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Efficient, Stable, Small, and Water-Soluble Doped ZnSe Nanocrystal Emitters as Non-Cadmium Biomedical Labels

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ABSTRACT

Mn^{2+}-doped ZnSe quantum dots (Mn:ZnSe d-dots) with a tunable photoluminescence (PL) peak position were made to be water soluble by coating them with a monolayer of mercaptopropionic acid, a very short hydrophilic thiol. If the dopant centers were located close to the surface, thiol-coating partially quenched the PL. With about 2–3 monolayers of pure ZnSe on the surface, the PL of d-dots was actually enhanced upon thiol coating. When the doping centers were placed reasonably inside a d-dot, with about four monolayers of pure ZnSe between the doping centers and the surface ligands, the thiol ligands did not quench the PL of the d-dots, even though they did completely quench the PL of intrinsic ZnSe quantum dots. The overall size of such d-dots/ligand complex is only about 7–8 nm, implying an excellent permeability in biological issues. These d-dots were found to be exceptionally stable against continuous UV radiation in air for at least 25 days. They were also stable in boiling water with air bubbling under room light for hours. Recognition of a biotin pattern by d-dots conjugated with avidine was carried to illustrate the suitability of these efficient (about 40% PL quantum yield), stable, small, and water-soluble d-dots as biomedical labeling reagents.

Luminescent semiconductor nanocrystals, or quantum dots (q-dots), have been widely explored as biomedical labeling reagents since 1998.[1−10] The spectral advantages of q-dots are apparent, narrow and symmetric photoluminescence (PL), a broad and intense absorption band, and tunable emission peak positions. Their photochemical stability has been improved to a level substantially better than that of organic dyes by several innovative ligand protection strategies.[9] However, despite some attempts at using non-cadmium q-dots,[11] cadmium chalcogenides, especially CdSe, and the related core/shell nanocrystals, are still the current workhorse for fluorescence biological labeling using q-dots. Experimental results indicate that any leakage of cadmium from the nanocrystals would be toxic and fatal to a biological system,[8] and cadmium-containing products are eventually environmentally problematic. In addition, the small-ensemble Stokes shift of intrinsic q-dot emitters makes self-quenching as a serious issue if the fluorescent labels must either be kept close by or be in a high absorbance. The other disadvantage of q-dot fluorescent labels is their excessively large physical size in comparison to organic dyes.[9,11]

This report intends to introduce a new class of potential fluorescence biomedical labels, which are based on transition metal ion-doped quantum dots (d-dots) without heavy metal ions, specifically using ZnSe and ZnS as the hosts. The results to be described below illustrate that, to a certain extent, d-dots offer potential solutions to all of the problems of q-dot fluorescent labels discussed above. In addition, the water-soluble d-dots to be discussed below also show fundamental differences from intrinsic q-dots in terms of ligand chemistry and photochemical stability, which should help to reach a better understanding of these important issues in general.

Transition metal ion-doped quantum dots have been studied for many years because of their unique optical properties[12−30] and potential for use in various applications other than biomedical labeling, such as spintronics.[31−33] The early report by Bhargava et al.[13] for Mn-doped ZnS in 1994 illustrated that it may be possible to obtain efficient emission from the dopant centers even if the host nanocrystals are not of high quality. On the basis of this and other encouraging results reported in literature by various research groups, we recently reported on the possibilities to decouple doping processes from nucleation and/or growth using Cu- and Mn-doped ZnSe nanocrystals as the model systems.[34] These decoupling strategies allow for the growth of d-dots in a

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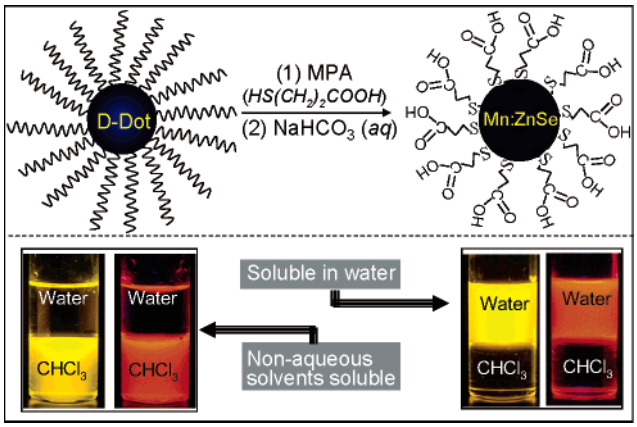

