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High-Temperature Synthesis of CdSe Nanocrystals in a Serpentine Microchannel: Wide Size Tunability Achieved under a Short Residence Time

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ABSTRACT: A three-dimensional serpentine microchannel was applied in the reaction part of a microreactor for the synthesis of CdSe nanocrystals (NCs). The local fluctuation of velocity in the turns created by the continuous variation of channel geometry was demonstrated to be effective to maintain a uniform residence time and monomer concentration for the constrained fluid under fast flow rates. Therefore, an enhanced growth rate for NCs within a narrow size distribution was accomplished with a short residence time. The triple-ligand system (trioctylphosphine oxide−oleic acid−oleylamine) was demonstrated to be powerful to achieve high-quality CdSe NCs with a short reaction time. The superior kinetic control achieved via the variation of precursor concentration and Se/Cd ratio provided effective control of the size of CdSe NCs, which allowed the rapid synthesis (8−10 s) of CdSe NCs in a wide size range with diameters ranging from 2.1 to 4.0 nm, while maintaining excellent color purity and a high photoluminescence (PL) efficiency (PL 483−600 nm, fwhm 27−35 nm, and quantum yields 12−50%).

Introduction

Nanocrystaline semiconductors are of great interest for both fundamental research and technical applications, due to their size-dependent properties and excellent chemical processibility.[1−3] In most cases, these advantages can only be exploited in relatively monodisperse samples. Controlling the sizes of nanocrystals (NCs) is an active research field that seeks to extend the emission range while maintaining the same chemical composition.[4−6] CdSe-based NCs have become the most extensively investigated NCs among a variety of semiconductors due to the tunability of their size-dependent photoluminescence (PL) across the whole visible spectrum. High-quality products are usually obtained by the organometallic approach and its alternatives under high temperatures.[7−14] Nevertheless, based on reported reaction recipes,[6,11−14] it can be difficult to prepare CdSe quantum dots (QDs) with diameters smaller than 2.5 nm. The elongated nucleation period under a low reaction temperature usually leads to polydisperse sizes for the products, while the realization of short reaction times is challenging due to the difficulties associated with quenching the reaction in a short period by the batch method.[15−21] As a result, the published, large-scale synthesis is restrained to medium-sized CdSe NCs.[22−24]

The recently introduced microfluidic methods can produce the reaction in a controlled time period, and the priorities of these methods in precise synthetic-condition control, online sample characterization, and parallel operation were demonstrated based on the study of CdSe, CdS, and CdSe/ZnS NCs.[25−35] But these reports simply adopted the well-established chemistry obtained from bath reactors to a microfluidic flow reactor. Consequently, the enhanced growth rate in a microenvironment coupled with insufficient focus on size distribution at a short residence time precluded the obtaining of high-quality CdSe NCs. Furthermore, using variations of flow rates to achieve
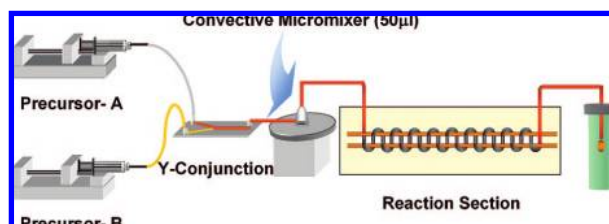
Figure 1. Set-up of the capillary microreactor with a serpentine channel in the heated section.

short residence times in a straight channel was not a trivial task, because the parabolic velocity profile can have a pronounced effect on residence time distribution. Using multiphase flow and constraining a droplet in another liquid media have been proven useful in achieving narrow residence time distributions (RTD),[32,33] but these processes usually involve complicated fabrication methods, and the product yields were low.

