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Cyclodextrin driven hydrophobic/hydrophilic transformation of semiconductor nanoparticles

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Quantum dots (QDs) have been the subject of considerable study in theoretical physics, and water soluble QDs now appear to have numerous applications in biological tagging, molecular electronic devices, and nanoscale engineering. The work reported here supports the notion that the aliphatic chains of the trioctylphosphine oxide molecules decorating these (CdSe)ZnS core-shell QDs are stabilized by the hydrophobic cyclodextrin (CD) lumen. Photoluminescence studies show a redshift of over 15 nm in the emission wavelength of the QDs upon complexation with the CD, and first-principles calculations reveal an exothermic exchange of the S in the ZnS shell with the CD hydroxyl oxygen. Unlike simple water-driven surface transformations, the directed bonding of hydroxyl groups to the ZnS shell results in stable structures, verified by photoluminescence and Fourier transform infrared spectroscopy. © 2005 American Institute of Physics.

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Surface chemical modification of semiconductor nanoparticles in solvent is thought to alter the thermodynamics of the formation/breakage of crystal coordinate bonds.¹ For example, surface water of hydrated ZnS nanoparticles has been shown to contribute to the exchange equilibrium of the crystal coordinate bonds of Zn-S and Zn-O.^{1,2} Methods for producing water-soluble quantum dots (QDs) have been limited to uncontrolled application of surface coatings consisting of thiol compounds^{3,4} and macromolecules.^{5,6} Active, soluble QDs stabilized by stoichiometric complexation with CDs should therefore be of considerable interest. Initially, we observed that ZnS or ZnS-shelled nanoparticles were strongly bound to hydroxylated chromatography packing materials. From this, we concluded that the modification of ZnS nanoparticles with hydroxyl-rich molecules would result in a high-energy gain. We explored the possibility that natural cyclodextrins, which have a hydrophobic pocket⁷ ringed by equatorial hydroxyls, may stabilize the aliphatic chains of trioctylphosphine oxide (TOPO) molecules decorating the surface of QDs and thus serve as a model molecule to demonstrate the energetics of exchange of ZnS crystal coordinate bonds.

TOPO (CdSe)ZnS QDs were synthesized following the method of Dabbousi and co-workers.⁸ In hexane or toluene, these QDs are typically 3.4–3.6 nm in diameter and exhibit good photoluminescence (PL) quantum yields (PLQY > 15%) with little or no evidence of deep-trap emission associated with surface defects. The TOPO-QDs were purified by precipitation and centrifugation in anhydrous methanol. The precipitates were washed with anhydrous methanol to remove residual TOPO. Aliquots of 0.85 mg QDs in 0.1 mL hexane were slurried in 1.0 mL anhydrous ethanol and slowly pervaporated to remove the hexane. To produce cyclodextrin- (CD) QDs, 0.5 mg γ -CD powder dissolved in 1 mL ethanol was added to the QD residue and stirred for

2–4 h at 60 °C. After stirring at 25 °C for 72 h, the CD-QD product was collected by centrifugation and transferred to water. Both β - and γ -cyclodextrins demonstrated the ability to react with these QDs; however, the γ -cyclodextrin-QDs were used for further investigation.

After interaction with cyclodextrins, the (CdSe)ZnS QDs appear to be well dispersed in water. The high-resolution atomic force microscopic (AFM) image of the γ -CD-QD preparation [Fig. 1(a)] clearly shows two distinct regions for each object, i.e., a bright (high z -axis) core region surrounded by a diffusive edge region, which is also visible in the height profile in Fig. 1(b). Analysis of these AFM images showed that these structures display a diameter of about 5.5 nm including an edge thickness of about 1 nm. Hence, the size of the object “core” can be estimated as $5.5 - (2 \times 1) = 3.5$ nm, which is in good agreement with estimates for TOPO-QD starting material.⁶ The observed dimension of the object “edges” (~ 1 nm) is consistent with the height dimension of the CD (0.78 nm).⁷

The PL spectra of the TOPO- and γ -capped CD-QDs were compared (data not shown) and we observed a sizable 15-nm redshift. We cannot rule out the possibility that the change of the capping group on the (CdSe)ZnS core-shell structure may have changed the PL emission. For example, changes in the emission of CdSe QDs have recently been reported to be related to both their surface chemistry and the surrounding environment.^{9,10} Still, because the TOPO and CD interaction is thought to be van der Waals-type, it is quite difficult to understand why such a redshift could result.

