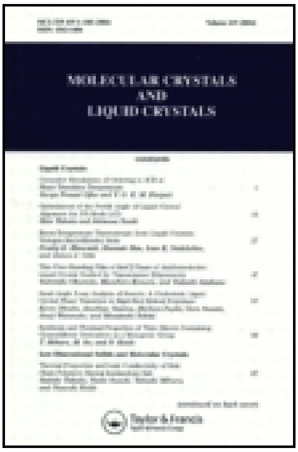

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Low Temperature Synthesis of CdSe Nanocrystal Quantum Dots using Paraffin Oil

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We report a simple and rapid route for synthesis of CdSe quantum dots at low temperature of 150°C by using the paraffin oil as a solvent in place of the conventional trioctylphosphine and trioctylphosphine oxide. The CdSe QDs were synthesized as a function of the growth temperature. UV-vis and PL data show a narrow emission peak at 552 nm with absorption peak of 533 nm, implying a uniform size distribution. The CdSe QDs reveal large blue-shifts in both UV-vis and PL data under the low temperature conditions, due to the quantum confinement effect depending on the smaller particle size.

Keywords Quantum dots; CdSe; nanocrystals; paraffin oil; low temperature synthesis

Introduction

Semiconductor nanoparticles known as quantum dots (QDs) have size-dependent optical properties [1] when the size of particles approaches to Bohr exciton radius. CdSe quantum dots have come into the spotlight [2,3] as new phosphors for displays because they can emit most visible spectrum by tuning the particle size, namely, the quantum confinement effect where electronic transitions depend on particle sizes. This is why many methods for the synthesis of CdSe quantum dots have been studied by several groups and ‘hot injection’ reaction method [4] calling ‘pyrolysis’ is mainly used. In spite of many efforts on the pyrolysis method, the high reaction temperatures make large-scale production of QDs still difficult and expensive. Moreover, the conventional pyrolysis method involves trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) which are known to be environmentally unfriendly, high-cost and dangerous solvent. Recently, TOP and TOPO have been substituted with natural, low-cost and more air-stable solvents [5–7]. Meanwhile, paraffin oil was proposed as a solvent which allows to work on simple and safe pyrolysis process [8–11].

In this study, we report CdSe nanocrystal QDs synthesized from CdO and Se at a low temperature of 150°C using paraffin oil as a solvent of the reaction mixture. Characterizing by XRD, TEM, UV-vis and PL spectroscopy, the effect of the synthesis temperature on the size and the size distribution of QDs are investigated.

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Experimental

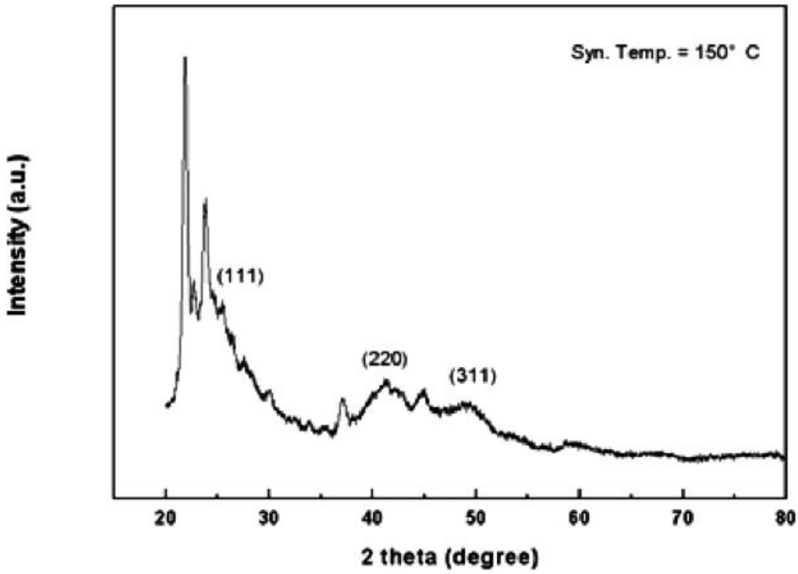
Among chemicals, cadmium oxide (99.99%), stearic acid (99.5%), and selenium powder (99.99%) were purchased from Aldrich while paraffin oil was from Fluka. All of the reagents were used as received. To prepare the Cd precursor solution, cadmium oxide (2 mmol), stearic acid (9 mmol) and paraffin oil (16 ml) were added into the two-neck flask and heated to 150°C with stirring to form optically clear solution. On the other hand, selenium (1 mmol) and paraffin oil (50 ml) were added into another flask and heated to 225°C above selenium melting point with stirring to form the Se precursor solution. When a dark Se precursor solution was formed, the temperature went down to 150°C. Then, the Se precursor solution was quickly taken out and injected into the Cd precursor solution. The temperature was maintained at 150°C during the synthesis process of CdSe QDs with vigorous stirring. The reaction mixture was rapidly cooled down to the room temperature to prevent further growth. Methanol was added to precipitate CdSe quantum dots and separated by centrifugation. The CdSe QDs were further washed with methanol several times and dried in a vacuum for XRD analysis or redissolved in chloroform for optical characterization. In order to compare with low temperature synthesis of CdSe QDs, same procedure was also carried out at high temperature of 225°C.

