Solvothermal Fabrication of Monodisperse Zinc-blende CdS Nanocrystals

Ming Chen,[1] Lijia Pan,*[1,2] Jieming Cao,*[1] Mingbo Zheng,[1]
Yongping Chen,[1] Yulin Cao,[1] and Haiqian Zhang[1]
[1]*College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nangjing 210016, P. R. China*
[2]*Department of Physics, Nanjing University, Nanjing 210093, P. R. China*

(Received September 4, 2006; CL-061012; E-mail: ljpan@nju.edu.cn)

Nearly monodisperse CdS semiconductor nanocrystals have been successfully fabricated by a simple solvothermal route using cheap and low-cost normal inorganic compounds as precursors. The reaction temperature is demonstrated to be critical for the fabrication of the monodisperse nanocrystals. The nanocrystals were characterized by XRD, TEM, UV–vis absorption and photoluminescence spectra. Without involving special conditions, this method can be expected to make considerable contribution to the fabrication of various nanocrystals and nanocrystals-related research.

Semiconductor colloidal nanocrystals as an important class of materials have attracted broad attentions in recent years due to their fundamental importance and potential important technological applications such as light-emitting diodes,[1] optoelectronic devices,[2] solar cells,[3] biological fluorescence labeling,[4] and so on. Colloidal nanocrystals exhibiting unique size-dependent characteristics, novel electronic and optical properties are suitable building blocks for the next generation device application.[5] In the past two decades, considerable efforts have been employed for fabricating many metal sulfide nanocrystals due to their quantum confinement effects and size-dependent photoemission characteristics.[6] Various chemical routes were reported to prepare nanocrystals, including the pyrolysis of (roughly 250–350 °C) single molecular organometallic compounds schemes or alternative approaches in organic solvents which have played a key role in the colloidal nanocrystals fabrication.[7] Very recently, An's group utilized a two-phase approach which was carried out under mild conditions with less toxic and inexpensive reagents, and have successfully fabricated highly luminescent and nearly monodisperse CdS nanocrystals, extremely small CdSe and CdS/CdSe core/shell nanocrystals.[8] However, this method requires careful design of Cd precursors. Moreover, Li and co-workers reported a general method to fabricate nanocrystals through a simple hydrothermal method which is based on a general phase transfer and separation mechanism occurring at the interfaces of the liquid, solid, and solution phase during the fabrication.[9] However, it is important to develop a convenient method for the fabrication of monodisperse CdS nanocrystals via a simple solution route without extreme conditions such as glovebox and inert atmospheres. Herein, we report the study of fabricating nearly monodisperse CdS nanocrystals using the traditional solvothermal method in the presence of oleic acid and octadecylamine, which is conducted simply by the reaction of $Cd(AC)_2 \cdot 3H_2O$ and S powder. Due to the special reactivity under high temperature and high pressure, S powder can be directly used as sulfur sources. We took advantage of solvothermal method to obtain a high temperature for the growth of CdS nanocrystals without using tedious size-selective process.

All of the chemicals are analytical or higher grade and used without further purification. In a typical reaction for the fabrication, a mixture of $Cd(AC)_2 \cdot 3H_2O$ (0.533 g), 1.080 g of octadecylamine (ODA) was added to 20-mL oleic acid to form an optically clear solution under heating and stirring, which was heated at 80 °C for about 3 h by water bath. A 0.032 g of S powder was added into the solution and stirred vigorously for about 1 h to dissolve S powder completely. The resulting mixture was then sealed in the stainless steel autoclave with a capacity of 25 mL and maintained at 220 °C for 3 h. Then, the autoclave was cooled naturally to ambient temperature after given reaction time. The product was washed several times with anhydrous ethanol followed by centrifugation, and yellow colored CdS nanocrystals were obtained. The as-prepared CdS nanocrystals could be easily redispersed in nonpolar solvents such as hexane and aggregated by adding anhydrous ethanol. The dispersion of CdS nanocrystals in 5-mL hexane yielded a yellow transparent homogeneous dispersion, which was stable for weeks at room temperature and showed no signs of aggregation. The structure and shape and size of the obtained CdS nanocrystals were characterized by transmission electron microscopy (TEM) and by powder X-ray diffraction (XRD). The optical properties of the sample were investigated by using UV–vis spectra and the photoluminescence spectra.

The powder XRD patterns of the as-synthesized CdS nanocrystals are shown in Figure 1, in which all of the detectable peaks are indexed to the standard bulk of CdS, confirming it to be pure cubic phase zinc-blende crystal structure. All of the peaks in the XRD patterns are apparently broadened because of the nanometer size of nanocrystals. It can be seen that the sample prepared at 200 °C shows much broader and less intense diffraction peaks due to its smaller size (Figure 1B).

