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Simple hydrolysis-photodeposition route to synthesize Ag/$BiOCl_{0.5}Br_{0.5}$ composites with highly enhanced visible-light photocatalytic properties

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ABSTRACT

A series of Ag/$BiOCl_{0.5}Br_{0.5}$ photocatalysts with different Ag contents were synthesized via a simple hydrolysis-photodeposition method. As-prepared products were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectra (DRS). The photocatalytic activities of Ag/$BiOCl_{0.5}Br_{0.5}$ composites were evaluated by the degradation of Methyl orange (MO) dye pollution and phenol non-dye pollution under visible-light ($\lambda > 420$ nm) irradiation. Results reveal that Ag/$BiOCl_{0.5}Br_{0.5}$ composites have much higher photocatalytic activities than pure $BiOCl_{0.5}Br_{0.5}$ and commercial TiO_2 (P25), that 1%-Ag/$BiOCl_{0.5}Br_{0.5}$ exhibits the highest photocatalytic activity and stability. The enhanced performance could be ascribed to the roles of Ag Nanoparticles (NPs) as electron traps and the surface plasma resonance effect, achieving the more effective charge transfer and separation derived from the Schottky barriers between Ag NPs and $BiOCl_{0.5}Br_{0.5}$ nanosheets. Finally, main active species and enhanced photocatalytic mechanism of Ag/$BiOCl_{0.5}Br_{0.5}$ were investigated.

1. Introduction

Semiconductor photocatalysis technique, as an increasing potential measure for the development of renewable energy technologies and for environmental protection and remediation, have been paid widespread attentions [1–3]. Thus, the exploration and investigation on the highly active photocatalyst systems for completely, rapidly, and directly harvesting the solar energy have been the most important part of photocatalytic technology.

In recent ten years, BiOXs (X = Cl, Br and I) semiconductors have been considered as the potential candidate materials for the efficient photocatalytic degradation removal of pollutants in air, water and biological contaminants, becasue of the scientific report on the more superior photocatalytic activity of BiOCl than one of P25, but the photocatalytic efficiency of individual BiOX still was far from efficient for practical applications under visible light irradiation [4–7]. Noted that different from doping of foreign atoms, the doping behavior of congeners used to exhibit the $BiOX_xX''_{1-x}$ solid solutions that enhance their catalytic properties owing to the formation of visible-light response, high dipole moment (value above 2.00 D), high redox potential of holes, low electron–hole recombination rates, Bi^{3+} vacancies and O vacancies [8–12]. For instance, Sohn et al. [8] synthesized hierarchical flower-like $BiOBr_xCl_{1-x}$ ($0 < x < 1$) catalysts with the band gaps between 3.2 and 2.73 eV, which were dependent on the relative compositions of Br and Cl. Huang et al. [9] reported that the $BiOBr_xCl_{1-x}$ ($0 < x < 1$) solid solutions exhibited the stronger photocatalytic activity than BiOCl and BiOBr, and reached the maximum activity at $x = 0.5$, which were attributed to the trapping of photogenerated carriers caused most likely by Bi^{3+} cation vacancies that generated hole states. Besides, a family of $BiOBr_xCl_{1-x}$ ($0 < x < 1$) compounds could be synthesized by a hydrothermal method, and exhibited unique photocatalytic activity for the degradation of Rhodamine B and acetophenone under visible light irradiation, 3 times higher rate than Degussa P25 in removing aqueous RhB over $BiOBr_{0.5}Cl_{0.5}$ photoactive material [10,11]. Nevertheless, the experimental data showed that the main active species were the photo-induced holes (h^+) during the photodegradation process, or superoxide radical ($\cdot O^{2-}$) and h^+ in the dye-sensitized photocatalytic mechanism, but hydroxyl radical ($\cdot OH$) had few contribution as confirmed through analyzing the valence band and conduction band combined with an indirect chemical probe method including the active species scavengers and photoluminescence [13,14]. Therefore, it is still necessary for further enhancing the transfer capacity of photo-induced electrons to reduce greatly the recombination of

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electron–hole pairs, to achieve the effective utilization of photo-excited quantum efficiency, and eventually, to improve their photocatalytic efficiency for practical applications.

