

Effects of reaction temperature on size and optical properties of CdSe nanocrystals

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Abstract. We report experimental results on the reaction temperature dependence of luminescence properties in size-controlled CdSe nanocrystals. Such reaction temperature dependent property is also size-dependent. The diameter of the CdSe nanocrystals is tuned from 4–11.0 nm by varying the reaction temperatures. The growth process and characterization of CdSe nanocrystals are determined by photoluminescence (PL) spectroscopy, ultraviolet-visible (UV–Vis) spectroscopy, X-ray photoelectron spectrometry (XPS), X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The influence of reaction conditions on the growth of CdSe nanocrystals demonstrates that low reaction temperature is favourable for the formation of high quality CdSe nanocrystals.

Keywords. Nanomaterials; semiconductors; optical properties; defect formation.

1. Introduction

Research on colloid semiconductor nanocrystals has been a distinguishable topic in the field of modern nanoscale science and technology (Steigerwald and Brus 1990; Wang *et al* 2006). Among the various semiconductor materials, colloidal CdSe nanocrystals are the most actively studied owing to their size-dependent emission in the visible range (Weller 1993), the advances in their synthesis and their potential applications in various fields, such as light-emitting diodes (Lee *et al* 2000; Schaller *et al* 2006), lasers (Schlamp *et al* 1997; Artemyev *et al* 2001; Maskaly *et al* 2006), solar energy cell (Kornowski *et al* 1996; Suri and Mehra 2007) and biomedical tags (Bruchez *et al* 1998; Zhang *et al* 2003; Alivisatos *et al* 2005; Michalet *et al* 2005). In practice, such extensive applications have great potential to promote the synthesis of CdSe nanocrystals to the well-developed level. Among various traditional synthesis methods of nanomaterials, the most conventional route to synthesize the high quality CdSe nanocrystals is colloid chemistry: in the early 1990s, dimethyl cadmium was used as the cadmium precursor to react with *bis* (trimethylsilyl)selenium in a coordinating solvent trioctylphosphine oxide (TOPO) (Murray *et al* 1993). Later on, Manna and co-workers (2000) have generally studied the influential factors in shape control of CdSe nanocrystals by changing the ratio of surfactants, injection amount, and time-dependent monomer concentration using

dimethyl cadmium as the cadmium precursor. Recently, the morphologies and optical properties of CdSe nanocrystals have been systematically studied by directly using CdO or Cd(Ac)₂ as cadmium precursor in different solvent systems, ratio of the precursor, injection rates and concentrations of the ligands (Peng and Peng 2001; Qu *et al* 2001; Peng 2002; Yu and Peng 2002).

However, the above studies discussed in detail the influential factors of CdSe nanocrystals synthesis except for reaction temperature. As part of the development of strategies for the synthesis of high quality colloidal nanocrystals, here we described the influence of the reaction temperature on colloidal CdSe nanocrystals synthesis at four different temperatures. The relationship between the optical properties of the as-prepared CdSe nanocrystals and a variety of growth conditions was also studied. Obtained CdSe nanocrystals were characterized by ultraviolet-visible (UV–Vis), photoluminescence (PL) spectra, X-ray photoelectron spectrometry (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) tomography.

2. Experimental

2.1 Chemicals

Se powder, stearic acid (SA), trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) were purchased from Alfa Aesar Chemicals and used without any purification. The solvents used and Cd(CH₃CH₂COO)₂·2H₂O were purchased from Chemical Reagent Corporation of Beijing.

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2.2 Synthesis

The synthesis of CdSe nanocrystals is similar to the methods reported by Qu and co-workers (2001). A typical synthesis is as follows. Cd(Ac)₂·2H₂O, 0.0133 g (0.05 mmol), and 1.0000 g SA were loaded into a 25 mL three-neck flask and heated to 120°C under nitrogen flow, after Cd(Ac)₂·2H₂O was completely dissolved, the mixture was allowed to cool to room temperature, 1.4332 g TOPO was added to the flask, and the mixture was heated to 200–280°C under argon flow to form an optically clear solution. At this temperature, the Se solution containing 0.0197 g (0.25 mmol) of Se dissolved in 0.8803 g (2.38 mmol) TOP and 0.2 g toluene was swiftly injected into the reaction flask. After the injection, the temperature was set at 200–280°C for the growth of nanocrystals. At various time intervals, aliquots with a needle-tip amount of the reaction mixture were removed and diluted by toluene. Insoluble white solid, if it existed, was separated by centrifugation and decantation prior to further measurements.

