DOI: 10.1002/anie.201206333

Core–Shell Structures

Bright and Stable Alloy Core/Multishell Quantum Dots[**]

*Shinae Jun and Eunjoo Jang**

Quantum dots (QDs) have been considered as an excellent light-emitting material for next-generation displays because of their high quantum efficiency (QE), broad absorption, highly saturated color, and simple color tunability.[1] The synthetic methods to prepare high-quality QDs in a colloidal phase have been continuously developed,[2] and it has been proposed that the advantages of the QDs can be practically realized in various optoelectronic devices in the near future.[3,4] In particular, red-light-emitting CdSe-based QDs have been significantly optimized in terms of emission wavelengths, QE, and tolerance against fabrication conditions such as high-temperature curing or chemical treatments.[5] The red-light-emitting QDs showed great potential as color converting phosphor for white-light-emitting diodes (LEDs) to improve the average color rendering index (R_a) up to 90, which is a quality standard for general illuminations.[6] The electroluminescent device employing red QDs as an active fluorophore, which endure a thiol cross-link process to increase the packing density, showed high brightness of 12380 $\mathrm{cd\,m^{-12}}$ and external QE (EQE) of 2.1 $\mathrm{Lm\,W^{-1}}$.[5] However, the QE and stability diminish rapidly as the size of QDs is reduced, because the density of the surface defects are more easily generated by a large surface-to-volume ratio and the steric hindrance of the capping ligands.[7] The commercially available CdSe/ZnS (Evident Technology) core/shell (C/S) QDs routinely showed a QE of 50% at 530 nm emission. The extremely small CdSe/CdS C/S QDs ($d \approx 2.8$ nm) showed a QE of 60% at 517 nm emission.[8] The alloy C/S CdZnSe/CdZnS QDs ($d \approx 3$ nm) showed 50–60% QE at 520 nm[9] and the CdZnSe/ZnS QDs ($d \approx 4.4$ to 6 nm) showed 60–70% QE at 520–535 nm.[10] The reverse type I ZnSe/CdSe C/S QDs ($d \approx 3.5$ nm) showed a 515 nm emission with comparable QE of about 40%.[11] Compared to the previously reported red QDs that showed a QE of 80–90%,[6,12] there is much room for improving the QEs of green QDs. And, the optical properties of the C/S QDs with a thin passivating shell layer easily degraded during the general fabrication processes such as ligand exchange,[13] incorporation into the solid states and exposure to a high dose of radiation.[14] Although multishell passivation is known as the most effective method to improve photostability, previously reported mutishell CdSe/CdS QDs (> 10 monolayers) showed only 50% of the initial QE,[13,15] resulting from interfacial strain between the CdSe core and the thick CdS shell.

Herein, we present a new green-light-emitting alloy core/multishell (AC/MS) QD structure that shows a high QE as well as a high photostability. The AC/MS QDs with peak emission at 520 nm showed a relatively large size ($d > 7$ nm) compared to previously reported C/S structures. The AC/MS QD solutions showed up a QE of up to 100% and the QD–silicone polymer composites, which were subjected to a 150 °C thermal curing process for 2 h, maintained the luminescence to exhibit a EQE of 70% as a green color converter on a 450 nm blue LED.

