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Preparation and optical properties of dispersible ZnSe nanocrystals synthesized by high energy ball milling

Jianping Li, Minqiang Wang *, Wang, Xiao Huo, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

ZnSe nanocrystals have been successfully synthesized by high energy ball milling method. X-ray diffraction patterns show a single zinc blende structure formed in the milling process. HRTEM images confirm that the formation of the ZnSe nanocrystals synthesized by high energy ball milling have a wide crystals distribution (3–20 nm). Using the aqueous solutions of Na_3PO_4, $(NaPO_3)_6$ and $Na_4P_2O_7$ to disperse the 40 h-milled samples, we have observed the gradual blue-shift of the absorption edge along with the different centrifuging speed. In PL spectras, two main bands peaked at about 1.95 and 2.35 eV are observed, the former band is related to the V_{Zn} defects emission; and the latter is related to the V_{Se} defects emission. The V_{Se} defects emission does not depend on the dispersants, but the V_{Zn} defects emission changes in different dispersants.

Keywords: ZnSe nanocrystals; High energy ball milling; Absorption spectra; PL spectra

1. Introduction

Since Efros and Efros [1] proposed the quantum confinement effect in semiconductor nanocrystals, the fundamental research and technical applications on nanostructure has become a flourishing field in material science. Theoretically, the semiconductor quantum dots (QDs) is strongly restricted when the dot diameter is comparable to or smaller than the Bohr exciton radius [2–4]. Theoretical calculations have given the relationship between the blue-shift of band gap energy and the diameter of the quantum dots [5–7].

ZnSe, an important wide band gap II–VI semiconductor material, has attracted a significant amount of interests recently [8]. ZnSe nanocrystals materials can obtain by sol–gel method [9,10], hydrothermal method [11], chemical vapor deposition method [12,13], and molecular beam epitaxy method [14,15]. High energy ball milling method with the advantage of low cost and out of chemical contamination form agents was widely used to produce nanometer materials [16]. Some semiconductor nanocrystals had been synthesized by this technique; all of them have revealed the novel quantum confinement effects in optical fields. However, the dispersants play an important influence upon nanomaterials' optical properties. Some organic dispersants (such as: MPA, THF, hexane, TOP/TOPO) have been used to disperse the nanocrystals [17–19], but these dispersant are poisonous and expensive. For achieving the intention of innocuity and inexpensive, inorganic dispersants were selected to take place the organic ones. In this paper, the aqueous solutions of phosphate were used to disperse the ZnSe nanocrystals synthesized by high energy ball milling and their optical properties under different dispersants were investigated.

2. Experimental procedure

Commercially available zinc and selenium elemental powder with a nominal purity of 99.999% were mixed together with atomic ratio of 1:1, and then the mixture powder and 10 mm diameter hardened steel balls were added into the hardened steel vial. Milling processes were performed in a Fritsch Pulverisette 4^{TM} vario-planetary high energy ball milling system. The milling speed of main and minor disk were set at 400 rounds per minute (rpm) and −800 rpm, respectively. Small amount of milled ZnSe nanocrystals were taken out of the vial within different time intervals for X-ray diffraction (XRD; Model D\max-2400, Rigaku) measurement. For the transmission electron microscopy (TEM; Model JEM-3010), the 40 h-milled sample should be dispersed in ethanol by ultrasonic for 20 min.

* Corresponding author.
E-mail address: mqwang@mail.xjtu.edu.cn (M. Wang).

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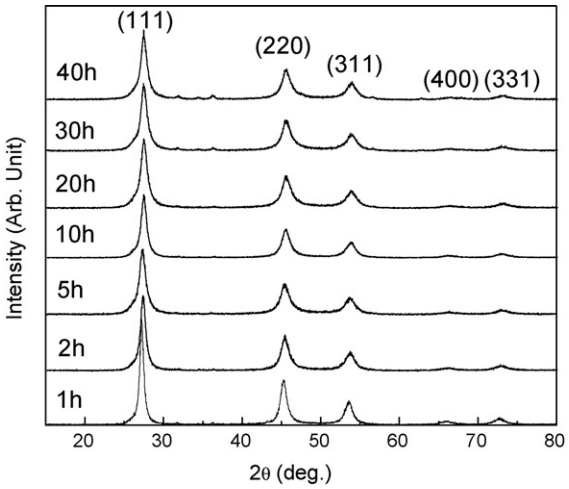

Fig. 1. XRD patterns of ZnSe nanocrystals for different milling time.