2.3 Characterization

The size and shape of these CdSe nanocrystals were examined using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). TEM and HRTEM images were obtained using Jeol-200CX (operating at 120 kV) and FET TECNAI F30 (operating at 200 kV), respectively. The sample for TEM was prepared by placing a drop of toluene dispersion of CdSe nanocrystals on the amorphous carbon-coated copper grids. The structure of the nanocrystals was investigated by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 X-ray diffractometer with CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$). Prior to the XRD measurements, the samples were prepared by spreading several drops of CdSe nanocrystals on the glass substrate. The surface of CdSe nanocrystals was measured by using a VG ESCALAB-5 X-ray photoelectron spectrometry (XPS) system. Optical absorption spectra were collected at room temperature on a PE Lambda 35 Ultraviolet-visible (UV-Vis) spectrometer using 1 cm quartz cuvettes. The toluene solvent was used for the background sample. Room temperature photoluminescence (PL) spectra were carried out on a SPEX Fluorolog-2 spectrometer of front face collection with 500- μm slits. PL spectra were collected between 400 and 700 nm at room temperature with 480 nm excitation energy.

3. Results and discussion

3.1 Absorption analysis

The growth kinetics of the nanocrystals was monitored by collecting samples from the reaction vessel at different

reaction times. After injection of the Se solution, the nucleation and growth of CdSe nanocrystals occurred at different reaction temperatures. The formation process of CdSe nanocrystals can be identified from both the colour change and the UV-Vis spectra of the solution. As the reaction progressed, the solution was observed to be from colourless to transparent light yellow to orange yellow and then red brown, which directly indicated the formation of different sized CdSe nanocrystals. Figure 1 shows shifts of the peak positions and the shapes of the UV-Vis absorption spectra during the whole reaction process at four different temperatures (200, 220, 240 and 280°C). During the whole reaction process, growth of the particles was clearly evidenced by the shift of absorption spectra to longer wavelengths as a consequence of the quantum confinement effect. With the raise of reaction temperature, the growth rate of the CdSe nanocrystals increases. The width of the absorption band reflects the size distributions of the nanocrystals in the crude solutions. The sharp absorption features suggested highly monodisperse samples. A substantial difference in the growth evolution was observed between four growth temperatures.

At lower reaction temperature (200°C), peak position of CdSe nanocrystals shifted to long wave when reaction time ranged from 2 min (495 nm) to 15 min (531 nm) (figure 1a). This result indicates that the size of CdSe nanocrystals gradually becomes larger with increase in reaction time. Similar results were obtained when the reaction temperature was increased to 220°C, as shown in figure 1b. Interestingly, at higher reaction temperature (240 or 280°C, the absorption peak did not attain any shape at all, and this phenomenon lasted for the entire growth course (figures 1c, d). Specifically, when the reaction temperature was increased to 280°C, the flat absorption peak ranged from 1 min (629 nm) to 10 min (649 nm). This result revealed that the size of CdSe nanocrystals gradually increased as reaction time prolonged. Later on, very little change was observed for the position of the peak, and the wavelength located at 650 nm (15 min), indicating that the nucleation and growth process took < 10 min (figure 1d). At the same initial time of reaction (1 min) in four reactions, the position of the absorption peak appeared at 495 nm (200°C), 533 nm (280°C), 585 nm (240°C) and 629 nm (280°C), respectively. These observations can be explained as due to the relative rates of nucleation and growth at low temperatures being slower than at high temperature, if the absolute value of monomer concentration was same. Moreover, when compared to the results shown in figures 1c and d, the sharper absorption peaks and smaller value of full-width at half maximum (FWHM) as shown in figures 1a and b, indicate that the size of CdSe nanocrystals can be close to monodisperse size distribution (Qu *et al* 2001). The possible reason is that high reaction temperature results in formation of irregular nanocrystals due to faster

