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Polyamine−Quantum Dot Nanocomposites: Linear versus Starburst Stabilizer Architectures

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Recently, a number of research groups have found that dendrimers are effective templates for the synthesis of inorganic nanomaterials (Sooklal, K.; Hanus, L. H.; Ploehn, H. J.; Murphy, C. J. *Adv. Mater.* **1998**, *10*, 1083. Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355. Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877.). Here, we report that linear polymer analogues of the dendrimer molecules can be used to make CdS nanocomposites with similar optical properties in solution, albeit with reduced quantum yield of emission. High local concentration of chelating nitrogens on the polymer or dendrimer is hypothesized to be the key feature for ultrasmall, defect-free CdS nanoparticle formation. Immobilization of the nanocomposites in a sol−gel glass is an effective means to capture them in a solid form.

Introduction

Semiconductor quantum dots have attracted much attention during the past few years because of their size-dependent chemical and physical properties.[1−6] Progress has been made in the chemical synthesis of relatively monodisperse nanometer-sized particles in various media.[7,8] For many applications, including optoelectronics and sensors, immobilization of quantum dots in a condensed phase is a requirement for robust and portable devices. Therefore, a variety of technologies have been developed for anchoring nanoparticles onto inorganic surfaces or trapping them within inorganic porous solids.[9−19]

Dendrimers are quasispherical organic molecules that have well-defined surface groups and can be synthesized in well-defined sizes on the nanometer scale.[20−22] Recently, several groups have explored the synthesis of inorganic nanoparticles using dendrimers as a soft organic template.[23−25] We have already shown that PAMAM starburst dendrimers are good matrices for

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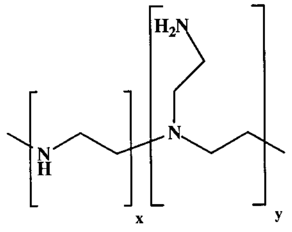
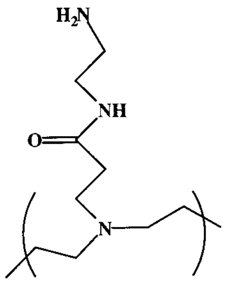
producing bright blue-emitting CdS quantum dots.[23] In this paper, we compare dendrimer- and linear polymer-stabilized CdS quantum dots having similar functional groups in order to explore the effect of polymer architecture, dendritic versus linear, on quantum dot formation and stabilization. The resulting nanocomposites have been immobilized in silica-based sol−gels to form solid optical materials that can retain their emissive properties for months.

Experimental Section

Preparation of Amine Polymer/Dendrimer-Quantum Dot Nanocomposites. The synthesis and properties of CdS quantum dots stabilized by dendrimers (starburst PAMAM dendrimers, generation 4, with 64 surface amine groups, Aldrich) have been reported previously.[23] A linear polymeric analogue of the Starburst amine dendrimer is polyethylenimine (PEI, MW = 7.5 × 10^5, Aldrich).



structure of PEI



structure of Starburst PAMAM dendrimer surface branch

Typically, 0.5 mL of a 2 × 10^{-3}M $Cd(NO_3)_2{\cdot}4H_2O$ in methanol stock solution was added to 10 mL of 1.14 × 10^{-4} M dendrimer or PEI stock solution in the appropriate solvent (methanol, water, or acidic methanol at pH = 3.4−3.5) at 10 °C, followed by addition of an 0.50 mL aliquot of 2 × 10^{-3} M Na_2S stock solution, to form CdS nanoparticles stabilized by either dendrimer or PEI. The Cd^{2+} and S^{2-} additions were repeated 10 times, so that the final concentration of CdS was 5 × 10^{-4} M. The nanocomposite solutions were colorless and emitted bright blue light upon irradiation with a blacklight. Solutions were stored at −20 °C.

Preparation of Polyphosphate-Stabilized CdS Quantum Dots. Polyphosphate-stabilized CdS quantum dots were prepared according to the following protocol: 96 mL of deionized water was purged with N_2 for 20 min. After the addition of 2.0 mL of 0.01 M sodium polyphosphate (Fisher) as the stabilizing agent and 2.0 mL of 0.01 M $Cd(NO_3)_2{\cdot}4H_2O$ (Baker), the pH was adjusted to 10.3 by the addition of 0.10 M NaOH (Aldrich). While the solution was vigorously stirred, 0.0016 g of Na_2S (Alfa) was added to form a bright yellow solution of CdS quantum dots, which did not precipitate for days. Under a blacklight, the solution emitted weak red-orange light.

