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Photoluminescent Polymer/Quantum Dot Composite Nanoparticles

Steven C. Farmer and Timothy E. Patten*

Department of Chemistry, University of California at Davis, One Shields Avenue, Davis, California 95616-5295

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Core−shell CdS/SiO_2 nanoparticles were prepared and modified with the atom transfer radical polymerization (ATRP) initiator 3-(2-bromopropionyloxy)propyl dimethylethoxysilane (BIDS). The initiator-modified nanoparticles were then used as macroinitiators for the polymerization of methyl methacrylate (MMA) catalyzed by $NiBr_2(PPh_3)_2$. These hybrid polymer/inorganic nanoparticles could be cast into films that retained the photoluminescence of the precursor CdS nanoparticles and showed even dispersal of the CdS/SiO_2 cores throughout the PMMA matrix. These hybrid nanoparticles are versatile structures: their films can be processed from solution and show uniform dispersion of the inorganic phase throughout the host organic matrix on the microscopic level. These nanoparticles also have components whose structures and compositions can be altered to introduce new properties to the material (i.e., the luminescence of the inorganic core or the conductivity of the polymer arms) and to allow for self-assembly of the material (via the structure and composition of the polymer arms).

Introduction

Inorganic nanoparticles display optical and magnetic properties that make them attractive candidates for devices.[1,2] Because inorganic nanoparticles are usually powders and lack favorable bulk mechanical properties and processing characteristics, host materials need to be developed to impart these properties as well as others, such as charge carrier mobility. Ideally, the final composite material should be processable from solution or from the melt with uniform dispersion of the inorganic phase on the microscopic level and should have components whose structures and compositions can be altered to allow for self-assembly of the material. The surface functionalization of nanoparticles serves to passivate the surface and improve their properties, as shown by the increase in photoluminescence quantum yield for organic or inorganic capped CdS nanoparticles.[3,4] Recently, research has focused on understanding how surface functionality can be used to direct the assembly of nanoparticles. Assembly strategies have utilized interactions with surfaces,[5−7] block copolymer microphase separation,[8−10] or DNA hybridization.[11−13] We have been exploring methods for grafting well-defined polymer chains from nanoparticle surfaces, with the intent of using the polymer layer both as a film-forming host and as a directing agent for assembly of the nanoparticles.[14] Here we report the synthesis of novel core−shell semiconductor nanoparticle (or quantum dot)/polymer hybrids and their use in forming photoluminescent films in which the nanoparticles are evenly dispersed on the microscopic level. These nanoparticles could be dissolved and recast repeatedly, while the films retained their dispersed morphology.

Experimental Section

Materials. The ATRP initiator, 3-(2-bromopropionyloxy)propyl dimethylethoxysilane (BIDS), was prepared by the catalytic hydrosilylation of allyl-2-bromo-2-methylpropionate with ethoxydimethylsilane. Methyl methacrylate was distilled under vacuum before use. Double distilled water was used in the CdS/SiO_2 nanoparticle syntheses. Unless otherwise stated, all materials were purchased from commercial sources and used without further purification.

Instrumentation. UV/vis spectra were recorded using an HP 8450A spectrometer and THF, CH_3OH, or cyclohexane as the solvent. Fluorescence spectra were collected using a

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* Corresponding author: Phone (530) 754-6181; Fax (530) 752-8995; e-mail patten@indigo.ucdavis.edu.

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Perkin-Elmer LS50B spectrometer and THF or chloroform as the solvent. Dynamic light scattering (DLS) data were collected on an IEM1 9863 detector and a Coherent DPSS 532 laser with either THF or CH_3OH as the solvent. Samples were prepared as follows: A small amount (0.100 g) of the material was added to a borosilicate test tube that had been cleaned of dust by refluxing THF onto the inverted tube for 20 min prior to use. Solvent (5 mL of a CH_3OH for the CdS/SiO_2 nanoparticles; 5 mL of THF for the initiator-modified CdS/SiO_2 nanoparticles and the CdS/SiO_2/PMMA composite nanoparticles) was added, and then the mixtures were sonicated for 10 min. The CdS/SiO_2 and initiator-modified CdS/SiO_2 nanoparticles were passed through a 0.100 μm syringe filter, and the CdS/SiO_2/PMMA composite nanoparticles were passed through a 0.450 μm syringe filter. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed using a Hitachi H-600 TEM at the UC Davis Facility for Advanced Instrumentation. For the CdS/SiO_2 nanoparticle samples, a drop of a CH_3OH suspension (100 mg of sample/3 mL of solvent) of the nanoparticles was placed on a Formvar-coated copper grid, and the solvent was allowed to evaporate. For the CdS/SiO_2/PMMA samples, a drop of a THF or toluene suspension (100 mg of sample/3 mL of solvent and the solution was filtered through a 0.45 μm syringe filter to remove dust particles) was placed on a carbon-coated copper grid, and the solvent was allowed to dry. IR spectra were recorded using neat samples on an NaCl plate and a Mattson Genesis II spectrometer. Number-averaged molecular weights (M_n), weight-averaged molecular weights (M_w), and molecular weight distributions (M_w/M_n) were determined using gel-permeation chromatography in THF at 30 °C; flow rate = 1.0 mL/min. Three Polymer Standards Services columns (100 Å, 1000 Å, and linear) were connected in series to a Thermoseparation Products P-1000 isocratic pump, autosampler, column oven, and Knauer refractive index detector. Calibration was performed using polystyrene samples (Polymer Standard Services; $M_p = 400-1\,000\,000$; $M_w/M_n < 1.10$). AFM samples were prepared by dissolving the sample in toluene and then spotting the sample onto a freshly cleaned mica disk. The AFM was performed using a Digital Instruments NanoScope IIIa (Santa Barbara, CA) in contact mode using a sharpened, gold-coated silicon nitride tip.

