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BiOCI/ultrathin polyaniline core/shell nanosheets with a sensitization mechanism for efficient visible-lightdriven photocatalysis

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ABSTRACT Photocatalytic technology holds great promise in renewable energy and environmental protection. Herein, we report the synthesis of a class of polyaniline-sensitized BiOCl core/shell nanosheets with visible-light photocatalytic activity by a one-step oxidative polymerization method and show how the hybrid nanosheet boosts the photocatalytic activity and stability for degradation of Rhodamine B (RhB). In this unique structure, the ultrathin polyaniline (PANI) as a shell with the thickness of about 1-2 nm, can widen the response of the catalyst to visible light to boost photocatalysis and the BiOCl core can promote the separation of photogenerated carriers from the PANI. We demonstrate that the optimized BiOCl/ PANI core/shell photocatalyst shows nearly three times higher photocatalytic activity for the degradation of RhB than pure BiOCl and also shows high stability. This work provides a new strategy for the design of a highly efficient hybrid photocatalyst driven by visible light.

Keywords: BiOCl, core/shell, nanosheets, photocatalysis, polyaniline

INTRODUCTION

Since Fujishima and Honda reported a semiconducting TiO_2 photochemical electrode for splitting water in 1972 [1], the use of semiconductors as photocatalysts has been well established for the mineralization of organic pollutants [2]. In recent years, there has been a sharp growth in the organic pollutants of air, water, and soil, which are seriously harmful to human beings [3,4]. Therefore, research on developing a "green" method to degrade pollutants is attracting widespread attention. Many semiconductors, including oxides (TiO₂ [5,6] and ZnO

[7,8]), sulfides (CdS [9], ZnS [10], and MoS_2 [11]), halides (AgCl [12] and AgBr [13]), and other classes of semiconductors (g-C₃N₄ [14] and Ag₃PO₄ [15]), have been used in applications such as photocatalysis for the degradation of organic pollutants [16]. However, these semiconductors suffer from three major problems: low degradation efficiency, lack of stability, and high toxicity.

Recently, certain two-dimensional (2D) materials [17-19], particularly bismuth-based compounds, such as BiOX (where X is Cl, Br, or I) [20]Bi₂O₃ [21], and BiVO₄ [22], have been widely used in photocatalysis and have attracted attention for their high photocatalytic performance in the treatment of organic pollutants and nitrogen fixation in water [23,24]. In particular, 2D BiOX nanomaterials have gained more interest in recent years. However, BiOX nanomaterials often have a poor visiblelight response due to their wide bandgaps, which limits their solar-energy conversion efficiency. On the other hand, conducting polymers with extending π -conjugated electron systems, such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT), have shown great potential for applications because of their wide visible-light range, high charge mobility, and long-term stability [25-29]. Therefore, creating interface materials between BiOX and PANI may open up a brand-new opportunity for achieving much better photocatalytic performance. However, how to construct a BiOX-PANI interface is still a great challenge.

Herein, we report the synthesis of a class of BiOCl/ PANI core/ultrathin-shell nanosheets by a one-step oxidative polymerization of aniline on BiOCl nanosheets. In the core/shell nanosheets, PANI acts as the sensitization

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center, which absorbs visible light and produces the photogenerated charges. The BiOCl nanosheets can capture the photogenerated electrons from the PANI layer to activate O_2 . The ultrathin shell presented here is more efficient at bringing organic pollutants into contact with the catalyst. The optimized BiOCl/PANI core/shell nanosheets show excellent visible-light photocatalytic activity for the degradation of Rhodamine B (RhB) with their degradation efficiency reaching nearly 100% after 25 min—much better than pure BiOCl (PB). The present work highlights the importance of designing interfacial photocatalytic materials for boosting the photodegradation performance of pollutants.

EXPERIMENTAL SECTION

Materials

All chemicals were of analytical grade and were used without further treatment. Bi(NO₃)₃·5H₂O (99%) was obtained from Energy Chemical. Polyvinylpyrrolidone (PVP, $M_w = 58,000$) and mannitol were bought from Sinopharm Chemical Ceagent Co., Ltd. NaCl and aniline (99.5%) were purchased from Xilong Chemical Co.

