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Water-Soluble CdS Quantum Dots Prepared from a Refluxing Single Precursor in Aqueous Solution

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The first aqueous preparation of luminescent CdS QDs from a single precursor is reported. These water-soluble CdS quantum dots with tunable sizes between 25 and 40 Å were produced from a readily prepared [(2,2'-bipyridine)Cd(SC{O}Ph)₂] complex by simply refluxing in an aqueous solution. The as-prepared nanoparticles are fairly uniform in size without the need of size sorting, and exhibit a quantum confinement effect. The size of the nanoparticles is tunable by varying the capping agent-to-precursor molar ratio. The green- and yellow-emitting quantum dots obtained via this simple route are water soluble and have OH functionality that is suitable for further applications. The particle aging kinetics was investigated by monitoring the optical band edge absorption and was found to follow the Ostwald ripening mechanism. When the amount of capping agent used is 10 mmol, unprecedented dimerization of some QDs upon prolong reflux to form nanocrystals double the size is detected. Thus, a common red shift of the absorption band edge is not detected and the growth of larger QDs seems to arise from the coalescence of two QDs.

Introduction

During the past decade, nanostructured semiconductor materials have been extensively studied due to their unique physicochemical and optical properties.^{1–5} Reliable methods which can reproducibly give a high yield of uniformly sized nanocrystals remain an active research goal in nanomaterials chemistry.^{6–12} In some cases, chemical manipulation toward both size- and shape-tunable preparation is successfully achieved.^{6–8,11}

Recently, injection of reagents into a hot coordinating solvent such as tri-*n*-octylphosphine oxide (TOPO), at high temperatures (200–400 °C), was used as an efficient route to prepare semiconductor quantum dots (QDs). For example, single precursors dithio- and diselenocarbamate complexes were injected into hot TOPO to synthesize various ME (M = Cd, Zn, Pb; E = S, Se, Te) QDs.¹² In all these reports, the crystallite size and size distribution of these TOPO-capped nanocrystals are very critically dependent on the proper control of injection and reaction temperature.¹³ The QDs obtained with this approach are only soluble in nonpolar organic solvents, unless their surfaces are further modified. This surface modification, however, often increases the effective hydrodynamic radii of the QDs. For biological^{14,15} and environmental applications,¹⁶ it is often desirable for the prepared nanocrystals to be water soluble.

In this paper, we describe a simple method to prepare monodispersed CdS QDs from a molecular precursor using water as solvent. While there have been many reports on the synthesis of CdS nanoparticles in water,^{17–25} as far as we know, this is the first report of preparing CdS QDs in aqueous solution directly from a single molecular precursor. Our approach produces water-soluble QDs in relatively high yields, and the particle size and its emitting color can be tuned easily by changing the feed ratio between capping agent and the precursor. The QDs prepared are fairly uniform in size, without the need of size-sorting such as for those carried out in some earlier reports on water-soluble preparations.^{17,19,23} To understand the

growth of QDs in our proposed aqueous method, we have investigated the growth kinetic using absorption spectroscopy.

Experimental Section

A. Chemicals. 1-Thioglycerol (98%, Fluka), thiobenzoic acid (95%, Fluka), ether, ethanol, chloroform (J. T. Baker), sodium bicarbonate (Dumont), acetonitrile, cadmium acetate (98%, Aldrich), 2-propanol (Merck), sodium hydroxide (99%, Dickson), and 2,2'-bipyridine (99%, Aldrich) were used as received.

B. Preparation of [(2,2'-bpy)Cd(SC{O}Ph)₂]. Sodium bicarbonate (0.8 g) was dissolved in 20 mL of water and 30 mL of acetonitrile. 0.7 mL of thiobenzoic acid was then added, and the solution was stirred for 5 min. Subsequently, 0.468 g of 2,2'-bipyridine (bpy) and 0.8 g of cadmium acetate were added. The mixture was stirred for 30 min and filtered. The crystals obtained were washed with ethanol, dried, and recrystallized from chloroform and ether. The compound was fully characterized by NMR, microanalysis, IR spectroscopy, and thermogravimetry. Single crystals were grown by slow diffusion of methanol into a DMSO solution of the compound. Crystal data: triclinic space group, *P*1̄; *a* = 8.6754(4) Å, *b* = 11.5986(6) Å, *c* = 11.7670(6) Å; α = 76.238(1)°, β = 75.934(1)°, γ = 84.019(1)°; *Z* = 2; *V* = 1114.1(1) Å³; ρ = 1.618 g/cm³; *R*1 = 0.0268; *wR*2 = 0.0643 for 280 parameters and 4923 data with *F*_o > 4σ(*F*_o).

C. Synthesis of CdS Nanoparticles in Aqueous Solution. 1-Thioglycerol (10 mmol) was dissolved in deionized water (25 mL) and the solution was adjusted to pH ca. 11 with 1 M sodium hydroxide. The solution was placed in a three-necked flask fitted with a septum and valve, then a certain amount of the precursor [(2,2'-bpy)Cd(SC{O}Ph)₂] was added into this solution. Subsequently, the solution was deaerated with N₂ bubbling and refluxed at ca. 100 °C for 15–30 min. The solution turned from turbidity to clear, and from colorless to pale yellow, indicating the decomposition of precursor and the generation of CdS nanoparticles. Three batches of CdS nanoparticles were synthesized with 0.25, 2.5, and 10 mmol of thioglycerol, respectively.

