

Synthesis of Monodisperse Nanocrystals via Microreaction: Open-to-Air Synthesis with Oleylamine as a Coligand

Hongwei Yang · Ningning Fan · Weiling Luan · Shan-tung Tu

Received: 19 October 2008 / Accepted: 8 January 2009 / Published online: 22 January 2009
© to the authors 2009

Abstract Microreaction provides a controllable tool to synthesize CdSe nanocrystals (NCs) in an accelerated fashion. However, the surface traps created during the fast growth usually result in low photoluminescence (PL) efficiency for the formed products. Herein, the reproducible synthesis of highly luminescent CdSe NCs directly in open air was reported, with a microreactor as the controllable reaction tool. Spectra investigation elucidated that applying OLA both in Se and Cd stock solutions could advantageously promote the diffusion between the two precursors, resulting in narrow full-width-at-half maximum (FWHM) of PL (26 nm). Meanwhile, the addition of OLA in the source solution was demonstrated helpful to improve the reactivity of Cd monomer. In this case, the focus of size distribution was accomplished during the early reaction stage. Furthermore, if the volume percentage (vol.%) of OLA in the precursors exceeded a threshold of 37.5%, the resulted CdSe NCs demonstrated long-term fixing of size distribution up to 300 s. The observed phenomena facilitated the preparation of a size series of monodisperse CdSe NCs merely by the variation of residence time. With the volume percentage of OLA as 37.5% in the source solution, a 78 nm tuning of PL spectra (from 507 to 585) was obtained through the variation of residence time from 2 s to 160 s, while maintaining narrow FMWH of PL (26–31 nm) and high QY of PL (35–55%).

Keywords Quantum dots · Microreaction · Reaction kinetics · Size control

Introduction

Nanocrystalline semiconductors exhibit unique size-tunable electronic and optical properties distinct from their bulk counterparts. Taking advantages of this nanoscale tunability on a macroscopic length scale could provide new classes of materials for scientific research and technological applications [1–5]. Owing to the size-dependent PL covering the whole visible spectrum, CdSe nanocrystals (NCs) have become the most extensively investigated target among various semiconductor materials. Since the milestone created by Murray et al. in 1993 [6–15], tremendous progresses have been made with regards to the size and shape control for CdSe NCs, and monodisperse products can be obtained with environmental-benign raw materials by fairly facile methods. Although the formed CdSe NCs can be stable in air at room temperature, but some key chemical ingredients utilized in the synthesis are air sensitive under high temperature, and the open-to-air synthesis of CdSe NCs by batch reaction usually leads to low quantum yield (QY) of PL [16]. As a result, most of the reported bath reaction concerning the synthesis of CdSe NCs were conducted in inert atmosphere (such as Ar and N₂). The difficulties associated with the oxygen-free operation lead to reduced flexibility and increased cost of the whole process, and the large-scale preparation can hardly be achieved without compromising the NC quality.

The recently introduced microfluidic methods can realize operation in closed systems, and the precise control of synthetic conditions offered by the strengthened heat and mass transfer makes the reproducible reaction achievable [17–19]. Furthermore, with several functional microdevices integrated in a miniature platform, multi-step reaction can be performed in a continuous manner [20, 21]. Recent studies have demonstrated that microfluidic reactors

H. Yang · N. Fan · W. Luan (✉) · S.-t. Tu
School of Mechanical and Power Engineering, East China
University of Science and Technology, Shanghai 200237, China
e-mail: luan@ecust.edu.cn

drastically outperform batch systems in the direct production of nanoparticles with short reaction time [22–30], and the open-to-air preparation of well dispersed CdSe NCs can be realized in a simple capillary microfluidic system [31]. However, as a result of the surface defects formed during the fast growth in microenvironment, CdSe NCs prepared by microreaction exhibited generally low QY of PL, and this situation was exacerbated for the reactions performed in open air [16, 31]. Various amines are known as favorable coligand to obtain highly luminescent CdSe NCs [13, 32–34], among which octadecylamine and hexadecylamine showed impressive results to improve both the size distribution and emission efficiency for CdSe NCs. For primary amines, a long organic chain length is required to obtain a boiling point compatible with the high temperature needed for the synthesis of CdSe NCs. As a result, these ingredients are in solid state at room temperature, and their applications in microreaction would result in the clogging of microchannels. OLA was a favorable ligand for the synthesis of CdSe NCs via both batch reactions and microreactions [24, 35], and fairly high QY of PL (25–50%) was observed. But the reported methods were conducted in inertial environment, and high quality products can only be favored under long residence time, high temperature, and small microchannel (inner diameter <250 μm). Meanwhile, for CdSe NCs synthesized with OLA, the observed reaction kinetics varied from each other. The kinetics observed by Yen et al. followed the classical diffusion-controlled growth theory. While an unusually long-term fixation of particle size and size distribution has been reported by Zhong et al. [35]. Furthermore, the qualitative study for the influence of OLA on the property of CdSe NCs was in scarcity, resulting in the experiential determination of OLA concentrations in different reports.

In this study, OLA was utilized as coligand to realize the open-to-air preparation of highly luminescent CdSe NCs via microreaction, and qualitative investigation of the influence of OLA on the PL property as well as size distribution was carried out to optimize the synthesis. The influence of OLA on the reaction kinetics was evidenced by the collected absorption spectra. The high quality of the obtained CdSe NCs has been confirmed by PL spectroscopy, powder X-ray diffraction (P-XRD) and transmission electron microscopy (TEM).

Experimental Section

Raw Materials

Cadmium oxide (CdO, SCR, 99.9%), selenium powder (Se, SCR, 99.5%), trioctylphosphine (TOP, Fluka, 90%), 1-octadecene (ODE, Fisher, 90%), oleic acid (OA, SCR, 90%),

oleylamine (OLA, Fluka, $\geq 75\%$), analytic grade methanol, and chloroform (SCR) were used directly without further treatment.

