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Article

Novel SiO₂ nanoparticle-decorated BiOCl nanosheets exhibiting high photocatalytic performances for the removal of organic pollutants

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ARTICLE INFO

Article history:

Received 23 January 2019

Accepted 20 March 2019

Published 5 August 2019

Keywords:

SiO₂/BiOCl

Nanosheets

Organic pollutant

Photocatalysis

Interface

ABSTRACT

Novel SiO₂/BiOCl composites were fabricated by decorating BiOCl nanosheets with SiO₂ nanoparticles via a simple hydrothermal process. The as-prepared pure BiOCl and SiO₂/BiOCl composites were intensively characterized by various techniques such as XRD, FT-IR, SEM/TEM, BET, UV-vis, DRS, XPS, and photocurrent measurements. The SiO₂/BiOCl composite nanosheets displayed high photocatalytic activity and excellent stability in the degradation of organic pollutants such as phenol, bisphenol A (BPA), and rhodamine B (RhB). With respect to those over bare BiOCl, the degradation rates of RhB, BPA, and phenol over 1.88% SiO₂/BiOCl increased 16.5%, 29.0%, and 38.7%, respectively. Radical capturing results suggested that h⁺ is the major reactive species and that hydroxyl (•OH) and superoxide (•O₂⁻) radicals could also be involved in the degradation of organic pollutants. The enhanced photocatalytic performances of SiO₂/BiOCl composites can be mainly attributed to the improved texture and the formation of intimate SiO₂/BiOCl interfaces, which largely promoted the adsorption of organic pollutants, enhanced the light harvesting, and accelerated the separation of e⁻ and h⁺.

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1. Introduction

The organic pollutants in water have become a major source of environmental pollution in waste fields. Organic pollutants

such as phenol, bisphenol A, and dyes may cause various adverse effects on aquatic organisms even at low exposure levels. For example, bisphenol A (2,2-bis(4-hydroxyphenyl)propane; BPA) is a key building block of epoxy and polycarbonate resins

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We acknowledged the funding from the National Natural Science Foundation of China (21567008, 21707055), the Program for Innovative Research Team of Guangdong University of Petrochemical Technology, the Yangfan talents Project of Guangdong Province, the Innovation-driven “5511” Program in Jiangxi Province (20165BCB18014), the Funding Program for Academic and Technological Leaders of Major Disciplines in Jiangxi Province (20172BCB22018), the Program for New Century Excellent Talents in Fujian Province University, and the Natural Science Foundation for Distinguished Young Scholars of Hunan Province, China (2017JJ1026).

DOI: S1872-2067(19)63359-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 8, August 2019

and has been widely used in commercial products. A large amount of BPA has been released into the aquatic environment [1]. However, it is a typical endocrine-disrupting chemical. The organic pollutants are difficult to eliminate through conventional water treatment technologies. They can only be decomposed slowly by acids, alkalis, heating, or employing biological methods. Therefore, identifying the optimal way to handle organic pollutants in wastewater is an important issue for environmental protection [2–7]. Photocatalytic degradation, as an advanced oxidation technology, is one of the most promising methods for the degradation of organic pollutants owing to its extremely high degradation rate, high mineralization efficiency, and low toxigenicity, and ideal production of CO_2 and H_2O as the end-products [8–13].

Although great progress has been made in photocatalysis in the past few decades, most of the current photocatalysts cannot meet the requirements for practical wastewater treatment or other environmental purifications. There are two main problems that largely limit the large-scale application of photocatalysis. One is the low quantum efficiency of the photocatalytic reaction, attributable to the high recombination probability of the photogenerated electrons (e^-) and holes (h^+). Due to this, in a heterogeneous photocatalytic process, most of the photogenerated e^- and h^+ will recombine in the bulk to produce thermal energy and only a few of them will migrate to the surface and react with the species adsorbed over the surface of a photocatalyst to induce a series of oxidative reactions. Another problem is that most of the developed photocatalysts are semiconductors having large bandgaps, which implies that light of short wavelengths is required to initiate the formation of e^-h^+ pairs. For example, the most frequently employed TiO_2 photocatalyst has a large bandgap of ~ 3.2 eV. Therefore, wavelengths below 400 nm are necessary for excitation and only a small UV fraction of solar light, approximately 2%–3%, can be utilized, which considerably restricts the use of natural solar light or artificial visible light.