The Na_3PO_4, $(NaPO_3)_6$ and $Na_4P_2O_7$ were chosen as the dispersants, and then the aqueous solutions with concentrations of 0.4 wt% were prepared. The pH values of above three solutions are 10.0, 6.6 and 7.8, respectively. Then, 0.1 wt% of 40 h-milled ZnSe nanocrystals was added to the three solutions in sequence. After being operated by ultrasonic and centrifugation, the upper layer solutions were transferred to the quartz vessels for UV–vis spectrophotometer (Model V-570, Jasco) and photoluminescence spectrometer (Model LS55, Perkin-Elmer) experiments.

3. Results and discussion

3.1. Crystal structure and microstructure

XRD patterns for different milling time are shown in Fig. 1. The diffraction peaks of (1 1 1), (2 2 0) and (3 1 1) associated to zinc blende phase can be observed. A broadening of the diffraction peaks is detected, which is indicated the average size of ZnSe nanocrystal had reduced to nanometer. The image of TEM (Fig. 2a) shows that the ZnSe nanocrystals often aggregate, which makes it impossible to show individual particles or obtain the grain size distribution. In the HRTEM image (Fig. 2b), the (1 1 1) lattice planes can be observed; and some smaller nanocrystals less than 10 nm can also be frequently observed, for example, 6 nm particle (marked B), 3 nm particle (marked C). These results are referred to a wide crystallite sizes distribution, which has been previously observed in other semiconductors materials synthesized by high energy ball milling [11,12].

3.2. Optical properties

Fig. 3 shows the absorption spectra of 40 h-milled ZnSe nanocrystals dispersed in Na_3PO_4, $(NaPO_3)_6$ and $Na_4P_2O_7$ solutions, respectively. With the centrifuging speed increased, the absorption edges shifted to higher energy gradually. On the other hand, the color of solutions changed from bright-yellow to slight green-yellow, which indicates the grain sizes dispersing in the solutions become smaller. According to following Brus's formula [5] and absorption edges, we can calculate the minimum grain size in each solution.

$$E(R) = E_g + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon_2 R} + \frac{e^2}{R}\overline{\sum_{n=1}^{\infty}\alpha_n\left(\frac{S}{R}\right)^{2n}}$$

where E_g is the band gap energy of bulk ZnSe material (2.58 eV), ε_2 is the dielectric constant between nanoparticle and medium, and m_e and m_h are effective masses of electron and hole. The result shows the minimum grain size in Na_3PO_4, $(NaPO_3)_6$ and $Na_4P_2O_7$ solutions are 1.5, 2.4 and 1.6 nm, respectively.

In Fig. 3, the solutions without centrifuging and with 1200 rpm centrifuging have a broadening absorption curves. These phenomena can be attributed to surface state absorption of nanocrystals, because the absorption lies below the absorption edge of the nanocrystals and the absorption energy is lower than the band gap (2.58 eV) of the bulk ZnSe [20]. Comparing with the 40 h-milled powder sample's absorption spectra (Fig. 4), it also has a broadening absorption curves in region of 500–800 nm.

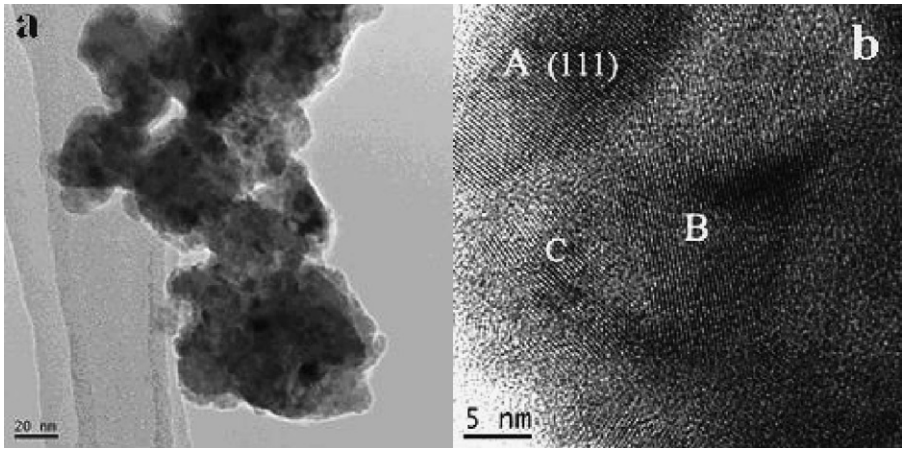

Fig. 2. TEM and high-resolution TEM (HRTEM) images of 40 h-milled ZnSe nanocrystals.

