

Aqueous synthesis of highly luminescent CdSe quantum dots with narrow spectra using hydrazine hydrate reduction selenium

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Highly luminescent CdSe quantum dots (QDs) with narrow spectra were synthesised by the reaction of CdCl₂·2.5H₂O, Se and hydrazine hydrate (N₂H₄·H₂O), respectively, in water and in the presence of 3-mercaptopropionic acid as the stabiliser. The effects of the experimental conditions, including the refluxing time and the selenium to cadmium molar ratio, on the luminescent properties of the obtained QDs have been investigated. Furthermore, the obtained QDs were characterised by UV–vis absorption spectra, photoluminescence (PL) spectra, X-ray powder diffraction and transmission electron microscopy, respectively. The results showed that the proposed method led to the formation of the cubic CdSe QDs with a narrow fluorescence full-width at half-maximum (47 nm) and a high PL quantum yield (up to 16%), respectively.

1. Introduction: Owing to their unique optical properties such as a broad absorption and a narrow emission with the peak positions tunable by their sizes, quantum dots (QDs) have gained increasing attention in the fields of chemical analysis [1], biolabelling [2], photocatalysis [3] and solar cells [4] and so on. The CdSe QDs are one of the most important group II–VI semiconductor nanomaterials, which can be prepared in either aqueous or organic solutions. One of the most successful organic synthesis methods is to grow the CdSe QDs in a solution from the molecular precursors in the presence of tributylphosphine (TBP) or oleylamine (OLA) at a high temperature [5, 6]. These methods are able to produce CdSe with several advantages such as a high photoluminescence (PL), a quantum yield (QY) and a narrow full-width at half-maximum (FWHM) of the PL spectra, respectively. However, these CdSe QDs are only soluble in some non-polar organic solvents, making them difficult to be used for biological applications. Among the aqueous routes, the use of various molecules as the stabilising agents in the preparation of the cadmium chalcogenide (CdS, CdSe and CdTe, respectively) QDs has been extensively investigated [7–9]. However, CdSe QDs prepared in an aqueous solution often exhibit a low emission efficiency and a wide FWHM of the PL spectra, respectively, compared with the QDs obtained via organic synthesis. For example, Song *et al.* [10] prepared mercaptosuccinic acid capped CdSe QDs with a QY of 30% through the microwave irradiation technique, but the FWHM of the PL spectra was in the range from 117 to 123 nm, respectively. Yu's group [11] prepared citrate stabilised CdSe QDs with a narrow FWHM (37–50 nm), but the photoluminescence quantum yield (PLQY) was only 4% after irradiation for 30 days.

Hydrazine hydrate is a weak base having reductive and complexing properties. There are some reports that hydrazine hydrate is used as a reducing agent rather than a complexing agent to prepare the metal selenide crystals, particularly the nanorods and the fractal nanocrystals [12–14]. However, very few studies have been reported on the synthesis of QDs using hydrazine hydrate as a reductant in an aqueous solution [15, 16]. In this Letter, we report a convenient synthetic method based on a complex reaction in an aqueous system, which can produce 3-mercaptopropionic acid (MPA) capped CdSe QDs with a narrow fluorescence FWHM (47 nm) and a high PLQY (up to 16%), respectively. CdCl₂·2.5H₂O, Se powder and the reductant N₂H₄·H₂O, respectively, are used as the reactants in this method.

2. Experimental: A cadmium chloride solution (100 ml, CdCl₂: 0.01 mol/l) was added to a three-necked flask and a 0.15 ml (1.7 mmol) MPA was added under magnetic stirring. The pH of the solution was then adjusted to 11.0 by a dropwise addition of a 1 mol/l NaOH solution. In a small flask, the required amount of the Se powder was dissolved in 2 ml of N₂H₄·H₂O (80%) in the open air, when the colour of the solution turned dark brown. It was injected using a syringe into the cadmium and thiol solution, and then the final solution was refluxed under the open air conditions. The typical molar ratio of the Cd²⁺/Se²⁻/MPA was 1:0.3:1.7. Aliquots of the sample were taken at different time intervals and used to record the UV–vis and the PL spectra without any post-preparative treatment.

After the samples were diluted, the absorption and the PL spectra were measured using a UV-2102PC spectrophotometer and a RF-5301 fluorescence spectrophotometer, respectively. The PLQY of the different QDs were determined by a comparison with rhodamine 6G and by using the procedure given in [17]. The as-prepared QDs were precipitated for 10 min by adding a threefold volume isopropyl alcohol, and the sediment was collected after centrifugation at 4000 rpm for 10 min. After drying, the obtained powder was used for an XRD analysis. The sample powder was placed onto sample holder plates, and the XRD spectra were carried out using a Rigaku /Dmax-2500 X-ray diffractometer with the CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The QDs solution was spread on an ultrathin carbon coated film on 200 mesh copper grids and left to dry in air. The sample was then visualised using FEI-TF30 transmission electron microscopy (TEM) with an operating voltage of 300 kV.

