

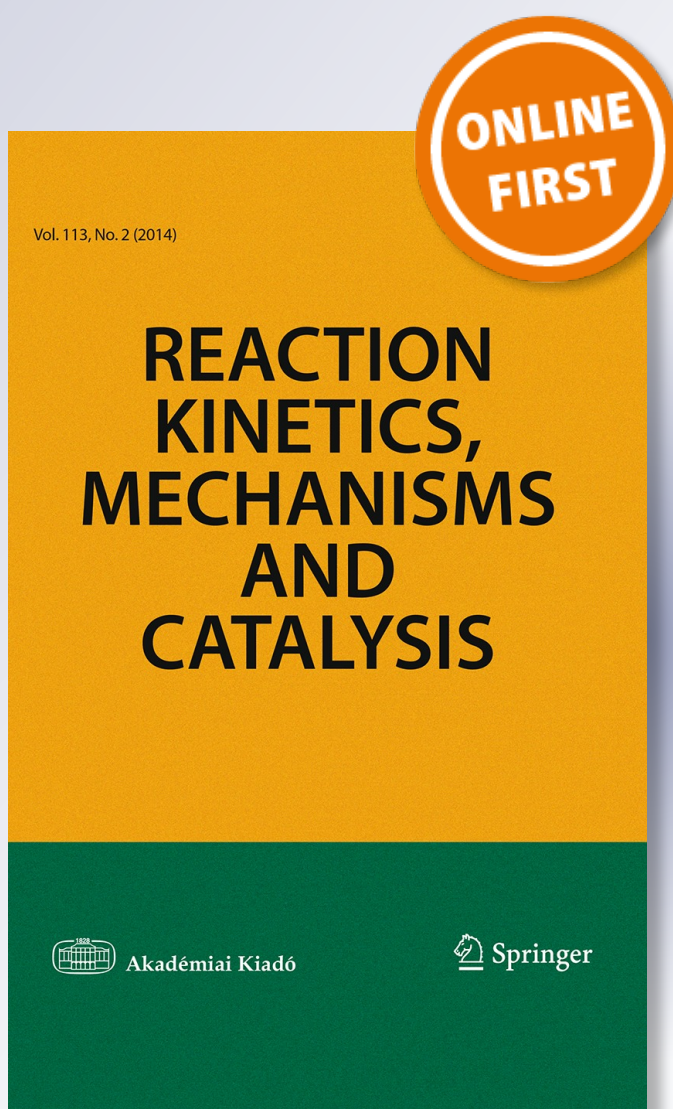
*Synthesis and characterization
of composition-gradient based
 $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y}$ heterostructured
quantum dots*

**Zoltán Győri, Zoltán Kónya & Ákos
Kukovecz**

**Reaction Kinetics, Mechanisms and
Catalysis**

ISSN 1878-5190

Reac Kinet Mech Cat
DOI 10.1007/s11144-014-0813-0



Your article is protected by copyright and all rights are held exclusively by Akadémiai Kiadó, Budapest, Hungary. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".

Synthesis and characterization of composition-gradient based $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y}$ heterostructured quantum dots

Zoltán Györi · Zoltán Kónya · Ákos Kukovecz

Received: 30 September 2014 / Accepted: 21 November 2014
© Akadémiai Kiadó, Budapest, Hungary 2014

Abstract In this paper, we describe a one-pot synthesis method to produce $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y}$ heterostructured quantum dots (QDs) with chemical composition gradient. The synthesized QDs have either CdSe rich cores with ZnS rich shell or CdSe–CdS hybrid cores with ZnS rich shell, which are formed simply due to the differences in reactivities of the precursors. The obtained QDs were characterized using TEM, PL spectroscopy, UV–Vis, XRD and EDX. The heterostructured QDs emit brightly in the 478–603 nm spectral window and the emission wavelength is tunable by changing the crystal size and the precursor ratios. The photoluminescent emission peaks are narrow (FWHM ~ 35 nm) due to the good size and shape uniformity of the particles.

Keywords Quantum dot · Core–shell · Alloy · Single-step synthesis · $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y}$

Introduction

Quantum dots are semiconductor fluorescent nanocrystals. Their properties are between those of bulk semiconductors and discrete atoms, with unique optical and

Z. Györi · Z. Kónya · Á. Kukovecz (✉)
Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1,
Szeged 6720, Hungary
e-mail: kakos@chem.u-szeged.hu

Z. Györi · Á. Kukovecz
MTA-SZTE “Lendület” Porous Nanocomposites Research Group, Rerrich Béla tér 1, Szeged 6720,
Hungary

Z. Kónya
MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1,
Szeged 6720, Hungary

electronic properties [1]. QDs are also known as zero-dimensional materials because their excitons are confined in all spatial dimensions. They attracted a lot of attention recently because of their unique optical and electrical properties, which are due to the quantum confinement effect. Their size-dependent optical properties make them ideal materials for many technical applications [2]. It is possible to produce light-emitting diodes [3, 4], lasers [5], photovoltaic cells [6] based on QDs and they can be applicable as single-photon sources [7] or probes in biological imaging [8].

