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Facile synthesis of Ag–Cu_2O composites with enhanced photocatalytic activity

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ABSTRACT

Silver–cuprous oxide (Ag–Cu_2O) microcomposites are successfully prepared by a facile low-cost solution method. The obtained materials were characterized by X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FESEM), ultraviolet–visible (UV–vis) spectroscopy, X-ray photoelectron spectroscopy (XPS). Experiments demonstrated that the formation of Ag–Cu_2O microcomposites was significantly influenced by the concentration of $AgNO_3$, and with increasing the concentration of $AgNO_3$, the optical absorption of the composites becomes strong. The photocatalytic activity of the prepared Ag–Cu_2O composites was determined by measuring the degradation of methyl orange solution under visible light, to find out its potential application in waste water treatment. The results reveal that the photocurrent of the composite is about 4 times higher than that of pure Cu_2O and the visible light photocatalytic activity of the composite is enhanced greatly on degradation of methyl orange. The reason for improvement in photocatalytic activity of the Ag–Cu_2O composites was also discussed.

1. Introduction

As a significant and typical p-type semiconductor with a direct band gap of 2.0–2.2 eV [1] cuprous oxide (Cu_2O) is of unique optical and magnetic properties [2,3], which has potential applications in solar energy conversion [4], electrode materials [5,6], gas sensors [7,8], visible-light driven photocatalyst of organic pollutants [9–11]. However, pure Cu_2O is not an ideal photocatalyst in terms of its limited actual photocatalysis efficiency. A proposed reason is that photogenerated electron generated in micronsized Cu_2O grains cannot be efficiently transferred to the crystal surface but is easy to recombine with hole. To overcome this limitation, modification of Cu_2O with noble metals is one of the most efficient ways.

Recently, semiconductor-noble metal heterostructures has attracted much current interest because of their excellent photocatalytic activities [12–15]. It is believed that in the semiconductor-metal composites, the photoinduced electrons can transfer to the metal deposits, while the photoinduced holes can remain on the semiconductor surface. Therefore the recombination of the electrons and holes can be prevented, and the photocatalytic efficiency of the semiconductors is improved. The formation of TiO_2–Au [16,17], ZnO–Ag [18], and CuO–Ag [19] composites has been reported to enhance the photocatalytic activity. However, these studies have mainly focused on TiO_2 and ZnO. Therefore, it is of interest to fabricate Cu_2O-based photocatalysts active under visible light irradiation and understand the underlying photocatalytic mechanism.

In this paper, octahedral Cu_2O microparticles were first synthesized. Then, well contacted heterostructures composing of Ag nanoparticles and Cu_2O microparticles were successfully prepared using wet-chemical precipitation method. And the crystal structures, morphologies, optical and photocatalytic properties of Ag–Cu_2O microcomposites were studied in detail.

2. Experimental

2.1. Synthesis

Copper(II) sulfate ($CuSO_4·5H_2O$), silver nitrate ($AgNO_3$), Sodium hydroxide (NaOH), hydroxylamine hydrochloride ($NH_2OH·HCl$), polyvinyl pyrrolidone (PVP, 99% hydrolyzed) surfactant were of analytical grade and used without further purification. In a typical procedure, 25 mL of 1 M NaOH and 0.2 g of PVP were added into 100 mL of 0.25 M $CuSO_4$ with vigorous stirring. The color of the solution turned blue quickly. Then 25 mL of 0.2 M $NH_2OH·HCl$ was

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added into the above-mentioned solution under vigorous stirring for 30 min. The color of the solution changed from blue to green to red. When the reaction ended, the products were separated by centrifugation, washed with distilled water and absolute ethanol for 4 times. Next, 0.05 g of Cu_2O particles were immersed into 50 mL of 0.05 M $SnCl_2$ ethanol solution. After 30 min of magnetic stirring at room temperature, the activated Cu_2O particles were obtained. Then, the activated Cu_2O particles were immersed into an $AgNO_3$ solution with a certain concentration for 30 min, the color of changes from red to black. After that, the obtained Ag–Cu_2O composites were separated by centrifugation, washed several times with alcohol, and dried under vacuum at 50 °C for 12 h. Samples prepared with 0 mM, 0.2 mM, 0.4 mM and 0.8 mM of $AgNO_3$ were herein referred to as sample A, B, C, D, respectively.

2.2. Characterization

X-ray powder diffraction (XRD) patterns of pure Cu_2O particles and Ag–Cu_2O composites were conducted on a Dmax-3β diffractometer with nickel-filtered Cu Kα radiation (λ = 1.54178 Å) The morphology and microstructure of the as-prepared products were characterized by field emission scanning electron microscope (FESEM; JEOL-6300F) and energy-dispersive X-ray spectroscopy (EDX). The UV–vis diffuse reflectance spectra (DRS) were obtained on a Lambda 35 UV–vis spectrometer. $BaSO_4$ was used as a reflectance standard in the UV–vis DRS experiment. The X-ray photoelectron spectroscopy (XPS) was collected on the ESCALab MKII X-ray photoelectron spectrometer (K-Alpha 1063).