For kinetic studies, aliquots were taken from the refluxing mixture at different time intervals and UV/vis spectra were recorded immediately. Alternatively, the nanoparticles can be

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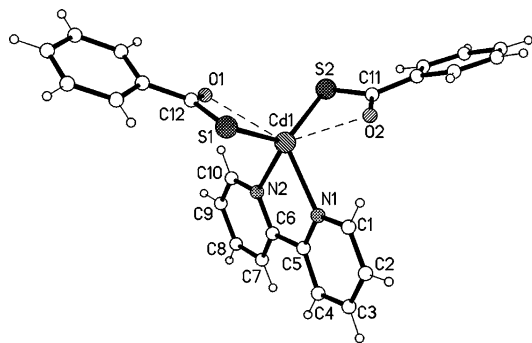


Figure 1. Structure of the precursor. Selected bond distances (Å) and angles (deg): Cd(1)–S(1), 2.476(1); Cd(1)–S(2), 2.502(1); Cd(1)–N(1), 2.331(2); Cd(1)–N(2), 2.339(2); Cd(1)··O(1), 2.780(2); Cd(1)··O(2), 2.631(2); S(1)–Cd(1)–S(2), 129.93(2); N(1)–Cd(1)–N(2), 70.45(7).

isolated by first precipitation with the addition of 2-propanol, followed by centrifugation and washing with ethanol and acetone. The vacuum-dried yellow to pale yellow powder can be used for XRD and TEM measurements or redissolved in water for other studies.

D. Characterization. Thermogravimetric analysis (TGA) was recorded on a SDT 2960 Simultaneous DTA-TGA. Approximately 10 mg of the precursor was measured under a flow of inert N₂ gas (flow rate 90 mL/min) at a heating rate of 10 deg/min. IR spectra were recorded with an FTS 165 Bio-Rad FTIR spectrophotometer in the range 4000–400 cm^{−1} on KBr pellets or Nujol mulls. UV–vis absorption spectra were obtained with a Shimadzu UV-2550 spectrophotometer. Photoluminescence (PL) spectra were collected with a Perkin-Elmer LS55 luminescence spectrometer, using a pulsed Xe lamp. Powder X-ray diffraction (XRD) patterns of the nanoparticles were recorded on a Siemens D5005 X-ray powder diffractometer with Cu Kα radiation (40 kV, 40 mA). The powdered sample was mounted on a sample holder and scanned with a step size of 2θ = 0.01° in the range 20–60°. Transmission electron micrographs (TEM) were obtained with a 300 kV Philips TEM microscope. The samples were prepared by placing a drop of the nanoparticles dispersed in acetone on a copper grid with carbon film and were allowed to dry in desiccators.

Result and Discussion

A. Formation of CdS Nanoparticles from the Precursor.

The precursor [(2,2'-bpy)Cd(SC(O)Ph)₂] we used is an air-stable crystalline complex, of which the molecular structure has been determined by X-ray crystallography as illustrated in Figure 1. In this mononuclear compound, the Cd atom is in a highly distorted tetrahedral geometry if weak interactions between Cd and the carbonyl oxygen atoms are neglected.

TGA of the precursor in a nitrogen environment showed weight loss in the region 200–240 °C corresponding to the formation of CdS. Hence, in solvents such as TOP and TOPO, the compound was found to decompose to CdS when the temperature is raised above 200 °C. In the aqueous preparation reported here, nevertheless, the precursor readily decomposed in water by refluxing at 100 °C in the presence of a base and 1-thioglycerol. Bases were normally added in the preparation of thiol-capped nanoparticles to facilitate the –S– capping.^{17–19,23} We have found that the precursor did not decompose without the base, even after refluxing for a long period in aqueous 1-thioglycerol solution. Thus the basic condition has facilitated the breaking down of the precursor, possibly via an initial attack of the base onto the carbonyl carbon, which thus weakens the C–S bond.

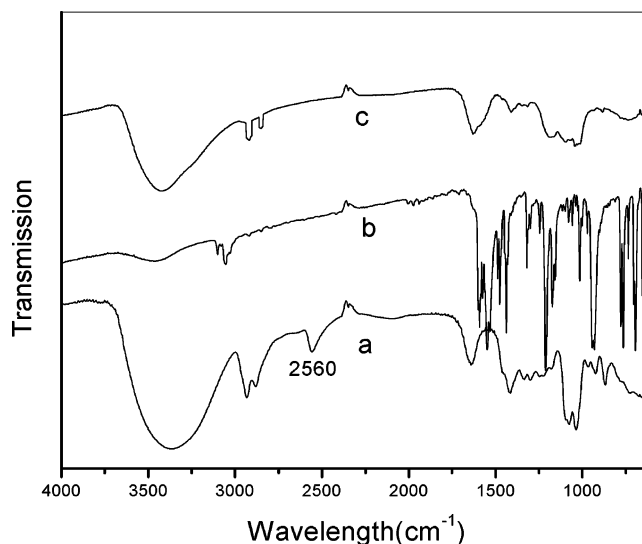


Figure 2. FTIR transmission spectra of (a) thioglycerol, (b) the precursor, and (c) a typical CdS QDs sample.

When the precursor is decomposed into CdS and other fragments in the basic refluxing solution, the surrounding 1-thioglycerol capping molecules readily chemisorbed onto the growing particles and impeded further growth. The amount of capping agent present in the reaction mixture was found to directly control the size of QDs produced (*vide infra*). While thiol groups are commonly used as capping agents, most of the other colloidal or sol–gel preparations in aqueous solutions produce nanoparticles with wide size distributions or low product yields. The yield of our preparation is about 60–70%. The prepared QDs are fairly monodispersed, and the results shown in this paper were obtained directly without any size-selective precipitation.

