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Facile Sonochemical Synthesis of Highly Luminescent ZnS−Shelled CdSe Quantum Dots

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The sonochemically driven synthesis of CdSe quantum dots (QDs) and their subsequent sonochemical ZnS shelling is described. By adapting the use of $Cd(OAc)_2$, TOPO, and hexadecylamine to an ultrasound-driven synthesis and by applying a subsequent sonochemical ZnS shelling procedure to CdSe QD cores using Zn-ethylxanthate, highly luminescent QDs with quantum yields of 50% to 60%, narrow emission spectra (fwhm ∼25 nm), and size distributions of ∼10% were obtained. Furthermore, QD synthesis via ultrasound has several attractive features, such as a straightforward process control in the absence of any outside heat source and the ability to achieve nucleation and growth at bulk temperatures notably lower than those required for thermal techniques. The approach presented herein is accessible to laboratories with limited synthetic expertise to create CdSe/ZnS QDs.

Introduction

The recent widespread interest in semiconductor quantum dots (QDs) is due largely to their distinct optical properties, including broad absorption bands, narrow, size-tunable, emission bands, and excellent photostabilities.[1] Physically, the quantum properties of QDs (a size-dependent fluorescence emission) occur if electron−hole pairs (excitons) are confined to dimensions that are smaller than the electron−hole distance (exciton diameter).[1−3] As a result of this condition, the state of free charge carriers within a nanocrystal is quantized and the spacing of the discrete energy states (emission colors) is linked to the size of the nanoparticle. The combination of small size, high photostability, and size-tunable emission properties makes quantum dots highly attractive probes for biological, biomedical, and bioanalytical imaging applications.[4−7] Among different quantum dot materials, ZnS-shelled CdSe QDs have played a particularly important role because high-quality quantum dots with narrow emission bands can be created that span the whole optical spectrum.

In their early development, syntheses of high-quality CdSe quantum dots involved heating mixtures of pyrophoric precursors such as $Cd(CH_3)_2$ and elemental Se in trioctylphosphine (TOP)/trioctylphosphine oxide (TOPO) at reaction temperatures of 250−350 °C for 24 h, followed by a size-selective precipitation step.[8,9] More recently, it has been shown that Cd-containing quantum dots can be formed from non-pyrophoric precursors such as CdO, $Cd(OAc)_2$, and $CdCO_3$.[10,11] In addition, to enhance the quantum yields and photostabilities of such quantum dots, shells of a higher band gap semiconductor material like ZnS have been added thermally to existing core materials.[12−14] More recently, the focus on QDs has been toward their biofunctionalization, thus shifting QD development from traditional chemistry laboratories exclusively to research groups with biological, biomedical, and engineering expertise. Unfortunately, such laboratories are often limited in their ability to participate actively in the development of new QD-based imaging probes because they lack the expertise in synthetic chemistry and the appropriate equipment required to generate quality core−shell QDs for further modification. For these groups, commercially available quantum dot probes typically are not a viable option due to their high price. The current study seeks to eliminate this deficiency by presenting a facile sonochemical synthesis procedure for ZnS-shelled CdSe QDs which makes quantum dots with attractive photophysical properties available at low cost to research labs with minimal synthetic expertise.

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As an alternative to thermally driven syntheses, sonochemistry has been applied successfully to a variety of chemical reactions,[15] including those that impact the fields of materials science and nanoscience. For example, sonochemical techniques have been used to prepare a wide range of materials including latex particles,[16] Fe/FeC particles,[17] Ag nanofibers,[18] and both Si[19] and Au[20] nanoparticles. Overall, while sonochemical syntheses of quantum dots and other nanomaterials have been reported,[21−25] including a CdSe synthesis using a sonoelectrochemical technique,[26] in comparison to the strategies reported herein, these procedures often result in QDs of varying morphologies or aggregated crystals with comparably poor luminescent properties, such as broad emission bands. Indeed, a recent review[27] that surveyed the latest productive routes to high-quality quantum dots did not include sonochemical methods. In the study described herein, we show that sonochemistry can indeed provide a very powerful strategy for the synthesis of high-quality CdSe−ZnS core−shell quantum dots and offers several advantages over traditional thermally driven approaches. In particular, these advantages include lower reaction temperatures and a straightforward process control, thus making quantum dot materials with quantum yields (QYs) of 50−60%, ∼25 nm fwhm emission spectra, and ∼10% size distributions accessible to an increased number of research labs.

Experimental Section

Methods. Absorbance spectra of quantum dot solutions were measured using a Lambda 19 UV/VIS/NIR Spectrometer (Perkin-Elmer). Samples were prepared by first precipitating freshly prepared quantum dots out of their coordinating solvents (3×) with a 50:50 acetone/methanol solution. The resulting precipitant was then dispersed in chloroform. Solutions were placed into quartz cuvettes and were scanned over a 400−700 nm wavelength range.

