Behavior of Bi₂S₃ under ultrasound and visible light irradiation for Rhodamine B dye degradation

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Abstract

In this study, we have demonstrated that Bi₂S₃ semiconductor under ultrasound is transformed into a piezoelectric material, facilitating the transfer of electrons and holes, which can enable the formation of oxidizing agents. Bi₂S₃ has no photocatalytic activity in the presence of light, which results in 2.5% of Rhodamine B (RhB) decomposition, which in turn, with ultrasound application results 40.6%. A possible mechanism to explain this behavior, based in the local charge polarization at the [BiS₇] clusters, is proposed.

1. Introduction

Piezocatalysis has developed as an emergent research field due to the easy operation, low cost, and the wide range of applications, such as organic compounds degradation [1,2], hydrogen evolution [3], bacterial disinfection [4], and others. Further, Wang *et al.* recently reported a practical and useful application of piezocatalysis by incorporating

BaTiO₃ nanoparticles into toothpaste and demonstrated a non-destructive form of tooth whitening with remarkable cleaning results [5], while Liang et al. have presented the advances in piezoelectric materials for catalytic/photocatalytic removal of pollutants [6].

Besides the most commonly used piezoelectric materials, which are the perovskite-type structure, such as BaTiO₃ [7], PbTiO₃ [8], and LiNbO₃ [9] that have the general formula of ABO₃, other classes of materials have been investigated for piezocatalytic response. These classes encompass binary oxide [10], metal chalcogenide [11], apatite [12], and so on. Recently, Liu and collaborators reported the activity of submicrorod particles of m-Bi₂O₄ for the piezocatalytic degradation of sulfamethazine antibiotic [13]. Yein and collaborators reported a highly piezocatalytic degradation of Eriochrome Black T dye by modulating the sulfur-vacancy in MoS₂ materials [14]. Also, Wei and collaborators developed a piezocatalyst material based on Fe surface loading on BiVO₄ nanoparticles for efficient degradation of p-chlorophenol [15].

Belonging to the metal chalcogenide class, the Bi₂S₃ is a semiconductor with orthorhombic structure and presents several applications, such as employed as heterojunction component for effective improvement of photocatalytic properties of materials for organic compounds degradation [16], hydrogen generation [17], and others. In this work, we investigate the piezocatalytic behavior for the first time of the Bi₂S₃ nanorods under ultrasound application for the degradation process of RhB dye. The material was synthesized by simple co-precipitation method and characterized by X ray diffraction (XRD), Raman spectroscopy, UV-Vis diffuse reflectance, Transmission electron microscopy (TEM), and, Atomic force microscopy-Piezoresponse force microscopy (AFM-PFM). The degradation tests were performed using light, ultrasound and both simultaneously.

2. Materials and methods

The Bi₂S₃ sample was synthesized by the chemical co-precipitation method. First, 2 mmol of Bi(NO₃)₃·5H₂O (0.9701 g) was dispersed in 100 mL of deionized water in a glass beaker and heated up to 60 °C. Then, 5 mL of HNO_{3(aq)} (70.0%) was added to dissolve the Bi(NO₃)₃·5H₂O. Separately, 3 mmol of thioacetamide (0.2277 g) was dissolved in 100 mL of deionized water in a glass beaker heated up to 60 °C. The Bi(NO₃)₃·5H₂O solution was added to the thioacetamide solution and the mixture was maintained at 60 °C for 3 hours under constant stirring. The resulting powder was washed with deionized water several times and dried at 60 °C for 12 hours in a drying oven. The photocatalytic, piezocatalytic and piezophotocatalytic activities of Bi₂S₃ sample was tested for Rhodamine B dye degradation. More details about the experimental section are in Supporting Information.

3. Results and discussion

The XRD pattern of Bi₂S₃ sample is shown in **Fig. 1a**. All the diffraction pattern of are in well agreement with the orthorhombic structure (stibnite) of Bi₂S₃ with *Pnma* space group, in accordance with the ICSD 153946 [18]. The sharp and well-defined diffraction peaks indicate a good crystallinity of the Bi₂S₃ sample. Further, no peaks related to any secondary or impurity phases were observed, confirming the pure phase. **Fig. 1b** shows the Raman spectrum at room temperature of the Bi₂S₃ sample. As can be seen, six bands related to the Raman modes were observed, which were centered at 141, 259, 306, 424, 604, and 967 cm⁻¹ [19]. These values are in agreement with the Raman modes reported for Bi₂S₃ nanostructures. Moreover, the Raman mode located at 141 cm⁻¹ is ascribed to stemming from surface optical phonon due to the nanoscale particles [20]. As seen in **Fig. 1b**, the high intensity of this mode indicates the formation of nanostructures. Considering the direct band gap of Bi₂S₃, the Tauc plot of the as-prepared sample is shown in **Fig. 1c**. The obtained energy value was of 1.57 eV, which is in agreement with those reported in the literature for the range of 1.3 to 1.7 eV [21].

