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CdS nanowires decorated with Cu_2O nanospheres: Synthesis, formation process and enhanced photoactivity and stability

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ABSTRACT

CdS/Cu_2O heterostructural materials were successfully synthesized by a solvent-thermal process followed by a chemical bath deposition process. Structures and morphologies of the obtained CdS/Cu_2O composites were characterized by XRD, SEM, and TEM; the experimental results indicate that the surface of CdS nanowires (NWs) is decorated with spherical Cu_2O whose diameter ranges from 100 to 200 nm. Through crystal shape-evolution, the formation process of these hierarchical nanostructures was rationally proposed. Briefly, in the chemical bath deposition process, $Cu(OH)_2$ colloids generate firstly, and then the colloids transform into nanobelts after adding ascorbic acid (AA). With the reaction time further increasing, nanobelts aggregate together to form the hierarchical nanospheres on the surface of CdS NWs. The photoactivity of CdS/Cu_2O composite for methyl orange (MO) photodegradation was investigated in detail. The obtained high photocatalytic efficiency can be attributed to the heterojunction structure, which results in the efficient separation of photo-generated electrons and holes.

1. Introduction

With the development of economy and society, environmental pollution is increasing seriously, especially for water pollution. Photocatalytic technology is a very effective method for the treatment of environmental pollutants [1–5]. Heterogeneous photocatalysis using nano-semiconductor has become the most compelling technology, because it can fully catalyze and degrade various organic and inorganic substances in air and wastewater [6–9]. For example, TiO_2 photocatalyst has received much attention for the past several decades, especially in water treatment technology [10–12]. However, because of the large band gap of TiO_2, its practical application is limited due to the need of an ultraviolet excitation source, which accounts only a small part (3–5%) of solar light. Therefore, developing visible-light-driven photocatalyst is necessary for photocatalysis application.

CdS is an n-type semiconductor with a band gap of about 2.4 eV and can be excited by visible light. It has a wide range of applications, including photocatalysts [13,14], solar cells [15–17], biological labeling [18,19], and environmental sensors [20]. However, it is known that the CdS is unstable upon light illumination, and photo-corrosion may occur on catalyst surface during photocatalytic process. There are several ways to modify CdS to overcome its drawback, such as the hybridization with other semiconductors [21–24], metal ion doping [25–27], and deposition [28–30]. Notably, metal ion doping and deposition have attracted intensive research attention with the goal of enhancing charge separation. However, previously reported studies often use noble metals, which are scarce in nature and expensive. A more cost-effective approach is to create band structure-matched heterojunctions, for example, type II heterojunctions, and then to facilitate the charge separation [31]. Cu_2O is a p-type semiconductor with a small energy band gap of around 2 eV, and it has been extensively studied as an excellent photocatalytic material because of its outstanding spectral response to visible light [32–36]. However, the role of Cu_2O in this work is to promote charge separation through forming a type II heterojunction with CdS nanowires. For the CdS/Cu_2O composites, there are little reports about degradation of organic pollutants, and the formation process is rarely discussed.

In this work, Cu_2O-decorated CdS nanostructures were prepared using a simple and low-cost chemical bath deposition method. A possible formation process of CdS/Cu_2O heterostructural composites was proposed according to the XRD, SEM, and TEM characterizations. Moreover, the photocatalytic activity of CdS/Cu_2O composites was evaluated though degrading methyl orange (MO) under visible-light irradiation. The reason of the

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superior photocatalytic performance for CdS/Cu_2O composites was discussed as well.

2. Experimental

2.1. Synthesis of CdS nanowires

Uniform CdS NWs were prepared through hydrothermal method [20]. 30 mL ethylenediamine was used as the solvent as well as capping reagent to direct the growth of CdS. To prepare CdS NWs, 1.28 g of cadmium nitrate and 0.947 g of thiourea were dissolved in 30 mL ethylenediamine. The resulting solution was then sealed in a steel container for the hydrothermal treatment, which proceeded at 180 °C for 30 h and then cooled down to room temperature. A yellow precipitate was filtered and washed several times with absolute ethanol and deionized water to remove the residue of organic solvent. After drying in an oven at 80 °C for 12 h, powders of CdS NWs were obtained finally.

2.2. Synthesis of CdS/Cu_2O composites

0.22 g $CuSO_4 \cdot 2H_2O$ was first dissolved in 10 mL of deionized water, and then KOH solution (10.0 mL, 6 mM) was added under constant magnetic stirring for about 10 min. In addition, 0.015 g of the as-prepared CdS NWs was well dispersed in 10 mL 0.3 mM CTAB solution by ultrasonication. Thereafter, the CdS solution was added dropwise to the as-prepared solution. After stirring the mixture solution at room temperature for about 10 min, 16 mL of ascorbic acid (AA) solution (8.5 mM) was added dropwise stirring continuously for 10 min. Thereafter, the solution was then put into a warm water bath that was maintained at a temperature of 60 °C for 1 h. Finally, the precipitates were rinsed twice with DI water and collected using a centrifuge, before being dried overnight in an oven at 80 °C.