Incorporation of Polymer/Dendrimer−Quantum Dot Nanocomposites in a Sol−Gel Matrix. Tetramethyl orthosilicate (TMOS, Aldrich) was partially hydrolyzed by mixing it with an equal amount of acidic deionized water (pH 3), with vigorous stirring, for 2 h at room temperature. The resulting solution became a clear and homogeneous sol. At this point, 3 mL of the sol was thoroughly mixed with 3 mL of the CdS−polymer solution. The sol was poured into plastic 1 cm × 1 cm cuvettes to a height of ~3 cm, covered with aluminum foil, and left for a day, becoming a gel. After days of drying at room temperature, a stiff transparent cubic gel with virtually no cracks was obtained.

Characterization of Sol−Gel Materials. Over the drying period, the sol−gels shrank to 0.5 × 0.5 × 1.5 cm, about $^1/_8$ of their original volume. The weight loss due to solvent evaporation was ~80%, consistent with the loss of nearly all of the original methanol/water solvent. The presence of the nanocomposite made little difference in these bulk properties. Fits of the BET isotherm to nitrogen adsorption data revealed that the gels had surface areas of 300 (dendrimer/ methanol nanocomposite), 280 (PEI/water nanocomposite), 290 (dendrimer/water nanocomposite), and 210 m^2/g (dendrimer/acidic methanol nanocomposite). These surface areas are relatively low but are comparable to other polymer/tetra(m)ethyl orthosilicate-derived sol−gel data in the literature.[26]

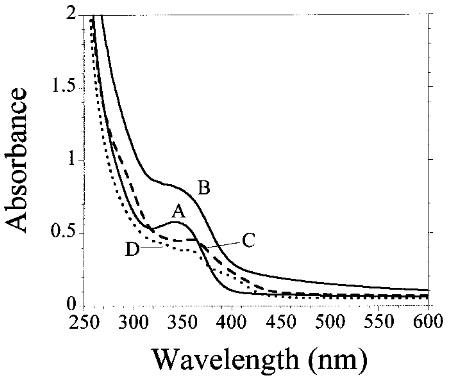


Figure 1. Absorption spectra of CdS quantum dots prepared in solution under different conditions: (A) PEI as stabilizer, in water; (B) dendrimer as stabilizer, in methanol; (C) dendrimer as stabilizer, in water (dashed line); and (D) dendrimer as stabilizer, in methanol at pH 3.4 (dotted line).

Instrumentation. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 14 ultraviolet−visible spectrophotometer. Emission spectra were acquired on an SLM-Aminco 8100 spectrofluorometer at room temperature and are uncorrected (the sharp drop at 500 nm is an instrumental artifact). Transmission electron microscopy (TEM) was carried out on a JEOL JEM-100CX II electron microscope at 80 kV; samples were prepared by placing a drop of the solution onto a nitrocellulose−copper grid and drying overnight at room temperature. Dynamic light scattering studies were performed as previously described.[23]

Results and Discussion

PAMAM Dendrimer versus PEI as a Template for CdS Quantum Dot Formation. To examine the effects of polymer architecture on quantum dot formation, PEI was chosen as a linear analogue to the PAMAM generation 4 starburst dendrimer. Sodium polyphosphate was chosen as a typical anionic water-soluble stabilizing agent with “no” architecture and little propensity to coordinate Cd(II). Figure 1 shows the UV−visible absorption spectra of the CdS quantum dots stabilized by PEI and the dendrimer under different conditions. All of the samples exhibited blueshifted absorption spectra relative to bulk CdS, indicating quantum confinement. The size of these CdS nanoparticles can be estimated from the absorption edge (from interception of slope at edge with wavelength axis) using Brus' effective mass model[1,2] (Table 1). Polyphosphate as a stabilizer led to larger CdS nanoparticles in water compared to those of both polyamines. Absorption data were reproducible from batch to batch.

