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Formation and spectroscopic characterization of mono-dispersed CdSe nanocrystals*

Miao Yan-Ming(苗雁鸣), Li Chao-Rong(李超荣), Cao Li(曹 立),
Liu Rui-Bin(刘瑞斌), He Yu-Ping(何玉平),
Xie Si-Shen(解思深), and Zou Bing-Suo(邹炳锁)†

Nanoscale Physics and Device Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, *China*

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In this article, mono-dispersed hexagonal structure CdSe nanocrystals with polyhedron shape were prepared by an open solvent thermal reaction. They show a discrete excitonic transition structure in the absorption spectra and the minimal photoluminescence (PL) peak full-width at half-maximum of 19 nm. The PL quantum yield is about 60%. Transmission electron micrographs, high-resolution transmission electron micrographs, x-ray powder diffraction patterns, UV-vis absorption spectra and PL spectra were obtained for the as-prepared CdSe nanocrystals. The size of the CdSe nanocrystals can be tuned by changing the reaction temperature or time. Due to the improved synthesis method, a different growth mechanism of the CdSe nanocrystals is discussed.

Keywords: mono-dispersed, nanocrystals, formation
PACC: 6146, 7280E, 3250

1. Introduction

There has been extensive interest in the investigation of cadmium selenide nanocrystals in the last ten years, due to the importance of many of their wide variety of applications in new lasers,[1] light emitting diodes,[2−3] biological and medical labelling,[4−7] DNA binding,[8−9] biological imaging and molecular recognition.[10] Compared to the traditional fluorescent dyes, the CdSe nanocrystals exhibit an efficient photoluminescence (PL), whose emission wavelength can be controlled by adjusting their sizes.[11] CdSe nanocrystals can also exhibit much higher photostability and their PL bandwidth depends strongly on the size distribution of the prepared nanocrystals.[12] Moreover, the surface of CdSe nanocrystals can be functionalized easily to enable them not only to be connected with other molecules but also dispersed in various solvents.[9,13,14] Consequently the synthesis of high-quality semiconductor nanocrystals plays a critical role in this active field. Many approaches have been carried out on the synthesis of high quality nanocrystals, including the organometallic one[15] and its alternatives such as using CdO as the precursor.[16] Recently, oleic acid has been used as a ligand to synthesize cadmium chalcogenide instead of trioctylphosphine oxide (TOPO).[17,18] All these approaches have impelled the progress of synthesis of high quality nanocrystals at corresponding times.

In our works, CdO and Se powder are used as the precursors and oleic acid is used as the ligand. Ethanol and liquid paraffin are introduced into the reaction as the solvent of Se powder and the reaction solvent respectively. Though an easily obtained solvent and a simple improved procedure are used in this reaction, the as-prepared CdSe nanocrystals are still uniform in size. Moreover their spectroscopic properties have also been studied. The PL quantum yield (QY) of the CdSe nanocrystals can reach 60% without any purification and further coating. The PL emission peak can be tuned from 460nm to 600nm by changing the reaction temperature and/or time. The mechanism of the nanocrystals' growth has been deduced from their PL spectra. The line-width of PL can be reduced to less

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†Corresponding author. E-mail: zoubs@aphy.iphy.ac.cn

than 20nm and no PL signal from the surface state (far from bandedge) has been observed.

2. Experimental

In our experiments, 0.05g cadmium oxide, and 0.5 mL of oleic acid were loaded into a 100 mL three-neck flask and then heated to 180°C under an argon flow. After CdO was completely dissolved, 50 mL liquid paraffin was added to the flask. Then the mixture was heated to 140°C for 2 hours under argon flow to form an optically transparent solution. The selenium solution containing 0.05 g of selenium powder and 5ml ethanol was heated to 80°C and swiftly injected into the reaction flask. After the ethanol had vaporized out of the reaction solution at a temperature below 140°C, the reaction temperature was set from 140°C to 320°C for the growth of the nanocrystals with different sizes. This improved step induces the different growth mechanism.

