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Noninjection, One-Pot Synthesis of Photoluminescent Colloidal Homogeneously Alloyed CdSeS Quantum Dots

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Colloidal photoluminescent CdSeS quantum dots (QDs) were readily prepared via a noninjection, one-pot approach, with air-stable compounds cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), elemental selenium (Se), and elemental sulfur (S) as Cd, Se, and S source compounds, respectively. The homogeneously alloyed CdSeS QDs were synthesized at 240 °C in a reaction flask containing the source compounds together with myristic acid, 2,2'-dithiobisbenzothiazole (MBTS), and 1-octadecene (ODE). All of these chemicals were loaded at room temperature with this newly developed approach. The effects of Cd/Se/S and S/MBTS feed molar ratios affecting the growth of the CdSeS QDs were investigated, via monitoring the temporal evolution of the optical properties (namely, absorption and emission) of the growing nanocrystals. The resulting ternary nanocrystals can be tuned easily to emit in the range of 470–550 nm of the electromagnetic spectrum; such an emission window is hard to manage with binary CdS and CdSe QDs alone. The bandgap engineering was accomplished readily via tuning the different Cd/Se/S and S/MBTS feed molar ratios. High Cd/Se/S feed molar ratios lead to an increase in both size and Se composition of the resulting CdSeS nanocrystals and, thus, a small bandgap; it is the composition that plays a relatively important role as compared to the size. Low S/MBTS feed molar ratios also lead to CdSeS QDs with a small bandgap, which is due to a high S activity, resulting in a fast growth in size. The CdSeS QDs were characterized by TEM, XPS, and XRD: they are homogeneous alloys with a cubic crystal structure. This noninjection, one-pot approach developed in our laboratories, which is the first regarding the synthesis of CdSeS QDs, features easy handling and large-scale production with excellent synthetic reproducibility.

1. Introduction

Colloidal photoluminescent (PL) semiconductor nanocrystals are fascinating nanoobjects which have attracted significant interest in both fundamental research and applied-oriented research.^{1–3} The synthesis of binary and ternary metal chalcogenide quantum dots (QDs) is a rapidly growing area in materials chemistry aiming at a fundamental understanding for practical applications, including quantum-confinement effects and nonlinear optical properties.^{4–11} A QD is one spherical semiconductor nanocrystal with its size less than or comparable to that of a photogenerated exciton in its corresponding bulk materials. Recently, investigation of the synthesis–structure–property relationship has become the major effort in our laboratories, with the development of noninjection approaches leading to high-quality colloidal PL quantum dots (QDs), including regular and magic-sized QD ensembles.^{9–11}

For the synthesis of colloidal PL II–VI QDs, earlier efforts focused more on binary systems, such as CdSe and CdS QDs, and recent efforts more on ternary systems, such as CdTeSe,⁷ CdSeS,⁸ ZnCdSe, and ZnCdS QD alloys.^{6,9} For the ternary QDs, bandgap engineering can be achieved via control of their sizes, constituent stoichiometries, and internal structures (such as homogeneous vs. gradient). For homogeneous ternary QDs, their

compositions play an essential role affecting both the confinement potential and the interfacial strain; thus, their bandgap energy can be tuned, even at a constant size. For example, alloyed CdSeS nanocrystals can be tuned readily to emit in the wavelength range of 480–540 nm, which is not easily achieved with binary CdSe or CdS QDs alone.^{4,5} Furthermore, homogeneously alloyed CdTeSe QDs emit at a relatively low energy, as compared to binary CdSe and CdTe QDs with similar sizes due to the optical bowing phenomenon.⁷

The ternary QDs reported by other research groups were from hot-injection approaches.^{6–8} Hot-injection approaches require rapid injection of a precursor solution and a fast decrease of the reaction temperature right after the injection to separate nucleation and growth stages for a narrow size distribution, during which strong stirring is mandatory for efficient mass transfer. The realization of these requirements is not easy; therefore, hot-injection approaches are not suitable for large-scale production and are poor in synthetic reproducibility. Accordingly, the development of noninjection-based synthetic approaches is in demand.

The recent advance in synthetic approaches to colloidal PL QD ensembles has led researchers to think more about applications, which in turn highlight more challenges in material synthesis, particularly in terms of the requirement of a certain size together with one certain bandgap energy. It is important for one QD ensemble to satisfy the requirement of both size and bandgap energy, from an application point of view. For

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example, for biological imaging, PL QDs have to be engineered with proper sizes to be compatible with biosystems, together with suitable emission colors.² To be incorporated into functional devices, QDs are often embedded into mesoporous materials with their sizes satisfying those of the pores.³ Therefore, it is fundamentally and practically important to construct alloyed ternary QDs whose change in the composition results in precise tuning of their electronic structure, even with a constant size.

Among II–VI PL colloidal QDs, CdSe QDs are probably the most extensively investigated (CdS QDs are the second most) regarding the development of the various synthetic routes including the hot-injection and noninjection approaches. At room temperature (300 K), CdSe has a bulk bandgap of ~ 1.73 eV (~ 715 nm) with its exciton Bohr radius of ~ 5.6 nm, whereas CdS ~ 2.48 eV (~ 500 nm) with its exciton Bohr radius of ~ 3.0 nm.¹² For zincblende CdSe and CdS, their lattice constants at room temperature are 6.050 and 5.835 Å, respectively.¹² Such a small lattice mismatch promises the formation of cadmium selenide sulfide (CdSeS) alloyed QDs, which are useful materials for studying nonlinear optical phenomena and for optoelectronic applications with tuneable optical and electronic properties in a wide range.

