High-Quality Violet- to Red-Emitting ZnSe/CdSe Core/Shell Nanocrystals

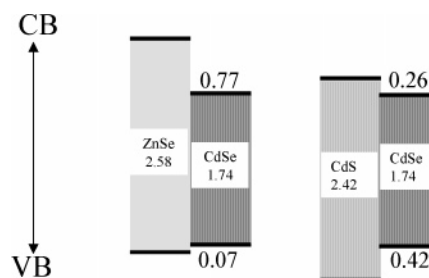Xinhua Zhong,*,[†,‡] Renguo Xie,[§] Ying Zhang,[‡]
Thomas Basché,[§] and Wolfgang Knoll*,[‡]

*Laboratory of Advanced Materials, Fudan University,
Shanghai 200433, People's Republic of China, Max-Planck
Institute for Polymer Research, 55128 Mainz, Germany, and
Institute of Physical Chemistry, University of Mainz,
55099 Mainz, Germany*

An important field in nanotechnology is the fabrication of composite structures comprising different semiconductor materials. Colloidal quantum dots (QDs) can be epitaxially coated with a shell of another material by various overgrowth methods. This gives rise to the so-called core/shell nanostructures. For many purposes, epitaxially grown core/shell semiconductor nanocrystals are of critical importance.[1] Thus far, extensive studies have been carried out on the so-called type-I QDs,[2−12] for which a wider band gap material is deposited to the core with a narrower band gap. As a result, both the electron and the hole are mostly confined in the core region, and consequently, the band gap almost remains constant or gives a small red-shift, while their photoluminescence quantum yield (PL QY) and stability can be greatly improved if compared with the plain core nanocrystals. Meanwhile several groups have attempted to fabricate the reverse type-I core/shell structure, where a material with narrower band gap was overgrown onto the core with wider band gap, and a significant red-shift of the band gap has been observed. The best-studied systems of the reverse type-I core/shell structure are CdS/HgS[13,14] and CdS/CdSe.[15] In the CdS/HgS system,[13,14] due to the undeveloped synthetic methods for the core and the shell growth, no distinctive absorption feature was observed, and the PL QYs were nearly zero. Even though the optical properties and the particle size

* Address correspondence to either author. E-mail: zhong@mpip-mainz.mpg.de (X.Z.); knoll@mpip-mainz.mpg.de (W.K.).
† Fudan University.
‡ Max-Planck Institute for Polymer Research.
§ University of Mainz.

(1) Rajeshwar, K.; Tacconi, N. R.; Chenthamarakshan, C. R. *Chem. Mater.* **2001,** *13,* 2765.
(2) Dabbousi, B. Q.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997,** *101,* 9463.
(3) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996,** *100,* 468.
(4) Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M.; Weller, H. *Nano Lett.* **2001,** *1,* 207.
(5) Mekari, T.; Banin, U. *Chem Mater.* **2003,** *15,* 3955.
(6) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997,** *119,* 7019.
(7) Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. *J. Am. Chem Soc.* **2003,** *125,* 12567.
(8) Mekis, I.; Talapin, D. V.; Lornowski, A.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2003,** *107,* 7454.
(9) Talapin, D. V.; Koeppe, R.; Götzinger, S.; Kornowski, A.; Lupton, J. M.; Rogach, A. L.; Benson, O.; Feldmann, J.; Weller, H. *Nano Lett.* **2003,** *3,* 1677.
(10) Reiss, P.; Bleuse, J.; Pron, A. *Nano Lett.* **2002,** *2,* 781.
(11) Cao, Y.; Banin, U. *J. Am. Chem. Soc.* **2000,** *122,* 9692.
(12) Cao, Y.-W.; Banin, U. *Angew. Chem., Int. Ed.* **1999,** *38,* 3692.

Figure 1. Schematic diagram of the band gap and band offsets (in eV) for interfaces between bulk ZnSe/CdSe and CdS/CdSe systems.

distribution of the recently reported CdS/CdSe system[15] have a significant improvement in comparison with the CdS/HgS, the optical properties of the CdS/CdSe system with a thin CdSe layer (<2 monolayer, ML) is still poor (no sharp distinctive feature in the absorption onset and almost no band-edge PL emission). Moreover, in the CdS/CdSe system the shell layer is grown layer by layer but not continuously, which renders it almost impossible to observe the effect of sub-monolayer shell (shell thickness <1 ML) on the core, and the obtained PL is not continuously tunable.