The decoration of composite photocatalyst materials with noble metal nanoparticles is becoming a more and more popular strategy [15–17], the reasons for that can not only trap efficiently the photoinduced electrons and reduce the probability of electron–hole recombination in the photocatalytic reaction, but also broaden their photoabsorption region through the surface plasmon resonance (SPR) effects and Schottky junction of noble metals (e.g. Ag, Pt, Pd, Au). Much research investigations on the Ag or Au-loaded BiOXs composition-dependent composite materials, such as $Ag/BiOBr_xI_{1-x}$, $Au/BiOBr_xI_{1-x}$ ($0 < x < 1$), had been reported to exhibit the excellent performance in the visible light region [18–21], but the fabrication of plasmonic $Ag/BiOBr_{0.5}Cl_{0.5}$ photocatalyst with higher stability and visible-light activity has no report for a rather promising material.

Based on our previous researches [22–24] and these reported works, the SPR metal Ag, a large work function, and the band gap structure are combined in the $Ag/BiOBr_{0.5}Cl_{0.5}$ photocatalyst in our present work. In addition to the synthesis and photocatalytic activity of BiOCl, BiOBr, $BiOBr_{0.5}Cl_{0.5}$ samples, we developed a facile hydrolysis combined with citric acid-assisted photodeposition method to prepare a series of Ag-loaded photocatalysts of nano-wt%-$Ag/BiOBr_{0.5}Cl_{0.5}$ ($0.5 < wt < 3$). The as-synthesized samples were characterized by XRD, SEM, XPS, UV–vis DRS, etc., and the MO dye and phenol non-dye pollutions were employed to evaluate their photocatalytic activities under visible-light irradiation ($\lambda > 420$ nm). The results revealed that $Ag/BiOBr_{0.5}Cl_{0.5}$ photocatalysts exhibited much higher photocatalytic activity than individual $BiOBr_{0.5}Cl_{0.5}$, while 1%-$Ag/BiOBr_{0.5}Cl_{0.5}$ possessed the best activity. Furthermore, reactive active species involved in the photocatalysis process were determined. Finally, the recycling stability of 1%-$Ag/BiOBr_{0.5}Cl_{0.5}$ photocatalyst, the possible enhanced photocatalytic decomposition mechanism of organic pollutions, and the effect of Ag deposition were investigated and discussed.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, ⩾99%), potassium bromide (KBr, ⩾99.5%), potassium chloride (KCl, ⩾99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd in Shanghai, silver nitrate ($AgNO_3$, ⩾99.8%), citric acid ($C_6H_8O_7{\cdot}H_2O$, ⩾99.5%), MO and phenol were purchased from Tianjin Guangfu Chemical Reagent Factory of China. All the chemicals were analytically of pure grade. Deionized water was obtained from a local supplier and used in the whole experiment.

2.2. Synthesis

$BiOBr_{0.5}Cl_{0.5}$ is synthesized by the hydrolysis precipitation method in deionized water. In a typical procedure, 4.85 g of $Bi(NO_3)_3{\cdot}5H_2O$ was added to 60 mL deionized water under magnetic stirring vigorously at room temperature. After 1 h, a white suspension was obtained. Then, a stoichiometric amount of KBr (1.19 g) and KCl (0.75 g) were added into the above suspension, respectively, stirred constantly for 24 h and aged another 24 h at room temperature in air. Finally, the resulting precipitates were collected by centrifugation, thoroughly washed with deionized water and ethanol, and dried at 80 °C for 12 h in air, obtaining the $BiOBr_{0.5}Cl_{0.5}$ powders.

