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Reactable polyelectrolyte-assisted preparation of flower-like Ag/AgCl/BiOCl composite with enhanced photocatalytic activity

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ABSTRACT

Ag/AgCl/BiOCl three-component visible-light-driven photocatalysts were successfully fabricated using the reactable polyelectrolyte, poly(allylamine hydrochloride) as the template by a simple solvothermal method for the first time. The influence of Ag content on the formation of Ag/AgCl/BiOCl was systematically investigated. The samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), scanning electron microscope (SEM), N_2 gas sorption, electron spin resonance (ESR) and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS). The formation mechanism of the Ag/AgCl/BiOCl materials which was mainly based on the self-assembly of polyelectrolyte was proposed. In addition, the photocatalytic activity of the as-fabricated Ag/AgCl/BiOCl was evaluated by the degradation of rhodamine B (RhB) and tetracycline (TC) under visible light irradiation. Compared to pure BiOCl, Ag/AgCl and Ag/AgCl/BiOCl obtained by traditional one-step chemical bath method, as-fabricated Ag/AgCl/BiOCl materials displayed more superior photodegradation efficiency, which might be attributed to the surface plasmon resonance (SPR) effect of Ag nanoparticles. According to the results of radical trapping experiments and ESR measurement, it can be concluded that the photogenerated holes and superoxide radical are the predominant active species in the photocatalytic process. Furthermore, the photocatalytic mechanism has been proposed based on the characterizations and analysis. The as-prepared Ag/AgCl/BiOCl exhibited enhanced photocatalytic ability in the degradation of dyes and TC, suggesting its superiority in the future practical industries. This route preparing the Ag/AgCl/BiOCl materials with special structure inspires a new approach to prepare the visible light driven photocatalysts with novel morphologies and advanced properties in addressing environmental protection problems.

1. Introduction

Along with urbanization and industrialization, energy shortage and environmental contamination have become a challenging problem all over the world [1–3]. Semiconductor photocatalysis technique as a green method provides a chance to solve this problem. Among the semiconductor materials, TiO_2 has been believed as a promising photocatalyst for the degradation of pollutants, due to the fact that it is non-poisonous, low-cost fabricated, and shows the excellent photocatalytic activity [4,5]. However, TiO_2 exhibits the relatively low quantum yield and high recombination rate of photogenerated electron-hole pairs, which limit the further application. Consequently, there is a pressing need to develop the visible light driven photocatalysts [6,7].

In recent years, deposited nanoparticles of noble metals (such as Au, Ag) on the wide band gap materials with suitable energetics have reported to be beneficial for improving the interfacial charge transfer and visible light responsive performance [8–10]. Among them, supported-AgX (X = Cl, Br, I) on ZnO, TiO_2 or other materials exhibit the enhanced photocatalytic activities [11–14]. It is noteworthy that AgX nanoparticles display the high stability under the protection of supports, which promote the transfer of photoexcited carriers. Moreover, the surface of AgX can be partially reduced to Ag nanoparticles, the resultant Ag/AgX dramatically enhance the absorption of visible light because of the surface

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plasmon resonance (SPR) of Ag [15–20]. Besides, Ag/AgX can use plasmonic noble metal nanoparticles to sensitize the semiconductor and trap the electrons, thus finally achieve improved solar light harvesting, which gives new opportunities for fabricating visible light driven photocatalysts.

BiOCl has been regarded as one of the promising bismuth oxyhalides to apply in photocatalytic process as the excellent photocatalytic properties [21–23]. Especially, the layered structure of BiOCl endows the self-built internal static electric fields, which is critical for reducing the recombination rate of the photogenerated electron-hole pairs [24–26]. Wang et al. [22] synthesized the porous BiOCl micro-flowers with a rapid degradation rate using KCl as Cl source by one-pot glycerol assisted solvothermal process. However, pure BiOCl is a UV light driven catalyst. To further improve the visible light photocatalytic ability, many attempts about constructing heterojunction with other semiconductors have been adopted, including Fe_3O_4/BiOCl [27], BiOCl/Bi_2O_3 [28] BiOI/BiOCl [29], and WO_3/BiOCl [30–32]. Especially, combining Ag/AgCl with BiOCl to develop the new Ag/AgCl/BiOCl catalyst is a potential way. Xiong et al. [33] prepared the flower-like Ag/AgCl/BiOCl composite by a one-step chemical bath method at low temperature for the first time. Ye and co-workers [6] reported the Ag/AgCl/BiOCl photocatalysts synthesized by a low-temperature chemical bath method. And these two kinds of Ag/AgCl/BiOCl displayed enhanced visible-light photocatalytic activity against RhB than Ag/AgCl or BiOCl due to the surface plasmon resonance of Ag particles. Therefore, it is effective to design a rational synthetic approach for preparing Ag/AgCl/BiOCl with the superior activity.

