

Tailoring heterostructures of Ag/Cu₂O hybrids for enhanced photocatalytic degradation



Yangang Sun^{*}, Liyuan Cai, Xijian Liu^{**}, Zhe Cui, Pinhua Rao

College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

ARTICLE INFO

Keywords:

Ag
Cu₂O
Heterostructures
Photocatalysis
Tailoring

ABSTRACTS

A facile solution deposition method using the etched Cu₂O truncated octahedrons as the substrates has been successfully demonstrated for tailoring Ag/Cu₂O heterostructures with excellent reproducibility, and Ag nanoparticles have been deposited on the surface of different Cu₂O particles including freshly prepared Cu₂O truncated octahedrons, the etched Cu₂O truncated octahedrons, Cu₂O cube assemblies and Cu₂O octahedron assemblies. The obtained tailoring Ag/Cu₂O heterostructures prepared by the etched Cu₂O truncated octahedrons exhibits enhanced photocatalytic activity for the degradation of MB solution under visible-light irradiation, and the photocatalytic activity of tailoring Ag/Cu₂O heterostructures was 3.1 and 5.7 times higher than those of the etched Cu₂O truncated octahedrons and bare Cu₂O truncated octahedrons. The enhanced photocatalytic activity of tailoring Ag/Cu₂O heterostructures can be attributed to tailoring surface of Cu₂O truncated octahedrons, the enhancement of UV–vis absorbance spectra and electron sink effect due to Ag nanoparticle deposition. The facilely prepared tailoring Ag/Cu₂O heterostructure products are promising materials in fields such as photocatalytic and optoelectronic applications.

1. Introduction

Metal-semiconductor or metal-metal-oxide heterostructures have been exhibited a series of intriguing optical, electronic, and catalytic properties [1–4] that arise from the nanoscale interactions between the metal and metal oxide [5,6]. The nanoscale interaction is significantly affected by the shapes, compositions, and especially interfaces of the heterostructures, and this variety could lead to improved properties [7–10]. For heterostructures, the interface is believed to play a key factor in many cases owing to its distinguished charge state, atomic arrangement, and so on [11]. A varied surface of metal and metal oxide might thus help us to obtain photocatalysts with enhanced activity and repeatability [12].

Cu₂O, a p-type oxide semiconductor, has been widely studied and applied as an excellent candidate for visible-light photocatalysis [13,14], because it is relatively inexpensive, easily prepared, and environmentally friendly. Up to now, various Cu₂O nanomaterials with different photocatalytic properties have been achieved [15]. However, there are several unfavorable issues that still restrict the application of Cu₂O catalytic material. For example, the high quantum efficiency in photocatalytic degradation is fundamentally challenging, because Cu₂O, with a short

hole-diffusion length, exists an easy recombination of photogenerated electron-hole pairs and the low quantum efficiency [16]. Therefore, many efforts have been made to improve the photocatalytic activity of Cu₂O, such as the fabrication of Cu₂O-based doping, composite, hybrid and heterogeneous materials with different charge separation efficiency [17–21]. Among these techniques, the combination of noble metals like Ag, Pd and Au with semiconductor to construct heterogeneous nanostructures is one of the most effective methods to prevent the recombination of the electrons and holes and to improve the photocatalytic efficiency. Several Ag/Cu₂O heterogeneous nanostructures with enhanced degradation properties have been reported for electron sink effect of relatively cheap silver Ag nanoparticles. For example, Zhang et al. [22] synthesized Ag/Cu₂O composite nanospheres using a one-pot room temperature method by adding AgNO₃ solution to fresh Cu₂O nanosphere solution in various ratios. The obtained Ag/Cu₂O nanospheres with tunable coverage of Ag nanoparticles exhibited superior catalytic properties under visible-light irradiation to Cu₂O nanospheres, because of enhanced light absorption and electron sink effect by Ag nanoparticles. Yang et al. [23] prepared two kinds of heterostructures of Ag/Cu₂O nano-corncocks and Ag@Cu₂O nanocables using Sn²⁺ absorbed on the surface of Cu₂O crystals to reduce Ag⁺ in ethanol solution. Two