During our study on CdSe NCs in a noncoordinating solvent with oleic acid (OA), the Se precursor prepared by air-exposed trioctylphosphine (TOP) was found to be able to shorten the reaction time for monodisperse CdSe NCs, coupled with considerable blue-shifted absorption peaks, while the whole process showed poor reproducibility. Dai et al. sought to resolve this problem by adding trioctylphosphine oxide (TOPO) into the reaction solvent to simulate the impurities in the air-exposed TOP.[36] However, the small NCs that formed exhibited significant trap emission in the PL spectra, and low PL quantum yields (QY) of less than 5% were observed. Furthermore, the reported recipe did not work well for large-sized CdSe NCs. Primary amines have shown the impressive ability of achieving high PL efficiencies for a variety of semiconductor NCs due to their high surface-bonding ability, and the adsorption of an alkylamine as a strong hole acceptor results in remarkable blue-shift and narrowing of the band gap absorption peak of small CdSe NCs, as was observed by Landes et al.[37]

In this study, a 3-D serpentine microchannel was applied to achieve narrow RTD and high mixing efficiency under fast flow

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rates, and a triple-ligand system (TOPO−OA−oleylamine) was designed to improve the stability of small CdSe NCs during the early reaction stage. The tailored kinetic control achieved by varying precursor concentrations and precursor feed ratios of Se to Cd allows the preparation of high-quality CdSe NCs in a wide size range, at short residence times. The high quality of the resulting CdSe NCs was confirmed by PL spectroscopy, powder X-ray diffraction (P-XRD), and high-resolution transmission electron microscopy (HRTEM).

Experimental Procedures

Chemicals. TOP (90%, Fluka), TOPO (98%, Fluka), CdO (99.9%, SCR), OA (90%, SCR), 1-octadecene (ODE, 90%, Fisher), oleylamine (OLA 70%, Fluka), analytical grade methanol (SCR), and chloroform (SCR) were used as received.

Set-up of the Capillary Microreactor. The setup of the microfluidic system is shown in Figure 1. Rapid mixing of the precursors was achieved by a convective mixer comprised of a magnetic bar and a miniature polytetrafluoro-ethylene (PTFE) chamber (50 μL). A 3-dimensional (D) serpentine microchannel was constructed by interlacing a PTFE capillary (300 μm I.D.) along two parallel metal bars (700 μm O.D.), while nucleation and growth of CdSe NCs were triggered by the heating provided by a thermally stable oil bath.

Synthesis of CdSe NCs. Independent processes were applied to prepare the precursors for different-sized CdSe NCs. A dilute Cd precursor solution was required to prepare small-sized NCs, in which CdO (6.42 mg, 0.05 mmol) was mixed with 0.2 mmol of OA, 0.5 g of TOPO, and 1 mL of OLA. The mixture was heated at 150 °C for 1.5 h to form a clear Cd precursor solution, and then further diluted with ODE to 3 mL. A Se stock solution was prepared by dissolving Se shot (0.5 mmol) in 1 mL of TOP and OLA to form a 3 mL solution. The as-prepared stock solutions were loaded into two syringes with various flow rates controlled by two separate syringe pumps (Harvard 22, USA). Before reaching the heated section, both flows were combined in a Y-conjunction and then mixed by turbulent flow. The homogeneously mixed precursors were heated in a thermally stable oil bath with the serpentine channel, and the formed CdSe NCs that flowed from the outlet were collected and diluted by chloroform for absorption and PL measurements.

For large-sized CdSe NCs, the Cd precursor solution was prepared by heating a suspension of CdO (64.25 mg, 0.5 mmol) in OA (0.80 mL), OLA (1 mL), TOPO (0.60 g), and ODE (3 mL in total). The influence of TOPO was tested by performing the same reaction while substituting various amounts of TOPO with ODE. In each evaluation, the volume of the Cd precursor was kept as 1 mL, while maintaining the same concentrations of CdO (21.42 mg), OA (0.27 mL), and OLA (0.33 mL). The influence of the addition of TOPO on reaction control was demonstrated by collecting the kinetic data from absorption spectra.[38]

Characterization. Absorption 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 with the organic dye (Rhodamine 6G and Rhodamine B). [11]

HRTEM images were taken on a JEM-2100F operated at 200 kV, and the sample was prepared by dipping an amorphous carbon−copper grid in a dilute solution of NCs dispersed in chloroform. P-XRD measurements were performed on a Rigaku D/max2550 operating with Cu Kα (λ = 0.154056 nm), with samples deposited as a thin layer on a Si wafer.