To better explain the observed redshift in PL, we performed first-principles density functional theory^{11,12} calculations for the interaction of the ZnS shell with the hydroxyls in the CD rings. To calculate surface reaction energy, we used first-principles pseudopotential methodology as implemented in the VASP codes. We used the ultrasoft pseudopotentials with a kinetic energy cutoff of 300 eV in the plane-wave basis expansion. The surface is modeled as ZnS(110) surface. We used slab geometry with 3×3 surface unit cell

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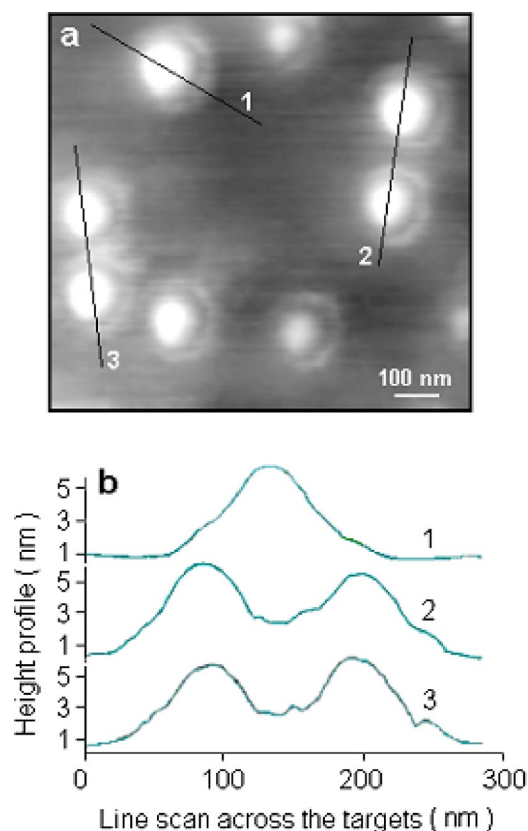


FIG. 1. (a) Atomic force microscopy (AFM) images of γ -CD-QDs and (b) height profiles of possible monomer (1), dimer (2), and trimer (3).

and six monolayers plus nine vacuum layers in the normal direction. One k -point is used in the Brillouin zone sum. All forces are minimized to less than $0.02 \text{ eV}/\text{\AA}$. For simplicity, we did not include in the calculation the curvature effect and lattice mismatch between CdSe and ZnS.

We studied the processes of hydroxyl binding and hydroxyl exchange with surface sulfur atoms where the hydroxyls come either from water (H_2O), methanol (CH_3OH), or glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). Figure 2 shows, as an example, the case for glucose interaction. In Fig. 2(a), the glucose is intact. In Fig. 2(b), it gives away a hydrogen atom to a surface sulfur and the exposed oxygen atom on the glucose binds to a surface zinc atom (“binding”). In Fig. 2(c), the glucose gives away a hydroxyl that replaces a surface sulfur atom. In return, the remainder of the glucose binds to the surface through the “give-away” sulfur atom (“exchange”). Interestingly, the sulfur atom in Fig. 2(c) is threefold coordinated including bonds with two of the surface zinc atoms. In the

case of binding, the reactions are endothermic with 0.67, 0.91, and 0.97 eV energy increases for water, methanol, and glucose, respectively. In the case of exchange, however, the reactions are exothermic with -0.2 , -0.35 , and -0.11 eV energy changes, respectively. As shown in Fig. 2(b) one can write $\text{Zn-S} + \text{H-O-R} \rightarrow \text{Zn-O-R} + \text{H-S}$ for the “binding” reaction. This reaction is not energetically favorable because of the high dissociation energy of the H-O bond. On the other hand, the “exchange” reaction is energetically favored because it avoids the break up of the H-O bond. Also, with a larger atomic size, the sulfur atom linked to glucose shown in Fig. 2(c) can form two, instead of one bond to the ZnS surface. In other words, surface energetics modeling suggests exchange reactions occurring on the QD surface between ZnS and glucose, forming a thin ZnO layer.

To study the effects of the surface reaction on the optical properties of the QDs, we used an effective mass (EM) model shown in Fig. 3(a).^{8,13} We solved three-dimensional Schrödinger equations for the electron and hole states separately, with charge and current continuity at the layer boundaries. We have determined experimentally that the (CdSe)ZnS core-shell QDs have a nearly uniform size with the core radius approximately $r_{\text{CdSe}} = 12 \text{ \AA}$ and the shell thickness $t_{\text{ZnS}} = 5 \text{ \AA}$. The thickness of the ZnS layer here corresponds to roughly two (110) monolayers. To be complete, we have considered below both the binding and exchange scenarios. In the former case, we allowed a new ZnO layer to grow over the existing ZnS layers with t_{ZnS} fixed; and in the latter case, we replaced the ZnS layers by ZnO layers, keeping $t_{\text{ZnS}} + t_{\text{ZnO}}$ fixed.