The samples for the UV–vis, PL and time-resolved PL spectra measurement were extracted with about 0.5 mL liquid from the solutions and diluted with 10 mL cold toluene (20°C) to stop further growth of the nanocrystals.

Images were obtained on a Philips CM200 transmission electron microscope.[19] X-ray powder diffraction patterns were acquired by the Rigaku D/max-2400 x-ray diffractometer with graphite monochromatized Cu Kα radiation with a weighted mean wavelength of 0.15405nm. The powder samples were prepared as follows. Twenty mL of petroleum ether was added into the solutions of CdSe nanocrystals and cooled to −10°C for 2 hours. After vigorous centrifugation, the precipitation from the cooled solutions were collected and desiccated at 60°C in a vacuum desiccator for 2 hours.

The UV–vis absorption spectra of the CdSe solution were measured with a Pgeneral TU-1901 spectrophotometer operating at a slit width of 1.0 nm. The PL spectra were recorded by using Shimadzu PTI-601 PL spectrophotometer. The PL QY measurements were carried out by comparing the integrated area of the emission peak of the nanocrystals in toluene with that of the fluorescent dye 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) in ethanol (PL QY 71%).

3. Results and discussion

By using the above method, monodispersed CdSe nanocrystals capped with surfactants have been obtained as seen by transmission electron micrograph (TEM) (Fig.1). From the high-resolution TEM (HRTEM), the shape of the single CdSe nanocrystal is not spherical (Fig.2). Most of them are polyhedral because the (100) surface planes are cadmium rich and the contrast increases from the base to the apex.[20] The inter-planar distance of the nanocrystals is 0.375 nm from the HRTEM, which is similar to that of the CdSe hexagonal structure between (100) (d=0.372nm). Hence the as-prepared CdSe nanocrystals are the hexagonal structure and the x-ray powder diffraction (XRD) patterns provide further evidence about that matter (Fig.3).

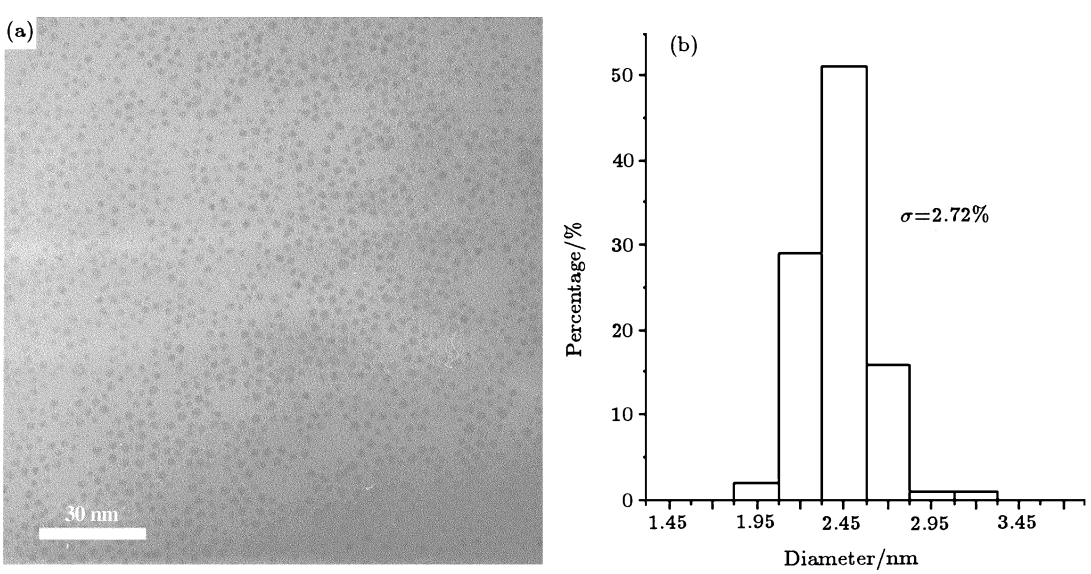


Fig.1. TEM of a sample of the as-prepared CdSe nanocrystals (a) and the corresponding size distribution histograms (b).