In order to enhance and retain their favorable optical properties, their surface must be protected, therefore, core–shell QDs are also researched besides bare dots. CdSe QDs are particularly intensely researched today for these practical applications because their emitted wavelengths cover the whole visible spectra. These QDs can be coated with a higher bandgap semiconductor shell, which not only protects the core but also reduces nonradiative recombination, thus resulting in brighter emission.

The main method to produce type-I core–shell dots (i.e. dots, in which both the photoinduced electrons and the holes are confined in the core) is a two-step mechanism, where we first make the core semiconductor QDs and then coat them with a higher band-gap semiconductor. This inorganic passivation can be very effective in removing the non-radiative recombination centers. In type-I core–shell QDs with CdSe cores, the shell commonly consists of several monolayers of ZnS [9–11] or CdS [12, 13]. The deposition of these shell layers requires an extra step in conventional QD synthesis. Furthermore, above a certain shell thickness the large lattice mismatch between the core and the shell can reduce the photoluminescence efficiency of the QDs by generating dislocations [14]. In the case of CdSe/ZnS core–shell QDs 1–2 monolayers of shell thickness is the most favorable [15]. Once the ZnS shell becomes thicker than 2 monolayers, the large lattice mismatch between the CdSe and ZnS lattices induces strain at the core–shell interface and this results effects the photoluminescence efficiency adversely. In special cases, when the chemical reactivities of the different constituents are favorable we can create core–shell QDs with a quick and simple one-pot method (or single-step synthesis), which yields QDs of a composition gradient based structure with CdSe rich cores and ZnS rich outer shells [16]. In this case the chemical composition gradient structure relieves the strain caused by the lattice mismatch between the CdSe rich core and the ZnS rich shell.

Here, we report on the properties of $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y}$ heterostructured QDs with fixed initial Cd-to-Zn ratio (1:4) and different initial Se-to-S ratios (1:1, 1:10, 1:30). With the applied Cd:Zn ratio, we were able to synthesize heterostructured QDs with Cd rich core and Zn rich shell with good size uniformity and narrow photoluminescent emission peak. The emission wavelength of the QDs was tunable across a wide window of the visible spectra (478–603 nm) by changing the Se:S ratio and the crystal size.

Experimental

Chemicals

Cadmium oxide (CdO, 99.5 %), zinc oxide (ZnO, 99.9 %), selenium (99.99 %, powder), sulfur (99.9 %, powder), trioctylphosphine (TOP, 90 %), oleic acid (OA,

90 %), 1-octadecene (ODE, 90 %) were purchased from Aldrich and all used as received.

The synthesis of the QDs is based on the one-pot synthesis method of Nag et al. with some modifications. [17]. In a typical synthetic procedure CdO (0.2 mmol) and ZnO (0.8 mmol) with fixed ratio of Cd:Zn = 1:4 were placed in a three-neck round bottom flask together with 3 mL oleic acid and 10 mL octadecene. This reaction mixture was heated to 150 °C while stirring and degassed under vacuum for 30 min. Then the reaction vessel was filled with nitrogen and heated up to 310 °C. At this temperature the solution became optically clear due to Cd-oleate and Zn-oleate formation. 2.2 mmol Se and S powder mixture (previously dissolved in 1.5 mL TOP and 0.5 mL ODE) was swiftly injected into the flask to promote uniform nucleation. Next the temperature was lowered to 300 °C to facilitate crystal growth. For making QDs with different emission color aliquots were taken at certain intervals (5, 15, 30 s, 1, 5, 15 min) and at three different Se:S ratios. These ratios were 1:1 (1.1 mmol Se, 1.1 mmol S), 1:10 (0.2 mmol Se, 2.0 mmol S) and 1:30 (0.07 mmol Se, 2.13 mmol S) for sample A, B and C, in order. The aliquots were quenched in cold hexane to stop the growth of QDs immediately, purified and precipitated with methanol and acetone and then redispersed in toluene.

Characterization

Transmission electron microscopy measurements were performed on a Philips CM10 microscope with ultrathin carbon film covered copper grids. The size distribution histograms were obtained by measuring the diameter of 200 individual QDs in each sample. The UV–Vis spectra were obtained on a Hitachi U-2001 spectrometer and the photoluminescence measurements were performed on a Hitachi F-2000 spectrofluorometer operating at 390 nm excitation wavelength. The crystal structure of the synthesized QDs was analyzed by X-ray diffraction (XRD) in a Rigaku MiniFlex II system using Cu K α radiation. Samples for XRD and SEM were prepared from toluene suspensions by precipitation with acetone. The composition of QDs was analyzed by energy dispersive X-ray spectroscopy (EDS) in a Hitachi S-4700 SEM Cold Field Emission SEM–EDS system.