Figure 1. Top: schematic representation of ligand exchange process using MPA. Bottom: digital pictures of Mn:ZnSe d-dots with two different colors before (left) and after (right) ligand exchange.

controllable fashion, thus yielding d-dots with pure dopant emission at a high efficiency. Systematic studies on the doping chemistry (results to be published separately) enabled us to further improve the PL quantum yield (QY) of the Mn-doped ZnSe d-dots to the level of typical CdSe q-dots, as high as 60−70% PL QY measured against organic dyes. While preparing this paper, we noticed that Cao's group reported that highly efficient d-dots (PL QY about 50%) can be obtained by isolating the CdS cores prior to doping the CdS/ZnS core/shell nanocrystals.[35]

Optimized synthesis of highly bright (PL QY between 40 and 60%) Mn-doped ZnSe (Mn:ZnSe) d-dots with tunable PL peak position from around 575 to 610 nm will be reported separately, and a brief description is provided as Supporting Information. After purification using the standard precipitation−dissolution procedure, the as-synthesized d-dots coated with the original amine ligands were dissolved in a minimum amount of chloroform and treated with mercaptopropionic acid (MPA). The resulting mixture was shaken for 20 min with sonication. The chloroform solution gradually became turbid as the original ligands with a long hydrocarbon chain were replaced by MPA. The MPA-coated d-dot precipitate was isolated by centrifugation and decantation. Excess MPA was further removed by washing the precipitate with chloroform and centrifugation. Finally, water with $NaHCO_3$ was added to the precipitate, and the nanocrystals were then dissolved in the water. The ligand exchange procedure is briefly illustrated in Figure 1 (top).

In Figure 1, Mn:ZnSe d-dots with two distinguishable colors are shown (bottom), both of which were successfully converted to be water soluble by using mercaptopropionic acid, a simple and small thiol ligand. The carboxylic groups at the outer surface of the nanocrystal−ligand complex render excellent water solubility for the d-dots after the thiol group has bonded to the zinc ions on the surface of the d-dots (Figure 1, bottom), which is similar to that reported for surface modification of typical semiconductor nanocrystals using similar ligands.[2,3,36] The same strategy also worked for copper-doped ZnSe nanocrystals (Supporting Information), which emit in the blue and green color windows.

It is interesting to see that, in Figure 1 and the results in the Supporting Information, thiol coating did not quench the PL of both Mn:ZnSe and Cu:ZnSe d-dots. It is well-known that thiol coating quenches the PL of plain CdSe nanocrystals completely,[36] as well as the PL of intrinsic ZnSe nanocrystals (Supporting Information). To better understand this issue, Mn:ZnSe d-dots with different thicknesses of a pure ZnSe outer layer on the same sized Mn^{2+}-containing core were subjected to the same ligand replacement process (Figure 2).

An interesting pattern (Figure 2) was revealed by this set of experiments. Mn:ZnSe d-dots with a thin pure ZnSe outer layer (Figure 2, left), about one monolayer, showed considerable quenching of the PL after ligand exchange with the thiol ligands. The PL QY for the d-dots with a thick pure ZnSe outer layer, about 5−6 monolayers, did not show much change to the surface ligand exchange (Figure 2, right). The most surprising observation was the significant PL enhancement of the sample with a medium pure ZnSe outer layer, about 2−3 monolayers. For this specific set of samples, the final PL QY for the water-soluble d-dots with either a medium or thick pure ZnSe outer layer was about the same, around 40% (Figure 2). It should be pointed out that the PL QY of the d-dots with thin and medium pure ZnSe outer layer was found to be less reproducible. The highest PL QY of water-soluble d-dots was above 60%.

Although the d-dots in water with a medium pure ZnSe outer layer could have a PL QY as high as that of the d-dots with a thick pure ZnSe outer layer (Figure 2), their photochemical stability was found to be substantially different (Figure 3a). The d-dots with a medium pure ZnSe outer layer were found to be not very stable in aqueous solution open to air under room light, while the ones with a thick pure ZnSe outer layer were stable for an extensive period of time under the same conditions. The corresponding UV−vis spectra for both samples in the same period of time did not show significant changes, indicating that no significant oxidation of the inorganic core was observed. This implies that the PL decrease upon aging was probably due to the loss of organic ligands on the surface of the nanocrystals. As discussed below, the PL QY of the d-dots with a medium pure ZnSe outer layer should be more sensitive to the surface ligand coverage.

