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Diethylenetriamine-assisted synthesis of CdS nanorods under reflux condition and their photocatalytic performance

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ABSTRACT

The morphologies and photocatalytic activity of the CdS nanostructures are sensitively dependent on the synthesis condition. Here, CdS nanostructures with various morphologies were synthesized by controlling the amine species under different reaction conditions. Especially, one-dimensional CdS nanorods with average diameter of ~10 nm and length of ~200 nm were successfully synthesized by a facile "one-pot" reflux method by using diethylenetriamine (DETA) as template and coordination agent. And the formation of CdS nanorods followed solvent coordination molecular template (SCMT) mechanism. By application of these materials as catalysts in photodegradation of methylene blue and photo-induced water splitting, it was found that the DETA-assisted synthesized CdS nanorods exhibit higher photocatalytic activities than the other CdS nanostructure. The favorable photocatalytic performance for the CdS nanorods should be ascribed to their anisotropic characteristic and good dispersion, leading to excellent photogenerated electron/hole separation ability.

1. Introduction

As an important II–VI group semiconductor, CdS has received much attention due to their potential application for photocatalytic reaction [1–3], photoelectric conversion in solar cells [4–6] and other optical devices [7–9]. Over the past few years, considerable efforts have been made to control the size and shape of CdS nanocrystals [10–16]. In particular, one-dimensional (1D) CdS nanostructures are intensively explored because of their unique physical–chemical properties [17–21]. Recently, the application of semiconductor for photocatalysis has become a hot subject [22–24]. In the photocatalytic process, one of the key points for increasing the photocatalytic activity is to suppress the recombination of photo-excited electron–hole pairs [25,26]. The 1D CdS nanostructures nanostructures has large specific surface area, high aspect ratio and anisotropic characteristics, so it would be benefit for separation of photogenerated electron–hole pairs and exhibit good photocatalytic activity when they were used as the photocatalyst.

So far, many techniques, including electrochemically induced deposition [27], sol–gel process [28], physical evaporation [29] and solvothermal method [30,31], have been employed to prepare 1D nanostructure. In these approaches, the solvothermal method has become the simplest method due to its high rate of product, good purity and less pollution [32,33]. However, solvothermal method was usually performed under high temperature and high pressure condition. Therefore, exploration of facile preparation method for CdS nanorods under relatively moderate conditions is desired.

In the process of solvothermal synthesis, the organic amines, usually as linking agents, play a crucial role on the CdS nanocrystals morphologies. For example, Yao et al. reported the special flower-like structure of CdS nanocrystals can be obtained under aqueous system containing with diethylenetriamine (DETA) [34]. When it was replaced by dodecylamine, nanorods, multipods, and triangular-like shape CdS nanocrystals becomes the main products [14]. While in the presence of ethanediamine (EN) template agent, CdS nanorods were synthesized and their growth followed the solvent coordination molecular template (SCMT) mechanism [35–37]. Therefore, the adoption of suitable amine species and clarification of the formation process in different amine media become the key step to design an efficient pathway for synthesis of 1D CdS nanorods.

In this work, series of CdS nanostructures with various morphologies were synthesized by changing the amine species and reaction condition. And the CdS nanorods with average diameter of ~10 nm and length of ~200 nm were synthesized via a DETA-assisted reflux route, the evolution process could be explained by SCMT mechanism. By application of these CdS nanostructures as

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catalyst in the systems of photodegradation of methylene blue and photocatalytic water splitting, it was found that DETA-assisted synthesized CdS nanorods photocatalysts with anisotropic characteristics exhibit higher photocatalytic activity than the other CdS nanostructures, resulting most likely from the good ability to suppress the recombination of photogenerated electron–hole pairs.

2. Experimental

2.1. Fabrication of CdS nanorods via DETA-assisted reflux route

All reagents in our experiments are analytically pure grade and used without further purification. In a typical synthesis procedure of nanorods, 0.028 mol $Cd(AC)_2{\cdot}2H_2O$ and 0.056 mol thiourea were added into a three-neck flask with 30 ml distilled water and continuously stirred about 5 min, subsequently 64 ml diethylenetriamine was introduced into the mixture solution. Then, the solution was refluxed for 13 h under stirring and cooled to room temperature. A yellow precipitate was filtered and washed several times with anhydrous ethanol and deionized water to remove the excess reactants. Finally, the sample was dried in a vacuum oven at 60 °C for 8 h. The as-prepared CdS nanorods were named by Rod-DETA-R. To investigate the influence of experiment parameters, the comparative experiments under different reaction temperature (70 and 90 °C) for 13 h and different time (1, 4 and 8 h) at refluxed temperature were also carried out.

2.2. Fabrication of other CdS nanostructure

The molar ratio of Cd $(AC)_2{\cdot}2H_2O$ and thiourea was similar to DETA-assisted reflux condition, the volume of added amine (EN or DETA) and water for reactions stay the same as DETA-assisted reflux method. Agminated CdS nanorods were prepared by EN-assisted reflux method for 13 h, which was substituted by Rod-EN-R. Short CdS nanorods were synthesized by EN-assisted solvothermal method, which was represented by Rod-EN-R. Detailed description as follows: the mixture was stirred to form a homogeneous solution and then placed in an autoclave with an inner Teflon lining. After that, the autoclaves were maintained at 180 °C for 13 h and cooled to room temperature. Finally, the sample was washed fully and dried in a vacuum oven at 60 °C for 8 h. Similarly, CdS nanospheres composed of nanoparticles was fabricated by DETA-assisted solvothermal method, which was named by Sphere-DETA-S.