Results and discussion

The TEM images reveal that the QDs have good shape and size uniformity with about 10–12 % standard deviation in diameter. Fig. 1 presents some representative samples of QDs after 1 and 15 min reaction time with the corresponding size distribution histograms. QDs sampled at the same time intervals exhibited a similar size distribution in all three sample series. After 5 s sampling time, the mean diameter of the QDs was 2.3 ± 0.2 nm, after 15 s 2.8 ± 0.1 nm and after 30 s 3.4 ± 0.1 nm. There was a minor size decrease in the early reaction stages when the initial sulfur ratio was raised from 1:1 to 1:30. This was attributed to the increasing amount of incorporated smaller S²⁻ ions instead of Se²⁻ ions. After 1 min sampling time, the mean diameter was 4.2 ± 0.4 nm, which is 2.5 nm smaller than the value

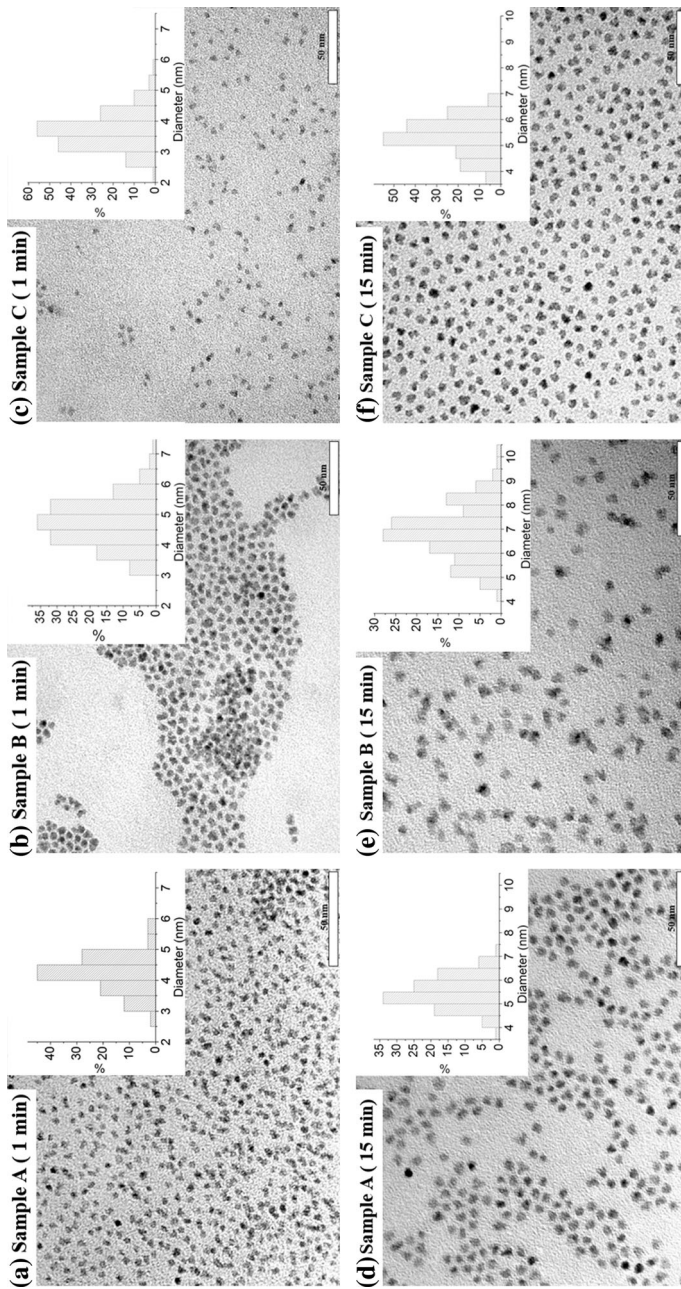


Fig. 1 TEM images with adherent histograms of the three sample series obtained with different Se:S ratios (Sample A: 1:1; Sample B: 1:10; Sample C: 1:30) after 1 and 15 min of crystal growth

Bae and coworkers got after 1 min crystal growth time (6.7 nm) [17]. After 5 min, the diameter was 4.5 ± 0.3 , 1.5 nm smaller than the corresponding value from Bae et al. (6.0 nm). We attribute the success in creating these relatively smaller sized QDs to the higher nucleation rate, which was caused by the higher initial Se^{2-} concentrations [18]. After 15 min crystal growth, the QDs had 5.9 ± 0.6 nm mean diameter.