Synthesis of CdS/SiO_2 Nanoparticles. All CdS/SiO_2 nanoparticles were synthesized via a modification of the method reported by Chang et al.[15] Initially two identical solutions of Igepal CO-520 (20.0 g, 19.2 mL) in cyclohexane (50.0 mL) were stirred to create clear reverse microemulsion phases. Igepal CO-520 (Aldrich) is the nonionic surfactant polyoxyethylene(5) nonaphenyl ether. A dilute $(NH_4)_2S$ solution (2.50 mL, 0.150 M, 0.375 mmol) was added to one microemulsion phase while a dilute $Cd(NO_3)_2$ solution (2.50 mL, 0.150 M, 0.375 mmol) was added to the other. [Caution: Cd(II) salts are suspected carcinogens. Care should be taken to eliminate possible contact with their solutions, and spill precautions should be in place when handling solid or solution forms of Cd(II).] After equilibration, the two microemulsions were mixed and allowed to stand overnight. The formation of CdS quantum dots was evident due to development of a bright yellow color typical for this material. The silica coating was generated by the addition of ammonium hydroxide (3.13 mL, 9.00 M, 28.1 mmol) and tetraethoxysilane (23.7 mL, 0.106 mol) to 140 mL of the CdS solution. After 18 h, the resulting CdS/SiO_2 nanoparticles were isolated by centrifugation and washed with cyclohexane and CH_3OH to produce 5.22 g of product.

Surface Modification of CdS/SiO_2 Nanoparticles. The CdS/SiO_2 nanoparticles were dispersed into dry THF from their original isolated state by dispersing the particles in fresh THF followed by centrifugation and decanting. This process was repeated until a clean dispersion in THF was assured. To the suspension was added 1.02 g (3.28 mmol) of BIDS, and the mixture was heated at reflux for 18 h. The resulting surface functionalized nanoparticles were centrifuged and washed repeatedly with pentane to remove any of the unreacted BIDS. Evaporation of the solvent produced 5.71 g of a pale yellow powder that could be resuspended in most nonpolar solvents.

Polymerizations and Analysis of the Polymer Attached to the Nanoparticles. The initiator functionalized CdS/SiO_2 nanoparticles (0.400 g) were added to a solution consisting of $NiBr_2(PPh_3)_2$ (0.210 g, 0.388 mmol) and methyl methacrylate (3.00 mL, 2.81 g, 28.0 mmol) in a Schlenk flask. The solution was degassed three times via freezing in liquid N_2, evacuation to 20 mTorr, thawing, and backfilling with nitrogen. The resulting mixture was heated at 100 °C for 3 h to graft poly(methyl methacrylate) chains from the surface of the nanoparticles. After precipitation in CH_3OH the composite nanoparticles were collected by filtration, and volatile materials were removed under vacuum, yielding 0.911 g of product. To detach the grafted polymer, some of the composite nanoparticle was dissolved in 5 mL of toluene, and 75 mg of Aliquot 336 was added as a phase transfer catalyst. A 5% aqueous HF solution (5 mL) was added, and the mixture was stirred for 2 h. The organic layer was removed, and the polymer was isolated by precipitation from CH_3OH, filtration, and removal of volatile materials under vacuum.