2.3. Photocurrent experiments

In brief, 10 mg of the as-prepared products were dispersed in 5 mL ethanol. After 30 min sonication, the slurries were dip-coated onto a 1 cm × 2 cm fluorine-doped tinoxide (FTO) glass electrode and dried at 50 °C. The prepared photocatalyst/FTO electrodes, saturation calomel electrode, and platinum electrode were chosen as the working electrode, reference electrode, and counter electrode, respectively. The measurements were carried out in Na_2SO_4 aqueous solution as anodic electrolyte. The working electrode was irradiated by a high pressure mercury lamp (160 W). The photocurrent tests of samples were measured using the electrochemical workstation (CHI660C, Chenhua, China).

2.4. Photocatalytic properties

The evaluation of photocatalytic activities of as-prepared samples rely on the methyl orange (MO) decomposition testings. In a typical photocatalytic experiment, the dye solution was prepared by dissolving the MO in de-ionized water with concentration of 20 mg/L. A 500 W Xe lamp was used as a light source. An optical filter was used to allow visible light (>420 nm) to pass through. Experiments were as follows: 0.05 g of the prepared products were dispersed in 40 mL of MO aqueous solution, before irradiation, the mixed solution was magnetically stirred in the dark for 30 min to ensure establishment of an adsorption-desorption equilibrium of dye on the sample surface. Afterwards, the solution was exposed to simulated sunlight by the Xe lamp, at given time intervals, the solution was sampled (2 mL), diluted (4 mL).

Then the solution was put into a quartz cell, and the absorption spectrum was measured with a UV-2401 spectrophotometer.

3. Results and discussion

3.1. XRD analysis

The composition of the prepared samples was examined by XRD. As shown in Fig. 1A, the diffraction peaks at 29.65°, 36.52°, 42.36°, 53.89° and 61.30° are assigned to Cu_2O (curve a), matching very well with JCPDS card no. 05-0667, and no other impurity peaks could be detected, indicating the pure phase of the Cu_2O crystals. Fig. 1A(b–d) shows XRD patterns of the corresponding samples synthesized at different concentrations of $AgNO_3$ (0.2 mM, 0.4 mM, and 0.6 mM respectively). All spectra show three additional peaks at 38.10°, 44.38° and 64.48° compared to pure Cu_2O (curve a), which can be assigned to the (1 1 1), (2 0 0) and (2 2 0) crystal planes of cubic structure of Ag (JCPDS card no. 1-1242). The XRD results show that Ag crystals were successfully deposited on the surface of Cu_2O. Moreover, with increasing concentration of $AgNO_3$, the intensity of the diffraction peaks corresponding to Ag from the composites increase gradually, this may because of the continuous growth of Ag on Cu_2O crystals. In addition, there is no obvious shift of all the diffraction peaks, implying that Ag is not incorporated into the lattice of Cu_2O, but is present as metal deposits on the surfaces.

In order to determine the exact composition of composites, EDX test was carried out. Fig. 1B is an EDX spectrum of the Ag–Cu_2O composites (sample C), in which Cu, O, and Ag are all present. Meanwhile, the atomic ratio of copper and oxygen is close to 2:1, further confirming that the obtained products are Cu_2O crystals. The EDX spectra further confirmed that the Ag–Cu_2O heterostructure were successfully fabricated.

3.2. FESEM images and growth mechanism

FESEM images of pure Cu_2O and Ag–Cu_2O (sample C) micro-composites are shown in Fig. 2 Fig. 2a shows a FESEM image of the

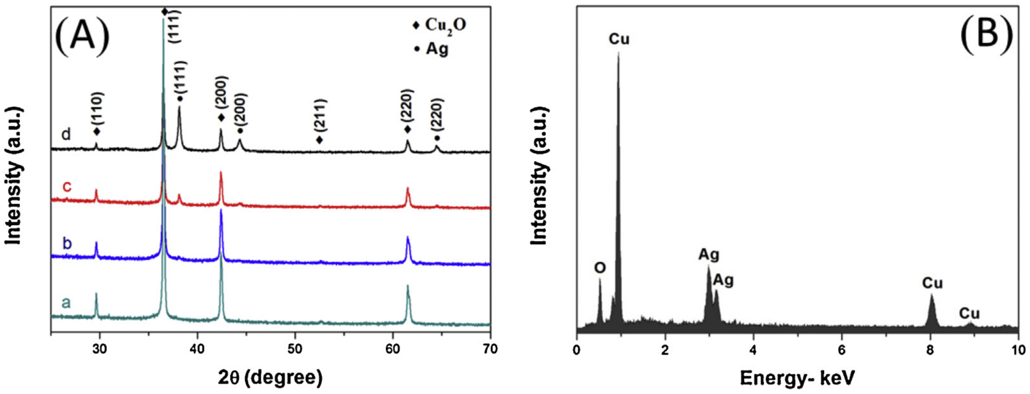

Fig. 1. (A) XRD patterns of Ag–Cu_2O composites (a: sample A; b: sample B; c: sample C; d: sample D). (B) EDS spectrum of Ag–Cu_2O composites (sample C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)