Applied Surface Science 313 (2014) 558–562

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Ag/CdS heterostructural composites: Fabrication, characterizations and photocatalysis

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ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form 17 May 2014
Accepted 4 June 2014
Available online 11 June 2014

Keywords:
CdS
Ag/CdS
Methylene blue
Photocatalytic efficiency

ABSTRACT

Ag/CdS heterostructural materials were successfully synthesized by ultrasound-assisted polyols and hydrothermal method. Under hydrothermal condition, thiourea adsorbed on Ag nanowires releases S^{2-} ions, which react with vicinal Cd^{2+} ions to form CdS clusters on Ag nanowires. Thereafter, the Ag/CdS composites grow into core–shell structure through CdS aggregation, Ostwald ripening, and preferential growth. The obtained core–shell structures and morphologies were investigated by XRD, SEM, and TEM; the experimental results indicate that the composites are composed of Ag nanowires serving as the core and CdS particles as the shell. The photocatalytic property of Ag/CdS core–shell materials was then investigated in detail. Comparing studies on the degradation of methylene blue were employed by using pure CdS, pure Ag, and Ag/CdS composites, respectively. The results show that the Ag/CdS composites possess higher photocatalytic degradation efficiency. Moreover, the Ag/CdS composites show improved stability, and the photocatalytic activity remains almost unchanged after four recycles. The enhanced photocatalytic effect for Ag/CdS composites is mainly attributed to the photogenerated electron transfer from CdS to Ag nanowire, while photogenerated holes still remain in CdS's valence band. Consequently, the effective separation of photogenerated electrons and holes and the resulting OH radicals improve the photocatalytic efficiency of Ag/CdS composites greatly.

1. Introduction

In recent years, much attention has been focused on semiconductor photocatalysis, because this technique can make full use of the renewable solar energy to solve the environmental problems and energy crises [1–5]. CdS, a visible-light-driven photocatalyst with 2.4 eV band gap, has extended application prospects on degrading the organic pollutants regardless of limited photocatalytic efficiency due to recombination of photogenerated electrons and holes [6–10]. A number of efforts have been taken to effectively separate photogenerated electrons and holes, for example, one way is to compound by noble metals (e.g. Ag, Au, Pd, Pt) [11–15]. Metal deposition can fabricate metal/semiconductor heterostructures to promote the separation efficiency of photogenerated electrons and holes. Ag has been widely studied because it is cheaper than other noble metals [16–19].

Based on the advantages of CdS and Ag, a lot of attention has been paid to Ag-decorated CdS systems. Thakur et al. [20] reported that the emission of cysteine-mediated Ag–CdS nanocolloid was found to be enhanced and then quenched as the silver content increases because of Ag^{+} in substitution for Cd^{2+} in the CdS lattice. Shah et al. [21] described that thin films of CdS prepared by thermal evaporation technique showed polycrystalline structure with preferred growth in ⟨1 1 1⟩ direction. Further studies showed that silver doping strongly affects the morphology of samples and optical transmission decreases with the increasing quality of Ag. Wang et al. [22] successfully prepared CdS–Ag nanocomposite arrays by electrochemical approach based on CdS hierarchical nano-arrays as templates. The strong coupling between CdS and Ag not only is conducive to transfer charges, but also makes the nanocomposite have excellent electro-chemiluminescence (ECL) properties. In addition, Ag has been revealed to promote the separation of photogenerated electrons and holes and then to improve the photocatalytic activity [23,24]. For the Ag–CdS composites, although there are

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http://dx.doi.org/10.1016/j.apsusc.2014.06.022
0169-4332/

some reports about degradation of organic pollutants, the reaction mechanism is rarely discussed [8,24].

In this work, the combination of the hydrothermal approach with ultrasonic-assisted method was employed to fabricate the Ag/CdS core–shell heterostructural composites. A possible formation mechanism of Ag/CdS heterostructural composites was proposed through XRD, SEM, and TEM characterizations. Moreover, the photocatalytic activity of Ag/CdS composites was evaluated by degrading methylene blue (MB) under visible-light irradiation. The mechanism of the excellent photocatalytic performance for Ag/CdS composites was discussed as well.

2. Experimental

2.1. Synthesis of Ag nanowires

Ag nanowires (Ag NWs) were obtained by a simple hydrothermal method [25]. Firstly, the polyvinylpyrrolidone (PVP, 0.375 mM, MW ≈ 40 000) and Na_2S (5 mM) were dissolved into 50 mL ethylene glycol (EG), and then the mixed solution was stirred for about 10 min. This mixture was then added into a solution of $AgNO_3$ (0.5 mM) in EG (50 mL) under constant stirring. Secondly, the as-prepared solution was transferred to a microwave oven and heated for 5 min under 450 W. The final product was washed repeatedly with acetone and deionized water to remove EG and excess surfactant PVP. The Ag nanowires were separated from particles through centrifugation at 2000 rpm for ~20 min. Finally, purified Ag nanowires were dried in a vacuum oven.