The apparent difference of PL response to thiol ligands between intrinsic ZnSe q-dots (quenching completely, see Supporting Information) and the d-dots (the results in Figure 2 for Mn:ZnSe and in Supporting Information for Cu:ZnSe) can be understood by the different emission mechanisms for the two cases. When an intrinsic q-dot is excited by photons with energy higher than its band gap, an exciton (an electron−hole pair) will be generated. The direct recombination of the electron−hole pair, typically being quantum confined in the case of nanocrystals,[37] gives the well-known band edge emission, or exciton emission. However, the emission of a d-dot is fundamentally different. After the exciton is generated by the absorption of the host semiconductor nanocrystal, the energy of a photogenerated electron and hole pair will be transferred into the electronic levels of

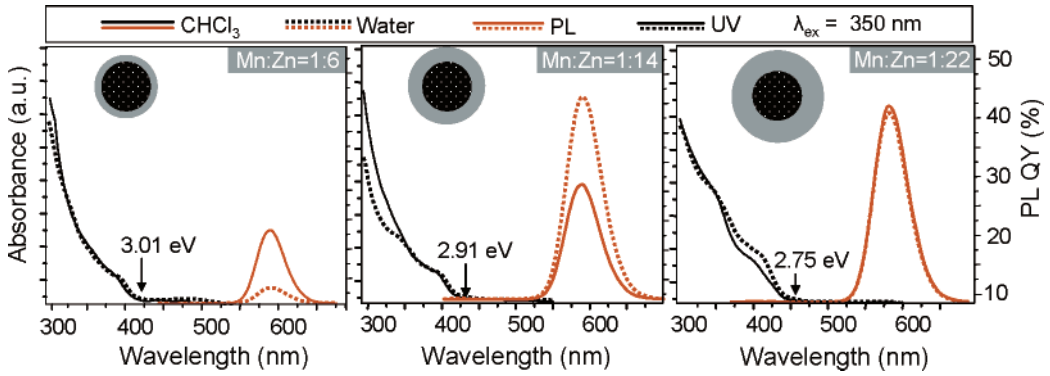

Figure 2. UV−vis and PL spectra of d-dots before and after the thiol ligand exchange. The three samples were with the same-sized Mn^{2+}-containing core and a different thickness of pure ZnSe coating.