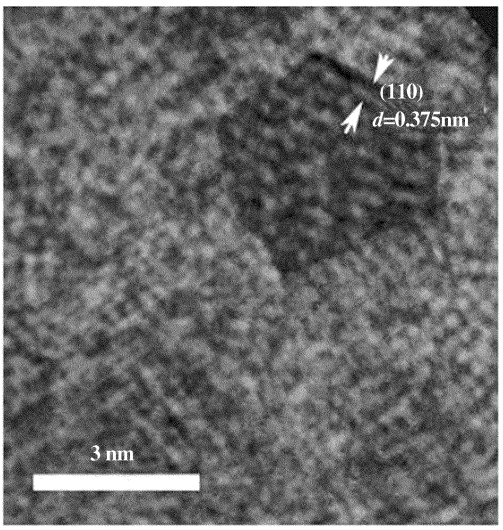


Fig.2. HRTEM of a single CdSe nanocrystal as prepared.

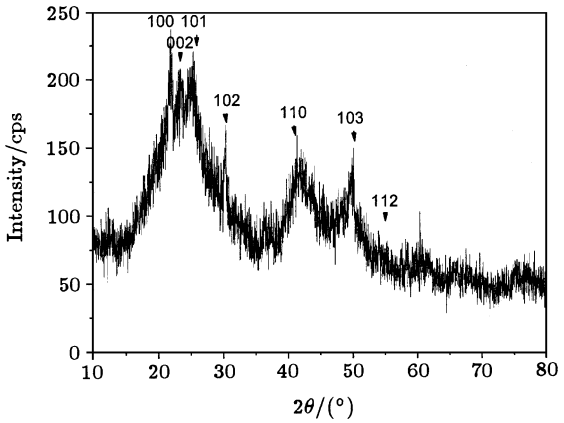


Fig.3. XRD data obtained from the CdSe nanocrystals as prepared.

Different sized CdSe nanocrystals can be prepared by changing the reaction temperature and/or the reaction time. The UV–vis absorption spectra reveal that the 1s–1s' absorption peaks vary between 450nm and 590nm (Fig.4) with the excitonic absorption due to quantum confinement.