In our previous work, flower-like BiOCl were fabricated by using the poly(allylamine hydrochloride) as the template instead of the conventional Cl source [34]. In order to boost the visible light photocatalytic activity, the Ag/AgCl/BiOCl three-component photocatalysts using poly(allylamine hydrochloride) as the template were prepared by a simple solvothermal method. Compared with the conditional one-step chemical bath method, Ag particles of the as-prepared Ag/AgCl/BiOCl materials originated from two sources, including the reduction of $AgNO_3$ and the reduction of the surface of AgCl. The morphology of as-prepared BiOCl materials was characterized, and the effects of Ag/AgCl concentration to the structure of BiOCl materials were studied. Besides, the photocatalytic abilities of the Ag/AgCl/BiOCl materials were assessed in the degradation of the rhodamine B (RhB), tetracycline hydrochloride (TC) under visible light irradiation. Furthermore, the structure-activity relationships and the mechanism of enhancement of photoactivity for Ag/AgCl/BiOCl were studied.

2. Experimental section

2.1. Chemicals

All chemicals were analytical grade and were used without further purification. The polyelectrolyte poly(allylamine hydrochloride), Phenol rhodamine B (RhB), and tetracycline hydrochloride (TC) were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Synthesis of Ag/AgCl/BiOCl materials

In a typical synthesis, 0.38 g $AgNO_3$ was dispersed in 20 mL of oleylamine and 0.4 mL of oleic acid, and then the mixture kept stirring at 120 °C for 15 h. After cooled down to room temperature, the final product was precipitated by using 30 mL acetone. Finally, 20 mL of hexane was added to the product to obtain solution A, which included Ag particles and Ag^+.

0.5 g of polyelectrolyte and a certain amount of solution A (1, 1.5, 2, 3 mL) was dispersed into 40 mL of ethylene glycol, 2 mmol Bi $(NO_3)_3 \cdot 5H_2O$ was dissolved into above mixture under vigorous stirring and then the mixture kept stirring for another 1 h. The suspension was transferred into 50 mL Teflon-lined autoclave and maintained at 150 °C for 24 h. The products were washed and dried at 50 °C overnight. The final powder was denoted as Ag/AgCl/BiOCl-X, in which X represented the volume of solution A. As a comparison, the sample without BiOCl, solution A and the sample using $AgNO_3$ instead of the solution A were also prepared and denoted as Ag/AgCl, BiOCl and Ag/AgCl/BiOCl, respectively.

2.3. Characterization

Transmission electron microscopy (TEM) images were recorded using a JEM-2010 instrument with an accelerating voltage of 100 kV. Morphological analysis was performed by a JEOL JSM-5600L SEM instrument with an electron voltage of 3.0 kV. The crystallographic properties of the products were measured on a Bruker D8 Advance Diffractometer (Germany) with Cu-Kα radiation ($\lambda = 1.5418$ Å) in the 2θ range from 10° to 90°. The Brunauer-Emmett-Teller (BET) surface area analysis was adopted at 77 K to obtain surface areas with ASAP 2020 apparatus (Micromertics USA). UV–vis diffuse reflectance spectroscopy (UV-vis DRS) of the samples were recorded on a UV–vis spectrophotometer (UV-3600, Shimadzu) with an integrating sphere attachment. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB MKII X-ray photo-electron spectrometer using Mg Kα radiation. The PL spectra were monitored using the room temperature photoluminescence with a 300 nm He-Cd laser excitation wavelength (Shimadzu RF-5301).

2.4. Photocatalytic activity

The photocatalytic activities of Ag/AgCl/BiOCl materials were evaluated by the photocatalytic decompositions of RhB (10 mg/L), TC (10 mg/L) under visible light irradiation ($\lambda > 400$ nm). The visible light was obtained from a 500 W Xe lamp with a 400 nm cutoff filter. In the photocatalytic experiments, 40 mg and 20 mg of BiOCl photocatalyst was added into 50 mL of RhB and 50 mL of TC solution, respectively. The mixture was stirred in the dark for 30 min to ensure absorption-desorption equilibrium before irradiation. At given time intervals, 3 mL of mixture was sampled and centrifuged to remove the photocatalyst particles. The concentration of RhB and TC was analyzed by a UV–vis spectrophotometer (UV-3600, Shimadzu) according to its absorbance at 553 nm and 356 nm, respectively.

2.5. Photoelectrochemical measurements

The photocurrent was studied by preparing the modified electrodes in a standard three-electrode system which included Ag/AgCl (saturated KCl) as the reference electrode, Pt wire as the counter electrode and prepared samples as the working electrodes. The working electrodes were prepared by deposition 20 μL of the suspension containing as-prepared materials (2 mg), ethanol (0.2 mL) and ethylene glycol (0.2 mL) onto a fixed area of 0.5 cm^2 ITO slice. A 500 W Xe arc lamp was used as the light source. And the photocurrent was performed in phosphate buffer solution (PBS, 0.01 M, pH 7.2).

3. Results and discussion

3.1. Structure and morphology

The phase structure of as-prepared Ag/AgCl/BiOCl materials was analyzed by the XRD technique (Fig. 1A). All the diffraction peaks are indexed to JCPDS card no. 06-0249 of tetragonal phase of