Photoluminescence spectra were recorded using a Cary Eclipse Fluorescence Spectrophotometer (Varian) and an SLM 48000 Spectrofluorometer (SLM/ISS) with all samples excited at 400 nm and emissions monitored between 450 and 800 nm. To acquire photoluminescence spectra, samples were prepared in the same fashion as described for absorbance spectra. To determine quantum yields, laser quality Rhodamine B (quantum yield: 90%) was used as a reference dye.

Transmission electron microscopy (TEM) micrographs were taken using a FEI/Phillips CM-100 TEM operated at 100 kV and a JEOL 2010F field-emission TEM operated at 150 kV. High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL 2010F field-emission TEM operated at 200 kV. TEM samples were prepared by depositing a droplet of the QD solution (as prepared for absorbance and photoluminescence studies) onto holey carbon grids (Ted Pella, Inc.). The chloroform solution was allowed to evaporate, leaving the nanocrystals on the grid.

X-ray diffraction data were obtained using a D5000 Automated Powder X-ray Diffractometer with a Cu anode and a graphite monochromator (Siemens/Bruker AXS). Prior to their examination, quantum dot samples were washed and centrifuged 6× with an acetone:methanol (50:50) mixture to remove excess coordinating solvent. The final precipitant was suspended in chloroform for deposition onto Zero Background Plates made of quartz. Thin films of evenly dispersed core and core/shell nanocrystals were cast on quartz and placed in the diffractometer and scanned from 15° to 60°. Data for each sample was acquired at 2 s/step and 50 steps/°. To improve the signal-to-noise ratio, scans were continuously repeated with data averaging for approximately 24 h.

Quantum Dot Core Synthesis. To compare directly the efficiency of the sonochemical method described herein to established thermal techniques, the approach of Peng and co-workers[10,11] was adapted to the ultrasound synthesis of TOPO-coated CdSe quantum dots using $Cd(OAc)_2$, TOPO, and stearic acid (SA), as well as $Cd(OAc)_2$, TOPO, and hexadecylamine (HDA), thus comparing different coordinating solvent conditions. HDA was chosen as a capping agent because it was reported to result in high-quality quantum dots.[28] In contrast, $Cd(OAc)_2$ + SA was used because of its rapid growth kinetics during thermal syntheses.[10] In all cases, the Cd:Se ratio was held at 1:5, and the overall Cd concentration in the coordinating solvent was 0.33 mol/kg. A typical synthesis was carried out as follows: TOP and selenium powder were placed in a sidearm test tube which was purged continuously with argon (note that nitrogen is *not* an inert atmosphere when sonication is used[14]) and the selenium powder was dissolved by sonicating for 2 min using a high-energy sonifier (Branson, Model 450) equipped with a micro-tip operated at a frequency of 20 kHz and an ultrasonic power of 9−10 W. Subsequently, $Cd(OAc)_2$, TOPO, and stearic acid (60:40 TOPO:SA) or $Cd(OAc)_2$, TOPO, and HDA (75:25 TOPO:HDA)[29] were placed in identical Ar-purged reaction vessels. These reactants were heated gently to melt the mixture, and the previously prepared Se/TOP solution was injected into the melt. At that time, sonication was initiated using a specific ultrasonic power (in the range of 9−30 W; frequency: 20 kHz) chosen so as to effect the desired reaction kinetics, and product aliquots were taken as the reaction color was observed to change from pale yellow to deep red. The aliquots were washed (3 × 5 mL) with acetone/methanol and dried under high vacuum. Before use, the product material was dispersed in dry chloroform and centrifuged to precipitate any remaining particulate matter. Typically, Tech-grade HDA and TOPO were used, but batch-to-batch variability was observed.

ZnS Shelling of Core Quantum Dots. ZnS shell formation over a CdSe core was carried out using zinc ethylxanthate synthesized via the procedure of O'Brien, et al.[30] The zinc nitrate hexahydrate and potassium ethylxanthate used in this preparation, as well as

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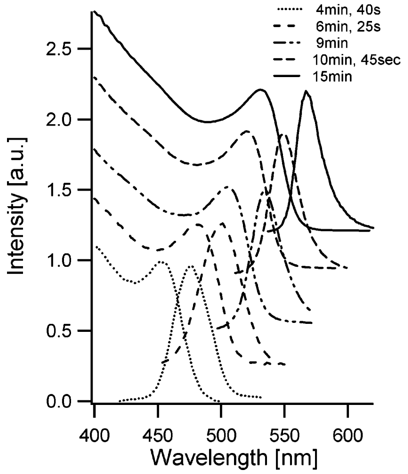