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(26) Surface areas of 300−1000 m^2/g are common for typical gels: Brinker, C. J.; Scherer, G. W. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: San Diego, 1990. Varying the synthesis conditions can greatly affect the resulting material's surface area; for example, see: (a) Harmer, M. A.; Farneth, W. E.; Sun, Q. *J. Am. Chem. Soc.* **1996**, *118*, 7708. (b) David, I. A.; Scherer, G. W. *Chem. Mater.* **1995**, *7*, 1957.

Table 1. Analysis of Absorption Spectra of CdS Quantum Dots Synthesized under Different Conditions

stabilizing agent/solvent	band gap energy (eV)	CdS particle size (nm)[a]
dendrimer/methanol	3.2	2.8
PEI/methanol	3.2	2.8
dendrimer/water	2.8	3.7
PEI/water	3.1	3.0
dendrimer/methanol pH 3.4	2.7	4.2
PEI/methanol pH 3.5	2.6	4.4
polyphosphate/water	2.5	5.0

[a] See Brus.[1,2]

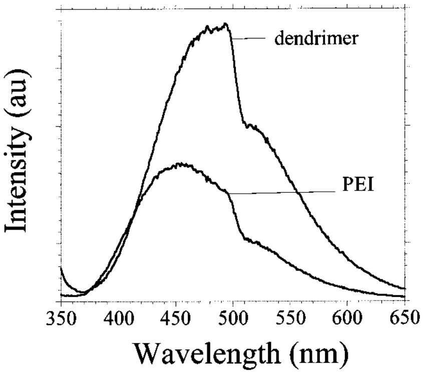

Figure 2. Photoluminescence spectra of CdS quantum dots prepared in solution with either PAMAM generation 4 dendrimer (in methanol) or PEI (in water) as a stabilizer. Samples were excited at 340 nm.

The solvent effects for PEI (methanol vs water vs acidic methanol) as a stabilizer of CdS quantum dot formation were similar to those for the dendrimer (Table 1); CdS particle size increased in the order methanol < water < acidic methanol. The difference between water and methanol solvents is much more subtle in the case of PEI, as the linear polymer does not aggregate substantially in water like the dendrimer (see below). Otherwise, PEI functions much as the dendrimer does to stabilize ultrasmall CdS nanoparticles and keep them soluble. We have also found that the generation of the dendrimer (2, 3, or 4, having respectively 16, 32, or 64 surface amine groups) has little effect on the optical properties of the resulting nanocomposites;[27] this suggests that the interior nitrogens of the dendrimer (and, presumably, of PEI) are important for CdS nanoparticle stabilization.

Previous work in our laboratory showed that CdS quantum dots stabilized by dendrimers aggregated into surprisingly soluble nanocomposite particles that were hundreds of nanometers in diameter (by dynamic light scattering and transmission electron microscopy);[23] individual CdS particles were not resolvable in these samples by these techniques. In water, the dendrimers alone aggregated extensively, as judged by transmission electron microscopy and dynamic light scattering,[23] resulting in larger CdS quantum dot formation compared to that with methanol as a solvent.

Both polyamine stabilizers, PEI and dendrimer, yielded CdS nanocomposite solutions that emitted in the blue region (λ_{max} ~450−480 nm; Figure 2). The emission of the resulting nanocomposite with PEI as the stabilizer was not as intense as the dendrimer-stabilized material for identical CdS concentrations (relative quantum yield of PEI-stabilized CdS to dendrimer-stabilized CdS is ~0.5; Figure 2), but the spectral distributions were similar. This result is distinctly different from that found for monomeric amines (ethylenediamine or *N*,*N*-diacetylethylenediamine) as stabilizing agents for CdS nanoparticle formation.[23] CdS nanoparticles stabilized by the monomeric amine in water or methanol were not emissive and precipitated after formation.[23] Polyphosphate as a stabilizer led to larger CdS nanoparticles that had more defects, as judged by their redshifted absorption spectra and dull orange-red emission (λ_{max} at 590 nm upon photoexcitation at 340 nm) compared to PEI and dendrimer.