Synthesis of CdSe NCs

The CdSe NCs were prepared using a modification of previously reported method [31]. Typically, a Se stock solution was prepared by dissolving 39.50 mg of Se powder in TOP (1.00 mL) and OLA (1.50 mL). The obtained solution was further diluted with 0.50 mL ODE. Meanwhile, a suspension of 12.85 mg CdO, 0.12 mL OA, 1.50 mL OLA, and 1.38 mL ODE were heated at 150 $^{\circ}\text{C}$ with stirring to prepare a clear yellow cadmium precursor solution. Before being drawn into the syringes, the two stock solutions were thoroughly degassed. During the optimizing process for OLA concentration, various amounts of OLA were replaced with ODE, while maintaining the constant solution volume. The whole process was performed in open air.

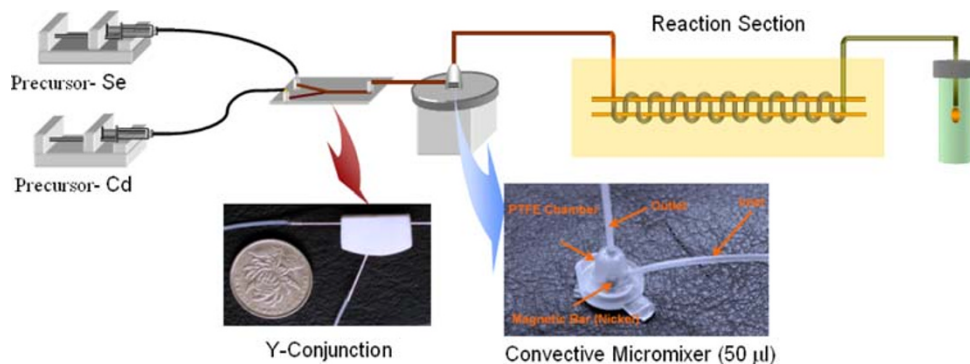
The microfluidic system comprised a convective micromixer and a 3D serpentine polytetrafluoroethylene (PTFE) capillary (300 μm I.D.), as shown in Fig. 1. Magnetic stirring in a miniature PTFE chamber with a volume of 50 μL facilitates the efficient mixing for the Cd and Se precursors under low flow rate, and stable heating source for the nucleation and growth of NCs was provided by a thermal-stable oil bath. During the operation, the as-delivered precursors firstly passed through a convective micromixer, and then entered the heating zone to initiate the nucleation, after dwelling in the heating section for different periods, the solutions flowed out of the outlet and were collected and diluted with chloroform for analysis.

Characterization

UV–Vis. spectra were acquired using a Varian Cary 100 UV–VIS spectrometer, and PL spectra were recorded with Varian Cary Eclipse. QY of PL was obtained by comparing the integrated PL intensities of the NCs and the organic dye (Rhodamine 6G) [36]. All measurements were performed on original QD samples without any purifying process.

To obtain samples for TEM and XRD characterization, the formed CdSe NCs were precipitated by adding methanol into the chloroform solution and were further isolated and purified by repeated centrifugation and decantation. HRTEM images were taken on a JEM-2100F microscope operated at 200 kV, and the sample was prepared by dipping an amorphous carbon–copper grid in a dilute chloroform dispersed NCs solution, then sample was left to evaporate at room temperature. XRD measurements were performed on a Rigaku D/max2550 operating with Cu K α ($\lambda = 0.154056$ nm), samples were deposited as a thin layer on a Si wafer.

Fig. 1 Schematic graph of the microfluidic capillary reactor



Results and Discussion

To fully characterize the stability of the microreaction system, two discrete operations were conducted based on the same precursor solutions and operation parameters. Figure 2 demonstrates the absorption and PL spectra of CdSe NCs obtained at 280 °C under a residence time of 20 s. The resulted spectra of the NCs samples prepared in these conditions clearly indicate narrow size distributions, which stand out in the samples prepared in microreactions and are comparable to the best results obtained by the batch processes [6–15, 22–30]. The sharp band-edge absorbance and several higher transitions are clearly resolved, besides, pure band-gap emissions with very narrow FWHM (26 nm) were observed. Moreover, two independent operations resulted in nearly the same spectra, which showed fairly good reproducibility with regards to peak location (1 nm), peak width (0.3 nm), and peak intensity (1/150).

During the preparation of precursors, equal volume of OLA was applied in the following three cases: (1) add OLA solely in Se precursor, (2) add OLA both in Se and Cd stock

solution, and (3) add OLA solely in Cd precursor. The resulted UV–Vis and PL spectra in those three cases were provided as shown in Fig. 3. Generally, applying OLA only in Cd side leads to the medium PL peak width (FWHM, 30 nm) and CdSe concentration (5.15×10^{-6} M). The best-quality samples were obtained by adding OLA both in Se and Cd side, as indicated by the very sharp absorption peak and up to three higher transitions observed in UV–Vis spectra. CdSe NCs synthesized with OLA in Se side possessed the widest PL peak (FWHM, 35 nm) and the lowest molar concentration (4.16×10^{-6} M) of products, as shown in Table 1. The presented phenomena can find their justifications in diffusion-controlled reaction. For CdSe NCs synthesized involved amines as coligands, the increased reactivity of Cd monomer by the formation of Cd–amine complex has been generally observed [13, 32–34]. As a result, applying OLA in Cd side would result in the formation of Cd–amine complex during the heating process for the preparation of precursors, and the monomer activity can be promoted. However, OLA is the most viscous ingredient among all the utilized reagents, and the addition of OLA