Therefore, in the past few decades, in order to overcome these drawbacks, much efforts have been devoted to designing and fabricating highly efficient photocatalysts with novel structures [14–21]. Among the numerous photocatalysts, Bi-based photocatalytic materials, e.g., Bi_2O_3 [22,23], Bi_2S_3 [24,25], Bi_2WO_6 [26–28], bismuth oxyhalide (BiOX , $X = \text{Cl}$, Br , and I) [29–34], and BiPO_4 [35], have been given much importance. BiOCl is a white-colored ecofriendly semiconductor that exhibits an anisotropic layered structure. Under UV light irradiation, it can display pronounced photocatalytic activity. However, the photocatalytic efficiency of pure BiOCl is relatively low and the recombination probability of its photogenerated e^-h^+ is very high [36]. To increase the photocatalytic efficiency of BiOCl , different BiOCl -based composite systems have been developed by applying bandgap engineering. Recently, Zhang et al. [37] reported a novel attapulgite- BiOCl - TiO_2 photocatalyst fabricated by a simple in situ deposition technique. This environmentally friendly composite photocatalyst displayed efficient UV and visible light activity for the degradation of methyl orange (MO). Another $\text{BiPO}_4/\text{BiOCl}$ heterojunction composite was prepared via a facile one-step hydrothermal

method [38]. This $\text{BiPO}_4/\text{BiOCl}$ composite exhibited a much higher photocatalytic activity for MO degradation than single BiOCl and BiPO_4 under simulated sunlight irradiation. The large enhancement in the photocatalytic activity could be mainly ascribed to the surface junction of $\text{BiPO}_4/\text{BiOCl}$, which can effectively increase the e^-h^+ separation speed during the photocatalytic process. Besides, the coupling of other materials with BiOCl , e.g., C_3N_4 [39], graphene oxide [40], and BiVO_4 [41], can significantly enhance its photocatalytic activities for the degradation of various pollutants.

With the aim of developing BiOCl as an efficient photocatalyst for the degradation of OPs, we prepared $\text{SiO}_2/\text{BiOCl}$ composite nanosheets by the facile hydrothermal process. The photocatalytic performances of $\text{SiO}_2/\text{BiOCl}$ for the degradation of BPA, phenol, and rhodamine B (RhB) were remarkably enhanced after the SiO_2 coupling. Furthermore, the role of the SiO_2 coupling in promoting the photocatalytic activity and stability was revealed based on the results of various physicochemical characterization techniques and analysis of the radical species involved in the reaction. This work reveals that the coupling of SiO_2 is a versatile method of improving the photocatalytic efficiency of BiOCl for the degradation of organic pollutants that would be helpful in the development of large bandgap semiconductors as efficient photocatalytic materials.

2. Experimental

2.1. Synthesis of the catalyst materials

For the preparation of SiO_2 NPs, 20 mL tetraethyl orthosilicate was dissolved in 100 mL absolute ethyl alcohol with constant stirring to obtain solution A. Further, 20 mL ammonium hydroxide and 40 mL deionized (DI) water were dissolved in 100 mL absolute ethyl alcohol, and the resulting solution was added dropwise to solution A at 45 °C. Then, the produced suspensions were further stirred for 3 h at constant temperature, and the resulting powder was collected by filtration, before being washed with DI water and ethanol several times. Finally, the SiO_2 NPs (Fig. S1) were obtained after drying at 100 °C for 8 h.