Synthesis of BiOCl nanosheets

The BiOCl nanosheets were synthesized using a method proposed by Xiong *et al.* [30] with modification. Using this modified method, 0.278 g of mannitol was firstly dissolved in 12.5 mL of ultrapure water and stirred for 30 min at room temperature, followed by the addition of 0.20 g of PVP and 0.243 g of Bi(NO₃)₃·5H₂O. The mixture was stirred for 1 h, followed by the addition of 2.5 mL of saturated NaCl solution, yielding a uniform white suspension. The mixture was transferred into a 25-mL Te-flon-lined stainless-steel autoclave after stirring for 30 min and further heated to 160°C for 3 h. After cooling down naturally to room temperature, the prepared white BiOCl nanosheets were centrifuged and washed several times with ultrapure water and ethanol before finally being dried at 80°C overnight.

Synthesis of BiOCl/PANI core/shell nanosheets

The BiOCl/PANI nanosheets were synthesized using a hydrothermal method. Typically, 0.278 g of mannitol was dissolved into 12.5 mL of ultrapure water and stirred for 30 min at room temperature, followed by the addition of 0.20 g of PVP and 0.243 g of Bi(NO₃)₃·5H₂O. The mixture was stirred for 1 h, followed by the addition of 2.5 mL of saturated NaCl solution and aniline solution (where the aniline solution was at 0, 0.5, 1, and 1.5 wt%, relative to

Bi(NO₃)₃·5H₂O, and the obtained samples are consequently named as PB, PB-0.5, PB-1, and PB-1.5, respectively). After being stirred for 30 min, the mixture was transferred into a 25-mL Teflon-lined stainless-steel autoclave and then heated at 160°C for 3 h in an oven. After the reaction, the autoclave was cooled naturally to room temperature. The as-prepared white BiOCl/PANI nanosheets were centrifuged and washed several times with ultrapure water and ethanol before finally being dried at 80°C overnight.

Characterization

X-ray diffraction (XRD) patterns were recorded using a PANalytical X-ray diffractometer that used Cu Ka radiation ($\lambda = 1.5406$ Å). UV-vis diffuse reflectance spectra (DRS) of the samples were carried out at room temperature using the Hitachi spectrophotometer UH4150. The structural information of the samples was measured using a Fourier transform infrared (FTIR) spectrometer (ThermoFisher Nicolet iS50). The spectrum was collected over the wavenumber range of 4,000 to 400 cm⁻¹. Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi SU8010 scanning electron microscope. Transmission electron microscopy (TEM) images were taken using a Hitachi HT7700 transmission electron microscope operated at an acceleration voltage of 100 kV. High-resolution TEM (HRTEM) and corresponding selected area electron diffraction (SAED) analyses were carried out using a JEM-2100F field emission transmission electron microscope (FE-TEM) at an acceleration voltage of 200 kV.

Photocatalytic measurement

The photocatalytic activity of the BiOCl/PANI samples was evaluated by measuring the degradation of RhB. A 300-W Xe lamp (MICROSOLAR300, Park Philae Technology Co., Ltd., Beijing) served as the light source and a glass filter was added to allow visible light ($\lambda > 420$ nm) to pass through. In a typical experiment, 5 mg of the PB photocatalyst was dispersed into the solution of RhB (100 mL, 3 mg L^{-1}). Before the measurement, the suspensions were stirred for 60 min in the dark to reach adsorption-desorption equilibrium. For each suspension, 5 mL was withdrawn every 5 min under irradiation and centrifuged to remove the catalyst. The degraded solutions were analyzed by their UV-vis absorption spectra. The characteristic absorbance of RhB at 550 nm was used to describe the measure of RhB present in the solution. The catalyst was used in three cycles. After each cycle, the sample was washed with deionized water three times and



Figure 1 (a) XRD patterns of the as-synthesized BiOCl/PANI photocatalysts: PB, PB-0.5, PB-1 and PB-1.5. (b) FT-IR spectrum of PANI, PB and PB-1. (c) UV-vis DRS of PB and PB-1 composite.

then dried in a 60°C oven before the next test.