Figure 1. Absorbance and photoluminescence spectra of sonochemically synthesized CdSe QDs obtained via the HDA approach. The varying values of λ_{max} for each emission spectrum and the corresponding shift of the exciton absorbance peak in the absorbance spectra correlate to different sonication times during CdSe core synthesis.

tributylphosphine (PBu_3), were purchased from Aldrich and used without further purification. To obtain ZnS-shelled quantum dots, aliquots of freshly synthesized CdSe core material were removed (4 mL) and placed into a separate reaction vessel. Zinc ethylxanthate (0.10 g, 0.53 mmol) was then dissolved in PBu_3 (2.0 mL, 8.1 mmol) and added to the 4 mL aliquot of CdSe core solution. No purification steps were performed on the core solution prior to this addition. We have determined that small amounts of oxygen and water potentially remaining after an argon purge do not significantly affect the reaction when using our rapid, low-temperature sonochemical synthesis. The two solutions were combined at 60 °C and sonicated continuously at 9 W for 12 min, reaching a final temperature of 120 °C. Small aliquots were removed at various intervals, noting the time and temperature as sonication progressed.

Results and Discussion

CdSe Core Quantum Dots. To explore the ultrasound-driven formation of CdSe nanocrystals with size-dependent emission properties, small aliquots were removed from sonicated core synthesis reaction mixtures at various time intervals to characterize their photoluminescence and absorbance spectra. Figure 1 shows representative absorbance and photoluminescence spectra, as obtained via the HDA-based synthesis procedure, for different sonication times (photoluminescence spectra were obtained using an excitation wavelength of 400 nm). The spectra in Figure 1 show the characteristic feature of quantum dots synthesized in solution, a red shift with increasing reaction time; simple observation of the sonicated reaction mixture also revealed color changes indicative of QD growth. Unlike absorbance spectra reported for thermally synthesized CdSe QDs, which show multiple resolvable exciton absorption peaks,[11,13] those illustrated in Figure 1 reveal one; however, both, thermally and sonochemically synthesized QDs based on HDA show narrow photoluminescence spectra of comparable line widths.[11,13,31−33]

Interestingly, CdSe QDs synthesized sonochemically based on HDA vs SA show quite different photoluminescence properties (photoluminescence spectra of CdSe QDs synthesized via SA-based sonochemistry are shown in the Supporting Information). To illustrate the spectral differences

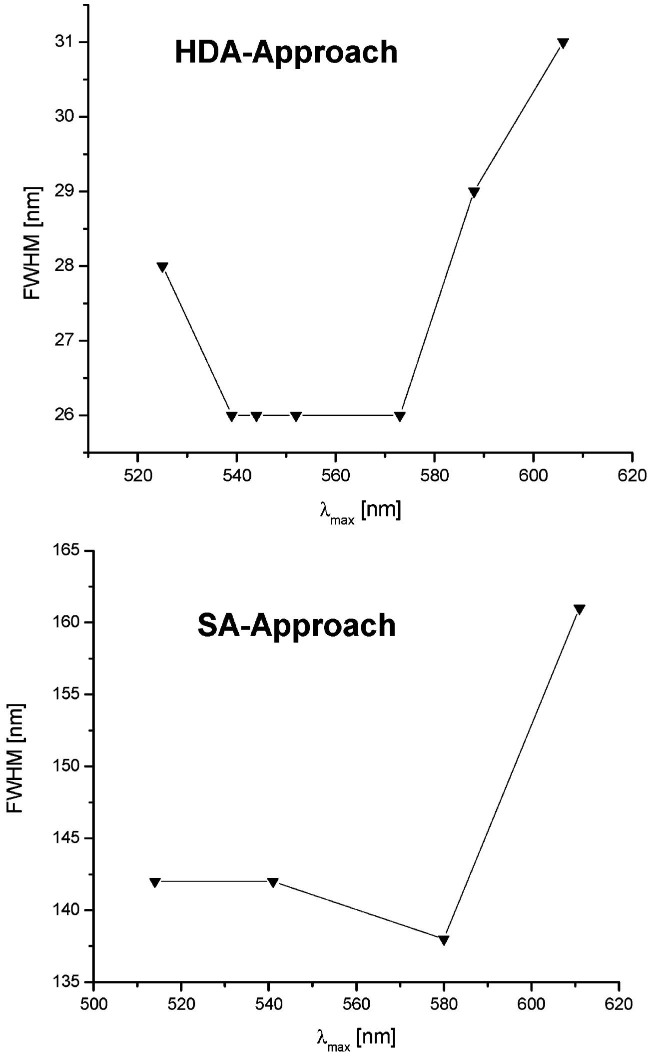

Figure 2. fwhm values of fluorescence spectra obtained during sonochemical formation of CdSe QDs using HDA and SA.