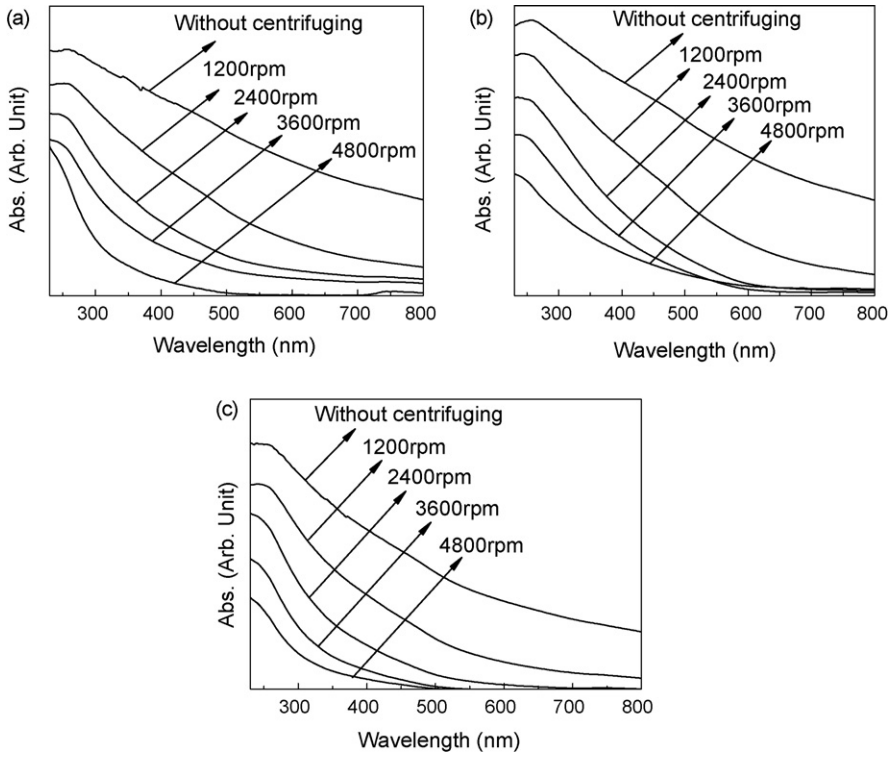

Fig. 3. The 40 h-milled ZnSe nanocrystals dispersed in Na_3PO_4 (a), $(NaPO_3)_6$ (b) and $Na_4P_2O_7$ (c) solutions, respectively.

At overview, PL spectras (Fig. 5) show several emission bands. The band located at 2.88 eV is assigned to double of the excitation wavelength (208 nm). The emission band located at 2.35 eV exists in all three samples, which is due to the V_{Se} defects. This fact is supported by Fernandez and Piqueras, they had reported [21] that a decrease in the intensity of the 2.3 eV emission in CL spectra upon thermal treatments in Se rich atmospheres, which confirmed the 2.3 eV emission is due to V_{Se} defects. Moreover, in the milling process, no only V_{Se}, but also the V_{Ze} were formed. In paper [22,23], they also observed in the milled ZnSe nanocrystals the CL emission peaked at 1.9 eV,

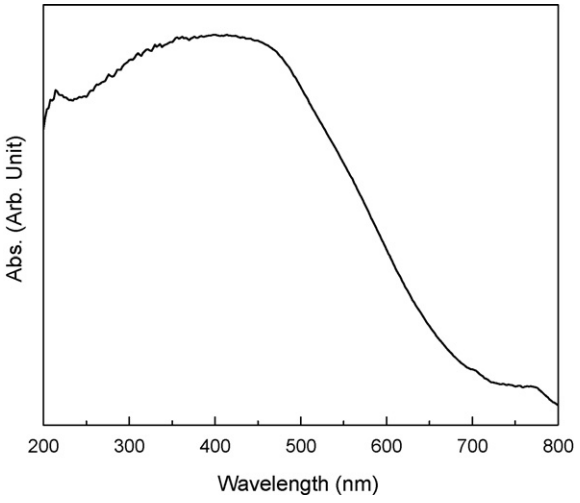

Fig. 4. The absorption spectra of 40 h-milled ZnSe nanocrystals.

