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Communication

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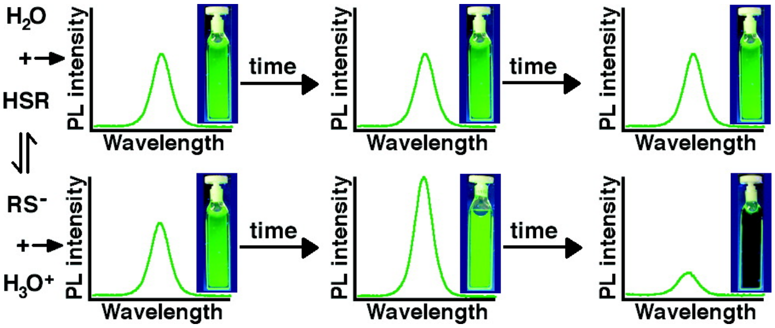

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Effect of the Thiol−Thiolate Equilibrium on the Photophysical Properties of Aqueous CdSe/ZnS Nanocrystal Quantum Dots

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As-prepared,[1] hydrophobic NQDs are soluble in a variety of nonpolar solvents. Transfer from the organic phase to the aqueous phase can be effected by ligand exchange. In the most frequently used and simplest procedure, the original ligands are replaced with bifunctional thiol ligands. This method has been widely used in biomolecular tagging and biosensing applications.[2]

The impact of thiol ligands on the photophysical properties of CdSe NQDs is complicated and often deleterious. Thiol−ligand exchange leads to reduced photoluminescence (PL) compared to the starting hydrophobic NQDs.[3] Further, it has been reported that thiol-derivatized CdSe NQDs are not temporally stable, losing solubility over time. This was attributed to photocatalytic oxidation of the thiol ligands to disulfides.[4] Improved thiol ligand systems, for example, poly(ethylene glycol)-terminated dihydrolipoic acid compounds, provide significantly enhanced NQD stability, but the exchange reaction still leads to diminished PL.[5] Recently, Hohng and Ha reported an unexpected effect of thiol (β-mercaptoethanol, BME) when they added small amounts to streptavidin-conjugated polymer-encapsulated CdSe/ZnS core/shell NQDs.[6] They observed complete suppression of blinking in single-dot studies of thiol-treated NQDs. The issue of NQD blinking is critical for applications that rely on single-dot emission. To better understand the contradictory reports regarding the effect of thiols on NQD photophysics, we studied PL efficiency and carrier (electron and hole) dynamics as functions of thiol concentration, time, and pH. Under such controlled conditions, we conclude that thiolates, rather than thiols, comprise the “active” species that affect NQD optical properties.

We prepared CdSe/ZnS core/shell NQDs following standard literature procedures[1a,7] and subsequently transferred them to the aqueous phase using a polymer encapsulation method[8] that employed 40% octylamine-modified poly(acrylic acid).[9] This method allowed us to avoid the use of thiol as the solubilizing agent, as thiol ligand exchange reactions require exposure of the NQDs to high thiol concentrations (∼neat). The NQDs had a core diameter of 3.0 nm, with the lowest, 1S absorption feature at 530 nm and a PL maximum at 546 nm.[10] Polymer encapsulation allowed retention of high as-prepared quantum yields (QYs) in emission (45% in hexane to 37% in water) and provided a more direct analogy to the Hohng and Ha report in terms of NQD chemistry. NQD−thiol samples were mixed well prior to analyses, and samples were stored in the dark. MES (pH 5.5 and 7.2) and borate (pH 9.2) buffers (100 mM) were used to control pH over three pH ranges.[10] While continuous wave (*cw*) PL was used to characterize QYs, a combination of time-resolved transient-absorption (TA)[11] and PL (*t*-PL) measurements[12] was used to monitor dynamics of photoexcited electrons and holes.

The influence of BME on PL was highly concentration-dependent (Figure 1). Lower concentrations (25−500 mM) resulted in PL enhancement, up to 1.7×, with a concentration-dependent decline observed over time. PL enhancement was temporally delayed for the lowest BME concentration (25 mM); however, once achieved, the high QYs were stable (>12 days). The highest studied concentration (2500 mM) produced an immediate drop in PL, with no luminescence measurable within a day. This BME concentration provides the closest comparison with traditional ligand-exchange reactions, which also result in diminished PL.

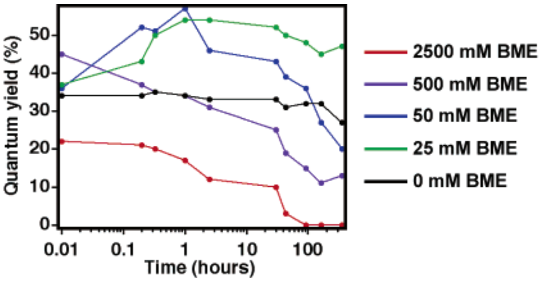

Figure 1. Effect of BME concentration and time on PL QYs of CdSe/ZnS NQDs (pH 7.2; NQD concentration is 0.02 μM, determined optically[13]).

