

Synthesis and characterization of CdSe nanorods using a novel microemulsion method at moderate temperature

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Abstract

CdSe nanoparticles have been successfully synthesized using a novel microemulsion method at moderate temperature. It is found that with a combination of the surfactant AOT and hydrazine hydrate, it is possible to control the morphology of the nanoparticles. The hydrazine hydrate acts as both a reducing agent and a templating agent that favors the formation of a rodlike structure. The composition, morphology and optical properties of the CdSe nanoparticles were investigated using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), ultraviolet–visible (UV–vis) absorption spectroscopy, photoluminescence (PL) spectroscopy, energy dispersive X-ray spectroscopy (EDX) and Fourier transform infrared (FT-IR) spectroscopy. The nucleation and growth mechanism for this system is also proposed based on a time-dependent study. This synthesis route provides a moderate temperature (100 °C) method for synthesizing rodlike CdSe, hence reducing the possibility of oxidation of this chalcogenide compound.

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1. Introduction

Cadmium selenide (CdSe), which is a narrow band gap material with an energy bandgap of 1.75 eV at 300 K [1], is one of the most important Group II–VI semiconductors. This material has been widely used for photoelectronic devices [2]. In the past decade, a great deal of research has been done on controlling the size, shape and crystal structure of CdSe nanocrystals because their electrical and optical properties are strongly related to their morphology. Many methods have been used to prepare the nanorods and they can be broadly divided into two groups: hot coordinating solvent method and hydrothermal method.

Alivisatos and co-workers [3] have developed a high temperature (around 300 °C), non-aqueous based method using organometallic precursors to control the shapes of CdSe nanocrystals. This method can generate nearly monodisperse CdSe nanorods due to the separation of the nucleation and growth stages. Several other shapes of CdSe nanocrystals, such

as rod-, tetradrod- and tetrapod-, have also been prepared by carefully controlling the nucleation and growth rate in a mixed surfactant system [4,5]. There are some disadvantages relating to this organometallic synthesis method [6]. The temperature for the synthesis is high and the nanoparticles produced have poor reproducibility. On top of this, extremely dangerous reactants (e.g., dimethylcadmium) are used. Another drawback of this method is the high cost compared to the microemulsion method [7]. Recently some changes have been made to this process such as the replacement of dimethylcadmium with cadmium oxide. But the complicated procedures involved in the method and the requirement for accurate temperature control at such high temperatures is still a concern.

Peng et al. first employed sodium selenite (Na_2SeO_3) as the Se source in their synthesis where Na_2SeO_3 is reduced to highly reactive Se by hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). They found that at 140 °C, CdSe with a mixed morphology of both branch-shaped fractals and nanorods was produced mainly, and at 180 °C, the products are mainly CdSe nanorods [8]. Chen et al. used a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) via hydrothermal method at 180 °C to synthesize CdSe

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nanorods. They used the same precursor and reducing agent as Peng et al. [9]. However, the synthesis of CdSe nanorods at moderate temperature has been less frequently researched [10]. In their work, they also synthesized nanoparticles in the micelles and dispersed them with the aid of ultrasound at low temperature. Both nanorods and spherical particles coexist in the products.

In this work, an anionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (see Fig. S1), and a reducing agent, hydrazine hydrate, are used in a water-in-oil microemulsion synthesis route for CdSe nanorods at the moderate temperature of 100 °C. The nanoparticles synthesized using this route are typically spherical in morphology. However, Pileni et al. [11] have synthesized copper nanorods with a combination of AOT and hydrazine hydrate by carefully controlling the water content at a constant hydrazine hydrate concentration.