In order to identify the chemical composition of the QDs, EDX spectra were recorded. The composition ratios of Cd-to-Zn and Se-to-S as a function of time can be seen in Fig. 2. It is observable in Fig. 2a that the incorporated amount of Cd precursor in the early reaction stages is higher in all three sample series than the amount of reacted Zn precursor even if the initial ratio of Zn was four times higher. This reveals that Cd-oleate is more reactive than Zn-oleate [19] under the applied reaction conditions. This finding agrees well with literature data [16, 17, 20]. After 15 min of crystal growth, the amount of incorporated Zn was about 3 times higher than the incorporated amount of Cd. This final ratio reveals that heterostructured QDs after 5 min reaction time have initially formed Cd-rich cores and Zn-rich shells, which are formed later at all three tested Se/S ratios. Hence, by using a smaller initial Cd-precursor ratio we succeeded in preparing heterostructured QDs with shells containing no or minimal amount of Cd. In contrast, earlier literature results were focused on using a higher Cd:Zn ratio ($\sim 1:1.6$), which resulted in a ZnS–CdS hybrid shell [16]. Fig. 2b shows the amount of incorporated Se and S for the three different Se:S ratios. In the first case, when the initial ratio of Se:S was 1:1, the amount of reacted Se-TOP was 70.8 % right after the nucleation and remained at high values along the whole crystal growth. Therefore, we probably got both Se-rich cores and S-rich shells (possibly including some Se as well) when using this high Se/S ratio. When the Se:S ratio was decreased to 1:10 the amount of incorporated Se was also high in the initial reaction stage with about 51.9 %, which reveals that at this smaller Se ratio the cores of the heterostructured QDs contained a higher amount of sulfur than in the case of 1:1 Se:S ratio. When the Se:S ratio was decreased further to 1:30, the large initial S concentration forced more sulfur into the cores. Hence, the incorporated amount of Se was only 19 % after 5 s and the S content was more than 94 % after 5 min. Therefore these QDs are closer to the CdS/ZnS structure than to CdSe/ZnS. The final Cd:Zn:Se:S ratios of the synthesized QDs did not match the initial ratios completely. However, they exhibited a similar trend. The initial ratios for sample A, B and C were 1.0:4.0:5.5:5.5; 1.0:4.0:1.0:10.0 and 1.0:4.0:0.35:10.65 and in the final product the ratios as determined by EDX were 1.0:3.1:2.8:2.1; 1.0:2.7:0.6:3.1 and 1.0:3.1:0.3:4.5. The incorporated ratio of Cd:Zn was close to 1:3 in all three cases, confirming that the initial 1:4 Cd:Zn ratio was low enough to create composition gradient based structures with Cd rich cores and Zn rich shells. The Se:S content was most favorable with 1:1 Se:S ratio, where the QDs had large amounts of Se in the cores and contained S rich shells. However, the possibility of minor Se incorporation into the shell layers could not be excluded completely.

The PL spectra in Fig. 3 are in good agreement with the EDX data, indicating that the amount of incorporated sulfur increased drastically as the initial Se:S ratio decreased. Spectra recorded at the same absorbance value are presented in Fig. 3.

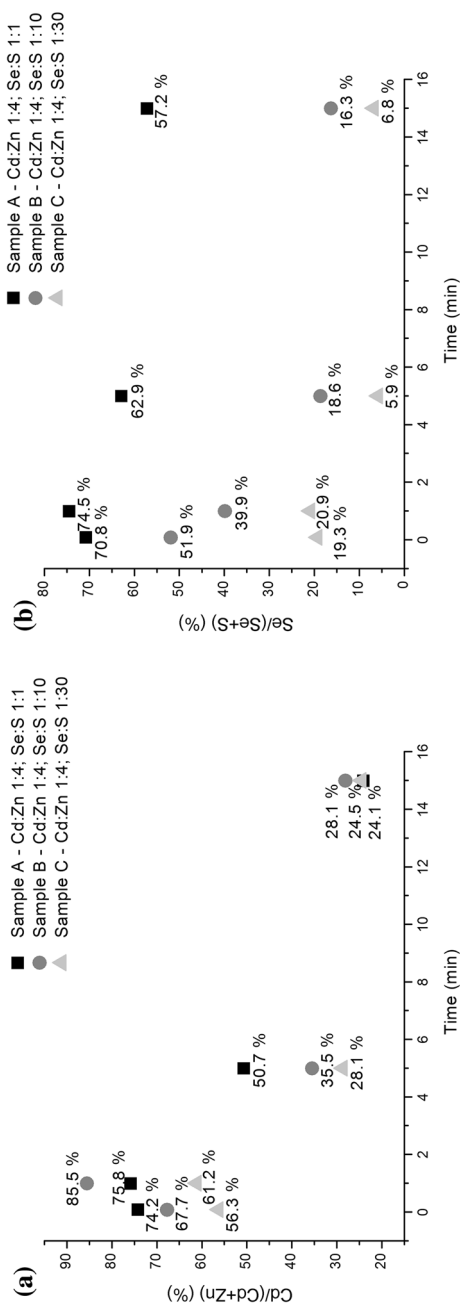


Fig. 2 Energy dispersive X-ray spectroscopy based composition analysis of QDs discussed here. Cd:Zn (a) and Se:S (b) composition ratios are depicted as functions of synthesis time