Figure 2 compares the IR spectra of 1-thioglycerol and the precursor with an as-prepared CdS QDs sample. 1-Thioglycerol (Figure 2a) has characteristic peaks at ~2560 and 3400 cm^{−1}, which are assigned to the SH and OH stretching vibrations, respectively. The precursor (Figure 2b) has many vibration bands in the range of 1500–1000 cm^{−1}, mainly arising from the stretching and bending modes of the bipyridyl group. The IR spectrum of the as-prepared QDs in Figure 2c showed major bands due to 1-thioglycerol, except for the SH stretching band at ~2360 cm^{−1}. While the bipyridyl group was reported to also act as a coordinating capping group,^{12a} our IR analysis did not indicate any sign of the bipyridyl group. The disappearance of the –SH vibration of 1-thioglycerol clearly indicates that this reagent is chemisorbed onto the QDs, and that the OH functional groups remain intact on the particles. The QDs are thus hydrophilic and water soluble, and the OH functionalities are available on the surface for further chemical modification or attachment.

B. Morphology and Characterization of the QDs. High-resolution TEM (HRTEM) images as shown in Figure 3 suggest that spherical particles are obtained and the average sizes of the QDs depend on the amount of capping agent used in the preparation. Generally, a higher amount of capping agent produces smaller QDs. From the HRTEM analysis, the size distribution of our QDs is estimated as ca. ±10%. This is comparable to earlier reports on the preparation of CdS QDs in aqueous solution after size-sorting precipitation.^{17,22–23} Clear crystalline lattices of the QDs are observed in Figure 3d, showing the 3.3 Å separated (111) planes extending over ~30 Å. The side fringes are less prominent indicating incomplete crystallization at the edges.

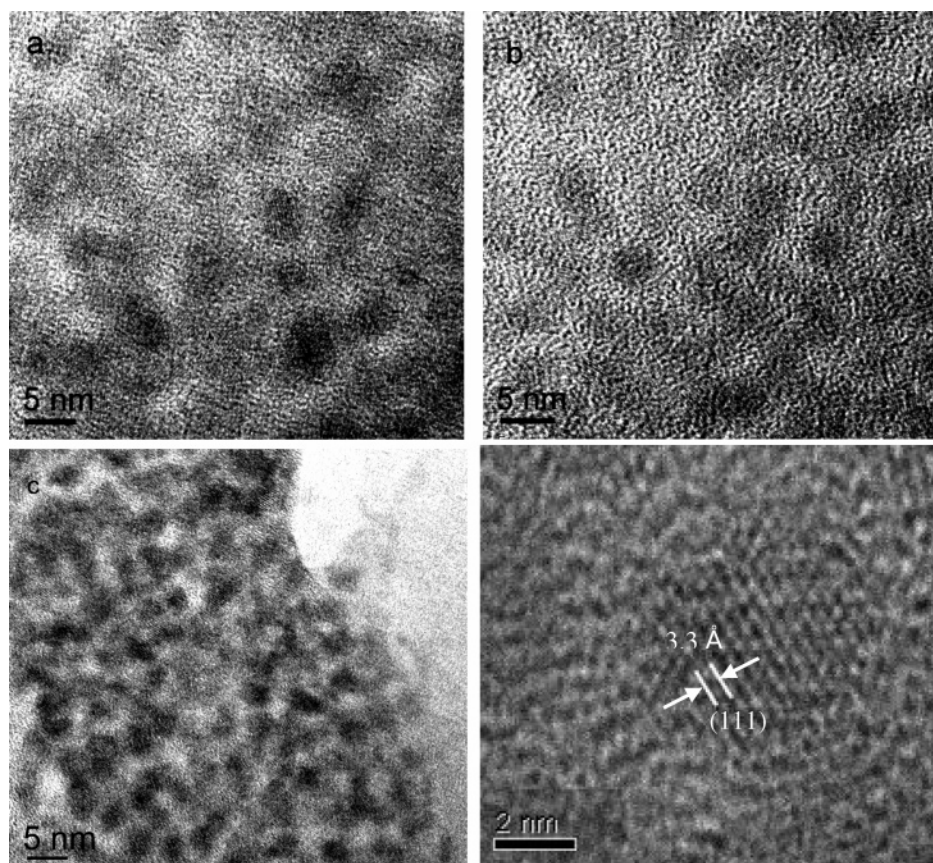


Figure 3. HRTEM images of various CdS QDs prepared by refluxing the precursor for 15 min, using various amounts of 1-thioglycerol: (a) 0.25 mmol, average particle size = 37 Å; (b) 2.5 mmol, average particles size = 30 Å; and (c) 10 mmol, average particle size = 26 Å. (d) Higher magnification image showing a single CdS nanocrystal with (111) lattices.