ZnSe, with a room temperature bulk band gap of 2.58 eV, has long been a material of choice for blue diode lasers. High-quality ZnSe nanocrystals with UV-blue emission have been reproducibly synthesized.[16] In addition, monodisperse, highly luminescent CdSe/ZnSe core/shell nanocrystals have been prepared.[10] Furthermore, ZnSe-based alloyed nanocrystals show superior PL properties.[17,18] These results prompted us to synthesize the ZnSe/CdSe system. As a core/shell heterostructure, ZnSe/CdSe would be superior to the newly reported CdS/CdSe. In the ZnSe/CdSe system, the same anion at the surface leads to a larger band offset in the conduction band (0.77 eV);[19] therefore, the wave function of the electron can dislocate in the shell completely. While in the CdS/CdSe system, the band offsets in the conduction band is only 0.26 eV,[19a] which results in only a partial dislocation of the charge carriers (Figure 1). Herein, highly luminescent (QYs = 40−85%) ZnSe/CdSe core/shell nanocrystals were prepared by the addition of Se/Cd precursors into a diluted ZnSe nanocrystals reaction solution. With the overcoating of CdSe shell onto the ZnSe cores, the emission colors of the obtained core/shell nanocrystals can be tuned consecutively from violet to red. The overcoating of a shell material with narrower band gap onto a core material with wider band gap would open a new route to produce

(13) Mews, A.; Eychmüller, A.; Giersig, M.; Schooss, D.; Weller, H. *J. Phys. Chem.* **1994,** *98,* 934.
(14) Braus, M.; Burda, C.; E1-Sayed, M. A. *J. Phys. Chem. A* **2001,** *105,* 5548.
(15) Battaglia, D.; Li, J. J.; Wang, Y.; Peng, X. *Angew. Chem., Int. Ed.* **2003,** *42,* 5035.
(16) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem. B* **1998,** *102,* 3655.
(17) Zhong, X.; Han, M.; Dong, Z.; White, T. J.; Knoll, W. *J. Am. Chem. Soc.* **2003,** *125,* 8589.
(18) Zhong, X.; Zhang, Z.; Liu, S.; Han, M.; Knoll, W. *J. Phys. Chem. B* **2004,** *108,* 15552.
(19) (a) Wei, S.-H.; Zunger, A. *Appl. Phys. Lett.* **1998,** *72,* 2011. (b) McCaldin, J. O.; McGill, T. C.; Mead, C. A. *Phys. Rev. Lett.* **1976,** *36,* 56. (c) Frensley, W. R.; Kroemer, H. *Phys. Rev. B* **1977,** *16,* 2642.

Communications

Chem. Mater., Vol. 17, No. 16, 2005 4039
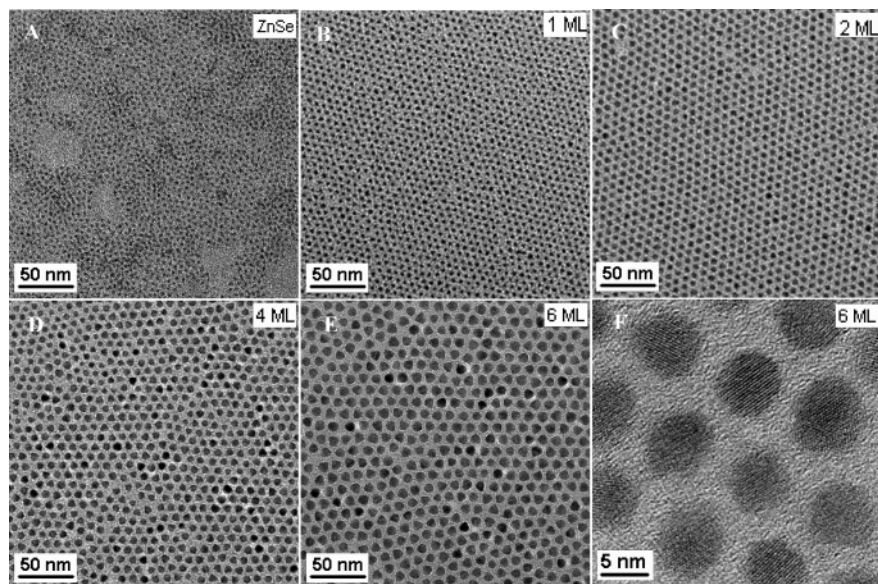
Figure 2. TEM images of plain ZnSe core nanocrystals and the corresponding ZnSe/CdSe core/shell nanocrystals with different shell thickness but identical cores: (A) wide-field TEM image of 2.8 nm ZnSe core nanocrystals; (B−E) wide-field TEM images of ZnSe/CdSe nanocrystals with 1, 2, 4, and 6 ML of CdSe, respectively (thickness of 1 ML CdSe = 0.7 nm in diameter); (F) HRTEM of ZnSe/CdSe nanocrystals with 6 ML of CdSe.

nanocrystals with tunable emission colors. The obtained high-quality ZnSe/CdSe nanocrystals can have practical applications in replacing CdSe-based QDs as desired emitters.