Results and Discussion

The microfluidic flow reactor offers a direct way to change reaction time by varying flow rates, but this simple operation causes some problems. For single-phase, laminar flow in a straight microchannel, the shear force imparted by the channel walls will induce a parabolic velocity profile over the cross section, which yields an RTD for the liquid flowing through the channel. Meanwhile, for the fluid in a channel that involved reaction, the discrete flow rates over the channel cross section
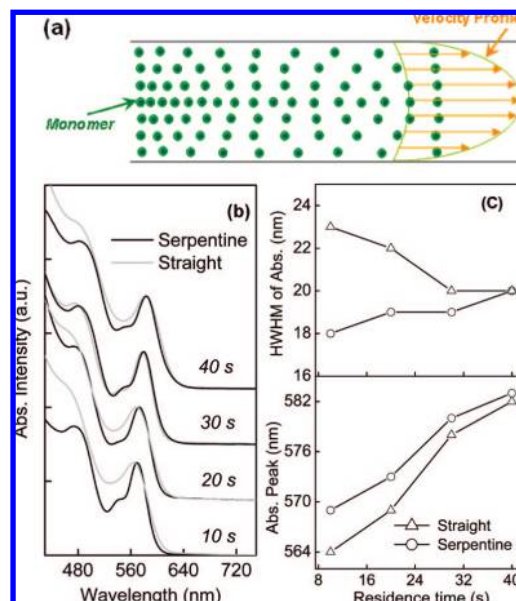
Figure 2. (a) Residence time distribution (RTD) and concentration gradient (CG) effects of a laminar flow in a straight microchannel; (b) absorption spectra of CdSe NCs prepared in serpentine and straight channels; (c) abs. half-width-at-half-maximum (HWHM) and abs. peak location of CdSe NCs prepared in serpentine and straight channels. For all the experiments, concentrated precursor solutions were used, maintaining the same channel length at 35 cm (Cd/Se = 1, T = 285 °C).

also imply different precursor consumptions between the wall and the center of the channel. If the diffusion rate of the precursor is not comparable to the reaction rate, the RTD can also induce a concentration gradient (CG) over the cross section of a channel, as shown in Figure 2a. For the reactions involved in the synthesis of solid particles, the implications of the RTD and CG are reflected in the size distribution of the final products. Furthermore, numerical simulation and experiments confirmed that the improved flow rate would result in wide RTD.[27] The serpentine channel has been proven to be useful for improving the mixing efficiency at the micro scale, and the local fluctuations of velocity can be achieved by the recirculation around the turns, mainly due to the continuously "stretching" and "refolding" of solute volumes induced by the variation in channel geometries.[39] Theoretically, the periodic fluctuations can avoid the dead volume near the channel wall and achieve narrow RTD in general. Inspired by this, a 3-D serpentine channel was utilized in the heating section of a capillary microreactor to ameliorate the RTD and improve the mixing efficiency in situ.

Figure 2b compares the absorption spectra for CdSe NCs prepared both in straight and serpentine channels. The resulting spectra of the NCs prepared in serpentine channels indicate narrow size distributions and are similar to the best results obtained by the batch process.[22−24] The sharp band-edge absorbance and several high transitions are clearly resolved, while wide absorption peaks are generally observed for the samples prepared using a straight channel. The more-pronounced behavior observed at short times results from the fact that the RTD broadens significantly with flow rate for single-phase flow in a straight channel,[27] whereas the RTD was meliorated by the second flow created by the periodic variation of channel geometry for the serpentine channel in the fast flow rate case. Figure 2b reveals an additional reason for the large improvement in size distribution at shorter reaction times. In a 3-D serpentine
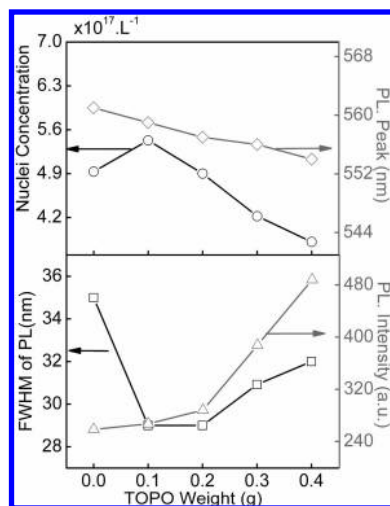
Figure 3. Influence of TOPO weight on the nuclei concentration and PL properties of CdSe NCs (residence time is 10 s, Cd/Se ratio is 0.5, and reaction temperature is 285 °C).