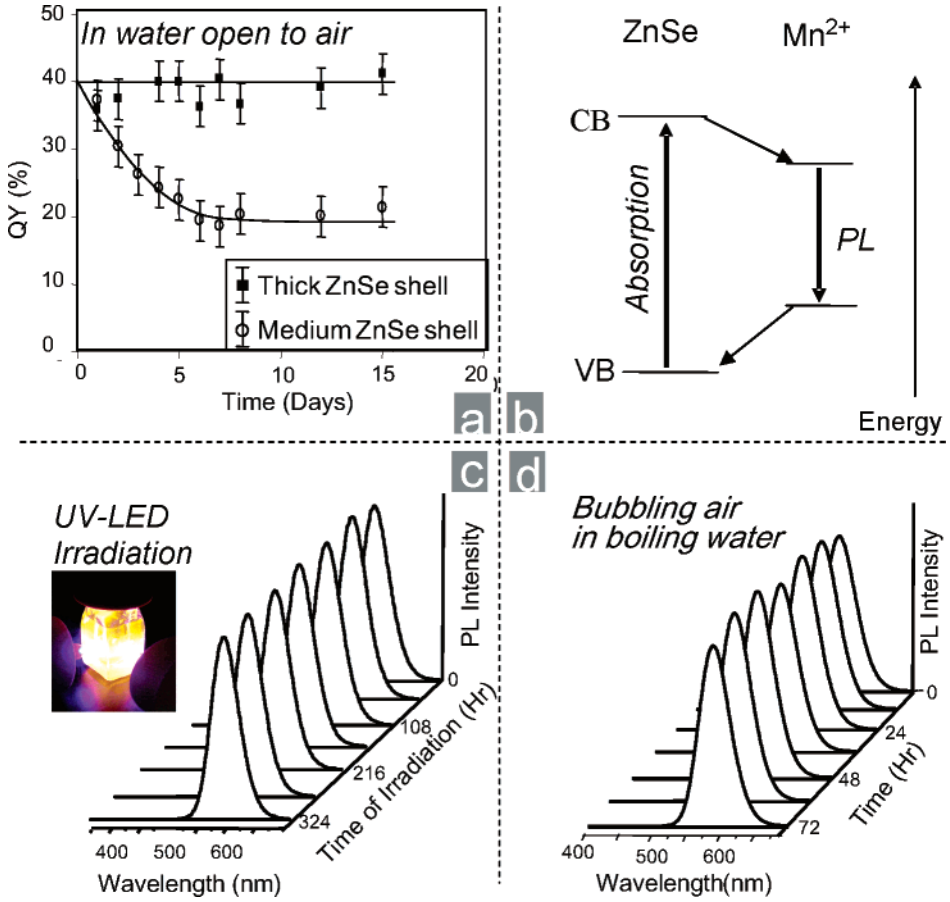

Figure 3. (a) Photochemical stability of water-soluble d-dots with different thickness of pure ZnSe coating. (b) Schematic representation of electron−hole recombination in Mn:ZnSe nanocrystals. (c) Stability of d-dots in water under UV irradiation by two 8 mW LEDs at 395 nm. The optical density (OD) of the solution at 350 nm was 4.1. (d) Photochemical stability of d-dots dissolved in boiling water and in the presence of bubbling air. OD of the solution at 350 nm was 2.9.

the Mn^{2+} ions. The recombination in a Mn^{2+} ion center leads to the characteristic dopant emission from the Mn^{2+} ion, namely the $^4T_1$ to $^6A_1$ transition (Figure 3b).

The quenching of the excitonic emission of intrinsic q-dots by thiol ligands has been regarded as the trapping of the photogenerated holes by the deprotonated thiol groups (negatively charged) on the surface of nanocrystals,[36] which in turn decays nonradiatively. For the case of d-dots, this trapping process must compete with the hole−electron transfer from the host into the split d-orbitals of the dopant ions. When the pure ZnSe outer layer was thin, this competition was more favorable toward the surface ligand trapping, which reduced the PL QY of the thiol-coated d-dots, although it did not quench the PL completely. When the pure ZnSe outer layer was more than four monolayers (Figure 2, right), the trapping into the dopant ions became dominant, which resulted in a hole spatially separated from the surface ligands by the relatively thick ZnSe outer layer. Consequently, the dopant emission did not change after the thiol ligand exchange. For d-dots with the intermediate pure ZnSe outer layer, the enhancement may be associated with the electron passivation provided by the deprotonated thiol

ligands. According to the current picture of quantum confinement,[37] the electron is more delocalized than the hole in a nanocrystal and should thus "feel" more of the negative field of the deprotonated ligands (thiolate). As a result, the negatively charged ligand layer should provide an extra barrier for confining the electron to the interior of the nanocrystal. This should increase the possibility of the electron to fall into the d-orbital and subsequently enhance the dopant emission (Figure 2, middle). For the d-dots with a thick pure ZnSe outer layer, the dopant centers were sufficiently far away from the surface, thus the additional thiol ligand layer did not adversely affect the electron localization. This explanation seems to be reasonable at a qualitative level, but additional experiments for these unique emitters are needed to fully clarify this issue.

The comparatively better stability of the d-dots with a thick pure ZnSe outer layer invited us to further test their stability for practical applications. Figure 3c shows the photostability of the nanocrystals in water under the continuous irradiation of two relatively intensive UV LEDs (8 mW each, emission peak at 395 nm) for an excessively long period of time, over 25 days (data for 300 h included in Figure 3c). The PL QY was found to be stable at about 44% for the entire period of irradiation. The second test was conducted in room light at an elevated temperature (~100 °C) with air bubbling into the d-dot aqueous solution for 72 h (Figure 3d). Both tests demonstrate that the d-dots were exceptionally stable under such extreme conditions. It should be pointed out that it would not be possible for the intrinsic II−VI q-dots coated with mercaptopropionic acids to withstand such harsh tests for more than 1 h. For example, CdSe nanocrystals coated with the same ligands precipitated from the solution after UV irradiation for about 1 h at room temperature.[36] As the early quantitative experiments revealed, MPA typically does not provide much diffusion barrier for oxygen, the MPA-coated semiconductor nanocrystals are thus very unstable against photocatalytic oxidation of the thiolate ligands.[36]

The exceptional photophysical and photochemical stability of the d-dots with a thick pure ZnSe outer layer coated with short thiol ligands (Figure 3a,c,d) is consistent with the emission mechanism of d-dots discussed above. Early reports indicate that the photochemical instability of thiol-coated q-dots is due to the photocatalytic oxidation of the thiol ligands into disulfides,[36] a poor surface-binding species. As discussed above, the unaffected PL brightness of the d-dots with a thick pure ZnSe outer layer upon thiol ligand exchange (Figure 2, right) implies that the necessary hole-trapping step for photocatalytic oxidation of the thiol ligands could not occur for the d-dots. As a result, the nanocrystal−ligands complex should be robust against the commonly known photocatalytic oxidation process.