We hypothesize that the high local concentration of basic nitrogens on the dendrimer and on PEI chelate the introduced Cd(II) ions and effectively capture the growing CdS particles upon sulfide addition; the resulting CdS nanoparticles are extremely small and well-stabilized from growth and defects by the amine ligands. Solvent-accessible amine groups keep the entire nanocomposite soluble in polar solvents. Polyphosphate, in contrast, lacks the amine groups that can compete well for Cd(II) in an aqueous environment, and polyphosphate-stabilized CdS nanoparticles are larger and have more surface defects. Monomeric amines do not provide a high enough local concentration for effective nanoparticle stabilization and, furthermore, present hydrophobic ethylene groups to the solvent once coordinated to the nanoparticle, leading to eventual precipitation. Overall, the G4 dendrimer as a stabilizer of CdS quantum dots is somewhat superior to PEI in solution, in terms of the resulting CdS photoluminescence intensity.

Transmission electron microscopy of the PEI−CdS nanocomposite (Figure 3) revealed that the average feature size was ~20 nm, considerably larger than the CdS size (~3 nm) calculated from the optical data. This is reminiscent of the results for the dendrimer nanocomposites.[23] Much larger features are also apparent in the micrograph. Many of these particles are heterogeneous, and some appear to have a core−shell structure, which may be consistent with a CdS core and a polymer shell. Dried films of the CdS−PEI nanocomposite still emitted in the blue region, as the solution did, suggesting that the CdS portion of the composite was well-passivated and the CdS particle size was far smaller than the TEM particle size.

Dynamic light scattering studies of the PEI−CdS nanocomposites in solution showed that their hydrodynamic diameters were 90−110 nm in the three solvent conditions (water, methanol, and acidic methanol), similar to that of PEI alone under those conditions. This result is distinctly different from the dendrimer stabilizer: the formation of CdS quantum dots in dendrimer solution resulted in large, soluble aggregates much larger than the individual dendrimer size, consistent with many dendrimer molecules surrounding CdS quantum dots in a probable weblike structure.[23] The physical solution properties of high-molecular-weight PEIs are evidently unaffected by the presence of CdS quantum dots within the polymer structure. The hydrodynamic diameter of PEI alone was independent of concentration

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(27) Sooklal, K.; Huang, J.; Murphy, C. J.; Hanus, L.; Ploehn, H. J. submitted to *Mater. Res. Soc. Symp. Proc.*

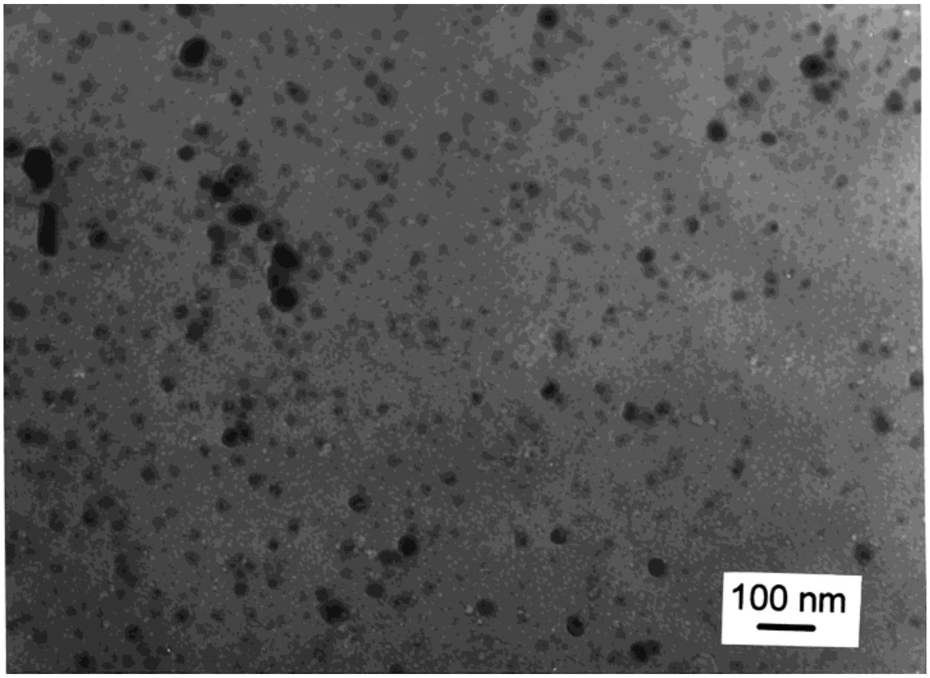

Figure 3. Transmission electron micrograph of the CdS−PEI nanocomposite. The scale bar is 100 nm; average particle size is 20 nm.

