

Sol-gel synthesis and particle size characterization of CdSe Quantum dots

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Abstract. In this article, we report on the preparation of CdSe quantum dots (QDs) by sol-gel method and their optical properties. The average size of QDs is also estimated by using various ways, such as the Scherer's formula, The Effros-Brus-Kayanuma's theoretical expression, TEM etc. The TEM images of samples show that the mean sizes of QDs are 4 nm. The mean sizes of QDs are smaller than that of other methods and arranging from 2 to 3.6 nm.

1. Introduction

Size-dependent optoelectronic properties of CdSe quantum dots (QDs) make them ideal candidates for tunable absorbers and emitters in application, such as nanoscale electronics, laser technology, and biological fluorescent labeling.

The properties of QDs are strongly influenced not only by the composition and structure of the matrix, but also by the preparation technique. The band-edge emission of CdSe QDs in a strongly confined regime has been generally attributed to electron transitions from the highest occupied to the lowest non-occupied molecular orbital [1]. Therefore, there exist many methods that have been applied to synthesize CdSe quantum dot. A variety of methods has been employed to synthesize semiconductor nanorods in recent years. These methods include the hot coordination solvents method using tri-*n*-octylphosphine oxide (TOPO) and trioctylphosphine (TOP) [2], the hydrothermal or solvothermal method [2,3] and the micelle or reverse micelle method [3]. The electrical and optical properties of nanoparticles are affected by the chemistry involved in their synthesis. Bottom-up approaches such as those using surfactants or micelles as the regulating agents are very effective for the synthesis of one-dimensional nanostructure because of their high efficiency, controllability, simplicity and versatility. Hydrothermal techniques have been widely applied for the synthesis of conventional and advanced materials. The advantages of this method include the relatively low temperature required for processing, the possibility of controlling particle morphology and the good crystalline of the products. Peng et al. first employed ammonium as a completing agent for cadmium ions to synthesize cadmium selenide (CdSe) nanocrystals using the hydrothermal method. They found that at 140 °C, CdSe with a mixed morphology of branch-shaped fractals and nanorods was produced,

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and at 180 °C, the products were mainly CdSe nanorods [4]. Chen et al. used a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) via a hydrothermal method at 180 °C to synthesize CdSe nanorods. They found that the concentration of CTAB is a key parameter in the control of nanoparticle morphology [5]. However, to investigate the size effect we need the sample with homogeneous distribution in particle size. Besides that, the hydrothermal method requires the long time reaction and its distribution in particle size is in the broadening range.

In this article, we report on the preparation of CdSe quantum dots (QDs) by sol-gel method and investigate their optical properties. This is a new route to get CdSe QDs and also very economic. We also estimate the average size of QDs by using various ways, such as the Scherer's formula, The Effros-Brus-Kayanuma's theoretical expression, TEM etc.

2. Experiment

The method used to prepare QDs CdSe was presented in previous paper [6]. The crystalline processes happened from 1 to 15 minutes, and QDs CdSe were dispersed in toluen solvent.

Powder X-ray diffraction (XRD) patterns were recorded using a D 5005 (Siemens) X-ray diffractometer using CuK α radiation ($\lambda = 0.15406$ nm). Transmission electron microscopy (TEM) was carried out using a microscope. Ultraviolet-visible (UV-vis) absorption spectra of the nanoparticles were recorded by using a Jasco V670 spectrophotometer.

3. Result and discussion

To calculate the particle size of QDs we use some following models:

+ Using absorption spectra to estimate the mean sizes of QDs:

The Effros, Brus and Kayanuma's theoretical expression shows the relation between mean size and specific parameters of QDs [7]:

$$E_g(a) = E_g + \pi^2 R_y^* \left(\frac{a_B}{a} \right)^2 - 1,786 R_y^* \left(\frac{a_B}{a} \right) - 0,248 R_y^* \quad (1)$$

where $E_g(a)$ is the effective band gap of QDs with radius of a , the band gap E_g , Bohr exciton radius a_B and Bohr exciton energy R_y^* are the specific parameters of bulk material. From absorption spectra, we can determine the $E_g(a)$ of QDs, hence can estimate the mean size of QDs.