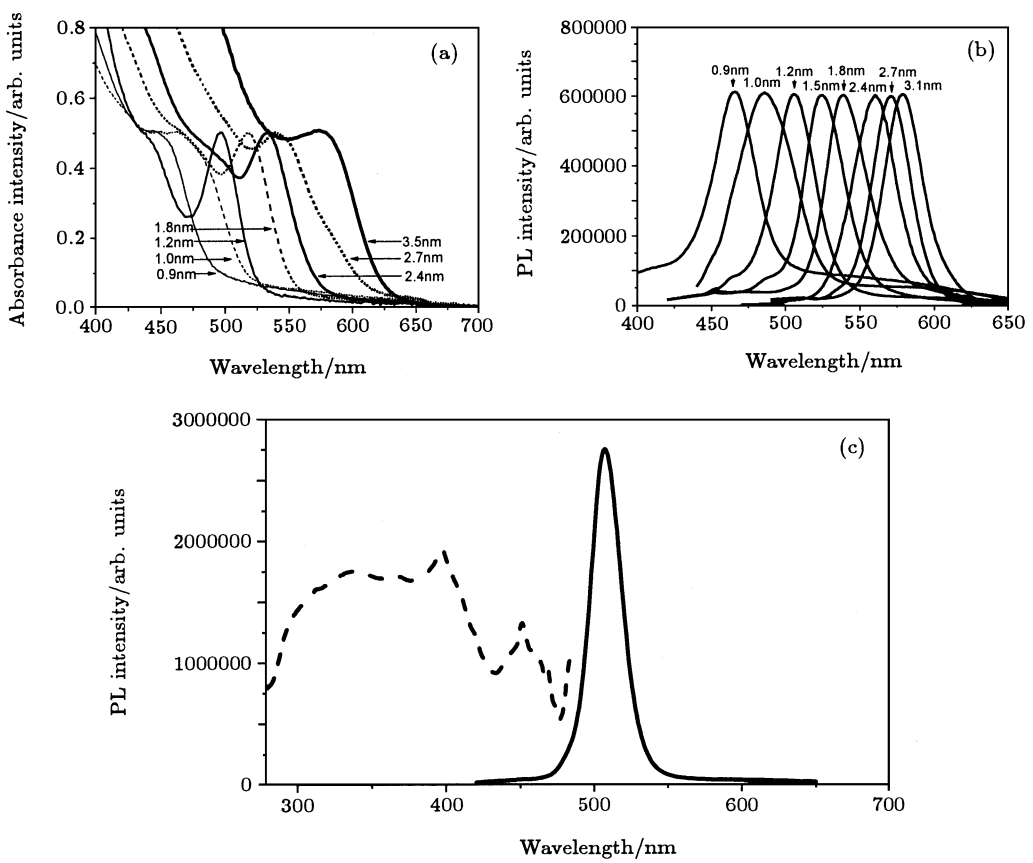


Fig.4. UV–vis adsorption spectra (a) and PL spectra (b) of different sized CdSe nanocrystals as prepared. PL spectra of the sample with the minimal FWHM (c).

From the PL emission spectra of the different sized CdSe nanocrystals, the peaks of eigen-transition varying from 460nm to 600nm can be observed and the peak of the surface state (far from bandedge) cannot be detected, which indicates that the surfaces of the nanocrystals are well capped and the confinement effect is dominant (Fig.4). The minimal PL peak full-width at half-maxmum (FWHM) is 19 nm (Fig.4), which also reveals the narrow size distribution of nanocrystals as prepared. The PL QY of the CdSe nanocrystal is about 40%–60% without any purification or further coating. To get higher PL QY (more than 60%), the nanocrystals need to be heated at a relatively low temperature (such as 140°C) for a long time.

In this reaction, liquid paraffin, a non-polar solvent, is used as the medium. The existence of the polar solvent affects negatively the luminescence of the CdSe nanocrystals. For the samples prepared by using 1-octadecanol or 1-octanol as the Se solvent and without vaporizing it out from the reaction flask, only the UV–vis absorption peaks can be detected but no or poor PL peaks are recorded. Ethanol is the appropriate solvent because it can be easily separated before or during the reaction.

In our experiments, we found something interesting about reaction temperature. Below 140°C, the reaction will not occur. And above 320°C, the CdSe nanocrystals will decompose. The decomposition temperature will be affected by the initial concentration ratio of CdO:OA. The larger the initial concentration ratio of CdO and OA becomes, the higher the decomposition temperature will be. If there is lots of unreacted OA in the flask, the decomposition temperature will be lower.

The size of CdSe nanocrystals grows with increasing reaction temperature or prolonged reaction time, when the concentrations of cadmium precursor and selenium precursor are fixed.

To study the size temperature-dependent properties, we design the experiment as follows. After the ethanol has been vaporized out of the reaction solutions at the temperature below 140°C, reaction temperature is increased quickly from 140°C to 260°C. The samples were extracted at the temperatures of 140°C, 170°C, 200°C, 230°C and 260°C and quenched in cold toluene promptly to stop the reaction. UV–vis absorption and PL measurements were carried out on the samples (see Fig.5 and Table 1).

Table 1. Temperature evolution of UV–vis and PL peak of the samples as prepared.

Temperature/°C	140	170	200	230	260
UV–vis peak/nm	447	463	492	518	534
PL peak/nm	466	486	506	525	539

From Fig.5, we find that the UV–vis absorption peaks and PL peak shifts from 140°C to 260°C and vary nearly linearly with the temperature. And in the range 260°C–320°C the size changes nonlinearly with temperature.