There are a few reports on the syntheses of CdSeS QDs via hot-injection approaches, with some information on the synthesis–structure–property.⁸ In 2003, the synthesis of CdSeS QDs was first reported. This reported approach involved one rapid injection of a premixed solution of (S + Se)/TOP (TOP = trioctylphosphine) into a CdO/oleic acid/trioctylamine solution at 300 °C. The resulting CdSeS QDs (with growth periods of 10 s to 4 min) were claimed to have quantum efficiency up to 85% and PL fwhm ~ 34 nm. Meanwhile, the authors stated that it was hard to conclude the structure of their QDs to be either core/shell or gradient, although there seemed to be a CdSe-rich core due to the fast formation of CdSe at the initial reaction stage.^{8a} Another pyrolytic synthesis of homogeneously alloyed $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals, which involved a swift injection of the mixture of S/ODE and Se/tributylphosphine into a CdO/oleic acid/ODE solution at 315 °C followed by the growth at 275 °C, was reported in 2006. The resulting CdSSe QDs exhibited fine absorption structures, depending on their size and composition; however, they exhibited significant deep-trapping emission, along with their bandgap emission with fwhm of 30–38 nm and quantum yield (QY) of ~ 1 –30%.^{8b} In 2007, the synthesis of alloyed CdSeS QDs was reported with an injection of a premixed solution of TOPSe and TOPS precursors into a cadmium oleate solution in various reaction coordinating media, including trioctylphosphine oxide, trioctylphosphine, triphenylphosphine, oleylamine, hexadecylamine, dioctylamine, and trioctylamine, and noncoordinating 1-octadecene at 230–300 °C. The resulting CdSeS QDs (with their growth temperature at 230–300 °C) exhibited absorption and emission between 500 and 600 nm with PL fwhm of ~ 29 nm and QY of ~ 30 –80%.^{8c} Basically, all of the syntheses reported so far on CdSeS QDs have been from hot-injection approaches, deriving from those to CdSe and CdS QDs with modifications.^{4a,5a}

This manuscript reports, for the first time, a noninjection, one-pot approach resulting in homogeneously alloyed CdSeS nanocrystals. On the basis of our latest improvement in the development of noninjection, one-pot approaches to CdS, ZnCdS, and PbS regular QDs as well as CdSe, CdTe, and CdTeSe magic-sized QDs in our laboratories,^{9–11} this newly developed noninjection approach engages air-stable compounds cadmium

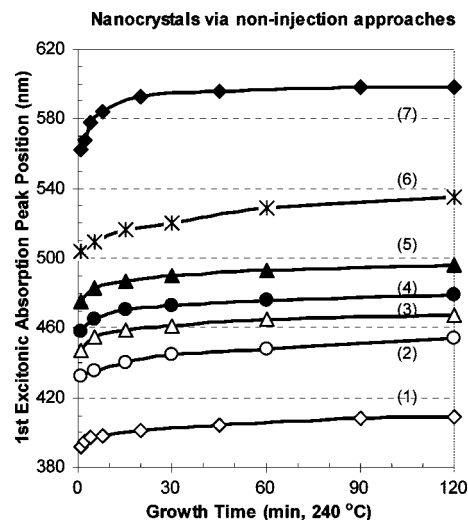


Figure 1. The effect of the feed molar ratios of Cd/Se/S on the growth of the nanocrystals via our noninjection approaches. The various feed molar ratios are 1Cd/0Se/1S (1, \diamond), 2Cd/0.6Se/1.4S (2, \circ), 3.5Cd/0.6Se/1.4S (3, \triangle), 2Cd/1Se/1S (4, \bullet), 3.5Cd/1Se/1S (5, \blacktriangle), 3.5Cd/1.4Se/0.6S (6, \times), and 2Cd/1Se/0S (7, \blacklozenge). The growth periods, in minutes, are presented on the x axis, and the first absorption peak positions, in nanometers, on the y axis. All these syntheses had the same experimental setup, with a 16S/1MBTS feed molar ratio (except for curve 6, 9.3S/1MBTS) and with a growth temperature of 240 °C (except for curve 7, 220 °C). The nanocrystals were dispersed in toluene, and the excitation wavelength was 350 nm. The preparation of the alloyed CdSeS QDs is presented in Supporting Information Table S1, and the temporal evolution of the optical properties of the growing CdSeS nanocrystals from the five ternary synthetic batches is addressed in Supporting Information Figure S1.

acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), elemental selenium (Se), and elemental sulfur (S) as Cd, Se, and S source compounds, respectively. All of the source chemicals were loaded in a reaction flask at room temperature, together with myristic acid (MA), 2,2'-dithiobisbenzothiazole (MBTS), and 1-octadecene. The homogeneously alloyed CdSeS QDs were synthesized at 240 °C, with the bandgap engineering achieved by various Cd/Se/S and S/MBTS feed molar ratios; the growth kinetics was monitored via the temporal evolution of the optical properties of the growing nanocrystals. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD) characterization were performed, suggesting that the resulting CdSeS QDs are homogeneous alloys with a cubic crystal structure. This noninjection, one-pot approach developed in our laboratories features easy handling and large-scale production with excellent synthetic reproducibility; in addition, it is a green approach with the avoidance of phosphines.

2. Experimental Section

All of the chemicals are commercially available and were used as received. They are cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, Alfa Aesar, 99.999%), elemental selenium (325 mesh, Alfa Aesar, 99.5%), elemental sulfur (Anachemia, precipitated), 2,2'-dithiobisbenzothiazole (Aldrich, 99%), myristic acid (Sigma, 99%), and 1-octadecene (Aldrich, tech. 90%). Photoluminescent CdSeS QDs were synthesized with various Cd/Se/S and S/MBTS feed molar ratios. In a typical synthesis with a feed molar ratio of 2Cd/0.6Se/1.4S and 16S/1MBTS, Se (2.38 mg, 0.03 mmol), S (2.46 mg, 0.07 mmol), MBTS (1.49 mg, 4.375 μmol), and ODE (~ 3 g) were sonicated together for 1 h. Afterward, this dispersion was added into a three-necked,