A green-light-emitting, zinc blend structured CdSe QD 3.5 nm in diameter consists of 790 cadmium and selenium atoms, and among them 245 atoms are located on the crystal surface (see Section S1 in the Supporting Information). The inorganic shell is supposed to passivate 30% of the atoms with dangling bonds to cover the defects efficiently, but still a large interface remains between the core and the shell layers. Thin shell passivation is insufficient to cover all the surface defects, and thick shell passivation causes strained interfaces. Therefore, to obtain efficient and stable green QDs, a nanostructure with inherently larger core and smaller surface area than CdSe with 3.5 nm diameter is more favorable. For example, the preparation of blue-light-emitting ZnSe or ZnS cores followed by additional growth of smaller band-gap materials such as CdS could be one of the choices for the larger green QDs.[16] Here, we used a previously reported CdSe//ZnS interfused gradient alloy structure as a blue core (PL = 458 nm).[17] The gradient alloy CdSe//ZnS QDs have two benefits. Compared to the ZnSe or ZnS QDs, it is more convenient to prepare uniform CdSe cores through the well-known synthetic method.[18] Furthermore, the CdSe//ZnS QDs have relatively stable ZnS outermost shells so that the storage and further synthetic processes do not change the properties of the optical core. The additional crystal layer was grown on the surface of the blue-light-emitting CdSe//ZnS QDs with Cd-, Zn-, and S-containing precursors to build CdSZnS multishells. Since CdS has a smaller energy band gap than the alloy core and excitons can be delocalized all over the CdSe//ZnS/CdS crystalline structure,[19] the emission of the CdSe//ZnS/CdSZnS QDs shifts to lower energy depending on the thickness of the CdS layer. And, the outermost ZnS shell enhances the QE as well as the stability. Figure 1a represents the conceptual structures of CdSe/ZnS C/S (A), CdSe core (B), CdSe//ZnS alloy core (C), and CdSe//ZnS/CdSZnS AC/MS QDs with different CdS thicknesses depending on the Cd precursor concentrations (D; marked with the millimolar concentration of the Cd precursor used under defined conditions). The thickness of the CdS interlayer determines the entire size of the QDs as well as the energy

---

[*] Dr. S. Jun, Dr. E. Jang
Advanced Material Research Center
Samsung Advanced Institute of Technology
Samsung Electronics Co., Mt.14-1, Nongseo-Dong
Giheung-Gu, Yongin-Si, Gyeonggi-Do, 449-712 (Korea)
E-mail: ejjang12@samsung.com

[**] The authors thank Y. Ham at Samsung Electronics for the ICP-AES analyses and for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206333.

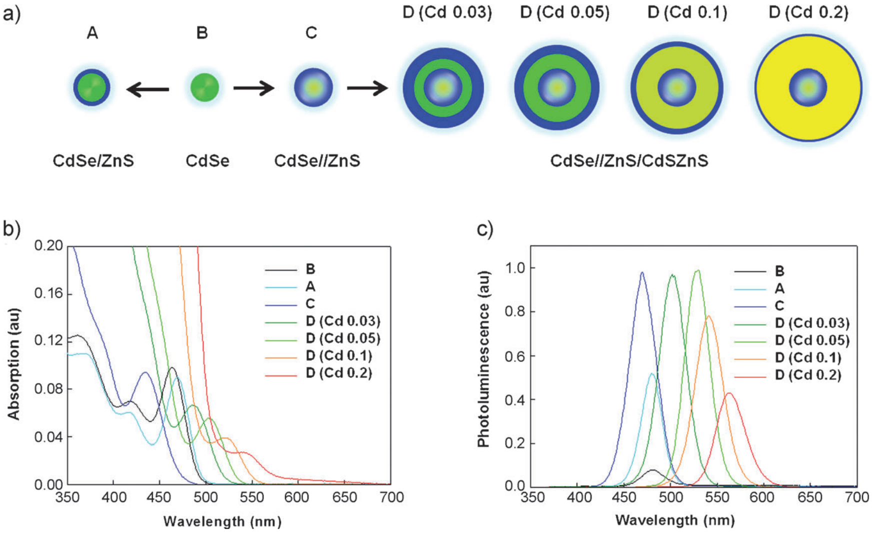

Figure 1. a) Schematic structures of CdSe/ZnS (A), CdSe (B), CdSe//ZnS (C), and CdSe//ZnS/CdSZnS (D). QDs prepared at various Cd precursor concentrations. b) UV/Vis absorption spectra. c) Photoluminescence spectra of the QDs.

band gap, therefore, the degree of the red-shift from the wavelength of the blue-light-emitting alloy core can be controlled by the growth of a CdS layer. Figure 1 b and c shows the UV/Vis absorption and photoluminescent emission properties of the QDs. The CdSe/ZnS C/S showed the same emission wavelength to the CdSe core at 481 nm with improved QE of 52 %, but the CdSe//ZnS alloy showed a stronge blue-shifted emission at 458 nm with a highly improved QE up to 100 %. Since the CdSe//ZnS interfused alloy structure has a reduced lattice strain between core and shell to provide more uniform and stable passivation, it reached the best efficiency ever reported for blue-light-emitting QDs (Section S2).

