Short communication

Novel application of Ag/PbBiO₂I nanocomposite in piezocatalytic degradation of rhodamine B via harvesting ultrasonic vibration energy

Ziyu Li b, 1 , Qingle Zhang b, 1 , Linkun Wang b , Jiuyang Yang b , Ying Wu a, *, Yiming He a, b, *

a Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China
b Department of Materials Science and Engineering, Zhejiang Normal University, Jinhua 321004, China

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ABSTRACT

Ag/PbBiO₂I nanocomposite was synthesized and firstly applied in piezocatalytic degradation of rhodamine B (RhB) under ultrasonic vibration. The two-dimensional structure endows PbBiO₂I nanosheets piezoelectric property, so that it can drive the piezocatalytic reaction under ultrasonic vibration. The loading of Ag nanoparticles forms Schottky barriers between the Ag-PbBiO₂I contact region, which improves the separation of charge carriers and subsequently increases the piezocatalytic efficiency. The RhB degradation rate of the optimal Ag/PbBiO₂I sample is 0.0165 min⁻¹, which reaches 6.8 times that of pure PbBiO₂I. This work indicates that the PbBiO₂I nanosheet shows promising potential in utilizing ultrasonic vibration energy.

Energy crisis and environmental pollution are two major problems facing the world today. The use of sustainable energy to resolve the above two issues is considered the most ideal approach. Therefore, photocatalytic technology using solar energy has been rapidly developed in recent decades. Recently, piezoelectric catalytic technology has also received widespread attention because it can be carried out in the dark and can utilize the abundant low-frequency mechanical energy source in nature. The piezoelectric effect is the fundamental reason of a piezocatalyst for driving the piezoelectric catalytic reaction. Under the action of external force, the distortion of the piezocatalyst crystal triggers the generation of a piezoelectric potential, so that heat-excited free charge carriers are enriched on the surface of the catalyst, thereby triggering the electrochemical reaction [1,2]. Since Domen firstly reported the piezocatalytic water splitting reaction over NiO and Cu₂O catalysts in 1988 [3], many piezoelectric catalysts including ZnO [4,5], KTa₃Nb₂₆SO₃ [6,7], SrTiO₃ [8], and Pb(Zr₁₁-ₓTiₓ)₂O₃ [9] have been reported and applied in dye degradation, hydrogen production, nitrogen fixation, and CO₂ reduction. These piezoelectric catalysts usually have asymmetric centers, which is the cause of the piezoelectric effect. However, some non-piezoelectric bulk materials such as BiOCl and BiOBr may also present piezoelectric catalytic properties when they are thinned to a nanosheet structure [10–11]. The ultrathin two-dimensional (2D) structure can transform the 3D symmetry of the bulk materials to a non-centrosymmetric point group, thereby giving the nanosheets piezoelectric characteristics [10].

Just like BiOX, PbBiO₂I also belongs to the layered Bi-based structural compound and consists of interlacing [PbBiO₂I] slabs and double [I] slices. The layer structure endows PbBiO₂I an internal electric field to separate electron-hole pairs, and hence it presents good photocatalytic activity [12–13]. Meanwhile, the weak nonbonding (van der Waals) forces between [PbBiO₂I] and [I] slabs indicate that PbBiO₂I easily forms an ultrathin 2D structure (nanoplates), thereby presenting piezoelectric property. In other words, PbBiO₂I nanosheets may be a promising piezoelectric catalyst that can achieve water purification via harvesting mechanical vibration energy. Based on the above discussion, PbBiO₂I nanosheets were synthesized and firstly applied in piezocatalytic degradation of RhB. Ag nanoparticles were photodeposited on the PbBiO₂I surface to improve the piezocatalytic performance [14,15]. The as-prepared Ag/PbBiO₂I performed excellent piezocatalytic efficiency for Rhodamine B (RhB) degradation under ultrasonic vibration. A systematic characterization was also performed to understand the nature of the enhanced piezocatalytic activity of the composite.

PbBiO₂I nanosheets were synthesized via a hydrothermal method based on the previous literature [13]. Ag/PbBiO₂I composite was prepared by a photodeposition method with AgNO₃ as Ag sources [16]. The piezocatalytic activities of the Ag/PbBiO₂I catalysts were evaluated by...
measuring the degradation rate of RhB solution (10 ppm) under ultrasonic vibration. The detailed information about the catalyst preparation, the piezocatalytic reaction, and the catalyst characterization was presented in the supplementary materials.