between the HDA and SA systems in more detail, Figure 2 shows fwhm values of the emission spectra for HDA- and SA-based syntheses as a function of the maximum emission wavelength, λ_{max}. With HDA as the coordinating solvent, the bandwidth initially decreases with increasing sonication time (wavelength of maximum emission, λ_{max}) until it reaches a minimum of about 25 nm. Notably, these narrow bandwidths are comparable to values reported for high-quality CdSe quantum dots synthesized using thermal procedures.[11,13,31−33] Spectra obtained from sonochemically driven reactions using SA as a coordinating solvent, on the other hand, were observed to exhibit broad emission peaks of fwhm ~ 150 nm, thus being different with respect to previously reported thermal synthesis procedures using identical reagents.[10] Obviously, identical reagents and coordinating solvents in thermal and sonochemical syntheses do not necessarily lead to identical photophysical properties.

With respect to their quantum yields, the products of sonochemical syntheses via HDA and SA show very similar

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features. In both cases, the quantum yield is very wavelength-dependent. While the HDA system shows an average quantum yield value of 9.3% and a maximum value (at 504 nm) of 32.4%, the SA-based counterpart is characterized by an average quantum yield of 11.1% and a maximum value (at 572 nm) of 35.8%. Interestingly, the maximum quantum yields determined are similar to those for the corresponding thermal synthesis approaches using the same[10] or very similar reactants and solvents,[28] though it has been shown that under carefully selected reaction conditions quantum yields of up to 85% can be achieved as well.[34]

The above results provide two important findings. First, some mixtures of reactants, which are well-established in thermal synthesis procedures, do not necessarily result in high-quality quantum dots using ultrasound. For example, CdSe quantum dots prepared by the SA procedure do not show the narrow emission peaks observed by thermal synthesis, even though the same reagents and coordinating solvents were used.[10] Second, if appropriate reagents and coordinating solvents are chosen, sonochemistry can result in CdSe quantum dots with photophysical properties similar to those of their thermally synthesized counterparts.[10,28] This indicates that ultrasound is a convenient and powerful tool for the synthesis of CdSe quantum dots with properties comparable to those obtained via thermal syntheses. Moreover, the use of ultrasound has two additional benefits, as discussed below.

One advantage of the sonochemical procedure is that the growth rate of nanocrystals can be controlled via the ultrasound intensity in a more precise manner than is possible via thermally driven syntheses. In the latter case, the growth processes often are characterized by high initial growth rates, making size control difficult. Sonochemistry is thus particularly relevant for cases where rapid growth kinetics of quantum dots occurs. For example, upon injection of the starting materials into the hot coordinating solvent, spectral shifts of 100 nm within less than 20 s have been observed.[10] Figure 3 shows $\lambda_{\max}$ vs time plots for sonochemically generated SA- and HDA-based CdSe quantum dots. The increasing values of $\lambda_{\max}$ with time indicate the growth process of quantum dots due to continuing ultrasound exposure. The plots illustrate different growth kinetics of SA- and HDA-based CdSe QDs, thus highlighting the well-known fact that different reagents and coordinating solvents often result in varying growth kinetics.[10,31] Furthermore, as illustrated for both SA-based and HDA-based QDs (Figure 3), quantum dot growth can be controlled by ultrasound power in a very straightforward way. While similar growth kinetics are observed for sonochemically and thermally synthesized quantum dots when high ultrasound intensity is used (e.g., ultrasound intensity ≥ 30 W, though the thermal method[10] under identical reactant/solvent conditions generally always results in more rapid growth kinetics), slower growth rates can be achieved via sonochemistry by simply reducing the ultrasound power. The ability to slow QD growth in a facile and controlled manner using ultrasound makes the synthesis of quantum dots of any desired size particularly attractive for reaction systems which otherwise are characterized by fast reaction kinetics.

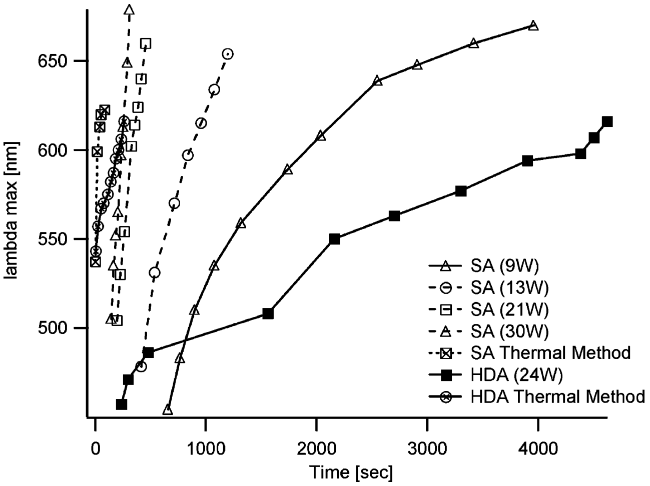

Figure 3. Growth kinetics for CdSe quantum dots obtained via HDA and SA illustrating the influence of ultrasound energy and coordinating solvent on growth kinetics. A comparison with the data obtained from the SA-based[10] and the HDA-based thermal synthesis procedures shows that sonochemistry has the potential to control the growth kinetics in a facile manner by adjusting the sonication power.