From this formula, the standard curve and measured absorption spectra, we can estimate the mean size of QDs.

Based on the analysis it has been expressed the experimental formula to estimate the mean sizes of QDs CdSe as:

$$D = 1,6122 \times 10^{-9} l^4 - 2,6575 \times 10^{-6} l^3 + 1,6242 \times 10^{-3} l^2 - 0,4277 l + 41,57 \quad (2)$$

where, D (nm) is the size of a given nanocrystal sample, and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample.

+ The second one, we estimate the mean size of QDs by the Scherer's formula [8]:

$$r = \frac{kl}{D \cos q} \quad (3)$$

where, D (rad) is the half width at half maximum of the XRD peak; λ - the X-ray diffraction wavelength (with radiation $\text{CuK}\alpha$: $\lambda = 1,5406 \text{ \AA}$); θ : the diffractive angle and k - constant ($k = 0,9$).

The structure and morphologies of the CdSe nanoparticles were characterized using transmission electron microscopy. The morphologies of the CdSe nanoparticles were mainly affected by the Cd:Se ratio, the reaction temperature and time. From TEM image on fig. 1, we can see CdSe QDs are dispersed in toluen solvent and have the spherical shapes with the mean diameter of about 4 nm.

A typical XRD pattern from the prepared CdSe nanoparticles and the positions of the X-ray peaks for CdSe FCC are shown in Fig. 2. All the diffraction peaks from the CdSe nanoparticles are consistent with the wurtzite structure of CdSe with measured lattice constants of $a = 6.1 \text{ \AA}$ (this can be compared to the lattice constants of $a = 6,077 \text{ \AA}$ from JCPDS file No. 19-0191). The sharp diffraction peaks also indicate that the products are highly crystalline. XRD analysis revealed no impurities such as Se and SeO_3 in the sample.

As expected, the width of the diffraction peaks is considerably broadened and can be determined easily because the size effect is exhibited very clear. By using the Scherrer formula, we can calculate the mean sizes of the CdSe QDs from the peak width at half-maximum. Particle sizes obtained from the width of the (111) diffraction are depicted in the table 1.

Table 1. Particle size of samples with reaction time 5 and 10 min

Samples	2θ	D (radian)	$\cos\theta$	d (nm)
5 minutes	25,381	0,0697	0,97555	2,039
10 minutes	25,402	0,06806	0,97553	2,088

These results show that the particle sizes are about 2 nm. When the crystalline time increased from 5 to 10 minutes, the peaks become broadening but not very considerably.

The mean sizes of samples obtained from XRD patterns are smaller than those of these samples obtained from TEM image. In this method, we did not eliminate the system standard error. In addition, in this XRD method, the mean sizes are obtained from all the structural layers of samples

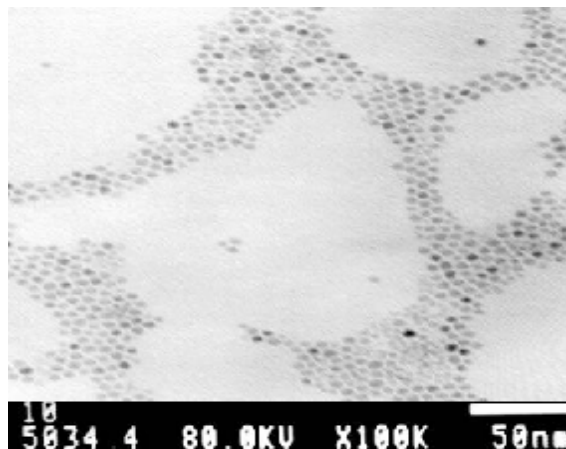


Fig. 1. TEM image of CdSe QDs.