ZnSe core nanocrystals of a size range between 2.8 and 4.5 nm were prepared via a modified literature method.[16] Typically, 5.0 g of octadecylamine (97%, Aldrich) was heated to 310 °C under Ar flow. At this temperature, 0.3 mmol of Se in 2.0 mL of trioctylphosphine (TOP, 90%, Aldrich) was added to the reaction flask. After the temperature returned to 310 °C, 0.3 mmol of ZnEt$_2$ (95%, Strem) in 1.0 mL of TOP was swiftly injected into the reaction vessel. The reaction mixture was stirred at 300 °C for 10 min before the heating was stopped to terminate the reaction. The reaction solution was diluted to 25.0 mL by adding octadecene (ODE, 90%, Aldrich) at ∼70 °C before solidification took place. By this approach one can obtain ZnSe QDs with an average size of 2.8 nm and an emission wavelength at $\lambda = 375$ nm.

In a typical synthesis of ZnSe/CdSe core/shell nanocrystals, 2.5 mL of the crude ZnSe nanocrystals reaction solution (containing 0.03 mmol of ZnSe), 4.5 mL of ODE, and 0.5 mL of oleylamine (97%, Aldrich) were mixed together and heated to 230 °C. Equimolar amounts of the Cd and Se stock solutions (0.1 M Se stock solution was obtained by dissolving Se powder with TOP in ODE; 0.1 M Cd stock solution was prepared by dissolving CdO with 6-fold of oleic acid in ODE) were mixed and loaded in a syringe and added dropwise (about 1 drop in every 2−3 s) to the vigorously stirred solution of ZnSe core nanocrystals via a syringe pump over a period of 2−3 h. Periodically small aliquots were removed in order to monitor the shell growth. With the addition of the Se/Cd precursors, the originally colorless solution turned slightly yellow, then dark yellow, and finally deep red. The addition rate of the precursors plays a critical role for the epitaxial growth of a CdSe shell onto the ZnSe cores. Slow addition can lead to all the Cd/Se precursors growing heterogeneously onto the existing ZnSe nuclei instead of undergoing independent homogeneous nucleation.

Slow addition ensures a quantitative use of the injected Cd/Se precursors. This can be used to determine the nanocrystal size in samples with very thin shells (<1 ML).

Figure 2 shows wide-field transmission electron microscopy (TEM) images of 2.8 nm plain ZnSe cores and four representative core/shell nanocrystals images with 1, 2, 4, and 6 ML of CdSe shell derived from the same batch of 2.8 nm ZnSe cores (thickness of a CdSe monolayer = 0.7 nm in diameter). The sizes of the nearly dot-shaped core/shell nanocrystals in Figure 2 approximately match the theoretical thickness calculated from the amount of injected stock solution, which gives strong evidence for the epitaxial growth of CdSe onto the ZnSe cores and excluding the independent homogeneous nucleation of CdSe. The nearly monodisperse core/shell nanocrystals formed good, well-ordered long-distance two-dimensional (2D) superlattices and exhibited hexagonal packing in most areas as shown in the TEM images. This demonstrates that the size and shape of the obtained core/shell particles are uniform. All the as-prepared ZnSe/CdSe core/shell nanocrystals with shell thicknesses ranging from 1 to 6 ML have a narrow size distribution with a relative standard deviation (σ) of 3−5% without any post-preparation fractionation or size sorting. The corresponding size distribution histograms are available in the Supporting Information. This size distribution is comparable to or even better than that of the best results of the most advanced and frequently studied plain CdSe system. It should be noted that the size distribution of the core/shell QDs is significantly improved in comparison with that of the corresponding ZnSe core particles. This observation is contrary to the commonly reported shell growth procedures, for which by the increase of the shell thickness, the size distribution of the resulting core/shell particles usually deteriorates severely.[2−5] The nearly uniform size and shape distribution in the obtained ZnSe/CdSe core/shell nanocrystals mainly originate from the higher stability of the shell precursors used (elemental Se and CdO). The higher stability of the precursors provides an extended period of existence for the free precursors,