Figure 4. (a) Absorption spectra; (b) PL property for CdSe NCs prepared at various temperatures while maintaining a constant residence time of 10 s; (c) absorption spectra; and (d) PL property of CdSe NCs prepared at different residence times (with a constant reaction temperature of 260 °C).

channel, the mixing time scale is governed by both diffusion and chaotic advection, and the latter process can be promoted considerably by fast flow rates.[39] Therefore, a shorter reaction time (i.e., a faster flow rate) is compensated by more intense mixing. The inverse relationship between mixing efficiency and reaction time is manifested in the absorption peak curves shown in Figure 2c. The increased growth rate causes the red-shifted absorption peak (corresponding to large NC sizes) and drives the NCs' distribution to focus more quickly than in the straight channel. As a result, the difference in the two curves in Figure 2c is more pronounced at short times. At low flow rates, the local velocity fluctuations in the turn is suppressed, but the reaction time is longer, and thus the abs. peak curve converges with that for a straight channel.

TOPO is an important ingredient for the synthesis of small-sized CdSe NCs, even though its total elimination has been demonstrated in the preparation of CdS, InP, and InAs NCs.[8,40] Figure 3 exhibits the influence of the amount of TOPO on the nuclei concentrations as well as PL properties for CdSe NCs. The addition of a small amount of TOPO in the Cd precursor solution can result in significant improvement of both size distribution and PL efficiency for the obtained CdSe NCs, without sacrificing the nucleation yield. The improved PL efficiency resulted from TOPO-induced passivation for highly reactive Se sites on the surface of the NCs.[41] However, a large excess of TOPO leads to decreased concentration of nuclei, implying reduced monomer reactivity in this situation. Furthermore, amounts of TOPO in excess of 0.2 g deteriorate the size distribution, as indicated by the continuously widened fwhm of PL. The sizes of the NCs seem inertial to the variation of TOPO concentration, and only a 7 nm blue shift of the PL peak was observed for CdSe NCs prepared with 0.4 g of TOPO. Previous experiments in our laboratory indicated that the ligand-system involving TOPO did not work well for large-grained CdSe NCs because of the adsorption of Cd monomer on reactive Se sites can be hindered by TOPO. Indeed, monodisperse, red-luminescent CdSe NCs have been synthesized with oleic acid and oleylamine as dual ligands.[22] On the contrary, TOPO is indispensable for the synthesis of small CdSe NCs, because TOPO can effectively suppress the shrinkage of small particles by specifically binding high-energy Se vacancies that would otherwise be particularly vulnerable to solvent attack.[41]
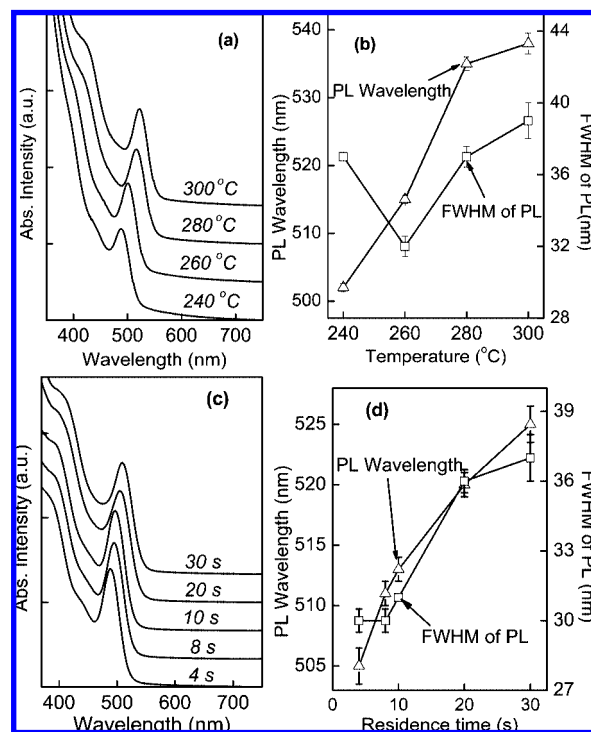
OLA has been proven to be a favorable ligand for the synthesis of CdSe NCs via microreaction,[27,32,33] since its low melting point, strong packing density, low reactivity in air facilitate the synthesis of high-quality NCs.[42] Furthermore, the improved monomer reactivity that resulted from the amine-Cd complex was observed in our former research. The reaction recipe demonstrated herein favors the preparation of small-sized CdSe NCs with diameters less than 2.6 nm. The presence of OLA is important to achieve high PL QY of the NCs as prepared, and the reaction temperature needed to form the high-quality CdSe NCs is significantly lower. Meanwhile, a small, blue-shifted absorption peak and high particle concentrations induced by the addition of OLA were observed. During the synthesis of small-sized CdSe NCs, the high molar ratio of Se to Cd is indispensable, and the concentration of oleic acid should be considerably low (with the molar ratio varying between 2 and 4). In this way, extensive nucleation can be achieved, and the slow growth of TOPO-stabilized CdSe NCs was achieved by diluting the precursor solution with noncoordinating solvent (ODE). On the basis of the microfluidic reactor, some reaction parameters, such as residence time and temperature, were investigated. For the optimization of each parameter, three independent experiments were conducted, and the standard deviations of the obtained data were set as error bars, as shown in Figure 4.