Although this representation offers the best comparison of actual PL emission performances, it should be noted that equal absorbance does not necessarily mean equal concentration in QD spectroscopy, as the extinction coefficient is size-dependent. The PL spectra reveal that as the incorporated S content increases, the emitted wavelength decreases at the same sampling time. For all sample series, there is a considerable red shift in the emission wavelength at the early stages of the reaction because of the increasing QD diameters. The PL peak of the QDs after 15 s reaction time is red-shifted by an average of 31 nm relative to that of the QDs measured after 5 s growth time. After a further 15 s of growth time (samples with 30 s), the PL peaks are red-shifted by a further 19 nm and after more 30 s (samples with 1 min) again by a further 15 nm. After 1 min, the growth slows down, therefore, PL peak positions hardly change any more as depicted in Fig. 4a. This can be explained by the fact that the leakage of carriers to the shells is suppressed by the outer shells made of the larger band gap material [16]. At 1:1 Se:S ratio, there is a 0.2 nm increase in the diameter of QDs after 5 min of growth time relative to the sample of 1 min crystal growth, however, a slight blue shift of 2 nm is observable. In the next 10 min of growth, the mean diameter increased from 4.41 to 5.49 nm and the PL peak was blue-shifted by 2 more nanometers. At 1:30 Se/S ratio the crystal size increased by 0.5 nm from 1 to 5 min (7 nm blue shift) and by a further 1.1 nm in the next 10 min of growth (2 more nm blue shift in PL peak position). These blue shifts can be attributed to an alloying mechanism involving Zn diffusion from the outer shells into the core induced by the high temperature and the long reaction time. [21]. At 1:10 Se:S ratio there was a 0.3 nm and a 1.8 nm increase in the diameter at growth times 5 and 15 min and 5–5 nm red shift in the PL peaks.

In sample A, the PL emission maximum was at 555 nm after 5 s growth time and at 603 nm after 15 min growth time. In sample B, the QDs emit from 497 to 578 nm and in sample C with 1:30 initial Se:S ratio from blue to green (478 nm after 5 s, 565 nm after 15 min). The full width at half maximum (FWHM) of the PL peaks averaged at 35 nm. The decreasing emission peak wavelength at the same sampling times confirms our hypothesis about the increasing S content of the QDs while moving from sample A though sample B to sample C (Fig. 4b). Let us now compare the PL emission maximum of these composition gradient based QDs synthesized with 1:1 Se:S ratio and 15 min crystal growth time with that of the compositionally most similar CdSe/ZnS QDs. The CdSe/ZnS core/shell QDs feature a similar emission peak maximum at 590–600 nm and a similar FWHM at the same crystal size (e.g. ~ 6 nm size with 4.8 nm CdSe core coated with about 1–2 monolayer ZnS shell) [15]. However, at reduced Se content (1:10 and 1:30 Se:S ratios), the performance of the QDs is no longer comparable directly with that of the CdSe/ZnS system because of the increased amount of S incorporation into the core.

UV–Vis absorption spectra of the heterostructured QDs with different initial S ratios are presented in Fig. 5. There is a systematic blue shift in the band-edge excitonic energy of the comparable samples taken from series A, B and C. This is caused by the increasing S content, because these crystals are very similar in size. A gradual red shift is observable in the single sample series at all tested Se:S ratios due to the increasing crystal size. All samples feature multiple excitonic peaks at the initial stages of the reaction. These excitonic peaks gradually disappear with

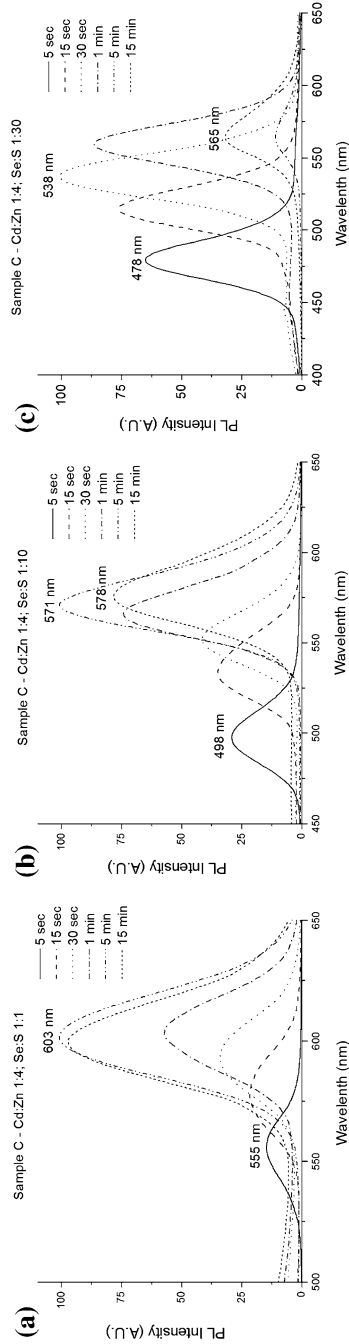


Fig. 3 Temporal evolution of photoluminescence spectra of samples A, B and C recorded at 390 nm excitation

