Preparation and Characterization of Dendrimer-Encapsulated CdS Semiconductor Quantum Dots

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Received August 22, 2000

We report the preparation and characterization of dendrimer-encapsulated CdS nanoparticles (DE-CdS). These luminescent assemblies are prepared using dendrimers as both nanoreactor and stabilizer. That is, the dendrimer first acts as a nanoreactor that sequesters Cd^{2+} ions, and then after reaction with S^{2-} it stabilizes the resulting CdS nanoparticles by preventing agglomeration. Because the size of the nanoparticle (or quantum dot, QD) is related to the size (or generation, G) of the dendrimer template used to prepare it, and because the optical properties of QDs are size-dependent, the absorptive and emissive properties of the QDs are a function of the generation of the dendrimer template used to prepare them. Additionally, the numerous reactive groups on the surface of the dendrimer can be used to render the composites soluble in essentially any solvent, including water, organic solvents,[1] fluorous phases,[2] and even supercritical fluids,[3] and as synthetic handles for attachment of ligands to direct binding of the composites to surfaces,[4] biological ligands,[5] DNA,[6,7] and other targets.

New methods for preparing useful luminescent QDs have recently been described. Three particularly significant findings are relevant to our work. First, means for closely controlling the size of CdS and CdSe QDs have been discovered. For example, the high-temperature organometallic route reported by Bawendi provides a high degree of control over both particle size and monodispersity.[8] Second, it was found that "capped" or core-shell (e.g., (CdSe)ZnS) structures result in enhanced stability and much higher quantum efficiency compared to uncapped CdS or CdSe nanocrystals.[9−11] Finally, methods for attaching biologically sensitive structures to the semiconductor surface have been reported.[12,13] These highly luminescent nanoparticles have photophysical properties superior to organic dyes (increased quantum yield and photostability), but the high temperature required to synthesize them can be problematic for some applications. It has also been found that attachment of biologically active groups requires multiple steps, and that the resulting composites have lower quantum yields than unmodified QDs.

Murphy was the first to report using dendrimers to control the size of QDs.[14−17] These materials have been shown to be agglomerates of spatially segregated QDs stabilized by multiple dendrimers. That is, in these *inter*dendrimer composites, many dendrimers surround multiple QDs to yield large, aggregated structures.[14] This geometry is very different than the nonaggregated CdS nanoparticles that are sequestered *within* individual dendrimers that we describe here. Both families of materials have their virtues, but the latter afford control over absorbance and emission characteristics through dendrimer-mediated, size-induced quantum confinement effects. DE-CdS composites also lend themselves to straightforward chemical modification of the dendrimer periphery. The fact that they are discreet nanoscopic entities is also critical to their future use as luminescent labels for biochemical applications.

The preparation of DE-CdS composites is similar to that of the dendrimer-encapsulated metal nanoparticles we have reported previously.[18−20] The latter are prepared by extraction of metal ions into the interior of dendrimers, followed by chemical reduction. DE-CdS composites are prepared by alternating dropwise addition of Cd^{2+} and S^{2-} (16 mM $Cd(NO_3)_2$ and 16 mM Na_2S in methanol) to a solution containing hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers of various generation (Gn-OH). The final concentrations of Gn-OH (given in parentheses) and Cd^{2+} and S^{2-} are as follows: G4-OH (0.1 mM), 1.6 mM; G6-OH (0.05 mM), 3.2 mM; and G8-OH (0.012 mM), 3.1 mM. These relative dendrimer/ion ratios were chosen to maintain a constant ratio of the ion concentration to the number of dendritic tertiary amines present in the outermost shell of the dendrimer. The G6-OH and G8-OH DE-CdS nanocomposites require no purification after preparation, while the G4-OH-encapsulated particles require aqueous washing or a size-selective photoetching[21] step to remove bulk CdS stabilized by multiple dendrimers.[14,16,17]

Figure 1 shows absorption and luminescence spectra of DE-CdS assemblies prepared using three different generations of dendrimers (G4, G6, and G8). For example, G4-OH DE-CdS (spectrum a) results in a sharp absorbance band at 280 nm and an emission peak at 320 nm. When higher generation dendrimers are used as templates, larger CdS QDs result. QDs prepared in G6-OH templates yield absorbance and emission maxima at 350 and 470 nm, respectively (spectrum b), while a CdS QD encapsulated within a G8-OH dendrimer absorbs and emits at 370 and 510 nm, respectively (spectrum c). The apparent diameters of the DE-CdS composites, as inferred from their optical absorbance spectra,[22,23] are 1.3 nm for G4-OH/CdS, 1.8 nm for G6-OH/CdS, and 2.3 nm for G8-OH/CdS. These particle sizes are consistent with those of the dendrimer-encapsulated metal nanoparticles we reported previously.[18,24] This high degree of

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(1) Chechik, V.; Zhao, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 4910−4911.