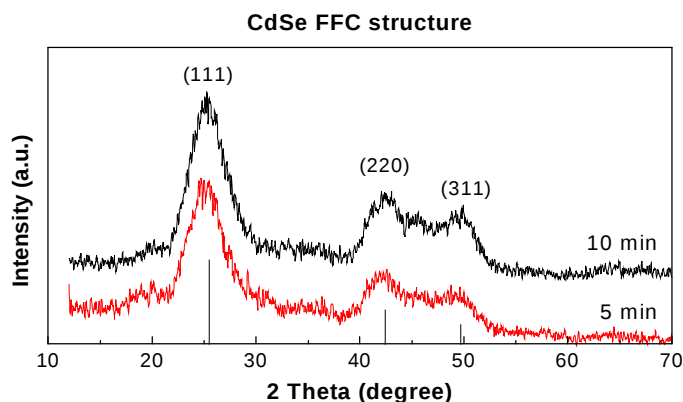


Fig. 2. XRD patterns of QDs CdSe with crystalline times of 5 and 10 minutes.

involved diffraction process, so the results are the diameters of crystal cores. In the other methods, there are some other objects which are involved in the shell of CdSe cores so it may be larger.

Fig. 3 shows absorption spectra, of the prepared CdSe QDs. It can be seen from Fig. 3 that with increasing growing time, the redshift of the spectra can be clearly observed and optical absorption in the visible region due to CdSe QDs is demonstrated. The average diameters of the CdSe QDs for each growth time interval is estimated using the effective mass approximation giving diameters ranging from 2.2 nm to 2.6 nm. These values are comparable to those obtained by TEM and by the wavelength of the first excitonic absorption peak (Table 2).

The deviation of the peaks in absorption spectra is about 50 nm, which may be due to the difference of surface states of these QDs. It is also thought that the strong intensity from the CdSe QDs can be attributed to their high crystallinity [9], which is in good agreement with the XRD patterns discussed earlier and the presence of good surface states on the QDs.

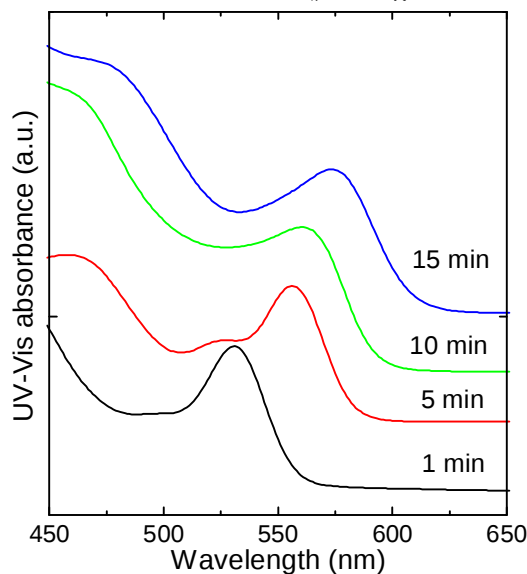


Fig. 3. UV-vis absorption spectra of CdSe QDs with various crystalline times.

Table 2. The parameters of the CdSe QDs vs. growing time

Ratio Cd:Se	Name	crystalline time (minute)	The wavelength of the first absorption excitonic peak (nm)	The mean diameter of CdSe QDs using formula (1) (nm)	The mean diameter of CdSe QDs using formula (2) (nm)
1 : 8 (260°C)	CdSe	1	520	2.2	2.6
	CdSe	5	557	2.5	3.2
	CdSe	10	561	2.5	3.3
	CdSe	15	574	2.6	3.6

Summary

In summary, QDs of CdSe with a diameter of 2.2 - 2.6 nm have been successfully synthesized through a novel method at a relative low temperature. The morphologies of the prepared nanoparticles can be controlled by the reaction time, the amount of Cd:Se ratio and the reaction temperature.

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