RESULTS AND DISCUSSION

The composition and phase purity of the synthesized BiOCl and BiOCl/PANI core/shell nanosheets were confirmed by XRD analysis. The as-prepared BiOCl nanosheets show diffraction peaks at 12.9°, 16. 3°, and 16.7° (Fig. 1a), ascribed to the (001), (101), and (102) lattice planes of the tetragonal structure of BiOCl, respectively (JCPDS card No: 06-0249). The enhanced relative intensity of the (110) peak clearly reveals a highly preferred (110) orientation in the BiOCl nanosheets. The FTIR spectrum of PANI in Fig. 1b shows characteristic peaks at $1,553 \text{ cm}^{-1}$ (C=C stretching mode for the quinonoid unit), 1,485 cm⁻¹ (C=C stretching mode for the benzenoid unit), 1,288 and 1,215 cm⁻¹ (C-N stretching mode of the benzenoid unit), and 1,100 cm⁻¹ (a plane-bending vibration of C-H). For the FTIR spectrum of PB-1, peaks aligning with the characteristic peaks of PANI at 1,553, 1,485, 1,288, 1,215, and 1,100 cm⁻¹ are observed [31], proving the existence of PANI in the PB-1 composite. The absorbance peak of BiOCl at 511 cm⁻¹ is also observed in the PB-1 composite (Fig. 1b) [32]. The color of the catalyst varies with the addition of aniline: with increasing content of aniline, the color of the samples changes from white to gray (inset of Fig. 1c). Fig. 1c shows the UV-vis DRS spectra of the prepared PB and PB-1 composites. The optical absorbance band edge of PB-1 shows a red shift relative to that of PB. Thus, it can be deduced that the presence of PANI significantly affects the visible-light absorption of BiOCl/PANI. The band-gap energies of PB-1 and PB, estimated from a plot of $(\alpha h v)^{1/2}$ versus the photon energy (hv) [33], are approximately 3.25 and 2.8 eV, respectively (Supplementary information (SI) Fig. S1). The narrower band-gap energy of the PB-1 catalyst demonstrates that it has an enhanced visible-light response.

X-ray photoelectron spectroscopy (XPS) is an important technique for studying the electronic structure of condensed matter and is widely used for quantitative surface analysis. The XPS survey spectrum in Fig. S2a shows that BiOCl/PANI is primarily composed of bismuth, oxygen, chlorine, carbon, and nitrogen. The two characteristic peaks for Bi 4f, located at 164.2 and 158.9 eV in Fig. S2b, are attributed to Bi $4f_{5/2}$ and Bi $4f_{7/2}$, respectively, corresponding to Bi³⁺ in the crystal structure [34]. On the other hand, the peaks at 539.6 and 531.4 eV (Fig. S2c) can be ascribed to the oxygen in BiOCl. For the

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Figure 2 (a) SEM and (b) AFM images of PB and (c) PB-1.

spectra of Cl 2p (Fig. S2d), the peaks with binding energies at 197.6 and 199.2 eV are ascribed to Cl $2p_{3/2}$ and Cl $2p_{1/2}$, respectively, characteristic of Cl⁻ [35]. In the C 1s spectrum of Fig. S2e, three peaks are observed at 284.8, 285.8, and 287.6 eV. The first peak, at 284.5 eV, is attributed to C atoms bound only to other C atoms or H atoms. Two other peaks correspond to the chemical groups of C–N and C=N of PANI, respectively. Fig. S2f shows that N atoms exists in PB at binding energies of 399.4 and 400.1 eV. These results suggest that PANI is coated on the BiOCl surface [36,37].

