, it affects photosynthesis, harms aquatic ecosystems and also the health and wellbeing of humans. Worse still, some of them are highly cytotoxic for the mammalian tissues [3]. Methylene blue (MB)
is a basic dye, usually used for dyeing wool and silk. Like other dye materials, its removal from effluents is one of the major challenges in the industry. Different techniques, such as coagulation-flocculation processes, membrane filtration and ion exchange [4] have been developed to effect the remediation of water from toxic compounds. However, these methods are not suitable for industries that operate at a small scale due to high operational costs and sustainability. Therefore, techniques that are efficient, stable, and could operate at low cost continue to garner research interest.

Photo-enhanced degradation of pollutants by semiconductors is a new and effective technique for the removal of dyes from water. Under light irradiation, semiconductor-based photocatalysts could effectively decompose dyes. This occurs when the semiconductors are irradiated with photons whose energy is higher or equal to the photocatalyst’s band gap energy [5]. Bismuth sulfide (Bi$_2$S$_3$) is a typical environmentally friendly semiconductor photocatalyst. It is stable, has direct band gap energy of 1.30 eV, and possess a lamellar structure that makes it possible to be applied in photocatalysis [6, 7]. As an n-type semiconductor, it has great electron mobility and is applied in many areas, including supercapacitor electrodes, sensors, photodetectors, and thermoelectric devices, due to its reasonably low band gap energy [8, 9]. It has a great absorption coefficient in the range 104–105 cm$^{-1}$, and a good incident photon to conversion efficiency of ($\sim$5%) [10, 11]. It is possible to adjust the direct band gap energy by simply varying the size of the particles and shape, consequently resulting in some changes in the properties of the material. In addition, the band edges fall within the visible region of the solar energy spectrum. This makes it a very suitable material for devices that convert solar energy [12].

The introduction of dopants into semiconductor nanomaterials is significant since it impacts on the electrical, optical, catalytic, and magnetic properties of the host material [13]. It is also a strategy for improving the utilization of solar light for semiconductors, either by modifying the band gap structures or indirectly exchanging the energy. Band gap modification could be realized by creating impurity levels in the forbidden band of semiconductors or shifting the valence band edge. This method has been successfully employed to extend the light absorption range of some wide band gap semiconductors from UV to visible light, with appropriate metals or non-metal dopants [14]. In addition, the introduction of a suitable metal ion into a substrate such as a semiconductor host material suppresses the recombination of electron–hole pairs, thereby prolonging the lifetime of charge carriers. Consequently, the photocatalytic activity is improved efficiently and the apparent quantum efficiency can be enhanced [15].

Different transition metal-doped bismuth sulfide nanoparticles have been reported. Anasane and Ameta reported manganese (Mn$^{2+}$) doped Bi$_2$S$_3$ nanoparticles of different morphologies [16]. A simple synthesis of Eu-doped Bi$_2$S$_3$ nanoparticles, in various ratios, through the breakdown of dual single source precursors: Bi(III) dithiocarbamate and Eu(III) dithiocarbamate complexes has been described [17, 18]. Microspheres of Sn-doped Bi$_2$S$_3$ (TDBs), composed of nanosheets consisting of Sn-doped Bi$_2$S$_3$ with a bit of Sn$^{4+}$ substitution at Bi$^{3+}$ sites within the Bi$_2$S$_3$ lattice has been reported [19]. Silver doped bismuth sulfide (AgBiS$_2$) nanoparticles have been reported by single source precursor approach using bismuth diethyldithiocarbamate as the precursor under reflux condition in the presence of hexadecylamine [20]. The long chain amine acted as both the capping agent as well as shape directing coordinating solvent because it has been shown to control the rate of particle growth and size when used as a capping agent [21]. The good solar light absorbing potency of Bi$_2$S$_3$ has increased the research interest on its photocatalytic degradation of organic contaminants [22–24]. In this study, we present the synthesis, characterization and the photocatalytic degradation of methylene blue using undoped and Sn doped Bi$_2$S$_3$ nanomaterials.

**Experimental**

**Materials**

Analytical grade bismuth(III) chloride dihydrate, aniline, sodium hydroxide, carbon disulfide and ethanol were purchased from Merck. All reagents and solvents were analytical grade and used as received without further purification.