Based on TEM images (Section S3) and inductively coupled plasma atomic emission spectroscopy analysis (Section S4), structural information of the QDs was obtained and the thickness of each shell layer was calculated (Table 1) based on the assumption that the fast growing CdS formed the inner shell and relatively slow growing ZnS formed the outermost shell.[20] Although the real CdS and ZnS multishells might not form sharp edges, as shown in Figure 1, the thickness of each shell layer gives important information about the boundary conditions for the preparation of QD structures under different reaction conditions.

The blue-light-emitting CdSe//ZnS QDs have a larger band gap and a larger particle size than the CdSe core or the CdSe/ZnS C/S QDs. Assuming a crystalline lattice distance of ZnS ($a = 0.312$) based on the (111) surface of the cubic structure, more than one monolayer of ZnS was coated on the CdSe surface of the CdSe/ZnS C/S QDs and more than two monolayers of ZnS were coated on the CdSe surface of CdSe//ZnS alloy core QDs, and these correlates well with each elemental ratio increase of Zn and S for the QDs. To control the wavelength of the AC/MS QDs, the amount of Cd precursor was increased from 0.03 to 0.2 mmol at a fixed amount of Zn precursor. The emission wavelengths of the AC/MS QDs were observed in the range of 502 to 563 nm and the QEs was found in the range of 100 to 43 %. From the blue-light-emitting CdSe//ZnS to the green-light-emitting CdSe//ZnS/CdSZnS (amount of Cd = 0.05 mmol) the QE showed almost unity, but the QE declined when the amount of Cd was increased to more than 0.1 mmol (Section S2). Based on the ICP-AES analyses, the relative Cd ratio in the QDs increased with an increasing amount of Cd precursors. However, the relative ratio of Zn decreased slightly as the amount of the Zn precursor was fixed. This observation was explained by the fact that Cd and Zn react with S competitively and that the excess amount of Cd retarded the reaction of Zn and S.[20] As the size of the QDs evolved to render the CdS layers thicker, the fixed amount of ZnS became deficient to passivate the increased surface area. When an amount of 0.2 mmol of Cd precursor was used, the thickness of the outermost ZnS shell was less thick than a monolayer which resulted in a severely reduced QE. Therefore, it was expected that the QEs of the AC/MS QDs with a thick CdS interlayer could be enhanced as the amount of the Zn precursor increased with increasing amount of Cd precursor. When 0.2 mmol of Cd precursor was used, supplemental Zn precursor was added after 30 minutes of the reaction. This resulted in an improved QE up to 96 % as well as an increased thickness of the ZnS shell (Section S5).

The stability of the AC/MS QDs against intense UV radiation and high-temperature curing processes was tested. Both AC/MS QDs and C/S QDs, having fluorescence with same peak wavelength at 520 nm, were drop-casted on the quartz substrate and exposed to 365 nm UV radiation of 3 mW cm^{-2} intensity. After 200 h, the AC/MS QDs maintained 95 % of the initial luminescence although the C/S QDs retained only 20 % (Figure 2 b and e). When the QDs absorbed high-energy photons continuously, the organic ligands coor-

Table 1: Size and thickness of each layer in the multishell of the different QD structures.

