



Bi₂O₂S nanosheets for effective visible light photocatalysis of anionic dye degradation

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ABSTRACT

Herein, we introduce the first investigation into the photocatalytic properties of ultrathin Bi₂O₂S nanosheets prepared by a hydrothermal method. These nanosheets demonstrate exceptional efficiency in degrading congo red (CR) and rose bengal (RB) when exposed to visible light. The degradation rates reached approximately 82 % for CR and 80 % for RB, respectively. The rate constants for CR and RB degradation were found to be $1.8 \times 10^{-2} \text{ min}^{-1}$ and $1.3 \times 10^{-2} \text{ min}^{-1}$, respectively, during a 75 and 150-minute exposure to Bi₂O₂S nanosheets.

1. Introduction

The discharge of untreated wastewater from textile, pharmaceutical, dyeing and paper printing industries leads to an increased amount of dyes in the water sources, causing a severe threat to the environment [1,2]. To get rid of these dyes, various degradation approaches like membrane filtration, oxidation, adsorption and photocatalysis have been successfully developed and demonstrated [3,4]. Photocatalytic degradation is considered as the most preferred technique due to its degradation efficiency, free photon energy and simple process. A variety of nanomaterials including metal oxide, chalcogenides, oxynitrides and oxychalcogenides have been studied for photocatalytic degradation [5–8]. Recently, bismuth oxychalcogenides (BOXs) have emerged as novel semiconductors for their application in optoelectronics and photocatalysis [9–12]. Among which, bismuth oxysulfide (Bi₂O₂S) is a semiconductor with an indirect bandgap of ~1.1 eV and has excellent air stability [13]. Bi₂O₂S offers a long carrier lifetime, excellent charge dissociation and transport properties, which makes it a potential candidate for photocatalytic and photodetection applications. So far, only a limited number of reports have explored the photocatalytic activity of nanocomposites containing Bi₂O₂S [14–16]. However, the photocatalytic properties of standalone Bi₂O₂S nanosheets for dye degradation have not been previously reported. Herein, we report the photocatalytic behavior of Bi₂O₂S nanosheets for the oxidative photodegradation of organic pollutants under visible light. Congo red (CR) and rose bengal (RB) were chosen for this study due to their widespread industrial use, environmental challenges, and notable efficiency in our dye degradation experiment's initial screening.

2. Experimental

CR and RB were purchased from Fisher Scientific. Bi(NO₃)₃·5H₂O, CH₄N₂S, KOH, NaOH, and cupric nitrate (CN) or Cu(NO₃)₂·3H₂O (99–104 %) were purchased from Sigma-Aldrich. Isopropyl alcohol (IPA), benzoquinone (BQ), and disodium ethylenediaminetetraacetate acid (Na₂-EDTA) were purchased from VWR. Bi₂O₂S nanosheets were synthesized using a simple solution process in ambient conditions. The detailed synthesis process is described in Fig. S1, (supporting information). Further, the structural, optical, morphological and photocatalytic characterizations were performed. Visible light irradiation experiments for photocatalytic degradation were conducted using an LS-150-Xe system with a cutoff filter L42 (Newport Corporation). The spectra were recorded using a VWR UV3100-PC UV–visible spectrophotometer.

3. Result and discussion

3.1. Material characterizations

Fig. 1a depicts the crystal structure of layered Bi₂O₂S, which comprises alternative layers of bismuth oxide (Bi₂O₂)²⁺ and sulfur (S²⁻). The atomic model is designed using the 3D visualization tool VESTA and the source file was imported from the materials project library. Fig. 1b shows the XRD pattern of Bi₂O₂S nanosheet powder, where the indexed peaks confirm its orthorhombic phase (JCPDS # 00–034–1493). Fig. 1c shows the UV–Vis-DRS spectra of Bi₂O₂S nanosheets and the value of bandgap obtained using the Kubelka Munk function as shown in Fig. 1c (inset). The calculated value of the bandgap of Bi₂O₂S is ~1.17 eV.

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Fig. 1d show the FESEM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets indicating the morphology of the material and confirming the nanosheet formation with the lateral dimensions of ≥ 100 nm. The elemental mapping image and atomic ratio of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets was obtained using EDS (see Fig. S2, supplementary information). Fig. 1e shows the TEM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets indicating the standalone nanosheets with weak electrostatic force between the layers.