X-ray diffraction (XRD) spectra were collected on a powder diffractormeter (PANalytical, X'pert PRO MPD) operating in the Bragg configuration using Cu Kα radiation. The morphological images of samples were taken from transmission electron microscopy (TEM) (Hitach, H-7100). UV-visible absorption spectra were obtained from optical spectrometer (M1461 OMA system, Cary 5G). Fluorescence spectra were obtained from photoluminescence spectrophotometer (Acton Research, Spectra PRO 2150i) with a Xe lamp (λ = 488 nm) as the excitation source. Quartz cuvettes with a 10mm path length were used in both measurements. All measurements were carried out at room temperature.

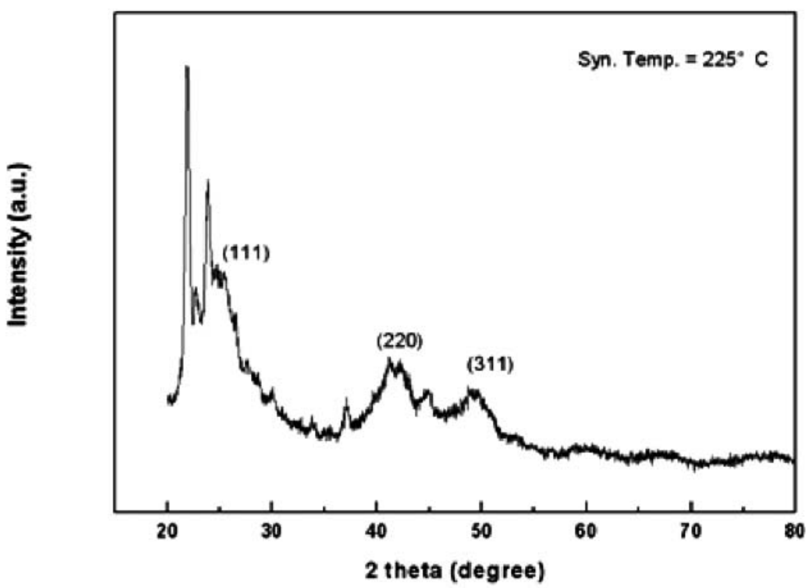
Results and Discussion

Figure 1 represents the XRD data for CdSe quantum dots synthesized under the low and high temperature conditions. The sharp peaks seen at 22°, 24° and 38° are known to be originated from cadmium stearate and stearic acid, which are organic components in the precipitate of the CdSe QDs [9]. Because cadmium stearate and stearic acid act as impurities in the CdSe QDs, a suitable way to remove them is required. The patterns except the sharp peaks are in accord with those of cubic CdSe with zinc-blende structure. The peaks seen at 25.3°, 42° and 49.7° correspond to the (111), (220) and (311) planes, respectively. Synthesis temperature is a critical factor in determining the crystal structure, and the synthesis temperature below 300°C may favor the formation of zinc-blende structure in the paraffin route [8,10]. In thermodynamics, it is notable that zinc-blende is the most stable form at lower temperature, while wurtzite is more stable in high temperature (about 300°C) [12]. As seen in Fig. 1, it is found that the both results are not suitable for estimating the size of QDs with the Scherrer equation because the excesses of cadmium stearate and stearic acid are present in the samples.