According to the phase diagram [12], the current system employed is on the *n*-heptane-rich side. Therefore reverse micelles are formed in the synthesis. In our case, water droplets with two precursors, Na₂SeO₃ and Cd(NO₃)₂, are dispersed in the *n*-heptane separately and stabilized by a shell formed by AOT. The stability of these micelles is greatly enhanced due to the high concentration of AOT and the existence of hydrazine hydrate. The concentration of AOT in this system is far above the CMC, which is 0.0025 mmol/ml [13]. It was found by several groups that hydrazine hydrate is not only a reducing agent, but also acts as a component of the templating agent in the formation of CdTe and a nickel nanorod structure [14,15]. Besides, it also can prevent oxidation of CdSe nanoparticles after preparation due to its reducing capability [16]. However, the detail of the mechanism is still unclear at this time. In this work, we attempt to study the mechanism of growth for these crystals at low temperature. In order to monitor the change in the reaction in this paper, two molar ratios were considered:

$$R = [\text{H}_2\text{O}]/[\text{AOT}],$$

$$S = [\text{hydrazine hydrate}]/[\text{AOT}].$$

Based on the experimental results, the mechanism for the formation of CdSe nanoparticles will be proposed in the final part of this paper.

2. Experimental

2.1. Materials

Cadmium nitrate-tetrahydrate (Cd(NO₃)₂·4H₂O, 99%) was purchased from Merck. Both sodium selenite (Na₂SeO₃, 99%) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 96%) were purchased from Sigma-Aldrich. Hydrazine monohydrate (N₂H₄·H₂O, 98%) and *n*-heptane (CH₃(CH₂)₅CH₃, 98%) was purchased from Kanto Chemical Co. Inc. and Lab-scan respectively. All chemicals were used without further purification and/or treatment. Deionized water was used in all experiments.

2.2. Synthesis of CdSe nanocrystals

In this synthesis, a series of *R* and *S* molar ratios are studied. The *R* value ranges from 5.0 to 8.5, while the *S* value ranges from 4.0 to 9.0. In a typical synthesis, where *R* = 5.0, and *S* = 5.2 and the molar ratio of [Cd(NO₃)₂·4H₂O]/[Na₂SeO₃] is equal to 1:1, the amount of reactants and the procedure for the synthesis are as follows: 10 mmol of AOT was dissolved in 50 ml of *n*-heptane in a three-necked flask to which is attached a condenser and a septum plus valves. The mixture was deaerated by bubbling with N₂, initially at room temperature. 0.45 ml of Cd(NO₃)₂·4H₂O aqueous solution (2.78 mmol/ml) was dropped into the above solution while the system was stirring and heated. When the temperature of the solution reached around 100 °C, a mixture of 2.55 ml of hydrazine hydrate (52.4 mmol) and 0.45 ml Na₂SeO₃ aqueous solution (2.78 mmol/ml) was added using a syringe over a duration of 30–45 s. The reaction took place under a N₂ environment and the solution was refluxed with continuous stirring for about 6 h. The color of the final solution changed rapidly from yellow to orange to red and then to deep dark red indicating the successful synthesis of CdSe nanoparticles. After the reaction was completed, the deep dark red precipitate was washed repeatedly with deionized water and ethanol to remove any ions that may still be present in the sample. Finally, the product was dried overnight in a vacuum oven at 60 °C to remove the remaining water from the sample.

2.3. Characterization

The ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra of the nanoparticles were obtained using a Shimadzu UV2501PC spectrophotometer and a Shimadzu RF-5301 PC fluorometer, respectively. The excitation wavelength for PL was 475 nm. All the optical measurements were performed at room temperature under ambient conditions. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were carried out using a JEOL 2010 microscope fitted with a LaB₆ filament using an acceleration voltage of 200 kV. TEM samples were prepared by dropping one or two drops of the nanoparticles in ethanol solution onto carbon-coated copper grids. Powder X-ray diffraction (XRD) patterns were recorded using a Shimadzu LabX-XRD-6000 X-ray diffraction instrument at a scanning rate of 4°/min with 2θ ranging from 10 to 80°, using CuKα radiation (λ = 0.1542 nm) radiation operating at 40 kV and 60 mA.

3. Results and discussion

3.1. Phase analysis

A typical XRD pattern of the as-prepared CdSe nanoparticles along with the position of the hexagonal CdSe peaks from the JCPDS is shown in Figs. 1a and 1b. All the reflections from the CdSe nanoparticles can be indexed to hexagonal CdSe with lattice constants of *a* = 0.4264 nm and *c* = 0.7014 nm (JCPDS file No. 08-0459, *a* = 0.4299 nm and *c* = 0.7010 nm).

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