3.2. Photocatalytic degradation studies

The UV–visible spectra of 30 ppm of CR and RB were recorded with and without $\text{Bi}_2\text{O}_2\text{S}$ photocatalyst as shown in Fig. 2a–d. Fig. 2a and 2b show the degradation of CR and RB without photocatalysts respectively. From the UV–visible spectra, we observe the $\sim 16\%$ and $\sim 49.5\%$ degradation of CR and RB dyes, respectively. After controlled degradation, $\text{Bi}_2\text{O}_2\text{S}$ nanosheet powder (1 mg/mL) was added to both the dye solution and stirred for 45 min in the dark to obtain equilibrium. The photodegradation was carried out under a 150 W Xe arc lamp with a UV filter to pass only visible light. The same time intervals were kept for degradation studies as for control degradation shown in Fig. 2c–d. The photodegradation for CR and RB was $\sim 82\%$ and $\sim 80.6\%$ as shown in Fig. 2c and 2d respectively. The degradation values adhere to a first-order pseudo-kinetic model, as represented by the following equation:

$$\ln(C_i/C_o) = -kt \quad (1)$$

where C_o is the equilibrium concentration of the reaction solution before

irradiation, and C_t is the concentration of the reaction solution at reaction time (t). The photodegradation processes of CR and RB in all their respective photocatalysts, as depicted in Fig. 3a and 3b respectively. The degradation rate constant (k) values for the degradation of CR and RB dyes were determined to be $1.8 \times 10^{-2} \text{ min}^{-1}$ and $1.3 \times 10^{-2} \text{ min}^{-1}$.

3.3. Scavenger test and degradation mechanism

Fig. 4a shows the effect of IPA, BQ, $\text{Na}_2\text{-EDTA}$, and CN on the photocatalytic degradation of CR dye by $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. These scavengers help to find the dominant radicals responsible for degradation [17]. $\text{Bi}_2\text{O}_2\text{S}$ nanosheets exhibited $\sim 82\%$ degradation efficiency without any scavengers. The inclusion of IPA, EDTA, BQ, and CN led to a decrease in the degradation efficiency, yielding percentages of 24.3 %, 41 %, 54.6 %, and 36 % respectively. The findings confirm the dominance of $\bullet\text{OH}$ radicals in photodegrading CR. The valence band (VB) potential of $\text{Bi}_2\text{O}_2\text{S}$ was reported at 1.81 V vs. the reversible hydrogen electrode (RHE). [18] The conduction band (CB) potential was calculated by combining the bandgap (1.17 eV) and the calculated CB potential was 0.64 V vs. RHE.

The photodegradation mechanism as shown in Fig. 4b can be expressed as follows: when visible light irradiates $\text{Bi}_2\text{O}_2\text{S}$ nanosheets, electron-hole pairs are generated on the surface. The adsorbed water and hydroxyl molecules react with generated charge carriers to form $\bullet\text{OH}$ radicals. The effective interaction between these radicals and dye molecules leads to the degradation of the dye.