TEM images of the CdSe QDs dispersed in pyridine on the copper grid are shown in Fig. 2. The respective size distributions were obtained from statistical TEM analysis of 50–80 particles per sample. As seen in Fig. 2, we can confirm a shape uniformity with spherical form and the narrow particle size distribution of 3 nm and 3.4 nm in average size under the low and high temperature conditions, respectively. It should be noted that the low temperature synthesis process gives smaller QDs in size.



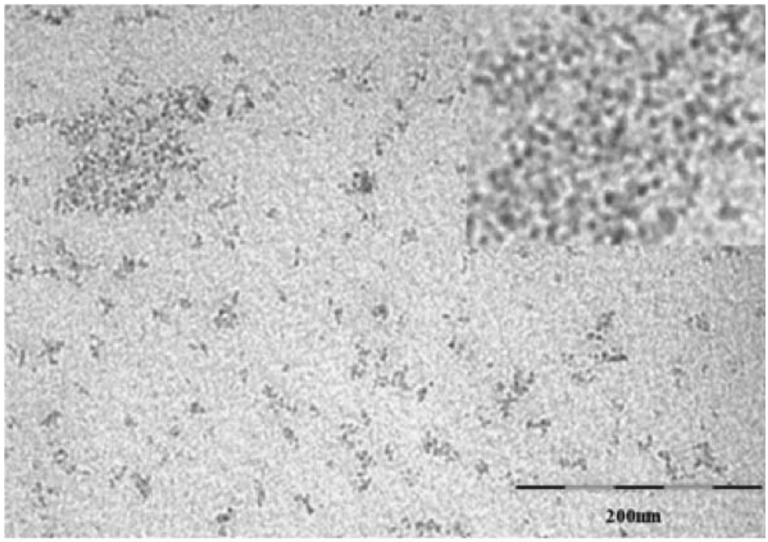
(a)



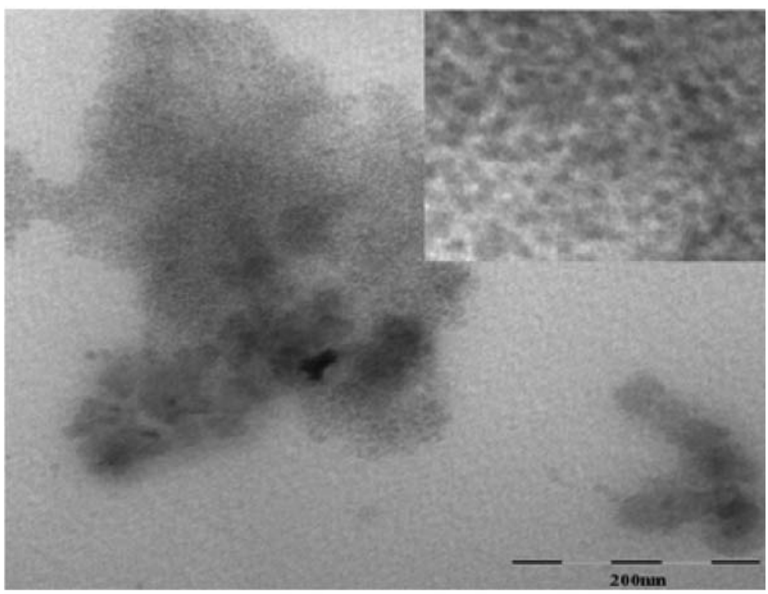
(b)

Figure 1. XRD patterns of the CdSe QDs synthesized at (a) 150°C and (b) 225°C.