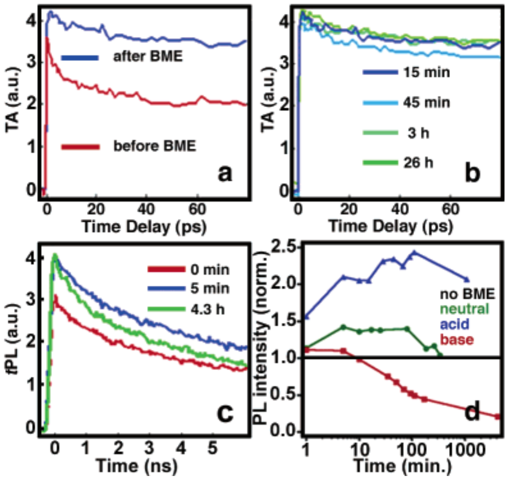

Figure 2. (a) Upon addition of BME to a pH-neutral CdSe/ZnS NQD solution, the electron decay channel (fast 2 ps time constant) disappears. (b) Electron dynamics (up to 1 ns) are stable, with no return of the fast component over many hours. (c) Time-resolved PL demonstrating the appearance over several hours of a new decay channel (1.6 ns dynamics). (d) PL intensity as a function of time and pH (total [BME]: 250 mM).

Employing time-resolved spectroscopic techniques allowed us to gain insight into the mechanism of PL increase and subsequent decrease upon BME addition. First, we studied TA by measuring time-dependent changes in 1S absorption after excitation of an NQD solution (100 fs time resolution),[11] where TA is sensitive only to changes in electron dynamics.[14] Upon BME addition to a solution (pH 7.2) of polymer-coated NQDs, a fast component (decay time ∼2 ps) present in the original sample disappears (Figure 2a) and does not return over time (Figure 2b). This indicates the stable passivation of electron traps upon BME addition. Second, we studied *t*-PL,[12] which is sensitive to both electron and hole dynamics (70 ps time resolution). We observed an increase in PL amplitude

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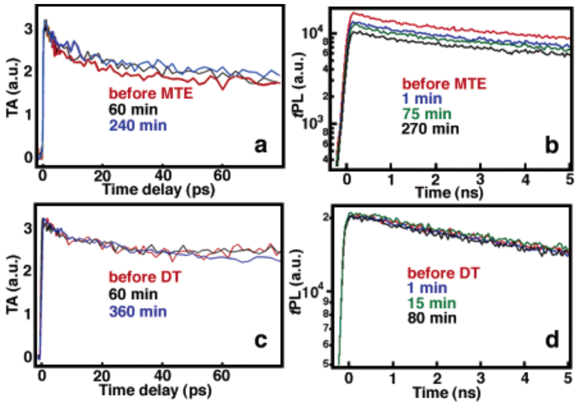

Figure 3. Control experiments. (a, b) TA and *t*-PL for aqueous solutions (pH 7.2) before and after MTE addition. (c, d) TA and *t*-PL for hexane solutions before and after DT addition. Dynamics unchanged in all cases.

immediately following BME addition without a change in nanosecond dynamics (Figure 2c). The amplitude enhancement is consistent with the passivation of electron traps observed in the TA experiment. Significantly, within a few hours, an additional decay channel (decay time ~1.6 ns) appeared (Figure 2c). As the TA data did not indicate any change in the electron dynamics on the nanosecond scale, the new decay channel is attributed to hole dynamics (see below). The time-resolved measurements correlate well with *cw*-PL measurements (Figure 2d, pH 7.2), where an initial PL increase can be explained as a reduction in the number of electron traps and subsequent PL decline as formation of hole traps. The direct observation of electron trap passivation and its correlation with enhanced PL is unique in terms of connecting a specific thiol−NQD interaction with a positive impact on NQD PL and may also assist in explaining the previously reported blinking suppression that was observed for similar low BME concentrations.[6]

BME dissociates in aqueous solution to thiolate (pK_a of 9.6).[15] To determine which moiety contributes to the observed PL changes, we first studied the pH-dependency of PL (Figure 2d). Starting with a total BME concentration of 250 mM, the relative thiol and thiolate concentrations were controlled by pH.[10] In basic conditions (pH 9.2), where the thiolate concentration is ~100-fold higher than in neutral solution, a strong PL decrease was observed. Whereas in acidic conditions (pH 5.5), where the thiol−thiolate equilibrium strongly favors the protonated species, PL increased dramatically and was temporally stable (Figure 2d). Results from pH-neutral solutions were intermediate. The dramatic decline in PL in basic conditions implied that thiolate provided the observed hole traps. However, the results in pH-neutral and acidic conditions were insufficient to conclude which species was responsible for the observed enhancement in PL.