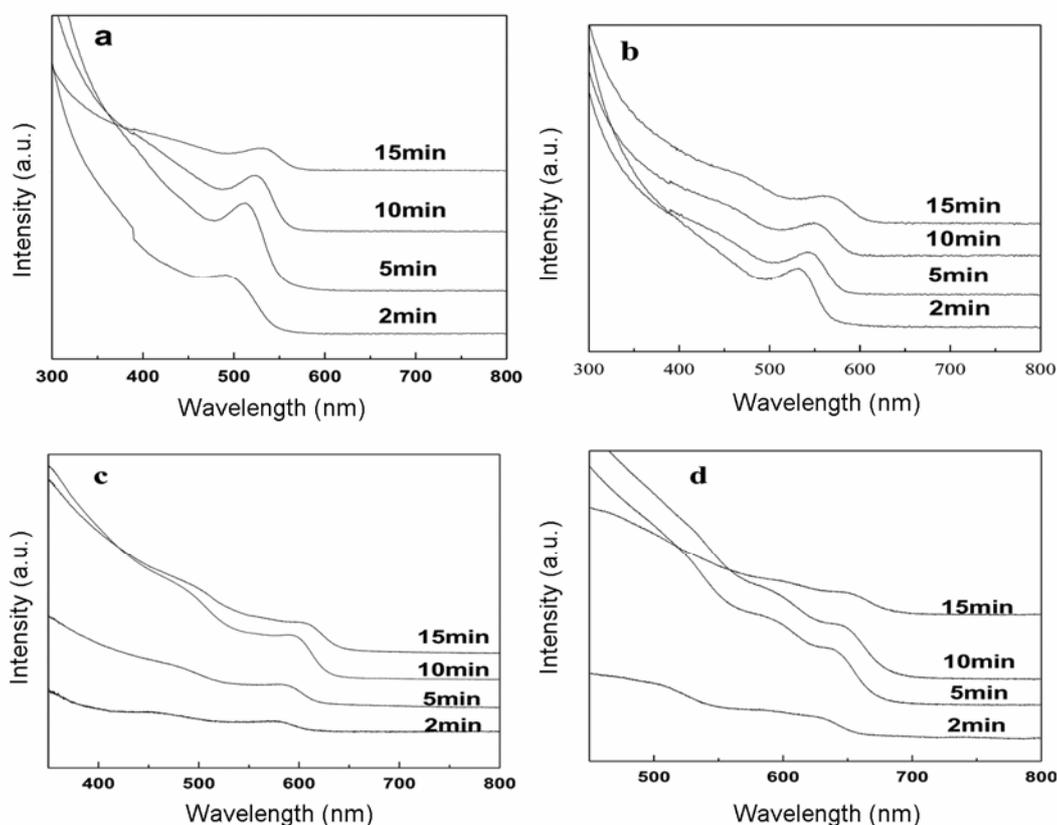


Figure 1. Temporal evolution of the absorption spectra of colloidal CdSe nanocrystals during their growth at different temperatures. **a.** 200°C, **b.** 220°C, **c.** 240°C and **d.** 280°C.

nucleation and growth of nanocrystals. Taken together, these facts clearly suggest that the CdSe nanocrystals with desired size will form at the lower reaction temperature. Therefore, it is believed that the reaction temperature plays a major role in determining nucleation and growth of the as-synthesized CdSe nanocrystals.