**Physical measurements**

The infrared spectral studies of the complex were carried out using a Fourier-transform infrared (FTIR) spectrometer (Nicolet 560), in the wavenumber range of 4000–500 cm$^{-1}$ at room temperature. The Nuclear Magnetic Resonance (NMR) spectra were recorded using a 600 MHz Bruker Avance III NMR spectrometer for $^1$H and $^{13}$C NMR analyses. The melting point measurement was done using a Gallenkamp melting point instrument. The absorption spectra of the bismuth sulfide nanoparticles were obtained using a Varian UV–vis spectrophotometer. The photoluminescence (PL) spectra were measured using Perkin Elmer LS 45 Fluorimeter. Powder X-ray diffractogram (XRD) of the nanoparticles were recorded on a Bruker D8 Advanced XRD machine, equipped with a proportional counter using Cu Ka radiation ($\lambda = 1.5405$ A, nickel filter). Samples were added on
a flat steel sample holder and scanned from 10 to 80 °C. The diffraction peaks at several values were matched with other recorded standards in JCPDS. The morphology of the nanoparticles was studied using transmission electron microscopy-TEM (Hitachi HF–2000 TEM at 200 kV and FEI Tecnai G² Twin at 20 kV).

Synthesis of sodium N-phenylthiocarbamate
A solution of NaOH (0.8 g, 0.02 mol) in 10 mL of distilled water was prepared in a round bottom flask. To this solution, aniline (1.86 g, 0.02 mol) was added and the mixture was stirred at a low temperature range ≤ 4 °C. After about 5 min, carbon disulfide (1.21 mL, 0.02 mol) was added slowly to the mixture. The faint yellowish-white solid product, which formed, was then filtered, rinsed with small portions of ether, and recrystallized in acetone.

Yield: 1.39 g, 85.93%; M.pt: 153–154 °C; Selected FTIR, ν (cm⁻¹): 1442 (C≡N), 1281 (C=N–N), 986 (C≡S), 3009 (≡CH), 3400 (–NH), 1526 δ (NH).

Synthesis of bismuth(III) tris(N-phenylthiocarbamate)
The complex was prepared by reacting an aqueous solution of the ligand with an aqueous solution of BiCl₃·2H₂O in 3:1 mol ratio (ligand to metal salt). Then, the precipitate formed was filtered, washed thoroughly using a mixture of ethanol (50 mL) and water (150 mL). The pure product, which formed, was then filtered, rinsed with small portions of ether, and recrystallized in acetone.

Yield: 1.39 g, 85.93%; M.pt: 153–154 °C; Selected FTIR, ν (cm⁻¹): 1485 (C≡N), 1232 (C=N–N), 1012 (C≡S), 2790 (≡CH), 3007 (≡CH), 3197 (NH), 1524 δ(NH); ¹H NMR (CDCl₃) δ (ppm) = 7.91 (s, 3H, HN–C₆H₅), 7.35–7.18 (m, 15H, N–C₆H₅); ¹³C NMR (CDCl₃) δ (ppm) = 179.97 (–NCS₂), 137.13, 127.04, 129.56, 125.22 (HN–C₆H₅); Anal. calc.C₂₁H₁₈N₃S₆Bi (713.76): C, 35.34; H, 2.54; N, 5.89; S, 26.95; Found: C, 35.23; H, 2.14; N, 6.01; S, 26.34.

Synthesis of pristine Bi₂S₃
In a typical procedure, 0.25 g of the bismuth complex was dispersed in 4 g oleylamine (OLA) in a 250 mL round-bottomed flask. This suspension was degassed for about 30 min, and then heated up to 180 °C under nitrogen, and maintained for 1 h. Thereafter, the reaction was terminated and the solution was allowed to cool down to 65 °C. Excess methanol was then added in order to precipitate the OLA capped bismuth sulfide nanorods. The product was isolated by centrifuging, rinsed 3 times with methanol and allowed to dry.

Synthesis of Sn doped Bi₂S₃
Sn(IV) doped Bi₂S₃ were prepared by introducing Sn(IV) chloride (0.037 g) into a beaker containing the bismuth dithiocarbamate complex (0.25 g) and oleylamine (7.5 mL). The obtained solution was transferred into a 100 mL capacity Teflon-lined autoclave sample reactor vessel, and heated up to 180 °C. The reaction was maintained for 8 h. Thereafter, the solution was allowed to cool to room temperature, ethanol was added and the precipitate obtained was centrifuged and washed with ethanol. The precipitation process with ethanol and centrifuging was carried out three times and the samples were dried in air.

