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Enhanced photocatalytic degradation of bisphenol A by Co-doped BiOCl nanosheets under visible light irradiation

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ABSTRACT

Bismuth oxychloride (BiOCl) is a typical UV-light-sensitive photocatalyst with a unique layered structure, but exhibits no response towards visible light. This is a main limitation for its practical applications in photocatalytic degradation of pollutants. Among various methods to expand the light absorption region, doping modification is an efficient approach because it can tailor the band structure by forming a doping energy level without changing the layered structure substantially. In this case, the static electric field in the BiOCl crystal can be retained. Since cobalt (Co) exhibits good electrochemical properties, it is an ideal element for doping modification to expand the light absorption region and enhance the charge separation efficiency of BiOCl. In this work, Co-doped BiOCl nanosheets were prepared using a simple hydrothermal route. The doped Co expanded the light absorption region and enhanced the charge separation efficiency by forming a doping energy level in the band gap of BiOCl. As a result, the Co-BiOCl nanosheets exhibited an outstanding photocatalytic performance in degrading bisphenol A (BPA) under visible light irradiation with a degradation rate of 3.5 times higher than that of BiOCl. On the basis of the experimental results and density functional theory calculations, the mechanism of visible-light-driven catalytic BPA degradation by the Co-BiOCl nanosheets was elucidated. Therefore, the feasibility of Co-doping modification for BiOCl was confirmed, and a novel and efficient strategy was provided for the design and synthesis of high-performance photocatalysts.

1. Introduction

Photocatalysis is recognized as an efficient technology for water purification using solar energy and has attracted extensive interests in recent years [1–4]. Among various photocatalysts, bismuth oxychloride (BiOCl) possesses a unique layered structure, in which a $[Bi_2O_2]^{2+}$ layer is sandwiched by two $[Cl_2]^{2-}$ layers in the crystal [5–7]. As a result, the static electric field perpendicular to $[Bi_2O_2]^{2+}$ and $[Cl_2]^{2-}$ layers caused by the difference in electronegativities can induce the separation of photogenerated electron-hole (e^--h^+) pairs, which contributes to a good photocatalytic activity [8–10]. Although BiOCl has been reported to be able to degrade some organic dyes under visible light irradiation with the help of dye-sensitization, BiOCl is a typical UV-light-driven photocatalyst with a wide band gap of approximately 3.4 eV but shows no responses towards visible light, which is dominant in solar light [11–13]. Since most organic pollutants are non-dye molecules, BiOCl is helpless to fight against these colorless pollutants under visible light irradiation. This has become a main limitation for its practical application [14]. Therefore, a simple and efficient modification method for BiOCl is highly desired to achieve a remarkable photocatalytic activity without dye-sensitization under visible light irradiation.

So far, many efforts have been made to improve the light absorption property of BiOCl. Our previous works show that coupling BiOCl and BiOBr to form a solid solution of $BiOCl_xBr_{1-x}$ and oxygen-rich modification of BiOCl to form $Bi_{12}O_{15}Cl_6$ and $Bi_{12}O_{17}Cl_2$ are effective ways to enhance the photocatalytic performance of BiOCl under visible light irradiation [15–17]. Furthermore, introduction of oxygen vacancies as lattice defects, formation of Schottky junctions with metallic elementary substances and tailoring the size, morphology or exposed facets have also been tried to make BiOCl a visible-light-responsive photocatalyst [9,18–23]. However, several drawbacks still remain to be overcome. For example, tailoring morphology does not change the intrinsic light absorption property of BiOCl, forming heterojunction is difficult to obtain a highly homogeneous distribution, and changing phase may destroy the layered structure and thus weaken the contribution of the static electric field in BiOCl crystals [24–27].

Doping modification is an effective strategy as it affects the band

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structure by forming a doping energy level without changing the host crystal structure substantially [28–31]. It has been reported that the doped Fe element could narrow the band gap of BiOCl nanosheets and activate the photogenerated H_2O_2, and thus enhanced the photocatalytic performance of BiOCl [32]. Moreover, C-doping modification of BiOCl could also achieve response towards visible light [33]. Inspired by these works, we assume that cobalt (Co) should be another promising element to be doped into BiOCl, which has not been reported yet. Since Co exhibits good electrochemical properties, the light absorption region of BiOCl might be expanded and the charge separation efficiency is also probable to be enhanced by doping Co element [34–36].

Therefore, in this work, Co-BiOCl nanosheets were synthesized via a simple hydrothermal route for the first time. The as-prepared Co-BiOCl nanosheets were characterized systematically by various techniques. More importantly, the role of doped Co element was evaluated in terms of light absorption, charge separation and charge injection. Additionally, density functional theoretical (DFT) calculation was also performed to further demonstrate the impact of Co doping on the modification of the energy band structure. In order to verify the feasibility for practical applications, bisphenol A (BPA), a typical non-dye endocrine disrupter in environments, was chosen as the target pollutant to examine the photocatalytic activity of the Co-BiOCl nanosheets under visible light irradiation. The active species responsible for the degradation of BPA over the Co-BiOCl nanosheets was detected, and a BPA degradation pathway was found out. In this way, an efficient strategy for the design and synthesis of high-performance visible-light-sensitive photocatalysts was proposed.