QD Structures	*d* [nm][a] by TEM	*d* [nm][a] by ICP	CdS[b] Thickness [nm]	ZnS[b] Thickness [nm]
CdSe[b]	2.95 ± 0.24		–	–
CdSe/ZnS	3.81 ± 0.31	3.63	–	0.34
CdSe//ZnS	4.30 ± 0.31	4.43	–	0.74
AC/MS Cd 0.03[c]	6.73 ± 0.33	7.00	0.28	1.01
AC/MS Cd 0.05[c]	7.17 ± 0.60	7.39	0.74	0.74
AC/MS Cd 0.1[c]	8.29 ± 0.30	8.04	1.36	0.45
AC/MS Cd 0.2[c]	9.30 ± 0.41	9.45	2.32	0.19

[a] Diameter of the QDs. [b] The detailed procedure for calculating each shell layer is given in Section S4. [c] Amount of Cd in mmol.

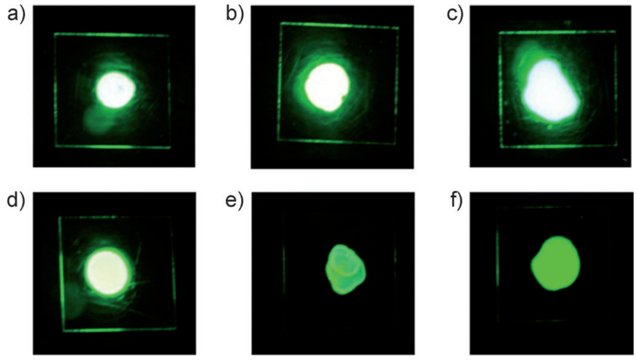

Figure 2. Photos taken under exposure to 365 nm UV light: a) AC/MS QD, initial. b) AC/MS QD, UV exposure 200 h. c) AC/MS QD, after a silicone curing process. d) C/S QD, initial. e) C/S QD, UV exposure for 200 h. f) C/S QD, after a silicone curing process.

dinated on the QD surface could be easily degraded or detached to generate surface defects that caused luminescence quenching or oxidation of the structure.[19] Therefore, the strong photostability of the AC/MS QDs is attributed to the inorganic shell, which is compact enough to be unaffected by alterations of the organic ligands. This property is also important for the preparation of robust QD–polymer composites for fabrication of practical devices such as LED encapsulation. The PL of the C/S QDs decreased significantly when the C/S QDs were mixed with a polymer resin and cured at high temperatures. The degree of PL quenching was dependent on the compatibility of the QDs with the polymer resins and the curing temperature. Acrylate polymers are beneficial for maintaining the initial luminescence[3] because the acrylic acid functional group can coordinate on the QD surface. However, the acrylate polymers are not stable as an encapsulating material used for long-term operating optical devices such as LEDs. Silicone polymers are generally used for LED encapsulants because of their thermal stability, transparency, and resistance to oxygen and UV light. For practical LED applications, QDs are required that can be mixed with a silicone encapsulant and maintain their original optical properties after packaging processes. Both AC/MS and C/S QDs were mixed with the silicone resin (Dow Corning, EG6301)[18] and cured at 150 °C for 2 h. The AC/MS QDs showed 71 % of the initial luminescence after curing. However, the C/S QDs retained only 10 % of the initial luminescence (Figure 2 c and f). Therefore, the new structure of the AC/MS green-light-emitting QDs showed an improved performance as a color-converting material for LED applications with a QE of 100 % in solution, a high stability against photobleaching under UV-light exposure, and thermal curing even in the silicone polymer composites.

We prepared a QD-LED package (Figure 3 a) by dispensing a mixture of 1 wt % of green-light-emitting AC/MS QDs (PL peak at 522 nm) and silicone resin (Dow Corning, EG6301) on the blue LED chip (emission peak at 450 nm, Seoul Semiconductor Co.). The blue LED and the QD-LED were operated with a 60 mA current at 3.3 V and both spectra are shown in Figure 3 b. The green emission from the AC/MS QDs slightly shifted to 530 nm and the full width at half maximum (FWHM) was 35 nm. The EQE of the AC/MS QD-LED was 70 % which is the best efficiency ever reported for green QD-LEDs. The color coordination of the green spectrum was marked at (0.209, 0.742) in the CIE1931 color space (Figure 3, inset), which is located far outside the sRGB color triangle ((xR, yR) = (0.64, 0.33), (xG, yG) = (0.30, 0.60), (xB, yB) = (0.15, 0.06)). This finding indicates that a highly color-saturated LED display can be realized by using the green QDs because the color coordinate of the green spectrum of the QD-LED covers an area larger than the sRGB color space.