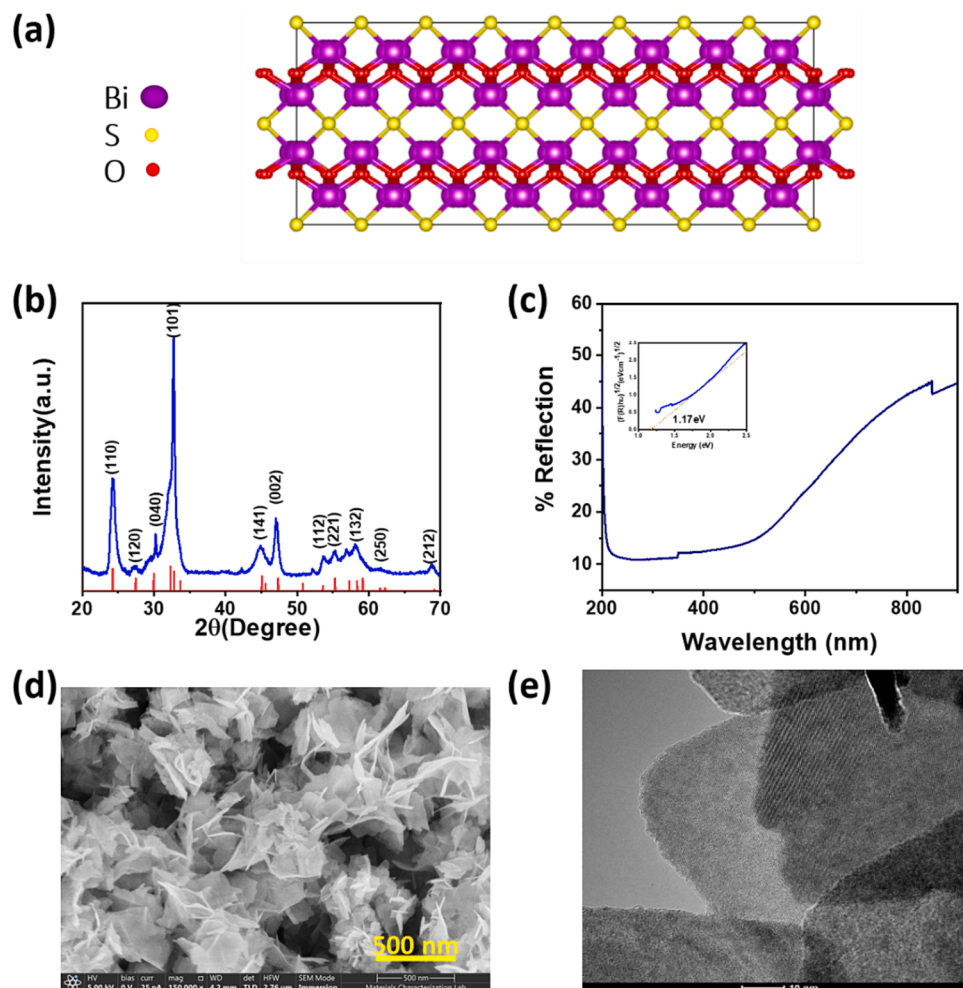


Fig. 1. (a) Atomic model of layered $\text{Bi}_2\text{O}_2\text{S}$, (b) XRD pattern of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets, (c) UV–Vis-DRS spectrum of $\text{Bi}_2\text{O}_2\text{S}$ (bandgap diagram), (d) FESEM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets, and (e) TEM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets.

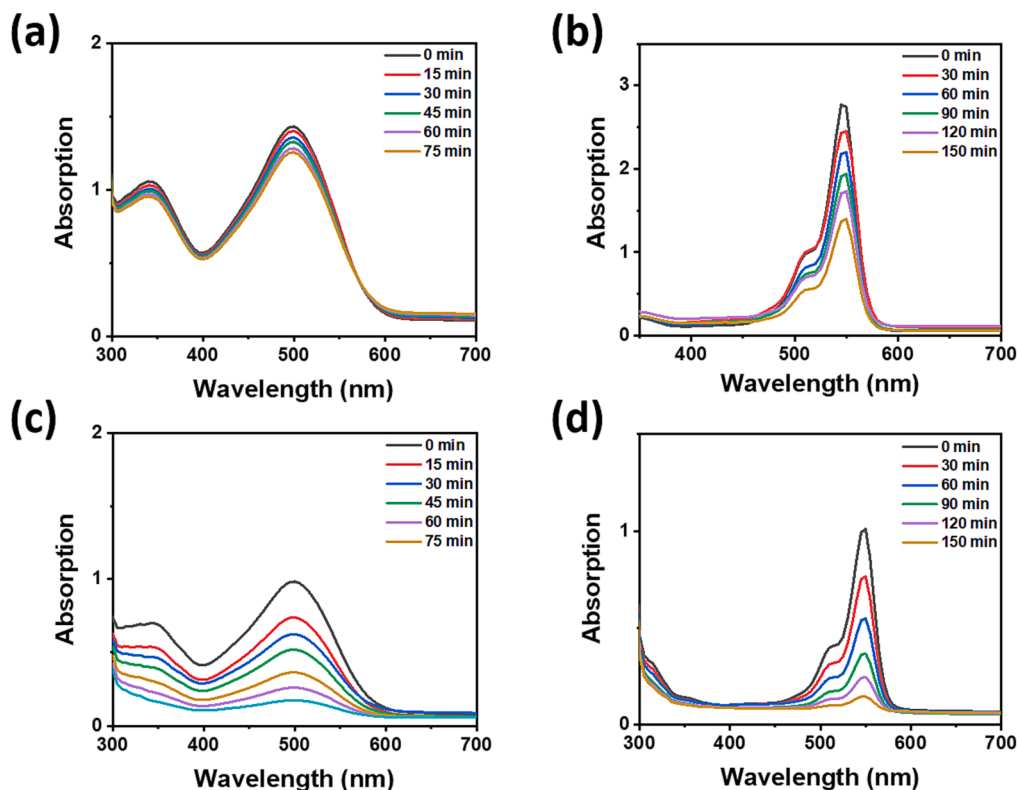


Fig. 2. Photodegradation characteristics (without catalyst) (a) CR and (b) RB. Photocatalytic degradation using $\text{Bi}_2\text{O}_2\text{S}$ (c) CR and (d) RB.