As we all know, every UV–vis absorption and PL emission peak reflects corresponding grain size due to the quantum confinement effect. Quantum confinement effect can be described with the Brus formula,[21]

$$E(r) = E_{\mathrm{g}}(r=\infty) + \frac{\hbar^2\pi^2}{2\mu r^2} - \frac{1.786e^2}{\varepsilon^* r} - 0.248E^*_{\mathrm{Ry}},$$

where $E(r)$ is the absorption band gap of nanosemiconductor particles, E_{g} is the bulk CdSe band gap energy, r is the radius of the particle, $\mu = \left[\frac{1}{m_{\mathrm{e}^-}} + \frac{1}{m_{\mathrm{h}^+}}\right]^{-1}$ is the exciton reduced mass, where m_{e^-} and m_{h^+} are the effective masses of the electron and hole, $\varepsilon^* = \varepsilon^0/\varepsilon^1$ is the relative dielectric constant, where ε^0 and ε^1 is the dielectric constants of bulk CdSe and the capping OA respectively, $E^*_{\mathrm{Ry}} = \frac{\mu e^4}{2\pi^2\hbar^2}$ is the Rydberg energy.

The first band in the UV–vis absorption spectra of CdSe nanocrystals is attributable to transition levels of a complicated nature,[22] so sometimes they do not reveal the size distribution well. The bandedge emissions mainly come from the 1s–1s' transition defined by the above equation. Therefore, the emission bands near bandedge are better used to reveal the size distribution of as-studied nanocrystals than their absorption bands, if the radiation transition dominates. The position of the PL emission is determined by $E(r)$ or r. Consequently we can obtain the peak-positioned nanocrystals of specific size and size distribution by adjusting the reaction temperature and terminating the reaction swiftly. It is easy to control the size of CdSe nanocrystals by grasping the temperature-dependent formation processes, which is important for their industrial production.

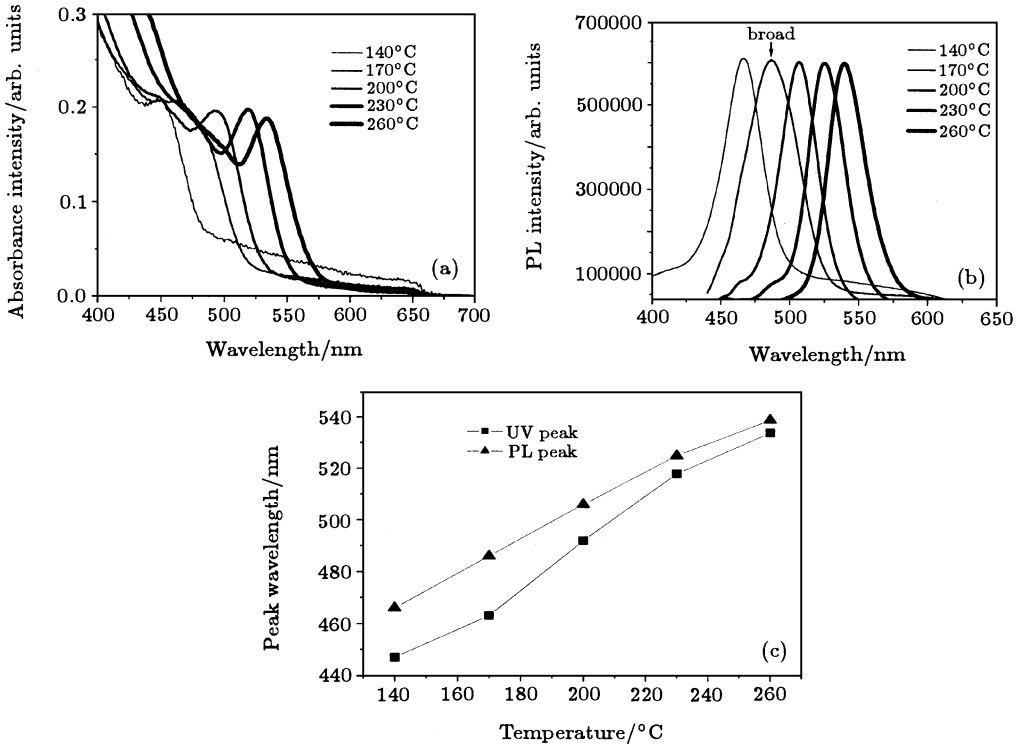


Fig.5. Temperature evolution of UV–vis spectra (a) and PL spectra (b) of the samples removed. Curves of peaks of temperature evolution of UV–vis and PL spectra of samples as prepared (c).