$Ag/BiOBr_{0.5}Cl_{0.5}$ samples are prepared by the citric acid-assisted photodeposition process. The detailed synthetic processes (as seen in Scheme 1) are as followings: Firstly, 1.00 g as-synthesized $BiOBr_{0.5}Cl_{0.5}$ powders were dispersed in 20 mL deionized water with 0.01 g citric acid under ultrasonic stirring for 5 min. Then, 20 mL of 0.01 mg L^{-1} $AgNO_3$ solution was added to the suspension and stirred in dark for 24 h. Secondly, the continual stirring suspension was irradiated by the simulated sunlight for 45 min. Finally, the light gray $Ag/BiOBr_{0.5}Cl_{0.5}$ precipitates were separated by centrifugation, washed several times with water and ethanol, dried at 80 °C for 12 h. All the products are denoted as 0.5%-$Ag/BiOBr_{0.5}Cl_{0.5}$, 1%-$Ag/BiOBr_{0.5}Cl_{0.5}$, 2%-$Ag/BiOBr_{0.5}Cl_{0.5}$, 3%-$Ag/BiOBr_{0.5}Cl_{0.5}$ on the basis of the different deposition amount of $AgNO_3$ solution, respectively.

2.3. Characterization

The crystalline phase of the as-synthesized samples was evaluated using XRD equipment (Rigaku, D/max-2550) with the Cu Kα radiation ($\lambda = 0.15406$ nm) in the 2-theta range of 20°–80°. The accelerating voltage and applied current were 40 kV and 30 mA separately and the scan rate was 8°/min. The surface chemical composition and electronic states were analyzed by XPS on a V.G. Scientific ESCALAB250 with Al Kα radiation ($h\nu = 1486.6$ eV, 150 W) as the exciting source, where the binding energies were calibrated by referencing the C 1s peak (284.6 eV) to eliminate the charge effect. The surface and microstructure morphologies of $Ag/BiOBr_{0.5}Cl_{0.5}$ samples were analyzed using SEM (America FEI nanosem-430). The optical absorption properties were obtained on via UV–Vis spectrophotometer (Varian, Cary-300) using $BaSO_4$ as a reference.

2.4. Photocatalytic activity measurements

The photocatalytic activities of as-synthesized samples were evaluated by the photocatalytic degradation of the MO dye and phenol non-dye pollutions under visible light irradiation ($\lambda > 420$ nm) at room temperature using a 500-W Xenon arc lamp (Shanghai Lansheng Electro-Optical Device Co. Ltd. China, Illumination intensity = 119 klx) as a light source. A typical photocatalytic degradation process was arranged in this way: 0.05 g photocatalyst was dispersed in 100 mL 10 mg L^{-1} MO aqueous solution in a quartz glass beaker. The mixture suspension was continuously stirred for 60 min to ensure the adsorption–desorption equilibrium of degradation products before turning on the light source. The 500 W Xenon lamp was placed horizontally above the liquid surface, and the vertical distance between the lamp and the surface of the beaker was 19 cm. At certain time intervals, 3 mL suspension was collected and centrifuged at 10,000 rpm for 10 min to remove the catalyst particles. The supernatant was analyzed using UV–Vis spectroscopy.

3. Results and discussion

3.1. Crystal structure and morphology

The phase structures of all the as-synthesized samples were analyzed by the XRD technique and presented in Fig. 1. The diffraction peaks of BiOCl (bottom) and BiOBr (top) samples are well indexed to the standard cards of BiOCl (JCPDS-ICDD No. 82-485) and BiOBr (JCPDS-ICDD No. 9-393), respectively. Fig. 1a reveals that the patterns of $BiOBr_{0.5}Cl_{0.5}$ samples are different from pure BiOCl and BiOBr, but all the samples display sharp diffraction peak shapes, indicating their high crystallinity. In addition to the successive shift of XRD patterns for $BiOBr_{0.5}Cl_{0.5}$, the diffraction peaks show the formation of solid solutions rather than the simple mixture of BiOBr and BiOCl phases [9,19]. Fig. 1b displays all the XRD