For sonication, different amounts of SiO_2 NPs (0.01, 0.025, and 0.05 g) and 5 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dispersed in the as-prepared solution (16 mL absolute ethyl alcohol and 32 mL DI water). Furthermore, 5 mmol NaCl was dissolved in 32 mL DI water, and the resulting solution was added dropwise to the above solution. The suspension solution was poured into a Teflon-lined autoclave after stirring for 5 h, before being heated to 140 °C for 14 h. After cooling to room temperature, the solvent was removed by filtration, and the catalyst was washed alternately with DI water and ethanol several times, before it was dried at 100 °C for 5 h to obtain the product. The catalyst loaded with x wt% SiO_2 was denoted as $x\%\text{SiO}_2/\text{BiOCl}$. Under the condition of no SiO_2 , pure BiOCl was synthesized using the abovementioned method.

2.2. Catalyst characterization

The physicochemical properties of the as-prepared catalyst materials were intensively characterized by various techniques such as N₂ physical adsorption (BET; Micromeritics ASAP 2020 physical adsorption apparatus), X-ray diffraction (XRD; Bruker D8 advance X-ray diffractometer), scanning electron microscopy (SEM; MLA650F scanning electron microscope), transmission electron microscopy (TEM; TECNAI G2F20 microscope), Fourier transform infrared spectroscopy (FT-IR; ALPHA FT-IR spectrometer), UV-visible diffuse reflectance spectroscopy (UV-vis DRS; UV-2550 UV-vis spectrophotometer), X-ray photoelectron spectroscopy (XPS; ESCALAB 250 XPS system), and photoelectrochemistry measurements (photocurrent, CHI660E electrochemical work station). Further details are provided in Supplementary Information.

2.3. Photocatalytic performance

Different organic pollutants such as BPA, phenol, and RhB were used as the degradation targets to evaluate the photocatalytic activities of the as-prepared catalyst materials. The photocatalytic reaction was carried out in an XPA photochemical reactor purchased from Nangjing Xujiang Electromechanical Plant. Specifically, 20 mg of the catalyst was dispersed in 50 mL of 20 mg·L⁻¹ aqueous BPA or phenol solution by magnetic stirring in the dark for 40 min prior to 300 W irradiation using a mercury lamp. Taking ~2 mL aliquots of the suspension at regular intervals, the solids were removed by high-speed centrifugation. The concentration of contaminants in the clear upper layer was determined by UV-vis spectrophotometry. In RhB degradation, a 350 W xenon lamp (simulated sunlight) was applied as the light source. Here, 20 mg of the as-prepared samples was added to 50 mL of aqueous RhB solution (concentration: 20 mg·L⁻¹).

3. Results and discussion

3.1. Materials characterization

The XRD patterns of the BiOCl and SiO₂/BiOCl samples are shown in Fig. 1a. The main characteristic peaks of BiOCl at 12.0°, 24.1°, 25.9°, 32.5°, 33.5°, 40.9°, 46.7°, 49.7°, 54.1°, 55.1°, and 58.6° can be indexed to the (001), (002), (101), (110), (102), (112), (200), (113), (211), (104), and (212) crystal planes of BiOCl (JCPDS no. 85-0861, lattice constants $a = b =$

Table 1

Average crystallite sizes and specific surface areas of the samples.

Sample	Specific surface area (m ² ·g ⁻¹)	Crystallite size (nm)
BiOCl	4.62	45.28
0.76%SiO ₂ /BiOCl	11.51	38.75
1.88%SiO ₂ /BiOCl	13.79	41.54
3.69%SiO ₂ /BiOCl	15.56	43.81