Analysis for Possible Unbound Chains after Polymerization. A standard polymerization was performed. After precipitation of the polymer-grafted nanoparticles from the polymerization solution into CH_3OH, the composite nanoparticles were collected by filtration. Removal of volatile materials under vacuum yielded 1.01 g of product. Part of the product (0.100 g) was treated with HF as described above in order to cleave the polymer from the nanoparticles. This yielded 0.051 g of isolated polymer. Another part of the product (0.410 g) was placed in a centrifuge tube and then dissolved in 50 mL of THF. The tube was sonicated for 15 min to suspend the particles, and the suspension was centrifuged at 3000 rpm for 20 min. The supernatant was separated from the sediment, and the process was repeated three times. The final sediment was dissolved in THF, precipitated into CH_3OH, and filtered. The polymer chains were cleaved from the CdS/SiO_2 nanoparticles and isolated using the same procedure as described above. The supernatant (~40 mL) from the first wash was placed in an ultracentrifuge tube and was spun at 20 000 rpm for 20 min. No additional sediment was observed. The solution was slightly turbid and emitted orange light under irradiation from a UV lamp, indicating that some nanoparticles remained suspended in solution. The solution was passed through a 100 nm pore size syringe filter to separate the remaining nanoparticles from any polymer in solution. The filtered solution did not emit orange light under irradiation from a UV lamp. The solvent was removed by rotary evaporation to yield 0.004 g of a white solid. Polymer from the sample precipitated directly from the final polymerization mixture: $M_n = 1.55 \times 10^5$, $M_w/M_n = 1.32$. Polymer from the sediment: $M_n = 1.75 \times 10^5$, $M_w/M_n = 1.36$. Polymer from the supernatant: $M_n = 8.37 \times 10^5$, $M_w/M_n = 2.21$.

Attempted Polymerization of MMA in the Absence of Surface Initiator. The control polymerization followed the same procedure as the standard polymerizations except that CdS/SiO_2 nanospheres (0.400 g) without surface initiator was used. A 0.250 mL sample was drawn from the initial and final reaction mixture (after 3 h) and added to separate solutions of 5.00 mL of THF with 0.100 mL toluene. The final polymerization conversion was determined using GC, and it was found that the polymerization had reached 3.8% conversion. Removal of volatile materials under vacuum of the 3.8% conversion solution yielded 0.380 g of material. This material underwent the HF etch and isolation procedure discussed above. $M_n = 7.52 \times 10^5$, $M_w/M_n = 1.44$.

Results and Discussion

The first step in the synthesis was the covalent attachment of a polymerization initiator to the surface

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Scheme 1. Synthetic Scheme for the Synthesis of CdS/SiO$_2$/PMMA Composite Nanoparticles

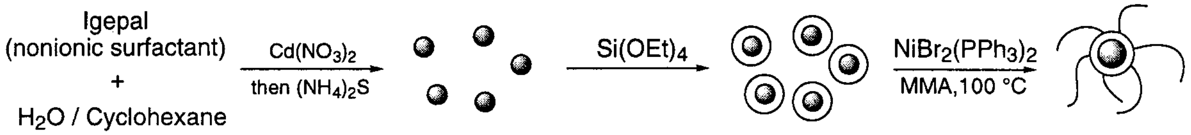

Table 1. Selected Area Electron Diffraction Data for the Precursor CdS Nanoparticles[a]

hkl	measd *d* (Å)	CdS *d* (Å)[b]	*hkl*	measd *d* (Å)	CdS *d* (Å)[b]
013	1.83	1.90	002	3.30	3.36
110	1.98	2.07	010	3.52	3.59
012	2.54	2.45			

[a] Camera length = 1.60 m; voltage = 100 kV. [b] From Standard X-ray Diffraction Powder Patterns, U.S. Dept. of Commerce, National Bureau of Standards, Washington, DC, 1985.

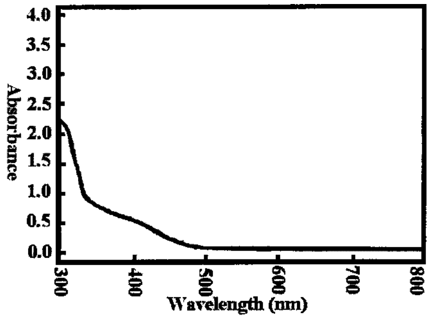

Figure 1. UV−vis spectrum of the precursor CdS nanoparticles (solvent = cyclohexane).

of a semiconductor nanoparticle, preferably CdS or CdSe due to the wealth of knowledge about these quantum dots. The attachment needed to be sufficiently robust that it would withstand the subsequent polymerization conditions, including elevated temperatures and the presence of redox active metal complexes. Such conditions have been shown to be adverse for thiol-capped CdS or CdSe nanoparticles.[16] Consequently, we opted to passivate the nanoparticle with a layer of silica (SiO$_2$), which would also permit the thermally robust, covalent attachment of polymerization initiators to the nanoparticle surface via silane coupling agents.[14] Additionally, silica coating has been shown to enhance the stability of the CdS cores to photodegradation.[17]