2. Experimental section

2.1. Synthesis of Co-BiOCl nanosheets

All chemicals used in this work were analytical-grade reagents and purchased from Shanghai Chemical Reagent Co., China. They were used without any further purification. In a typical synthesis procedure of Co-BiOCl nanosheets, 0.485 g of $Bi(NO_3)_3$•$5H_2O$ (1 mmol) and 0.5 mL of Triton X-100 were added into 15 mL of ethylene glycol (EG). After being vigorously stirred and sonicated for 30 min, the mixture became homogeneous and colorless. On the other hand, 0.0238 g of $CoCl_2$ (0.1 mmol), 0.117 g of NaCl (2 mmol) and 0.546 g of mannitol (3 mmol) were added into 15 mL of distilled water under vigorous stirring for several minutes until a homogeneous solution was formed. Then, these two solutions were mixed with vigorous stirring and an obvious suspension was formed immediately. The suspension was kept stirring for another 15 min to insure the sufficient mixing of all these reactants. After that, the suspension was transferred into a 50-mL autoclave with Teflon linear and heated at 160 °C for 12 h. After naturally cooling to room temperature, the resulting solid powders were collected through centrifugation and respectively washed with distilled water and alcohol for three times to remove the residual ions and organics. Finally, the product was dried at 70 °C in vacuum for 12 h prior to characterization. For comparison, BiOCl was also prepared using the same procedure without the utilization of $CoCl_2$.

2.2. Physicochemical characterization

The X-ray powder diffraction (XRD) measurement of the samples was performed using a Philips X' Pert PRO SUPER diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.541874 Å). The inductive coupled plasma (ICP) emission spectrometer (Optima 7300 DV, PerkinElmer Co., USA) was used to determine the doping amount of Co element. Scanning electron microscopy (SEM) images were taken with an X-650 scanning electron micro analyzer and a JSM-6700F field emission SEM (JEOL Co., Japan). Transmission electron microscopy (TEM) (JEM-2011, JEOL Co., Japan) and high-resolution transmission electron microscopy (HRTEM) (JEOL-2010, JEOL Co., Japan) analyses were performed to characterize the morphology and crystal structure of the samples, and the applied acceleration voltages of TEM and HRTEM were both 200 kV. Additionally, in order to find out the distribution of each element in the products, energy dispersive spectrometer (EDS) spectrum and the EDS mapping image were obtained using TEM and HRTEM, respectively. The surface areas were measured using a Builder 4200 instrument (Tristar II 3020 M, Micromeritics Co., USA) with the Brunauer-Emmett-Teller (BET) method. The X-ray photoelectron spectroscopy (XPS) (ESCALAB250, Thermo Fisher Inc., USA) was used to investigate the chemical compositions and the valence states of constituent elements. The diffuse reflectance spectra (DRS) were measured using a UV/Vis/NIR spectrophotometer (Solid 3700, Shimadzu Co., Japan). The inductively coupled plasma emission spectrometer (ICP) (Optima 7300 DV, Perkin-Elmer Co., USA) was used to measure the amount of doped Co. Raman spectra were obtained using a Raman spectrometer (LabRAM HR Evolution, Horiba Instruments Inc., USA) with a 633 nm laser at ambient temperature.

2.3. Electrochemical characterization

All electrochemical measurements were carried out using a home-made three-electrode system, and the Ag/AgCl (KCl, 3 M) and the Pt wire were used as the reference electrode and the counter electrode, respectively. The sample on glass carbon was used as the working electrode for Mott-Schottky plots determination and electrochemical impedance spectroscopy (EIS) analysis, and the sample on F doped SnO_2 (FTO) conductive glass was as the working electrode for the photocurrent test. In this work, EIS analysis was performed by applying an alternating current (AC) voltage amplitude of 5 mV in 0.5 M $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ aqueous solution within a frequency range from 10^6 to 10^{-2} Hz. Mott-Schottky plots were obtained in 0.1 M Na_2SO_4 aqueous solution by impedance measurement at a fixed frequency of 1 kHz between the applied voltage range of 0-1.0 V (vs Ag/AgCl). The photocurrent responses of the samplse in 0.1 M Na_2SO_4 aqueous solution with or without 0.1 M $K_2S_2O_8$ were determined by amperometric *i–t* curve measurement with a bias voltage of 0.2 V (the open-circuit voltage of the samples) for 850 s. All these experiments were conducted using a computer-controlled potentiostat (CHI 660E, CH Instrument Co., China) with a three-electrode glass electrochemical cell. The light source applied in the photocurrent measurement was the same as that used in photocatalytic measurements with a UV filter, which is shown in the following section.

2.4. Photocatalytic performance evaluation

The photocatalytic activity of the samples for the BPA degradation was evaluated using a 500 W Xe arc lamp with a 420 nm cutoff filter as the light source at ambient temperature, and the measured radiation flux was approximately 85 mW cm^{-2}. In a typical procedure, 20 mg of the powder as a photocatalyst was added into 30 mL aqueous solution containing 10 mg L^{-1} of BPA. Then, the mixture was sonicated and vigorously stirred in dark for approximately 60 min to ensure sufficient adsorption/desorption equilibrium. After that, the mixture was continuously stirred under light irradiation and the samples were collected at given time intervals. The BPA concentration was measured using a high performance liquid chromatography (HPLC) (1260 Infinity, Agilent Inc., USA) with an Agilent Eclipse XDB-C18 column (4.6 × 150 mm), and the column temperature was 30 °C. Additionally, 50% acetonitrile and 50% deionized water (containing 0.1% formic acid) were used as the mobile phase at a flow rate of 1.0 mL min^{-1}, and the detection wavelength was 273 nm. Furthermore, the electron spin resonance (ESR) (JES-FA200, JEOL Co., Japan) was used to detect reactive radicals. The fluorescence emission spectra were obtained on a fluorescence spectrophotometer (Aqualog-C, Horiba Instruments Inc.,

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