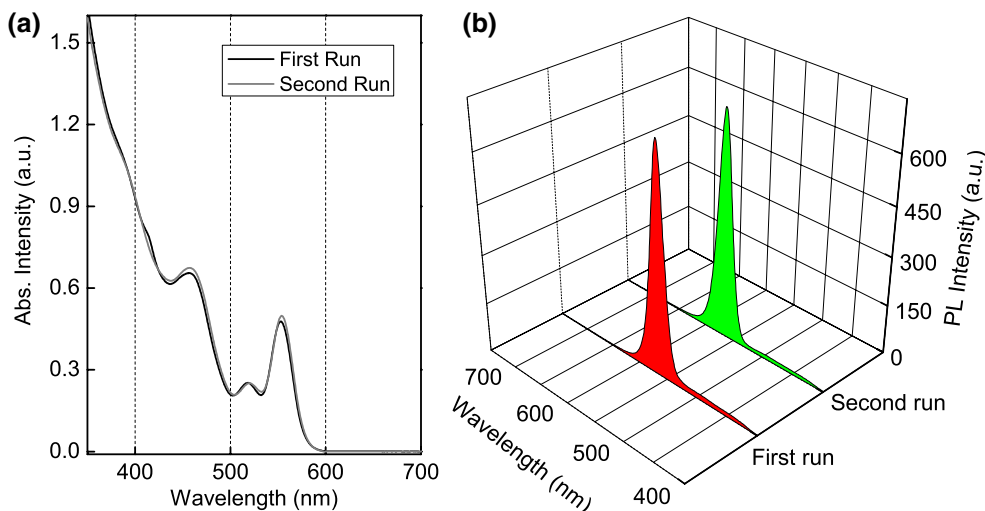


Fig. 2 **a** Absorption and **b** PL spectra of CdSe NCs prepared in two independent operations under the same reaction condition ($\text{vol.}_{\text{OLA}}\% = 37.5\%$, $T = 280$ °C, $t = 20$ s)

Fig. 3 **a** Absorption and **b** PL spectra of CdSe NCs prepared with OLA being added in different sources (vol._{OLA}% = 37.5%, $T = 280\text{ }^{\circ}\text{C}$, $t = 10\text{ s}$)

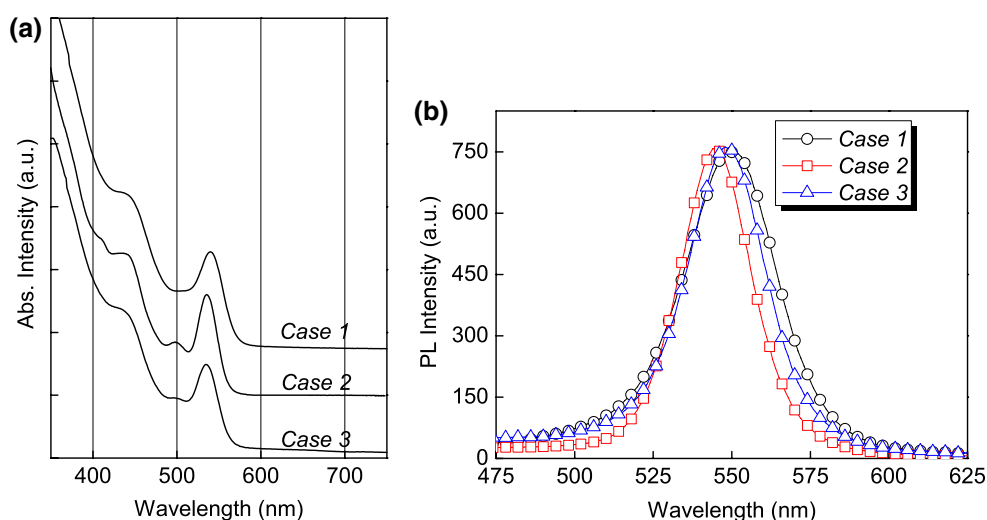


Table 1 Obtained results of CdSe NCs prepared with OLA being added in different source (vol._{OLA}% = 37.5%, $T = 280\text{ }^{\circ}\text{C}$, $t = 10\text{ s}$)

Defined case	FWHM of PL (nm)	CdSe concentration (10^{-6} M)
Case 1	35	4.16
Case 2	27	5.50
Case 3	30	5.15

solely in one side would hinder the diffusion of Se and Cd precursors during the reaction, resulting in low product yield. The above two competing factors justified the medium CdSe molar concentration ($5.15 \times 10^{-6}\text{ M}$) observed in Case 3. As for Case 1, cadmium oleate acted as Cd monomer in the early reaction stage, and its residence time in the heating microchannel was not enough for the formation of large amount of Cd–amine complex, this led to the lowest CdSe molar concentration. In contrast, adding OLA both in Se and Cd side have the dual function of forming Cd–amine complex and promoting the diffusion for the involved precursors, and the high monomer concentration facilitates the focusing of size distribution, which induced the highest CdSe concentration ($5.50 \times 10^{-6}\text{ M}$) and the narrowest PL peak observed in Case 2.

In order to investigate the influence of OLA systematically, OLA was partly replaced by ODE, and the temporal evolution of UV–Vis. and PL spectra were recorded to reflect the influence of OLA amount on the mean particle size and size distribution of CdSe NCs. The kinetic data with regards to CdSe molar concentration and mean particle diameter were obtained by the methods reported by Yu and his colleagues [37]. To establish a baseline for comparison of the different reaction conditions studied, initial experiment using OA as the sole ligand was also conducted.

Absorption spectra recorded for CdSe NCs prepared under various residence time and different volume percentage of OLA (the whole OLA volume percentage in

both Se and Cd side) are shown in Fig. 4. In the early reaction stage, dramatic red shifts of absorption peaks were observed with the increase of residence time, indicating the fast growth rate during this phase, and these shifts slowed down with the further increase of residence time. For the samples prepared with OA as a sole surfactant, generally wide absorption peaks were observed, which pointed to the wide size distribution of NCs. With the increase of OLA amount, the wide absorption peaks gradually became sharp, accompanying with the resolution of several different electronic transition states.