3.890 Å and $c = 7.370$ Å), respectively, and no other impurity phases are detected, indicating that pure tetragonal BiOCl phase has been obtained. Though the sample also contained trace SiO₂ (0.76%), no characteristic diffraction peaks of SiO₂ are observed for the 0.76%SiO₂/BiOCl composite. However, weak diffraction peaks at 22.2° can be observed for 1.88%SiO₂/BiOCl and 3.69%SiO₂/BiOCl. These peaks are indexed to the (020) plane of monoclinic SiO₂ with the space group C₂ (lattice parameters: $a = 6.621$ Å, $b = 7.996$ Å, and $c = 5.412$ Å), indicating the presence of the SiO₂ phase in the SiO₂/BiOCl composite. Fig. 1b compares the relative strengths of the (110) and (102) crystal planes. Interestingly, a comparison revealed that 1.88%SiO₂/BiOCl exhibited the highest exposure percentage of the (110) crystal plane. The average crystallite size of the as-prepared catalysts was calculated using the Scherrer equation. Table 1 summarizes the obtained results. Pure BiOCl and 3.69%SiO₂/BiOCl display similar average crystallite sizes: 45.28 nm for pure BiOCl and 43.81 nm for 3.69%SiO₂/BiOCl. Coupling of trace amounts of SiO₂ (0.76% and 1.88%) slightly decreases the average crystallite size. In general, the introduction of SiO₂ had little effect on the average crystallite size of BiOCl.

In order to further characterize the surface chemical bond information of SiO₂, BiOCl, and 1.88%SiO₂/BiOCl composite samples, FT-IR spectrum analysis was carried out, and the results are presented in Fig. 1c. The absorption peak at 528.7 cm⁻¹ is attributed to the typical stretching vibrations of Bi–O [42]. For SiO₂ and 1.88%SiO₂/BiOCl, the characteristic peak observed at 1090.3 cm⁻¹ is attributed to the typical stretching vibrations of Si–O–Si [43]. It further reveals the coexistence of SiO₂ and BiOCl (hybrid) phases in the obtained SiO₂/BiOCl composite.

The SEM and TEM images of the typical samples, BiOCl and 1.88%SiO₂/BiOCl, are shown in Fig. 2. No distinct difference is observed between the BiOCl (Fig. 2a and 2b) and

Fig. 1. (a, b) XRD patterns of BiOCl and SiO₂/BiOCl samples; (c) FT-IR spectra of BiOCl, SiO₂, and 1.88%SiO₂/BiOCl samples.

Fig. 2. (a, b) SEM images of BiOCl; (c) Low-magnification TEM image, (d) HRTEM image, and (e) FFT pattern of 1.88%SiO₂/BiOCl; (f) EDX spectrum of 1.88%SiO₂/BiOCl.

1.88%SiO₂/BiOCl (Fig. 2c) samples. Both samples are composed of nanosheet particles with diameters 200–300 nm and thickness 30–40 nm. In the high-resolution (HR) TEM image (Fig. 2d) of 1.88%SiO₂/BiOCl, two clear lattice spacings are identified. One interplanar spacing is about 0.275 nm, which corresponds to the (110) crystallographic plane of BiOCl. Another small lattice fringe with the spacing of 0.399 nm matches with that of the (020) crystal plane of SiO₂. These confirmed the coexistence of BiOCl and SiO₂ crystal phases, with close integration of both in 1.88%SiO₂/BiOCl. The spot points confirmed

that (110) is the main growth plane (Fig. 2e), which is in agreement with the XRD observations. The EDX spectrum of 1.88%SiO₂/BiOCl is shown in Fig. 2f; the elements bismuth, chlorine, oxygen, and silicon are attributed to BiOCl and SiO₂. In addition, except for copper, which originated from the tested copper net, no other elements were detected, which indicated the high purity of 1.88%SiO₂/BiOCl.

The chemical composition of the 1.88%SiO₂/BiOCl photocatalyst was investigated by XPS analysis. In Fig. 3a, the Bi 4f XPS pattern displays peaks at the binding energies of 164.8

Fig. 3. XPS spectra of the as-prepared 1.88%SiO₂/BiOCl sample. (a) Bi 4f, (b) O 1s, (c) Cl 2p, (d) Si 2p.

Fig. 4. N_2 adsorption and desorption isotherms of (a) BiOCl and (b) 1.88%SiO₂/BiOCl. Insets: the corresponding pore size distributions.