Fig. 2a shows an SEM image of the as-prepared PB-1 with a thickness of 10-12 nm. In an effort to assess the thickness of PB, the sample was taken to the ambient environment of an atom force microscope (AFM) where imaging was performed at multiple locations across the sample. From the AFM images (Fig. 2b, c), it can be seen that the sample had the morphology of nanoplates and its thickness was determined to be 12-14 nm by its height profile, which suggests that PANI is coated on the BiOCl surface with a thickness of about 1-2 nm. An energydispersive X-ray (EDX) spectrum of PB-1 is shown in Fig. S3. The composite materials obtained were composed of the elements of bismuth, chlorine, oxygen, carbon, nitrogen, and aluminum (the Al peaks come from the supporting aluminum grid). Therefore, the EDX results further demonstrate that PANI is coated on the surface of BiOCl. Fig. 3a shows an HRTEM image of PB-1. Fig. 3b exhibits distinct lattice fringes of the BiOCl nanosheets, corresponding to the (110) crystal lattice plane of BiOCl. The angle between adjacent spots labeled in the SAED pattern (Fig. 3c) is 45°, identical to the theoretical value of the angle between the (110) and (200) lattice planes of tetragonal BiOCl. Additionally, the distinct lattice fringe with an interplanar lattice spacing of 0.275 nm (Fig. 3b) indicates that PB nanosheets are exposed with (001) facets. Furthermore, the edge or thickness of the BiOCl/ polyaniline core/shell nanoplates can be tuned by changing the amount of aniline added (Fig. 3d-g). The photocatalytic activity of the BiOCl/PANI core/shell nanosheets was investigated by degrading RhB under



Figure 3 (a) TEM, (b) HRTEM and (c) SAED pattern images of the PB-1. TEM images of (d) PB, (e) PB-0.5, (f) PB-1 and (g) PB-1.5.

visible-light irradiation.

The degradation activity for RhB with different photocatalysts is displayed in Fig. 4a. No photodegradation activity is observed in the absence of a catalyst of any sort. Out of all of the samples, the PB-1 nanocomposite exhibits the best visible-light photocatalytic activity toward the degradation of RhB. After 25 min of irradiation, RhB is almost completely degraded with a photocatalytic conversion ratio of 99%. The specific surface areas of PB and PB-1 are similar (Fig. S4), and the Brunauer-Emmett-Teller (BET) normalized degradation rates are determined to be 20.4%/m²g and 39.6%/m²g, respectively. However, for the PB, it is found that the photocatalytic conversion ratio of RhB is only 55% under the same conditions. To further study the photodegradation process of RhB, the UV-vis spectra and the colors of the RhB aqueous solution, as a function of visible-light irradiation time in the presence of photocatalysts, are illustrated in Fig. S5. It can be seen from the UV-vis spectra changes



Figure 4 (a) Photocatalytic degradation activity for different catalysts. (b, c) Cycling curve of (b) PB-1 and (c) PB.

that the strong absorption peak at 554 nm for the RhB solution steadily decreases and shows a blueshift with increasing irradiation time. The initial orange color of the solution gradually turned to transparent because the RhB was photodegraded to intermediates under the visible-light irradiation and then the intermediates were themselves partially photodegraded [38]. This further indicates that the BiOCl/PANI composites exhibit excellent photocatalytic activity for RhB decomposition under visible-light irradiation.

Kinetic plots and corresponding kinetic constants (*k*) are given in Fig. S5. The photodegradation process is fitted for pseudo first-order kinetics by linear transforms of $\ln(C_0/C_t) = kt$, where C_0 is the adsorption equilibrium concentration of RhB, C_t is the concentration of RhB at time *t*, and the apparent rate constant, *k*, is 0.0357, 0.0823, 0.1532, and 0.0369 for PB, PB-0.5, PB-1, and PB-1.5, respectively. The removal efficiency of PB-1 is much faster than other samples, in agreement with the results in Fig. 4a.