The crystal structure of the synthesized Ag/PbBiO$_2$I was investigated via XRD analysis (Fig. 1a). Pure PbBiO$_2$I presents strong diffraction peaks at 29.6, 31.3, 40.1, 44.7, 51.6, 54.6, 61.5, and 66.4°, corresponding to the (203), (210), (205), (020), (216), (223), (415), and (209) planes of orthorhombic structure of PbBiO$_2$I (PDF# 42-1105). Compared with the standard card, it can be noted that the peak corresponding to the (203) plane of the synthesized PbBiO$_2$I is much stronger, which indicates that the synthesized PbBiO$_2$I have special anisotropic growth along the (203) plane and may present a special morphology such as nanosheet or nanorod. Ag/PbBiO$_2$I composites present nearly the same XRD patterns as pure PbBiO$_2$I. The peak at 29.6° is slightly weakened. Nevertheless, the $I_{(203)}/I_{(205)}$ value is still very small, indicating that the photodeposition process shows little effect on the PbBiO$_2$I structure. No peak corresponding metal Ag is observed, which may be ascribed to the low concentration of Ag.

Compared with the XRD technique, XPS is more sensitive to the detection of the low-content phase. Hence, the Ag/PbBiO$_2$I with different Ag contents was investigated via XPS. The survey spectrum of PbBiO$_2$I shows that all signals of Pb, Bi, O, and I are detected (Fig. S1), confirming its elemental composition. For Ag/PbBiO$_2$I composite, in addition to the aforementioned elements, Ag signals are also detected. The high resolution XPS spectra of the Ag/PbBiO$_2$I composites indicate that the binding energy (BE) of Ag 3d$_{5/2}$ and 3d$_{3/2}$ are 368.0 and 374.0 eV (Fig. 1b), respectively, corresponding to metal Ag species [16]. This result definitely verifies that metal Ag nanoparticles are successfully loaded on the PbBiO$_2$I surface via the photodeposition method. As the increase of Ag theoretical concentration, the Ag 3d peak increases gradually. The real Ag contents are calculated to be 0.15%, 0.28%, and 0.36% for the Ag/PbBiO$_2$I with Ag contents of 0.1, 0.2, and 0.4%, respectively. The XPS spectra of Pb2p, Bi4f, O1s, and I3d are presented in Fig. S2. The BE of Pb4f$_{7/2}$, Bi4f$_{7/2}$, I3d$_{5/2}$, and O1s of PbBiO$_2$I are examined to be 137.0, 158.0, 618.2, and 528.6 eV, respectively (Table S1). Based on the reported literature [12–13,17], the valence states of Pb, Bi, I, and O are determined to be +2, +3, −1, and −2.

![Fig. 1. XRD patterns (a) and Ag 3d XPS spectra (b) of Ag/PbBiO$_2$I composite with different Ag contents, EDS element mapping (c) and TEM images (d, e) of 0.2%Ag/ PbBiO$_2$I composite.](image-url)
respectively, which is consistent with the structure of PbBiO$_2$I. The Ag/ PbBiO$_2$I samples present almost the same XPS spectra as pure PbBiO$_2$I, indicating that the deposition of metallic Ag does not change the valence state of the consisting elements of PbBiO$_2$I. However, it can be noted that the BE values of each element of the Ag/PbBiO$_2$I samples are slightly higher than that of pure PbBiO$_2$I, demonstrating that the electron density of the PbBiO$_2$I phase is reduced after the loading of metallic Ag. This phenomenon can be ascribed to the different work functions of Ag and PbBiO$_2$I. Metal Ag presents a higher work function than most semiconductors [18]. When metal Ag is closely contacted with PbBiO$_2$I, electron migration from the semiconductor to metal Ag would occur which leads to the decreased electron density around PbBiO$_2$I and the formation of a Schottky barrier in the Ag-PbBiO$_2$I contact region. This barrier is beneficial to the separation of electron-hole pairs in the composite [14–16].

The morphology and the microstructure of 0.2%Ag/PbBiO$_2$I are investigated via SEM and TEM. Pure PbBiO$_2$I mainly manifests the appearance of nanosheets with a size of 200–300 nm (Fig. S3 a and b), which is consistent with the inference based on the XRD patterns. The 0.2%Ag/PbBiO$_2$I sample presents the same appearance as pure PbBiO$_2$I, indicating that the photodeposition process shows little effect on the PbBiO$_2$I (Fig. S3c and d). No Ag particles are observed due to their small size. However, the EDS element mapping image clearly shows that the Ag element is uniformly dispersed on the PbBiO$_2$I surface, just like Pb, Bi, O, and I elements (Fig. 1c). The Ag atomic content is estimated to be 0.26%, which is close to the theoretical value and the XPS result. The TEM pictures of the 0.20%Ag/PbBiO$_2$I sample are shown in Fig. 1d and e. Some nanoparticles appear on the surface of PbBiO$_2$I nanosheets. A clear lattice fringe of 0.2296 nm and 0.7103 nm are observed in the nanoparticles and nanosheet, which can be assigned to the (111) plane of metal Ag and the (002) plane of PbBiO$_2$I, respectively. Similar interfaces between Ag nanoparticle and PbBiO$_2$I are also observed in other TEM images (Fig. S4), which definitely proves the successful deposition of Ag nanoparticles and the formation of the Ag/PbBiO$_2$I composite catalyst.