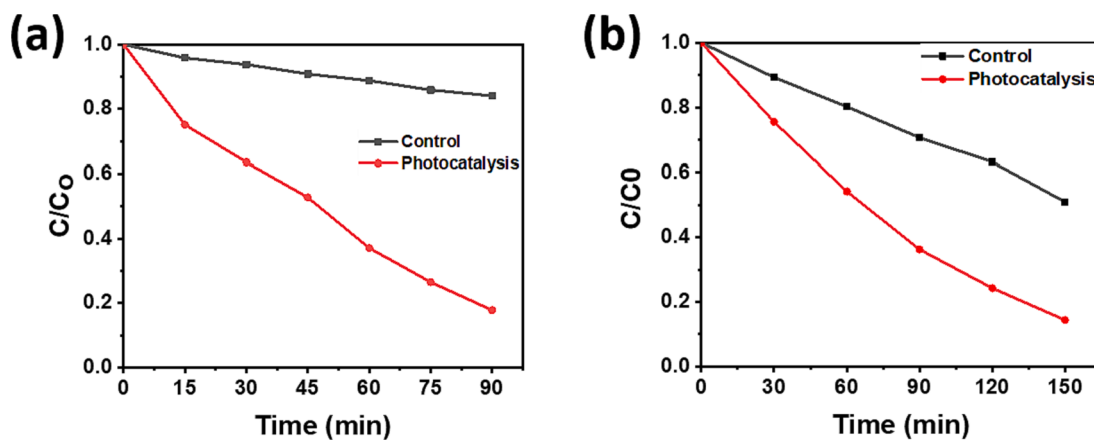


Fig. 3. C/C_0 plots for (a) CR and (b) RB.

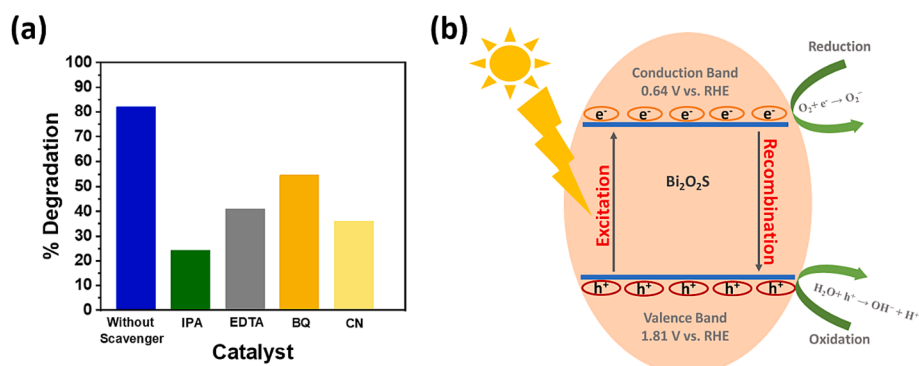
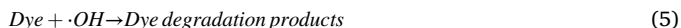


Fig. 4. (a) Percent degradation of CR dye in the presence of different scavengers, and (b) schematic representation of photocatalytic degradation mechanism.



It is noteworthy that the decrease in dye absorption observed in the presence of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets is partially influenced by photoreduction. The reduction in dye absorption under visible light is a complex phenomenon influenced by various factors, such as electronic transitions, photochemical reactions, conformational changes, photodegradation, and solvent effects.

4. Conclusions

To summarize, we have investigated the photocatalytic properties of ultrathin $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. The structural, optical and morphological characterizations confirm the crystalline phase, band gap and nanostructure of the synthesized nanosheets. $\text{Bi}_2\text{O}_2\text{S}$ nanosheets show ~82 % and ~80.6 % degradation efficiency for CR and RB dyes under visible light illumination. The report shows the potential of the $\text{Bi}_2\text{O}_2\text{S}$ nanosheets as efficient catalysts that can be used for the treatment of effluents and water sources.

CRediT authorship contribution statement

Tank R. Seling: Data curation, Investigation, Methodology. **Amit Kumar Shringi:** Data curation, Writing – original draft, Investigation, Formal analysis. **Ke Wang:** Data curation, Methodology. **Ufana Riaz:** Methodology, Project administration, Resources. **Fei Yan:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

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

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2024.136136>.

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