(166.1) and 159.6 (160.9) eV, which correspond to Bi 4f_{5/2} and Bi 4f_{7/2}, respectively, of the Bi³⁺ in BiOCl [44]. There are two different oxygen species present on the surface of the SiO₂/BiOCl composite sample (Fig. 3b). The peak at 532.9 eV is due to the Bi–O bond in BiOCl, whereas the peak at 530.9 eV corresponds to the surface hydroxyl groups on 1.88%SiO₂/BiOCl [45]. The binding energies of Cl 2p at 199.7 and 198.2 eV can be assigned to Cl[−] as Cl 2p_{1/2} and Cl 2p_{3/2}, respectively (Fig. 3c). Fig. 3d shows the Si 2p spectrum and the two peaks at 104.5 and 103.6 eV are assigned to Si 2p_{1/2} and Si 2p_{3/2}, respectively, of the Si⁴⁺ in SiO₂.

The BET specific surface areas of BiOCl and SiO₂/BiOCl composites were investigated with the help of N₂ adsorption and desorption isotherms (Fig. 4). The corresponding pore size distributions of the samples have also been inserted in Fig. 4; no narrow pore size distribution was observed, suggesting the presence of irregular pores in the fabricated samples. The BET surface areas (S_{BET}) of the different catalysts are listed in Table 1. The specific surface area of BiOCl is extremely small, 4.62 m²·g^{−1}. However, 0.76%SiO₂/BiOCl, 1.88%SiO₂/BiOCl, and 3.69%SiO₂/BiOCl exhibit relatively high specific surface areas (11.51 to 15.56 m²·g^{−1}). Large surface areas of photocatalysts inevitably favor the adsorption of reaction substrates and facilitate light harvesting in aqueous suspension systems, which lead to enhancements in the photocatalytic performances.

UV-vis DRS was applied to analyze the optical absorptions of the as-prepared samples. As clearly observed in Fig. 5a, the spectra of pure BiOCl and SiO₂/BiOCl display almost the same absorption edge at ~370 nm, corresponding to the bandgap energy (E_g) of 3.35 eV, which was calculated by Kubelka-Munk

method [46]. Pure SiO₂ displays weak light absorption in the UV and visible light range (Fig. S2). Analogous crystal structures and morphologies might result in all the as-prepared samples possessing similar band structures [47]. It was observed that BiOCl and SiO₂/BiOCl revealed strong light absorption ability in the UV wavelength range; in particular, 0.76%SiO₂/BiOCl and 1.88%SiO₂/BiOCl displayed slightly stronger light absorption ability in the UV range.

Transient photocurrent response was used to analyze the charge separation efficiencies of the photocatalysts. Fig. 5b shows a comparison of the I - t curves of the BiOCl and 1.88%SiO₂/BiOCl samples for several on-off cycles under intermittent xenon lamp light irradiation. The 1.88%SiO₂/BiOCl sample exhibited ~4 times higher photocurrent intensity than BiOCl, which suggested that the composite interface accelerated the migration of the photogenerated e[−]. Furthermore, peak photocurrent density ($I(\max)$) was observed in the samples when light was turned on, and, when light was turned off, the photocurrent density rapidly decayed to its trough value ($I(ss)$). Here, the apparent surface-recombination probability (SPR) of photogenerated e[−]-h⁺ could be calculated based on the formula $SPR = [I(\max) - I(ss)]/I(\max)$ [48], and the calculated values are summarized in Table 2. The SPR of BiOCl is 42.4%, which is higher than that of 1.88%SiO₂/BiOCl (21.2%), indicating that the utilization ratio of e[−] and h⁺ over 1.88%SiO₂/BiOCl is about 56% higher than that over BiOCl. This result revealed that over 1.88%SiO₂/BiOCl, a distinct improvement in e[−]-h⁺ separation was obtained.

Fig. 5. (a) UV-vis diffuse reflectance spectra of BiOCl and SiO₂/BiOCl samples; (b) Photocurrent densities obtained under simulated solar light irradiation (with a xenon lamp) for BiOCl and 1.88%SiO₂/BiOCl samples.