3. Results and discussion: The temporal evolution of the size of the CdSe QDs was studied by taking the samples from the reaction mixture at different intervals of time, and monitored via the UV–vis absorption and the PL spectra, respectively. The diameters of the QDs were calculated from the absorption peak by using the empirical equation [18], which is provided as follows

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \quad (1)$$

where D (nm) is the size of the CdSe QDs and λ (nm) is the

excitonic absorption peak, respectively. Fig. 1 shows the development of the absorption and the PL spectra of the CdSe QDs, respectively, as a function of the refluxing time. The absorption peaks of the CdSe QDs are quite obvious, with the reflux from 0.5 to 9 h and the absorption peaks are 431, 450, 467, 483 and 491 nm, respectively. Compared with the CdSe bulk material (716 nm) [19], the absorption peaks of the CdSe QDs have a significant blue shift, which show an obvious quantum confinement effect. According to the empirical formula, the mean diameters were estimated to be 1.8 (0.5 h), 2.0 (1.5 h), 2.1 (3 h), 2.2 (6 h) and 2.3 nm (9 h), respectively. The particle size increases from 1.8 to 2.3 nm over a period of 9 h, which indicates that the growth kinetics is slow. This is due to the fact that the MPA acts as an effective capping agent in producing stable colloids, which is an important aspect of the processing of the QDs. At the beginning of the refluxing, almost no fluorescence was detected. Until refluxing for 0.5 h, the PL spectra showed a very broad surface trap PL centred about 550 nm and a bandgap PL centred at \sim 466 nm, respectively. As the reflux time increases, the peaks of the bandgap PL spectra of the QDs are gradually red-shifted and the bandgap PL became stronger whereas the surface trap PL decreased. After about a 6 h refluxing, the bandgap luminescence is completely dominant, and the surface trap PL reduces to zero. With the reflux time increasing from 1.5 to 9 h, the bandgap PL peak of the CdSe QDs shifts from 485 to 514 nm, and the FWHM of the PL spectra are 54, 52, 50 and 47 nm, respectively. This suggests that the growth of the CdSe QDs was via an Ostwald ripening. After nucleation, further particle growth occurs through a dissolution of the smaller particles with less stability, which resulted in the size distribution becoming narrower as the reflux time was prolonged. The obtained CdSe QDs exhibited a narrow FWHM of 47 nm,

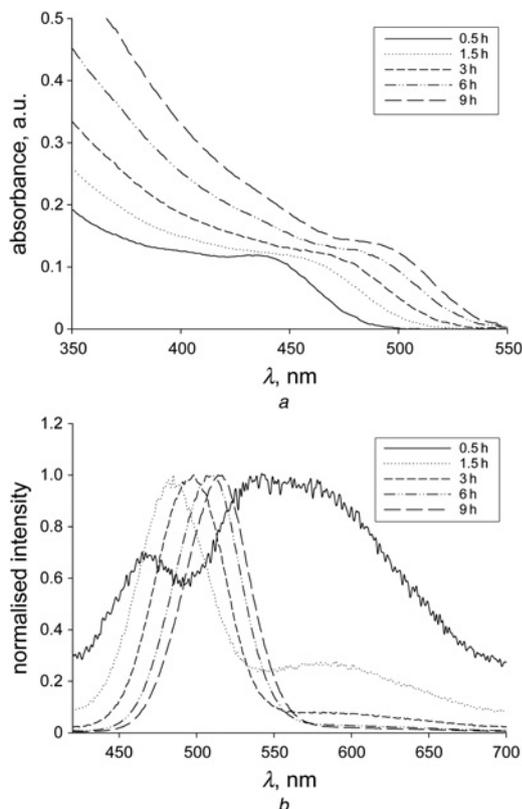


Figure 1 Temporal evolution of UV-vis absorption and normalised PL spectra of CdSe QDs prepared at Cd²⁺:Se²⁻:MPA molar ratio of 1:0.3:1.7
a UV-vis absorption
b Normalised PL spectra

almost comparable to the CdSe QDs prepared by organic synthesis [20, 21].