The obtained data shown in Fig. 5 supplies the further evidence for OLA-induced kinetic control. Generally, the increased volume percentage of OLA in the source solution led to small particle size and high particle concentration. Under the constant residence time as 20 s, the addition of 50.0 vol.% OLA in the source solution resulted in 0.4 nm decrease of mean diameter compared with the samples prepared without OLA, coupling with the significant increase of particle concentration from $1.16 \times 10^{17}/\text{L}$ to $1.87 \times 10^{17}/\text{L}$. The observed results were mainly resulted from the formed amine–Cd complex and the strong bonding of OLA on the NCs surface. With the increased amount of OLA in the source solution, the formed Cd–amine complex led to the increased reactivity of Cd monomer, and large quantity of nuclei were formed in the early reaction period. However, during the subsequent heating process in solution with large amount of free OLA, the increased coverage of OLA on NCs surface would hinder the absorption of CdSe monomer on the NCs surface, and the resulted slow growth led to small CdSe NCs [38].

The influence of OLA volume on the emission property of CdSe NCs was elucidated by the temporal evolution of PL spectra (Fig. 6), while QY and FWHM of PL were served as indirect measures for the emission efficiency and size distribution of CdSe NCs, respectively.

Fig. 4 Absorption spectra of the samples monitored during the evolution of residence time and the volume percentage of OLA (OLA both in Cd and Se side, $T = 280\text{ }^{\circ}\text{C}$)

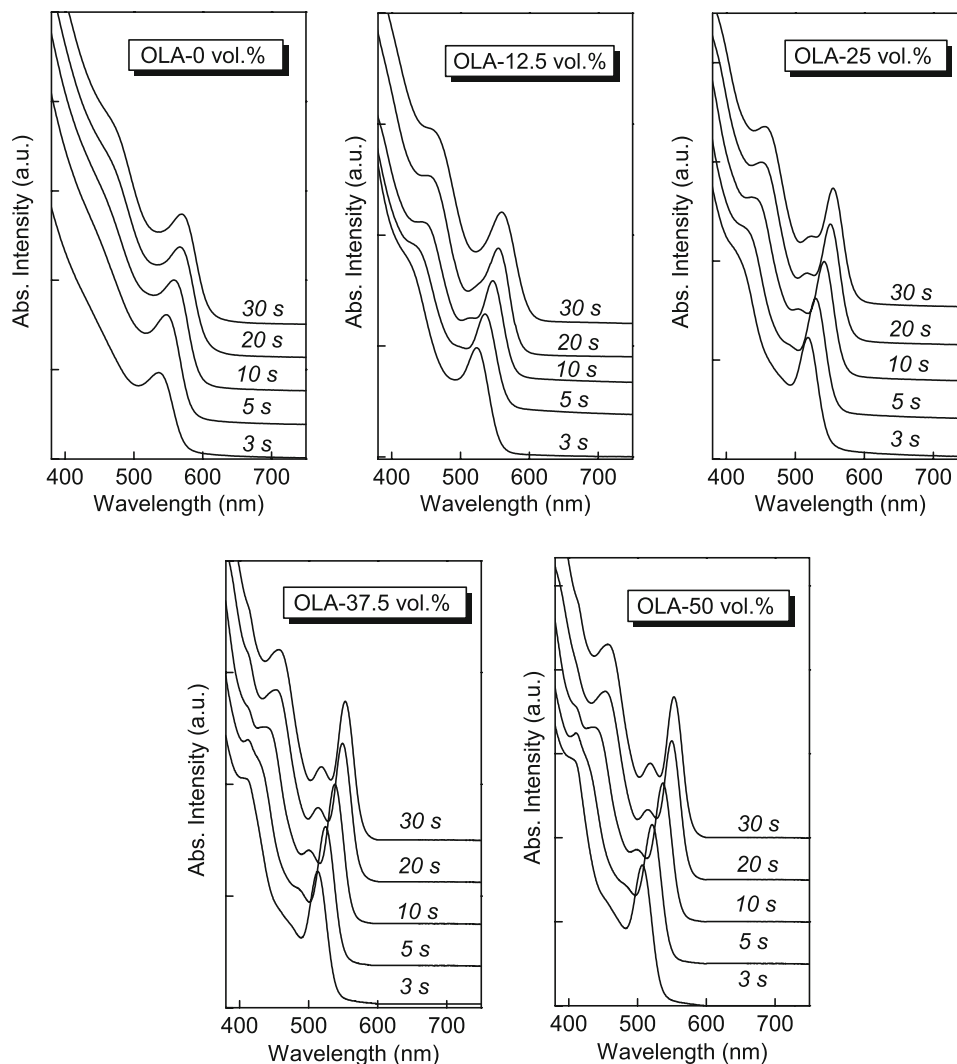


Fig. 5 a Mean diameter, **b** particle concentration of the CdSe samples obtained during the evolution of residence time and volume percentage of OLA (OLA both in Cd and Se sources, $T = 280\text{ }^{\circ}\text{C}$)