SiO$_2$-coated CdS nanoparticles were prepared via modification of a method reported by Chang, Liu, and Asher (Scheme 1).[15] Solutions of Cd(NO$_3$)$_2$ and (NH$_4$)$_2$S were added to a reverse microemulsion. Confirmation of the formation of CdS quantum dots was obtained from selected area electron diffraction (SAED) patterns (Table 1) and UV−vis spectra of the isolated nanoparticles. The experimental SAED patterns matched, within experimental error, the literature data. The UV−vis spectrum (Figure 1) showed an absorption onset at 480−490 nm, which was consistent with CdS quantum dots in the 6−8 nm diameter range.[18] When tetraethoxysilane was added to the reverse microemulsion, a coating of SiO$_2$ was deposited on the CdS nanoparticle surface. TEM micrographs (Figure 2) confirmed that the final nanoparticles possessed a core−shell morphology and an average diameter of 53 nm (standard deviation of 4.6; 50 particles measured). The diameter of the CdS core averaged 6.2 nm (standard deviation of 0.6 nm, 50 particles measured), which was consistent with the diameter estimated from the UV−vis spectrum. The majority of the nanoparticles had only one CdS core, but a few of the nanoparticles clearly contained two CdS nanoparticles. Fluorescence emission spectra (Figure 3) showed a signal at 610 nm that was not present in corresponding spectra of SiO$_2$-only nanospheres but matched the emission maximum of the precursor CdS nanoparticles. The photoluminescence from these nanoparticles was consistent with that of other aqueous preparations of CdS nanoparticles.[3] The core−shell SiO$_2$/CdS nanoparticles were stable indefinitely under air and withstood heating at 100 °C without loss of photoluminescence.

The surfactant was removed from the microemulsion solution by four cycles of centrifugation and resuspension of the nanoparticles in methanol. The methanol solvent was then exchanged for THF by three cycles of centrifugation and resuspension in THF. The polymerization initiator, 3-(2-bromopropionyloxy)propyl dimethylethoxysilane (BIDS), was then deposited on the surface of the nanoparticle (Scheme 1).[14] The THF suspension was sonicated for 5 min, and then BIDS was added to the solution, which was heated at reflux overnight. Once modified, the nanospheres could be evaporated to dryness without agglomeration and could be suspended in most nonpolar solvents. Confirmation of attachment of the initiator to the silica surface was shown by elemental analysis for bromine, UV−vis

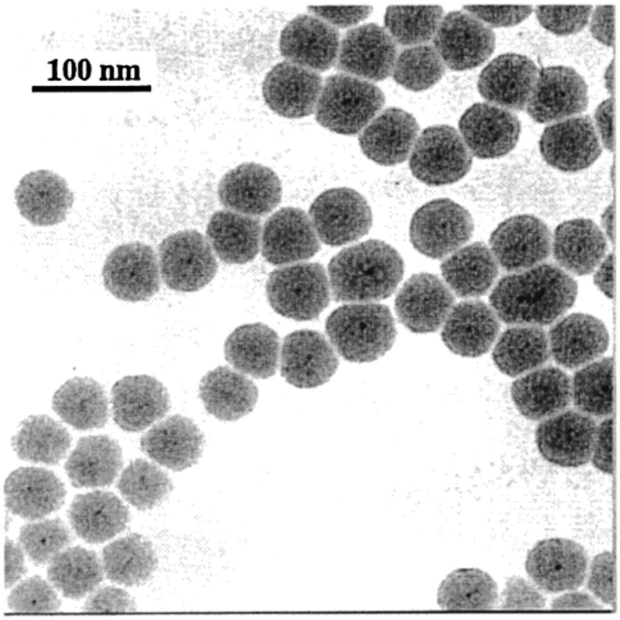

Figure 2. TEM micrograph of the unmodified core−shell CdS/SiO$_2$ nanoparticles.

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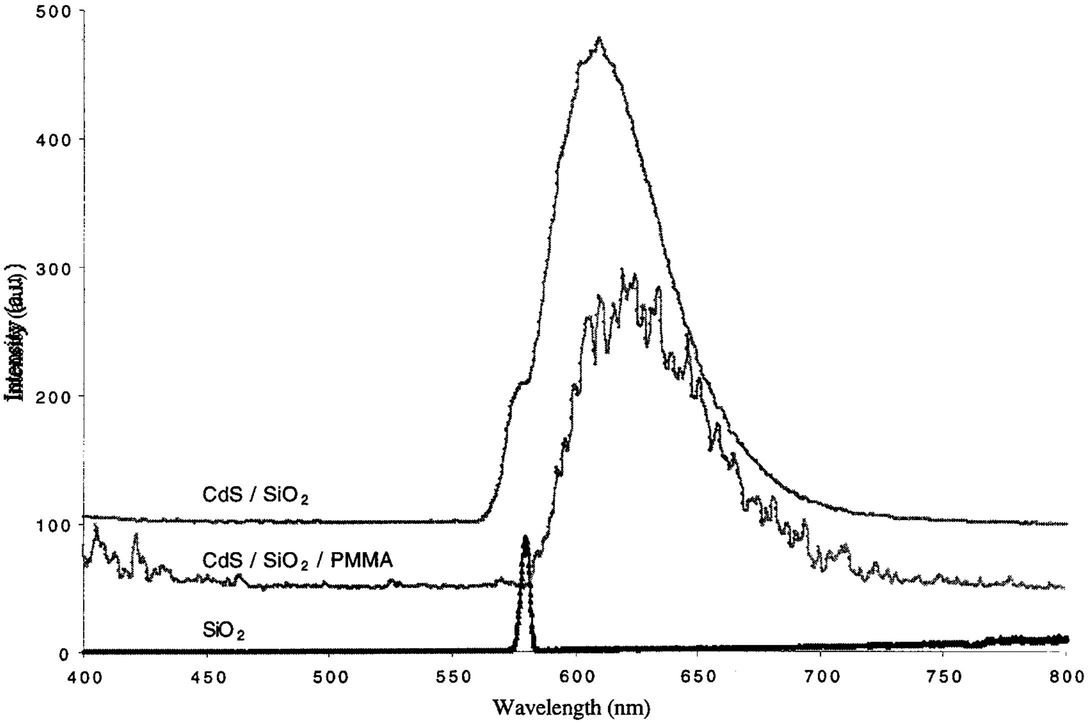

