Int. J. Electrochem. Sci., 7 **(2012)** 8473 - 8480

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Enhanced Ripening Behaviour of Cadmium Selenide Quantum Dots (CdSe QDs)

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Received: 19 March 202 / *Accepted:* 29 July 2012 / *Published:* 1 September 2012

In this research, cadmium selenide quantum dots (CdSe QDs) are synthesized successfully in the absence of trioctylphosphine (TOP) for 46 minutes and characterized by TEM and XRD analysis. The TEM image reveals that the CdSe QDs are spherical, compact with a dense stucture. The ripening behaviour of CdSe QDs is monitored using the red-shift characteristic in the UV-visible absorption peaks, and their size variations are estimated by the quantum confinement theory. The coarsening effect of CdSe QDs can be observed clearly from LSW plots due to the increase in ripening time and ripening temperature. The ripening coefficient is obtained to be 6.84 (10^{-3}) nm^3/min. The Arrhenius plot provides the activation energy value of the ripened samples, which are very low compared to the sample prior ripening, and is attributed to the domination of volume diffusion through the liquid phase.

Keywords: Semiconductors; nanostructures; chemical synthesis; optical properties.

1. INTRODUCTION

Many studies have been carried out on III-V and II-VI semiconductor quantum dots (QDs) all over the world. For II-VI QDs, in particular, the CdSe QDs prepared by chemical methods are by far, the most popular [1-3]. Recently, a new method has been developed for the synthesis of CdSe QDs without the use of TOP solvent [4-6]. The method is inexpensive, safer and produces CdSe QDs of high quality. Furthermore, the process can be operated in open atmosphere [7]. It is noteworthy that non-TOP based routes produce colloidal CdSe QDs with high-quality zinc blend structures and have attracted a great deal of interest due to their size-tunable photoemission characteristics. The photoemission characteristics originated from the quantum confinement effect of both electron and hole in all three dimensions, leading to an increase in effective energy band gaps of nanocrystals [8-11]. In addition, CdSe QDs exhibit almost full-range visible light emission within a reasonable size range. This, in turn, leads to numerous intensive studies on CdSe QDs for applications such as light-emitting diodes, laser, and biological labels [12-15].

It has been shown that at the initial nucleation and growth stage, the size of nanocrystal is primarily determined by the precursor concentration, capping ligand and precursor anion types, and temperature [16,17]. However, after nucleation and growth, ripening dominates between the nanoparticles. The final size of nanocrystals is thus determined by the temperature and the time period of ripening, as well as the colour of the emitting light [18,19]. Hence, the precise control of ripening is a critical issue for the applications of CdSe.

In line with the above motivation, the objectives of this work are to synthesize CdSe QDs in the absence of TOP solvent and to investigate the influence of ripening process on the size of CdSe QDs and their optical properties after a reaction time of 46 min.

2. EXPERIMENTAL

CdSe QDs were prepared using CdO and Se as precursors. 0.5 g of CdO, 25 ml of paraffin oil and 15 ml of oleic acid were loaded into a three-neck round bottom flask. The solution was heated to 160 °C and stirred until the CdO was completely dissolved, and a light yellow homogeneous solution was obtained. Following this, 0.079 g of Se in 50 ml of paraffin oil was carefully heated to 220 ºC with rapid stirring in another three-neck round bottom flask. The solution turned orange and then wine red. Following this, approximately 5 ml of Cd solution was injected swiftly into the Se solution during rapid stirring. The temperature dropped to 210 °C immediately after injection, and then rose to 220 °C. The temperature was maintained at 220 °C for the growth of CdSe QDs at 46 min. Finally, the precipitate was isolated from solvents and unreacted reagents via centrifugation, further washed with methanol several times and was dried in air at 50°C.

The CdSe QDs samples were reheated at 230, 240 and 250 °C for different ripening times, 15, 30, 60, 120, 180 and 240 min, respectively. The absorption spectra of each ripened sample were obtained using UVIKON 923 Double Beam UV-vis spectrophotometer.

