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Short Communication

Synthesis of novel Z-scheme AgI/Ag/AgBr composite with enhanced visible light photocatalytic activity

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ABSTRACT

Novel Z-scheme AgI/Ag/AgBr composite was synthesized through a facile in-situ ion exchange method along with light reduction. The as-prepared AgI/Ag/AgBr was characterized by XRD, SEM, DRS, XPS, EDS, BET and PL technology to study its phase structures, morphologies, optical properties, element components and surface areas. AgI/Ag/AgBr displayed excellent photocatalytic activity for the degradation of methyl orange under visible light ($\lambda > 420$ nm), which can be ascribed to the efficient separation of photogenerated electrons and holes through Z-scheme system composed of AgI, Ag and AgBr. The photocatalytic mechanism investigation demonstrates that $\bullet O_2^-$ was the main reactive species for methyl orange (MO) degradation.

1. Introduction

Nowdays, environmental depravation compels us to develop new and efficient approaches that can eliminate more and more kinds of pollutants, especially large quantity of non-biodegradable contaminants in wastewater. Among the existing strategies, semiconductor photocatalysis is highly expected to be an ideal “green” technology [1]. After 40 years of persistent investigation, different novel photocatalysts working under visible light have been discovered except for “conventional TiO_2” to obtain high photocatalytic activities [2–4].

In recent years, silver halide (AgX, X = Cl, Br, I) formerly applied in photography field have drawn extensive interests of researchers owing to its good photocatalytic performance in degradation of organic dyes [5–7] and volatile organic compounds [8], inactivation of bacteria [9–11] or reduction of CO_2 [12], etc. Generally, silver nanoparticles (Ag^o NPs) will be formed unavoidably because of the decomposition of AgX. Ag^o NPs not only can be adopted as efficient electron traps but also display the surface plasmon resonance (SPR) effect [13–15]. Due to the in-situ generation of Ag^o NPs on the surface of AgX, it facilitates the separation of photogenerated electrons and holes efficiently.

Differently, Z-scheme system is another important class of composite with excellent photocatalytic activities. Some reported Z-scheme system included CdS–M–TiO_2 (M = Ag, Au, Ru, Pd, Pt) [16–18], $CaFe_2O_4$/Ag (or ITO)/WO_3 [19,20], AgBr–Ag–Bi_2WO_6 [21,22], $H_2WO_4 \cdot H_2O$/Ag/AgCl [23] and other types [24–26]. Owing to their strong oxidation and reduction abilities, Z-scheme system exhibited higher photocatalytic performance than the single photocatalyst [16]. Therefore, Z-scheme composite is a fascinating photocatalytic system. However, the kinds of visible-light-driven Z-scheme photocatalysts are still limited. It is of importance and urgency to further develop novel Z-scheme photocatalysts.

Herein, we report a novel Z-scheme AgI/Ag/AgBr composite for the first time. The photocatalytic activity of AgI/Ag/AgBr synthesized via a facile in-situ ion exchange method was evaluated with degradation of methyl orange (MO) under visible light ($\lambda > 420$ nm). Furthermore, a possible mechanism of photocatalytic activiy enhancement of AgI/Ag/AgBr was proposed.

2. Experimental

2.1. Preparation of AgI/Ag/AgBr photocatalyst

All reagents were of analytical purity and were used without further purification. Deionized water was used throughout this study.

AgBr was prepared in advance. 0.904 g of $AgNO_3$ was dissolved in 100 ml deionized water. Then 0.547 g of NaBr dissolved in 20 ml deionized water was added to the $AgNO_3$ solution drop by drop with stirring. After stirring for 30 min, the resulting AgBr precipitates were collected, washed and dried at 80 °C in air. The whole preparation process was carried out in a dark room.

AgI/Ag/AgBr was obtained according to the following procedure. 1.000 g of AgBr was dispersed in 100 ml deionized water and sonicated for 20 min. Subsequently, 0.088 g of KI in 20 ml deionized water was added dropwise into the AgBr suspension with stirring magnetically for 30 min. The resulting suspension was vigorously stirred for

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1 h. Finally, the product was filtered, rinsed with deionized water and dried at 80 °C for 24 h. The obtained AgBr/AgI powders were dispersed into 50 ml of methyl orange (MO) solution (3.0×10^{-5} M) and then irradiated with a 500 W Xe lamp for 20 s to form a quantity of Ag^{o} NPs. Finally, the product of AgI/Ag/AgBr was filtered, washed with deionized water for several times and dried at 80 °C for 24 h.

Moreover, Ag/AgBr and Ag/AgI were synthesized through light reduction of pure AgBr and AgI, respectively.

2.2. Characterization of AgI/Ag/AgBr photocatalyst

The powder X-ray diffraction (XRD) analysis of the as-prepared catalysts was carried out with a Bruker D8 Advance X-diffractometer using Cu Kα radiation (λ = 1.5406 Å), operated at 40 kV and 40 mA. The UV–Vis diffuse reflectance spectra (DRS) were obtained by a Pgeneral TU-1901 UV–Vis spectrophotometer equipped with an integrating sphere assembly. $BaSO_4$ was used as a reflectance standard. Scanning electron microscopy (SEM) measurements were recorded on a FEI Sirion 200 field emission scanning electron microscope with 5.00 kV scanning voltages. Oxford instruments INCA X-act energy-dispersive spectroscopy (EDS) was employed to determine the Ag/Br/I molar ratio in the AgI/Ag/AgBr. NOVA 2000e surface areas, and a pore size analyzer (Quantachrome Instruments) was used to measure the Brunauer-Emmett-Teller (BET) surface areas of the samples at liquid nitrogen temperature (77.3 K). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 with Al Kα (1486.6 eV) line at 150 W. To compensate for surface charges effects, binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV. Fluorescence emission spectra were recorded on a JASCO FP-6500 type fluorescence spectrophotometer with 260 nm excitation source over a wavelength range of 350–650 nm.