Figure 3. Unnormalized fluorescence emission spectra for (1) SiO_2 only nanoparticles (solvent = CH_3OH), (2) core–shell CdS/SiO_2 nanoparticles (solvent = CH_3OH), and (3) core–shell-shell CdS/SiO_2/PMMA nanoparticles (solvent = $CHCl_3$). Excitation wavelength = 271 nm. The sharp signal at ~570 nm in the SiO_2 spectrum is due to light scattering.

spectra, and solid-state ^{29}Si CP-MAS spectra. Elemental analysis indicated that the starting nanoparticles contained <0.05% bromine and that the BIDS-modified nanoparticles contained, on average, 1.16% bromine. This difference translated into an average of 0.145 mmol of initiator/g of nanoparticles. The UV–vis spectrum showed an absorption centered around 225 nm which corresponded to the characteristic $n \rightarrow \pi^*$ absorption for aliphatic esters (~210 nm)[19] and coincided with the λ_{max} for BIDS at 229 nm ($\epsilon = 82$ M^{-1} cm^{-1}). The solid-state ^{29}Si CP-MAS spectrum (Figure 4) showed a signal at 12.8 ppm characteristic for an $R_3Si{-}O{-}Si$ species, and the line width was ~3 ppm, indicating that the silicon nucleus sampled a range of local environments and consistent with the initiator being bound to a surface.

The initiator-modified nanoparticles were used successfully as initiators in the atom transfer radical polymerization (ATRP) of styrene according to previous procedures.[14] However, the resulting material did not exhibit photoluminescence. It has been demonstrated that the layer of silica deposited on a nanoparticle is porous and that electrochemical and chemical transformations of the core materials are possible through the outer layer.[20] Thus, the loss of photoluminescence in our samples was probably due to a redox reaction between the CdS core and the CuBr/2dNbipy (4,4′-di(5-nonyl)-2,2′-bipyridine) catalyst. A control experiment in which the initiator-modified nanoparticles were heated with only CuBr/2dNbipy in toluene also resulted in quenching of the CdS photoluminescence. Complexes of many different transition metals are effective ATRP catalysts,[21] so we surmised that using a metal complex with a lower reduction potential might allow for the controlled growth of polymer chains from the nanoparticle surface without reacting with the CdS core. Recently, methyl methacrylate has been grafted from silicon wafers using $NiBr_2(PPh_3)_2$,[22] so we tested this ATRP catalyst. A polymerization of methyl methacrylate was performed using 0.400 g of the initiator-modified nanoparticles with 100.0 mg (0.212 mmol) of $NiBr_2(PPh_3)_2$ and 3.00 mL (28.0 mmol) of methyl methacrylate. The reaction solution was heated at 100 °C for 3 h, after which time there was 28% conversion of monomer. After precipitation using methanol and removal of volatile materials, 0.911 g of a powder was obtained. An IR spectrum (Figure 5) of the product showed signals characteristic for both PMMA (ν(C=O) at 1733 cm^{-1}) and silica (ν(Si–O) at 1101 cm^{-1}), and a fluorescence emission spectrum (Figure 3) showed that the product retained its photoluminescence ($\lambda_{max} = 568$ nm).

To analyze the poly(methyl methacrylate) (PMMA) part of the composite nanoparticle, a toluene suspension of the nanoparticles was treated with 5% aqueous HF and Aliquot 336 phase transfer catalyst in order to etch the inorganic core. Monitoring of the etching process indicated complete loss of the 1101 cm^{-1} signal after approximately 1 h with no change in the appearance of the signal at 1733 cm^{-1}. GPC analysis of the isolated polymer showed that the grafted polymer had a molecular weight of $M_n = 86\,000$ and a molecular weight distribution of $M_w/M_n = 1.30$. The narrow molecular