Choosing an appropriate temperature range is one of the key steps in the synthesis of colloidal NCs, because low temperatures cannot overcome the energy barrier to form the reactive monomer species required for nucleation and growth, while too high a temperature may result in uncontrolled growth. Changing the temperature provided easy control of the PL range. With an increase of temperature from 240 to 300 °C, a 36-nm shift in the PL peak was observed. The dependence of size distribu-
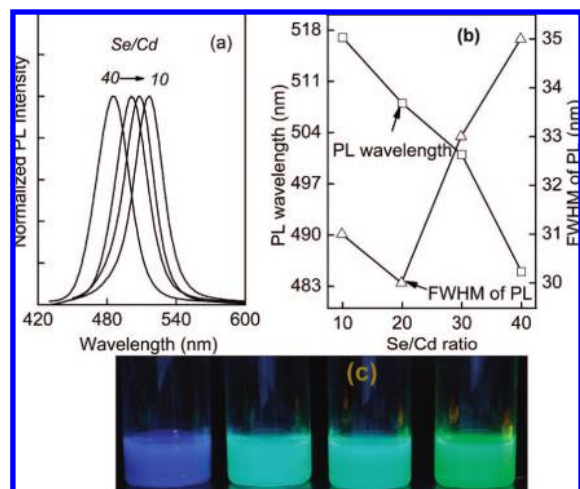
Figure 5. (a) PL spectra; (b) obtained result; (c) photo demonstration for size series of small CdSe NCs prepared with Se/Cd molar ratios ranging from 10 to 40 (with a residence time of 8 s and a reaction temperature of 260 °C).

Figure 6. (a) Absorption spectra, (b) PL spectra, and (c) obtained result for size series of CdSe NCs prepared with concentrated precursor solution for Cd/Se molar ratios from 0.1 to 3 (at a residence time of 10 s and a reaction temperature of 285 °C).

tion on temperature was not monotonic, and the crossover temperature was 260 °C, as confirmed by the sharpness of the first absorption (Figure 4a) and PL observation (Figure 4b). At temperatures below 260 °C, the whole reaction stage was characterized by mixed nucleation and growth, which resulted in a wide fwhm of PL and improved reactivity of the intermediate complexes (also called monomers). CdSe NCs prepared at 260 °C exhibited the narrowest fwhm, which was 32 nm (Figure 4b). However, further increases of temperature over 260 °C led to defocused size distribution, and the Ostwald ripening, which was promoted at the higher reaction temperatures, was provided as a justification.[34,35,43] Below 285 °C, the whole synthesis exhibited good reproducibility, but when the temperature was increased to 300 °C, some instability was observed, mainly due to the gas induced by the impurities in the solvent.

On the evaluation of residence time, the length of the capillary in the heating section was changed continuously from 14 to 105 cm to achieve residence times from 4 to 30 s, while maintaining the same flow rate (8.92 mL/h) of the precursor solutions. In this way, the influence of flow rate on the mixing process was eliminated. Changing the residence time from 4 to 30 s resulted in a 20 nm shift of the absorption peak (Figure 4c), and the turning point of fwhm was observed at 8 s. The elongated time over this threshold resulted in a continuously widened fwhm of the PL, as can be observed clearly in Figure 4d. The observed result indicated that the focus of size distribution can take place in the early reaction stage with the demonstrated triple-ligand system.