The samples for TEM observation were prepared by placing a drop of a dilute methanol suspension of CdSe QDs onto the surface of a 300-mesh copper grid which was then dried for five days. TEM images were acquired using LEO LIBRA operating at 120 kV. X-ray diffraction (XRD) analysis was carried out using SIEMENS D500 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å) irradiated with a scanning rate of 0.02 $°s^{-1}$.

3. RESULTS AND DISCUSSION

Fig. 1 shows a typical TEM image of CdSe QDs for a reaction time of 46 min. The QDs are observed to be spherically shaped, compact and dense in structure, with an increasing tendency of agglomeration. In the top insert, the SAED pattern confirms the crystallized nature of the CdSe QDs. The size of the CdSe QDs are found to be approximately 9 nm as shown in Fig. 2, which significantly deviates from the crystallite size calculated from the XRD data, which is obtained to be approximately 4.1 nm. The typical nano size CdSe growth island is in fact a cluster of several smaller nanocrystals (size ~2-4 nm), with each surface passivated by oleic acid. Due to extremely small dimensions and high surface energy, the nanocrystallites agglomerate to give a resultant average size of 9 nm [19].

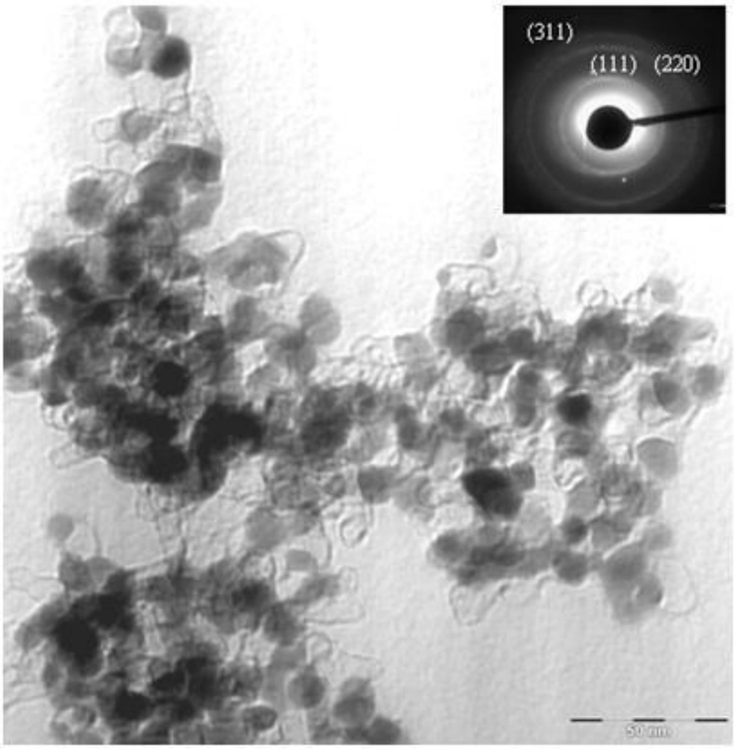

Figure 1. TEM micrograph and SAED pattern of CdSe QDs for a reaction of time 46 min.