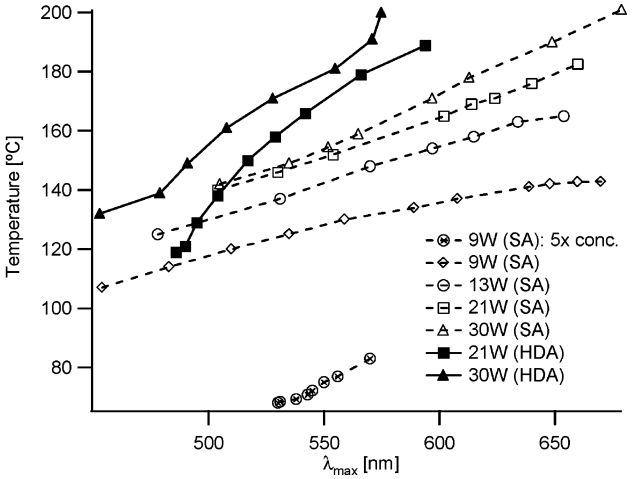

Figure 4. Temperature vs $\lambda_{\max}$ plots obtained during sonication of the reaction mixture using the SA and HDA approaches. The temperature was determined using a temperature sensor positioned in the reaction vessel during the sonication process. The increasing temperature with progressing sonication time indicates the moderate bulk heating of the sample due to ultrasound and the fact that the reaction tube is surrounded by air without connection to a heat sink. However, the temperatures detected are still notably below values necessary for the formation of CdSe QDs via thermal techniques. As shown for the case of QD formation via SA, increased concentrations of reagents lead to QD growth at notably lower temperatures, thereby reaching temperatures less than 100 °C.

Another important advantage of the sonochemical approach over thermally driven reaction procedures is that quantum dots can be formed at significantly lower reaction temperatures using ultrasound when the same reactants and solvents are used. This interesting feature of sonochemistry is illustrated in Figure 4 for SA-based CdSe quantum dot syntheses. Figure 4 shows that ultrasound intensities of 9−30 W are associated with a temperature range in the sample of 110−190 °C, with products thereby covering a spectral range of $\lambda_{\max} \sim 450-680$ nm. Similarly, HDA-based CdSe quantum dots were synthesized over a spectral range of $\lambda_{\max} \sim 450-620$ nm using a temperature range of 110−190 °C and ultrasound intensities of 21 and 30 W. In contrast, the

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corresponding thermally driven synthesis approaches were shown to provide best results if temperatures of 300−360 °C (SA-based CdSe QDs)[10] and 250−310 °C (HDA-based CdSe QDs), respectively, were used.[28] Our experimental results also indicate that quantum dot growth occurs at notably lower temperatures (for a given λ_{max}) if the concentration of reactants is increased. For example, we were able to synthesize CdSe quantum dots at a temperature of only 68 °C using a lowered ultrasound intensity of 9 W when the concentrations of Cd and Se were increased 5-fold (Figure 4). Importantly, the ability to conduct CdSe quantum dot syntheses at reduced temperature *provides an opportunity to include temperature-sensitive reagents in a one pot synthesis* where moderate reaction conditions are needed. However, it should be stated that sonochemical syntheses below 100 °C, as described in this study, result in a notable broadening of the photoluminescence spectra and in reduced quantum yields. Therefore, we did not study the concentration dependence of the quantum dot synthesis in more detail.

CdSe/ZnS Core−Shell Quantum Dots. As mentioned earlier, the formation of a semiconductive shell over a quantum dot core structure greatly enhances the photophysical properties of the QD. This is due, in part, to the large band gap of the shell material, which results in passivation of deep traps at the crystal surface.[12−14] Thus, one commonly used capping agent for CdSe nanocrystals is ZnS, which has a band gap of 3.68 eV at 300 K as compared to the CdSe band gap of 1.70 eV at the same temperature.[12]

Therefore, in a natural extension of our ultrasound-driven QD core synthesis, we also explored sonochemistry for the shelling of CdSe QDs. Here, we focused mostly on the shelling of CdSe QDs created via the HDA approach because these materials showed very promising properties characteristic of high-quality quantum dot imaging probes. To extend the concept of a facile synthesis, we did not want to use the pyrophoric reagents commonly used for ZnS shell synthesis, such as $Zn(CH_3)_2$. Instead, we have found that ultrasound in conjunction with zinc ethylxanthate can also accomplish the efficient ZnS shelling of CdSe quantum dot cores in a one-pot synthesis procedure. In our strategy, to prevent ZnS nucleation, the shelling process was conducted using low-intensity ultrasound (9−10 W).