With the fixed MPA/Cd molar ratio at 1.7: 1 and the pH value at 11.0, respectively, we investigated the influence of the various Se/Cd molar ratios on the optical properties of the CdSe QDs and the obtained experimental results are shown in Fig. 2. As can be seen, in all the cases, the PL spectra showed a very broad surface trap PL and a narrow bandgap PL for the samples prepared at a reflux time less than or equal to 1.5 h, and the bandgap PL increased with the decreasing of the Se/Cd molar ratio. The aqueous synthesis of the QDs is often based on the Ostwald ripening phenomenon, and the formation of the QDs in the solution involves two stages: nucleation and growth. At the nucleation stage, the number of the CdSe nuclei was dependent on the Se precursor concentration. At a lower Se precursor concentration, fewer nuclei were formed, and more Cd monomers remained for the growth of the nuclei. Thus, the more remaining Cd monomers probably caused the effective passivation of the particle's surface defects, which induced the strong bandgap PL and the weak surface trap PL, respectively.

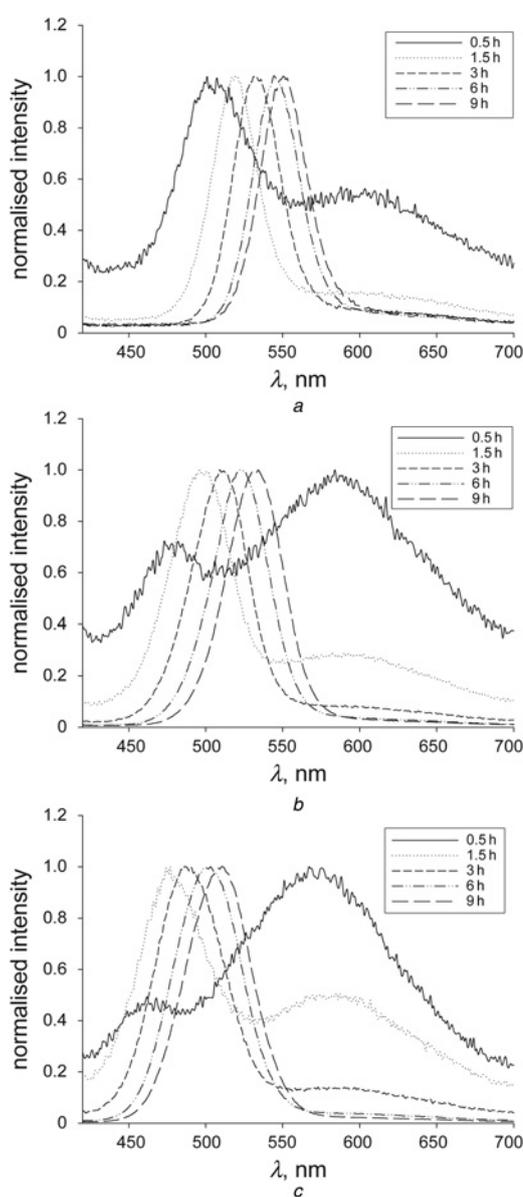


Figure 2 Normalised PL spectra of CdSe QDs prepared at various Se/Cd molar ratios
a 0.1:1
b 0.2:1
c 0.4:1

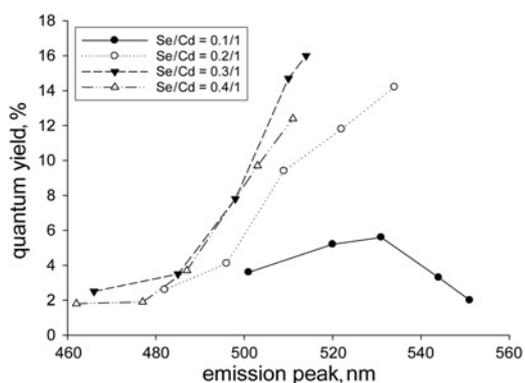


Figure 3 PLQY of CdSe QDs prepared at different Se/Cd molar ratios
Experimental conditions: Cd/MPA = 1:1.7, pH = 10.0, from left to right, the QDs are obtained for refluxing times of 0.5, 1.5, 3, 6 and 9 h, respectively

The PLQYs of the CdSe QDs prepared at the different Se/Cd molar ratios are shown in Fig. 3. It can be seen that the QDs show the distinguishing PLQY dependent on the reflux time and the stoichiometric ratio of the Se to Cd precursors used in the synthesis process. When the reflux time was less than or equal to 1.5 h, the PLQY of the CdSe QDs prepared at the Se/Cd molar ratio of 0.1:1 were relatively high because of the strong bandgap PL. As shown in Fig. 3, after a long time (≥ 3 h) refluxing, the bandgap luminescence is completely dominant whereas the surface trap PL reduces to almost zero, and we observed that when the Se/Cd molar ratio was 0.1:1, the CdSe QDs grew rapidly. A relatively fast crystal growth would lead to more defects and the surface states of the QDs [22], which decreased the PLQY. Therefore, when the reflux time was greater than or equal to 3 h, the PLQY of the CdSe QDs prepared at the Se/Cd molar ratio of 0.1:1 were lower than that of the CdSe QDs prepared at the other three Se/Cd molar ratios.