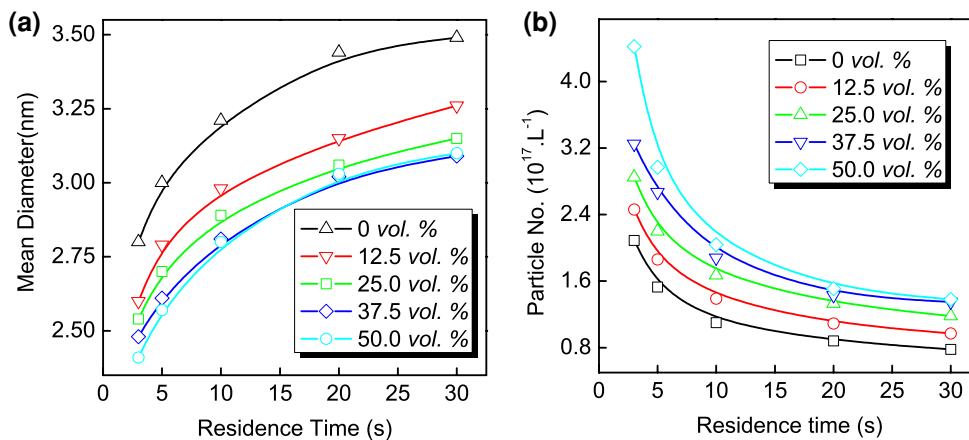
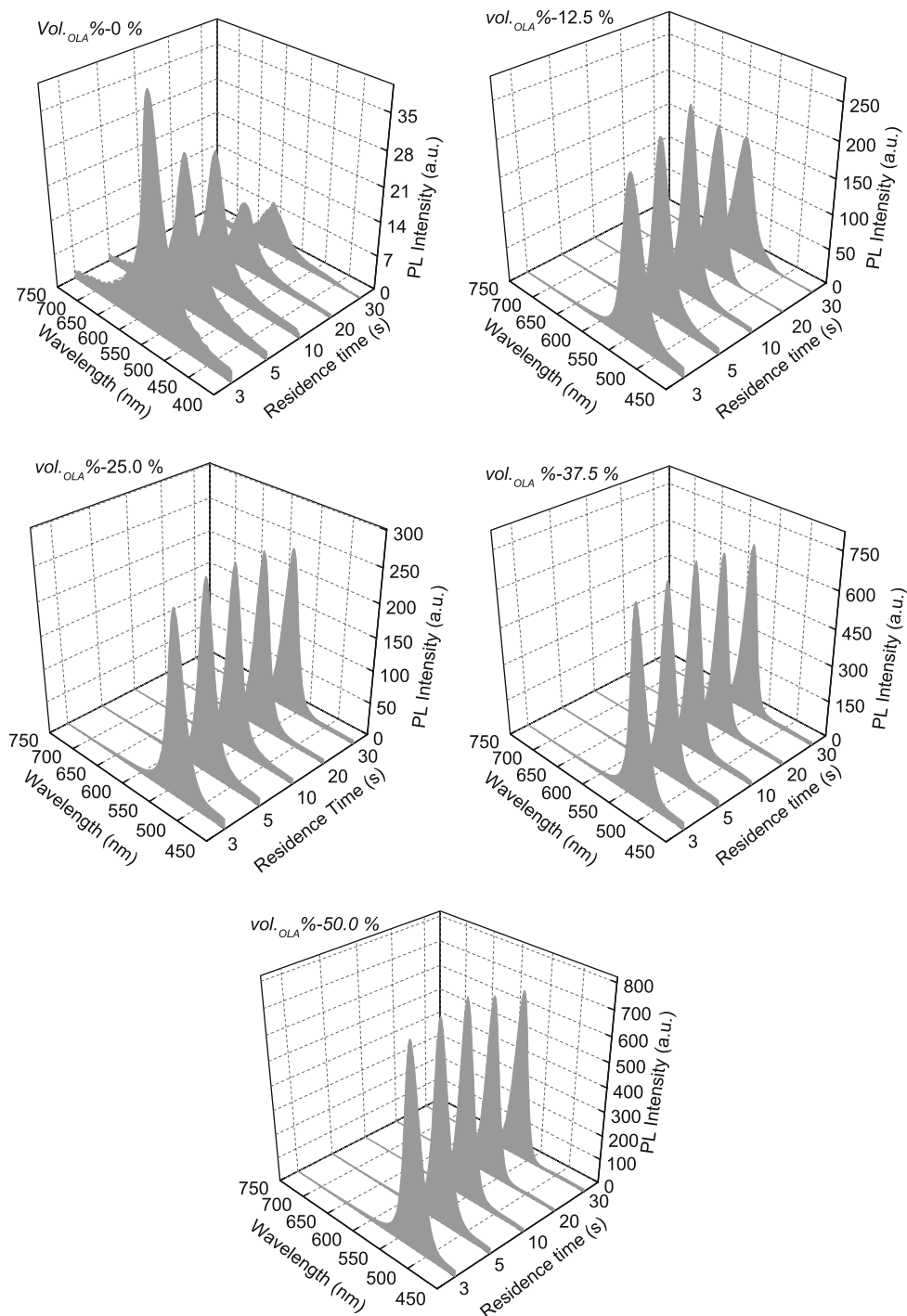


Figure 7a and b plots the FWHM and QY of PL as a function of residence time. Significant differences were observed in the comparison of these values among the different reaction sets. CdSe NCs synthesized without OLA demonstrated quite wide PL peaks (40–48 nm), and the very

low QYs of PL (below 6%) were observed. With the increase of OLA volume, the PL peaks gradually narrowed down, coupling with the significant improvement in QY. Under the same residence time as 3 s, changing the volume percentage of OLA from 0% to 50.0% provided a radical increase of QY

Fig. 6 PL spectra of the CdSe samples monitored during the evolution of residence time and volume percentage of OLA (OLA both in Cd and Se side, $T = 280\text{ }^{\circ}\text{C}$)

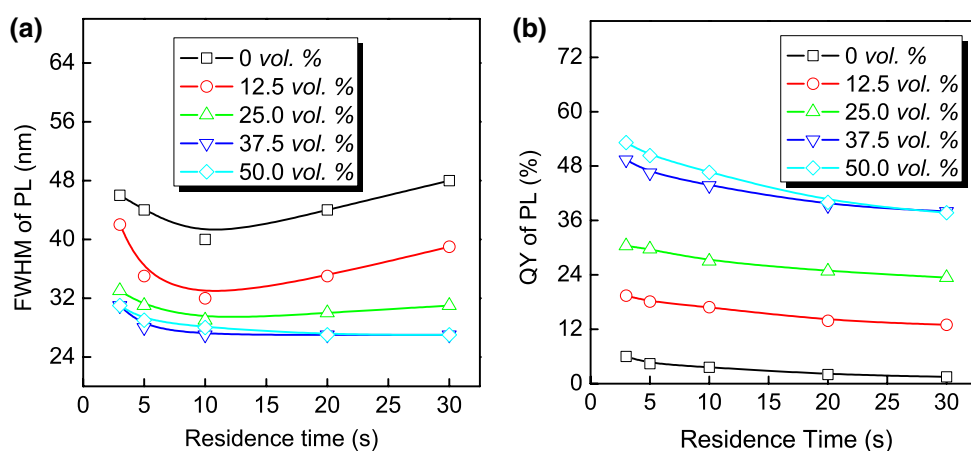


from 6% to 53%, accompanying with the narrowed FWHM from 46 nm to 31 nm. This enhancement of the band edge PL in comparison with OA-capped CdSe NCs may be due to the strong bonding of the amines to the NC surface, which allows its better passivation. Less sterically hindered amines may improve surface capping and, hence, the passivation of traps by creating larger capping densities [32, 33].