from 10^{-4} to 10^{-6} M, suggesting that the nanocomposite samples were in the dilute regime. Other workers have found that a slightly higher molecular weight PEI (MW = 1.0×10^6) is 52 nm in diameter in 100 mM KCl at pH 7, according to dynamic light scattering.[28] These workers also note that PEI size increases as the pH decreases and ionic strength decreases, consistent with our larger diameters of PEI alone in water, without salt. As the 90−110 nm diameter CdS−PEI nanocomposites were dried for obtaining TEM data, it is certainly likely that solvent loss could collapse the polymer structure to give ~20 nm particle diameters, as observed in the TEM.

Incorporation of Nanocomposites into Sol−Gel Glasses. For incorporation into sol−gel glasses, we examined CdS quantum dots that were stabilized by dendrimer, PEI, and polyphosphate. The absorption edge of polyphosphate-stabilized CdS did not change over time upon incorporation in the sol−gel and subsequent drying (data not shown). This result suggests that the CdS quantum dots neither grew nor shrank upon immersion in the initially acidic sol−gel medium. Upon excitation of the polyphosphate−CdS sol−gel nanocomposite at 340 nm, emission peaks were observed at both 400 and 670 nm (Figure 4). The emission peak located at 400 nm was also observed in the silica alone; other workers have suggested that carbon impurities in the sol−gel act as luminescence centers.[29−31] The emission peak at 670 nm is due to the CdS nanoparticles, but its intensity was weak due to (presumably) relatively large numbers of surface defects.[32] In solution, these nanoparticles emitted at 590 nm upon photoexcitation at 340 nm; the more redshifted emission maximum of the CdS in the glass is another indication of increased surface defects. Thus, polyphosphate is not an adequate protective agent for the CdS quantum dots under these conditions.

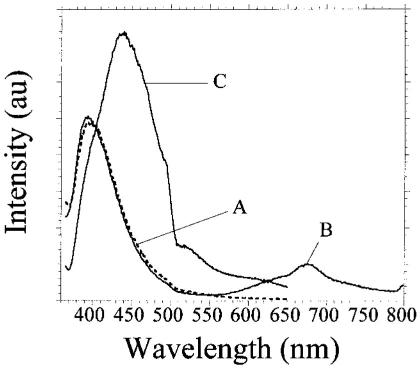

Figure 4. Photoluminescence spectra of (A) silicate sol−gel glass alone (dashed line), (B) polyphosphate-stabilized CdS quantum dots in a silicate sol−gel glass, and (C) CdS−dendrimer nanocomposite (methanol solvent) in a silicate sol−gel glass. Samples had been aged for 10 days at the time these spectra were taken. The emission at ~400 nm in spectrum C is in part due to the glass. Samples were excited at 340 nm.

The incorporation of the PEI−quantum dot and dendrimer−quantum dot nanocomposites in sol−gel glasses was monitored spectroscopically. The absorption results were similar to those of the polyphosphate-stabilized CdS quantum dots: the change in CdS absorption edge was negligible upon incorporation into the glass (data not shown), suggesting that, on average, the CdS nanoparticles were not aggregating nor dissolving upon contact with the initially acidic sol.

The emission of the sol−gel-derived materials was intense (Figure 5) but was surprisingly dependent on initial conditions. CdS nanocomposites made under PEI/aqueous and dendrimer/methanolic conditions were

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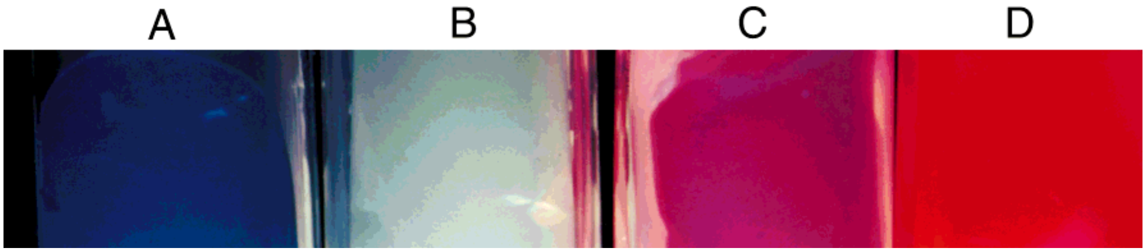