Changing the Se-to-Cd molar ratio offered a convenient mechanism for tuning the reaction conditions. A 34-nm shift of emission peak (from 483 to 517 nm) was observed as the molar ratio was varied from 10 to 40 (Figure 5a) while maintaining a narrow PL width (Figure 5b), and the resulted samples demonstrated bright emission from blue to green under a UV lamp (Figure 5c). In principle, if a large excess of the Se precursor is used, the cationic precursor should be rapidly consumed,[27,44] resulting in small-sized CdSe NCs. Meanwhile, an excessively high Se monomer concentration in the solution could improve the stability of the small NCs formed.[45] If a Se-to-Cd molar ratio less than five were utilized, only medium-sized (abs. peak >520 nm) NCs were obtained, although an extremely short residence time was utilized. Here, the superiority
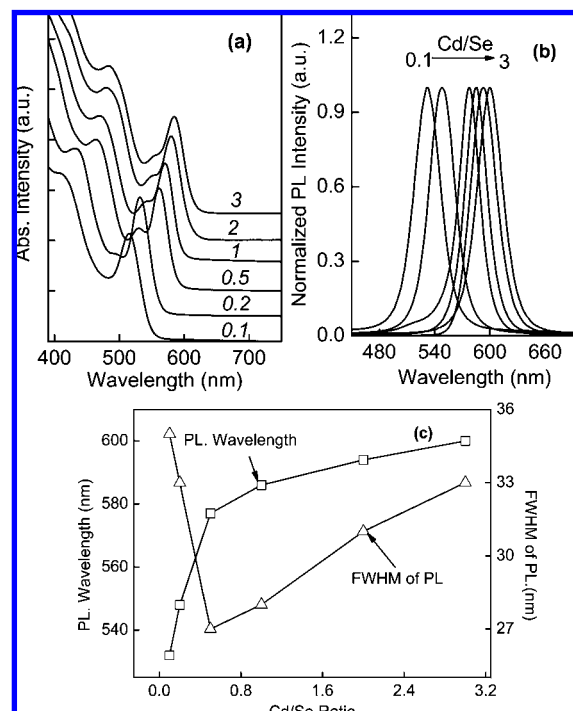
of microreaction technology for screening through the reaction parameters was demonstrated. Just by changing the feed ratio of each precursor while keeping the total flow rate constant, an arbitrary variation for the molar ratio of Se/Cd can be achieved. The strong packing density of the triple-ligand system was demonstrated by the fairly high QY of PL (12−35%) for these small CdSe NCs. Moreover, the PL spectra were free of any noticeable trap state emission even for CdSe NCs as small as 2.1 nm, as is shown by the PL spectra in Figure 5a.