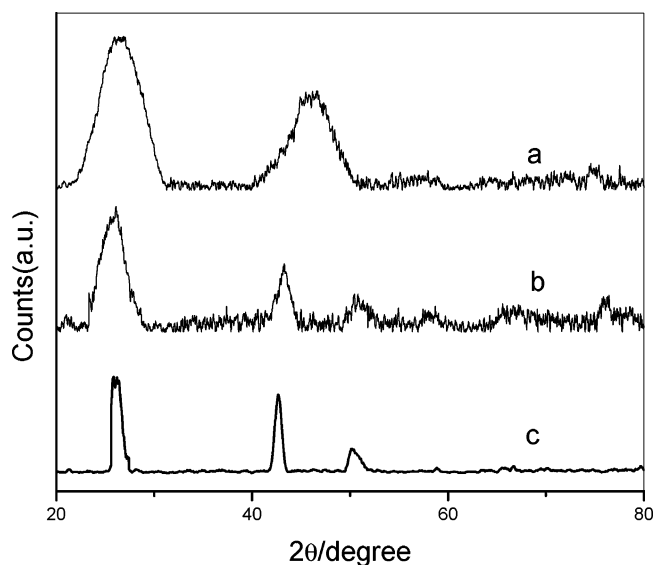


Figure 4. XRD patterns for CdS QDs prepared by refluxing the precursor for 15 min, using various amounts of 1-thioglycerol: (a) 10, (b) 2.5, and (c) 0.25 mmol.

The wide-angle XRD patterns for the different QDs prepared are shown in Figure 4. Diffraction peaks at $2\theta = 26.2^\circ$, 43.3° , and 51.2° are clearly observed for samples b and c, and can be readily assigned to the (111), (220), and (311) planes of bulk cubic CdS. This is often the observed phase of CdS prepared with thiols as the capping group.^{23,26,27} For the smallest QDs shown in Figure 4a, diffraction peaks between 40° and 50° seem to have merged into a broad peak. This is similarly observed in other reports for very small CdS QDs, and it is often difficult

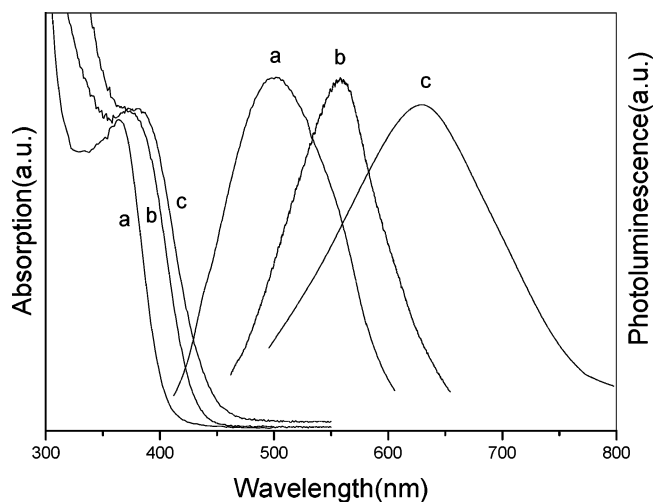


Figure 5. Optical absorption and PL spectra of CdS QDs prepared by refluxing the precursor for 15 min, using various amounts of 1-thioglycerol: (a) 10, (b) 2.5, and (c) 0.25 mmol. Excitation wavelength for the PL spectra is 380 nm.

to ascertain whether it is a pure cubic or a mixture of cubic and hexagonal phases.^{17,23} Applying the Debye–Scherrer formula²⁸ using the width of (111) peaks, we estimated the average sizes of the QDs as 17, 23, and 31 Å for samples a, b, and c, respectively. These values follow the same trend, but are consistently smaller than those obtained from TEM analysis. This could be due to incomplete crystallization of our QDs at the edges and surfaces.

In Figure 5, the optical absorption and photoluminescence (PL) spectra of the various QDs prepared are presented. The

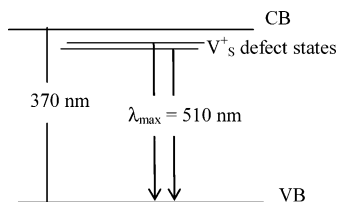


Figure 6. Schematic energy transfer diagram for the PL emission of sample a.

sharp absorption edges and the well-defined excitonic features exhibited confirm the narrow distribution of particle sizes. The absorption onsets are dependent on the average sizes: 370 (sample a), 410 (sample b), and 425 nm (sample c), which correspond to band gaps of 3.35, 3.02, and 2.92 eV, respectively. These onsets clearly show a blue-shift relative to that of bulk CdS at 515 nm (2.42 eV) due to the quantum size confinement effect.

As shown in Figure 5, the PL emission maximum is also red-shifting with increasing particle size; the λ_{\max} is respectively 510 (sample a), 560 (sample b), and 630 nm (sample c). It is noted that all these samples emit at similar intensity, but the emission peak width of sample c is relatively broader. A broad emission in the 500–700-nm region is often detected for CdS nanocrystals, and has been attributed to recombination of trapped electrons/holes in some surface defect states.^{29–33} For example, $S_{(s)}^-$ trap states, which were located at about 1.5 eV above the valence band, may be formed when photogenerated holes migrate to the surface of CdS clusters.³² V_s^+ defect states, on the other hand, are formed by electrons trapped in anionic vacancies and located about 0.7 eV below the conduction band of CdS.³³ In our samples, the emission λ_{\max} are red-shifted by about 0.8–1.0 eV from their respective excitonic absorption edges. One would thus expect the emission to arise from energy transfer within the forbidden band gap as shown schematically in Figure 6. It is commonly known that an improvement in crystallinity is beneficial to luminescence.³⁴ Since our TEM and XRD results have indicated incomplete crystallization of the QDs, lattice defects are expected and the emission peaks are broadened. Indeed we believe that in sample c, which was prepared by using the least amount of capping agent, substitutional defects may also be present and thus give rise to an overall broader band.³⁵