Figure 5 shows fluorescence emission spectra taken as a function of sonication time during the ZnS shelling of CdSe QDs. The spectra exhibit the well-known features of a successful shelling process: a moderate red shift of the emission spectra and a pronounced increase in the emission band intensity.[35,36] Furthermore, it can be seen that the fluorescence reaches a maximum value upon a specific reaction time after which a decrease in the emission band intensity is observed. Here the maximum intensity has been attributed to a core/shell system, which has a completed ZnS shell.[13,37]

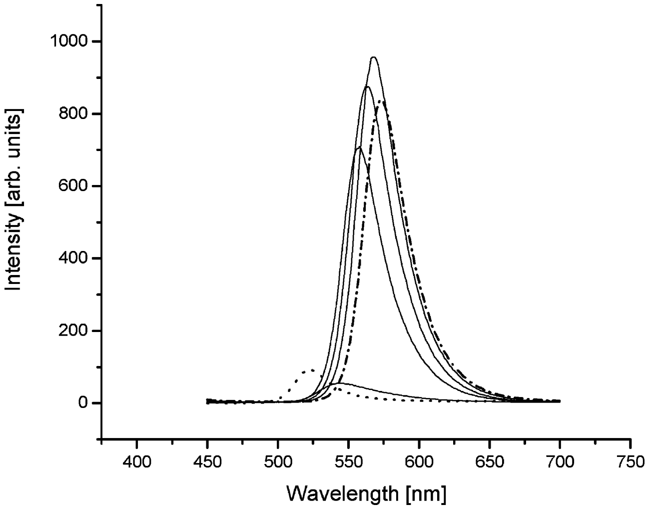

Figure 5. Photoluminescence spectra of reaction aliquots removed during sonochemical ZnS shelling. CdSe core starting material (t_0), dotted line; aliquots at $t = 7$, 9, 10, and 12 min (increasing luminescence, solid lines); and 17 min (dash−dot line).

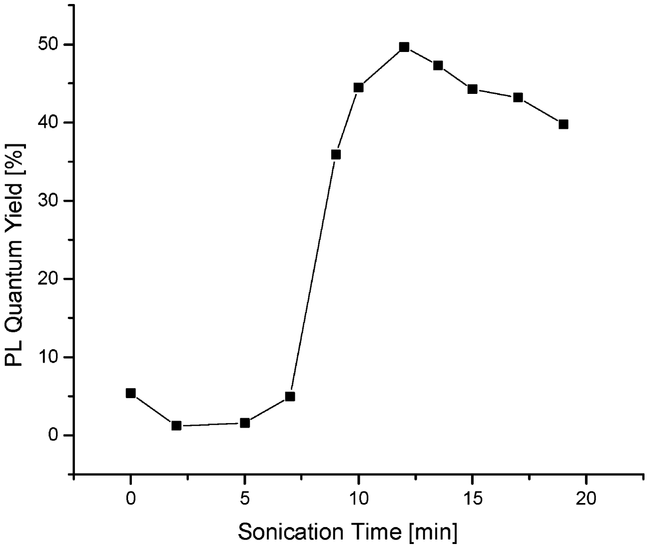

Figure 6. Plot exhibiting the relationship between quantum yield and sonication time during the ZnS shelling process. The data are based on the fluorescence spectra shown in Figure 5. The corresponding absorption spectra required for the quantum yield analysis are not shown.

Most importantly, sonochemical ZnS shelling leads to a dramatic increase in the quantum yield (QY) of the core QD, with QYs of 50−60% being achieved routinely. Figure 6 illustrates a representative plot of quantum yield versus sonication time during ZnS shelling of CdSe QDs. These data clearly support the established picture that the QY remains low (<10%) prior to the completion of a protective shell and that only after formation of a complete protecting layer is a notable increase in QY observed. As discussed above, the slightly decreased QY values that occur after longer sonication times are linked to the fact that the further