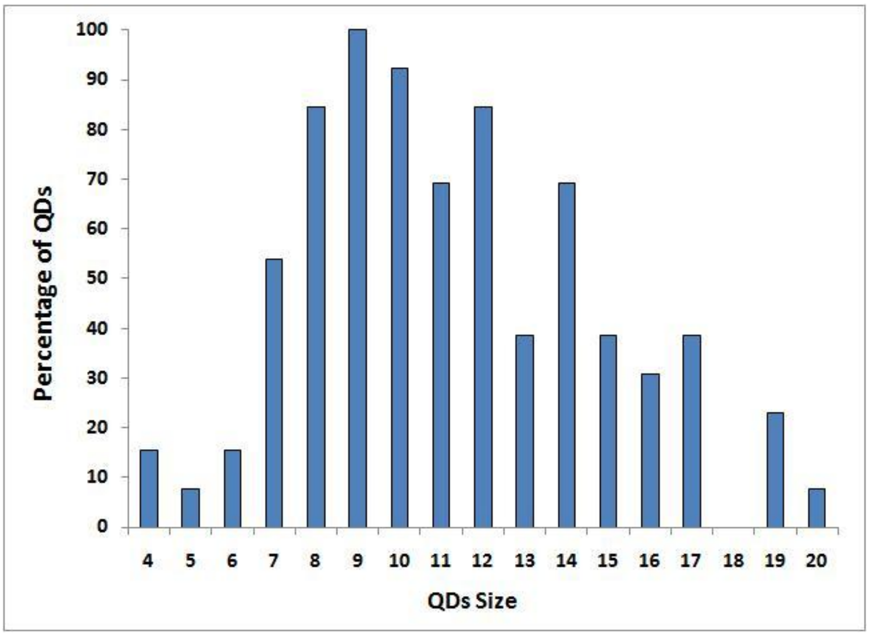

Figure 2. Particle size distribution of CdSe QDs for a reaction of time 46 min.

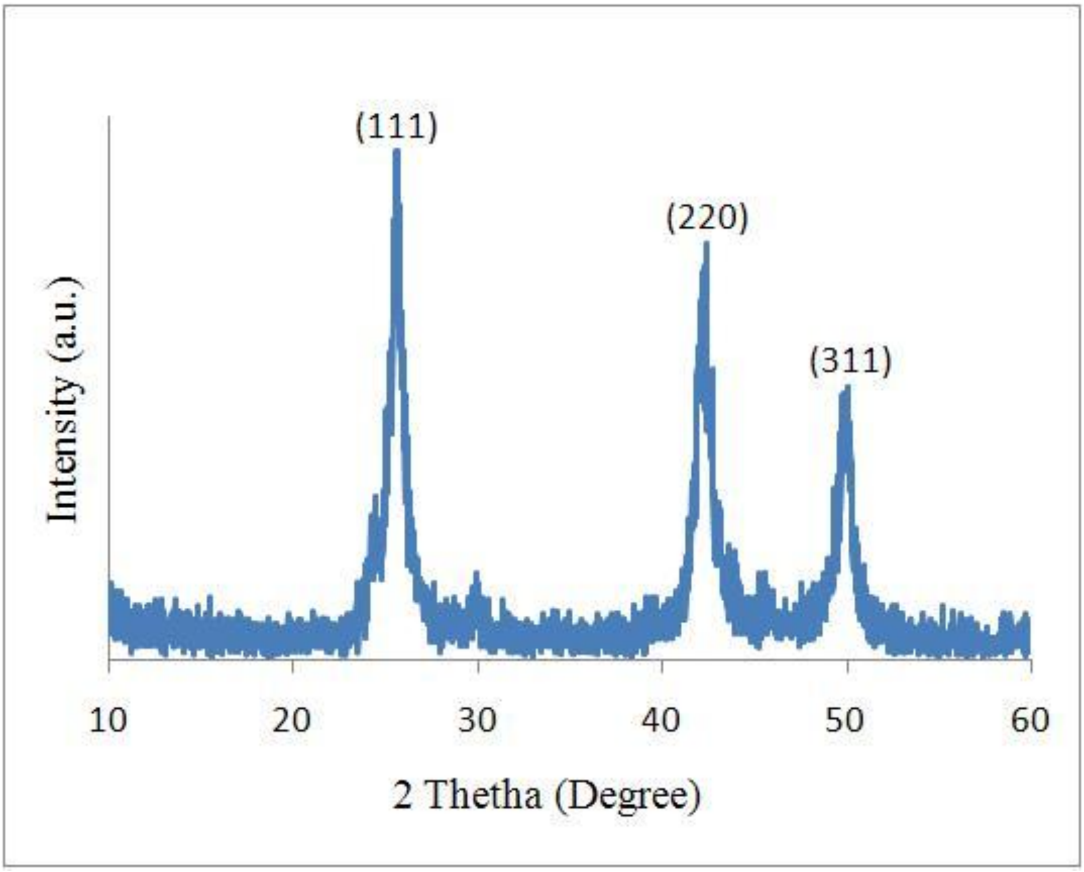

Figure 3. XRD patterns of CdSe QDs for a reaction of time 46 min.