The locale piezoelectric response of the Ag/PbBiO$_2$I composite is investigated by the piezoelectric force microscope (PFM) technique. Fig. 2a–c display the atomic force microscope (AFM) image, PFM amplitude image, and PFM phase image of the 0.2%Ag/PbBiO$_2$I sample, respectively. The images do not provide the morphological information of the composite material as clear as SEM. Only several nanoparticles can be observed. However, the locale hysteresis loop (Fig. 2d) indicates these particles (0.2%Ag/PbBiO$_2$I sample) presents a phase angle change of about 150° under the reversal of 10 V DC bias field, indicating that the 0.2%Ag/PbBiO$_2$I composite has the piezoelectric property and can drive the piezoelectric catalytic reaction.

The charge separation efficiency is an important factor that influencing the photo/piezocatalytic reaction. A serial of electrochemical experiments was thus implemented to investigate the variation of charge separation in the Ag/PbBiO$_2$I composite. The transient photocurrent (PC) responses of PbBiO$_2$I and Ag/PbBiO$_2$I composites with different Ag contents are shown in Fig. 3a. Ag/PbBiO$_2$I composites possess much higher photocurrent than pure PbBiO$_2$I. 0.2% Ag/PbBiO$_2$I electrode presents the highest photocurrent, indicating its best charge separation ability [19–20]. Considering that the electron migration from PbBiO$_2$I to Ag is the main reason for the improved charge separation efficiency, the 0.2% Ag/PbBiO$_2$I sample may have a suitable Ag content, which leads to the most Schottky barriers in the composite and efficiently boosts the

![Fig. 2. The AFM picture (a), PFM amplitude image (b), PFM phase image (c), and hysteresis loop (d) of the prepared 0.2% Ag/PbBiO$_2$I composite.](image-url)
charge separation. A similar result is also obtained in the electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) analyses (Fig. S5).

Fig. 3b demonstrates the piezoelectric current response of PbBiO$_2$I and 0.2%Ag/PbBiO$_2$I composite. An obvious current response is observed under periodic ultrasonic vibration, confirming the piezoelectric property of the two samples. Nevertheless, the piezoelectric current is only about 0.1% of the photocurrent, which can be ascribed to the low content of the heat-excited free electrons in the samples. The 0.2%Ag/PbBiO$_2$I composite generates a higher piezoelectric current than PbBiO$_2$I, which definitely proves that the decoration of metal Ag improves the separation of piezoelectric induced charge carriers in the PbBiO$_2$I [21–22].

The piezocatalytic activity of the synthesized Ag/PbBiO$_2$I was evaluated via piezocatalytic degradation of RhB under ultrasonic vibration, and the result is shown in Fig. 3c. It can be seen that the RhB degraded under ultrasonic vibration can be ignored. In the presence of PbBiO$_2$I or Ag/PbBiO$_2$I, the RhB content is obviously reduced as the vibration time increases, indicating that the two samples can induce the piezocatalytic reaction, which is consistent with the PFM analysis. The degradation rate of PbBiO$_2$I is estimated to be 0.0024 min$^{-1}$ (Fig. S6a). The Ag/PbBiO$_2$I composite has a higher piezocatalytic activity than pure PbBiO$_2$I, indicating that there is a synergy effect of Ag and PbBiO$_2$I. The piezocatalytic activity of the Ag/PbBiO$_2$I composites (Fig. 3d). The good piezoelectric property of PbBiO$_2$I (Fig. 3d) can significantly improve the separation and utilization of free charge carriers, thereby increasing the piezocatalytic activity in RhB degradation.

In summary, Ag nanoparticles were uniformly loaded on the PbBiO$_2$I surface and formed Schottky barriers in the contact region, which endows the synthesized Ag/PbBiO$_2$I composite stronger electronic migration and separation capability than pure PbBiO$_2$I. Hence, the Ag/PbBiO$_2$I nanocomposite shows much higher efficiency in harvesting ultrasonic vibration energy for RhB degradation. In addition, the Ag/PbBiO$_2$I nanocomposites used as a piezocatalyst also maintains stable catalytic efficiency in cyclic test, indicating its high practical application potential in water purification.
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CRediT authorship contribution statement

Ziyu Li: Writing – original draft, Investigation, Formal analysis, Data curation. Qingle Zhang: Writing – original draft, Investigation, Data curation, Validation. Linkun Wang: Investigation. Jieyu Yang: Investigation. Ying Wu: Conceptualization, Resources, Methodology, Writing – review & editing. Yiming He: Conceptualization, Supervision, Project administration, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105729.

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