Figure 1 – (a) XRD patterns, (b) Raman spectrum, (c) Tauc plot, (d) TEM image, (e) HRTEM image, and (f) Fast Fourier Transform (FFT) of selected HRTEM image region of Bi₂S₃ sample.

Fig. 1d shows a TEM image of the as-prepared sample, presenting the obtained nanorods particles of Bi_2S_3 , which are similar to those reported by Kaltenhauser and are quite common shapes for solution-driven synthesis [22]. The high-resolution TEM (HRTEM) image of Bi_2S_3 nanorod shown in **Fig. 1e** indicates the formation of a well-crystalline structure as can be seen by its periodic fringes along the nanorod particle. The correspondent Fast Fourier Transform (FFT) of the HRTEM image is shown in **Fig. 1f**. According to the analysis, only the orthorhombic structure of Bi_2S_3 was observed. Furthermore, the well-defined and parallel lines of the pattern spots indicate single-crystallinity in the Bi_2S_3 nanorod.

Fig. 2a shows the unit cell representation and the two constituent clusters $[\text{Bi}_7]$ of the orthorhombic structure of Bi_2S_3 . As can be seen, both clusters present highly asymmetry and structural distortions. **Fig. 2b** shows the AFM topography image of the pellet surface of Bi_2S_3 and its height profile along 3 μm is inset. **Fig. 2c** shows the PFM result of tip displacement against applied voltage for the as-prepared sample, indicating a hysteresis with butterfly shape, which is a characteristic and direct evidence of the piezoelectric response of the Bi_2S_3 nanorods [12,23].

Figure 2 – (a) Unit cell and composing clusters of orthorhombic Bi_2S_3 structure, (b) AFM topography, and (c) PFM displacement-voltage curve of the as-prepared sample.

Fig. 3a-c show the absorbance spectra of RhB along the reaction time for the experiments without catalyst with visible light irradiation, ultrasound, and both simultaneously, respectively. The absorbance spectra of RhB along the reaction time using Bi_2S_3 nanorods and with visible light irradiation, ultrasound, and with both simultaneously are shown in **Fig. 3d-f**, respectively. As can be seen, the RhB degradation in all processes without Bi_2S_3 are almost neglected. It can be observed that only the light irradiation has no significant contribution for the degradation of RhB using Bi_2S_3 nanorods, which has already been reported [24]. Once the valence band maximum of Bi_2S_3 has no potential to oxidize water molecules to produce hydroxyl radical ($\cdot\text{OH}/\text{H}_2\text{O}$, $E = 2.72 \text{ eV}$) [25], **NOTACION** the production of oxidizing species is hindered. However, the experiments with ultrasound radiation showed a higher degradation percentage of RhB compared to only visible light.

Figure 3 – Absorbance spectra of RhB without catalyst using (a) light, (b), ultrasound, and (c) light and ultrasound irradiation, and using Bi₂S₃ with (d) light, (e) ultrasound, and (f) light and ultrasound irradiation. RhB degradation performance without (g) and with (h) Bi₂S₃.

The valence ($E_{VB} = 1.55$ eV) and conduction ($E_{CB} = -0.015$ eV) bands potentials were calculated using the Mulliken's electronegativity relationship [26], by using $\chi = 5.27$ eV, and the energy band diagrams for Bi₂S₃ were constructed, as shown in **Fig. 4**. According to the results, the E_{CB} minimum has no potential to reduce O₂ molecules ($O_2/\cdot O_2^-$, $E = -0.16$ eV) [27], thus only the electrons excited above it can perform the reaction. Furthermore, in photocatalysis, the electrons and holes migrate in random directions, decreasing the probability of these to reach the particle surface and hence decreasing the degradation performance. In contrast, the application of ultrasound in the Bi₂S₃ generates the piezo-polarization, in which the valence and conduction bands are tilted and the electrons and holes migrate in opposite directions toward an internal electrical field, increasing the probability of these to reach the particle surface.