4040   *Chem. Mater., Vol. 17, No. 16, 2005*

Communications
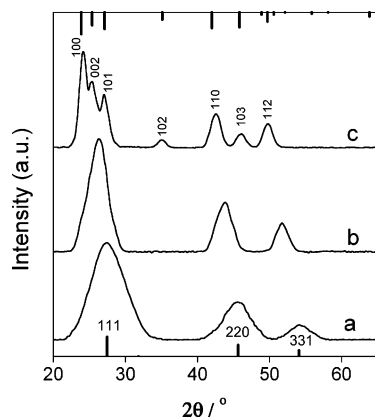
Figure 3. Powder XRD patterns of the plain ZnSe core nanocrystals with a diameter of 2.8 nm (a) and ZnSe/CdSe core/shell nanocrystals with a CdSe shell thickness of 2 ML (b) and 6 ML (c). The line XRD spectra correspond to bulk zinc blende ZnSe (bottom) and bulk wurtzite CdSe (top), respectively.

leading to the smaller particle bearing a larger shell growth rate, and resulting in the size focusing similar to the previously studied "focusing" mechanism for the growth of binary nanocrystal systems.[20−22] The higher stability of the precursors can also promote the even deposition of shell molecules to all core nanocrystals, resulting in shell layers with nearly the same thickness around each core nanocrystal. The high-resolution TEM images (Figure 2F) of the obtained ZnSe/CdSe core/shell structures reveal uniform spherical nanocrystals with well-resolved lattice fringes, demonstrating the highly crystalline nature of the nanocrystals.

Powder X-ray diffraction (p-XRD) patterns for the ZnSe core and for ZnSe/CdSe core/shell nanocrystals with increasing shell thickness are presented in Figure 3. As reported in the literature, the ZnSe XRD pattern consists of the characteristic peaks of zinc blende (cubic) ZnSe, which are broadened due to the finite crystalline size. The p-XRD patterns of the ZnSe/CdSe core/shell nanocrystals shifted from a zinc blend ZnSe-like to a zinc blend CdSe-like, and further to a wurtzite CdSe-like pattern upon the increase of the CdSe shell thickness. When a thin CdSe shell (<4 ML) is overgrown onto the cubic ZnSe template, the general pattern of the cubic lattice is maintained in the core/shell structures, but the diffraction peaks shift to smaller angles consistent with the larger lattice constant for CdSe compared with ZnSe. In addition, the diffraction peaks get narrower. This narrowing indicates that the crystalline domain for the core/shell structure is larger, which provides direct evidence for the epitaxial growth mode of the shell.[2−9] Because CdSe nanocrystals in these growth conditions preferentially form the wurtzite (hexagonal) structure,[7,15] with the increasing of the CdSe shell thickness, the diffraction pattern of the core/shell nanocrystals shift from a zinc blend pattern to a wurtzite one. The diffraction pattern of the core/shell structure with 6 ML CdSe shell is almost the same as the wurtzite CdSe nanocrystals of the same size. The domination of the CdSe pattern for the core/shell nanocrystals with 6 ML CdSe shell

is expected given that the CdSe:ZnSe ratio is ∼15:1 in these nanocrystals.

The most direct and immediate evidence for the shell growth comes from the absorption and PL spectra. Both single PL emission peak in the PL spectra and no CdSe correlated absorption peak in the absorption spectra can rule out any separate homogeneous nucleation of CdSe nanocrystals. Figure 4 shows the evolution of the absorption and the PL spectra measured for aliquots taken from the reaction solution during the growth of the CdSe shell on the same batch of ZnSe cores with an average diameter of 2.8 nm. With the increase of the CdSe shell thickness around the ZnSe cores, both the absorption onsets in the absorption spectra and the band-edge PL emission peaks in the PL spectra shift systematically to the red (or lower band gap energy). The small Stokes shift (∼15 nm) between the emission peaks and the corresponding first excitonic absorption onsets indicates the dominant band-edge luminescence from the core/shell nanocrystals without the appearance of deep trap emission at the long-wavelength side. With the increase of the shell thickness to 0.1, 0.2, 0.5, 1, 2, 4, and 6 ML, the corresponding PL peaks shift to $\lambda = 418, 473, 515, 566, 614, 654$, and 674 nm, respectively, from the original $\lambda = 375$ nm corresponding to the ZnSe cores. The PL emission from these core/shell nanocrystals spans the whole visible spectrum from the violet to the red. On the basis of the effective mass approximation theoretical approach developed by Brus and co-workers,[23] Haus et al.,[24] and Weller and co-workers,[25] the band gap energy of this type of core/shell system depend on the radius of the core, the shell thickness, the conduction band offsets of the materials, and the effective masses of the charge carriers in the respective materials. Due to the larger conduction band offset in the ZnSe/CdSe system (the conduction band of CdSe shell is 0.77 eV lower than that of the core ZnSe), the charge carriers are mostly delocalized into the CdSe shell material with narrower band gap, especially if thicker shells are formed. The finding that identical emission wavelengths of the obtained ZnSe/CdSe core/shell nanocrystals cannot be obtained by the binary ZnSe or CdSe system or by the alloyed $Zn_xCd_{1−x}Se$[17,18] nanocrystals with the same particle size as the ZnSe/CdSe nanocrystals gives our claimed core/shell structure further support.