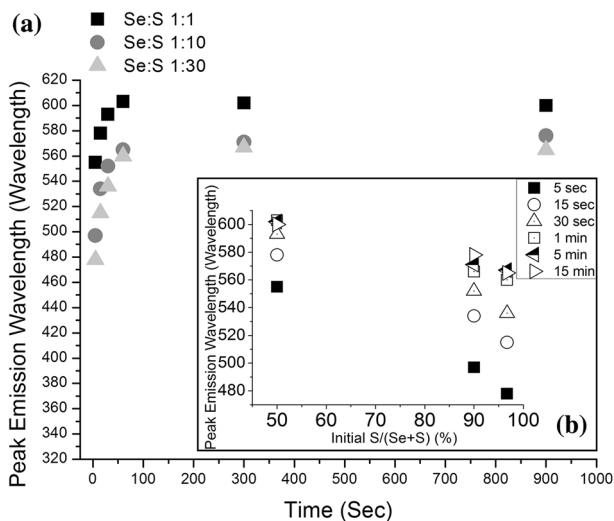


Fig. 4 Photoluminescence peak positions as a function of time **(a)** and as a function of sulfur ratio **(b)** for samples A, B and C

increasing diameter. Furthermore, these excitonic peaks start to disappear earlier with increasing initial S ratio. QDs of large diameters exhibit almost the same featureless absorption spectra as their bulk counterparts indicating that the quantum confinement effect (QCE) is weak. As the particle size approaches the corresponding exciton Bohr radius, weak excitonic absorption peaks are observed which indicates the existence of a limited QCE. [22]. The exciton Bohr radius for the bulk ZnS is 2.2 nm, for CdS is 3.0 nm, for ZnSe is 3.8 nm and for CdSe is 5.6 nm [23]. With 1:1 Se to S ratio, the samples have bright emission at all crystal sizes, especially after 5 and 15 min sampling time (with 4.41 and 5.49 nm) because these CdSe rich QDs are smaller than the corresponding exciton Bohr radius. It is well known that synthesizing bare, red-emitting CdSe QDs of good quality is experimentally challenging [24]. On the other hand, red-emitting QDs with bright emission are easily obtainable with our method, because here the ZnS rich outer shell reduces the amount of surface dangling bonds which act as surface traps. At 1:10 ratio above 4.9 nm crystal size (after 5 min of growth time), the QDs exhibit weak emission and at 1:30 ratio for the QDs with Cd and S rich cores, above 3.46 nm (after 30 s) the emission of the samples is very weak as indicated by their bulk-like spectra.

The crystallinities of the QDs were investigated by X-ray diffraction. The XRD patterns of the QDs obtained after 1 and 15 min at different Se:S ratios are shown in Fig. 6. These patterns reveal that the QDs have cubic zinc blende structure, which agrees well with the findings of Bae et al. [16] and Nag et al. [17]. The XRD patterns of bulk zinc blende CdSe and ZnS are also shown as references in the figures at the bottom and the top, respectively. The XRD results rule out the possibility of separate nucleation of binary QDs. The characteristic peaks of the

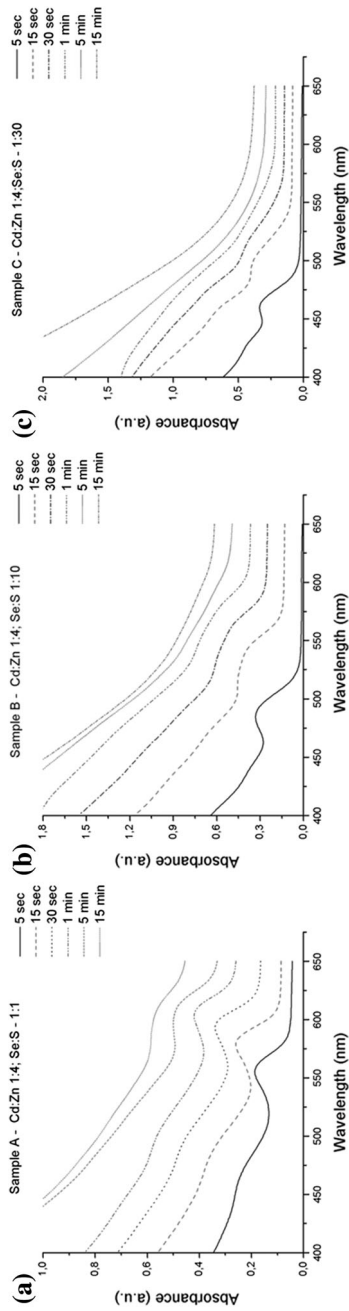


Fig. 5 UV-Vis absorption spectra of the sample series with the different Se:S ratios (1:1, 1:10, 1:30)