It is known that most crystal structures containing the Bi³⁺ cation are highly asymmetric due to its lone pair of electrons that implies in a requirement for spatial arrangement [28]. Hereupon, several Bi³⁺ based materials have been investigated and employed for piezocatalytic applications, such as BiOCl [29], Bi₂O₂(OH)(NO₃) [30], *m*-Bi₂O₃ [13], and BiOBr [31]. According to the piezoelectric fundamentals [32,33], the piezo-polarization induced by ultrasound in the Bi₂S₃ can be understood as the displacement of Bi³⁺ cation from its centroid position in the highly asymmetric [BiS₇] clusters. This displacement generates a shift of the electronic density around the Bi³⁺ cation, leading to the formation of a region with high electronic density and in an opposite direction, a region with low electronic density, resulting in internal dipoles in the structure. These dipoles induced by ultrasound arises from the structural order-disorder effects in the [BiS₇] clusters. According to the Kröger-Vink notation [34], electrically neutral disordered $[BiS_7]_d^x$ clusters donate an electron to electrically neutral ordered $[BiS_7]_o^x$ clusters, thus generating the $[BiS_7]_d^{\bullet} - [BiS_7]_o^{\cdot}$ dipoles, which act as hole and free electron, respectively, for the RhB degradation reactions. Bi₂S₃ without external perturbation or irradiated with visible light has very low oxidizing activity. However, when mechanical shocks occur, the disordered clusters become polarized and increase the

charge carrier transfer by piezoelectricity. According to the general mechanism for degradation of organic compounds based on the main active species, a mechanism has been proposed for Bi₂S₃ as shown in equations 1 to 5. Herein, the disordered cluster transfers an electron to the neighboring ordered cluster, and facilitates the formation of oxidizing radicals from the water and oxygen molecules.

Seria ·O₂⁻, ·OH, H⁺, ·O₂H

With α meaning Bi₂S₃ without external perturbation, where $[\text{BiS}_7]_{\text{d}}^{\text{x}} \gg [\text{BiS}_7]_{\text{d}}^{\cdot}$, β meaning with visible light irradiation, where $[\text{BiS}_7]_{\text{d}}^{\text{x}} \leq [\text{BiS}_7]_{\text{d}}^{\cdot}$, and γ meaning with ultrasound application, where $[\text{BiS}_7]_{\text{d}}^{\text{x}} \lll [\text{BiS}_7]_{\text{d}}^{\cdot}$. **COC ?**

Figure 4 – Schematic representation of energy band diagram for Bi₂S₃ (a) without external perturbation, (b) with visible light, and (c) ultrasound irradiation.

The piezo-polarization induced by ultrasound in the Bi₂S₃ leads to an effective charge separation at the **[BiS₇]** clusters, with a charge transfer from the **disorganized to the organized cluster**. This separation of charge from the valence band to the conduction band is due to the internal electric field generated by the displacement of the Bi³⁺ in the disordered cluster. This quantum effect decreases the activation energy for the **decomposition of H₂O, allowing** the formation of oxidizing agents such as **·OH and ·O₂H** that will degrade RhB. Bi₂S₃ nanoparticles under ultrasound present a variation effect of

the polarization **with respect to the bulk**. This polarization must be reversed in the hysteresis cycle, in which there is an **increase/decrease** in the charge density in the crystal, **and the formation of an electron/hole pair, which promoted** the degradation of RhB reaching 40.6%. Then, there was a "polarization fatigue", which can be defined as the decrease in polarization remaining after several polarization/depolarization cycles in the **degradation process**.

Therefore, we demonstrate for the first time that the RhB degradation performance of Bi_2S_3 can be notably improved under **ultrasound due to the formation of internal dipoles** at the $[\text{BiS}_7]$ clusters. Since the RhB degradation performance are practically quenched due to the polarization fatigue, this effect could be improved by several methods, such as doping, semiconductor and/or metal heterojunctions, and others. **We hope that present findings can contribute for the design and development of novel Bi_2S_3 -containing materials with enhanced properties**.

Conclusions

For the first time, we report the behavior of Bi_2S_3 nanorods under ultrasound **application for the degradation process of RhB**. The as-prepared material presented a significant difference in piezo and photocatalytic activities that arises from its band tilting and formation of internal dipoles in $[\text{BiS}_7]$ clusters by piezo-polarization, decreasing the activation barrier for the reactions that drive the degradation of organic compounds. However, after achieving the polarization fatigue, the degradation rate was notably quenched. Herewith, the present work strongly contributes for the construction of novel Bi_2S_3 -containing materials with improved properties by ultrasound application.

Acknowledgments

The authors acknowledge the financial support of the Brazilian agencies: Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, 2013/07296-2; 2019/01732-1), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, 142035/2017-3), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES, Finance Code 001; PrInt - 88887.588736/2020-00). **J.A. acknowledges Universitat Jaume I (project UJI-B2019-30), and the Ministerio de Ciencia, Innovación y Universidades (Spain) (project PGC2018094417-B-I00) for financially supporting this research.**

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