3.2 PL analysis

Figure 2 indicates PL spectra of CdSe nanocrystals synthesized at different reaction temperatures. The PL spectrum is red-shifted compared to the absorption spectrum, which indicated the large Stokes shift of the nanocrystals. With the raise of the reaction temperature, the PL spectra occurrence dramatically changed. At lower reaction temperature (200°C), the PL spectrum shows narrow FWHM value from reaction 5 min (32 nm) to 15 min (36 nm) as shown in figure 2A, which indicated growth of crystallites with few electronic defects sites. Similar results were obtained from 2 min (31 nm) to 15 min (35 nm) when the reaction temperature was increased to 220°C (figure 2B). At high reaction temperature (240°C), there had been two exciton peaks at 560 nm and from 576 nm extended to the region of near infrared from reaction time of 2 min to 10 min (figure 2C). The appearance of the first exciton peak around 560 nm originates from the

band edge of the as-prepared CdSe nanocrystals. In addition to the excitonic emission, the broad band emission from 576 nm extended to the region of near infrared arises from the defect states of CdSe nanocrystals. When the reaction temperature was increased to 280°C, there also emerged two exciton peaks at 559 nm and 650 nm (figure 2D). These weaker and broader emission spectra suggest a large percentage of defects are located at the surface of CdSe nanocrystals. Why does this phenomenon appear? Taking into account the kinetics of the particle formation, the reaction temperature can effect the surface configuration of the nanocrystals on the packing of surface ligands. The higher reaction temperature is in favour of the capping groups attaching and detaching from the surface of CdSe nanocrystals, which results in a faster growth rate and larger big miscellaneous nanocrystals cannot be perfectly passivated. While the lower reaction temperature may make the ligands to have no enough energy to shed from the surface, which is propitious to form well-proportioned nanocrystals. Thus, high quality CdSe nanocrystals were successfully prepared at low reaction temperature.

3.3 TEM analysis

The diameter and narrow size distribution of the crude CdSe nanocrystals synthesized in this work were also