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: syg021@sues.edu.cn (Y. Sun), liuxijian@sues.edu.cn (X. Liu).

kinds of heterostructures of Ag/Cu₂O exhibited better photocatalytic activity compared with the Cu₂O particles due to Ag core nanowires as an excellent conductor effectively leading to the separation of photo-generated electron-hole pairs on the Cu₂O. Sharma et al. [24] fabricated Ag@Cu₂O core-shell materials as visible-light catalysts for carrying out palladium free Suzuki-Miyaura and Suzuki type cross-coupling reactions at room temperature. Ren et al. [25] showed that sandwiched ZnO@Ag@Cu₂O nanorod films with enhanced photocatalytic performance were synthesized by a three-step method of successive electrodeposition, magnetron sputtering and the second electrodeposition. Xu et al. [26] reported that hierarchical structures of Ag/Cu₂O/reduced graphene oxide (rGO) with enhanced photocatalytic activities and recyclability are developed through a one-pot, two-stage reduction synthetic route at room temperature without any surfactant. We notice that surface etching has provided an efficient way to prepare a diversity of controlled interfaces for other material to nucleate and grow on specific sites [27]. However, the heterostructures consisted of Ag nanoparticles and Cu₂O with different tailoring surfaces, which can exhibit excellent physical and chemical properties, have rarely been reported. Consequently, it is necessary to develop a facile method to tailor Ag/Cu₂O heterostructures with enhanced photocatalytic properties.

In this paper, Cu₂O truncated octahedrons with different surfaces by the aging/etching technology were first synthesized. Different heterostructures composing of Ag nanoparticles and Cu₂O particles of various surfaces and shapes were successfully prepared using a facile solution deposition method. And the crystal structures, morphologies, optical and photocatalytic properties of tailoring Ag/Cu₂O heterostructures were studied in detail.

2. Experimental section

2.1. Preparation of Cu₂O truncated octahedrons and tailoring Ag/Cu₂O heterostructures

All of the chemicals were of analytical purity and used as received without further purification. Cu₂O was fabricated by the typical approach reported previously [28]. Firstly, a reaction solution composed of copper sulfate (2.0 mL of 0.68 M), PVP (1.5 mmol, K-30, $M_w = 30\,000$) and 33.2 mL distilled water was prepared in a glass ask by constant strong stirring for 15 min, and then 2.0 mL of mixture solution (0.74 M sodium citrate and 1.2 M anhydrous sodium carbonate) was dropped into the above reaction solution, resulting in a dark blue color change. After about 10 min, 8 mL of a 1.0 M glucose solution was slowly injected into the reaction with further stirring for 15 min; lastly, the reaction solution was immersed in a water bath at 80 °C for 0.5 h to drive the reduction process. The mother solution is obtained. If the mother solution was exposed to air for 0 day (without aging), 1 day, 4 days, 8 days and 20 days at room temperature, then the precipitation in the mother solution was collected by centrifugation, and rinsed with distilled water and ethanol several times, and dried in a vacuum at 60 °C overnight. The samples of Cu₂O truncated octahedrons with different etched surfaces are prepared. If AgNO₃ of 0.2 mM was directly added into the mother solution exposed to air for different days (0 day, 1 day, 4 days, 8 days) at room temperature with vigorous for 20 min. Then, the precipitation was collected by centrifugation, and rinsed with distilled water and ethanol several times, and dried in a vacuum at 60 °C overnight, and different tailoring Ag/Cu₂O heterostructures were formed. By comparison, the varied PVP concentrations were also investigated while maintaining other parameters, and the corresponding different Cu₂O crystals (Ag/Cu₂O heterostructures) with various morphologies were prepared.