Fig. 3 shows the evolution of XRD patterns for CdSe QDs at for a reaction time of 46 min. The peaks located at $2\theta = 25.9^{\circ}, 42.5^{\circ}$ and 50.3° can be attributed to the (111), (220) and (311) planes of the zinc-blend phase of CdSe. This structural assignment is consistent with the SAED pattern shown in Fig. 1. It is interesting to note that the CdSe QDs synthesized by this route possesses a different crystal structure from those synthesized by TOP-based route (wurtzite) [1]. A relatively lower growth temperature (260-220 °C) compared to the TOP-based route (300 °C) may play an important role in the formation of the zinc-blend phase. The QDs crystallite size were determined from the (111) reflection using Scherrer`s formula [3].

The ripening behaviour of CdSe QDs samples were observed using UV-vis spectroscopy. Fig. 4 shows the absorption spectra of different ripening time for 230, 240, 250 and 260 °C ripening temperatures. The peak shifts were used to estimate the variations in the energy band gap, which were then used for the estimation of size variation based on quantum confinement theory [20], as follows. The results are tabulated in Table 1.

$$E_{g\,(dot)} = E_{g\,(bulk)} + \frac{h^2}{2\,m^*\,d^2} - \frac{1.8e^2}{2\,\pi\,\varepsilon\,\varepsilon_0 d} \qquad (1)$$

$$\frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h} \qquad (2)$$

Table 1. Radius of CdSe QDs at different ripening time and temperature.

Ripening Time (min)	Radius of QDs for various ripening temperature (nm)		
	230 °C	240 °C	250 °C
0	2.42	2.24	2.42
15	2.67	3.17	4.09
30	2.74	3.28	4.34
60	2.81	3.4	4.64
120	2.89	3.54	5
180	2.98	3.7	5.49
240	3.07	3.79	6.13