2.3. Photocatalytic activities test

In each experiment, 0.10 g of photocatalyst was added to 50 ml of MO solution (3.0×10^{-5} M). Prior to illumination, the suspension was magnetically stirred in the dark for 30 min to reach adsorption-desorption equilibrium of MO on catalyst surfaces. At every irradiation time intervals of 4 min in a photoreaction apparatus under visible light (λ > 420 nm), as shown in Fig. S1, 3 ml of the suspension was collected, then centrifuged at 4000 rpm for 30 min and filtered through a 0.2 μm millipore filter to remove the photocatalyst particles. The catalyst-free MO solution was analyzed with a 722 s spectrophotometer (Shanghai Precision and Scientific Instrument Company, China). The concentration of MO was determined from its maximum absorption at a wavelength of 464 nm for MO with deionized water as a reference sample.

In addition, the examination of reactive species (h^{+}, •OH and •O_2^{-}) is similar to the photodegradation experiment. Different scavengers were introduced into the MO solution prior to addition of the catalyst. Furthermore, the terephthalic acid photoluminescence (TA-PL) probing technique was also used for the detection of ·OH radicals, the procedure can refer to our previous study [7].

3. Results and discussion

3.1. Characterization of AgI/Ag/AgBr

Fig. 1a shows the XRD patterns of as-prepared AgI/Ag/AgBr that can be indexed to face-centered cubic AgBr (JCPDS 06-0438) and a mixed crystal of AgI including β-AgI (JCPDS 85-0801) and γ-AgI (JCPDS 09-0399). The diffraction peaks of AgI in AgI/Ag/AgBr were of little difference from those of Ag/AgI sample, due to the different growth conditions. In addition, no peaks assigned to Ag^{o} were found

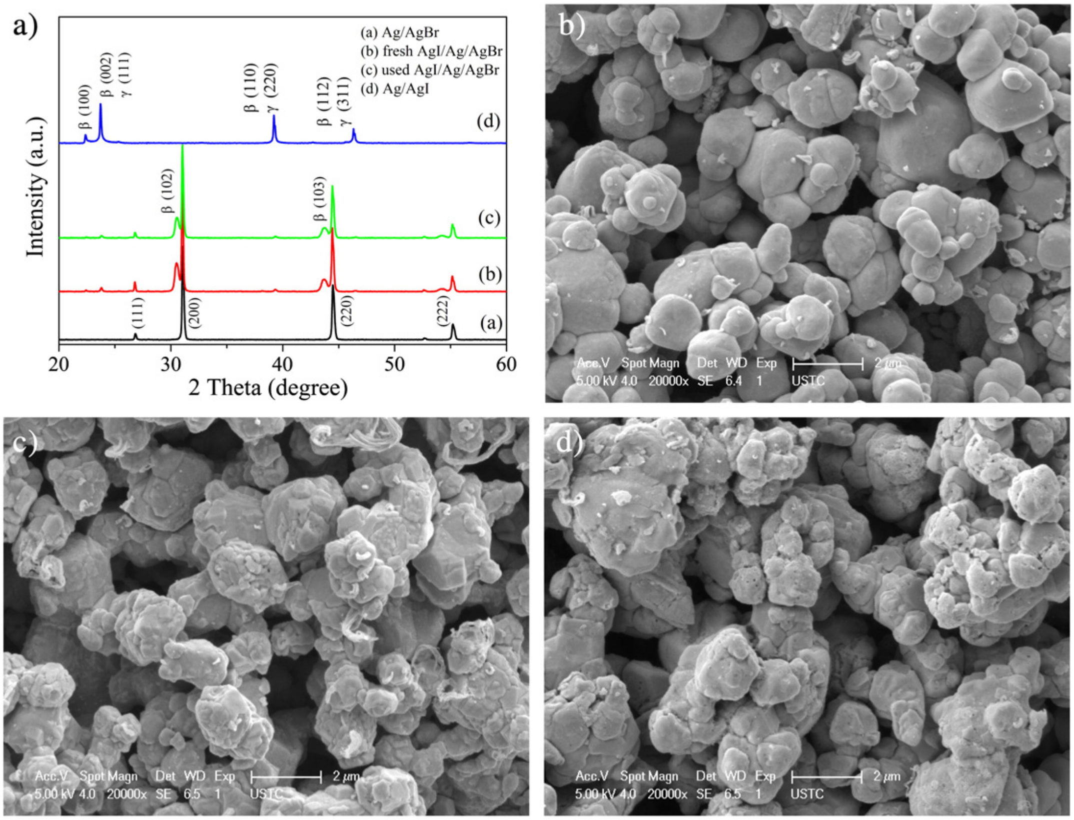

Fig. 1. (a) XRD patterns of the as-prepared photocatalysts. SEM images of (b) Ag/AgBr, (c) fresh AgI/Ag/AgBr and (d) used AgI/Ag/AgBr.