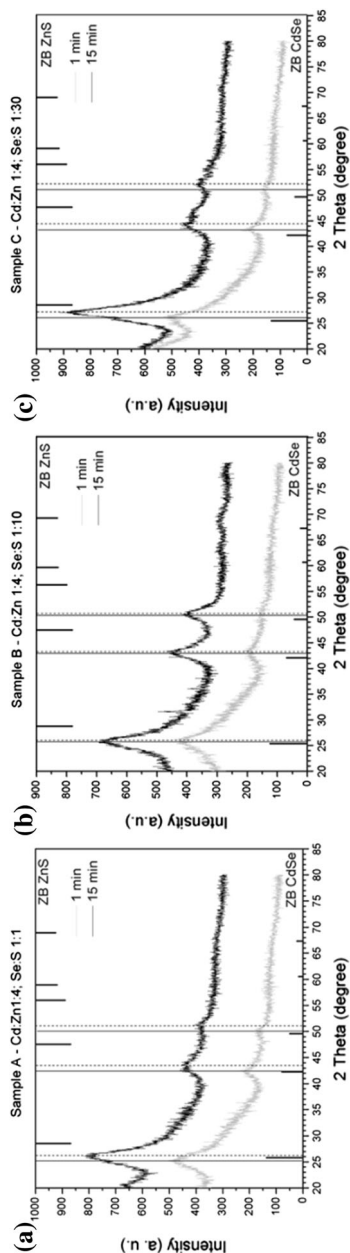


Fig. 6 XRD patterns of the heterostructured QDs with the adherent patterns of bulk zinc-blende CdSe and ZnS marked by *line* indicators at the *bottom* and the *top* of the figures, respectively

QDs shifted slightly towards higher angles after 15 min of growth, which is attributed to the increasing zinc and sulfur content: interplanar distances decrease as smaller S^{2-} and Zn^{2+} ions are gradually incorporated into the CdSe structure. The corresponding interplanar distances for sample A after 1 min are 3.50, 2.13, 1.83 Å and after 15 min: 3.41, 2.09, 1.78 Å; for sample B after 1 min: 3.45, 2.10, 1.81 Å and after 15 min: 3.44, 2.09, 1.80 Å; and for sample C after 1 min: 3.39, 2.09, 1.78 Å and after 15 min: 3.29, 2.04, 1.75 Å. The bulk interplanar distances for the zinc blende phase of CdSe are 3.50, 2.14, 1.83 Å, for CdS: 3.36, 2.06, 1.76 Å, for ZnSe: 3.26, 2.00, 1.70 Å and for ZnS (3.13, 1.92, 1.64 Å). The shift of the XRD peaks towards higher angles due to the decreasing interplanar distances confirms our hypothesis that core-shell quantum dots featuring a composition gradient can be grown in a single-step reaction if the synthesis conditions are controlled tightly. The success of this method is due to the different reactivities of the precursors.

Our results confirm that it is possible to synthesize composition gradient based heterostructured QDs with 1:4 initial Cd-to-Zn ratio in a single-pot reaction, which results in the preferred Cd rich cores and Zn rich shells. The most favorable ratio to the Se:S was 1:1, because at this ratio the Se content in the core of the QDs was high enough yet the S rich outer layers were also adequately formed. By decreasing the Se:S ratio, the amount of incorporated S increases rapidly, which results in the blue shift of the peak emission wavelengths of the QDs with similar size. These composition tunable emission peaks are favorable when the application requires having uniformly sized QDs with different emission wavelengths, e.g. in biological imaging [25].

Conclusions

Various heterostructured $Cd_xZn_{1-x}Se_yS_{1-y}$ quantum dots featuring chemical composition gradients were successfully synthesized in a one-pot reaction with CdSe rich core and ZnS rich shell structure. The size of these QDs was smaller than that of the comparable composition gradient based QDs synthesized under similar reaction circumstances but with different precursor ratios. The synthesized QDs were confirmed to exhibit variable photoluminescence emission wavelengths with the variation of initial Se:S ratio and/or with crystal size across the crystal growth time. The obtained QDs exhibited good size and shape uniformity and bright photoluminescence emissions. This synthesis method could be beneficial when it is more important to obtain CdSe-based QDs of good quality by an easy and rapid synthesis procedure than to have a precise control over the shell thickness like that offered by the conventional two-step synthesis method of core/shell QDs.

Acknowledgments The financial support of the OTKA NN 110676 project is acknowledged.