Table 2

Values of the peak photocurrent densities ($I(\max)$) and transient photocurrent densities ($I(ss)$), and the apparent surface-recombination probabilities of BiOCl and 1.88%SiO₂/BiOCl samples.

Sample	$I(\max)$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	$I(ss)$ ($\mu\text{A}\cdot\text{cm}^{-2}$)	SPR (%)
BiOCl	0.132	0.076	42.4
1.88%SiO ₂ /BiOCl	0.485	0.382	21.2

3.2. Performance test

Phenol and BPA were first used as the photodegradation model organic pollutants under mercury lamp illumination. From the degradation curves of phenol (Fig. 6a) and BPA (Fig. 6c), we can see that pure BiOCl exhibits a very low photocatalytic activity. Nevertheless, the coupling of SiO₂ distinctly enhanced the photocatalytic activity, and the largest degradation rates of phenol (83.3%) and BPA (88.9%) were observed over 1.88%SiO₂/BiOCl (Fig. 6d). With respect to BiOCl, the degradation rates of phenol and BPA increased 38.7% and 29.0%, respectively. In Fig. 6b, the characteristic peak of 270 nm corresponded to phenol, which indicated that 1.88%SiO₂/BiOCl showed good photocatalytic activity for the degradation of phenol.

In addition, we evaluated the photocatalytic activities of the SiO₂/BiOCl composite materials for the degradation of RhB dye. Fig. 7a displays the changes in the concentration of RhB for different xenon lamp illumination times, whereas Fig. 7b presents the corresponding RhB degradation rates after 100 min illumination. It was found that the coupling of SiO₂ into BiOCl

greatly enhanced its photocatalytic activity. In particular, 1.88%SiO₂/BiOCl showed the highest photocatalytic activity. Fig. 7c exhibits the degradation dynamic curves of RhB; the maximal rate constant of RhB degradation over 1.88%SiO₂/BiOCl reaches 0.012 min⁻¹, which is 1.7 times that over pure BiOCl (0.007 min⁻¹). Furthermore, the photocatalytic activity of SiO₂/BiOCl for RhB degradation could be increased in weakly acidic conditions (Fig. S3).

From the viewpoint of practical application, good renewable photostability of a material is the precondition for its industrial application. Therefore, the stabilities of BiOCl and 1.88%SiO₂/BiOCl samples in the photodegradation of RhB were tested by recycling them in the photocatalytic reactions. The photocatalysts were recycled by centrifugation and reused under the same conditions. Fig. 7d shows that both BiOCl and 1.88%SiO₂/BiOCl display high stabilities, even though slight declines in the performances are observed with the increase in the recycling time, which indicate the excellent photostabilities of BiOCl and 1.88%SiO₂/BiOCl under simulated sunlight irradiation. Similarly, 1.88%SiO₂/BiOCl shows good stability in the photodegradation of phenol and BPA (Fig. S4), which indicates that the SiO₂/BiOCl composite is an efficient and durable photocatalyst that is promising for application in the decomposition of OPs.

To understand the photodegradation mechanism of the OPs over the composites, radical trapping tests were performed by using iso-propyl alcohol (IPA; a quencher of $\cdot\text{OH}$) [49], benzoquinone (BQ; a quencher of $\cdot\text{O}_2^-$) [50], and triethanolamine (TEOA; a quencher of h^+) [51] as quenchers in the photocatalytic degradation of RhB over 1.88%SiO₂/BiOCl. As shown in

Fig. 6. (a) The photocatalytic performance of samples in degradation of phenol; (b) UV-vis absorption spectra of phenol under different reaction time in the presence of 1.88%SiO₂/BiOCl; (c) The photocatalytic performance of samples in degradation of BPA; (d) The comparison of degradation rates of phenol and BPA under BiOCl and 1.88%SiO₂/BiOCl samples.

Fig. 7. (a) The photocatalytic performance of samples in degradation of RhB; (b) The comparison of degradation rates of RhB under different samples; (c) Reaction kinetics of degradation of the RhB over different samples; (d) Photocatalytic degradation of RhB by BiOCl and 1.88%SiO₂/BiOCl samples in repeated experiments under xenon lamp irradiation.