(2) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243−1244.

(3) Yeung, L. K.; Crooks, R. M. *J. Am. Chem. Soc.* Submitted for publication.

(4) Chechik, V.; Crooks, R. M. *Langmuir* **1999**, *15*, 6364−6369.

(5) Wilbur, D. S.; Pathare, P. M.; Hamlin, D. K.; Buhler, K. R.; Vessella, R. L. *Bioconj. Chem.* **1998**, *9*, 813−825.

(6) Kukowska-Latallo, J. F.; Bielinska, A. U.; Johnson, J.; Spindler, R.; Tomalia, D. A.; Baker, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 4897−4902.

(7) Bielinska, A. U.; Chen, C.; Johnson, J.; Baker, J. R. *Bioconj. Chem.* **1999**, *10*, 843−850.

(8) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(9) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649−5655.

(10) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem.* **1996**, *100*, 468−471.

(11) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattousi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463−9475.

(12) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013−2016.

(13) Chan, W. C. W.; Nie, S. *Science* **1998**, *281*, 2016−2018.

(14) Sooklal, K.; Hanus, L. H.; Ploehn, H. J.; Murphy, C. J. *Adv. Mater.* **1998**, *10*, 1083−1097.

(15) Lackowics, J. R.; Gryczynski, I.; Gryczynski, Z.; Murphy, C. J. *J. Phys. Chem. B* **1999**, *103*, 7613−7620.

(16) Huang, J.; Sooklal, K.; Murphy, C. J.; Ploehn, H. J. *Chem. Mater.* **1999**, *11*, 3595−3601.

(17) Hanus, L. H.; Sooklal, K.; Murphy, C. J.; Ploehn, H. J. *Langmuir* **2000**, *16*, 2621−2626.

(18) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877−4878.

(19) Zhao, M.; Crooks, R. M. *Adv. Mater.* **1999**, *11*, 217−220.

(20) Zhao, M.; Crooks, R. M. *Chem. Mater.* **1999**, *11*, 3379−3385.

(21) Torimoto, T.; Konati, H.; Sakata, T.; Mori, H.; Yoneyama, H. *Chem. Lett.* **1999**, *5*, 379−380.

(22) Vossmeyer, T.; Katsikas, L.; Girsig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmuller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665−7673.

(23) Vossmeyer, T.; Reck, G.; Katsikas, L.; Haupt, E. T. K.; Schulz, B.; Weller, H. *Science* **1995**, *267*, 1476−1479.

(24) Zhao, M.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 364−366.
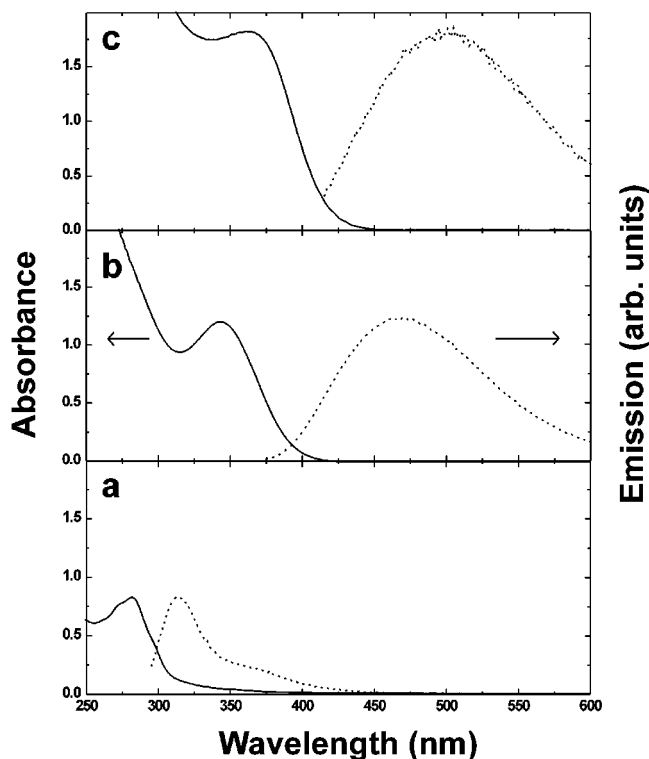
Figure 1. Absorption (solid line) and emission (dotted line) spectra of dendrimer-encapsulated CdS quantum dots prepared within different generation dendrimers: (a) G4-OH; (b) G6-OH; and (c) G8-OH. A rising baseline characteristic of nanoscale semiconductor particles obscures spectral data at wavelengths significantly lower than the absorption maximum.