The crystallinity and the structure of the CdSe QDs were characterised by X-ray powder diffraction (XRD), as displayed in Fig. 4. The resulting CdSe QDs belonged to the cubic (zinc) structure, which was also the dominant crystal phase of the bulk CdSe. However, the positions of the XRD reflexes are intermediate between the values of the cubic CdSe and CdS phases. The reason was fully discussed in [23]. Briefly, during the refluxing of the aqueous solutions of the CdSe QDs in the presence of an excess of thiols in the basic media, a partial hydrolysis of the thiols leads to the incorporation of sulphur from the thiol molecules into the growing nanoparticles. Mixed CdSe(S) QDs, most probably with some gradient of sulphur distribution from inside the

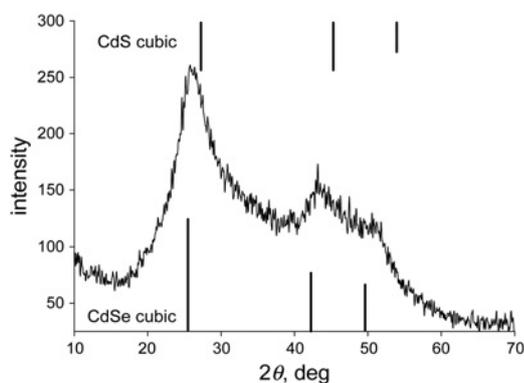


Figure 4 XRD patterns of CdSe QDs refluxed for 9 h
Standard diffraction lines of cubic CdSe and CdS, respectively, also shown for comparison

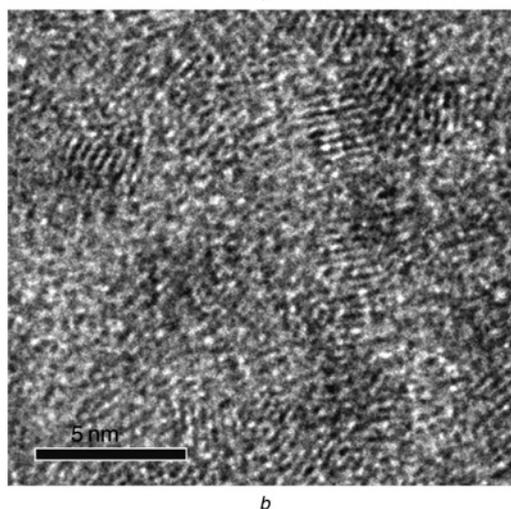
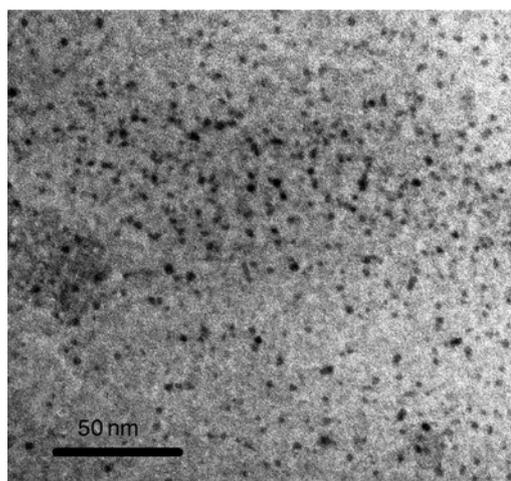


Figure 5 TEM and HRTEM images of as-prepared CdSe QDs
a TEM image
b HRTEM image

QDs to the surface, were formed under the refluxing. From Fig. 4, it can also be seen that the XRD peaks of the CdSe QDs are comparatively wider than that of the bulk materials because of the finite crystalline size.

Fig. 5 shows the TEM and the high-resolution TEM (HRTEM) images of the CdSe QDs prepared at the $\text{Cd}^{2+}:\text{Se}^{2-}:\text{MPA}$ molar ratio of 1:0.3:1.7, and refluxed for 9 h. Fig. 5a indicates that the CdSe appeared as spherical particles with excellent monodispersity. Moreover, the existence of well-resolved lattice fringes in the HRTEM image (Fig. 5b) confirmed the excellent crystalline structure of the obtained CdSe QDs.

4. Conclusion: A new route for the precursor of the selenium ions, that is, hydrazine hydrate reduction selenium, is proposed, and highly luminescent CdSe QDs capped with MPA were prepared in an aqueous solution. It is found that the obtained CdSe QDs are homogeneous, spherical and small and the CdSe QDs prepared by our method show very narrow and symmetric PL spectra with the FWHM of the PL peaks at about 47 nm. Without any post-treatments, the PLQY of the as-prepared CdSe QDs can reach up to 16%.

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6 References

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