In conclusion, we have synthesized novel AC/MS CdSe//ZnS/CdSZnS structures of larger size with a surface area reduced relative to the simple C/S CdSe/ZnS QDs, which have a simlar energy band gap. The AC/MS QDs employ a blue-light-emitting CdSe//ZnS alloy core and the emission wavelength can be controlled by an additional CdS shell. In the green-light-emitting region, AC/MS QDs showed the best luminescence efficiency of 100 % with both improved photo- and chemical stabilities. The green-color-converting QD-LED shoowed an excellent color gamut and the highest EQE ever reported.

Experimental Section

Synthesis of AC/MS QDs (CdSe//ZnS/CdSZnS Cd 0.05): CdO (0.4 mmol, Aldrich, 99.99 + %) and octadecylphosphonic acid (0.8 mmol, Alfa) were mixed in trioctylamine (16 g, Aldrich, 95 %). The mixture was degassed, heated to 150 °C under rapid stirring, and then the temperature was further increased to 300 °C under N_2 flow. The Se precursor was prepared from a Se powder (Alfa, 200 mesh 99.999 %) and trioctylphosphine (Aldrich, 90 %) as a 2.0 M solution. The CdSe core QD was prepared by quick injection of 1 mL of Se precursor into the Cd-containing reaction mixture at 300 °C. After 2 minutes, the reaction mixture was cooled to 50–60 °C. An organic residue was precipitated from the reaction mixture by single centrifugal separation. Ethanol (Fisher, HPLC grade) was added to the CdSe solution until the opaque flocculation was observed. The CdSe cores were separated by a further centrifugal step and the precipitates were dispersed in toluene (Sigma Aldrich, anhydrous 99.8 %). The optical density of the 100-times diluted CdSe core solution was adjusted to 0.1 at the first absorption maximum (463 nm). Zinc acetate (0.4 mmol, Aldrich, 99.99 %) and andoleic acid (0.8 mmol, Aldrich, 90 %) were mixed in 16 g of trioctyl-

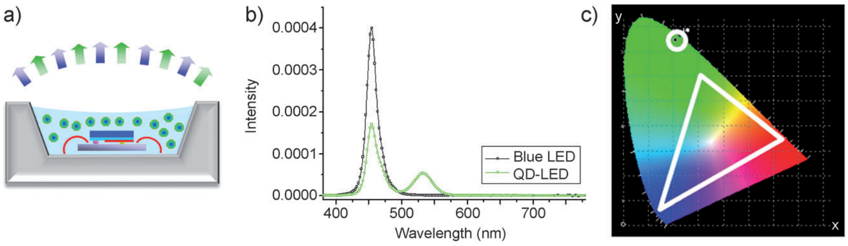

Figure 3. a) Side view of a QD-LED. b) Spectra of a blue LED and a green color converting QD-LED operated with 60 mA current at 3.3 V. c) Color coordination of the green spectrum (black spot with white circle) and sRGB color triangles (white line) on the CIE 1931 color space.

amine. The mixture was heated and degassed at 150 °C, and further heated to 300 °C under N_2 flow. The CdSe core solution (1 mL) was injected into the Zn-containing solution at a rate of 0.5 mL min^{-1}. After core injection, 1.6 mmol of *n*-octanethiol in 2 mL of trioctylamine (TOA) was added at a rate of 1 mL min^{-1}. ZnS was grown for 40 min, and the reaction mixture was cooled to room temperature.[17] The prepared CdSe//ZnS alloy cores were separated by the addition of ethanol and centrifuged. The CdSe//ZnS QDs were dispersed in toluene and the optical density of the 100-times diluted solution was adjusted to 0.1 at the first absorption maximum (434 nm). Cadmium acetate (0.05 mmol), zinc acetate (0.4 mmol), and oleic acid (1.5 mmol) were mixed in 20 mL TOA. The mixture was degassed and heated to 120 °C, and then the temperature was further increased to 320 °C under N_2 flow. The CdSe//ZnS solution (0.6 mL) was injected into the Cd- and Zn-containing solution. Right after injection of the alloy core, 2 mL of 0.4 M sulfur in trioctylphosphine was added to the reaction mixture at a rate of 1 mL min^{-1}. The mixture was rapidly stirred for 30 minutes by keeping the reaction temperature. Then the CdSe//ZnS/CdSZnS AC/MS QDs were separated by adding ethanol, centrifuged, and dispersed in toluene. To control the wavelength of the green emission, the amount of cadmium acetate was varried from 0.03 to 0.2 mmol.