Photocatalytic evaluation of the Bi₂S₃ and Sn doped Bi₂S₃
The photocatalytic activities of the Bi₂S₃ and Sn doped Bi₂S₃ were studied by measuring the degradation of methylene blue (30 mL, 10 mg/L) under visible light irradiation. 50 mg of the catalyst and dye solution, for each measurement, were mixed inside a Pyrex glass vessel. Then, the mixture was stirred in the dark cupboard for about 1 h to ensure that adsorption–desorption equilibrium was fully established between the dye and the catalyst. After 30 min, the solutions were exposed to the visible light with constant stirring in the compartment designated for the photocatalytic reaction. The efficiency of the degradation of the dye was analysed using UV–vis spectrometer by measuring the absorbance of aliquots taken at specific time intervals.

Results and discussion
Spectral studies
The FTIR spectrum of the ligand showed vibrational bands at 1479 cm⁻¹ attributed to the stretching vibrations of C–N characteristic of dithiocarbamate compounds (Additional file 1). In the spectrum of the complex, a shift in the position of this band to around 1485 cm⁻¹ occurred [25]. The position of this band was indicative of a partial double bond character of the C–N stretching vibrational band. The appearance of a single symmetric peak for the (C=S) stretching vibration around 1000 indicated a bidentate coordination fashion between the metal and the sulfur atoms of the dithiocarbamate ligand [26]. The stretching vibrations around 3009 cm⁻¹ in the ligand was ascribed to the (=C-H) of the aromatic ring and these bands shifted upon complexation to a lower frequency, 3007 cm⁻¹. The stretching vibrational band of N–H bond, observed at 3400 cm⁻¹ in the spectrum of the ligand, shifted to 3197 cm⁻¹ in the complex.

The ¹H-NMR spectra of the complex (Additional file 1) showed the protons of the aromatic ring as multiplet in the range 7.10–7.35 ppm. The proton of the –NH group resonated at 7.91 ppm due to its attachment to nitrogen atom, similar to previous report [27]. In the ¹³C NMR spectra, the complexes showed carbon signal at 179 ppm, ascribed to the carbon of the thioureide.
bond. The appearance and position of this peak show the contribution of the double bond character in the complexes to a formally single N–C bond of the dithiocarbamate moiety [28]. The phenyl carbons from the dithiocarbamate moiety were affected by the coordination of the bismuth metal. Coordination of the bismuth atom to the respective ligands caused a decrease in the partial double bond character of the nitrogen–carbon bond as well as the movement of electron density towards the nitrogen from the carbon atom of the dithiocarbamate group. The additional deshielding of carbon sites upon complexation is a consequence of this electron movement [27].

XRD studies of the nanomaterials

Figure 1a and b present the X-ray pattern of the undoped and Sn doped Bi₂S₃. Notable peaks observed at 2θ values of 23.39°, 24.92°, 28.60° and 31.79° could be indexed to the reflection pattern of (220), (130), (211) and (221) respectively of orthorhombic crystal structure of Bi₂S₃ with a JCPD No. 17-0320 [12]. Bi₂S₃ tends to crystallize in an orthorhombic system, with Pcnm space group, as it contains a thin layer arrangement of infinite chains of alternating Bi³⁺ and S²⁻. The intensity of the diffraction peaks of the Sn doped Bi₂S₃ are lower than that of the undoped Bi₂S₃. In addition, the diffraction peaks of the Sn doped Bi₂S₃ tend to be mildly displaced toward the zero mark of the 2θ value, indicating the doping of Sn into the lattice of Bi₂S₃.

TEM analysis

The method of synthesis of nanomaterials influences the morphology and size. Figures 2a and b show low and high magnification images of the TEM micrograph of the Bi₂S₃, which displayed rod morphology. The inset in Fig. 2c shows clearly the lattice fringes of Bi₂S₃, which confirmed the crystalline nature of the nanorods. The particles size distribution histograms in Fig. 2d and e present the length and width of the nanorods, with average length and width size of 85.39 and 13.4 nm, respectively. The calculated aspect ratio for the nanorods was 6.3, and they were fairly monodispersed with less than 40 percent superimposition on one another. The rod-like morphology exhibited by the Bi₂S₃ is partially due to the chain type structure of Bi₂S₃ nanoparticles, which is known to form band structures as Bi units interlinked with weaker van der Waals forces [29].