UV-vis absorption spectra of the CdSe QDs prepared under the low and high temperature conditions are plotted in Fig. 3. One can find three distinct electronic transitions and especially sharp absorption peaks at around 533 nm in case of low temperature condition while at around 552 nm in case of high temperature condition, indicating sufficiently narrow



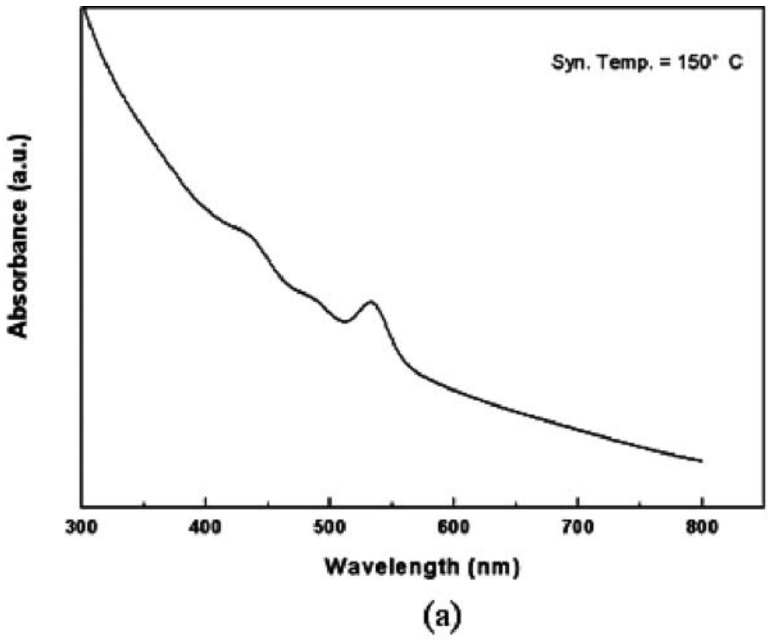
(a)



(b)

Figure 2. TEM images of the CdSe QDs synthesized at (a) 150°C and (b) 225°C.

size distribution of the as-prepared CdSe QDs. This means that the growth of the QDs stops in the "focusing of size distribution" regime [13]. And absorption peak positions of the QDs are determined by bulk band gap energy and quantum confinement. Thus, we can know the size dependence of the band gap energy for the QDs as quantum confinement equation with



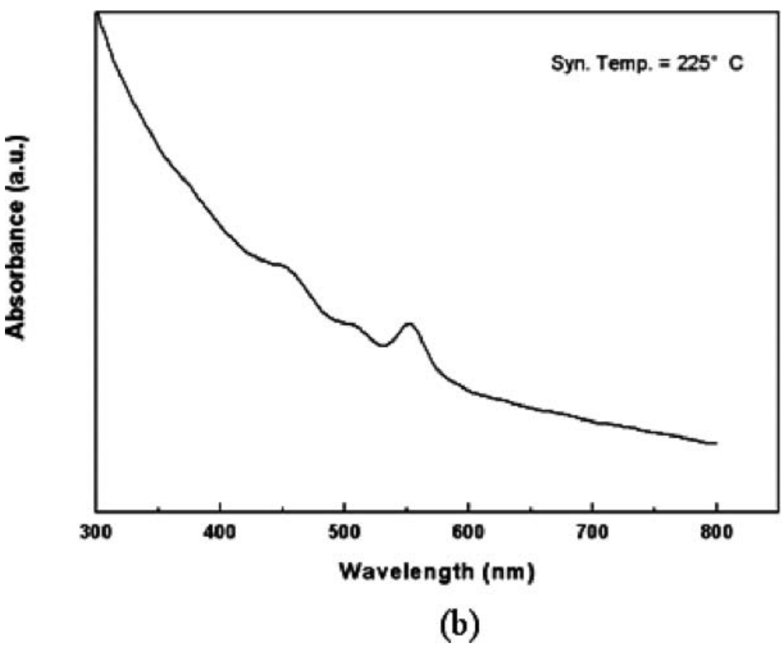


Figure 3. UV-vis spectra of the CdSe QDs synthesized at (a) 150°C and (b) 225°C.

the absorption peaks. In addition, the obvious blue shift toward shorter wavelength was observed with decreasing the growth temperature. Therefore, these results tell that the low temperature condition yields smaller particle size of the QDs and the blue shift originates from the quantum confinement effect of smaller particles.