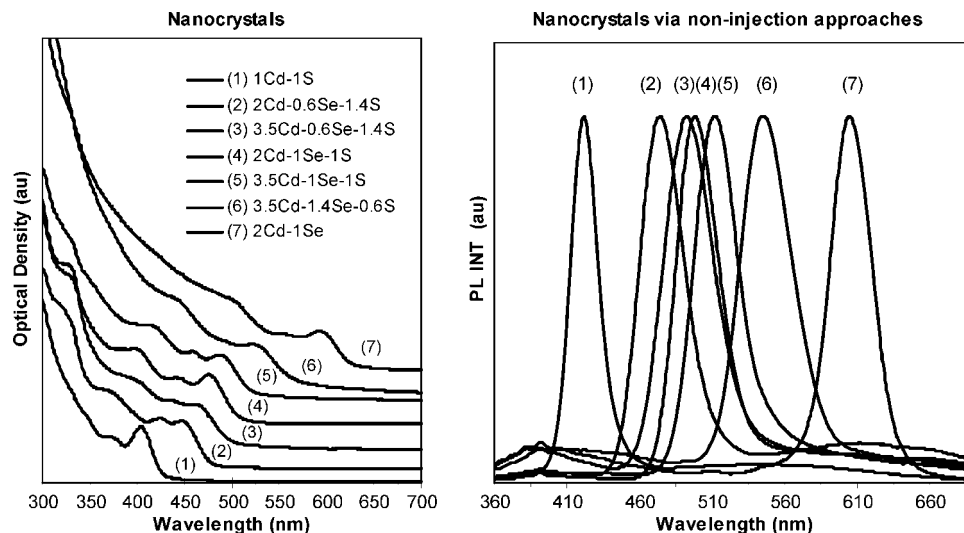


Figure 2. The UV-vis absorption (left, offset) and photoluminescence (right, normalized) spectra of the nanocrystals from the seven synthetic batches shown in Figure 1. Again, the feed molar ratios are 1Cd/0Se/1S (1), 2Cd/0.6Se/1.4S (2), 3.5Cd/0.6Se/1.4S (3), 2Cd/1Se/1S (4), 3.5Cd/1Se/1S (5), 3.5Cd/1.4Se/0.6S (6), and 2Cd/1Se/0S (7). The excitation wavelength was 350 nm. These ternary CdSeS nanocrystals were synthesized at 240 °C with a growth period of 30 min; the binary CdSe, at 220 °C with a 20-min growth period; and the binary CdS, at 240 °C with a 45-min growth period. The CdSeS nanocrystals from the synthetic batch with a relatively high Cd/Se/S feed molar ratio exhibit relatively small bandgap with relatively red-side absorption and emission.

round-bottom flask containing $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (26.84 mg, 0.1 mmol), MA (45.85 mg, 0.2 mmol), and ODE (~ 2 g) at room temperature. The mixture was heated to 120 °C with stirring under vacuum (~ 30 mTorr) and allowed to stay at this temperature for ~ 2 – 2.5 h to get a clear yellow solution. The resulting solution was further heated to 240 °C at a rate of 10 °C/min under a flow of purified nitrogen. The growth time was counted once the temperature reached 240 °C, and the growth was kept at this temperature for the growth/annealing process of the CdSeS QDs. Similar noninjection, one-pot synthetic protocols have been successfully used in the syntheses of cubic CdS, ZnCdS, and magic-sized CdSe nanocrystals in our laboratories.^{9–11}

To monitor the growth of the nanocrystals, small aliquots (~ 0.2 mL) of the reaction mixture were taken quickly at 240 °C at different growth periods (such as 1, 5, 15, 30, 60, and 120 min); each aliquot taken was then dispersed in toluene with a proper concentration, such as 20 $\mu\text{L}/3$ mL to achieve ~ 0.1 optical density at the excitation wavelength. Optical absorption spectra were collected with a Perkin-Elmer Lambda 45 ultraviolet-visible (UV-vis) spectrometer using a 1-nm data collection interval. Photoluminescent emission experiments were performed on a Fluoromax-3 spectrometer (Jobin Yvon Horiba, Instruments SA), with a 450 W Xe lamp as the excitation source, an excitation wavelength of 350 nm, an increment of data collection of 2 nm, and slits for excitation and emission of 3 nm. For the emission peak, baseline-subtracted and Gaussian-fitted integration was performed, with built-in DataMax software, to yield the peak position, full width at half-maximum (fwhm), and peak area for the calculation of quantum yield. PL QY was determined by comparing the integrated emission of a given QD sample in dilute toluene dispersion with that of quinine sulfate in 0.05 M H_2SO_4 (lit. QY ~ 0.546). Corrections were made for the refractive indices of the difference solvents.

Structural and compositional characterizations were performed by TEM, XPS, and powder XRD. Intensive purification of the nanocrystals samples was carried out before these characterizations. It is necessary to point out that large-scale syntheses were carried out to get enough materials for the XRD and XPS characterizations. Our noninjection approach exhibits very good

reproducibility and is easy to scale up, as illustrated in the Supporting Information. TEM was performed on a JEOL JEM-2100F electron microscope operating at 200 kV and equipped with a Gatan UltraScan 1000 CCD camera. A TEM sample was prepared by drying a purified-QD dilute dispersion in toluene on a 300-mesh carbon-coated TEM copper grid. Powder XRD patterns were recorded at room temperature on a Bruker Axis D8 X-ray diffractometer using Cu K radiation in a θ – θ mode. The generator was operated at 40 kV and 40 mA, and data were collected between 5° and 80° in 2θ mode with a step size of 0.1° and a counting time of 5 s per step. An XRD sample was prepared by depositing purified nanocrystals on a low-background quartz plate. XPS was performed using a Kratos Axis Ultra XPS equipped with a monochromated Al X-ray source. The purified QDs were deposited on a silicon wafer substrate; afterward, the substrate was mounted with doubled-sided copper tape. For each sample, three analyses were performed with data collected on three local areas. The data collection was carried out using an accelerating voltage of 14 kV and a current of 10 mA consisting of an initial survey scan performed at a pass energy of 160 eV to identify all the species present and a following survey scan with high resolution at a pass energy of 40 eV for the species identified and of interest. During the data collection, the pressure in the analysis chamber was 2.0×10^{-9} Torr; meanwhile, charge build-up was compensated with the use of an Axis charge balancing system. Peak-fitting was performed using a CasaXPS (version 2.2.107) data processing software. All analyses were calibrated to C 1s at 285 eV. Quantification was performed using sensitivity factors provided by CasaXPS's Scofield element library.