References

1. Alivisatos AP (1996) Semiconductor clusters, nanocrystals, and quantum dots. *Science* 271:933–937
2. Peng X, Manna L, Yang W, Wickham J, Scher E, Kadavanich A, Alivisatos AP (2000) Shape control of CdSe nanocrystals. *Nature* 404:59–61

3. Zhao J, Zhang J, Jiang C, Bohnenberger J, Basché T, Mews A (2004) Electroluminescence from isolated CdSe/ZnS quantum dots in multilayered light emitting diodes. *J Appl Phys* 96:3206–3210
4. Li Y, Rizzo A, Mazzeo M, Carbone L, Manna L, Cingolani R, Gigli G (2005) White organic light-emitting devices with CdSe/ZnS quantum dots as a red emitter. *J Appl Phys* 97:113501–113504
5. Burda C, Chen X, Narayanan R, El-Sayed MA (2005) Chemistry and properties of nanocrystals of different shapes. *Chem Rev* 105:1025–1102
6. Gur I, Fromer NA, Geier ML, Alivisatos AP (2005) Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science* 310:462–465
7. Michler P, Imamoglu A, Mason MD, Carson PJ, Strouse GF, Buratto SK (2000) Quantum correlation among photons from a single quantum dot at room temperature. *Nature* 406:968–970
8. Dahan M, Laurence T, Pinaud F, Chemla D, Alivisatos AP, Sauer M, Weiss S (2001) Time-gated biological imaging by use of colloidal quantum dots. *Opt Lett* 26:825–827
9. Hines MA, Guyot-Sionnest P (1996) Synthesis and characterization of strongly luminescing ZnS-capped CdSe nanocrystals. *J Phys Chem* 100:468–471
10. Talapin DV, Rogach AL, Kornowski A, Haase M, Weller H (2001) Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine–triethylphosphine oxide–triethylphosphine mixture. *Nano Lett* 1:207–211
11. Reiss P, Bleuse J, Pron A (2002) Highly luminescent CdSe/ZnSe core/shell nanocrystals of low size dispersion. *Nano Lett* 2:781–784
12. Peng X, Schlamp MC, Kadavanich AV, Alivisatos AP (1997) Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility. *J Am Chem Soc* 119:7019–7029
13. Mekis I, Talapin DV, Kornowski A, Haase M, Weller HJ (2003) One-pot synthesis of highly luminescent CdSe/CdS core–shell nanocrystals via organometallic and “greener” chemical approaches. *Phys Chem B* 107:7454–7462
14. Chen XB, Lou YB, Samia AC, Burda C (2003) Coherency strain effects on the optical response of core/shell heteronanostructures. *Nano Lett* 3:799–803
15. Dabbousi BO, Rodriguez-Viejo J, Mikulec FV, Heine JR, Mattoussi H, Ober R, Jensen KF, Bawendi MG (1997) (CdSe)/ZnS core–shell quantum dots: synthesis and characterization of a size series of highly luminescent nanocrystallites. *J Phys Chem B* 101:9463–9475
16. Bae W, Char K, Hur H, Lee S (2008) Single-step synthesis of quantum dots with chemical composition gradients. *Chem Mater* 20:531–539
17. Nag A, Kumar A, Kiran PP, Chakraborty S, Kumar GR, Sarma DD (2008) Optically bifunctional heterostructured nanocrystals. *J Phys Chem C* 112(22):8229–8233
18. Peng ZA, Xiaogang Peng (2002) Nearly monodisperse and shape-controlled CdSe nanocrystals via alternative routes: nucleation and growth. *J Am Chem Soc* 124:3343–3353
19. Cundari TR, Fu WT (1999) Reaction pathways for model II–VI precursors: a computational study. *Int J Quantum Chem* 71:47–56
20. Lee H, Yang H, Holloway PH (2007) Single-step growth of colloidal ternary ZnCdSe nanocrystals. *J Lumin* 126:314–318
21. Zhong X, Han M, Dong Z, White TJ, Knoll W (2003) Composition-tunable Zn_xCd_{1-x} nanocrystals with high luminescence and stability. *J Am Chem Soc* 125:8589–8594
22. Zhong X, Feng Y, Knoll W, Han M (2003) Alloyed Zn_xCd_{1-x} S nanocrystals with highly narrow luminescence spectral width. *J Am Chem Soc* 125:13559–13563
23. Gaponenko SV (1998) Optical properties of semiconductor nanocrystals. Cambridge University Press, Cambridge
24. Zhong Xinhua, Feng Yaoyu, Zhang Yuliang (2007) Facile and reproducible synthesis of red-emitting CdSe nanocrystals in amine with long-term fixation of particle size and size distribution. *J Phys Chem C* 111:526–531
25. Bailey RE, Nie SM (2003) Alloyed semiconductor quantum dots: tuning the optical properties without changing the particle size. *J Am Chem Soc* 125:7100–7106