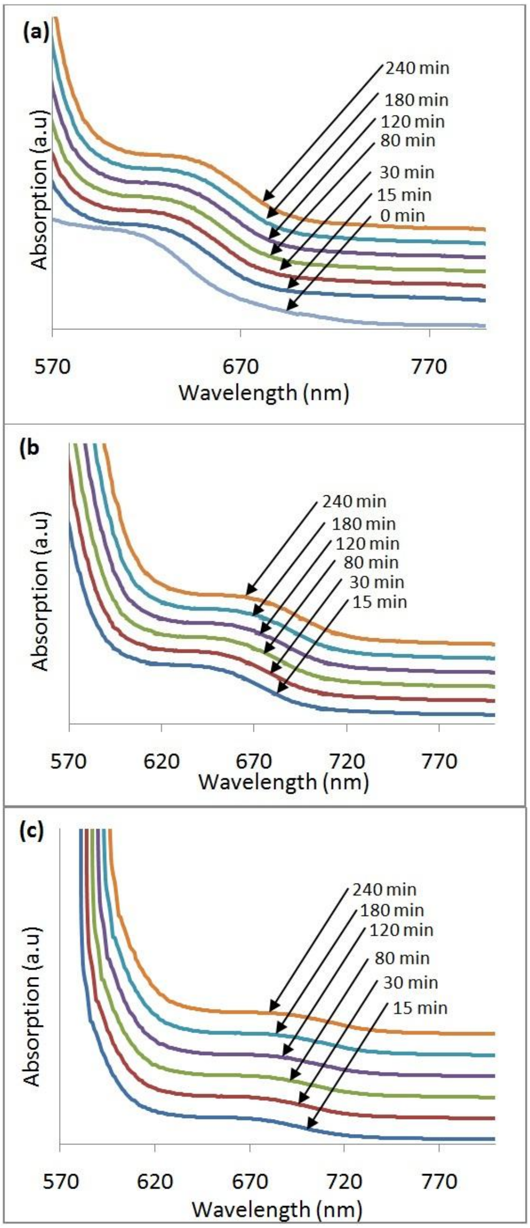

Figure 4. UV-visible absorption spectra for a ripening temperature of: (a) 230 °C, (b) 240 °C and (c) 250 °.

In this equation, $E_{g\,(dot)}$ is the energy band gap of a nanocrystal QDs, $E_{g\,(bulk)}$ is the energy band gap of a bulk semiconductor, h is the Planck constant, m^* is the reduced mass of exciton, m_e is the effective mass of an electron, m_h is the effective mass of a hole, d is the diameter of a nanocrystal, e is the electron charge, ε is the relative dielectric constant and ε_o is the space dielectric constant.

The coarsening effect can be observed clearly in each of the absorption spectrum as the ripening time increases. This also shows that the coarsening of CdSe QDs can be influenced by an increase in ripening temperature, which consequently increases the particle size. The size variation was used to determine the ripening rate coefficient for each ripening temperature using Lifshitz-Slyozov-Wagner (LSW) kinetic equation [20] as follows:

$$r^3 - r_o^3 = Kt \qquad (3)$$

where r_o is the average initial size of the original QDs before ripening occurs (i.e. 9 nm), r is the average size of nanocrystals after ripening occurs and K is the ripening rate coefficient. The ripening rate coefficient is represented by:

$$K = K_o\, exp\left(-\frac{Q}{RT}\right) \qquad (4)$$

In this equation, K_o is a rate constant and Q is the activation energy for ripening. By plugging the K values obtained from the LSW plots (Fig. 5) into Eq. 3, the Arrhenius is obtained, as shown in Fig. 6. The activation energy for ripening (Q) and the constant values (K) are summarized in Table 2.

Table 2. Coarsening kinetic variables for CdSe QDs before ripening and after ripening.

Kinetic Variables	CdSe Before Ripening	CdSe After Ripening
K_o (nm^3/min)		684 x 10^3
Q (kJ/mol)	310 [20]	36

The activation energy of the ripened samples is found to be very low compared to the samples prior to ripening. The result is attributed to the domination of volume diffusion through the liquid phase solution during the ripening reaction compared to the un-ripened CdSe QDs samples. The dissociating of Cd-Se bonds in un-ripened samples required higher activation energy due to the domination of lattice diffusion. In comparison, volume diffusion through the liquid phase solution was much easier than lattice diffusion through the solid phase.

