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Full Length Article

Improving visible light driving degradation of norfloxacin over core-shell hierarchical BiOCl microspherical photocatalyst by synergistic effect of oxygen vacancy and nanostructure

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ABSTRACT

In this article, A core-shell hierarchical microspherical BiOCl photocatalyst was prepared by a one-step solvothermal method in acid solution. Abundant of oxygen vacancies existed on the surface of BiOCl microspherical, which shortened the band gap to 1.77 eV and broadened the light absorption range to 700 nm. More importantly, the modified BiOCl showed greatly improved photon capture capability in the visible light region due to the synergistic effect of the oxygen vacancy and hierarchical structure of BiOCl. The BiOCl photocatalyst synthesized at 140 °C showed the best photocatalytic degradation performance for norfloxacin (NOR), and it can completely mineralize NOR to CO_2 and H_2O in four hours under the visible light. Thus, the synergistic effect of the oxygen vacancy and hierarchical structure is considered as a potential method to improve the photocatalytic performance of a wide band gap semiconductor.

1. Introduction

Photocatalytic technology is attracting more and more attention because of its potential to solve energy crisis and environmental pollution. In recent years, it has been found that BiOCl has better photocatalytic degradation performance than TiO_2 under ultraviolet light due to its larger band gap and more negative reduction potential [1]. Meanwhile, the built-in electric field formed by $[Bi_2O_2]^{2+}$ and Cl elements in BiOCl can reduce the recombination rate of photogenerated electrons and holes effectively [2–4]. However, the band gap of BiOCl is so large that it cannot absorb visible light [5], which greatly limits its application in the field of photocatalysis.

At present, elemental doping [6–7], coupled surface plasmon resonance [8–11,46,49], dye sensitization [12–13,47] composite material with visible light response [14–16,34–35,44], construction of heterostructure [40,45] and control the morphology [39,48] and phase [41] are the main methods to enhance the photocatalytic activity of BiOCl under visible light irradiation. But these modification methods require the assistance of other materials. It has been found that appropriate amount of defects not only does not introduce any impurity element, but also maintains the intrinsic crystal structure of the material, which is more conducive to the improvement of the absorption in the visible light region and the photocatalytic activity of the semiconductor photocatalysts [17–20]. Therefore, fabrication of defects is a valid method to improve the photocatalytic performance of semiconductor photocatalysts under visible light irradiation. The impurity energy levels formed by the oxygen vacancy state between valence band (VB) and conduction band (CB) would reduce the bandgap of the semiconductor, and the light absorption and electron excitation can be realized under visible light, which is the main reason for the enhancement of the photocatalytic activity [21–23]. In addition, the oxygen vacancies with charge properties are favorable for electron transfer, so the electron-hole pairs are easy to be separated and lead to favorable visible light photocatalytic activity. A BiOCl nanosheets with oxygen vacancies were prepared by Li et al. [24], the light absorption range of which extended from 361 nm to 386 nm. Weng et al. [25] prepared a BiOCl with oxygen vacancies by driving surface complex under visible light in air, accompanied with the extension of the light absorption range from 370 nm to 380 nm and a weak light absorption in the visible light area.

In this paper, oxygen vacancy-rich BiOCl were prepared by a one-step solvothermal method. The light absorption range of the

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oxygen vacancy modified BiOCl photocatalyst extended to 700 nm, and its absorption intensity was the highest in the ever reported BiOCl materials [24–25,31]. The higher visible light absorption of BiOCl is attributed to the high concentration of the oxygen vacancies. The oxygen vacancy-rich BiOCl can completely mineralized norfloxacin (NOR) into carbon dioxide and water under visible light irradiation. Therefore, it has potential in the field of environmental catalysis.

2. Experimental

2.1. Chemicals and materials

Bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, 99.99%) and Sodium sulphate (Na_2SO_4, 99%) were purchased from Sinopharm Reagent Co., hydrochloric acid (HCl, 36–38%) and ethylene glycol ($C_2H_6O_2$, 99.5%) were purchased from Tianjin Bodi Chemical Limited by Share Ltd. Ethanol (C_2H_6O, 99.7%) was purchased from Laiyang economic and Technological Development Zone Fine Chemical factory. All reagents were used directly without further purification.

2.2. Preparation of oxygen vacancy-rich BiOCl by solvothermal method

The BiOCl with rich oxygen vacancies are prepared by the solvothermal method as follows: firstly, 0.4 mmol $Bi(NO_3)_3$ was dissolved in 80 mL ethylene glycol containing 0.4 mmol HCl, followed by stirred for 30 min. Then it was added to a 100 mL autoclave and heated to 120 °C, 140 °C, 160 °C and 180 °C and kept for 24 h. After the auto-clave naturally cooled to room temperature, the products were washed with deionized water and anhydrous ethanol several times to remove impurities. Finally, the oxygen vacancy-rich BiOCl were obtained after dried at 80 °C in the air, and the final samples were labeled as BiOCl-120, BiOCl-140, BiOCl-160 and BiOCl-180, respectively. To remove the oxygen vacancy, a BiOCl-140 sample was annealed at 400 °C in air for 2 h, which is labeled as BiOCl-140-400.