Received: August 7, 2012
Revised: October 29, 2012

Keywords: core–shell structures · light-emitting diodes · nanocrystals · quantum dots · semiconductors

[1] a) L. Spanhel, M. Haase, H. Weller, A. Henglein, *J. Am. Chem. Soc.* **1987**, *109*, 5649 – 5655; b) V. L. Colvin, A. P. Alivisatos, J. G. Tobin, *Phys. Rev. Lett.* **1991**, *66*, 2786 – 2789; c) A. P. Alivisatos, *J. Phys. Chem.* **1996**, *100*, 13226 – 13239; d) A. P. Alivisatos, *Science* **1996**, *271*, 933 – 937.

[2] a) C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* **1993**, *115*, 8706 – 8715; b) A. A. Guzelian, U. Banin, A. V. Kadavanich, X. Peng, A. P. Alivisatos, *Appl. Phys. Lett.* **1996**, *69*, 1432 – 1434; c) Z. A. Peng, X. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 183 – 184; d) T. Trindade, P. O'Brien, N. L. Pickett, *Chem. Mater.* **2001**, *13*, 3843 – 3858; e) M. A. Hines, P. Guyot-Sionnest, *J. Phys. Chem. B* **1996**, *100*, 468 – 471; f) X. Peng, M. C. Schlamp, A. V. Kadavanich, A. P. Alivisatos, *J. Am. Chem. Soc.* **1997**, *119*, 7019 – 7029; g) B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen, M. G. Bawendi, *J. Phys. Chem. B* **1997**, *101*, 9463 – 9475; h) E. Jang, S. Jun, Y. Pu, *Chem. Commun.* **2003**, 2964 – 2965; i) J. Lim, S. Jun, E. Jang, H. Baik, H. Kim, J. Cho, *Adv. Mater.* **2007**, *19*, 1927 – 1932; j) R. Xie, D. Battaglia, X. Peng, *J. Am. Chem. Soc.* **2007**, *129*, 15432 – 15433.

[3] J. Lee, V. C. Sundar, J. R. Heine, M. G. Bawendi, K. F. Jensen, *Adv. Mater.* **2000**, *12*, 1102 – 1105.

[4] a) J. Ziegler, S. Xu, E. Kucur, F. Meister, M. Batenschuk, F. Gindele, T. Nann, *Adv. Mater.* **2008**, *20*, 4068 – 4073; b) M. Ali, S. Chattopadhyay, A. Nag, A. Kumar, S. Sapra, S. Chakraborty, D. D. Sarma, *Nanotechnology* **2007**, *18*, 075401; c) E. Jang, S. Jun, H. Jang, J. Lim, B. Kim, Y. Kim, *Adv. Mater.* **2010**, *22*, 3076 – 3080; d) S. Coe, W. K. Woo, M. Bawendi, V. Bulovic, *Nature* **2002**, *420*, 800 – 803; e) P. O. Anikeeva, J. E. Halpert, M. G. Bawendi, V. Bulovic, *Nano Lett.* **2009**, *9*, 2532 – 2536; f) M. Bruchez, M. Moronne, P. Gin, S. Weiss, A. P. Alivisatos, *Science* **1998**, *281*, 2013 – 2016; g) Q. Sun, Y. A. Wang, L. S. Li, D. Wang, T. Zhu, J. Xu, C. Yang, Y. Li, *Nat. Photonics* **2007**, *1*, 717 – 722; h) J. Kwak, W. K. Bae, D. Lee, I. Park, J. Lim, M. Park, H. Cho, H. Woo, D. Y. Yoon, K. Char, S. Lee, C. Lee, *Nano Lett.* **2012**, *12*, 2362 – 2366.