Because of the significant energy differences between the band gap of the host semiconductor and the energy gap of the excited states of of the dopants (Figure 3b), the absorption and emission spectra of d-dots are well separated (Figure 2). It is thus possible to obtain different color emitters in the low-energy window beyond the bulk exciton emission of ZnSe (around 470 nm) such as green, yellow, and orange-red colors. Furthermore, this large ensemble Stokes shift also stops self-quenching due to either Forster energy transfer or reabsorption, which is an advantage for certain applications when the emitters need to be either close to each other or at a high absorbance, such as molecular barcoding using beads loaded with differently sized nanocrystal emitters.[4]

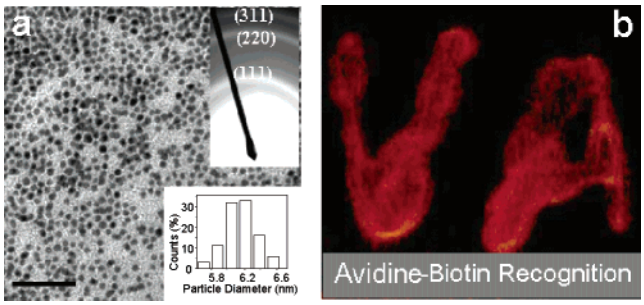

Figure 4. Left: TEM picture of d-dots in water, the size distribution histogram (bottom insert), and the electron diffraction pattern (top insert). Scale bar = 50 nm. Right: Digital image of a biotin pattern (UA) on a glass slide illustrated by the PL of MPA capped d-dots conjugated with avidine. A blue filter was used for removing the excitation light.

The total size of the nanocrystal−ligand complex determines the physical permeability of the nanocrystals in a biological system, which is an important parameter for a fluorescence label.[9] In addition to their bright emission and robust stability, the mercaptopropionic acid coated d-dots are also small in physical size. Because of the photochemical instability of intrinsic q-dots, such as CdSe, and their sensitive PL properties against ligand exchange, intrinsic q-dots must be made in core/shell forms for biomedical fluorescence labeling.[1−10] In addition, the thiol ligands, mostly used in the field, must be reasonably bulky for a reasonable stability.[36] Alternatively, polymer wrapping and micelle formation[1,3,5,6,9,10] have also been employed to provide a significant diffusion barrier to prevent photo-oxidation of the core/shell nanocrystal−ligand complexes. These two factors make the physical size of the nanocrystal−ligand complexes relatively large. For instance, for similar emission colors discussed here, with a peak from 580 to 610 nm, the inorganic part (typically 8 nm, 4 nm for the CdSe core,[38] and 4 nm for about five monolayers of shell with a high band gap) would be slightly larger than the typical size of the stable d-dot emitters shown in Figure 4a, about 6.2 nm. The organic ligand shell, however, would be much thinner for the d-dots reported here, around 0.5 nm (MPA) vs several to tens of nanometers for the typical ligands needed for q-dots. Bawendi's group[11] recently reported one solution to this problem by developing an InAs/ZnSe nanocrystal system with an extremely small InAs core size, <2 nm in diameter, and coated with relatively small organic ligands, either dihydrolipoic acid (DHLA)[3] or dihydrolipoic acid conjugated to a short poly(ethylene glycol). The overall size of their nanocrystal−ligand complex is slightly larger than our water-soluble d-dots shown here, but in one case, their dots have a short poly(ethylene glycol) on the surface to improve biocompatibility of the resulting dot−ligand complexes. It is expected that the final size of our water-soluble d-dots

might also need to have such short poly(ethylene glycol) terminal groups for in vivo applications. In any case, the efficient, stable, and water-soluble d-dots reported here should be at least of a size not much larger than that of the InAs/ZnSe dots reported by Bawendi's group.