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(35) To streamline our synthesis procedure, CdSe quantum dots were not purified prior to the shelling process. The one-pot synthesis approach could provide an alternative explanation for the relatively large red shift (~40 nm) of the photoluminescence spectra that was observed after ZnS shelling because blending of the quantum dot shell could have occurred. (See comparison of absorbance and photoluminescence spectra before and after ZnS shelling, Supporting Information.) For example, an even more pronounced red shift of 47 nm was reported for a synthesis procedure that also relies on a single shelling precursor [$Zn(S_2CNMeHex)_2$ and $Zn(Se_2CNMeHex)_2$] without prior purification of the core quantum dots.[36]

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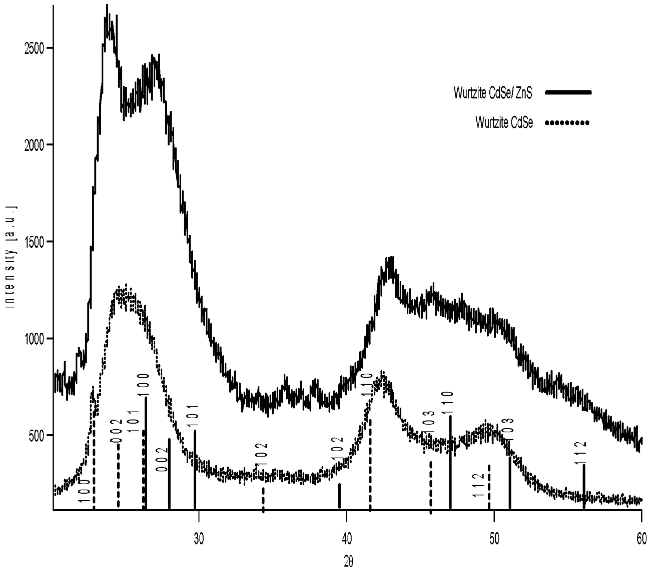

Figure 7. X-ray diffraction (XRD) pattern comparing CdSe and CdSe/ZnS quantum dots, which were synthesized using sonochemistry. The XRD data show the characteristic features reported previously for core and core/shell systems, respectively.[13] The dashed and solid lines represent the XRD powder patterns of CdSe and ZnS wurtzite structures, respectively.

increase in thickness of an already complete QD shell reduces fluorescence and quantum yield, respectively.[13,37] It should be mentioned that the QYs obtained through the ultrasound procedure are comparable to shelling procedures of CdSe cores using established thermal techniques.[37−40]

While the photoluminescence data presented in Figures 5 and 6 point to the successful sonochemical ZnS shelling of CdSe quantum dots, X-ray diffraction (XRD) patterns and TEM/HRTEM analyses that compare our CdSe and CdSe/ZnS nanocrystals more conclusively verify the presence of a ZnS shell. The XRD spectra in Figure 7 show the typical diffraction patterns reported previously for CdSe core and CdSe/ZnS core/shell systems.[13] As reported for other syntheses, the comparably broad features within XRD patterns do not exactly correspond to the calculated powder patterns of CdSe (dashed) and ZnS (solid) wurtzite structures.[13] However, by comparing the powder spectra of CdSe and CdSe/ZnS quantum dots with their calculated powder wurtzite patterns (dashed lines: CdSe; solid lines: ZnS), one can observe the influence of the ZnS shell on the overall XRD pattern (e.g., the enhanced intensities at the 110 and 112 ZnS lines). The relatively moderate changes in the XRD pattern due to ZnS shelling are not surprising because ZnS has a smaller scattering factor than CdSe.[13] In addition, Figure 8 compares TEM images of sonochemically synthesized CdSe core QDs and CdSe/ZnS core/shell systems. Here the core system is compared to a core/shell system which shows the maximum QY (compare Figure 6). The insets in each TEM image show representative HRTEM micrographs, which illustrate the high crystallinity of both types of nanocrystals obtained through sonochemistry. Figure 8 also includes size distribution histograms of CdSe and CdSe/ZnS QDs, as determined from TEM micrographs. The observed size shift between core and core/shell QDs of 1.0 nm provides direct experimental evidence for the presence of the ZnS layer. Furthermore, given that the distance between adjacent planes along the [002] axis in bulk ZnS wurtzite is 3.1 Å,[13] the observed size shift corresponds to ~1.6 ZnS monolayers. This result agrees well with earlier findings, which reported that CdSe/ZnS QDs and nanorods show their maximum QY if their shell consists of ~1.5 monolayers.[13,41]