For CdSe NCs synthesized with small amount of OLA below 37.5 vol.%, there was clearly an optimal time for

FWHM of PL, a point after which the growth slowed down while the size distribution of the NCs widened. Increasing the volume percentage of OLA to 37.5% resulted in a long term (up to 5 min) fixing of FWHM, and the narrowest FWHM as 27 nm was obtained at a short residence time as 20 s, which was significantly shorter than the reported value in ref. [24]. The observed phenomenon resulted primarily from the kinetic issues. For steady-state, diffusion-controlled growth of spherical particles, there exist a

Fig. 7 **a** FWHM of PL and **b** QY of the CdSe samples obtained during the evolution of residence time and volume percentage of OLA (OLA both in Cd and Se sources, $T = 280\text{ }^{\circ}\text{C}$)



critical size (r_{cr}), and the focus of size distribution occurs when all the NCs sizes (r) are larger than r_{cr} . The high monomer concentration realized under elevated OLA amount is favorable to achieve large r_{cr} [39, 40]. In this way, the focusing of size distribution took place in the early reaction stage, and the shortened reaction time for monodisperse CdSe NCs was achieved. For CdSe prepared with higher volume percentage of OLA over 37.5%, high quality samples (FWHM 31 nm) were obtained under quite short residence time as 3 s. While in the subsequent heating phase, the FWHM of PL continuously narrowed down, and the narrowest FWHM (27 nm) was obtained at 20 s. The further increase of residence time resulted in little variation of PL wavelength and FWHM of PL. During the synthesis of NCs, the ligands are dynamically bonded onto the surface of NCs. In this case, the ligand needs to be able to exchange on and off the growing NCs, so that regions of the NCs surface are transiently accessible for growth, yet entire crystals are, on average, monolayer-protected to block aggregation [39]. In the early reaction stage, the chemical potential of the NCs was low, and the high monomer concentration in the precursor would promote the dynamical bonding of ligand, resulting in the growth of NCs. However, the prolonged growth led to significant reduction in monomer concentration and the decreased growth rate was observed. Furthermore, increase of the total OLA concentration in the solution should increase the number of ligands on the surface of each NC. This should also decrease the growth rate of the NCs. When the OLA was applied in large excess (more than 37.5 vol.% in this experiment), the increased coverage of ligand and the large amount of free amine in the precursor would hinder the “off” process of OLA. As a result, the new monomers were inaccessible for the NCs and the long-term fixing of size as well as size distribution NCs were thus made possible.

The PL efficiency of NCs prepared using $\text{vol.}_{\text{OLA}} > 25.0\%$ was maintained at a high level during the evolution of residence time. In our experiment, QYs of PL were

continuously decreased with the proceeding of reaction, and the “bright point” (corresponding to the crossover of QY) observed in batch reactions was not detected [36], this may be due to the lack of slow annealing process for NCs in microenvironment. From Fig. 7a and b, it was clear that CdSe NCs prepared with 37.5 vol.% and 50 vol.% OLA showed little difference. For the economical concern, 37.5 vol.% OLA were applied for the subsequent experiments.

An important consideration in CdSe NCs synthesis is the ability to vary NCs size reproducibly over a large range that facilitates broad spectral tuning. The observed long-term focusing of size leveling off of FWHM and QY of PL allowed the tuning of NCs size simply by the variation of residence time. Figure 8 exhibited CdSe NCs synthesized with varied residence time from 2 s to 160 s, and this

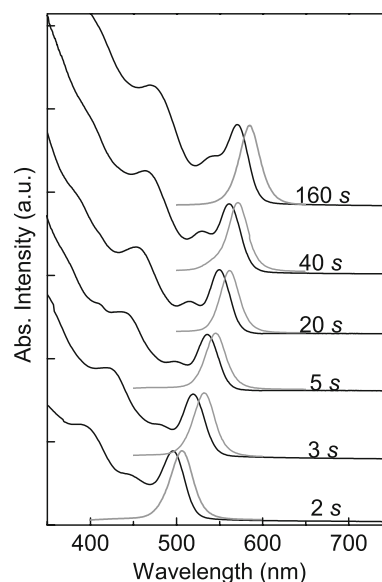


Fig. 8 A size series of CdSe NCs synthesized by the variation of residence time from 2 s to 160 s ($\text{vol.}_{\text{OLA}}\% = 3\text{ mL}$, $T = 280\text{ }^{\circ}\text{C}$)

Fig. 9 TEM images of 3.6 nm CdSe NCs synthesized at 160 s ($\text{vol.}_{\text{OLA}}\% = 37.5\%$, $T = 280\text{ }^{\circ}\text{C}$)