With the overcoating of the CdSe shell, the QYs of the core/shell nanocrystals increase steadily from ∼40% for the original core particles reaching the highest value of ∼85% after one full monolayer is formed and keeping this value till 3 ML.[26] If a shell with more than 3 ML is formed, the QY decreases gradually (the QY for 6 ML is ∼25%). The lower QYs of the thicker shelled ZnSe/CdSe QDs may originate from the weaker quantum confinement effect due to their larger particle sizes (the particle radius of the ZnSe/

(20) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
(21) Peng, Z. A.; Peng, X. *J. Am. Chem Soc.* **2001**, *123*, 1389.
(22) Talapin, D. V.; Rogach, A. L.; Haase, M.; Weller, H. *J. Phys. Chem. B* **2001**, *105*, 12278.

(23) Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327.
(24) Haus, J. W.; Zhou, H. S.; Honma, I.; Komiyama, H. *Phys. Rev. B* **1993**, *47*, 1359.
(25) Schooss, D.; Mews, A.; Eychmüller, A.; Weller, H. *Phys. Rev. B* **1994**, *49*, 17072.
(26) The PL QYs of QDs were determined by comparing the integrated emission of a given QD sample in dilute chloroform solution with those of fluorescent dyes with known photoluminescent efficiencies.
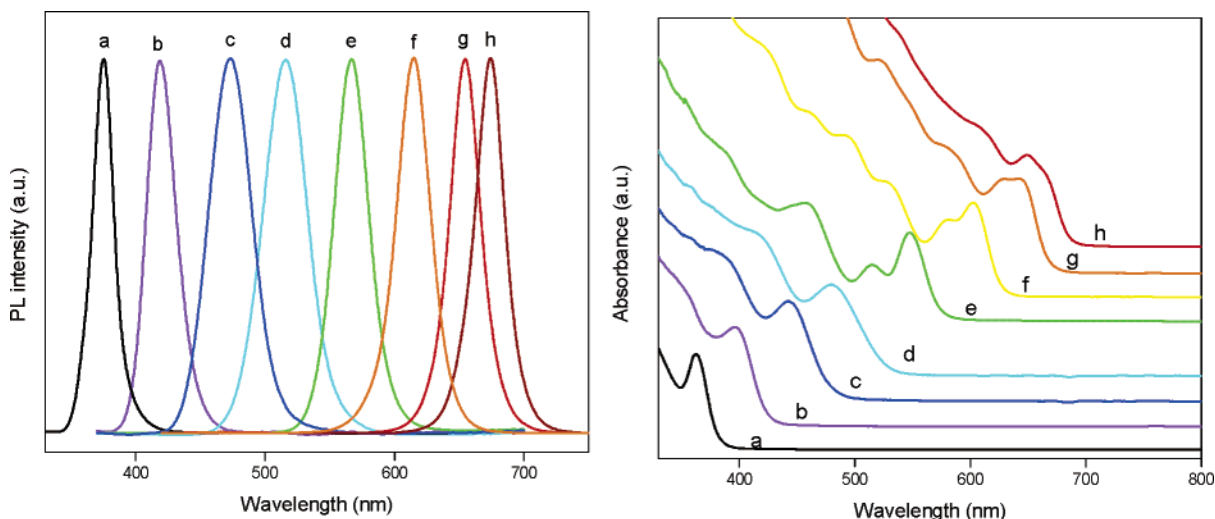
Figure 4. Normalized PL (left, λ_{ex} for ZnSe = 320 nm, for ZnSe/CdSe = 360 nm) and corresponding absorption (right) spectra of plain ZnSe core nanocrystals (a) and ZnSe/CdSe core/shell nanocrystals with different numbers of monolayers of CdSe shell: b, 0.1; c, 0.2; d, 0.5; e, 1; f, 2; g, 4; h, 6.
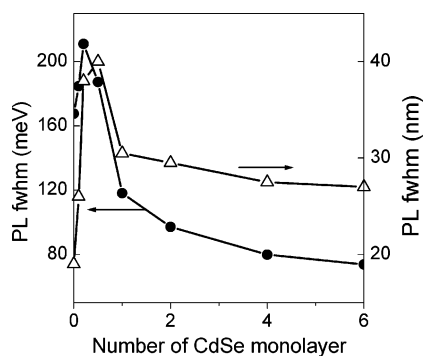
Figure 5. Evolution of PL fwhm in meV (solid circle, left) and in nm (triangle, right) of ZnSe/CdSe nanocrystals in the process of overgrowing CdSe layer.