3. Results and Discussion

This manuscript reports on our noninjection, one-pot synthesis of colloidal CdSeS nanocrystals emitting in the range of 470–550 nm with air-stable source compounds. To the best of our knowledge, it is the first report on a noninjection, one-pot approach to alloyed CdSeS nanocrystals. Our noninjection approach features easy handling and large-scale capability with high synthetic reproducibility and relatively mild synthetic

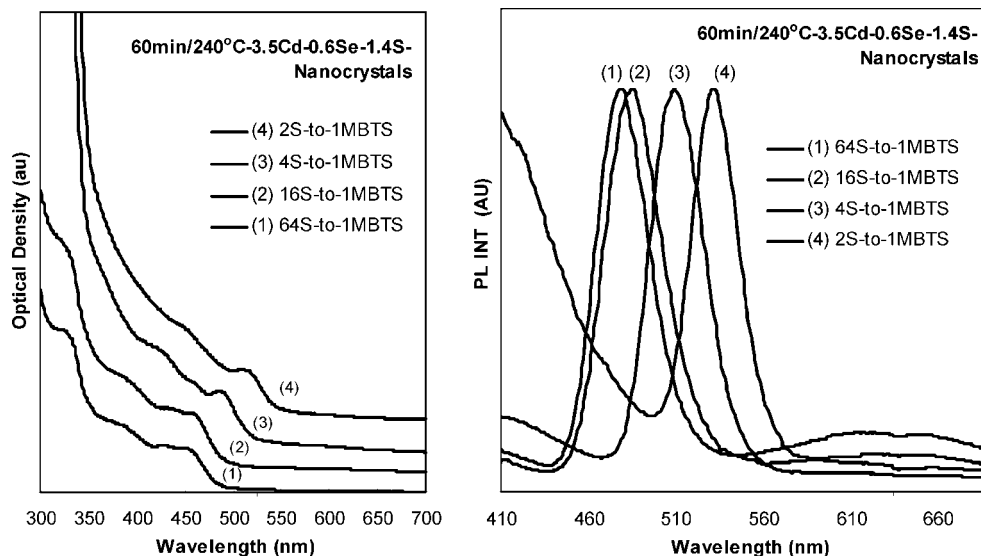


Figure 3. The UV-vis absorption (left, offset) and photo emission (right, normalized) spectra of the 60-min growth nanocrystals from our four synthetic batches with a fixed 3.5Cd/0.6Se/1.4S feed molar ratio but different S/MBTS feed molar ratios, which are 64S/1MBTS (1), 16S/1MBTS (2), 4S/1MBTS (3), and 2S/1MBTS (4). The excitation wavelength was 350 nm. These nanocrystals were synthesized at 240 °C with a 60-min growth period and were dispersed in toluene. The nanocrystals from the synthetic batch with a relatively small S/MBTS feed molar ratio exhibit a relatively small bandgap with relatively red-side absorption and emission. The temporal evolution of the optical spectra of the growing CdSeS nanocrystals from the four synthetic batches is presented in Supporting Information Figure S2.

conditions. It is easy to understand that various synthetic parameters and the interplay between them affect the growth of the CdSeS QDs. Accordingly, the first part (section 3-1) deals with the growth kinetics of the nanocrystals, addressing two major synthetic parameters: Cd/Se/S (section 3-1-1) and S/MBTS feed molar ratios (section 3-1-2), where MBTS is an activator of sulfur.^{5b,9,13} The two synthetic parameters affect the growth kinetics of the resulting QDs as well as their composition, which determines the bandgap mainly. The growth kinetics of the CdSeS QDs was monitored in terms of the temporal evolution of their optical properties, indicating that the bandgap of the resulting nanocrystals is readily engineered with these feed molar ratios, leading to the various tuneable emission colors; the higher the Cd/Se/S and lower S/MBTS feed molar ratios, the lower the bandgap of the resulting CdSeS QDs. The second part (section 3-2) presents the compositional and structural characterization of the synthesized CdSeS QDs; the CdSeS QDs are cubic in crystal structure, with Se and S homogeneously distributed in the whole nanocrystals. Furthermore, it is the composition of the CdSeS QDs that plays a major role in determining the bandgap, rather than their size.

3-1. Growth Kinetics of CdSeS Nanocrystals. 3-1-1.

Effect of Cd/Se/S Feed Molar Ratios. The effect of Cd/Se/S feed molar ratios on the growing kinetics of CdSeS QDs is summarized in Figure 1, which presents the temporal evolution of the first excitonic absorption peak positions (in nanometers) of the growing nanocrystals from seven synthetic batches, among which are five for ternary and two for binary. The detailed synthetic conditions are summarized in Supporting Information Table S1. Curves 1 and 7 in Figure 1 represent binary CdS and CdSe QDs, respectively. The Cd/Se/S feed molar ratios are different for the five ternary batches; they are 2Cd/0.6Se/1.4S (curve 2), 3.5Cd/0.6Se/1.4S (curve 3), 2Cd/1Se/1S (curve 4), 3.5Cd/1Se/1S (curve 5), and 3.5Cd/1.4Se/0.6S (curve 6). Figure 2 shows the absorption (left) and emission (right) spectra of the nanocrystals from the seven synthetic batches shown in Figure 1, with the growth period/temperature of 45 min/240 °C for CdS QDs (curve 1), 30 min/240 °C for

the ternary QDs (curves 2–6), and 20 min/220 °C for CdSe QDs (curve 7). Our CdSeS QDs via the noninjection approach exhibit fine absorption structures, which are similar to the best CdSeS reported with hot-injection syntheses.^{8b} It is noteworthy that no absorption was reported in refs 8a and 8c.

It is clear that the bandgap energy of our CdSeS QDs is smaller than that of our binary CdS QDs and larger than that of our binary CdSe QDs; the two binary ensembles were synthesized with a similar experimental setup and the feed molar ratios of 1Cd/1S and 2Cd/1Se. Thus, we successfully bridge the gap between the bandgap energy of binary CdS QDs and that of CdSe QDs; such an energy/wavelength range of the gap is hardly reached by regular CdS and CdSe QD ensembles, which are usually in the size range of 3–4 nm in diameter.