An important consideration in the synthesis of CdSe NCs is the ability to vary the size of the NCs reproducibly over a large range that facilitates broad spectral tuning. With slight modifications, the ligands system presented can be readily applied to synthesize green-to-red luminescent CdSe NCs. For the synthesis of medium- and large-sized CdSe NCs, concentrated precursor solutions were used, allowing a high concentration of monomer to remain after the nucleation, which can feed the growth of CdSe NCs and maintain the focus of size distribution over a fairly long time. Figure 6 shows the spectra of CdSe NCs prepared using Cd/Se precursors with various molar ratios. Precursors with an excess of Cd favored the formation of large NCs, but PL efficiency was decreased. Changing the Cd/Se molar ratio from 0.1 to 3 provided an amazing tuning of PL over 68 nm at the short residence time of 10 s (Figure 6b,c), while maintaining fairly high QY (35−50%) for bare CdSe NCs. During our experimental limit, the clearly observed sharp band-edge absorbance and several higher transitions pointed directly to the narrow size distribution of the NCs formed (Figure 6a), and the resulting narrow fwhm of PL (27−33 nm) are rarely achieved by microreaction at a residence time as low as 10 s. The change of residence time and reaction temperature can offer additionally wide optical tunability. It was believed that the fast synthesis achieved in this research would benefit the preparation of CdSe NCs in fairly high yield. For CdSe NCs prepared with Se/Cd as 1, the NCs concentration in the as-formed solution
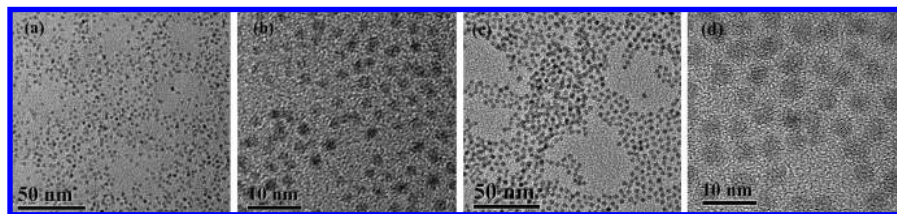
Figure 7. (a, b) TEM images of 2.2-nm-sized CdSe NCs synthesized using dilute precursor solutions; (c, d) TEM images of 4.0-nm-sized CdSe NCs prepared using concentrated precursor solutions.
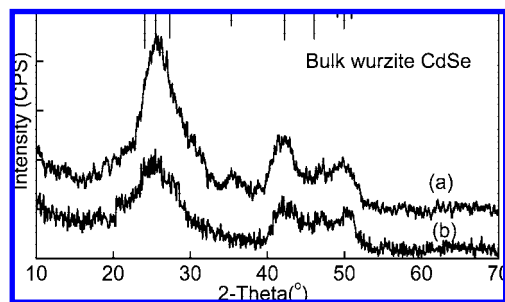
Figure 8. P-XRD patterns of (a) 2.2-nm-sized CdSe NCs prepared using dilute precursor solutions with a Se/Cd molar ratio of 30 and (b) 4-nm-sized CdSe NCs prepared using concentrated precursor solutions with a Se/Cd molar ratio of 3.

was calculated through the Lambert−Beer's law, using the extinction coefficient reported by Yu and his colleagues.[38] Here, the conversion rate of the precursors to NCs was calculated as 43%. Considering the feeding rate of precursor (1.5 mmol/h), the gram scale synthesis of CdSe NCs can be achieved in 10 h. Furthermore, it was believed that increasing the length of serpentine capillary in the oil bath coupled with the parallel operation of several capillaries could offer further increase of the yield for CdSe NCs.

The overview TEM images in Figure 7 illustrate clearly the narrow distribution and fairly spherical morphology of CdSe NCs with an average size of 2.2 nm in diameter (Figure 7a,b) and 4.0 nm in diameter (Figure 8c,d). Without any size sorting, the 2.2-nm CdSe NCs show a relative standard deviation of 10%, while a low value of 8% was obtained for 4.4-nm CdSe NCs. Furthermore, the distinguishable lattice planes shown in Figure 7d reveal the high crystallinity of the dots.

Figure 8 shows the P-XRD patterns of 2.2-nm and 4-nm CdSe NCs. As expected, the width of the diffraction peaks at wide angles is considerably broadened, and the appearance of well-resolved diffraction peaks at $2\theta = 25^o$, 42°, $46°$, and $50°$ confirmed the wurtzite structure of the formed dots.

Conclusions

A capillary microreactor using the 3-D serpentine channel was applied to achieve controlled reaction parameters, while achieving narrow RTD under a large flow rate and improving the mixing efficiency in situ. Meanwhile, a complex triple-ligand reaction system was designed to synthesize high-quality CdSe NCs with wide size tunability. The tailored kinetic control obtained via the variation of precursors concentration and precursors feed ratio of Se to Cd allows the rapid (residence times from 8−10 s) preparation of CdSe NCs with PL covering most of the visible spectrum (483−600 nm). Small CdSe NCs (PL, 483−517 nm; fwhm, 30−35 nm; and QY, 12−35%) were synthesized using dilute precursor solutions at a temperature of 260 °C and a short residence time of 8 s. Concentrated

precursor solutions, improved Cd/Se molar ratios, and elevated temperatures were applied to further extend the size range. As a result, high-quality CdSe NCs (fwhm 27−33 nm) with highly efficient PL (QY 35−50%) in the green-to-red spectra range (PL 532−600 nm) were obtained at a residence time of 10 s.

The reported approach would benefit the synthesis of high-quality QDs with increased yield. For 3.5 nm CdSe NCs (prepared using Se/Cd as 1), the gram scale synthesis was obtained in 10 h, and increasing the length of serpentine capillary in the oil bath coupling with the parallel operation of several capillaries would offer further increase of the yield.

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