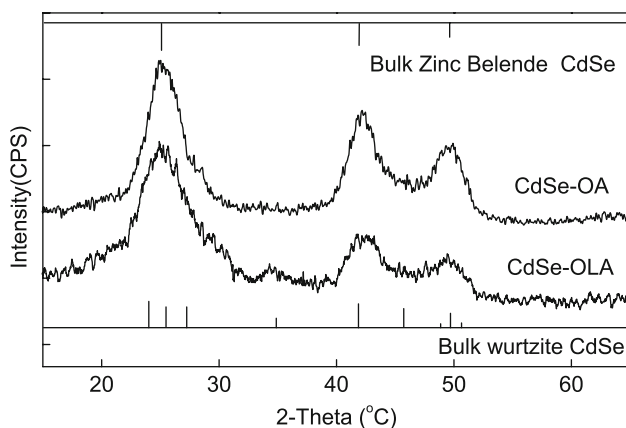
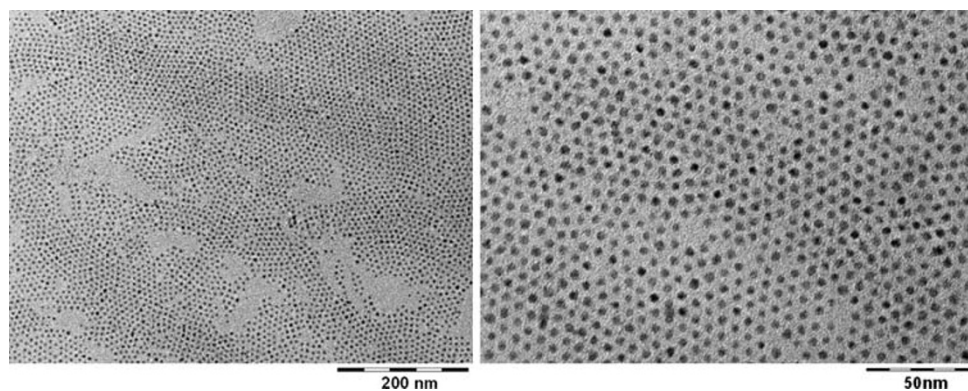


Fig. 10 XRD pattern of 3.6 nm CdSe NCs synthesized at 160 s ($\text{vol.}_{\text{OLA}}\% = 37.5\%$, $T = 280\text{ }^{\circ}\text{C}$)

simple operation offered a 78 nm tuning of PL maximum while maintaining the narrow FWHM (26–31 nm) and high QY (35–55%). The overview TEM images of CdSe NCs prepared under 160 s are presented in Fig. 9, which clearly illustrates the narrow size distribution and fairly spherical morphology of CdSe NCs with an average size of 3.6 nm in diameter. According to the statistics for 100 dots in a selected regime, the standard deviation of the average diameter was calculated as 6.0%.

Figure 10 compared the XRD spectra for CdSe NCs prepared using OA and OA-OLA. CdSe NCs prepared using OA as the sole ligand clearly exhibit the typical pattern of the zinc blende structure with three distinct features, the first peak at $2\theta = 25^{\circ}$ is due to the (111) reflection, and the other two features appearing at $2\theta = 42^{\circ}$ and 50° are due to the (220) and (311) reflections, respectively. For CdSe NCs prepared using OLA as the coligand, (102) reflection at $2\theta = 35^{\circ}$ was clearly observed, which points to the wurtzite structure of the NCs.

In conclusion, closed environment realized by microreactor was utilized to eliminate the requirement of inert atmosphere for the synthesis CdSe, and OLA was applied as a coligand to improve the size uniformity and PL efficiency of the products. The addition of OLA both in Se and

Cd side was demonstrated advantageous to increase the reactivity of Cd monomer and promote the diffusion of the two precursors, which resulted in CdSe NCs with quite narrow FWHM of PL. The addition of OLA in the source solution resulted in significant improvement of both size distribution and QY of CdSe NCs, and high OLA concentration is favored to prepare highly luminescent CdSe NCs with small size as well as narrow size distribution. When the applied volume percentage of OLA exceeded 37.5%, long-term fixing of FWHM was observed, and high QY of PL was maintained over a long period. The obtained results facilitate an easy tuning of PL range by the variation of residence time. With 3 mL OLA in the source solution, a size series (2.3–3.6 nm) of highly luminescent CdSe NCs (QY 35–55%) with narrow FWHM of PL (26–31 nm) were obtained under varied residence time from 2 s to 160 s.

Acknowledgment Authors appreciated the financial supports from the National Natural Science Fund of China (50772036) and the State Key Laboratory of Chemical Engineering at East China University of Science and Technology.

References

1. M. Bruchez Jr., M. Moronne, P. Gin et al., *Science* **281**, 2013 (1998). doi:10.1126/science.281.5385.2013
2. W.C.W. Chan, S. Nie, *Science* **281**, 2016 (1998). doi:10.1126/science.281.5385.2016
3. V.I. Klimov, A.A. Mikhailovsky, S. Xu et al., *Science* **290**, 314 (2000). doi:10.1126/science.290.5490.314
4. V.L. Colvin, M.C. Schlamp, A.P. Alivisatos, *Nature* **370**, 354 (1994). doi:10.1038/370354a0
5. A.P. Alivisatos, *Science* **271**, 933 (1996). doi:10.1126/science.271.5251.933
6. C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993). doi:10.1021/ja00072a025
7. W.W. Yu, X. Peng, *Angew. Chem. Int. Ed.* **41**, 2368 (2002). doi:10.1002/1521-3773(20020703)41:13<2368::AID-ANIE2368>3.0.CO;2-G
8. D. Battaglia, X. Peng, *Nano Lett.* **2**, 1027 (2002). doi:10.1021/ml025687v
9. C.B. Murray, C.R. Kagan, M.G. Bawendi, *Annu. Rev. Mater. Sci.* **30**, 545 (2000). doi:10.1146/annurev.matsci.30.1.545
10. C.D.M. Donega, S.G. Hickey, S.F. Wuister et al., *J. Phys. Chem. B* **107**, 489 (2003). doi:10.1021/jp027160c