Furthermore, it seems that there are two growth stages, before and after 30 min at 240 °C. The growth is relatively fast in the early growth periods of 30 min, as compared to that afterward. Moreover, a comparison of the absorption and emission demonstrates a straightforward relationship between the Cd/Se/S feed molar ratios and the bandgap energy of the resulting QDs. For example, the bandgap absorption position of the nanocrystals from batches 3, 5, and 6 moves toward long wavelength direction, with an increase in the Se/S feed molar ratios when the Cd amount is fixed; when the Se/S ratio is fixed (for batches 4 and 5), the bandgap absorption position also moves toward long wavelength direction with an increase in the feed Cd amount. Thus, the QDs from the batches with relatively large Cd/Se/S feed molar ratios exhibit a relatively small bandgap during the entire monitored growth periods of 120 min at 240 °C.

Accordingly, the bandgap of resulting CdSeS QDs is engineered efficiently with various Cd/Se/S feed molar ratios, leading to tuneable emission colors. For instance, the CdSeS QDs from batch 2 with the 2Cd/0.6Se/1.4S ratio exhibit bandgap emission centered at 470 nm (blue), whereas from batch 6 with the 3.5Cd/1.4Se/0.6S ratio shows bandgap emission centered at 550 nm (green). The change of the bandgap should be a result of both size and composition; our TEM, XRD, and XPS characterization

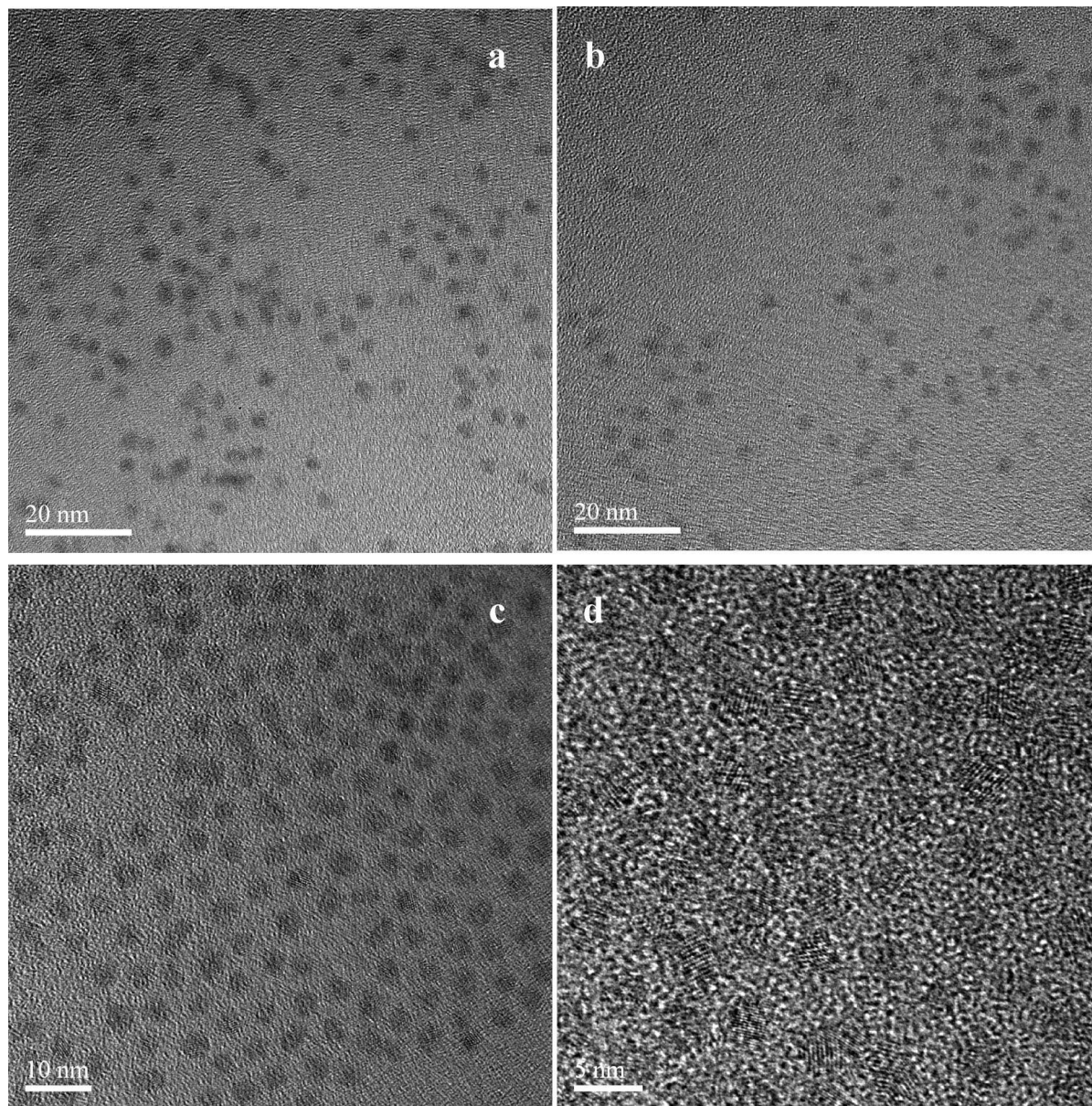


Figure 4. Typical TEM images of CdSeS alloyed QDs with a 120-min growth at 240 °C, from the synthetic batches with varied feed molar ratios of (a) 3.5Cd/0.6Se/1.4S (scale bar 20 nm), with the mean size 3.05 nm; (b) 3.5Cd/1Se/1S (scale bar 20 nm), with the mean size 3.33 nm; and (c) 3.5Cd/1.4Se/0.6S (scale bar 10 nm), with the mean size 3.70 nm. (d) High resolution of panel c (scale bar 5 nm). The increase in size with an increase in the Se feed ratio is consistent with the larger bond length of Cd–Se than that of Cd–S in the nanocrystals.

(presented in section 3-2-1) suggests that the composition of the resulting CdSeS QDs plays a major role for such a change in the bandgap. The temporal evolution of the optical spectra of the growing nanocrystals from the five ternary synthetic batches with the different Cd/Se/S feed molar ratios is shown in Supporting Information Figure S1.