To test how the reaction time affects the size of CdSe nanocrystals, the experiment was carried out as follows. After the ethanol was vaporized out of the reaction solutions at a temperature below 140°C, the reaction temperature was maintained at 140°C. The samples were extracted at the time of 10 minutes, 40 minutes, 90 minutes, 150 minutes, 210 minutes and 420 minutes and quenched promptly in the cold toluene to stop the reaction. UV–vis absorption and PL measurements were carried out on the samples (see Fig.6 and Table 2).

Table 2. Temporal evolution of UV–vis and PL peak of the samples as prepared.

Time/min	10	40	90	150	210	420
UV–vis peak/nm	436	456	474	480	486	493
PL peak/nm	455	474	489	499	501	507

The CdSe nanocrystals' size changes nonlinearly with the reaction time. During the initial 150 minutes, the size grows relatively fast. And the size grows slowly after 200 minutes. After 400 minutes, the size remains nearly unchanged.

The difference of our experiments from previous literature[16–18] is that when injecting cold Se solution into the hot solvent swiftly, the nuclei are produced explosively and the reaction temperature decreases so that the nuclei growth stops at that moment. After vaporizing the ethanol out of the reaction system at a temperature below 140°C, we start to increase the temperature so that the nuclei's growth can continue. But in Peng's work,[16–18] the nuclei come into being at a high temperature such as 300°C and the nuclei's growth occurs at a relatively low temperature such as 260°C, which accounts for the difference in the growth mechanism.

The size-dependent growth/dissolution rates may be caused by diffusion-controlled Ostwald Ripening (OR) and/or the surface reaction-controlled OR, which have been discussed in detail by Rogach *et al.*[23] This ripening occurs where the smaller particles dissolve and the monomer released thereby is consumed by the large particles. It implies that the largest particles have positive and the smallest ones have negative growth rates. They used the Lifshitz–Slyozov–Wagner theory to predict that OR finally leads to an asymptotic particle size distribution, which is independent of the initial conditions. There are two processes for different reaction control conditions. For the surface reaction control, the particle size distribution is broad, whereas the particle size distribution is narrow for the diffusion-controlled case (Fig.6(b)). However, an asymmetric negatively skived band occurs if the reaction time is long enough for both cases.