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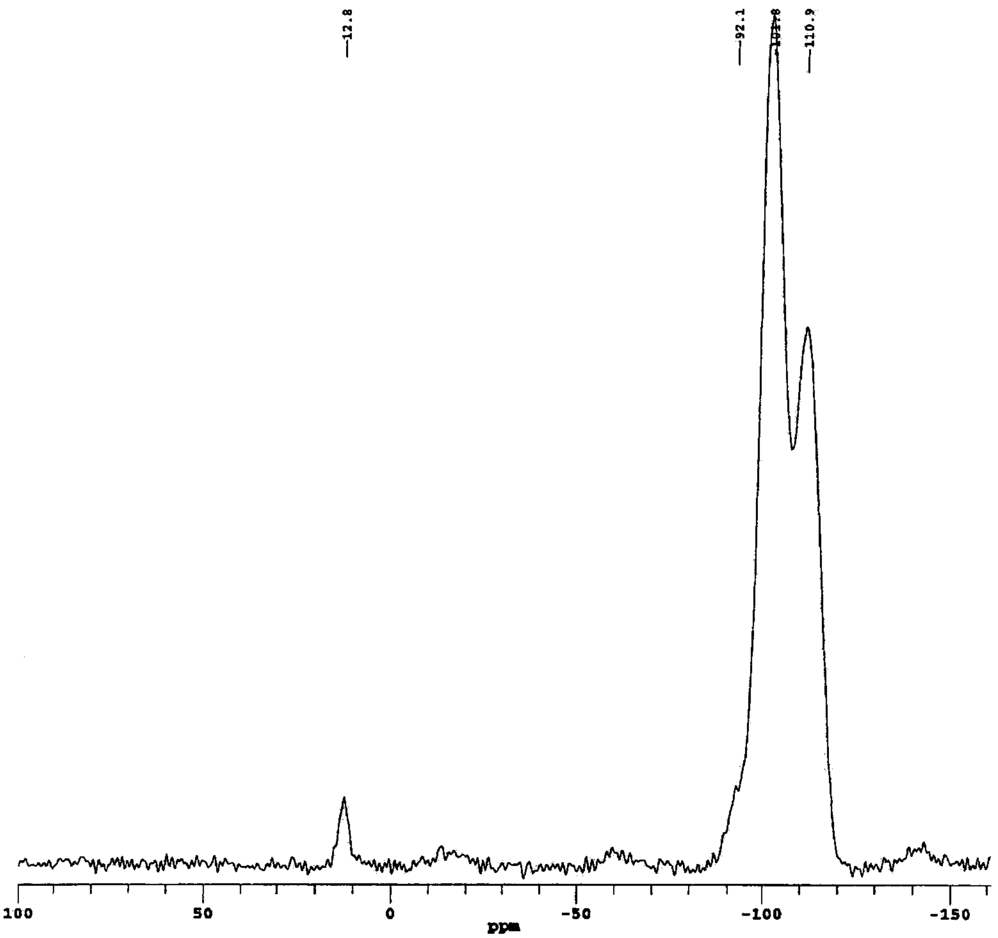

Figure 4. Solid-state ^{29}Si CP-MAS NMR spectrum of the BIDS-modified core−shell CdS/SiO$_2$ nanoparticles.

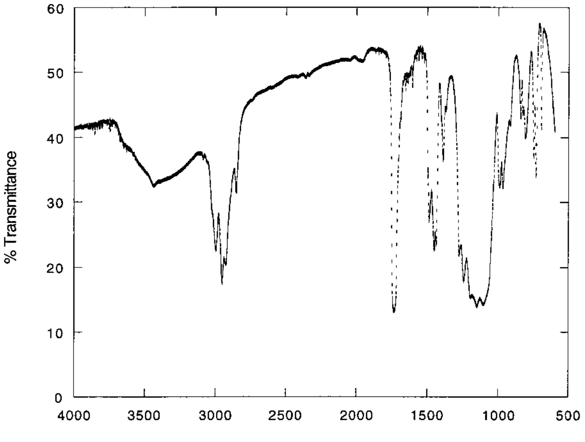

Figure 5. IR spectrum of the CdS/SiO$_2$/PMMA hybrid nanoparticle sample.

weight distribution was consistent with previous results[14] and with a controlled/living polymerization of methyl methacrylate from the silica surface. Dynamic light scattering (DLS) measurements also yielded results consistent with the grafting of PMMA from the nanoparticle surface. The CdS/SiO$_2$ nanoparticles had an average hydrodynamic diameter of 53 nm (standard deviation of 5.7), and after modification with BIDS the average hydrodynamic diameter increased marginally to 54 nm (standard deviation of 5.8). After polymerization, the average hydrodynamic diameter was 160 nm (standard deviation of 23).

There were two alternative explanations for the data that we needed to consider. First, the polymerization could have occurred only in solution, and the initiator-modified nanoparticles were only a spectator in the reaction. The DLS data argued against this possibility, but we also performed a control experiment. An identical polymerization reaction was conducted, except that nanoparticles without the surface layer of initiator were used. After 3 h very little polymerization had occurred (3.8% conversion), demonstrating that the initiator on the nanoparticle surface was necessary for polymerization to occur.