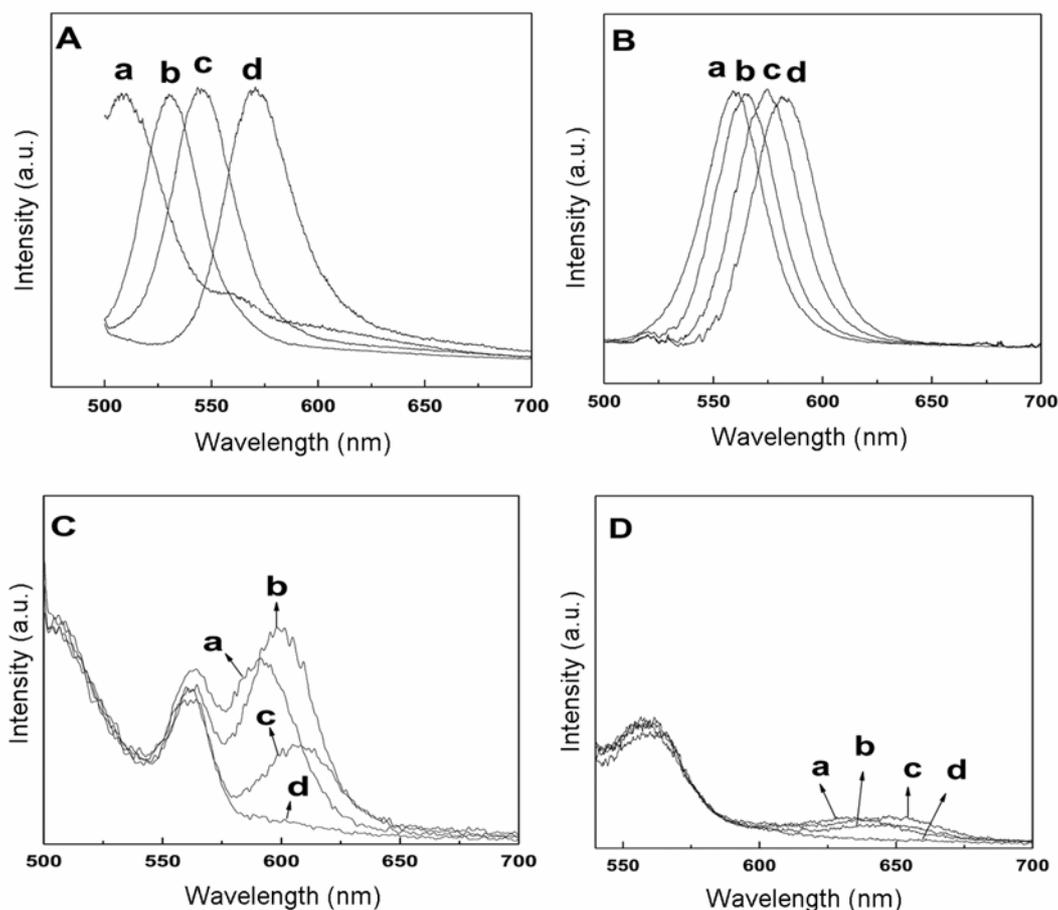


Figure 2. Photoluminescence spectra of colloidal CdSe nanocrystals during their different growth temperatures. **A.** 200°C, **B.** 220°C, **C.** 240°C, **D.** 280°C and for different reaction times **a.** 2 min, **b.** 5 min, **c.** 10 min and **d.** 15 min.

determined by TEM. With the raise of reaction temperature, diameter of CdSe nanocrystals becomes gradually big from 4.5–11.0 nm. A representative example was presented in figure 3, for samples of CdSe nanocrystals grown at different temperatures for a reaction time of 15 min. The average particle diameters were 4.5 nm at 200°C, 6 nm at 220°C, and 9.8 nm at 240°C, respectively. However, when the reaction temperature was raised to 280°C, the products became a mixture of big nanocrystals (60%) and small ones (40%) as shown in figure 3d. When the reaction temperature was at 200°C, the vague TEM image indicated the structure of CdSe nanocrystals to be incomplete owing to slower rates of nucleation and growth (figure 3a). While the reaction temperature was increased to 280°C, the nonspherical CdSe nanocrystals (figure 3d) were formed due to faster nucleation and growth of nanocrystals. These results also corresponded to the XRD data analysis. The HRTEM image (inset of figure 3b) showed an ensemble of CdSe nanocrystals assembled into a locally well-ordered close-packed array. It could be observed that the nanocrystals were well cry-

stallized, with interplanar distances of 3.5 Å, which was consistent with the (111) planes of cubic CdSe (viz. 3.510 Å). The crystal lattice appeared to be faultless in all the CdSe nanocrystals investigated.

3.4 XRD analysis

The crystallinity of the final products was detected by X-ray diffraction. Typical XRD patterns of the prepared CdSe nanocrystals (reaction time, 15 min) at different reaction temperatures are shown in figure 4. The three distinct diffraction peaks at $2\theta = 25.6^\circ$, 42.3° and 49.7° corresponded to the (111), (220) and (311) crystalline planes of cubic CdSe (JCPDS No. 19-191). The broadening of the diffraction peaks indicated the small size of the obtained CdSe nanocrystals, which was consistent with the result from the UV-Vis spectra and TEM. With the reaction temperature higher, the intensity of the XRD peaks increased, which may indicate that the reaction temperature has important influence on the crystallinity of CdSe nanocrystals.