CdSe dots with 6 ML of shell is 3.5 nm, which is close to the values of the corresponding exciton Bohr radii of ZnSe (4.5 nm) and CdSe (5.4 nm)). With the overcoating CdSe shell on the ZnSe cores, the spectral widths (full width at half-maximum, fwhm) of the resulting ZnSe/CdSe core/shell nanocrystals decreases systematically when more than one full monolayer is overgrown (from the original 168 meV corresponding to the initial ZnSe core decreasing to 74 meV corresponding to core/shell QDs with a 6 ML shell; Figure 5). When less than one full monolayer of CdSe shell is overgrown, the PL spectral width is a little widened in comparison with the cores. This may be due to the uneven distribution of the shell material around the cores. The systematic decrease of the PL spectral width of the ZnSe/CdSe core/shell nanocrystals with the overgrowing the CdSe shell originates from the size focusing of the resulting core/shell nanocrystals as well as from the weaker quantum confinement effect (QCE) due to the larger particle size. In the weaker QCE region, an identical size difference would translate into a relatively smaller variation in the band gap energy and, consequently, into a narrower emission spectral width.[27] The high QYs of the obtained ZnSe/CdSe QDs in organic media can retain for more than 1 year at ambient atmosphere. Due to the dislocation of exciton wave function

around the shell, the high luminescence of the obtained QDs cannot survive when transfer into aqueous media.

In the absorption spectra, all samples show a very sharp first excitonic absorption onset. After one full monolayer of shell is formed, up to five resolved electronic transitions are observed, which are comparable with the best CdSe samples.[2−10,28−30] This indicates a very narrow size distribution of the ZnSe/CdSe nanocrystals. In all samples, almost no observable absorption tail at the low energy side indicates that scattered light from the colloidal dispersions does not exist. Such distinct absorption feature has not ever been observed in the former similar cases.[13−15] The thicker overcoated particles show some increase in relative absorptivity over the ZnSe cores and the thinner coated particle in the blue light region of the spectrum as a result of the higher effective density of states expected due to their larger sizes. This absorbance increase in the short wavelength window has no contributions from small CdSe nanocrystals because the absorption spectra keep this feature even after careful size selection in order to get rid of the small particles should they exist.

In summary, high-quality (uniform in size and morphology, good crystallinity, high QY, sharp and narrow absorption onsets and PL peaks) ZnSe/CdSe core/shell nanocrystals have been prepared by the deposition of stable and inexpensive cationic and anionic precursors (CdO and elemental Se, respectively) into a diluted crude ZnSe nanocrystals reaction solution. This synthesis can be performed in one vessel and thus can easily be scaled up. Through an identical procedure, the emission colors can be tuned continuously from violet to red via a simple variation of the shell thickness of the core/shell nanocrystals. Both synthetic methods for the core and the shell overcoating are very facile and reproducible, and the reagents used are commonly available. The overcoating of a shell material with narrower band gap onto a core material with wider band gap would open a new

(27) Zhong, X.; Feng, Y.; Knoll, W.; Han, M. *J. Am. Chem. Soc.* **2003**, *125*, 13559.

(28) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

(29) Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.

(30) Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049.

way to produce emission color tunable nanocrystals. The optical properties of the obtained ZnSe/CdSe nanocrystals are comparable to or even better than the best results reported for the plain CdSe nanocrystals. The obtained high-quality ZnSe/CdSe nanocrystals can have practical applications in replacing CdSe based QDs as desired emitters.

Supporting Information Available: Corresponding size distribution histograms. This material is available free of charge via the Internet at http://pubs.acs.org.

CM050948Y