Our modeling results show that one can readily rule out the “binding” scenario not only because it requires additional zinc source, and is energetically unfavorable, but also because to get a 15 nm redshift, the thickness of the ZnO layer has to be at least 5 \AA or more. For the “exchange” scenario, the calculated redshift, $\Delta\lambda$, is depicted in Fig. 3(b), as a function of the thickness ratio, $t_{\text{ZnO}}/(t_{\text{ZnS}} + t_{\text{ZnO}})$. From this figure, we see that a 58% replacement of the ZnS shell by ZnO corresponds to a 15 nm redshift in the emission peak, or roughly one monolayer of the ZnS is replaced. The reason for the observed redshift lies in the characteristics of the conduction band shown in Fig. 3(a), where the replacement of ZnS by ZnO creates an outermost layer that significantly lowers the barrier height by 1.56 eV. In contrast, the same replacement of ZnS by ZnO results in an increase in the valance band barrier height by 1.0 eV. Consequently, holes become more localized and electrons become more delocalized as measured by the change in their wave vector, k . The quantum confinement effect in the optical transition is a

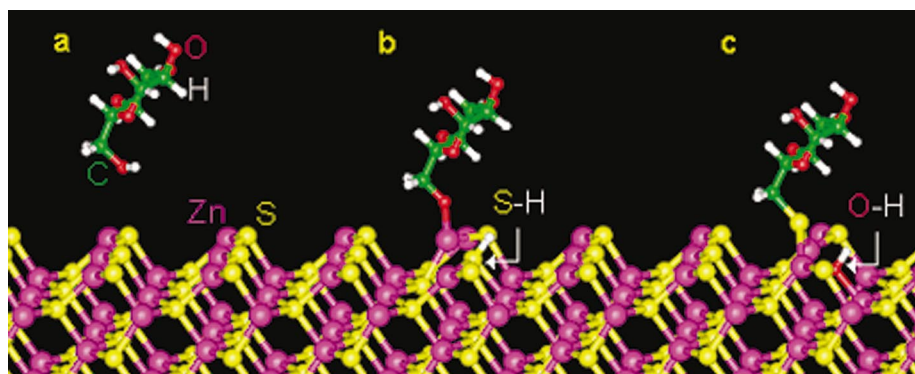


FIG. 2. (Color) Calculated atomic structures and energies for a glucose near the ZnS (110) surface. (a) Intact glucose taken as energy zero, (b) direct binding, and (c) S/O exchange configurations.

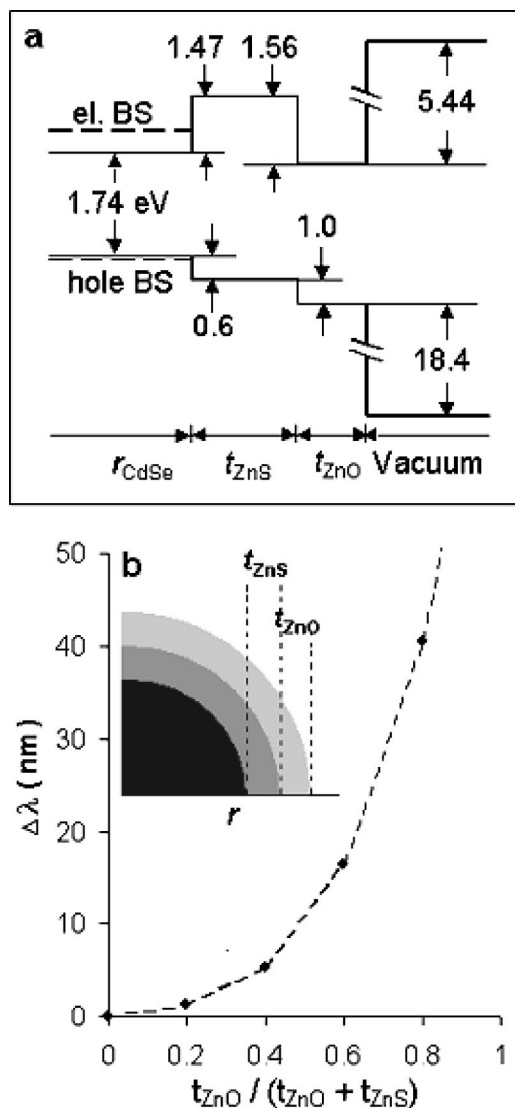


FIG. 3. (a) Radial band diagram used in the EM calculation and (b) calculated redshift as a function of the relative thickness of the ZnO layer to the (ZnO+ZnS) layer. Inset shows the exchange model in which t_{ZnS} represents the thickness of the ZnS layer, t_{ZnO} represents the thickness of the ZnO layer, and r_{CdSe} is the CdSe core size that does not change.