control over particle size allows the photophysical properties of these composites to be finely tuned by varying only the generation of the dendrimer and not the reaction conditions (reaction temperature, solvent, surfactant, or surfactant concentration).

Dynamic light scattering (DLS) measurements also confirm the presence of small, nonaggregated CdS particles. For example, Figure 2 shows DLS data for G8-OH in the presence and absence of an encapsulated CdS nanoparticle. The average radius of a G8-OH dendrimer is 5.0 nm, while for a G8-OH/CdS composite the value is slightly smaller (3.8 nm). Complete size distribution data for G4-OH, G4-OH/CdS, G6-OH, and G6-OH/CdS are provided in the Supporting Information; the average particle sizes are 2.3, 1.3, 2.5, and 2.5 nm, respectively. These data indicate that the dendrimer radius usually shrinks slightly in the presence of the encapsulated CdS nanoparticles. Importantly, and in contrast to previous reports of aggregates having radii generally in the range of 50−100 nm,[14,16,17] the DE-CdS materials do not aggregate (at least within the detection limit of DLS, which is ~1−2 nm). Finally, DE-CdS nanocomposites are exceptionally stable: there is no indication of aggregate formation (via DLS measurements) or particle growth (via absorption and emission experiments) after months of storage in the dark.
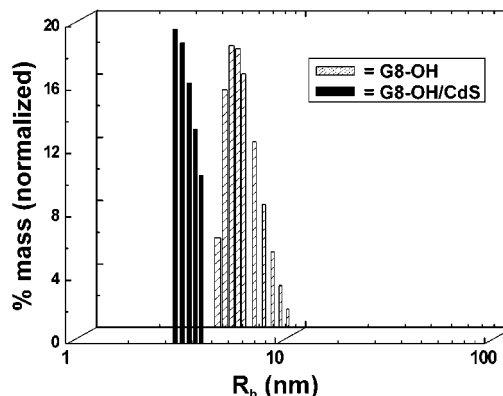
Figure 2. Dynamic light scattering (DLS) measurements of the hydrodynamic radius (R_h) of G8-OH dendrimer (shaded bars) and G8-OH/CdS (black bars) at 20 °C. DLS data for G6-OH and G4-OH, with and without encapsulated CdS nanoparticles, are provided in the Supporting Information.

We have found that DE-CdS QDs can be further modified with a ZnS shell to yield intradendrimer (CdS)ZnS nanocomposites.[9] As discussed earlier, such core-shell materials have been found to have superior luminescent properties and to be even more stable than the unclad analogues. ZnS capping is accomplished by addition of methanolic Zn^{2+} and S^{2-} to a solution of DE-CdS. After normalization at the absorbance maximum (280 nm), the quantum yield of the encapsulated (CdS)ZnS materials is about 20% higher than that of the dendrimer-encapsulated CdS-only nanocomposites (spectra are provided in the Supporting Information). The gain afforded by this modification promises to be even higher for encapsulated (CdSe)ZnS core-shell particles, where quantum yields approaching 50% have been reported.[10,11]

To summarize, we have described the synthesis and characterization of discreet, luminescent, dendrimer-encapsulated quantum dot assemblies. They are characterized by all of the advantages of quantum dot-based luminescent probes (high quantum yield, good photostability, and color tunability), but the synthetic conditions required to prepare them are less extreme than others that have been reported. Moreover, these composites come equipped with easily functionalized hydroxyl groups on the dendrimer periphery. We will report shortly on the application of these assemblies as luminescent biological probes and on the preparation and characterization of high-quantum-yield (CdSe)-ZnS core-shell dendrimer-encapsulated QDs.

Supporting Information Available: DLS data for G4-OH and G6-OH in the presence and absence of CdS nanoparticles and emission spectra obtained from dendrimer-encapsulated G4-OH/CdS nanocomposites and ZnS-modified G4-OH/CdS nanocomposites ((CdS)ZnS) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.