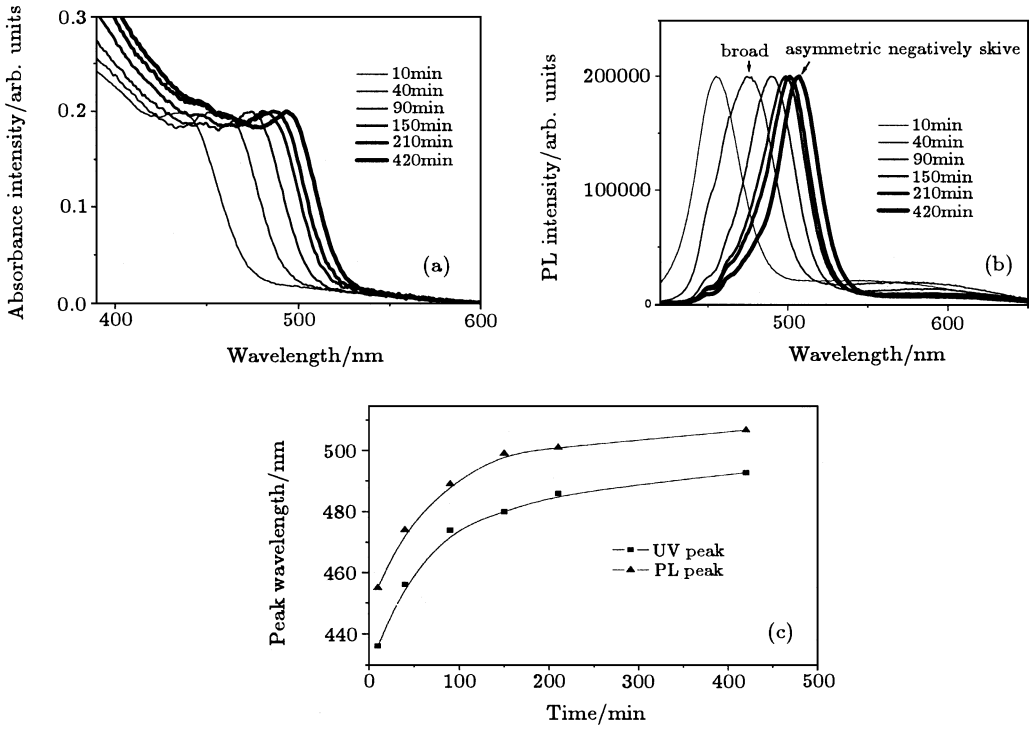


Fig.6. Temporal evolution of UV-vis spectra (a) and PL spectra (b) of the samples removed. Curves of peaks of temporal evolution of UV–vis and PL spectra of samples as prepared (bottom).

Based upon the theoretical prediction we find that the growth regime can be divided into three parts from Figs.5(b) and 6(b). At first, nucleation occurs and the small particles are uniform, and their PL band is narrow. Due to the high monomer concentration in the solution, the growth of the nanocrystals is under surface-reaction control. So the PL band broadens with time and/or temperature, as does the particle size distribution. After a while (the temperature beyond about 170°C or the time after about 40 minutes at 140°C), the monomer concentration reduces to a critical value and the particle concentration in the solution reaches a maximum. The diffusion control takes over the particle growth processes, which part is called "focusing".[23] The particle size distribution goes back to a narrow one and the PL band, too. When the over-saturation drops down to the equilibrium value, the OR mechanism governs the subsequent evolution. The PL band becomes an asymmetric negatively skived one after 420 minutes at 140 °C.

The FWHM changes of the PL bands are recorded in Fig.7. The optimal reaction temperature is acquired at about 230°C. The reaction process is like the hot injection condition[23,24] but the growth regime is

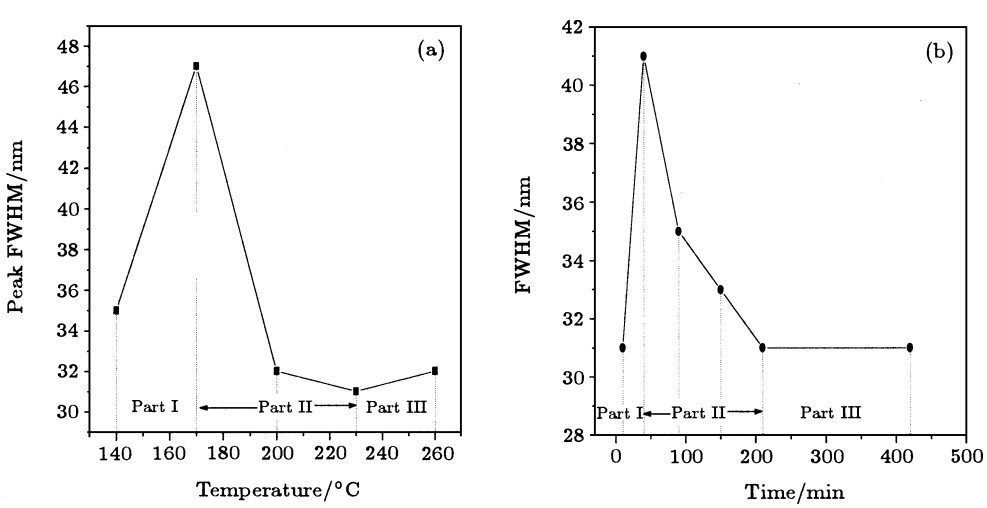


Fig.7. Changes of the peak FWHM of the PL spectra of the samples prepared with the changing (a) reaction temperatures and with the changing (b) reaction time.

a little like the additional injection one.[23,25] Along with the rising reaction temperature or evolving time, the size distribution initially increases then decreases and increases almost a constant value at last.[26−29]