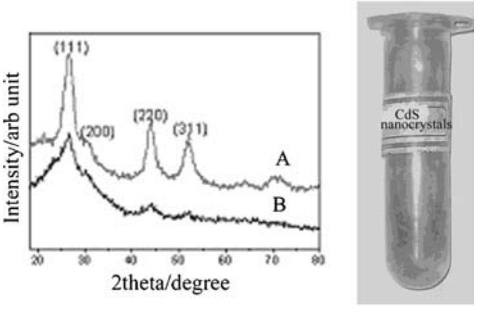

Figure 1. (Left) XRD patterns of CdS nanocrystals (A) at 220 °C; (B) at 200 °C; (Right) Picture showing transparent and stable solution of CdS nanocrystals.

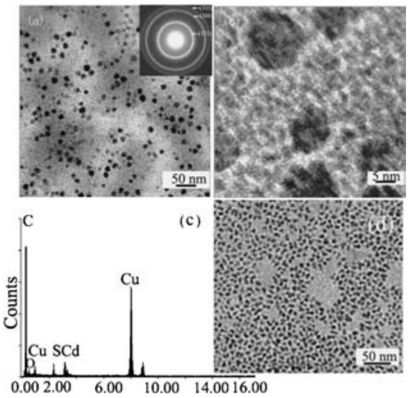

Figure 2. (a), (b) TEM images of CdS nanocrystals at 220 °C; The inset in (a) is an SAED image; (c) Energy dispersive spectroscopy (EDS) obtained from the CdS nanocrystals; (d) TEM images of CdS nanocrystals at 200 °C.

Nearly monodisperse CdS nanocrystals with an average size of around 13 nm were found in the TEM image (Figures 2a and 2b), which is consistent with the calculated particle sizes from the broadening of the (111) diffraction peak using Scherrer's formular. The TEM images revealed that the prepared CdS sample was consisted of polyhedron outer shape nanocrystals due to the selective absorption of capping ligand on certain cubic faces during the crystal growth.[10] The nanocrystals are quite well dispersed, indicating that the current method is effective in preventing the nanocrystals from agglomeration.

The selected area electron diffraction (SAED) pattern revealed that the nanocrystals are highly crystalline and can be indexed as the (111), (220), and (311) planes of typical cubic CdS nanocrystals, as shown in the set of Figure 2a. The energy dispersive spectroscopy (EDS) analysis of the product in Figure 2c demonstrated that they are composed of only Cd and S with the Cd/S atomic ration of about 1:1, indicating the nanocrystals were highly pure. The peaks of C and Cu signals are attributed to the carbon-coated copper grid.

In our experiment, the reaction temperature was crucial for the formation of the CdS nanocrystals. It is noticeable that when the reaction temperature was 220 °C, the poorer crystallinity of CdS nanocrystals was obtained, as can be seen from the XRD pattern (Figure 1B). The corresponding TEM (Figure 2d) showed that the sample had poorer dispersion and the smaller average diameter. Furthermore, the amount of the octadecylamine was found to be very important for the experiment. Without adding the octadecylamine in the reaction system, the CdS nanocrystals could not be obtained.

In the reaction system, oleic acid was used as solvent and ligand for stabilizing the nanocrystals. The oleic acid moleculars would be coated onto the outer surface of the nanocrystals through the interaction between the Cd^{2+} ions and carboxyl of the oleic acid with the hydrophobic alkyl chains left outside, which led to good dispersibility in nonpolar solvent.[11] Furthermore, oleic acid is used not only for the capping agent but also for preventing premature contact between Cd and S source under the lower temperature, which would benefit to form the uniform and nearly monodisperse nanocrystals.

The Figure 3 presents the room temperature UV–vis absorption spectra and photoluminescence spectra of the CdS nanocrystals. The absorption spectrum for the CdS nanocrystals shows the edge at 460 nm (2.69 eV), which is blue-shift compared with the absorption onset of bulk CdS (515 nm, 2.4 eV) because of the quantum size effect. The PL spectrum of the sample using an excitation wavelength of 325-nm He–Cd laser as excitation source is shown in Figure 3B. The PL spectrum shows a broad emission with a well-defined peak around 415 nm due to the band gap emission of CdS.

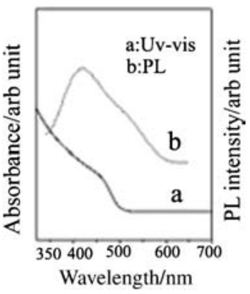

Figure 3. UV–vis and PL spectra of the CdS nanocrystals prepared using 220 °C.

In summary, we have demonstrated a simple solvothermal method to fabricate nearly monodisperse and uniform CdS nanocrystals. The advantages of this method for fabricating CdS nanocrystals lie in its safety, convenience, and low cost. The absorption and photoluminescence spectra nanocrystals show the blue-shift compared to bulk CdS. It is possible to extend this feasible method to prepare the other transition-metal sulfide semiconductor nanocrystals.

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