The micrograph of the Sn doped Bi₂S₃ shown in Fig. 3a and b, which appeared as needle-like structures covered by semi-transparent creased and wrinkle materials layers. The dimension of these needles was measured in terms of length and width. The observed average size of the width was 2.19 nm, while the length was 83.29 nm. Inset is the HRTEM that shows lattice fringes which indicated the crystallinity of the nanomaterial. The EDX spectrum presented in Fig. 4 shows peaks of Sn, Bi, and S which confirmed the formation of bismuth sulfide and a successful doping of the nanomaterial with Sn. The carbon peak could be attributed to the carbon tape used to hold the samples firmly to the stud during analysis.

Photocatalytic degradation of methylene blue

The wavelength of maximum absorption of methylene blue (MB) is 664 nm, which is due to the absorption of the π-system [30]. MB could be degraded either by oxidative degradation of its molecule or by a two-electron reduction [31, 32]. In the presence of a semiconductor such as Bi₂S₃, the degradation of MB is not a consequence of a direct redox reaction between the Bi₂S₃ and the dye molecules but results from the interaction of the dye molecules with radicals. The pathway for the photocatalytic degradation of MB in water has been proposed [33]. During photo-enhanced degradation, the electrons generated in the Bi₂S₃ under the irradiation of visible light, would either recombine with the holes of the valence band or react with the adsorbed oxygen on the surface of Bi₂S₃. In the latter case, oxygen ions are created, which in turn combine with the adsorbed water molecules to form hydroxyl radicals ‘OH. Eventually, the reactions of MB with the radicals cause the degradation of the dye molecules. The sequence of this process could be itemized as follows:
Fig. 2. TEM micrograph of Bi$_2$S$_3$(2) nanorods at (a) low magnification, (b) high magnification, (c) inset-HRTEM showing lattice fringes; with corresponding particle size histogram showing (d) width and (e) length of the nanorods.

Fig. 3. TEM images of Sn doped Bi$_2$S$_3$(2) at (a) low magnification, (b) high magnification, inset-HRTEM showing lattice fringes.
In the first equation, the activation of Bi$_2$S$_3$ by incident light ($h\nu$) generates excitons (electron–hole pairs), which are powerful oxidizing and reducing agents, respectively [34]:

\[
\text{Bi}_2\text{S}_3 + h\nu \rightarrow e^- + h^+
\] (1)

This is followed with the oxidation of the adsorbed water molecules on the surface of Bi$_2$S$_3$, which then results into the production of hydroxyl radical according to reaction:

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \cdot \text{OH}
\] (2)

This process is followed with the reduction and oxidation reactions as follows:

\[
\text{Reduction} - \cdot \text{OH}^- + h^+ \rightarrow \text{OH}\ 
\] (3)

\[
\text{Oxidation} - \text{O}_2 + e^- \rightarrow \cdot \text{O}_2^- \ 
\] (4)

Finally, the degradation of the organic compound (MB) occurs:

\[
\text{MB} + \cdot \text{OH} \rightarrow \text{products}
\]

\[
\left(\text{CO}_2 + \text{H}_2\text{O} + \text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-\right)
\] (5)

The photodegradation efficiency of the synthesized Bi$_2$S$_3$ on the MB is shown in Fig. 5, while that of the Sn doped Bi$_2$S$_3$ is presented in Fig. 6. The UV–vis spectra of the original and degraded MB solutions were determined by a UV–vis spectrophotometer at 15 min time interval and over a 150 min period. The Figures showed pronounced reduction with time in the absorption peaks of the MB solutions at 664 nm in the presence of the nanoparticles, due to an oxidative degradation process [9], suggesting a breakdown of the chromophore in the reaction process. The photocatalytic activity of Bi$_2$S$_3$ photocatalysts for MB photodegradation was calculated using the equation:

\[
\text{Degradation \%} = \frac{A_c - A_t}{A_c} \times 100
\] (6)

where $A_c$ is the initial solution of dye concentration and $A_t$ is the final solution of dye concentration after treating with the photocatalyst.