Figure 5. Photograph showing the emission of silicate sol–gel glasses in which are embedded nanocomposites prepared under different reaction conditions: (A) CdS–PEI in water, (B) CdS–dendrimer in methanol, (C) CdS–dendrimer in water, and (D) CdS–dendrimer in methanol at pH 3.4. The samples were irradiated with 366 nm light from a UV lamp.

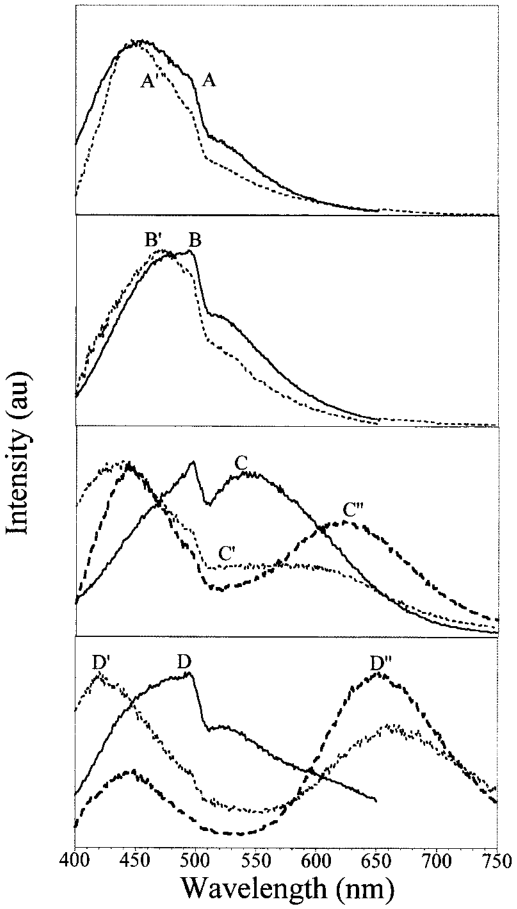

Figure 6. Normalized emission spectra of different CdS nanocomposites embedded in silicate sol–gel glasses upon excitation at 340 nm. The background from the sol–gel alone has been subtracted out. (A) CdS–PEI nanocomposite prepared in water, spectrum in solution; (A′) CdS–PEI nanocomposite prepared in water, spectrum in sol–gel; (B) CdS–dendrimer nanocomposite prepared in methanol, spectrum in solution; (B′) CdS–dendrimer nanocomposite prepared in methanol, spectrum in sol–gel; (C) CdS–dendrimer nanocomposite prepared in water, spectrum in solution; (C′) CdS–dendrimer nanocomposite prepared in water, spectrum in sol; (C″) CdS–dendrimer nanocomposite prepared in water, spectrum in sol–gel; (D) CdS–dendrimer nanocomposite prepared in methanol at pH 3.4, spectrum in solution; (D′) CdS–dendrimer nanocomposite prepared in methanol at pH 3.4, spectrum in sol; (D″) CdS–dendrimer nanocomposite prepared in methanol at pH 3.4, spectrum in sol–gel. The total drying time was approximately 10 days.