For the three batches shown in Figures 1 and 2 with feed molar ratios of 3.5Cd/0.6Se/1.4S (batch 3), 3.5Cd/1Se/1S (batch 5), and 3.5Cd/1.4Se/0.6S (batch 6), the increase in the Se feed amount relative to S led to a decrease in the QY, together with a slight increase in the PL fwhm, as summarized in Supporting Information Table S2. Thus, it seems that the higher the Se feed amount relative to S, the more the Se in the resulting CdSeS QDs (see XPS part), and the lower the QY. For the two batches with the feed molar ratios of 2Cd/0.6Se/1.4S (batch 2) and 3.5Cd/0.6Se/1.4S (batch 3), as well as for the two batches with the feed molar ratios of 2Cd/1Se/1S (batch 4) and 3.5Cd/1Se/1S (batch 5), the higher the Cd feed amount, the higher the

QY, accompanied by an increase in the PL fwhm. In addition, with our experimental setup and conditions, the relatively high growth temperature and the relatively high acid/Cd feed molar ratio resulted in CdSeS QDs with relatively a high QY (as shown in Supporting Information Figure S3).¹¹

3-1-2. Effect of S/MBTS Feed Molar Ratios. The Cd/Se/S feed molar ratio has an evident effect on the growth kinetics of the nanocrystal, affecting the bandgap of the resulting CdSeS QDs. Elemental sulfur is activated here by MBTS; thus, it is apparently important to study the S/MBTS feed ratios. Actually, this parameter also plays an important role in the optical properties of the resulting CdSeS nanocrystals.

With the fixed 3.5Cd/0.6Se/1.4S feed molar ratio, we investigated the effect of the S/MBTS feed molar ratio on the growth of the nanocrystals from our noninjection approaches. The investigated S/MBTS ratios were (2–64)S/1MBTS, as shown in Figure 3. The absorption (left) and emission (right) spectra of the 60-min as-synthesized CdSeS QDs from the four

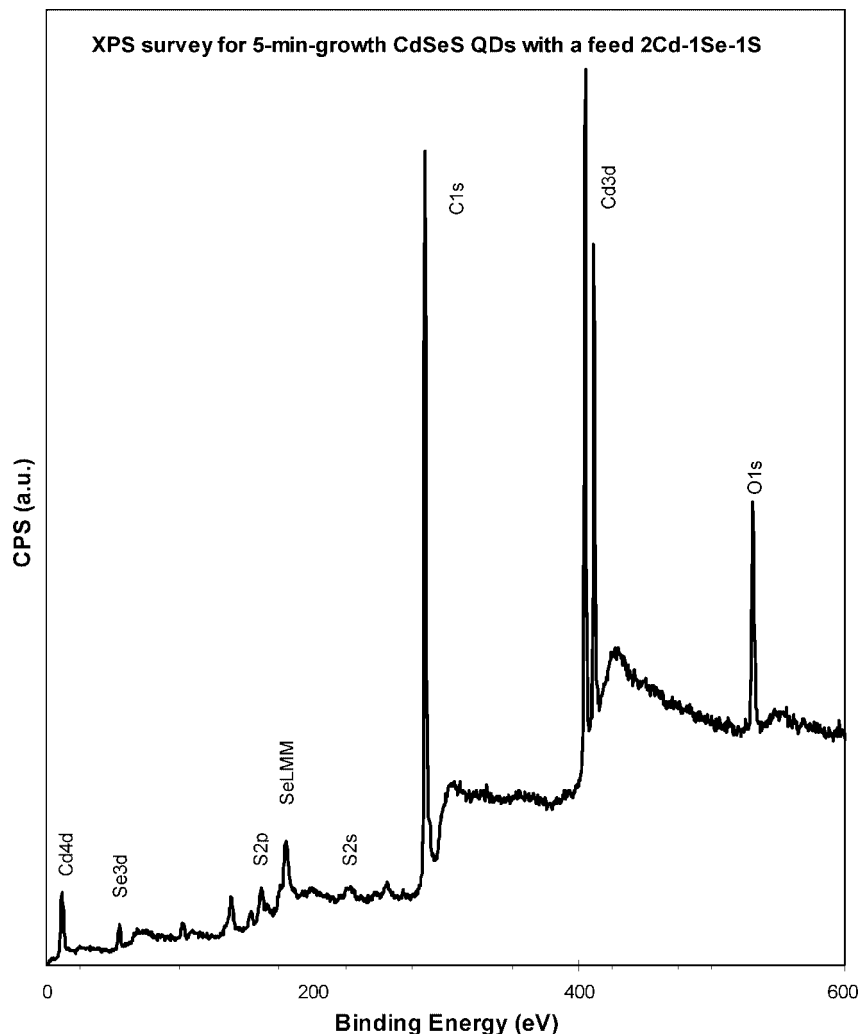


Figure 5. One typical XPS survey spectrum of the CdSeS nanocrystals prepared via our noninjection approaches. The sample is 5-min-growth/240 °C CdSeS QDs with a feed molar ratio of 2Cd/1Se/1S (whose optical spectra and TEM image are shown in Supporting Information Figure S5). The CdSeS nanocrystals are characterized as $\text{CdSe}_{0.45}\text{S}_{0.55}$. The Se amount is calculated from Se3d signals in the range of 52–58 eV (including oxidized Se if any), whereas S is from S 2p (159–167 eV) or S 2s (222–230 eV) (S 2p complicatedly overlaps with Se 3p, and the deconvolution of S 2s is easier with Se 3s).

synthetic batches with 64S/1MBTS (curve 1), 16S/1MBTS (curve 2), 4S/1MBTS (curve 3), and 2S/1MBTS (curve 4) demonstrate that relatively low S/MBTS feed molar ratios lead to relatively small bandgaps with relatively red-side absorptions and emissions. It is acknowledged that the bandgap of the CdSeS QDs depends on two factors: namely, their sizes and compositions. Larger size and more selenium should result in lower bandgap QDs. It is easy to understand that the more MBTS added, the higher the sulfur activity, which may lead to a higher S composition in the ternary QDs and larger QDs.^{5b} Obviously, via the present approach, it should be the increase in the nanocrystal size that is responsible for the decrease in the bandgap of the nanocrystals from the batches with low S/MBTS feed molar ratios. The temporal evolution of optical spectra of the nanocrystals from the four synthetic batches shown in Figure 3 are presented in Supporting Information Figure S2.

