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Fabrication of FeOOH/BiOCl Nanocomposites with Enhanced Visible Light Photocatalytic Activity

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Abstract. BiOCl as a two-dimensional layer ternary oxide semiconductor, has been widely used in energy and environmental area due to its non-toxicity, price and the good photocatalytic performance. However, BiOCl has a wide bandgap and can only absorb ultraviolet light, which limits its solar energy conversion efficiency for practical application. Herein, we report a facile synthesis of FeOOH/BiOCl nanocomposites by hydrothermal method. The results of XPS and FT-IR

Introduction

With the developed industrialization, more and more environment problems and energy problems have threatened our daily life.^[1] In 1972, the TiO₂ was used for photocatalytic splitting of water.^[2] After that using semiconductor photocatalyst to solve environment problems and energy problems has drawn a lot of attention.^[3] Two-dimensional semiconductor photocatalyst has attracted much attention due to its large specific surface areas, more catalytic sites and unusual electronic properties. These characters can increase more catalytic sites to contact with reactants, shorting the route of transmission of the photoinduced charges and reducing the recombination of electron and hole.^[4]

Recently a two-dimensional layer ternary oxide semiconductor bismuth oxychloride (BiOCl) due to the stable chemical property, cheap price and the excellent photocatalytic performance has drawn much attention.^[5] The open crystalline structure and layered structure of BiOCl was constituted of $[Bi_2O_2]^{2+}$ slabs sandwiched between double chlorine atoms slabs. A stable internal static electric field between the $[Bi_2O_2]^{2+}$ and chlorine slabs along the [001] direction is imparted by the layered structure, which can inhibit the recombination of photogenerated charge carriers.^[6] But BiOCl has a wide bandgap about 3.2 eV, which means it can only make use of UV-light and the conversion efficiency from solar energy to chemical energy of BiOCl is very low. Up to now, many efforts have been done to enhance the absorbance of visible-light for BiOCl, a promising approach to improve the visible photocata-

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indicated that FeOOH has been loaded on the nanocomposites. The chemical and optical properties of the nanocomposite are well-characterized. The nanocomposite showed much more excellent photocatalytic performance compared with the individual FeOOH and BiOCl single component. Reactive specie trapping experiment indicated that-O^{2–} and h⁺ were the two main active species during the photocatalytic process of FeOOH/BiOCl nanocomposites.

lytic activity is selecting suitable semiconductors to establish heterojunction.^[7]

FeOOH is a hydroxide of iron, which is a cheap, non-toxic and environmental friendly semiconductor.^[8] It has widely been used in photocatalytic degradation of organic pollutants due to a good absorption of visible light with a narrow bandgap, which is about 2.2 eV.

Herein, we report a facile and green hydrothermal method for the preparation of FeOOH/BiOCl nanocomposites with enhanced photocatalytic property. The BiOCl nanosheet as substrate and the FeOOH was synthesized in situ on the BiOCl nanosheet with a hydrothermal method. The chemical structure, morphology and optical properties of the FeOOH/BiOCl nanocomposites were characterized by XRD, XPS, FT-IR, SEM, UV/Vis absorption. The photocatalytic performance was investigated in depth by measuring the degradation of rhodamine B dye under visible light illumination in the presence of the resulting carbon nitrides.

Results and Discussion

Under high temperature, Fe^{3+} hydrolyzed to FeOOH on the surface of BiOCl nanosheet. For different molar mass of FeCl₃·6H₂O, the mass of FeOOH on the BiOCl nanosheet were different and that exhibits some different performance. In this study, there is no corresponding diffraction peak of FeOOH in the powder X-ray diffraction of the nanocomposites due to the poor crystallinity of FeOOH, as shown in Figure S1 (Supporting Information). But the results of XPS and FT-IR confirmed the existence of FeOOH.

The chemical states of Fe and O in the FeOOH/BiOCl nanocomposites were investigated by XPS. Figure 1 shows the XPS spectra of the Fe 2p and O 1s core levels of the FeOOH/ BiOCl-1. In Figure 1a, the peaks located at 725.1 eV and 711.6 eV correspond to the Fe³⁺ $2p_{3/2}$ and Fe³⁺ $2p_{1/2}$ and the satellite peak of Fe³⁺ at 719.5 eV is in good agreement with the binding energy values of Fe³⁺ in FeOOH.^[9] Furthermore, the O 1s peak can be deconvoluted into two major peaks at

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529.9 eV and 531.5 eV in Figure 1b, which can be respectively ascribed to oxide and hydroxide groups bounded to O of FeOOH.^[10]

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Figure 1. XPS spectra of FeOOH/BiOCl-1: (a) Fe 2p and (b) O 1s.

FT-IR spectroscopy of the nanocomposites could also indicate the existence of FeOOH. Figure 2 shows the FT-IR spectra of synthesized samples. The broad absorption bands at 3443 cm⁻¹ and the adsorption peak at 1640 cm⁻¹ can be attributed to O–H vibrations of absorbed water molecule.^[11] The peak at 530 cm⁻¹ is due to the stretching vibrations of Bi–O of BiOCl.^[12] The peak at 894 and 794 cm⁻¹ are allocated to the Fe–O–H bending vibration in FeOOH and the absorption bands presented at 631 cm⁻¹ are due to the Fe–O stretching vibration in FeOOH.^[8e,13] The results of XPS and FT-IR indicated the existence of FeOOH in the samples.