Second, the polymer chains may have become detached from the nanoparticle surface during polymerization, and the final molecular weight data actually reflected growth of the chains in solution rather than from the nanoparticle surface. Again, the DLS data argued against this possibility, but we also attempted to separate any free chains from surface bound chains. A polymerization using the initiator-modified nanoparticles was performed, and part of the product was treated with HF to cleave the polymer chains from the nanoparticle surface as described above. The starting composite contained 56 wt % of PMMA, and after etching we were able to isolate 51% of the starting mass of the composite in PMMA. Another part of the sample was centrifuged until a sediment had formed. The sediment was isolated by decanting the supernatant and washing with THF, and the sediment was subjected to the etching conditions as described above. The super-

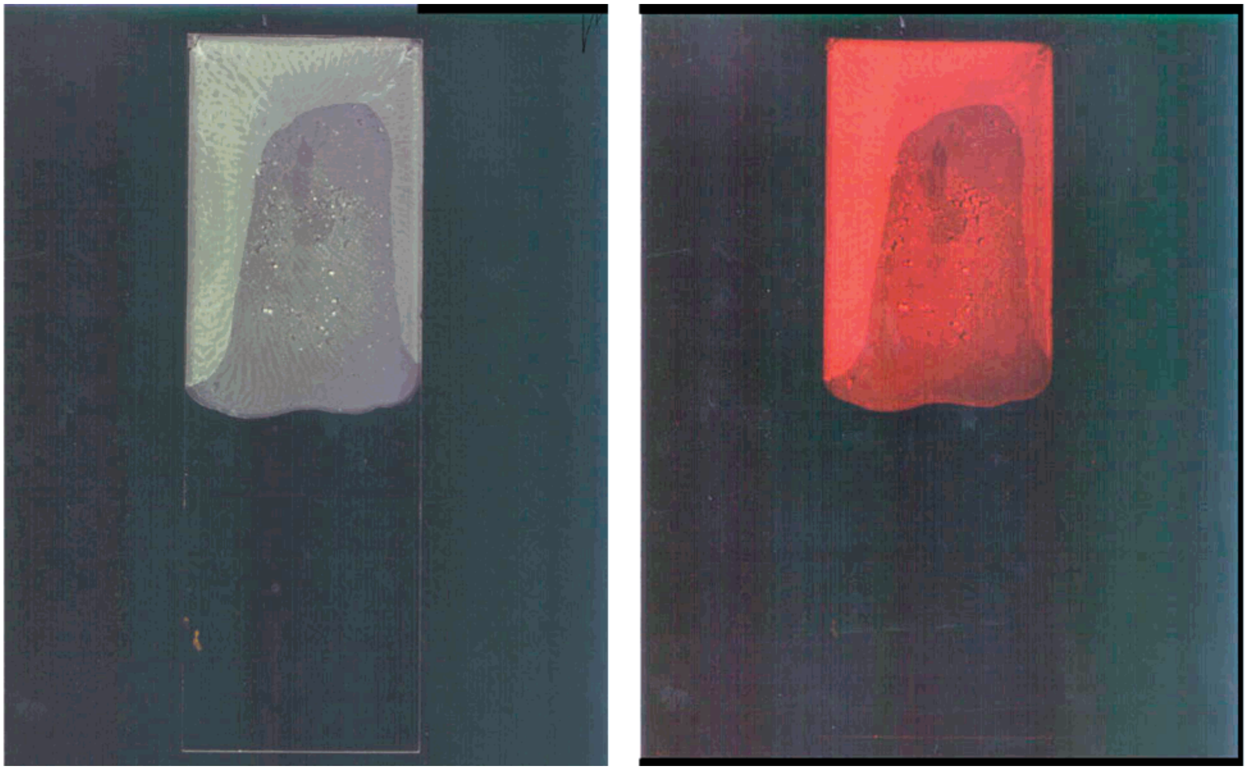

Figure 6. Photographs of a cast film of hybrid poly(methyl methacrylate)/SiO_2/CdS nanoparticles on a glass slide. The pictures were recorded (a, left) under ambient light and (b, right) under 365 nm UV light.

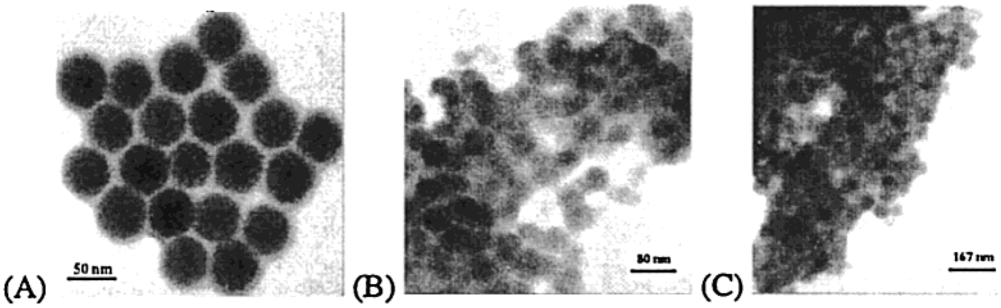

Figure 7. TEM micrographs of agglomerates of CdS/SiO_2/PMMA composite nanoparticles: (A) a small nanoparticle agglomerate cast from dilute solution showing the inorganic cores surrounded by an outer layer of PMMA; (B, C) larger agglomerates formed when cast from more concentrated solutions.