The transmission electron microscope (TEM) image in Figure 4 (left) indicates that the size distribution of the d-dots was reasonably uniform. Compared to the TEM image before ligand exchange (data not shown), the average size and size distribution of the d-dots after the ligand exchange remained the same. The selective area electron diffraction pattern (Figure 4a, inset) further indicates that the d-dots are in a zinc blende structure that is the same as undoped ZnSe nanocrystals[39] and the original nonpolar solvent soluble d-dots.[34]

To explore the suitability of biomedical labeling using the d-dots discussed here, a preliminary test was carried out (Figure 4b). D-dots conjugated with avidine were used for the recognition of a biotin pattern (UA) on the surface of a glass slide. Although the full slide was subjected to the treatment of an excess amount of the d-dots/avidine conjugates, the edges of the biotin pattern were reasonably sharp in the picture (Figure 4b). This indicates the selective binding of the d-dots to the substrate via avidine−biotin interactions.

In conclusion, transition metal doped ZnSe nanocrystals (d-dots) without any heavy metal ions can be made to be efficient, stable, small, and water soluble as potential fluorescent labels for biological systems. Even though thiol ligands are known as a PL quencher for intrinsic CdSe[36] and ZnSe q-dots, the PL of ZnSe-based d-dots responded to the thiol ligands according to the distance of the Mn^{2+} doping centers to the surface ligands, from partial quenching to significant enhancement, and then to no influence as the distance increased from one monolayer to above four monolayers of pure ZnSe. The D-dots with above four monolayers of pure ZnSe protected with mercaptopropionic acid were found to be exceptionally stable during photooxidation and continuous photoirradiation experiments. The interesting responses to the thiol ligands and exceptional stability of the d-dots coated with mercaptopropionic acid seem to be consistent with their unique emission mechanism, efficient trapping of the photoexcitation of the host nanocrystals into the dopant centers, followed by recombination of these trapped charges to give pure dopant emission. The water-soluble d-dots presented here are color tunable, thermally and photochemically stable, and small in size, and are thus promising second-generation emissive semiconductor nanocrystals for different applications, such as solid-state lighting,[13] lasers,[40] and light emitting diodes,[41,42] in addition to biomedical imaging.