2.3. Characterization

The morphologies and microstructures of the as-synthesized CdS NWs and CdS/Cu_2O 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. Chemical compositions were analyzed by X-ray energy-dispersive spectroscopy (EDS) equipped to the SEM. 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

A representative organic pollutant MO was chosen to evaluate the photocatalytic properties of CdS/Cu_2O composites. 50 mg of the as-synthesized CdS/Cu_2O composites were added to 200 mL of aqueous MO solution (20 ppm) under constant stirring. The suspensions were magnetically stirred overnight in dark to develop adsorption–desorption equilibrium between the MO and the photocatalyst. The photocatalytic reaction was conducted in homemade beaker-like glassware with double wall for cooling the reactor, using a 500 W halogen lamp as the visible light source. At given intervals (20 min), about 5 mL of the mixture was withdrawn and the catalysts were separated by centrifugation. Photocatalytic degradation process was monitored by an UV–vis spectrophotometer (Shimadzu UV-2450, Japan) to measure the absorption of MO at 465 nm.

3. Results and discussion

3.1. Morphological observations

Fig. 1 shows the XRD patterns of Cu_2O nanospheres, CdS NWs, and CdS/Cu_2O composites respectively. It is clearly seen that the crystal phase of Cu_2O nanospheres is cubic phase (Fig. 1a). No other diffraction peaks arising from possible impurities such as Cu and CuO were detected, indicating that the products were pure Cu_2O. As for CdS/Cu_2O composites, the cubic cuprite structure Cu_2O and hexagonal wurtzite CdS (Fig. 1c) coexist in the CdS/Cu_2O heterostructure crystals (Fig. 1b), and the XRD patterns match the JCPDS files No. 5-667 and No. 41-1049 respectively. No remarkable shifts in diffraction peaks are detected, which further confirms that the as-synthesized samples are composed of Cu_2O and CdS phases.

Fig. 2 shows the SEM images of the as-prepared CdS NWs and CdS/Cu_2O composites. Fig. 2a shows a typical FESEM image of the

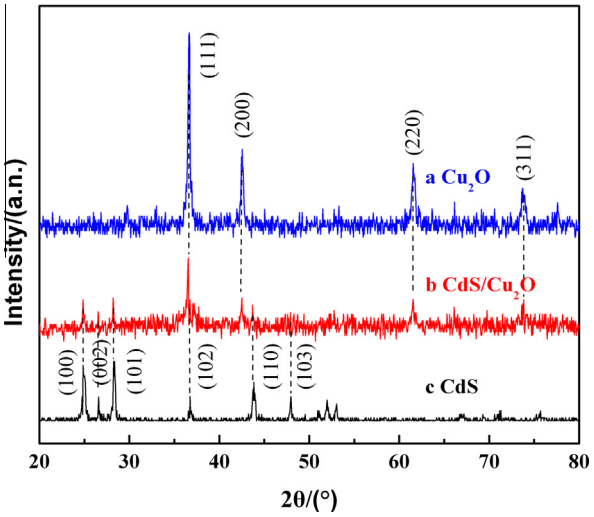

Fig. 1. XRD patterns of pure Cu_2O nanospheres (a), CdS/Cu_2O heterostructure (b) and CdS nanowires (c).

CdS NWs, in which most of CdS NWs have a diameter of 50 nm with length of several micrometers. For CdS/Cu_2O composites, the surface of CdS NWs is decorated with spherical Cu_2O and the diameter of the Cu_2O nanospheres ranges from 100 to 200 nm (Fig. 2b).

TEM and HRTEM images provide more information of the CdS/Cu_2O composites. Fig. 2c shows that Cu_2O nanospheres grow on the CdS NW, which has a diameter of about 50 nm. Fig. 2d shows a HRTEM lattice image of the interface. The measured lattice spacing of Cu_2O domain is 0.25 nm, which is in good agreement with the *d*-spacing value of the (1 1 1) facets of Cu_2O crystal [37,38]. The spacing of the CdS NW is 0.33 nm, corresponding to the (0 0 2) plane of hexagonal CdS [39].

Fig. 2e shows the EDS spectrum of CdS/Cu_2O composites. Elemental Cu, O, S and Cd are detected, and the corresponding atomic percentages are summarized in Table 1. The atomic ratio of Cu to O is roughly 2 to 1 and Cd to S is roughly 1 to 1, which confirm the stoichiometry of Cu_2O and CdS.

3.2. Formation process

In order to illustrate the growing process of the heterostructure, a series of time-dependent experiments were carried out. Fig. 3 shows the SEM images of the products obtained at different reaction stages. It can be obviously seen that the crystal shape-evolution depends on the reaction time.

Firstly, KOH was added to $CuSO_4$ solution to generate blue $Cu(OH)_2$ colloids [40]. When the CdS NWs were added to the colloids solution under constant stirring, there would be some colloids attached to the CdS NWs surface. Fig. 3a shows the SEM image of as-prepared $Cu(OH)_2$ colloids and CdS nanowires, centrifuged from the blue solution before adding AA. When the reaction time was 1 min after adding AA, the colloids transformed into nanobelts, furthermore, these nanobelts tended to aggregate to form the quasi-spherical nanostructures on the surface of CdS NWs (Fig. 3b). The primary hierarchical nanospheres subsequently formed by ripening mechanism at the aging time of 3 min, as demonstrated in Fig. 3c. With the reaction time further increased (5 min), complete hierarchical nanospheres with aggregated nanoparticles were generated on the surface of CdS NWs finally (Fig. 3d).