The effective mass approximation is commonly used to estimate particle size from absorption onset of semiconductor QDs.^{36–38} In the strong-confinement regime, the confinement energy of the first excited electronic state can be approximated by the Brus equation:

$$E = E_g^{\text{bulk}} + \frac{h^2}{8r^2} \left(\frac{1}{m_0 m_e^*} + \frac{1}{m_0 m_h^*} \right) - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 r}$$

Here, E is the absorption onset inferred from the UV spectra; E_g^{bulk} is the bulk band gap; h is Planck's constant; r is the particle radius; m_e^* and m_h^* are the effective mass of electrons and holes respectively; m_0 and e are the mass and charge of a free electron, respectively; ϵ_0 is the permittivity of free space; and ϵ is the relative permittivity. In this case, the particle size of CdS QDs can be calculated by taking $E_g^{\text{bulk}} = 2.42$ eV, $\epsilon = 5.7$, $m_e^* = 0.19$ and $m_h^* = 0.80$.³⁶ Thus, our prepared particle diameters are calculated as 28, 33, and 35 Å, for sample a, b, and c, respectively. These values are thus consistent with those obtained from TEM analysis.

C. Growth Kinetics of CdS QDs. While many reports focused on the synthesis and characterization of QDs, relatively few studies have reported on their growth kinetics. Searson et

al. studied the growth of ZnO nanoparticles in colloidal suspensions and found that the growth kinetics followed the Lifshitz–Slyozov–Wagner (LSW) theory for Ostwald ripening, i.e., large particles grow at the expense of dissolution of smaller ones.³⁹ Peng et al. reported a “focusing and defocusing” process for the growth of II–VI and III–V colloidal semiconductor prepared by using injection method.¹³ They found that a critical size (r^*) existed at equilibrium and played an important role to control the size distribution of the produced nanocrystals. When the monomer concentration was depleted, r^* became larger and the size distribution broadened (“defocusing”). The injection of additional monomer decreased r^* to a smaller value, which resulted in the process of “focusing”. Our method, while using a single precursor, is slightly different from this study in the sense that our precursor is continuously heated from room temperature until the solution refluxes. Thus the supply of monomers will be continuous throughout the heating period until the precursor is depleted.

To follow the growth kinetics of QDs, it is necessary to determine particle sizes as a function of time. In most kinetics studies, particle size inferred from absorption onset was conveniently used since good agreement with TEM analysis could often be found.^{39,40} In Figure 7, two typical time evolutions of the absorption band edge during our preparation are presented.

It should be pointed out that $t = 0$ in the plots refers to the onset of reflux, i.e., after continuous heating from room temperature for ~ 10 –15 min. During this heating period, the reaction mixture will slowly turn from a turbid to a clear yellowish solution, indicating the onset of decomposition of the insoluble precursor. The absorption band edge is already obvious at $t = 0$, suggesting that some nanoseeds are formed at the onset of reflux. The absorption edge progressively shifts to higher wavelength with time, indicating the gradual growth of these QDs in size.

At a fixed precursor concentration, the size-dependent growth rate can be obtained by considering the Gibbs–Thompson equation:^{13,39–41}

$$S_r = S_b \exp\left(\frac{2\gamma V_m}{rRT}\right) \quad (1)$$

Here, S_r and S_b are the solubility of the particles and the bulk solid respectively, γ is the interfacial energy, r is the radius of the particles, V_m is the molar volume of the materials, R is the gas constant, and T is the temperature. When diffusion is the rate-limiting step, the Gibbs–Thompson expression can be inserted into Fick's first law of diffusion and the growth law based on the LSW model^{42,43} is obtained:

$$r_{\text{av}}^3 - r_{\text{av},0}^3 = Kt \quad (2)$$

Here, r_{av} is the average particle radius, $r_{\text{av},0}$ is the average initial particle radius, t is the reaction time, and K is a constant related to the diffusion coefficient (D):³⁹

$$K = \frac{8\gamma D V_m^2 S_b}{9RT} \quad (3)$$

The equation thus predicts that the cubic term of r_{av} is linearly dependent on t . In Figure 8, we plot the cubic term of r_{av} inferred from the absorption band edges with time and the linear relationship obtained thus confirms that the growth of CdS QDs follows the LSW theory. The constant K value is calculated as $0.147(\pm 5) \times 10^{-3} \text{ nm}^3/\text{s}$ for sample a and $0.128(\pm 5) \times 10^{-3} \text{ nm}^3/\text{s}$ for sample b. The slight decrease of K in sample b agrees