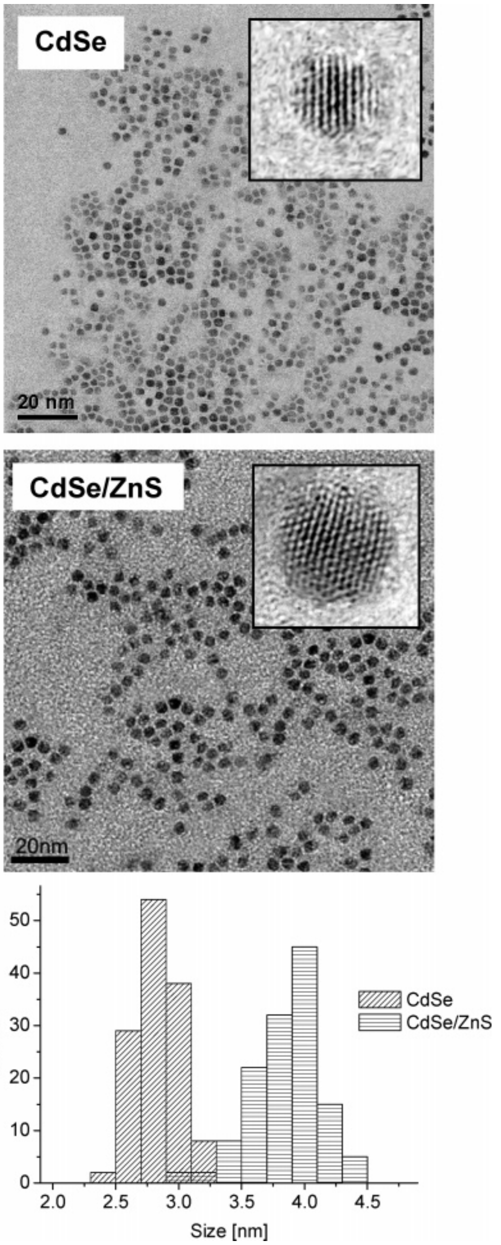

Figure 8. TEM and HRTEM (insets) of CdSe (top) and CdSe/ZnS QDs (middle) and size distribution histograms of core and core/shell systems (bottom). The observed size shift between CdSe and CdSe/ZnS QDs provides experimental evidence about the successful shelling of the core QDs using Zn-ethylxanthate. The size of the insets is 5.4 nm × 5.1 nm (W × H).

To verify that remaining excess core precursors did not lead to further core growth during the one-pot shelling process, we also studied $\lambda_{\max}$ of the photoluminescence spectra and QY over time using low-intensity ultrasound (9−10 W) without shelling precursors. Unlike in the presence

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of Zn-ethylxanthate, this control experiment showed no further red shift of λ_{max} and no change in QY (data not shown), thus indicating that the chosen ultrasound power is too low to drive further core growth and nucleation. Similarly, the photoluminescence spectra of CdSe/ZnS also show that the XRD signal related to ZnS crystal structures is not caused by ZnS quantum dots. Such ZnS nanocrystals show a notable emission in the range of 300−400 nm if excited at ∼250 nm,[42] which was not observed in the current study (data not shown). These controls provide further indirect experimental support, indicating successful ZnS shelling in the presence of Zn-ethylxanthate.

Conclusion

We have shown that CdSe quantum dots can be synthesized using high-energy ultrasound and that this technique can readily and conveniently add ZnS shells; these core/shell QDs are characterized by the following: (1) 50−60% QYs; (2) narrow emission line widths (fwhm ∼ 25 nm); (3) high crystallinities; and (4) narrow size distributions of ∼10%. The data presented here indicate that the core synthesis based on $Cd(OAc)_2$, TOPO, and hexadecylamine (HDA) and the subsequent QD shelling via zinc ethylxanthate represent a facile and inexpensive approach to the design and generation of these nanocrystals, thereby entirely relying on non-pyrophoric materials. Importantly, the procedures used are straightforward and readily accessible to researchers in a wide range of disciplines. In addition, sonochemistry also offers the opportunity to form CdSe/ZnS QDs using precisely controllable sonication conditions at relatively low reaction temperatures that, under specific conditions, can be less than 100 °C. This opens the door to the synthesis of high-quality quantum dots in the presence of temperature-sensitive reagents. Furthermore, the straightforward process control and low cost make it a viable method for the large-scale synthesis of quantum dots. Even though the findings presented here were focused on CdSe/ZnS QDs, we envision that this approach can be expanded to other materials[43] and reaction conditions. The facile sonochemical approach presented herein represents a viable alternative to existing CdSe/ZnS synthesis procedures. In particular, it could help laboratories that have biological and engineering know-how, but only limited synthetic expertise to become more actively involved in probe development and new applications involving these fascinating nanocrystals.

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Supporting Information Available: Photoluminescence spectra of sonochemically synthesized CdSe quantum dots via the SA-based synthesis approach are shown for different sonication times and absorbance and photoluminescence spectra are included which compare CdSe with CdSe/ZnS (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) We also have successfully applied the ultrasound method described to synthesize high-quality CdTe QDs.