Figure 3 shows the SEM of BiOCl and FeOOH/BiOCl nanocomposites. Figure 3a shows the SEM of pure BiOCl nanosheet: it has a smooth surface and rounded edges. When we added 0.1 mmol of FeCl₃·6H₂O, under high temperature, the Fe³⁺ eroded the surface and edges of BiOCl nanosheet, which made the surface and edges become rough and hydrolyzed to FeOOH nanoparticles on the surface of nanosheet, shown in Figure 3d. When the amount of FeCl₃·6H₂O increased to 0.5 mmol, the surface was completely covered with the FeOOH nanoneedle and the edges of the BiOCl nanosheet also



Figure 2. FT-IR patterns of the pure BiOCl, FeOOH and the FeOOH/ BiOCl nanocomposite.

exposed to the outside. When the amount of FeCl₃•6H₂O increased to 1 mmol, the FeOOH nanorod completely coated BiOCl nanosheet and there is a lot of agglomerated FeOOH.



Figure 3. SEM of BiOCl nanosheet (a), Fe/BiOCl-1 (b), Fe/BiOCl-0.5 (c), and Fe/BiOCl-0.1 (d).

The UV/Vis/NIR diffuse reflectance spectra of synthesized products were studied, as shown in Figure 4. BiOCl nanno-sheet displayed weak absorption in the whole visible region and all FeOOH/BiOCl nanocomposites show a strong absorption of visible light. The increased absorption of visible light would improve the photocatalytic performance.

The photocatalytic performance of the samples was evaluated by the photo-degradation of RhB under visible light irradiation ($\lambda > 400$ nm). As shown in Figure 5, all FeOOH/ BiOCl nanocomposites performed better than pure BiOCl and FeOOH, which is due to the heterojunction of FeOOH and BiOCl, and which promotes the performance. For the FeOOH/ BiOCl nanocomposites, with the increased amount of FeOOH, the photocatalytic performance firstly increased and then decreased, the Fe/BiOCl-0.5 has the best performance. For Fe/ BiOCl-0.5, RhB degradation was already achieved in 60 min,

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Figure 4. The UV/Vis diffuse reflectance spectra of samples.

whereas less than 80% RhB was degraded by Fe/BiOCl-0.1 and Fe/BiOCl-1 under the same condition. This can mainly be ascribed to the FeOOH totally wrap BiOCl up and lead to the reduction of catalytic site.



Figure 5. The concentration changes of RhB as a function of illumination time for BiOCl, FeOOH, and FeOOH/BiOCl nanocomposites.

It is generally accepted that hydroxyl radical (*OH), photogenerated holes (h⁺) and superoxide radical (•O²⁻) are the three main active species in photodegradation process.^[14] Reactive specie trapping experiments were performed to estimate the influence of these active species on the photocatalytic reactions, shown in Figure 6. Isopropanol (IPA), EDTA disodium salt (EDTA-2Na) and benzoquinone (BQ) were used as scavengers of •OH, h⁺, and •O²⁻, respectively.^[15] When IPA was added, there was no significant effect on degradation process, indicating that 'OH did not play an important role in the photocatalytic system. But when BQ and EDTA-2Na were added, a significant effect on the degradation process could be observed, indicating that •O²⁻ and h⁺ were the two main active species. In general, the RhB was degraded to CO₂, water and intermediate products, such as phenolic compounds and carboxylic acids, in the photocatalytic process.^[16] The possible working principle of photocatalytic activity enhancement was shown in Figure S2 (Supporting Information). The conduction bands (CB) of BiOCl and FeOOH are -0.51 V and -0.35 V vs. NHE, respectively, and the valence bands (VB) of BiOCl

and FeOOH are 2.75 V and 1.75 V vs. NHE, respectively.^[17] Under visible light irradiation, the photogenerated electrons in the CB of BiOCl transferred to the CB of FeOOH, then, those electrons react with O_2 to produce O^{2-} to degrade RhB. The holes in the VB of BiOCl transferred to the VB of FeOOH, resulting in the increased photodegradation of RhB.



Figure 6. Influence of various scavengers on the photocatalytic activity of Fe/BiOCI-0.5.

Conclusions

In this work, we used a facile method to develop a series of FeOOH/BiOCl nanocomposites photocatalyst. Under high temperature the Fe³⁺ hydrolyzed to FeOOH on the surface of BiOCl nanosheet, and the existence of FeOOH would enhance the photocatalytic performance of raw BiOCl. When the amount of added FeCl₃·6H₂O is 0.5 mmol in 200 mg BiOCl, the composite shows high visible light photocatalytic efficiency and good stability in the degradation of RhB dyes. We also investigated the photocatalytic activity mechanism of the FeOOH/BiOCl nanocomposites, which indicated that h⁺ and •O^{2–} are the main active species of RhB degradation process.

Supporting Information (see footnote on the first page of this article): The Experimental Section, XRD and photocatalytic mechanism of samples.

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Keywords: FeOOH; BiOCl; Bismuth; Photocatalysis; Nanocomposites

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