4. Conclusion

Using a thermal chemical method, we can synthesize the mono-dispersed hexagonal structure CdSe nanocrystals with a polyhedral shape by using CdO and Se as precursors, OA as the ligand, and liquid paraffin and ethanol as the solvents. As-prepared CdSe nanocrystals, also have high PL QY. The size of CdSe nanocrystals can be tuned by changing reaction temperature or time with a nearly linear change between 140°C and 260°C. The mechanism of the nanocrystals' growth can be divided to three parts. Along with the rising reaction temperature and passing time, the size distribution initially increases then decreases and increases almost a constant value at last.

References

[1] Brus L 1986 *J. Phys. Chem.* **90** 2555
[2] Colvin V L, Schlamp M C and Alivisatos A P 1994 *Nature* **370** 354
[3] Alivisatos A P 1996 *Science* **271** 933
[4] Bruchez M, Moronne M, Gin P, Weiss S and Alivisatos A P 1998 *Science* **281** 2013
[5] Chan W C W and Nie S 1998 *Science* **281** 2016
[6] Han M, Gao X, Su J Z and Nie S 2001 *Nat. Biotech.* **19** 631
[7] Wu X, Liu H, Liu J, Haley K N, Treadway J A, Larson J P, Ge N, Peale F and Bruchez M P 2003 *Nat. Biotech.* **21** 41
[8] Mitchell G P, Mirkin C A and Letsinger R L 1999 *J. Am. Chem. Soc.* **121** 8122
[9] Hamad-Schifferli K, Schwartz J J, Santos A T, Zhang S and Jacobson J M 2002 *Nature* **415** 1525
[10] Dubertret B, Skourides P, Norris D J, Noireaux V, Brivanlou A H and Libchaber A 2002 *Science* **298** 1759
[11] Alivisatos A P 1996 *J. Phys. Chem.* **100** 13226
[12] Kuno M, Lee K, Dabbousi B O, Mikulec F V and Bawendi M G 1997 *J. Chem. Phys.* **106** 9869
[13] Reiss P, Bleuse J and Pron A 2002 *Nano Lett.* **2** 781
[14] Gerion D, Pinaud F, Williams S C, Parak W J, Zanchet D, Weiss S and Alivisatos A P 2001 *J. Phys. Chem.* B **105** 8861
[15] Murray C B, Norris D J and Bawendi M G 1993 *J. Am. Chem. Soc.* **115** 8706
[16] Peng Z and Peng X 2002 *J. Am. Chem. Soc.* **123** 183
[17] Yu W W and Peng X 2002 *Angew. Chem. Int. Ed.* **41** 2368
[18] Yu W W, Wang A and Peng X 2003 *Chem. Mater.* **15** 4300
[19] Bailey R E and Nie S 2003 *J. Am. Chem. Soc.* **125** 7100
[20] Mews A, Banin U, Kadavanich A V and Alivisatos A P 1997 *Ber. Bunsenges. Phys. Chem.* **101** 1621
[21] Brus L 1986 *J. Phys. Chem.* **90** 2555
[22] Norris D J and Bawendi M G 1996 *Phys. Rev.* B **53** 16338
[23] Rogach A L, Talapin D V, Shevchenko E V, Kornowski A, Haase M and Weller H 2002 *Adv. Funct. Mater.* **12** 653
[24] Peng Z and Peng X 2001 *J. Am. Chem. Soc.* **123** 1389
[25] Peng X, Wickham J and Alivisatos A P 1998 *J. Am. Chem. Soc.* **120** 5343
[26] Hui P 2000 *Chin. Phys.* **9** 844
[27] Zhang H and Shi J 2004 *Chin. Phys.* **13** 2136
[28] Wang R, Wu X, Wu P, Zou B, Wang L, Xu J, Wang X, Wang Z and Chen J 1998 *Acta Phys. Sin.* (Overseas edition) **7** 203
[29] Volkov V V, Wang Z, Zou B and Xie S 2000 *Chin. Phys.* **9** 767