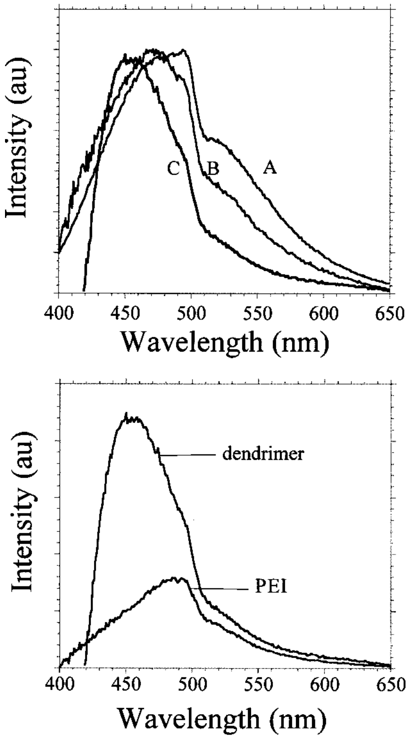

Figure 7. (Top) Normalized emission spectra of CdS–dendrimer nanocomposites in silicate sol–gel as a function of time. (A) initial time (sol stage), (B) 15 days (gel), (C) 2 months (gel). (Bottom) Emission spectra of CdS–dendrimer and CdS–PEI nanocomposites in silicate sol–gel glass after 2 months of aging. Samples were excited at 340 nm.

effectively trapped by the sol–gel and showed little change in spectral distribution upon initial immobilization (Figure 6A,B). For the samples in parts C (dendrimer/aqueous conditions) and D (dendrimer/acidic methanol conditions) of Figure 6, the emission spectra dramatically changed upon mixing with the silicate sol, and these spectra further evolved upon gel formation. Both of these samples gave final emission spectra that had a blue- and a redshifted component, compared to their respective initial emission spectra. The sample in Figure 6C, having a more intense blueshifted component, appeared visibly purple to the eye, whereas the sample Figure 6D appeared red. Thus, tuning of the intensity and color of the output light is possible by controlling synthesis conditions of CdS–dendrimer nanocomposites.

The mechanism behind these optical changes is likely complicated. The sol–gel process itself over time produces methanol and water, the two solvents used for the nanocomposite preparation. (However, the bulk properties of the resulting nanocomposite sol–gels were rather similar.) An altered emission spectral distribution in quantum dots can signal that the nature of the surface defects is changing, or it may be a sign of changing particle size. The lack of change in the absorption spectra upon incorporation into the sol–gel