change in the kinetic energy, k^2/m^* . Ignoring the effective mass m^* , this implies a small gap reduction because the electron and hole effect largely cancel each other. However, the effective mass of electron is significantly smaller than that of hole, $m_e^*/m_h^*=0.15$ for CdSe. This further magnifies the band gap reduction. First-principles density functional theory predicted a 0.1 eV energy gain for S/O exchange on the QD surface.

Fourier transform infrared (FTIR) spectra, collected using a Nicolet 20F Far IR FTIR spectrometer and KBr win-

dows, provided direct evidence for the CD and QD interaction. The spectral data (not shown) showed that both the QD and CD-QD samples displayed the IR band at 332 cm^{-1} thought to be due to ZnS, whereas the ZnS-related band at 357 cm^{-1} observed for CD-QDs was shifted from the 366 cm^{-1} band position observed for the QDs alone. IR bands at 445 cm^{-1} and $517\text{--}526\text{ cm}^{-1}$ could also be due to shifts of the original bands observed for the QDs. However, the IR bands observed at 400 cm^{-1} and $561\text{--}586\text{ cm}^{-1}$ for the CD-QDs were clearly absent before introduction of the CDs and are consistent with the ZnO^{14} and Zn-O stretching modes,¹⁵ respectively.

In summary, a new ZnO layer on the existing ZnS shell generated by crystal coordinate bond transformations with CDs or CD-water clusters¹⁶ resulted in water-soluble and stable QDs. Interestingly, this structure may serve to “direct” the cyclodextrin hydroxyls close to the ZnS surface.

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¹H. Z. Zhang, B. Gilbert, F. Huang, and J. F. Banfield, *Nature (London)* **424**, 1025 (2003).

²F. Huang, H. Zhang, B. Gilbert, and J. F. Banfield, *Pap. Am. Chem. Soc.* **225**, 431 (2003).

³S. Pathak, S. K. Choi, N. Arnheim, and M. E. Thompson, *J. Am. Chem. Soc.* **123**, 4103 (2001).

⁴H. Mattoussi, J. M. Mauro, E. R. Goldman, G. P. Anderson, V. C. Sundar, F. V. Mikulec, and M. G. Bawendi, *J. Am. Chem. Soc.* **122**, 12142 (2000).

⁵S.-Y. Ding, M. Jones, M. P. Tucker, J. M. Nedeljkovic, J. Wall, M. N. Simon, G. Rumbles, and M. E. Himmel, *Nano Lett.* **3**, 1581 (2003).

⁶A. P. Alivisatos, K. P. Johnsson, X. G. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez, and P. G. Schultz, *Nature (London)* **382**, 609 (1996).

⁷L.-Q. Gu, O. Braha, S. Conlan, S. Cheley, and H. Bayley, *Nature (London)* **398**, 686 (1999).

⁸B. O. Dabbousi, J. RodriguezViejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen, and M. G. Bawendi, *J. Phys. Chem. B* **101**, 9463 (1997).

⁹B. L. Abrams, J. P. Wilcoxon, S. G. Thoma, and J. M. Kraus, *Materials Research Society, Poster DD11.9, Annual Meeting, Boston, MA, 29 November–3 December, 2004*

¹⁰J. Lee, R. Li, B. Yang, T. A. P. Seery, and F. Papadimitrakopoulos, *Materials Research Society, Poster DD10.14, Annual Meeting, Boston, MA, 29 November–3 December, 2004*.

¹¹M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).

¹²G. Kresse and J. Furthmuller, <http://cms.mpi.univie.ac.at/VASP>.

¹³S. B. Zhang, S.-H. Wei, and A. Zunger, *J. Appl. Phys.* **83**, 3192 (1998).

¹⁴S. M. Liu, F. Q. Liu, H. Q. Guo, Z. H. Zhang, and Z. G. Wang, *Phys. Lett. A* **271**, 128 (2000).

¹⁵C. H. Fischer, H. J. Muffler, M. Bar, S. Fiechter, B. Leupolt, and M. C. Lux-Steiner, *J. Cryst. Growth* **241**, 151 (2002).

¹⁶T. Tabushi, Y. I. Kiyosuke, T. Sugimoto, and K. Yamamura, *J. Am. Chem. Soc.* **100**, 916 (1978).