Careful comparison shows that the nanocrystals from the four synthetic batches exhibit PL emission with different symmetry; the best is from batch 2 with a 16S/1MBTS feed molar ratio. The nanocrystals from batch 1 with a 2S/1MBTS feed molar ratio exhibit one additional emission at the blue side of bandgap emission, although their deep-trapping emission (at the red side of bandgap emission) seems to be suppressed; meanwhile, the

nanocrystals from batch 4 with a 64S/1MBTS feed molar ratio exhibit both the blue- and red-side emission, in addition to their bandgap emission. Therefore, the 16S/1MBTS feed molar ratio is preferred and is the most widely used in our laboratories.^{9,11} For the nanocrystals from the batches shown in Figure 3, the fwhm values are in the range of 36–39 nm, which are close to the best reported by hot-injection syntheses,⁸ whereas our QY values of 3.9–4.7% (except for batch 1, 0.7%) are close to the low-end 1–30% QY reported and lower than the high-end 30–80% QY reported.⁸ It is necessary to point out that different QDs exhibit different homogeneous broadening, in addition to inhomogeneous broadening. For example, one single PbS QD exhibits ~50 nm fwhm, but one single CdSe QD ~ 10 nm. Thus, it is helpful to compare the PL fwhm of CdSeS ternary QDs from various synthetic approaches when they are identical in structure (homogeneous vs gradient), composition, and size, but it can be problematic to compare QYs from various laboratories.

3-2. Structural and Compositional Characterization. In the research field of the development of colloidal PL nanocrystals, it is important to characterize the synthesized nanocrystals to know their size, crystal structure, and composition; for ternary systems, it is also necessary to determine their

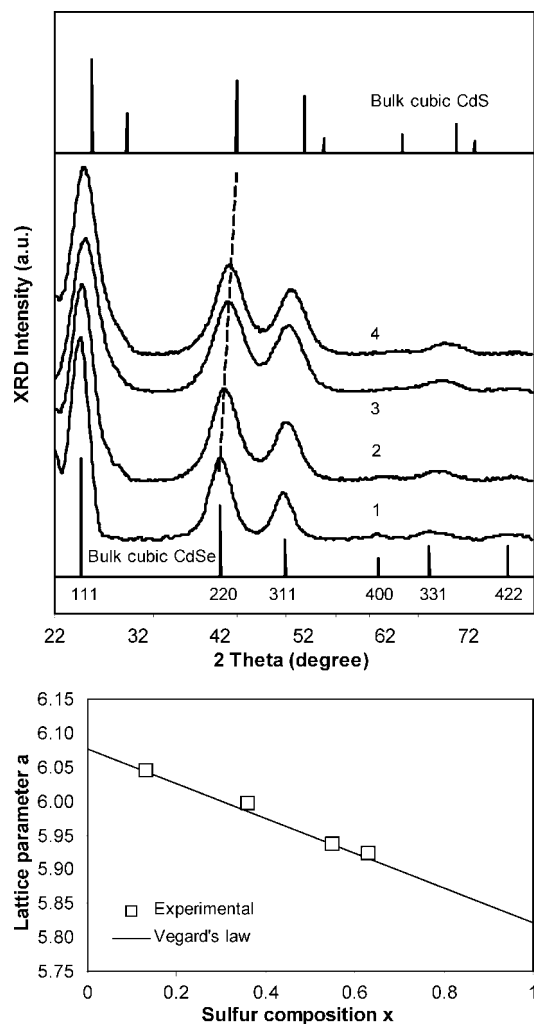


Figure 6. (top) Powder XRD patterns of CdSeS nanocrystals synthesized from the batches shown in Figures 4 and 5, with varied feed molar ratios of Cd/Se/S: 3.5Cd/1.4Se/0.6S (curve 1), 3.5Cd/1Se/1S (curve 2), 2Cd/1Se/1S (curve 3), and 3.5Cd/0.6Se/1.4S (curve 4). The standard patterns of bulk cubic CdSe and CdS are present as references. The diffraction peaks are indexed. (bottom) The dependence of lattice parameter *a* on *x*, the composition of sulfur, in the alloyed nanocrystals. The straight line represents the Vegard's law.

compositional structure (namely, homogeneous vs gradient) for the synthesis–structure–property relationship. Therefore, we performed TEM, XPS, and XRD characterization on our CdSeS QDs. It is important to point out that the QD samples used were from relatively large-scale synthetic batches, which are four times the synthetic volume of our regular-scale synthesis (see Supporting Information Table S1). It is noteworthy that our large-scale syntheses have excellent reproducibility, as illustrated by the comparison of the optical properties of the CdSeS nanocrystals from five batches with identical conditions, such as 3.5Cd/0.6Se/1.4S and 16S/1MBTS feed molar ratios (see Supporting Information Figure S4).

3-2-1. Transmission Electron Microscopy Together with X-ray Photoelectron Spectroscopy. Figure 4 shows typical TEM images of the purified CdSeS QDs from the synthetic batches of 3.5Cd/0.6Se/1.4S (a), 3.5Cd/1Se/1S (b), and 3.5Cd/1.4Se/0.6S (c and d); the three batches have an identical 16S/1MBTS feed molar ratio. The nanocrystals are spherical in shape with a narrow size distribution and high crystallinity. The mean size is 3.05 nm (a), 3.33 nm (b), and 3.70 nm (c and d), indicating an increase in size with an increase in the Se feed amount. Such

a relationship is consistent with the fact that the bond length of Cd–Se is larger than that of Cd–S. The as-synthesized QDs exhibit bandgap absorption peaking at 469 nm (a), 489 nm (b), and 529 nm (c and d). For the binary CdS and CdSe QDs at a similar size range of 3.05–3.70 nm, CdSe should exhibit bandgap absorption between 550 and 576 nm, whereas CdS should be between 389 and 409 nm.¹⁴ Accordingly, it is clear that the obtained nanocrystals are alloyed ternary in nature rather than binary CdS or CdSe QDs. Meanwhile, for the QDs in the same size range of 3.05–3.70 nm, the CdSe, CdSeS, and CdS QDs exhibit a bandgap difference of 26, 60, and 20 nm, respectively; thus, the composition in the ternary system should play an important role in bandgap energy.