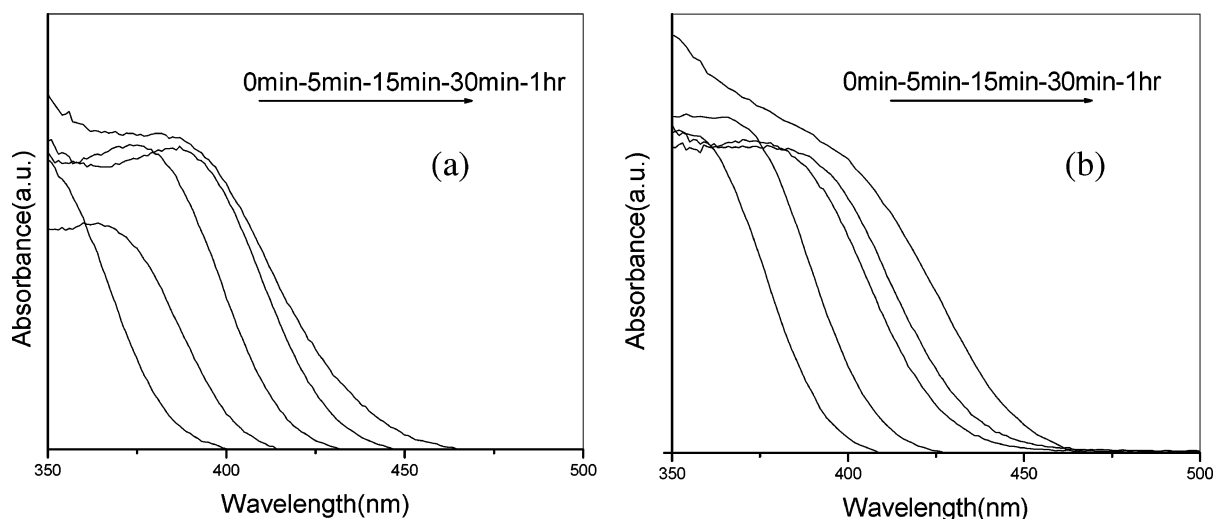


Figure 7. Time evolution for the absorption spectra of CdS QDs prepared with (a) 0.25 and (b) 2.5 mmol of 1-thioglycerol. Time = 0 refers to the onset of reflux of the reaction mixture.

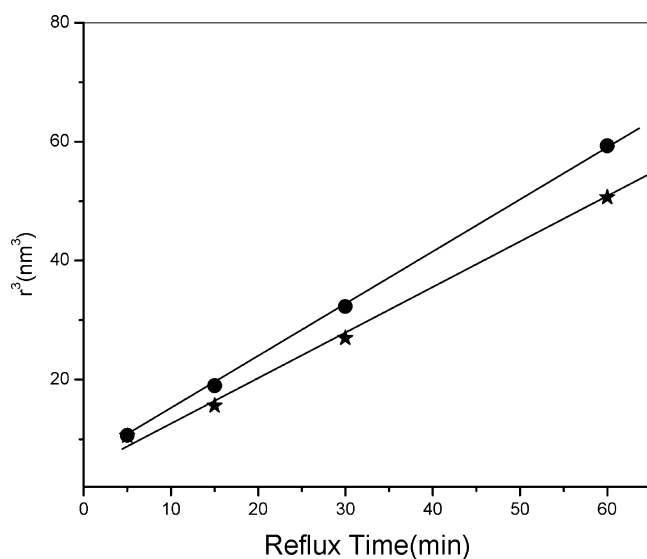


Figure 8. Plot of (particle radius)³ versus time for CdS QDs prepared with different amounts of 1-thioglycerol: 2.5 (stars) and 0.25 mmol (dots).

with the expectation that the presence of more capping agents will impede diffusion through the interfacial boundaries for coalescence to occur.

When the amount of capping agent was increased to 10 mmol, however, we observed an interesting phenomenon. Thus, as shown in Figure 9, the onset peak now remains at the same position instead of red-shifting for the first 1 h of reflux. From there on an additional peak is observed at higher wavelength and gradually grows in intensity. Thus after 5 h of reflux, the absorption spectrum indicated two distinct peaks: one at 367 nm (3.38 eV) and another at 467 nm (2.66 eV). When these band gap values are fitted into the Brus equation, two average particle sizes, 23 and 48 Å, respectively, are obtained. We have found that these two distinctly sized QDs can be easily separated by size-selective procedures and the individual absorption spectrum can be measured when the separated QDs are re-dispersed in water. In Figure 10, the individual spectrum is compared with the original composite spectrum obtained after 5 h of reflux.

It is interesting to note that the larger QDs are about twice the size of the smaller ones, and that the later practically does not grow in size upon reflux. Such a phenomenon does not occur for samples prepared with a lower amount of thioglycerol. Thus, based on the above results, we can propose the following kinetic

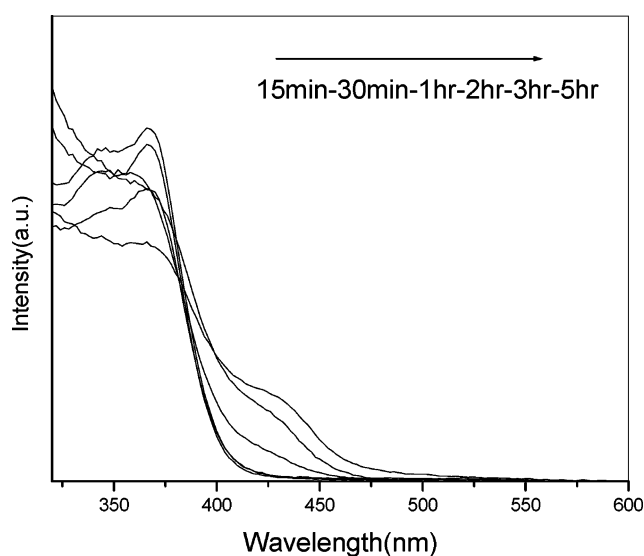
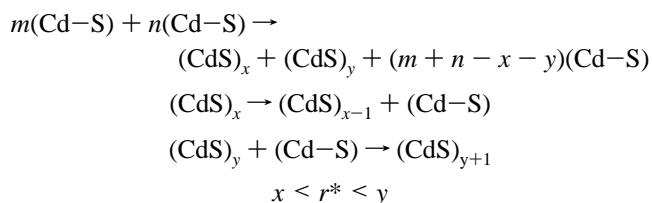


