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Urchin-like CdS microspheres self-assembled from CdS nanorods and their photocatalytic properties

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ABSTRACT

Urchin-like CdS microspheres were successfully prepared via a facile hydrothermal route. The CdS microspheres were self-assembled from CdS nanorods with average diameters of about 30 nm and lengths of about 200 nm. The volume ratio of water/ethylenediamine (water/en) played a key role in morphology of products including assembled nanorods and dispersed nanorods. In addition, we characterized the photocatalytic property of the urchin-like CdS microspheres under visible light, which showed good photocatalytic activities.

1. Introduction

The one-dimensional (1D) nanostructured materials, such as nanowires, nanorods, nanobelts and nanotubes have attracted considerable interest in the past decades because of their unique fundamental properties and potential applications in nanodevices [1–4]. However, the application of 1D nanomaterials depends not only on their quality (e.g., purity and crystallinity), but also on their spatial orientation and arrangement [5–7]. Recently, much attention has been focused on the assembly of nanoscale building blocks into 2D or 3D ordered superstructures or complex functional architectures for the fabrication of advanced nanodevices [8–10]. Various methods have been developed to produce the assembly of nanocrystals including nanospheres, nanorods, nanowires and nanobelts [11–14]. Among these methods, the self-assembly of nanocrystals driven by various interactions is of special interest due to its high efficiency and controllability [15,16]. However, few literatures reported the self-assembly process, and the synthesis of novel architectures using a facile, mild and effective way still remains a challenge.

As an important II–VI group semiconductor, CdS has attracted extensive studies for many years. CdS has a band gap of 2.42 eV, and displays good optical and photoconductive characteristics [17–21]. The CdS semiconductor materials can be used for the fabrication of solar cells, nonlinear optical materials, quantum size effect semiconductors, optoelectronic and electronic devices, biological labeling, and photocatalytic water-splitting [22–28]. Many methods have been developed to synthesize nanocrystalline CdS with diversified morphologies such as nanorods, nanowires, nanotubes and nanobelts [29–36]. Furthermore, much attention has also been paid on the self-assembly of CdS nanocrystals into self-assembled structures [37–39].

Herein, we present a simple and convenient one-step hydrothermal method for the fabrication of urchin-like CdS microspheres self-assembled from CdS nanorods. The urchin-like CdS microspheres are formed with the assistance of ethylenediamine tetraacetic acid disodium salt (EDTA) in a mixed solvent of water and ethylenediamine (en). The morphology of the products can be tuned from assembled nanorods to dispersed nanorods by controlling the volume ratio of water/en. The photocatalytic property of the as-prepared CdS microspheres under visible light is examined, which shows better photocatalytic activities toward commercial CdS powders.

2. Experimental

All chemical reagents were of analytical grade and used as received without further purification. In a typical procedure, 0.057 g $CdCl_2 \cdot 2.5H_2O$ and 0.200 g EDTA were dissolved in 39 mL distilled water under constant magnetic stirring, and then 1 mL en and 0.020 g thioacetamide were added and dissolved to form a clear solution. Next, the solution was transferred into a Teflon-

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lined stainless-steel autoclave with a capacity of 50 mL and heated in an oven at 180 °C for 4 h, then cooled to room temperature naturally. The obtained products were collected by centrifugation, washed with distilled water and absolute ethanol for several times each, and dried under vacuum at 50 °C for 2 h.

The photocatalytic degradation was conducted as the following procedure: 0.020 g of the as-prepared CdS sample was dispersed into an aqueous solution of eosin Y (0.01 g/L, 50 mL). A 500 W column-like iodine tungsten lamp was placed over the solution with a height of 20 cm, and the solution was irradiated with the lamp under constant magnetic stirring and fan cooling. At intervals of 20 min, 3 mL of the suspension was taken out, centrifuged, and the supernatant fluid was collected and analyzed with a UV–vis absorption spectrometer.

X-ray powder diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 0.15406$ nm). The scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 field emission scanning electron microscope. The high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were recorded on a JEOL-2011 high-resolution transmission electron microscope performed at an acceleration voltage of 200 kV. UV–vis absorption spectra were recorded with a Hitachi U-3010 spectrophotometer.

3. Results and discussion

The phase and purity of the as-obtained sample was examined by XRD. Fig. 1 shows a typical XRD pattern of the sample. All of the diffraction peaks in this pattern can be readily indexed to the hexagonal phase of CdS. The lattice constants calculated from this pattern are $a = 0.4150$ nm and $c = 0.6757$ nm, which are in good agreement with the reported values (JCPDS Card No. 41-1049, $a = 0.4140$ nm, $c = 0.6719$ nm). No impurities can be detected in this pattern, which indicates that pure CdS was obtained under the current synthetic conditions.