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Supporting Information Available: Experimental details, emission and absorption spectra of Cu:ZnSe d-dots, and comparative emission properties of intrinsic ZnSe q-dots and d-dots. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Bruchez, M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013−2016.
(2) Chan, W. C. W.; Nile, S. *Science* **1998**, *281*, 2016−2018.
(3) Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Anderson, G. P.; Sundar, V. C.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142−12150.
(4) Han, M.; Gao, X.; Su, J. Z.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631−635.
(5) Dubertret, B.; Skourides, P.; Norris, D. J.; Noireaux, V.; Brivanlou, A. H.; Libchaber, A. *Science* **2002**, *298*, 1759−1762.
(6) Wu, X.; Liu, H.; Liu, J.; Haley, K. N.; Treadway, J. A.; Larson, J. P.; Ge, N.; Peale, F.; Bruchez, M. P. *Nat. Biotechnol.* **2003**, *21*, 41−46.
(7) Kim, S.; Lim, Y. T.; Soltesz, E. G.; De Grand, A. M.; Lee, J.; Nakayama, A.; Parker, J. A.; Mihaljevic, T.; Laurence, R. G.; Dor, D. M.; Cohn, L. H.; Bawendi, M. G.; Frangioni, J. V. *Nat. Biotechnol.* **2004**, *22*, 93−97.
(8) Derfus, A. M.; Chan, W. C. W.; Bhatia, S. N. *Nano Lett.* **2004**, *4*, 11−18.
(9) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538−544.
(10) Cai, W.; Shin, D.-W.; Chen, K.; Gheysens, O.; Cao, Q.; Wang, S. X.; Gambhir, S. S.; Chen, X. *Nano Lett.* **2006**, *6*, 669−676.
(11) Zimmer, J. P.; Kim, S.-W.; Ohnishi, S.; Tanaka, E.; Frangioni, J. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2006**, *128*, 2526−2527.
(12) Becker, W. G.; Bard, A. J. *J. Phys. Chem.* **1983**, *87* (24), 4888−4893.
(13) Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. *Phys. Rev. Lett.* **1994**, *72*, 416−419.
(14) Sooklal, K.; Cullum, B. S.; Angel, S. M.; Murphy, C. J. *J. Phys. Chem.* **1996**, *100*, 4551−4555.
(15) Dinsmore, A. D.; Hsu, D. S.; Gray, H. F.; Qadri, S. B.; Tian, Y.; Ratna, B. R. *Appl. Phys. Lett.* **1999**, *75*, 802−804.
(16) Murase, N.; Jagannathan, R.; Kanematsu, Y.; Watanabe, M.; Kurita, A.; Hirata, K.; Yazawa, T.; Kushida, T. *J. Phys. Chem. B* **1999**, *103*, 754−760.
(17) St. John, J.; Coffer, J. L.; Chen, Y.; Pinizzotto, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 1888−1892.
(18) Mikulec, F. V.; Kuno, M.; Bennati, M.; Hall, D. A.; Griffin, R. G.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 2532−2540.
(19) Suyver, J. F.; Wuister, S. F.; Kelly, J. J.; Meijerink, A. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5445−5448.
(20) Azad Malik, M.; O'Brien, P.; Revaprasadu, N. *J. Mater. Chem.* **2001**, *11*, 2382−2386.
(21) Chen, W.; Sammynaiken, R.; Huang, Y.; Malm, J.-O.; Wallenberg, R.; Bovin, J.-O.; Zwiller, V.; Kotov, N. A. *J. Appl. Phys.* **2001**, *89*, 1120−1129.
(22) Norris, D. J.; Yao, N.; Charnock, F. T.; Kennedy, T. A. *Nano Lett.* **2001**, *1*, 3−7.
(23) Suyver, J. F.; van der Beek, T.; Wuister, S. F.; Kelly, J. J.; Meijerink, A. *Appl. Phys. Lett.* **2001**, *79*, 4222−4224.
(24) Raola, O. E.; Strouse, G. F. *Nano Lett.* **2002**, *2*, 1443−1447.
(25) Karar, N.; Singh, F.; Mehta, B. R. *J. Appl. Phys.* **2004**, *95*, 656−660.
(26) Lehmann, O.; Kompe, K.; Haase, M. *J. Am. Chem. Soc.* **2004**, *126*, 14935−14942.
(27) Yang, H.; Holloway Paul, H.; Cunningham, G.; Schanze Kirk, S. *J. Chem. Phys.* **2004**, *121*, 10233−10240.
(28) Erwin, S. C.; Zu, L.; Haftel, M. I.; Efros, A. L.; Kennedy, T. A.; Norris, D. J. *Nature* **2005**, *436*, 91−94.
(29) Radovanovic Pavle, V.; Barrelet Carl, J.; Gradecak, S.; Qian, F.; Lieber Charles, M. *Nano Lett.* **2005**, *5*, 1407−1411.
(30) Zu, L.; Norris, D. J.; Kennedy, T. A.; Erwin, S. C.; Efros, A. L. *Nano Lett.* **2006**, *6*, 334−40.
(31) Radovanovic, P. V.; Gamelin, D. R. *J. Am. Chem. Soc.* **2001**, *123*, 12207−12214.
(32) Norberg, N. S.; Kittilstved, K. R.; Amonette, J. E.; Kukkadapu, R. K.; Schwartz, D. A.; Gamelin, D. R. *J. Am. Chem. Soc.* **2004**, *126*, 9387−9398.
(33) Huang, X.; Makmal, A.; Chelikowsky, J. R.; Kronik, L. *Phys. Rev. Lett.* **2005**, *94*, 236801/1−23680.1/4.

(34) Pradhan, N.; Goorskey, D.; Thessing, J.; Peng, X. *J. Am. Chem. Soc.* **2005**, *127*, 17586−17587.
(35) Yang, Y.; Chen, O.; Angerhofer, A.; Cao, Y. C. *J. Am. Chem. Soc.* **2006**, *128*, 12428−12429.
(36) Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844−8850.
(37) Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 5566−5571.
(38) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.
(39) Li, L. S.; Pradhan, N.; Wang, Y.; Peng, X. *Nano Lett.* **2004**, *4*, 2261−2264.
(40) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H.; Bawendi, M. G. *Science* **2000**, *290*, 314−317.
(41) Mattoussi, H.; Radzilowski, L. H.; Dabbousi, B. O.; Thomas, E. L.; Bawendi, M. G.; Rubner, M. F. *J. Appl. Phys.* **1998**, *83*, 7965−7974.
(42) Schlamp, M. C.; Peng, X.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837−5842.

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