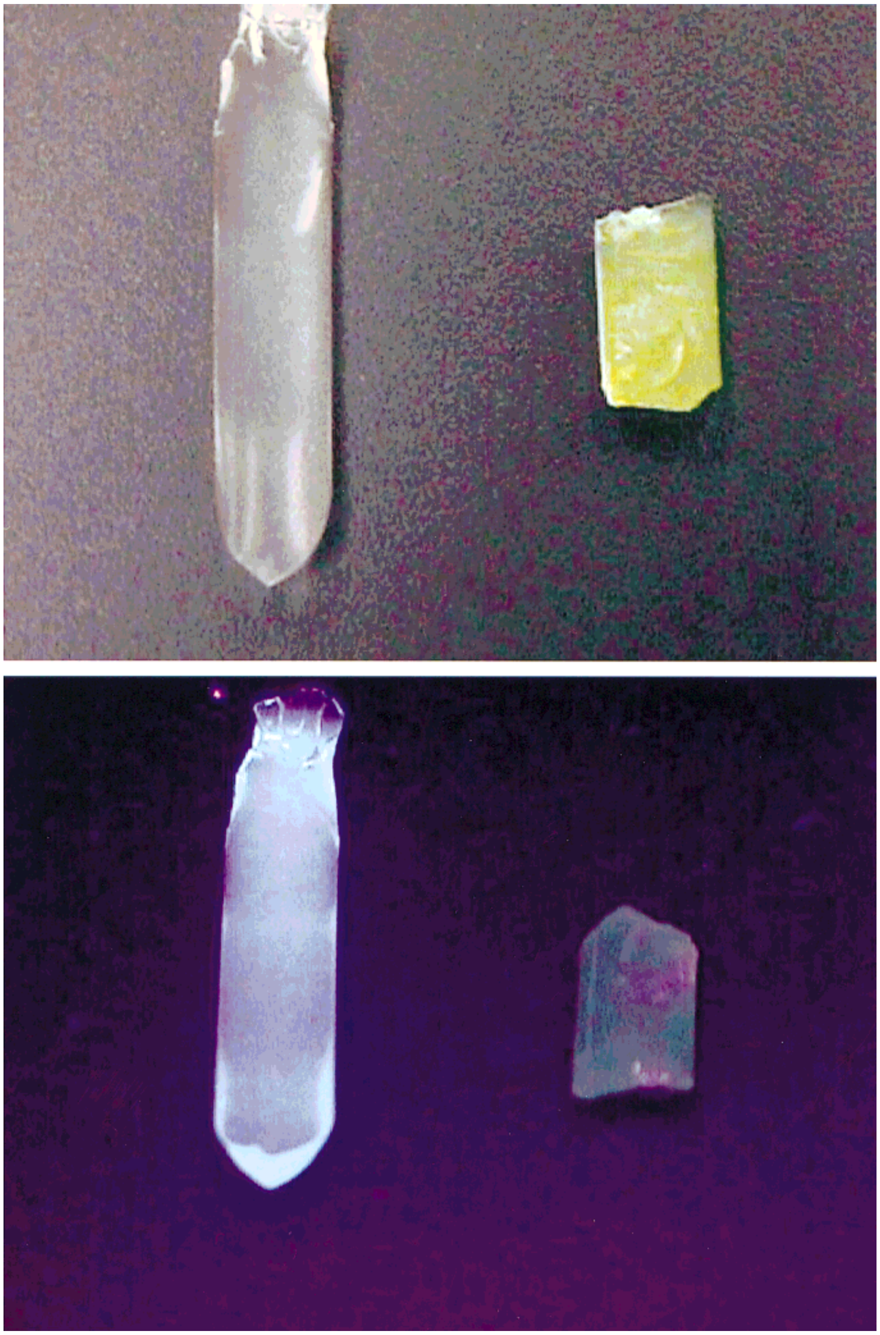

Figure 8. Photographs of sol−gel-immobilized CdS−dendrimer and CdS−PEI nanocomposites, taken in room light (top) and under ultraviolet light (bottom). The materials had been aged for 2 months. The CdS−dendrimer sol−gel nanocomposite is on the left in both pictures, and the CdS−PEI sol−gel nanocomposite is on the right.

suggests that average CdS particle size was not altered; thus, we propose that the dendrimer−CdS nanocomposites synthesized in either aqueous (Figure 6C) or acidic methanol (Figure 6D) conditions undergo surface modification in the sol−gel environment and are not protected as are their aqueous/PEI and methanol/dendrimer counterparts. Silicate polymer[15] and amine groups[33] have been found to effectively passivate nanoparticle surface states that promote radiationless recombination. Thus, one scenario for the optical "disproportionation" observed in the emission spectra is that one population of quantum dots winds up in either a silicate- or amine-rich environment (corresponding to the blueshifted component of the emission of aged samples), and the remaining quantum dots are more exposed to solvent or other species that produce defects (the redshifted component). Both samples in parts C and D of Figure 6 contain CdS quantum dots that are significantly larger than their aqueous/PEI and methanol/dendrimer counterparts (Table 1); perhaps, these larger particles are not as fully encapsulated by their stabilizing polymer.

The long-term stability of the PEI−CdS and dendrimer−CdS nanocomposites in sol−gels is illustrated in Figures 7 and 8. After 2 months, the dendrimer−quantum dot material had a slightly blueshifted emission maximum and the shoulder in the green was

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(33) Dannhauser, T.; O'Neill, M.; Johansson, K.; Whitten, D.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 6047.

reduced in intensity. After 2 months, the sol−gel containing the CdS−dendrimer nanocomposite was visibly clear under room light and emitted bright blue-violet upon ultraviolet irradiation. Older samples (7 months) showed the same behavior. The corresponding PEI material was visibly yellow under room light after 2 months, and its emission was quenched and redshifted (λ_{max} ∼500 nm; Figure 7). Overall, the dendrimer architecture appears to afford better protection of the CdS nanoparticles compared to the linear architecture of PEI.

Conclusions

Blue-emitting PEI/CdS nanocomposites have been prepared in solution that have similar optical properties, albeit with less intense photoluminescence, compared to dendrimer−CdS nanocomposites with similar functional groups. We ascribe the excellent stabilization of CdS nanoparticles in these media to high local concentrations of chelating nitrogen groups. We have successfully introduced CdS quantum dot−polymer/dendrimer nanocomposites into transparent silicate glasses. Depending on synthetic conditions, the spectral distribution of the emission of the immobilized quantum dot materials can be altered. The starburst dendrimer polymer can protect the CdS quantum dots from significant degradation of optical performance for months compared to the linear PEI stabilizer.

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