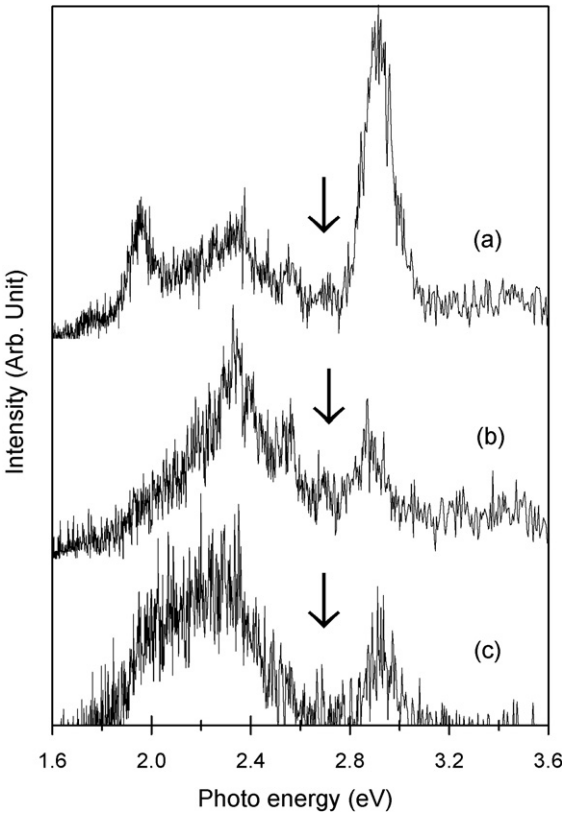

Fig. 5. The PL spectra of the 40 h-milled sample dispersed in $Na_4P_2O_7$ (a), Na_3PO_4 (b) and $(NaPO_3)_6$ (c) solutions, respectively (the band edge emissions have been marked by arrows).

close to the PL band peaked at 1.95 eV here, which are associated to V_{Zn} defects. In addition, there are two faint emission bands in the range 2.5–2.7 eV. The former peaked at 2.57 eV is attributed to a decoration effect of point defects around dislocations produced in the milling process as the nanocrystals size is reduced [24]; and the latter peaked at 2.68 eV is related to the band edge emission. As mentioned before, the three solutions have strong absorption above 2.5 eV, so the emissions above 2.5 eV look relative faint.

In Na_3PO_4 solution, the 2.35 eV emission band is sharp, but the 1.95 eV emission band is hardly observed, which is due to the V_{Se} defects adsorbed hydroxyl ions in the Na_3PO_4 solution; and the hydroxyl ions passivate the nonradiative centers on the nanocrystals surface and create a negatively charged barrier around the nanocrystals [24]. By contraries, in the $Na_4P_2O_7$ and $(NaPO_3)_6$ solutions, the 1.95 eV emission band and 2.35 eV emission band have the same magnitude, or even overlap together (Fig. 9C), probably due to an increase of the hydrogen ions adsorbed by the V_{Zn} defects. This assumption is supported by the fact that the 1.95 eV emission band intensity increases as the pH value decreases. These facts indicate that the hydroxyl ions in solution favor the V_{Se} defects emission; and the hydrogen ions favor the V_{Zn} defects emission.

4. Conclusions

Using the elemental Zn and Se mixture powders as the staring materials, we have successfully synthesized ZnSe nanocrystals of a single zinc blende structure through high energy ball milling method. Dispersing the 40 h-milled ZnSe nanocrystals in the Na_3PO_4, $(NaPO_3)_6$ and $Na_4P_2O_7$ solutions, we have observed the gradual blue-shift of the absorption edges under different centrifuging speeds. These facts indicate that aqueous solutions of phosphate can disperse the nanocrystals effectively; and centrifuging route can select the grain sizes dispersing in solutions. In PL spectra, two main emission bands at 1.95 and 2.35 eV are observed, which are related to the V_{Zn} and V_{Se} defects emissions. The V_{Se} defects emission does not depend on the dispersants, but the V_{Zn} defects emission changes in different dispersants. Overview, using the aqueous solutions of phosphate to disperse ZnSe nanocrystals synthesized by high energy ball milling is a novel way to exhibit their optical properties.

Acknowledgments

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