Fig. 8, in the presence of IPA and BQ, the degradation rates of RhB are maintained at 50.8% and 36.9%, respectively, which suggest that the hydroxyl ($\bullet\text{OH}$) and superoxide ($\bullet\text{O}_2^-$) radicals have certain effects on the photodegradation of RhB. However, when TEOA was added into the reaction solution, the photocatalytic degradation rate dropped to 3.4%. This could suggest that h^+ is the major reactive species in the 1.88%SiO₂/BiOCl system.

Based on the earlier analyses of the characterizations and the radical capturing results, a possible mechanism of e^- - h^+ separation and transport in the light-driven SiO₂/BiOCl composite was proposed. As shown in Fig. 9, the classical photoinduced e^- and h^+ separation process occurs in this SiO₂/BiOCl composite system, and then, a series of active substances, such as $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals, are formed under photochemistry

action. The produced $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals, and especially, photogenerated h^+ , are powerful oxidative species that can decompose organic pollutant molecules into smaller molecules such as CO₂ and H₂O. First, the introduction of SiO₂ increased the specific surface areas of SiO₂/BiOCl composites, enhanced the capacities to adsorb pollutants (Fig. S5), and could provide more active sites for the degradation of pollutants [52]. Then, the composite sample with highly exposed (110) crystal planes was obtained by the coupling of moderate SiO₂, which enhanced the efficiency of e^- and h^+ separation owing to these planes providing a high-speed channel for e^- migration [53]. More importantly, the photoexcited e^- can transfer to the SiO₂ surface through the closely contacted SiO₂/BiOCl interfaces and be effectively trapped by the defects and vacancy sites on the

Fig. 8. Effect of the addition of quenchers on photocatalytic degradation of RhB over 1.88%SiO₂/BiOCl.

Fig. 9. Proposed reaction mechanism for the decomposition of organic pollutants over SiO₂/BiOCl photocatalyst.

surface of SiO₂ [54]. Thus, recombination of the photoexcited e⁻ and h⁺ was effectively inhibited and more photoexcited e⁻ and h⁺ are available to participate in the photocatalytic reactions, which results in higher photocatalytic activities of the SiO₂/BiOCl composites.

4. Conclusions

Our research indicated that the coupling of trace SiO₂ into BiOCl nanosheets can largely increase the photocatalytic activity for the degradation of organic pollutants such as BPA, phenol, and RhB. The presence of SiO₂ effectively improved the texture property of the photocatalyst and resulted in a large surface area. Moreover, the defects and vacancy sites present on the surface of SiO₂ can effectively trap the photoexcited e⁻ through intimate SiO₂/BiOCl interfaces and thus promote the separation of the photoexcited e⁻ and h⁺, resulting in high photocatalytic activities of the SiO₂/BiOCl composites. This work indicates that the coupling of SiO₂ is an effective method for the development of efficient photocatalytic materials. Our work is expected to offer new insights into the rational design and synthesis of efficient bismuth oxychloride photocatalysts for the removal of organic pollutants.

Acknowledgments

We acknowledged the funding from the National Natural Science Foundation of China (21567008, 21707055), the Program for Innovative Research Team of Guangdong University of Petrochemical Technology, The Yangfan Talents Project of Guangdong Province, the Innovation-driven “5511” Program in Jiangxi Province (20165BCB18014), the Funding Program for Academic and Technological Leaders of Major Disciplines in Jiangxi Province (20172BCB22018), the Program for New Century Excellent Talents in Fujian Province University, and the Natural Science Foundation for Distinguished Young Scholars of Hunan Province, China (2017JJ1026).

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Graphical Abstract

Chin. J. Catal., 2019, 40: 1212–1221 doi: S1872-2067(19)63359-0

Novel SiO₂ nanoparticle-decorated BiOCl nanosheets exhibiting high photocatalytic performances for the removal of organic pollutants

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Novel SiO₂ nanoparticle-decorated BiOCl nanosheets with higher e⁻ transfer efficiencies were fabricated via the facile hydrothermal route. The SiO₂/BiOCl revealed significant enhancements in the photocatalytic activities for the degradation of organic pollutants.