11. P. Reiss, J. Bleuse, A. Pron, *Nano Lett.* **2**, 781 (2002). doi:[10.1021/nl025596y](https://doi.org/10.1021/nl025596y)
12. A. Eychmuller, *J. Phys. Chem. B* **104**, 6514 (2000). doi:[10.1021/jp9943676](https://doi.org/10.1021/jp9943676)
13. E.F. Foos, J. Wilkinson, A.J. Makinen et al., *Chem. Mater.* **18**, 2886 (2006). doi:[10.1021/cm052120h](https://doi.org/10.1021/cm052120h)
14. D.V. Talapin, S. Haubold, A.L. Rogach, *J. Phys. Chem. B* **105**, 2260 (2001). doi:[10.1021/jp003177o](https://doi.org/10.1021/jp003177o)
15. J. Hambrock, A. Birkner, R.A. Fischer, *J. Mater. Chem.* **11**, 3197 (2001). doi:[10.1039/b104231a](https://doi.org/10.1039/b104231a)
16. Q.Q. Dai, D.M. Li, S. Jiang et al., *J. Cryst. Growth* **292**, 14 (2006). doi:[10.1016/j.jcrysgro.2006.04.097](https://doi.org/10.1016/j.jcrysgro.2006.04.097)
17. A.J. de Mello, *Lab Chip* **4**, 11N (2004). doi:[10.1039/b403638g](https://doi.org/10.1039/b403638g)
18. A.J. de Mello, *Nature* **442**, 394 (2006). doi:[10.1038/nature05062](https://doi.org/10.1038/nature05062)
19. M. Brivio, W. Verboom, D.N. Reinhoudt, *Lab Chip* **6**, 329 (2006). doi:[10.1039/b510856j](https://doi.org/10.1039/b510856j)
20. C.-C. Lee, G. Sui, A. Elizarov et al., *Science* **310**, 1793 (2005). doi:[10.1126/science.1118919](https://doi.org/10.1126/science.1118919)
21. H.R. Sahoo, J.G. Kralj, K.F. Jensen, *Angew. Chem. Int. Ed.* **46**, 5704 (2007). doi:[10.1002/anie.200701434](https://doi.org/10.1002/anie.200701434)
22. J.B. Edel, R. Fortt, A.J. deMello, et al., *Chem. Commun. (Camb.)* 1136 (2002)
23. H. Nakamura, Y. Yamaguchi, M. Miyazaki, et al., *Chem Commun. (Camb.)* 2844 (2002). doi: [10.1039/b208992k](https://doi.org/10.1039/b208992k)
24. B.K.H. Yen, N.E. Stott, M.G. Bawendi et al., *Adv. Mater.* **15**, 1853 (2003). doi:[10.1002/adma.200305350](https://doi.org/10.1002/adma.200305350)
25. E.M. Chan, A.P. Alivisatos, R.A. Mathies, *J. Am. Chem. Soc.* **127**, 13854 (2005). doi:[10.1021/ja051381p](https://doi.org/10.1021/ja051381p)
26. B.K.H. Yen, A. Gunther, M.A. Schmidt et al., *Angew. Chem.* **117**, 5583 (2005). doi:[10.1002/ange.200500792](https://doi.org/10.1002/ange.200500792)
27. E.M. Chan, R.A. Mathies, A.P. Alivisatos, *Nano Lett.* **3**, 199 (2003). doi:[10.1021/nl0259481](https://doi.org/10.1021/nl0259481)
28. H.Z. Wang, H. Nakamura, M. Uehara et al., *Adv. Funct. Mater.* **15**, 603 (2005). doi:[10.1002/adfm.200400164](https://doi.org/10.1002/adfm.200400164)
29. S. Krishnadasan, J. Tovilla, R. Vilar, A.J. de Mello et al., *J. Mater. Chem.* **14**, 2655 (2004). doi:[10.1039/b401559b](https://doi.org/10.1039/b401559b)
30. H. Yang, W. Luan, S.-T. Tu et al., *Lab Chip* **8**, 451 (2008). doi:[10.1039/b715540a](https://doi.org/10.1039/b715540a)
31. W. Luan, H. Yang, Z.M. Wang et al., *Nanotechnology* **18**, 175603 (2007). doi:[10.1088/0957-4484/18/17/175603](https://doi.org/10.1088/0957-4484/18/17/175603)
32. M.A. Hines, P.J. Guyot-Sionnest, *J. Phys. Chem. B* **102**, 3655 (1998). doi:[10.1021/jp9810217](https://doi.org/10.1021/jp9810217)
33. D.V. Talapin, A.L. Rogach, A. Kornowski et al., *Nano Lett.* **1**, 207 (2001). doi:[10.1021/nl0155126](https://doi.org/10.1021/nl0155126)
34. K. Nose, H. Fujita, T. Omata et al., *J. Lumin.* **126**, 21 (2006). doi:[10.1016/j.jlumin.2006.04.009](https://doi.org/10.1016/j.jlumin.2006.04.009)
35. X.H. Zhong, Y.Y. Feng, Y.L. Zhang, *J. Phys. Chem. C* **111**, 526 (2007). doi:[10.1021/jp064797d](https://doi.org/10.1021/jp064797d)
36. L. Qu, X. Peng, *J. Am. Chem. Soc.* **124**, 2049 (2002). doi:[10.1021/ja017002j](https://doi.org/10.1021/ja017002j)
37. W.W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* **15**, 2854 (2003). doi:[10.1021/cm034081k](https://doi.org/10.1021/cm034081k)
38. N. Pradhan, D. Reifsnyder, R. Xie et al., *J. Am. Chem. Soc.* **129**, 9500 (2007). doi:[10.1021/ja0725089](https://doi.org/10.1021/ja0725089)
39. Y.D. Yin, A.P. Alivisatos, *Nature* **427**, 664 (2005). doi:[10.1038/nature04165](https://doi.org/10.1038/nature04165)
40. X. Peng, J. Wickham, A.P. Alivisatos, *J. Am. Chem. Soc.* **120**, 5343 (1998). doi:[10.1021/ja9805425](https://doi.org/10.1021/ja9805425)