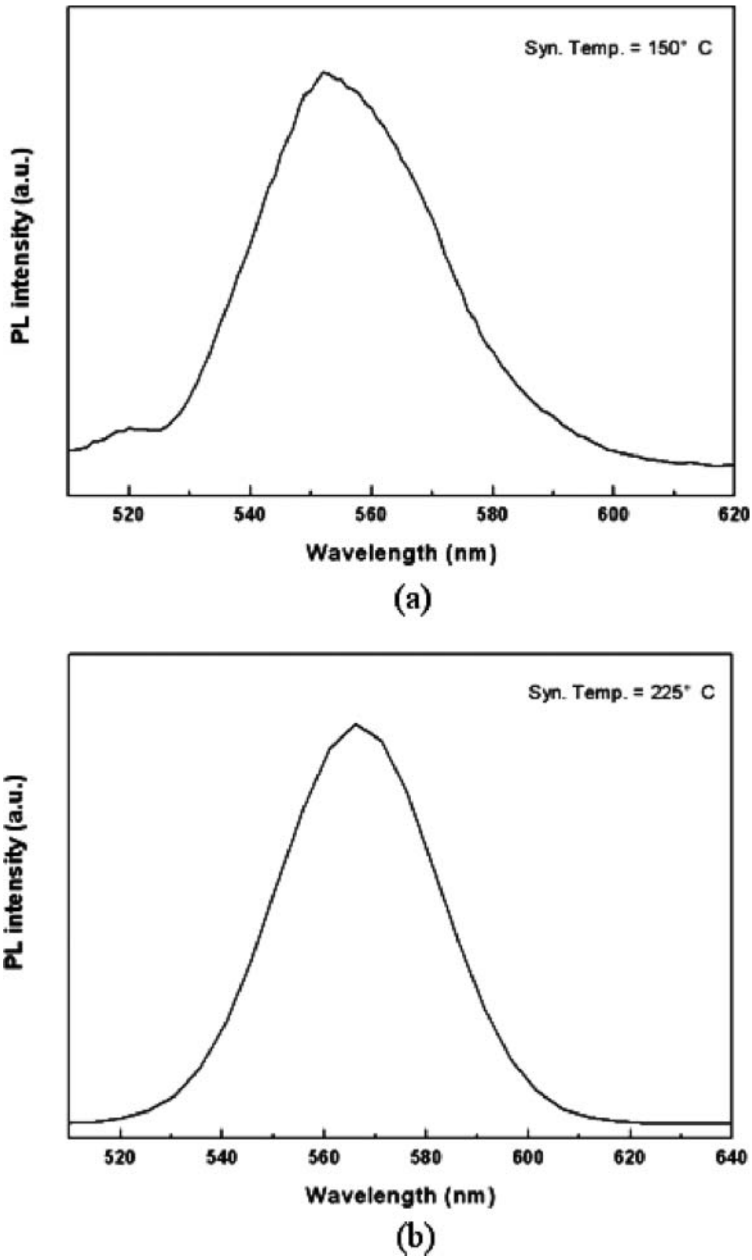


Figure 4. PL spectra of the CdSe QDs synthesized at (a) 150°C and (b) 225°C.

Figure 4 shows PL spectra of the as-prepared CdSe QDs prepared under the different temperature conditions. PL peaks were measured at 552 nm and 569 nm, depending on the temperature conditions and showing fairly symmetric shape. The PL peaks also reveal that the band gap energy was blue-shifted with decreasing the growth temperature because of the quantum confinement effect of smaller particles, corresponding well to the absorption peaks. The full width at half maximum (FWHM) of the PL spectra were about 38 nm and 37 nm under the low and high temperature conditions respectively, which means the size distributions are good as a whole and it is somewhat better in the case of the high temperature condition. In addition, as shown in Figs. 3 and 4, absorbance has shorter wavelength than emission by 17∼19 nm, because molecules with electrons in the ground state have stronger bonds than molecules with excited electrons, known as the Stokes shift.

Conclusions

We demonstrated a low temperature synthesis of CdSe quantum dots using paraffin oil as a solvent of the reaction mixture. The results of optical investigations indicate that it is feasible to synthesize CdSe QDs at a low temperature of 150°C, but a suitable way to remove the excess of cadmium stearate is required. Compared to the high temperature condition, the low synthesis temperature yields smaller sized QDs and somewhat wider particle distribution in size. It is of interest that the synthesis temperature played an important role for the size control of the CdSe QDs.

Acknowledgment

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