PB-1 shows a good stability for the degradation of RhB (Fig. 4b). After each run of three runs of the degradation reaction, the photocatalytic conversion ratio of RhB for PB-1 exhibits a similar degradation rate under visible

light. However, under the same condition, PB exhibits a decrease in the photocatalytic conversion ratio from 75% in the first cycle to less than 60% after the third cycle (Fig. 4c). The unstable RhB degradation performance of BiOCl nanosheets can be ascribed to the blockage of photocatalytic active sites by the strong adsorption of the dye intermediate [39]. To further investigate the photodegradation stability of the PB-1 photocatalyst, the XRD patterns of the photocatalyst before and after light irradiation were also analyzed, confirming its structure stability (Fig. S6). This indirectly verifies that the PANI exists in a very stable form on the surface of the BiOCl after reaction, in agreement with the results of the FTIR spectra of the PB-1 before and after irradiation. Therefore, this illustrates that the presence of PANI not only enhances the photocatalytic activity of PB in the degradation of organic dye pollutants but also exhibits excellent photocatalytic stability in the visible-light range.

Both BiOCl and BiOCl/PANI show photocatalytic activity under visible-light irradiation, but BiOCl/PANI shows much better photocatalytic performance for the degradation of RhB. The various types of dyes have different molecular structures, resulting in different degradation mechanisms [40]. The photocatalytic



Figure 5 Schematic illustration of the proposed photocatalytic mechanism of PB-1 under visible light irradiation.

mechanism of the BiOCl/PANI composites is illustrated in Fig. 5. The PANI and BiOCl have similar energy levels. The energy levels of PANI and BiOCl follow an order of $E_{\text{LUMO}} > E_{\text{CB}} > E_{\text{HOMO}} > E_{\text{VB}}$ [41]. Under visible-light irradiation, the PANI absorbs visible light and produces photogenerated electrons and holes. Although BiOCl, with a band gap of 3.2 eV, cannot absorb visible light, the photogenerated electrons can be spontaneously transferred into the conduction band (CB) of BiOCl. Then, the BiOCl can use the captured electrons to reduce O₂ into $\cdot O_2^{-}$, a highly active oxidant for degrading RhB. As there are holes left in the HOMO of PANI, the OH⁻ can react with them to produce ·OH, also contributing to the degradation of RhB [42,43]. Besides, it is possible that the holes in the HOMO of PANI can directly degrade RhB. It is proposed that a PANI-sensitized photocatalytic reaction mechanism occurs on the BiOCl/PANI core/shell nanoplates. The detailed generation and transfer mechanisms of photogenerated carriers in the BiOCl/PANI and PB are shown in Figs S7 and S8.

CONCLUSIONS

To summarize, we have demonstrated a simple method for making a class of BiOCl/PANI core/shell nanosheets as a highly efficient visible-light-driven photocatalyst for greatly enhancing the degradation efficiency of RhB. Our unique design takes advantage of the BiOCl nanosheets' structural feature, promoting the effective separation of the photoinduced electron-hole pairs from the PANI, while also providing a highly active surface for the degradation of RhB under visible light. The optimized PB-1 photocatalyst shows a catalytic activity for the degradation of RhB that is three times higher than that of PB and also exhibits enhanced photocatalytic stability. The present work highlights that the existence of a thin PANI shell on BiOCl nanosheets can not only lead to new possibilities for highly efficient photocatalysts under visible light, but can also provide a new strategy for improving the stability of photocatalysts.

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Author contributions Li H and Guo S designed and engineered this work; Tang Y performed the experiments and wrote the paper with support from Zhou P. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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一种光驱动下具有敏化性能的氯氧化铋/超薄聚苯胺核壳纳米片结构

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摘要 光催化技术在可再生能源和环境保护方面有巨大的潜力.本文通过一步氧化聚合法合成了一种超薄聚苯胺壳敏化氯氧化铋核纳米 片结构.该结构中约1-2纳米厚的超薄聚苯胺壳可以促进催化剂对可见光的响应,氯氧化铋核可以促进聚苯胺中光生载流子的分离,在可 见光驱动下对于降解罗丹明B具有较高的光催化活性和稳定性.优化后的氯氧化铋/超薄聚苯胺核壳催化剂的光催化降解罗丹明B的活性 比纯氯氧化铋高出近三倍,且稳定性更高.本工作为设计可见光驱动的高效混合光催化剂提供了一种新的策略.