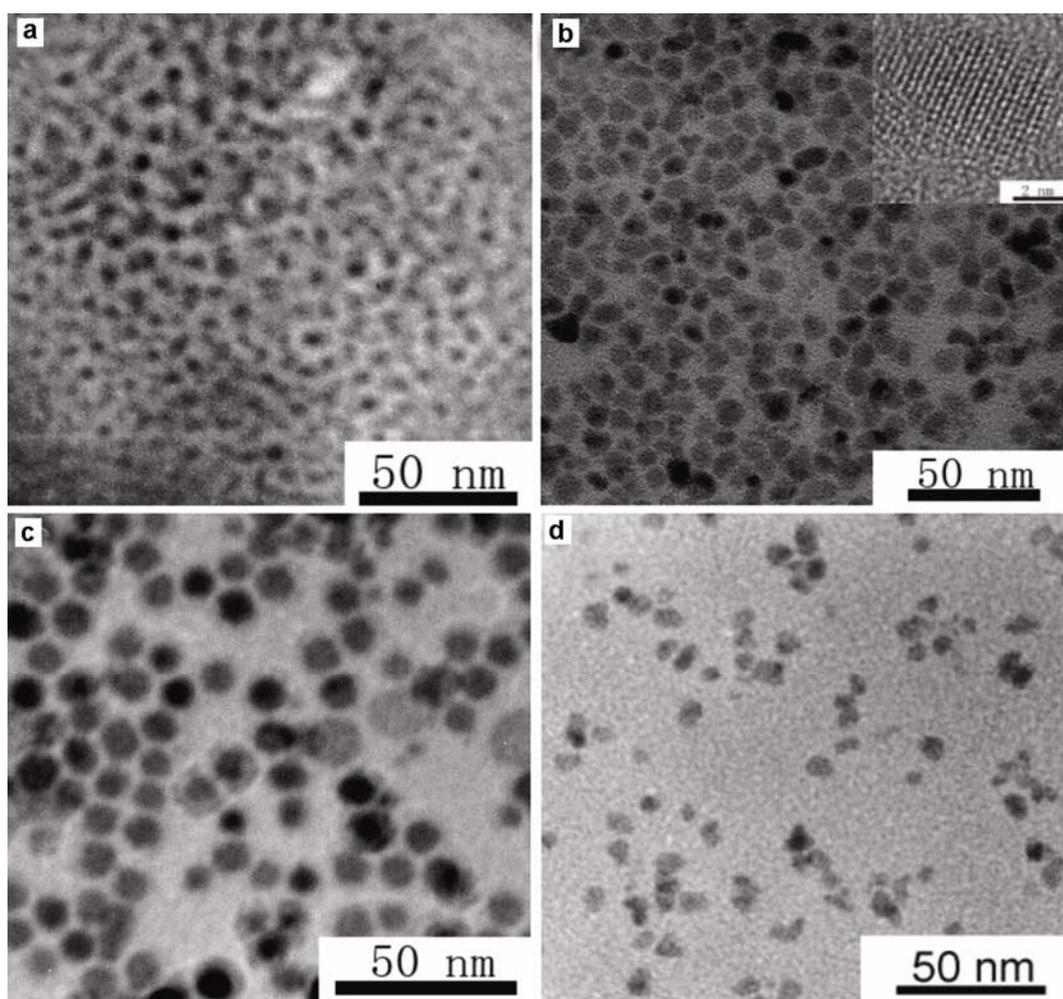


Figure 3. Typical TEM images of as-prepared CdSe nanocrystals under different reaction temperatures for reaction time of 15 min: **a.** 200°C; **b.** 220°C; **c.** 240°C and **d.** 280°C. Inset shows HRTEM image corresponding to 220°C.

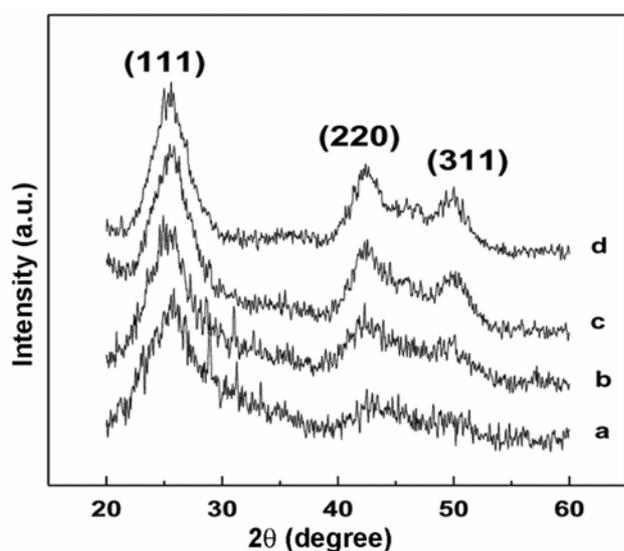


Figure 4. XRD patterns of CdSe nanocrystals obtained under different reaction temperatures for reaction time of 15 min: **a.** 200°C; **b.** 220°C; **c.** 240°C and **d.** 280°C.