natant was placed in an ultracentrifuge tube and was spun at 20 000 rpm for 20 min. No additional sediment was observed, but the solution was slightly turbid and emitted orange light under irradiation from a UV lamp, indicating that some nanoparticles remained suspended in solution. The solution was passed through a 100 nm pore size syringe filter to remove any suspended nanoparticles but not any free polymer, since the nanoparticles had a hydrodynamic diameter larger than the pore size. The filtered solution did not emit orange light under irradiation from a UV lamp. The solvent was removed by rotary evaporation to yield 0.004 g of a white solid, which was less than 1 wt % of the nanoparticle fraction used for the procedure. The polymer isolated from the original product (i.e., no separation procedure before etching) and from the sediment had similar molecular weights ($M_n = 1.55 \times 10^5$ vs 1.75×10^5, respectively) and molecular weight distributions ($M_w/M_n = 1.32$ vs 1.36, respectively). The small amount of polymer isolated from the supernatant had a larger molecular weight ($M_n = 8.37 \times 10^5$) and a very broad molecular weight distribution ($M_w/M_n = 2.21$). The results of this experiment were consistent with the conclusion that the majority of the polymer in the final sample was grafted from the nanoparticle surface.

These hybrid nanoparticles (CdS/SiO_2/PMMA) could be cast from organic solvents to form continuous films, which were transparent and had a faint yellow tint due to the presence of the CdS quantum dots. Figure 6 shows photographs of a film of hybrid CdS/SiO_2/PMMA nanoparticles cast from toluene onto a glass slide. The pictures were recorded before and after illumination with 365 nm UV light, and under this light, all regions of the film were observed to emit orange-red light. We obtained TEM images of small agglomeration domains formed from dilute THF solutions of the hybrid nanoparticles onto carbon-coated copper grids. Representative micrographs are shown in Figure 7, which show that the sample consisted of the inorganic nanoparticles surrounded by a PPMA matrix, and the inorganic cores were dispersed throughout the PMMA domains. No agglomeration of the inorganic cores independent of the

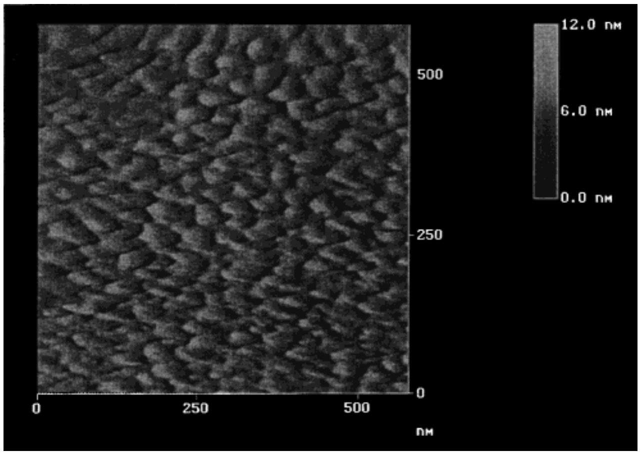

Figure 8. Contact mode AFM image of the surface of a film of the hybrid nanoparticles.

PMMA was observed, consistent with a two-phase system in which the inorganic particle is embedded within a PMMA shroud. The hybrid nanoparticles could be dissolved and recast with retention of the dispersed morphology. Both optical transparency and dispersion of the inorganic phase have been identified recently as important characteristics for photoluminescent polymer/semiconductor nanoparticle composites.[23] To confirm that the dispersed morphology was retained within the larger, continuous films, we imaged the surface of such films using AFM (Figure 8). As seen in the image, the surface texture and the average size of the features were consistent with inorganic particles imbedded and dispersed within a polymer film as observed in the TEM images.

In summary, we have demonstrated that controlled/living radical polymerizations can be used to graft PMMA, and presumably other vinyl polymers as well, from core−shell CdS quantum dot/SiO_2 nanoparticles. Films of these hybrid nanoparticles could be processed from solution (in contrast to composite films prepared using block copolymers), retained the photoluminescence of the precursor CdS nanoparticles, and showed dispersion of the CdS/SiO_2 cores throughout the PMMA matrix. These hybrid nanoparticles are versatile structures in that they have components whose structures and compositions can be altered to introduce new properties to the material (i.e., the luminescence of the inorganic core or the conductivity of the polymer arms) and to allow for self-assembly of the material (via the structure and composition of the polymer arms).

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Supporting Information Available: An SAED pattern for the CdS nanoparticles and UV/vis spectra of BIDS, core−shell CdS/SiO_2 nanoparticles, and BIDS-modified core−shell CdS/SiO_2 nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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