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SiO₂修饰强化BiOCl纳米片对有机污染物的光催化降解性能

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摘要: 许多有机污染即使在很低浓度下也可对水生生物造成各种不利影响。例如, 作为合成环氧树脂和聚碳酸酯重要原料的双酚A是一种典型的内分泌干扰化学物质, 当大量的双酚A被排放到水环境中时, 必将对水生生态环境造成不可修复的破坏。光催化技术具有催化效率高、矿化能力强和环境友好等优点, 是很有应用前景的有机污染物降解方法。但是, 目前大多数光催化剂尚难以满足实际有机废水处理或其它环境净化的需求。限制光催化剂大规模应用的原因可归结于以下两方面: 一是光催化反应中的量子效率较低, 大部分光生电子和空穴被复合而消耗掉, 这使得电子和空穴很难迁移到催化剂表面及与吸附的目标降解物发生氧化反应; 二是太阳光利用效率较低, 在光催化剂体系中, 宽带隙的半导体占有很大比重, 而宽带隙的光催化剂需要短波长的紫外光来激发电子跃迁, 这极大限制了自然太阳光或人工可见光的使用。

BiOCl是一种绿色、稳定的新型光催化剂, 具有材料易得、制备方法简单和形貌可控等诸多优点。为了进一步提高BiOCl光催化剂对有机污染物的降解活性, 本文从提高量子效率的角度出发, 采用SiO₂纳米粒子修饰BiOCl纳米片光催化剂, 以期提高光生电子和空穴分离效率, 进而增强BiOCl纳米片对有机污染物的光催化降解活性。我们首先采用水解法制备了SiO₂纳米粒子, 然后通过水热反应制备了SiO₂纳米粒子修饰的BiOCl复合光催化剂。利用XRD, FT-IR, SEM/TEM,

BET, UV-vis DRS, XPS和光电流等表征手段分析了样品的物理化学性质。催化活性测试表明, $\text{SiO}_2/\text{BiOCl}$ 在苯酚、双酚A和罗丹明B等有机污染物的光催化降解中表现出优越的光催化活性和稳定性。与单纯的BiOCl相比, 1.88% $\text{SiO}_2/\text{BiOCl}$ 样品对罗丹明B、双酚A和苯酚的降解率分别提高了16.5%, 29.0%和38.7%。

SiO_2 纳米粒子修饰使催化性能提升的主要原因如下: 首先, SiO_2 的修饰增加了复合材料的比表面积, 增强了污染物的吸附能力, 为污染物降解提供了更多的活性位点; 其次, 适当的 SiO_2 耦合有利于(110)晶面生长, 高暴露的特殊晶面为电子迁移提供了更加高速的通道, 从而提高了电子和空穴的分离效率; 最后, 光生电子可以通过紧密接触的 $\text{SiO}_2/\text{BiOCl}$ 界面转移到 SiO_2 表面, SiO_2 表面的缺陷和空位能有效捕获光生电子, 从而减小了光生载流子的复合几率, 使更多的光生电子和空穴参与到光催化降解反应, 进而提高了 $\text{SiO}_2/\text{BiOCl}$ 复合材料的光催化活性。

关键词: $\text{SiO}_2/\text{BiOCl}$; 纳米片; 有机污染物; 光催化; 界面

收稿日期: 2019-01-23. 接受日期: 2019-03-20. 出版日期: 2019-08-05.

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基金来源: 国家自然科学基金(21567008, 21707055); 广东石油化工学院创新团队发展计划资助计划, 广东省扬帆人才计划; 江西省5511科技创新人才计划(20165BCB18014); 江西省主要学科学术和技术带头人资助计划(20172BCB22018); 福建省高校新世纪优秀人才支持计划; 湖南省自然科学基金杰出青年基金(2017JJ1026).

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