3.5 XPS analysis

The XPS spectra shown in figure 5 give further evidence for the purity of the product. All the peaks were calibrated by using C (1s) (284.5 eV) as the reference. The two peaks located at 405.7 eV and 412.7 eV are assigned to Cd (3d) and that at 58.0 eV corresponds to Se (3d). These results are close to those of the pure CdSe. No impurities such as SeO₂, Cd₃P₂, CdO were detected in the XPS analysis, which was consistent with the XRD results.

4. Conclusions

We systematically investigated effects of reaction temperature on the size and optical properties of CdSe nanocrystals. The reaction temperature has important influence on optical properties due to the surface configuration of the nanocrystals on the packing of surface ligands. The size of CdSe nanocrystals may increase with the raise of

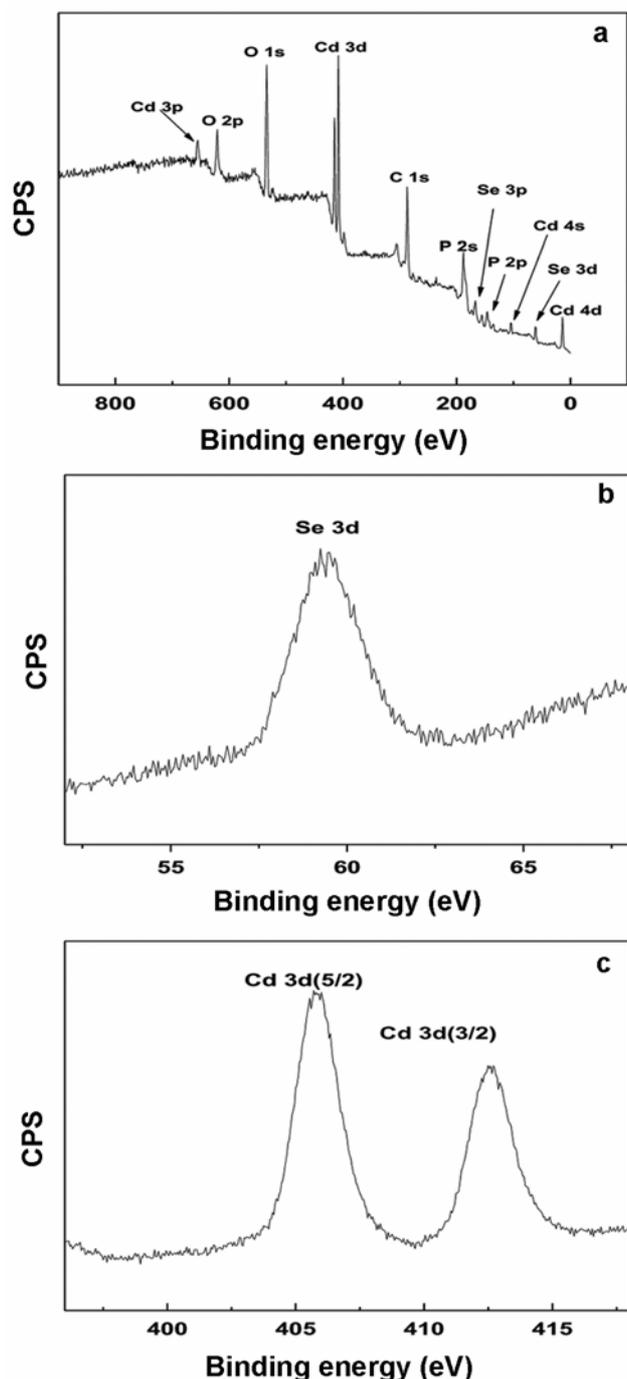


Figure 5. XPS spectra of organic molecule-capped CdSe nanocrystal obtained at 220°C for reaction time of 15 min: **a.** XPS full spectrum, **b.** Cd element and **c.** Se element.

reaction temperature because of different rates of nucleation and growth. It has also been seen that the different reaction temperatures lead to CdSe nanocrystals synthesized with the zinc blende structure. The unique optical properties suggest a promising future of the nanocrystals in practical applications.

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