The three samples shown in Figure 4 were characterized by XPS. Figure 5 shows one example of our characterization with XPS for atomic composition. For the 5-min-growth/240 °C nanocrystals from batch 2Cd/1Se/1S (whose optical spectra and one TEM image are shown in Supporting Information Figure S5, giving an absorption peak at 481 nm and a size of ~3.64 nm), the composition is CdSe_{0.45}S_{0.55}; for those from batch 3.5Cd/0.6Se/1.4S (a), 3.5Cd/1Se/1S (b), and 3.5Cd/1.4Se/0.6S (c and d), shown in Figure 4, the composition is CdSe_{0.37}S_{0.63} (a), CdSe_{0.64}S_{0.36} (b), and CdSe_{0.87}S_{0.13} (c, d).

Therefore, it seems conclusive that the composition (Se vs S) of the resulting CdSeS QDs, from our batches with the different Cd/Se/S feed molar ratios, plays a relatively important role in the bandgap, as compared to their size. For example, CdSe_{0.45}S_{0.55} QDs exhibit absorption peaking at ~481 nm with a size of ~3.64 nm, whereas CdSe_{0.87}S_{0.13} peaks at 529 nm with a size of ~3.70 nm. It is clear that the size variation is relatively small, but the composition and bandgap variation is relatively large. At the same time, it is necessary to point out that the increase in the Se feed amount leads to both the increase in size and the Se content in the nanocrystals; thus, the resulting nanocrystals exhibit low bandgap with red-side absorption and emission. It is also necessary to point out that under the condition with excess Cd feeding (such as batch 3.5Cd/1Se/1S shown in Figure 4), the reactivity of Se is relatively high as compared to that of S due to the fact that the Se/S ratio in the resulting CdSe_{0.64}S_{0.36} QDs is higher than the Se/S feed ratio. Under the condition without excess Cd feeding (such as batch 2Cd/1Se/1S shown in Figure 5), the reactivity of Se is similar to that of S due to the fact that the Se/S ratio in the resulting CdSe_{0.45}S_{0.55} QDs is nearly equal to the Se/S feed ratio. Subsequently, more Cd feeding promotes its reactivity more to Se than it does to S.

3-2-2. Powder X-Ray Diffraction. The XRD patterns of our CdSeS nanocrystals are shown in Figure 6 (top), together with those of bulk cubic CdS and CdSe for reference. The examined ternary QDs are the purified 120-min growth CdSeS QDs from the batches (shown in Figure 4) with 3.5Cd/1.4Se/0.6S (curve 1), 3.5Cd/1Se/1S (curve 2), and 3.5Cd/0.6Se/1.4S (curve 4) feed molar ratios and the 5-min growth CdSeS QDs from the batch (shown in Figure 5) with 2Cd/1Se/1S (curve 3) feed molar ratios.

It is obvious that our synthesized CdSeS nanocrystals have a cubic crystal structure, as indicated by the lack of diffraction peaks of (102) and (103) planes, which are characteristic of a hexagonal crystal structure. Moreover, the diffraction peaks of the resulting nanocrystals shift to the direction of large Bragg angles with increasing S feed amount; such an increase in 2θ indicates a decrease in the lattice parameters and an increase in the S content, which is incorporated into the CdSe lattice, leading to the formation of the CdSeS QDs.

Figure 6 (bottom) shows the relationship of the S atomic composition x ($x = S/(S + Se)$) and the lattice constant a (in angstrom, Å); the S composition is determined by XPS, and the lattice constant a is calculated from the (220) diffraction peak. It is acknowledged that homogeneous ternary alloys obey Vegard's law with a linear relationship between the compositions of solid–solution alloys and their lattice parameters, with the composition expressed as atomic percentage.^{9,15} Clearly, our CdSeS QDs satisfy such a relationship of Vegard's law. Accordingly, it is reasonable to conclude that our CdSeS alloyed QDs, with 5–120 min growth at 240 °C are homogeneous in composition; such homogeneity may be true throughout the whole reaction at 240 °C.

4. Conclusions

The present study reports, for the first time, the growth of CdSeS nanocrystals by a noninjection, one-pot approach using air-stable compounds. Such a “green” chemistry approach features easy handling and large-scale capability with mild reaction conditions and with great reproducibility. Colloidal homogeneously alloyed photoluminescent CdSeS QDs were readily synthesized via our noninjection approach. The effects of the feed molar ratios of Cd/Se/S and S/MBTS on the electronic properties of the resulting QDs have been studied. High Cd/Se/S feed molar ratios lead to a small bandgap with long wavelength PL emission, which is due to, mainly, the increase of Se composition accompanied by the increase in size. Low S/MBTS feed molar ratios also have a similar effect on the bandgap, which results from a fast growth rate with high S activity. Furthermore, the S/MBTS feed molar ratio plays an important role in the optical spectral shape of the nanocrystals. The obtained high-quality homogeneously alloyed CdSeS QDs have a controllable bandgap with limited size variation. A cubic crystal structure and homogeneous composition were verified by TEM, XPS, and XRD.

Note Added after ASAP Publication. This article was published ASAP on March 2, 2009. References 10b, 10d, and 11 have been modified. The correct version was published on March 6, 2009.

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Supporting Information Available: The details about the CdSeS QD preparation (namely, recipes) and the absorption and emission spectra of the growing CdSeS QDs from the various synthetic batches with the varied feed molar ratios of Cd/Se/S and S/MBTS are available in Supporting Information, together with the monitored reproducibility of the large-scale syntheses and some optical spectra and TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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