The efficiency of the pristine Bi$_2$S$_3$ for the dye degradation was 83%, and increased to about 94% with the Sn doped Bi$_2$S$_3$ samples. Considerable improvement in the photocatalytic activity of doped semiconductors in aqueous systems has been reported for the degradation of organic compounds [35–37]. The electronic structure in a semiconductor could be effectively modulated by the introduction of a dopant into its lattice. Since the ionic radius of Sn is smaller than that of Bi, the replacement of Bi atoms by Sn atom is promoted. The introduction of
Sn could form a new energy level below the CB, which could alter the equilibrium concentration of the carrier. The new energy level serves as electron-hole trapping site. Hence, electron transfer to the Sn causes a reduction in the carrier recombination rate, and allows an effective reaction between the electrons and the surface trapped holes. This is capable of suppressing the recombination rate of electron-hole pairs, and consequently enhances the degradation rates. This accounts for the improvement in the photocatalytic performance of the doped Bi$_2$S$_3$ compared with the pristine Bi$_2$S$_3$.

The degradation process, showing the energy diagram with the different band level positions are shown in Fig. 7. The doped Sn could promote the separation of electron-hole pairs, and consequently enhances the degradation rates. This accounts for the improvement in the photocatalytic performance of the doped Bi$_2$S$_3$ compared with the pristine Bi$_2$S$_3$.

Sn doping
of photo-excited electron–hole pairs effectively, thereby suppressing the recombination of electron–hole. Consequently, the photocatalytic degradation activity is enhanced by the doped Sn. Table 1 presents a summary of the efficiency of different metal and non-metal doped Bi₂S₃ in comparison with the results of the current study.

**Conclusion**

Orthorhombic Bi₂S₃ and doped Bi₂S₃ nanostructures have been prepared using a single source precursor complex in oleylamine. Both the diameter and length of the nanorods was observed to be decreased with doping with tin. The photocatalytic evaluation of the Bi₂S₃ and doped Bi₂S₃ nanomaterials showed good photocatalytic activity for the degradation of methylene blue. The doped Bi₂S₃ had higher degradation efficiency due to them having a new energy level, which can suppress the recombination rate of electron-hole pairs. The high photocatalytic activities is suggestive that the reported Bi₂S₃ nanostructures would be good candidates in the photocatalytic degradation of organic pollutants in aqueous solution.

**Supplementary Information**

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**Authors’ contributions**

DCO conceptualized and designed the project; VMN carried out the synthesis of the samples and their characterization; MAA interpreted the photocatalytic studies. All the authors participated in the writing of the manuscript. All authors read and approved the final manuscript.

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**Availability of data and materials**

Available on request. Contact the corresponding author.

**Declarations**

**Ethics approval and consent to participate**

Not applicable.

**Consent for publication**

Not applicable.

**Competing interests**

The authors declare that they have no competing interests.

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| Compounds          | Synthesis method | Morphology | Pollutants (dye) | Degradation (%) | Refs.     |
|--------------------|------------------|------------|------------------|-----------------|-----------|
| Sn-Bi₂S₃          | Hydrothermal     | Nanorods   | MB               | 83–94           | This work |
| Se-Bi₂S₃          | Hydrothermal     | Nanorods   | MB               | 88–96           | [38]      |
| Au-Bi₂S₃          | Facile one-pot   | Nanorods   | MO               | 72–80           | [39]      |
|                   |                  | Nanoflowers| MO               | 86–97           |           |
|                   |                  | Nanorods   | RhB              | 77              |           |
|                   |                  | Nanoflowers| RhB              | 95              |           |
| Sn-Bi₂S₃          | Solvothermal     | Microspheres| RhB            | 21–99           | [40]      |
| Mn-Bi₂S₃          | Wet chemical     | Nanorods   | MV               | 75–90           | [16]      |
| Eu-Bi₂S₃          | Solvothermal     | Nanoflowers| MB               | 4.6             | [17]      |

**Additional file 1:** Fig. S1. FTIR spectra of (a) sodium N-phenylthiocarbamate and (b) bismuth(III) tris(N-phenylthiocarbamate). Fig. S2. (a)¹H and (b)¹³C NMR spectra of Bi(III) tris (N-phenyldithiocarbamate) complex.
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