[5] K.-S. Cho, E. K. Lee, W.-J. Joo, E. Jang, T. H. Kim, S. J. Lee, S.-J. Kwon, J. Y. Han, B.-K. Kim, B. L. Choi, J. M. Kim, *Nat. Photonics* **2009**, *3*, 341 – 345.

[6] H. S. Jang, H. Yang, S. W. Kim, J. Y. Han, S. G. Lee, D. Y. Jeon, *Adv. Mater.* **2008**, *20*, 2696 – 2702.

[7] L. Qu, X. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 2049 – 2055.

[8] D. Pan, Q. Wang, S. Jiang, X. Ji, L. An, *Adv. Mater.* **2005**, *17*, 176 – 178.

[9] J. S. Steckel, P. Snee, S. Coe-Sullivan, J. P. Zimmer, J. E. Halpert, P. Anikeeva, L.-A. Kim, V. Bulovic, M. G. Bawendi, *Angew. Chem.* **2006**, *118*, 5928 – 5931; *Angew. Chem. Int. Ed.* **2006**, *45*, 5796 – 5799.

[10] M. Protière, P. Reiss, *Small* **2007**, *3*, 399 – 403.

[11] X. Zhong, R. Xie, Y. Zhang, T. Basché, W. Knoll, *Chem. Mater.* **2005**, *17*, 4038 – 4042.

[12] P. O. Anikeeva, J. E. Halpert, M. G. Bawendi, V. Bulovic, *Nano Lett.* **2007**, *7*, 2196 – 2200.

[13] a) Y. Chen, J. Vela, H. Htoon, J. L. Casson, D. J. Werder, D. A. Bussian, V. I. Klimov, J. A. Hollingsworth, *J. Am. Chem. Soc.* **2008**, *130*, 5026 – 5027; b) S. Jeong, M. Achermann, J. Nanda, S. Ivanov, V. I. Klimov, J. A. Hollingsworth, *J. Am. Chem. Soc.* **2005**, *127*, 10126 – 10127.

[14] a) S. J. Selvan, C. Bullen, M. Ashokkumar, P. Mulvaney, *Adv. Mater.* **2001**, *13*, 985 – 988; b) A. Y. Nazzal, X. Wang, L. Qu, W. Yu, Y. Wang, X. Peng, M. Xiao, *J. Phys. Chem. B* **2004**, *108*, 5507 – 5515.

[15] B. N. Pal, Y. Ghosh, S. Brovelli, R. Laocharoensuk, V. I. Klimov, J. A. Hollingsworth, H. Htoon, *Nano Lett.* **2012**, *12*, 331 – 336.

[16] S. Kim, J. Park, T. Kim, E. Jang, S. Jun, H. Jang, B. Kim, S. W. Kim, *Small* **2011**, *7*, 70 – 73.

[17] S. Jun, E. Jang, *Chem. Commun.* **2005**, 4616 – 4618.

[18] W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* **2003**, *15*, 2854 – 2860.

[19] a) A. Pandey, P. Guyot-Sionnest, *J. Chem. Phys.* **2007**, *127*, 104710; b) J. Li, L. W. Wang, *Appl. Phys. Lett.* **2004**, *84*, 3648 – 3652.

[20] S. Jun, E. Jang, J. Lim, *Nanotechnology* **2006**, *17*, 3892 – 3896.

[21] W. G. J. H. M. van Sark, P. L. T. M. Frederix, D. J. Van den Heuvel, H. C. Gerritsen, A. A. Bol, Joost, N. J. van Lingen, C. de Mello Donegá, A. Meijerink, *J. Phys. Chem. B* **2001**, *105*, 8281 – 8284.