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Preparation of $BiVO_4$/BiOCl heterojunction photocatalyst by in-situ transformation method for norfloxacin photocatalytic degradation

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ABSTRACT

In this study, we employed an in-situ transformation method to prepared a mesoporous spindle like $BiVO_4$/nanosheet BiOCl composite photocatalyst. The nanostructure and content of 2-D BiOCl could be facilely tuned by controlling the concentration of Cl^- ions in the reaction solution. The as-prepared $BiVO_4$-BiOCl photocatalyst showed an excellent photocatalytic norfloxacin degradation performance, and removed it in 1 h almost completely. Further research results indicated that a well-defined p-n heterojunction interface has been formed between $BiVO_4$ and BiOCl, to enhance the separation efficiency of photogenerated carriers. In addition, after the nanosheets BiOCl interlaced with the mesoporous $BiVO_4$ spindles, since the 2-D structure of the former, the charge transfer capacity of the composite would be improved to prolong the lifetime of the photoinduced carriers.

1. Introduction

Monoclinic bismuth vanadate ($BiVO_4$), with a band gap width of 2.4 eV, shows an excellent visible light absorption capacity. So, it is widely used in photocatalytic organic pollution degradation and water oxidation for O_2 evolution [1–4]. However, the dramatic recombination of the photogenerated carriers limited to increasing the quantum yield of this semiconductor [5,6]. In order to control this recombination process, except tuning the semiconductor characteristics of $BiVO_4$ [7,8], combining it with other suitable semiconductors to form a heterojunction system, has been widely considered as a simple and effective method [9–15].

Recently, except $BiVO_4$, other Bi-based semiconductors, bismuth oxyhalides (BiOX, X = Cl, Br, I), have drawn considerable research potential in the area of photocatalysis, which is owing to their adjustable band gap width, controllable nanostructure and facile synthetic process [16–23]. In the bismuth oxyhalides group, with the anions diameters decreasing, the band gap with of the BiOX increase gradually, such as BiOCl, a p-type semiconductor with a band gap width of 3.5 eV, it just can absorb UV light [24,25]. However, this material shows much higher photocorrosion stability than visible light absorbed BiOBr and BiOI. Furthermore, in its crystal of BiOCl, The $[Bi_2O_2]^{2+}$ layers, interleaved by double slabs of Cl atoms, to induce BiOCl crystal growth along [001] to form a two dimensional nanosheet structure [26–28]. Thus, the transfer process of the photogenerated carriers inside the crystal can be accomplished smoothly, to prolong the lifetime of the photoinduced carriers.

Composition of n-type $BiVO_4$ and p-type BiOX to form a p-n heterojunction photocatalyst has been widely considerable an effective method to increase the separation efficiency of the photogenerated electrons and holes [29,30]. As we know, the band gap widths of BiOBr and BiOI are smaller than BiOCl, meaning that the redox energy of photogenerated carriers of the BiOBr and BiOI are lower than that of BiOCl. Especially, since BiOBr or BiOI composite with $BiVO_4$ to form a p-n junction system, the corresponding photogenerated carriers redox energy would decrease further, so these composites were only able to treat some easy degradation organics such as RhB, MB etc. In order to treat some more obstinate environmental pollution by photocatalytic methods, such as antibiotic, $BiVO_4$/BiOCl composite is a better choice [31,32].

A favorable interface contact and a unique nanostructure can

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improve the photons adsorption, photogenerated charge separation and migration capacities of the p-n heterojunction photocatalyst. Ion exchange has been confirmed a utilized method to prepare heterojunction materials through a in-situ growth process [33,34]. Generally, a heterojunction photocatalyst with better interface contact and more effective nanostructure could be achieved by this method. Herein, we employed this facile ion exchange method to fabricate a novel $BiVO_4$/BiOCl (mesoporous spindle/nanosheet) composite. Specially, the micro morphology and the content of BiOCl in this composite can be easily controlled by tuning the Cl^- ion concentration in the reaction solution. The as-prepared $BiVO_4$/BiOCl composite in this work shows an excellent photogenerated carriers separation capacity and keeps a high redox energy of these carriers, to degrade the norfloxacin smoothly.

2. Experimental

2.1. Preparation of spindle like $BiVO_4$

The reagents and solvents used in this experiment were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. $BiVO_4$ powder was prepared by a hydrothermal method. 1.5 mmol $Bi(NO)_3 \cdot 5H_2O$ and 2 g polyvinylpyrrolidone (PVP, MW ~40 K) were dissolved in 50 mL ethylene glycol with sonicating for 20 min, which was marked as solution A. 1.5 mmol of NH_4VO_3 was dissolved in 20 mL of deionized water with sonicating for 10 min, and marked as solution B. Then, the solution B was added dropwise to solution A with stirring. The resulting mixture was then transferred into a 100 mL Teflon-lined stainless-steel autoclave, and heated at 180 °C for 10 h. After that, the liquid mixture was centrifugalized and repeatedly washed with deionized water and ethanol, dried at 60 °C for 5 h in air.