Figure 9. Time evolution for the absorption spectra of CdS QDs prepared with 10 mmol of 1-thioglycerol. Prolong reflux shows the growth of a new peak at longer wavelength.

growth model for the formation of CdS QDs in our reaction. First, the precursor is decomposed and monomers (denoted as Cd-S) are formed in the mixture. Some monomers come together to form nanoseeds initially (denoted with a subscript x or y) during reflux. The reaction is then followed by a competition between coarsening and dissolution (Oswald ripening), depending on whether the crystal size is smaller or larger than the equilibrium critical size (r^*). The competition mechanism may be shown as follows:



Peng et al. has proposed that r^* is the critical radius for which the solubility of the nanocrystals is exactly equal to the concentration of the monomers (i.e. the growth rate is zero).¹³ We have found that effectively r^* is inversely dependent on the amount

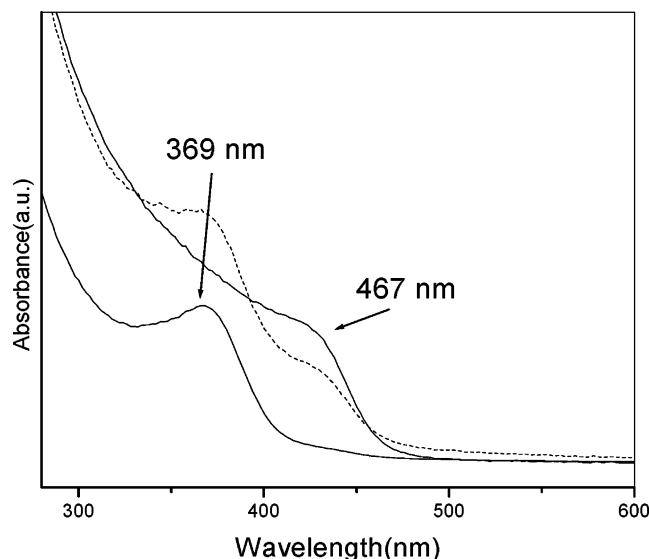


Figure 10. Comparison between the absorption spectrum for the separated QDs (solid) and the composite spectrum after 5 h of reflux in Figure 9 (dotted).

of capping agent present, since the amount of capping agent will affect the interfacial diffusion and hence the solubility of the nanocrystals. There seems to exist a saturation amount of capping agent, S^* , for the reaction. When the amount of capping agent is $>S^*$, the diffusion constant D will be lowered to near zero, and then according to eqs 2 and 3, $r_{av} = r_{av,0}$, i.e., the nanocrystal practically does not grow once formed. During prolonged reflux, some of these smaller QDs will probably collide with each other to form dimers: $(\text{CdS})_y + (\text{CdS})_y \rightarrow (\text{CdS})_{2y}$.

Since the dimers will have a lower surface-to-volume ratio compared to the smaller QDs, we expect some capping molecules are released into the reaction mixture in this process. While the smaller QDs are more or less *matured* (i.e. not growing) in the refluxing mixture, it will be interesting to investigate modifications/reactions that could be further carried out on these QDs. More work is now underway in this direction.

Conclusion

We have demonstrated a facile route to synthesize water-soluble CdS QDs using a new single-source precursor. The precursor is air-stable and relatively easy to prepare and purify. The produced QDs are fairly uniform and the particle size can be adjusted by either controlling the capping agent-to-precursor ratio or stopping the reaction at the appropriate time. The growth of these QDs was found to follow Oswald ripening during the reflux process. When the amount of capping agent used exceeds some saturation value, an unprecedented dimerization of QDs is detected. The first-grown QDs are found to have ceased growing except merging with one another to form QDs of double the size. Two distinctly sized nanoparticles can thus be isolated after prolonged reflux. This phenomenon is interesting as further modification of the QDs is now possible at elevated temperatures.