To determine whether thiolate played a dual role, both enhancing and decreasing PL, we performed three control experiments. First, BME in a nonpolar solvent (chloroform), where the thiol remains protonated, produced no PL changes. Second, we replaced BME with 2-methyl thioethanol (MTE), which cannot generate thiolate in aqueous solution. Finally, we exposed as-prepared NQDs in hexane, again, where the thiol−thiolate equilibrium is not supported, to 250 mM concentration of dodecanethiol (DT). In these latter two cases, we saw no changes in PL intensity nor any changes in TA and PL dynamics (Figure 3). These results support the supposition that thiolate, not thiol, both deactivates existing electron trap states at low concentrations (enhancing PL) and introduces new hole trap states at high concentrations (decreasing PL). This dual role may be attributed to a limited number of undercoordinated NQD surface sites that benefit from thiolate's electron-donating ability. Once these sites are saturated, additional thiolates play the role of hole traps. As reported previously, it is energetically favorable for a photogenerated CdSe hole to trap to a surface-bound "thiol" molecule.[16] While previous studies have not differentiated the roles played by thiols and thiolates, our results show that these distinctions are critical to the understanding of concentration, pH, and thiol chemical classification (i.e., primary versus secondary) effects.

The precise fate of the thiolate-trapped hole has yet to be determined. Hole transfer to a thiolate anion results in formation of a thyil radical (RS$^\bullet$), and RS$^\bullet$ can couple with a second RS$^\bullet$, generating a noncoordinating disulfide (RSSR).[16] Alternatively, the NQD electron and the thiolate-trapped hole can recombine radiatively (deep-trap emission) or nonradiatively, returning the NQD−thiolate pair to its original state but circumventing band-edge emission. Both disulfide formation and electron−hole recombination lead to reduced PL, and the two processes likely compete. The first is a bimolecular reaction whose rate depends on the concentration of the reacting molecules, which is directly related to thiolate concentration. At increasing thiolate concentrations, radical consumption by disulfide formation can dominate. Also, at high concentrations, thiolates can effectively displace a majority of the native TOPO/TOP ligands. In this case, subsequent loss of thiolates to disulfide can lead to ligand shell instability and NQD aggregation.[4] We observe aggregation only for the highest total thiol concentration (2500 mM).[10]

In summary, we have determined that the effect of thiols on NQD PL can be favorable or adverse, depending on the concentration of the thiolate anion, which is influenced by absolute initial thiol concentration, pH conditions, and/or thiol exposure times. The pH-dependent results, coupled with the concentration data, point to an optimal thiolate presence that can support long-term high QYs. Understanding the role of surface ligands is critical to the design of stable, high-QY, nonblinking NQDs.

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Supporting Information Available: Experimental details and preliminary results for ZnS-shell- and NQD-size-dependence of thiolate−NQD emission properties are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Murray, C. B.; Norris, D.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715. (b) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183−184.
(2) (a) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016−2018. (b) Mattoussi, H.; Mauro, J. M.; Goldman, E. R.; Mikulec, F. V.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 12142−12150.
(3) Gao, X.; Chan, W. C. W.; Nie, S. *J. Biomed. Opt.* **2002**, *7*, 532−537.
(4) Aldana, J.; Wang, Y. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844−8850.
(5) Uyeda, H. T.; Medintz, I. L.; Jaiswal, J. K.; Simon, S. M.; Mattoussi, H. *J. Am. Chem. Soc.* **2005**, *127*, 3870−3878.
(6) Hohng, S.; Ha, T. *J. Am. Chem. Soc.* **2004**, *126*, 1324−1325.
(7) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468−471.
(8) Wu, X.; Liu, J.; Liu, K. N.; Haley, J. A.; Bruchez, M. P. *Nat. Biotechnol.* **2003**, *21*, 41−46.
(9) Wang, K. T.; Iliopoulos, I.; Audebert, R. *Polym. Bull.* **1988**, *20*, 577−582.
(10) See Supporting Information for experimental details.
(11) Klimov, V. I.; McBranch, D. W. *Opt. Lett.* **1998**, *23*, 277−279.
(12) Balet, L. P.; Ivanov, S. A.; Piryatinski, A.; Achermann, M.; Klimov, V. I. *Nano Lett.* **2004**, *4*, 1485−1488.
(13) Leatherdale, C. A.; Woo, W. K.; Mikulec, F. V.; Bawendi, M. G. *J. Phys. Chem. B* **2002**, *106*, 7619−7622.
(14) Klimov, V. I.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. *Phys. Rev. B* **1999**, *60*, 13740−13749.
(15) Lamoureux, G. V.; Whitesides, G. M. *J. Org. Chem.* **1993**, *58*, 633−641.
(16) Wuister, S. F.; de Mello Donega, C.; Meijerink, A. *J. Phys. Chem. B* **2004**, *108*, 17393−17397.

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