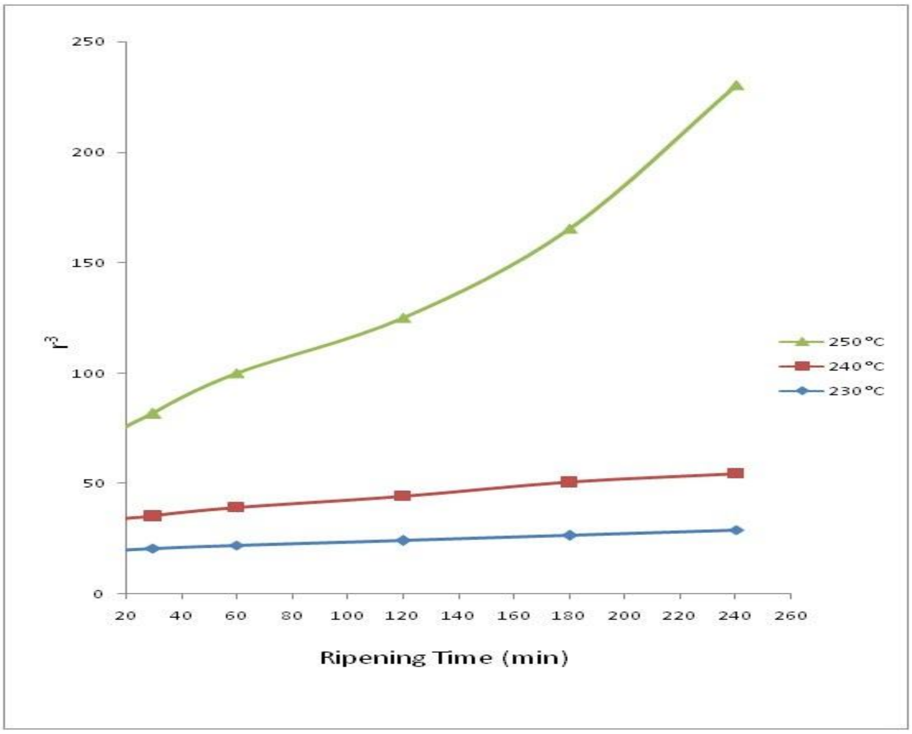

Figure 5. LSW plot showing the coarsening of CdSe QDs.

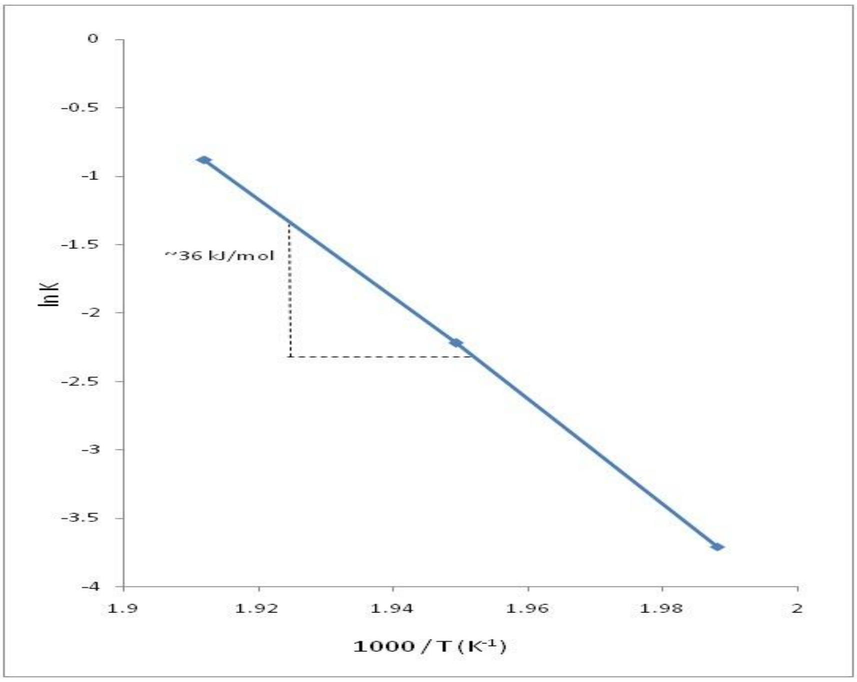

Figure 6. Arrhenius plot of CdSe QDs samples showing the activation energy for coarsening.

4. CONCLUSIONS

High-quality zinc blend CdSe QDs having spherical shapes have been synthesized successfully in this research. By changing the ripening time and ripening temperature, the size of the QDs is tunable. The domination of volume diffusion through the liquid phase gives significant effect in drastically lowering the activation energy of ripened CdSe QDs.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the Malaysian Ministry of Higher Education under the FRGS grant (No. FP015/2008C), University of Malaya PJP fund (No. FS211-2008A) and PPP fund (No. PS079/2008C and No. PS115/2010A).

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