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References and Notes

- (1) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.
- (2) Tolbert, S. H.; Alivisatos, A. P. *Annu. Rev. Phys. Chem.* **1995**, *46*, 595.
- (3) Beecroft, L. L.; Ober, C. K. *Chem. Mater.* **1997**, *9*, 1302.
- (4) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. *Chem. Rev.* **1995**, *95*, 735.
- (5) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
- (6) Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, *122*, 12700.
- (7) (a) Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59. (b) Yu, M. W.; Peng, X. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2368. (c) Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *123*, 183.
- (8) (a) Jun, Y.-W.; Koo, J.-E.; Cheon, J. *Chem. Commun.* **2000**, 1243. (b) Jun, Y.-W.; Choi, C.-S.; Cheon, J. *Chem. Commun.* **2001**, 101. (c) Lee, S. M.; Jun, Y.-W.; Cho, S.-N.; Cheon, J. *J. Am. Chem. Soc.* **2002**, *124*, 11244. (d) Jun, Y.-W.; Jung, Y.-Y.; Cheon, J. *J. Am. Chem. Soc.* **2002**, *124*, 615. (e) Jun, Y.-W.; Lee, S. M.; Kang, N. J.; Cheon, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 5150.
- (9) Joo, J.; Na, H. B.; Yu, T.; Yu, J. H.; Kim, Y. W.; Wu, F.; Zhang, J. Z.; Hyeon, T. *J. Am. Chem. Soc.* **2003**, *125*, 11100.
- (10) (a) Yan, P.; Xie, Y.; Qian, Y. T.; Liu, X. M. *Chem. Commun.* **1999**, 1293. (b) Wang, W. Z.; Geng, Y.; Yan, P.; Liu, F. Y.; Xie, Y.; Qian, Y. T. *J. Am. Chem. Soc.* **1999**, *121*, 4062.
- (11) Some other examples on size and shape control: (a) Lee, S. M.; Cho, S.-N.; Cheon, J. *Adv. Mater.* **2003**, *15*, 441. (b) Li, Y. C.; Li, X. H.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 2641. (c) Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001**, *124*, 3343. (d) Barrelet, C. J.; Wu, Y.; Bell, D. C.; Lieber, C. M. *J. Am. Chem. Soc.* **2003**, *125*, 11498.
- (12) (a) Trindade, T.; O'Brien, P.; Zhang, X. *Chem. Mater.* **1997**, *9*, 523. (b) Ludolph, B.; Malik, M. A.; O'Brien, P.; Revaprasadu, N. *Chem. Commun.* **1998**, 1849. (c) Trindade, T.; O'Brien, P.; Pickett, N. L. *Chem. Mater.* **2001**, *13*, 3843. (d) Nair, P. S.; Radhakrishnan, T.; Revaprasadu, N.; Kolawole, G. A.; O'Brien, P. *Chem. Commun.* **2002**, 564.
- (13) Peng, X. G.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.
- (14) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.
- (15) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016.
- (16) Mills, A.; Lehunte, S. J. *Photochem. Photobiol. A* **1997**, *1*, 108.
- (17) Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmuller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665.
- (18) Rockenberger, J.; Troger, L.; Kornowski, A.; Vossmeier, T.; Eychmuller, A.; Feldhaus, J.; Weller, H. *J. Phys. Chem. B* **1997**, *101*, 2691.
- (19) Kho, R.; Torres-Martinez, C. L.; Mehra, R. K. *J. Colloid Interface Sci.* **2000**, *227*, 561.
- (20) Sondl, I.; Siiman, O.; Koester, S.; Matijevic, E. *Langmuir* **2000**, *16*, 3107.
- (21) Sapra, S.; Nanda, J.; Sarma, D. D.; El-Al, F.; Hodes, G. *Chem. Commun.* **2001**, 2188.
- (22) Qi, L. M.; Colfen, H.; Antonietti, M. *Nano Lett.* **2001**, *1*, 61.
- (23) Rogach, A. L.; Kornowski, A.; Gao, M. Y.; Eychmuller, A.; Weller, H. *J. Phys. Chem. B* **1999**, *103*, 3065.
- (24) Barglik-Chory, C.; Buchold, D.; Schmitt, M.; Kiefer, W.; Heske, C.; Kumpf, C.; Fuchs, O.; Weinhardt, L.; Stahl, A.; Umbach, E.; Lentze, M.; Geurts, J.; Muller, G. *Chem. Phys. Lett.* **2003**, *379*, 443.
- (25) Chen, Y. F.; Rosenzweig, Z. *Anal. Chem.* **2002**, *74*, 5132.
- (26) Van Dijken, A.; Janssen, A. H.; Smitsmans, M. H.; Vanmaekelbergh, D.; Meijerink, A. *Chem. Mater.* **1998**, *10*, 3513.
- (27) Nanda, J.; Sapra, S.; Sarma, D. D.; Chandrasekharan, N.; Hodes, G. *Chem. Mater.* **2000**, *12*, 1018.
- (28) Azaroff, L. V. *X-ray diffraction*; McGraw-Hill: New York, 1974.
- (29) Chestnoy, N.; Harris, T. D.; Hull, R.; Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 3393.
- (30) Anderson, M. A.; Gorer, S.; Penner R. M. *J. Phys. Chem. B* **1997**, *101*, 5895.
- (31) Banin, U.; Bruchez, M.; Alivisatos, A. P.; Ha, T.; Weiss, S.; Chemla, D. S. *J. Chem. Phys.* **1999**, *110*, 1195.
- (32) Ginlet, D. S. *Photoelectrochemistry and Electrosynthesis of Semiconductor Materials*; Electrochemical Society: Pennington, NJ, 1988.
- (33) Vuyesteke, A. A.; Sihonen, Y. T. *Phys. Rev.* **1959**, *113*, 40.
- (34) Kitai, A. H. *Solid State Luminescence: Theory, Materials and Devices*; Hapman & Hall: New York, 1993.
- (35) Misawa, K.; Yao, H.; Hayashi, T.; Kobayashi, T. *Chem. Phys. Lett.* **1991**, *183*, 113.
- (36) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403.
- (37) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555.
- (38) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.
- (39) Wong, E. M.; Bonevich, J. E.; Searson, P. C. *J. Phys. Chem. B* **1998**, *102*, 7770.
- (40) Curri, M. L.; Agostiano, A.; Manna, L.; Monica, M. D.; Catalano, M.; Chiavarone, L.; Spagnolo, V.; Lugara, M. *J. Phys. Chem. B* **2000**, *104*, 8391.
- (41) Ratke, L.; Voorhees, P. W. *Growth and coarsening*; Springer: Berlin, Germany, 2002.
- (42) Lifshitz, I. M.; Slyozov, V. V. *J. Phys. Chem. Solids* **1961**, *19*, 35.
- (43) Wagner, C. Z. *Electrochem.* **1961**, *65*, 581.