2.2. Characterization

The crystal structures and purity of the as-prepared products were determined using X-ray powder diffractometer (XRD; Rigaku D/Max-2550 PC) with Cu K α radiation. The morphology and size of the samples

were observed using a scanning electron microscope (SEM, S-4800) with an X-ray energy dispersive spectrometer (EDS) and a JEM-2100F high-resolution transmission electron microscope. UV–Vis diffuse reflectance spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer, using BaSO₄ as the reference.

2.3. Photocatalytic activity experiments

For the evaluation of catalytic activity, degradation experiments of methylene Blue (MB) were carried out under visible light at room temperature (ca. 24 °C). The experimental procedures are as follows: 20 mg of sample was dispersed in 50 mL of MB solution with a concentration of 10 mg/L in a beaker (with a diameter of ca. 7.0 cm). Afterwards, the dispersion was kept in the dark under magnetic stirring for 30 min to reach adsorption/desorption equilibrium. Then, the dispersion under magnetic stirring was placed approximately 10 cm below a xenon lamp (500 W, Model PLSSXE300) with a cut-off filter that only emits visible light ($\lambda > 400$ nm). At each sampling time (5 min), about 3.5 mL of the dispersion was taken and centrifuged. The absorbance spectrum of residual MB solution was analyzed using a UV-1901 spectrophotometer (maximum absorption peak at 663 nm).

3. Results and discussion

The chemical composition and structure of the typical samples were characterized using X-ray powder diffractometer (XRD) and the energy dispersive X-ray spectrum (EDS). Fig. 1 shows the XRD patterns of Cu₂O truncated octahedrons of aging for 8 days and tailoring Ag/Cu₂O heterostructures. The sample is the etched Cu₂O truncated octahedrons, and the diffraction peaks at 29.32°, 36.30°, 42.11°, 52.43° and 61.26° are assigned to a pure cubic phase Cu₂O (Fig. 1a), matching very well with JCPDS card no. 05-0667. After Ag nanoparticles are deposited on the surface of the etched Cu₂O truncated octahedrons, the XRD pattern of tailoring Ag/Cu₂O heterostructures appeared new diffraction peaks at 38.0°, 43.9°, 64.3° and 77.3° as shown in Fig. 1b, and these new diffraction peaks can be indexed to the (111), (200), (220), and (311) planes of the face-centered cubic structure of Ag (JCPDS card no.04-0783). In addition, Fig. 2 presents EDS spectrum of the tailoring Ag/Cu₂O heterostructures, confirming the presence of Cu, O and Ag in the Ag/Cu₂O heterostructures. The XRD and EDS results indicate that Ag nanoparticles were successfully deposited on the surface of the etched Cu₂O truncated octahedrons.

The morphology and size of Cu₂O truncated octahedrons of aging for 8 days and tailoring Ag/Cu₂O heterostructures were observed in scanning electron microscopy (SEM) images, which are shown in Fig. 3. Fig. 3a is the SEM image of Cu₂O truncated octahedrons of aging for 8

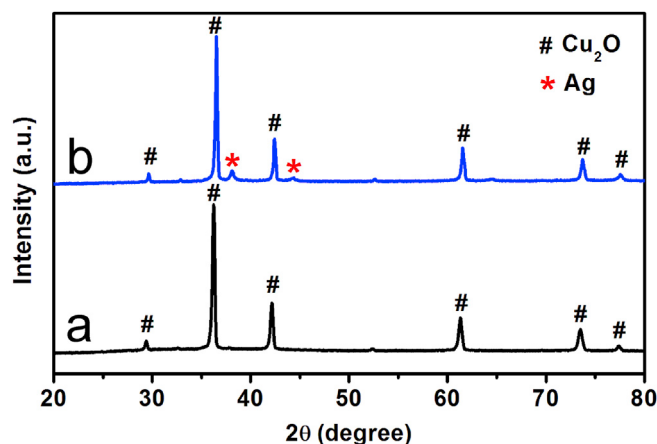


Fig. 1. XRD patterns of (a) Cu₂O truncated octahedrons of aging for 8 days and (b) tailoring Ag/Cu₂O heterostructures.

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