2.2. Preparation of $BiVO_4$/BiOBr composite photocatalyst

Simply, 1 mmol as-prepared $BiVO_4$ power and 1 g of PVP were mixed into 80 mL of deionized water with sonicating for 20 min. Then, a certain amount of concentrated HCl (0.1, 0.3, 0.5 and 0.7 mL) was added to above mixture under magnetic stirring. After 10 Min, the resulting mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 180 °C for 10 h. The final precipitations were collected by centrifugation, and washed by deionized water and ethanol for three times, then dried at 60 °C for 5 h. The samples were marked as $BiVO_4$-BiOCl-0.1, $BiVO_4$-BiOCl-0.3, $BiVO_4$-BiOCl-0.5 and $BiVO_4$-BiOCl-0.7, respectively.

2.3. Characterizations

The morphology and the microstructure of the prepared samples were analyzed by using a scanning electron microscope (SEM) (SEM, JSM-6700F, JEOL, Japan) and a high-resolution transmission electron microscope (HRTEM, Tecnai G2 F20, FEI Company, USA). The elemental compositions, the crystalline structures and bonding information of the prepared samples were analyzed by using X-ray diffraction (XRD, D/MAX-2500/PC, Rigaku Co., Tokyo, Japan) and XPS (Axis Ultra, Kratos Analytical Ltd., England). The optical absorption properties were tested by a UV/Vis diffuse reflectance spectrophotometer (UV–Vis DRS, UV-2600, Shimadzu, Japan). The fluorescence spectrum (PL, Fluoro Max-4) was employed to characterize the PL density of these photocatalysts.

2.4. Photocatalytic degradation of norfloxacin

0.05 g prepared photocatalyst was added into 100 mL norfloxacin solution with a concentration of 5 mg L^{-1} and kept stirring for 30 min under dark. The light source was a 150 W Xenon lamp (PLS-SXE300C, Beijing Bofeilai Co. Ltd., Beijing, China). A 420-nm cutoff filter was used to get visible light. The distance between the light source and the liquid level was 10 cm. A circulating water system was employed to control the operation process temperature at 25 °C. The concentration of the norfloxacin relative to photocatalysis time were tested by UV–Vis DRS.

2.5. Photoelectrochemical measurements

Photoelectrochemical measurements were performed in a three-electrode experimental system using CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The prepared series photoelectrodes, Ag/AgCl electrode, and Pt electrode acted as the working, reference, and counter electrodes, respectively. The light source was a 150 W Xenon lamp (PLS-SXE300C, Beijing Bofeilai Co. Ltd., Beijing, China). The variations of the photoinduced current density with time (i-t curve) were measured at a bias potential of 1.0 V (vs Ag/AgCl) during a 3-cycle light switching on and off. Electrochemical impedance spectroscopy (EIS) tests were performed at 0 V bias potential over the frequency range between 10^4 and 10^{-1} Hz, with an AC voltage magnitude of 5 mV, using 12 points/decade. All tests are carried out in 0.1 mol L^{-1} Na_2SO_4 electrolyte. Mott-Schottky plots were measured at the frequency of 1000 Hz with an AC voltage magnitude of 10 mV.

3. Results and discussion

The XRD results of the $BiVO_4$ and series of $BiVO_4$-BiOCl composite with different HCl adding contents are shown in Fig. 1. $BiVO_4$ curve shows a typical monoclinic phase. For the sample of $BiVO_4$-BiOCl-0.1, except monoclinic phase peaks of $BiVO_4$, a weak diffraction peak is found near 32.6, consistent with the tetragonal BiOCl, indicating that trace content BiOCl had formed in this sample with a low concentration of HCl in the reaction solution. With the HCl adding content increasing, we can find that the tetragonal BiOCl diffraction peaks density increase gradually. This phenomenon demonstrated that the content and crystallinity of the BiOCl in the composite of $BiVO_4$-BiOCl were increased with the HCl

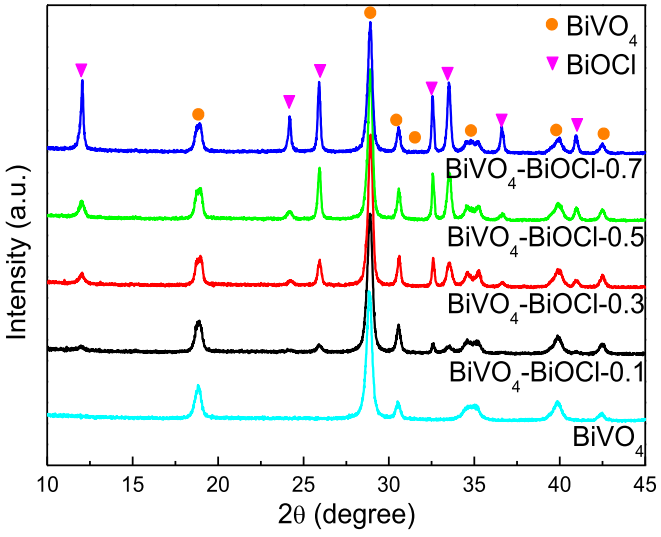

Fig. 1. XRD results of spindle $BiVO_4$ and series of $BiVO_4$-BiOCl composite with different HCl adding contents.