The morphology and microstructure of the as-prepared samples were examined by SEM, TEM and HRTEM. Fig. 2a shows a SEM image of a typical sample, in which a large number of microspheres with diameter of *ca.* 1 μm can be observed. A clear view of one of the CdS microspheres (Fig. 2b) demonstrates that the microsphere is assembled from many nanorods with average diameters of *ca.* 30 nm and lengths of *ca.* 200 nm. The nanorods are aligned and radially oriented with their growth axes perpendicular to the surface of the microsphere, which makes the CdS microsphere looks like an urchin. Fig. 2c shows a TEM image of one CdS microsphere, which further reveals that these urchin-like CdS microsphere are assembled from CdS nanorods. The HRTEM image (Fig. 2d) taken from a CdS nanorod shows its single crystal in nature. The interplanar spacing along the growth direction is 0.67 nm, which corresponds to the separation between (001) lattice planes of hexagonal CdS. The SAED pattern of this nanorod shown as an inset in Fig. 2d may be indexed to the [010] zone axis of hexagonal CdS, which also confirms that this nanorod grows along the [001] direction.

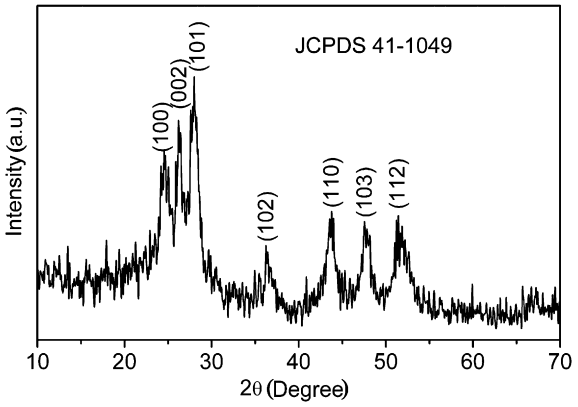

Fig. 1. XRD pattern of as-prepared CdS sample.

The previous reports on the synthesis of CdS nanorods employ the solvothermal method are mostly involving the use of en as a solvent [40–42]. It is believed that en molecules adsorbed on the surface of CdS play a critical role in the formation of CdS nanorods [40–43]. To make clear the role of en played in the formation of the urchin-like structure of CdS, a series of experiments were carried out by changing the volume ratio of water/en while kept the total volume of the mixed solvent constant. When only en was used as the solvent, many dispersed CdS nanorods with diameters of 20–30 nm were obtained (Fig. 3a). When a mixture of 20 mL en and 20 mL water was used as the solvent, many CdS nanorods still could be obtained (Fig. 3b), but some of the CdS nanorods are assembled together. With increasing the volume ratio of water/en, the assembly of CdS nanorods becomes more obvious. Fig. 3c displays a SEM image of the CdS sample obtained in a mixed solvent of 10 mL en and 30 mL water. In this figure, it may be observed that more CdS nanorods are assembled together. Fig. 3d shows a SEM image of the sample obtained in a mixed solvent of 0.5 mL en and 39.5 mL water, in which many urchin-like microspheres that assembled from CdS nanorods are presented, and no dispersed CdS can be observed. To obtain urchin-like CdS microspheres, an optimal volume of en added in the mixed solvent is 0.5–1 mL. When the volume of en in the mixed solvent is 0.25 mL or less, many irregular nanoparticles instead of nanorods or nanorods assemblies are obtained. From the above experimental results we learn that en is essential for the formation of CdS nanorods, and the self-assembly of CdS nanorods can be well controlled through adjusting the volume ratio of water/en.

The growth process of the urchin-like CdS microspheres was studied by quenching the Teflon-lined autoclaves with tap water after they had been heated at 180 °C for different periods of time. Fig. 4a shows a TEM image of the CdS sample obtained after heated for 10 min, in which many irregular nanoparticles with diameters of about 10 nm can be seen. The CdS nanoparticles are poorly crystallized according to XRD analysis (Curve I, Fig. 4b). In this sample, we also find some rod-like particles (Fig. 4c). TEM image of the CdS sample obtained after heated for 13 min is shown in Fig. 4d, in which some nanorods along with tiny nanoparticles can be seen. These nanorods tend to aggregate to form urchin-like CdS microspheres. Fig. 4e shows a TEM image of the sample obtained after heated for 15 min. We can see that more nanorods are assembled together. XRD analysis indicates the presence of hexagonal phase CdS (Curve II, Fig. 4b). Many urchin-like microspheres of CdS can be seen from the SEM image (Fig. 4f) of the sample obtained after heated for 20 min. Furthermore, we can observe that the microspheres are buildup of many nanorods along with some tiny nanoparticles. The nanorods have average diameters of about 10 nm. SEM images of the CdS sample obtained after heated for 30 min and 60 min are shown in Fig. 4g and h. It may be seen that the average diameter of the nanorods in the urchin-like microspheres increases with decreasing the content of nanoparticles. After heated for 4 h, the obtained urchin-like CdS microspheres are totally buildup of nanorods with average diameters of about 30 nm (Fig. 2a and b). The above results indicate that tiny CdS nanoparticles are formed in the early stage and then gradually converted to microspheres assembled from CdS nanorods.