2.2. Synthesis of Ag/CdS core–shell composites

Firstly, the thiourea (8 mM) was dissolved in 40 mL of deionized water. Secondly, the Ag nanowires (1 mM) were ultrasonically dispersed into 40 ml of deionized water and then were added into the as-prepared thiourea solution under constant stirring. After stirring at room temperature for about 20 min, the cadmium acetate (1.6 mM) was dissolved into the mixture solution. Thereafter, the mixture was transferred into a stainless steel autoclave (30 mL). The autoclave was sealed and heated at 120 °C for 10 h and then cooled down to room temperature. The resulted precipitates were centrifuged and washed using absolute ethanol and deionized water for several times, and finally dried in a vacuum oven at 60 °C.

2.3. Characterization

The morphologies and microstructures of the as-synthesized Ag nanowires and Ag/CdS core–shell composites were investigated by the field emission scanning electron microscopy (FESEM; JSM-6700F, Japan) and high-resolution transmission electron microscopy (HRTEM; JEM-2010, Japan). The crystal structure was determined by powder X-ray diffraction (XRD) with a 0.154178 nm Cu Kα rotating anode point source operating at 40 kV. Photoluminescence (PL; Renishaw1000, UK) spectra were measured at room temperature using a He–Cd laser as the excitation light source at 325 nm.

2.4. Photocatalytic activity measurement

The photocatalytic activity of the Ag/CdS composites was evaluated by the degradation of MB in aqueous solution. Firstly, 30 mg of Ag/CdS composites were ultrasonically dispersed into 200 mL of an aqueous MB solution (10 ppm). The mixture was magnetically stirred overnight in dark to establish the adsorption/desorption equilibrium between the photocatalyst and MB. Then, visible light irradiation was carried out with a 500 W halogen lamp. The photocatalytic reaction was conducted in homemade beaker-like glassware with double wall for cooling the reactor, which minimizes self-degradation of MB due to the thermal effect. After a given irradiation time, about 5 mL of the mixture was withdrawn and the catalysts are separated by centrifugation. Photocatalytic degradation process was monitored by an UV–vis spectrophotometer (Shimadzu UV-2450, Japan) to measure the absorption of MB at 664 nm.

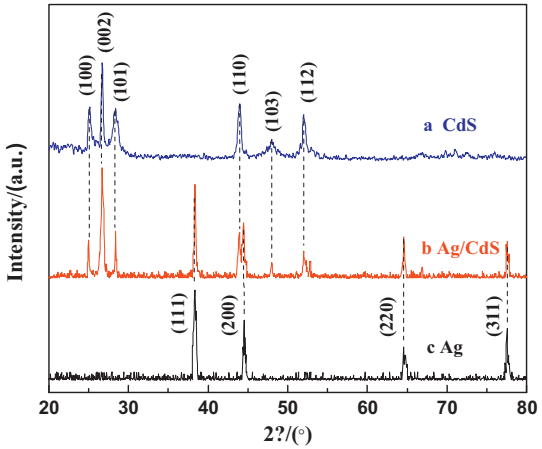

Fig. 1. XRD patterns of pure CdS nanoparticles (a), Ag/CdS heterostructure (b) and Ag nanowires (c).

3. Results and discussion

3.1. Morphological observations

Fig. 1 shows the XRD patterns of Ag nanowires, CdS particles, and Ag/CdS composites, respectively. It is clearly seen that the crystal phase of CdS particles is wurtzite phase (Fig. 1a). As for the Ag/CdS composites, all the diffraction peaks (Fig. 1b) can be indexed as a mixture of hexagonal wurtzite CdS and the face-centered-cubic (fcc) metallic Ag nanowires (Fig. 1c), which are well consistent with the JCPDS files No. 41-1049 and No. 04-783, respectively, revealing that the as-synthesized samples are composed of CdS and Ag constituents.

Fig. 2 shows the SEM images of the as-prepared Ag NWs and Ag/CdS composites. It can be clearly seen from Fig. 2a that the Ag NWs have diameters ranging from 100 to 150 nm with lengths of several micrometers. For Ag/CdS composites, the Ag NWs maintain the linear structures and the outer CdS partials have sizes from 100 to 200 nm.

TEM and HRTEM images further describe the Ag/CdS composites. As shown in Fig. 2c, an Ag NW with a diameter of about 150 nm is wrapped by CdS particles, which is in agreement with the above SEM observations. Fig. 3d shows a HRTEM image of the CdS nanoparticle as well as the Ag NW core. The estimated interlayer distance of the CdS domain is 0.33 nm, corresponding to the *d*-spacing in the (0 0 2) direction of hexagonal CdS [8]. The lattice fringes of Ag NW reveal an interlayer distance of 0.232 nm, in agreement with the *d*-spacing value of the Ag (1 1 1) plane [25].

3.2. Formation mechanism

On the basis of the above observations, a possible growth mechanism of the Ag/CdS heterostructure can be proposed. In this reaction process, thiourea acts as a sulfur source agent [26,27]. When the Ag NWs are added to the solution of thiourea under constant stirring, there will be some thiourea attached to the Ag NWs surface. Under hydrothermal condition, the C=S bonds of thiourea are easily broken by oxygen atoms of H_2O, releasing S^{2-} ions slowly.