2.3. Characterization

The morphology of samples were tested by scanning electron microscopy (SEM, JSM-6700F, JEOL, Tokyo, Japan). The crystal structure of samples were analyzed by X-ray diffraction analysis (XRD, D/MAX-2500/PC, Rigaku Co., Tokyo, Japan). The morphology and crystal structure of the samples were observed by high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20, FEI Company, USA). The elements composition and bonding information were tested through energy dispersive spectroscopy (EDS, FEI Tecnai G20; FEI Company, USA) and X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos Analytical Ltd., England). The optical absorption properties of samples were investigated by UV–Vis diffuse reflectance spectroscopy (UV–Vis, DRS, U-41000, HITACHI, Tokyo, Japan). The molecular structure information of samples were obtained by Raman spectroscopy (Raman, NanoZS90new, Malvern, England), and the excitation wavelength was 532 nm. Defect information were obtained by electron paramagnetic resonance (ESR, EMX-8/2.7, Bruker, Germany). Analysis of intermediates in photocatalytic degradation by liquid chromatography mass spectrometry (LC-MS).

2.4. Photocatalytic degradation of NOR

Photocatalytic activity could be characterized by photocatalytic degradation for NOR. The amount of prepared sample in the process of photocatalytic degradation was 0.05 g. The steps were as follows: 0.05 g of the prepared sample was added into 100 mL NOR with a concentration of 5 mg/L and stirring for 30 min without light irradiation to achieve adsorption equilibrium. The light source was a 300 W Xenon lamp (PLS-SXE300, Beijing Changtuo Co. Ltd., Beijing, China) with a 420-nm cutoff filter to filter out ultraviolet light below 420 nm, and the light intensity was 1000 mW/cm^2. The temperature of NOR was maintained at room temperature using circulating water. Samples were taken every 30 min during the degradation, and the absorbance was measured by UV–Vis DRS.

2.5. Electrochemical and photoelectrochemical (PEC) measurements

Electrochemical and photoelectrochemical measurements were performed in a three-electrode experimental system using CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The prepared photoelectrodes, a Ag/AgCl electrode and a Pt electrode acted as the working, reference and counter electrodes, respectively in 0.1 M Na_2SO_4 solution. The 300 W Xenon lamp was used in PEC test with a 420-nm cutoff filter to filter out ultraviolet light below 420 nm. The variations of the photoinduced current densities with time (i-t curves) were measured without bias potential, under intermittent lights witching on and off every 50 s for 3 cycles. The electrochemical impedance spectroscopy test was applied with a bias voltage of 0 V (vs. Ag/AgCl) and a frequency range of 10^5–10^{-2} Hz. The voltage range of Mott-Schottky test was 1.2–2.0 V (vs. Ag/AgCl) with frequency of 1000 Hz.

2.6. Theory calculation

BiOCl crystal structure were optimized based on density functional calculations by using the CASTEP code and a kinetic energy cutoff of 310 eV. Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was employed to describe the Exchange and correlation effects. The bulk crystal of BiOCl was relaxed by 300 eV energy cutoff, and a $7 \times 7 \times 4$ Monkhorst-Pack k-point mesh was employed. Both the atoms and the cell were allowed to relax. The energy, force, stress and displacement convergence criteria were set to 2.0×10^{-5} eV, 5.0×10^{-2} eV/Å, 0.1 GPa, and 2.0×10^{-3} Å, respectively. The structural model of oxygen vacancy modified BiOCl was built by cut the centered oxygen atom in a $(2 \times 2 \times 2)$ supercell of BiOCl.

3. Results and discussion

Fig. S1 presents the XRD results of the prepared samples. Curve S1a, b, c, and d are the corresponding XRD patterns of the BiOCl samples prepared at different reaction temperatures. When the reaction temperature is 120 °C, the diffraction peaks of BiOCl-120 correspond to tetragonal phase (PDF#06-0249), but the peaks intensity is relatively lower which indicates that the crystallinity of BiOCl is lower at this reaction temperature. When the reaction temperature rises to 140 °C, the intensity of the diffraction peaks of BiOCl-140 is obviously enhanced, which indicates the increase of the crystallinity of BiOCl-140. As the reaction temperature further increases, the crystallinity of BiOCl decreases. The diffraction peaks of the Bi appear at 160 °C, corresponding to the hexagonal phase of Bi (PDF # 44-1246), which is consistent with the previous reports [37]. With the further increases of the reaction temperature, the intensity of the diffraction peaks of Bi show an increasing trend, indicating that high reaction temperature can induce the formation of Bi monomer. In addition, BiOCl-140 sample were annealed at 400 °C in the air to remove oxygen vacancy defects on the surface of the material. The XRD patterns corresponding BiOCl-140-400 shown in Curve S1e showed that the crystal phase