2.3. Catalyst characterization

The as-prepared samples were characterized by transmission electron microscopy (TEM, JEOL JEM-2010) using an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns of the samples were obtained on a BRUKER D8 ADVANCE X-ray diffractometer (German) using Cu Kα radiation (λ = 1.5406 Å). Fourier transform infrared (FTIR) spectra were carried out on a Nicolet 380 spectrometer using KBr pallets at ambient temperature. To obtain the UV–Vis absorption spectra, the samples were performed on a Shimadzu UV–Vis–NIR spectrophotometer (UV-3600). Photoluminescence (PL) spectra were recorded at room temperature on a fluorescence spectrophotometer (Hitachi F-7000, Japan) using Xenon lamps as the excitation source, all samples were excited to a wavelength of 300 nm.

2.4. Photocatalytic tests

Photocatalytic degradation of methylene blue (MB) was carried out as follows: 0.1 g sample of catalyst was added to 100 mL of methylene blue (MB) aqueous solution (methyl blue concentration: 20 mg/L). The suspension was stirred in the dark for 2 h to reach the adsorption equilibrium prior to illumination. The light source was 300 W Xe lamps (Trusttech PLS-300UV, China) with a UV filter ($\lambda \geqslant 420$ nm). Approximately 4 mL of aqueous solution was collected at regular intervals and centrifuged. The concentration of methylene blue in the centrifuged aqueous solution was determined by measuring the absorption of methylene blue at 665 nm on a UV–Vis spectrophotometer, from which the photocatalytic activity was evaluated.

Water splitting reactions were carried out in a top-irradiation vessel connected to a closed gas circulation system made of glass. 0.1 g CdS photocatalyst powder was dispersed in a 100 mL 0.1 M Na_2S/Na_2SO_3 aqueous solution. The whole reaction process was cooled between 4 °C and 9 °C. The light source was a 300 W Xe lamp with a UV filter ($\lambda \geqslant 420$ nm). The amount of H_2 evolution was determined using a gas chromatography (Agilent Technologies: 6890 N).

3. Results and discussion

3.1. DETA-assisted synthesis of CdS nanorods and the influence of experiment parameters on the final products

Fig. 1 shows the XRD patterns of samples obtained at different reaction temperatures and times. All the products exhibit the hexagonal lattice of wurtzite CdS structure with prominent diffraction peaks corresponding to (100), (002), (101), (110), (103) and (112) planes (JCPDS Card File, No. 41-1049). By close inspection, it can be seen that the crystallinity for these CdS samples is rather different (the intensity and width of (002) plane), suggesting the crystal properties have been greatly affected by temperature and times. For example, the crystallinity of samples is poor at low temperature (70 °C), while it became a little better when the temperature rises to 90 °C. As the temperature reaches the boiling point of reaction mixture (118 °C), the growing increase in the intensity ratios of (002)/(100) and (002)/(101) indicates the products are oriented growth. The TEM and HRTEM images of CdS samples prepared at different temperatures were shown in Fig. 2. It can be seen from Fig. 2(a) that the samples synthesized at 70 °C exhibits irregular folding slices. When the reaction temperature is 90 °C, the irregular slice is still remained (Fig. 2(b)). Fig. 2(c) is the TEM image of the sample prepared at 118 °C under reflux condition, which shows the well-defined and uniform nanorods with diameter of ~10 nm and length of ~200 nm were found at refluxed temperature (118 °C). The HRTEM images shows that all of the synthesized products under different temperature have the same interplanar distance (0.34 nm) along the growth axis, consistent with the interplanar distance of (002) plane for the wurtzite structure of CdS. Further confirmation for the morphology of CdS was carried out by the field-emission scanning electron microscopy (FE-SEM) analysis (Fig. 1S). As it shown, the samples prepared at 70 °C were composed of a lot of slice, as the temperature reached, rod-like nanostructures would appear, and most of the nanorods can be observed when the reaction was carried out at the reflux temperature.

The influence of reaction time on the crystallinity and morphology of product has also been conducted. As shown in the XRD patterns, the sample obtained at 1 h (Fig. 1) had the poor hexagonal structure of CdS. With the time increasing, the intensity ratios of (002)/(100) and (002)/(101) became stronger, which can be ascribed to a preferential orientation along *c*-axis of the nanorods. Fig. 3 shows TEM images of the samples prepared at reflux temperature for different reaction times. The morphology of products prepared at reflux temperature for 1 h (Fig. 3(a)) was consisted some aggregated folding slices. As reaction time increased to 4 h (Fig. 3(b)), needle-like fragments begin to appear. Further, the sample obtained at reflux temperature for 8 h (Fig. 3(c)) showed some nanorods with a short length, and the dimensions became more uniform among nanorods orientation. When the reaction time

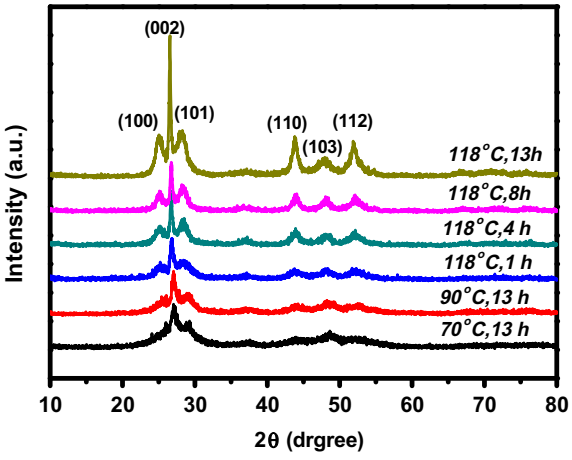

Fig. 1. XRD patterns of samples by DETA-assisted synthesis at different temperatures and times.