Nanotechnology

Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization from Unprotected Cadmium Selenide Nanoparticles**

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Advanced synthetic and spectroscopic techniques in nanoscience are providing a number of new nanostructured materials as well as unprecedented insight into their structures and properties. Polymer materials alone serve as components of a rich array of nanostructures, from block copolymer assemblies[1] to dendrimers[2] to a variety of core–shell materials.[3] Hybrid materials composed of polymers and nanoparticles add a level of complexity to these nanostructures, including the inherent functional capabilities of the particular nanoparticle, and the impact of interactions between the polymer and nanoparticle.[4] Semiconductor nanoparticles, or quantum dots, are especially interesting for use in such hybrid materials, for example as components of LEDs,[5] tunable lasers,[6,7] photovoltaic cells,[8–10] and biological tags.[11,12] This is due to the unique properties of the semiconductor nanoparticles, including their broad absorption spectra, narrow emission profiles, and discreet energy bands[13,14] that result from their quantum confined nature.

To further the progress of quantum dots from nanoscience into nanotechnology, versatile methods of ligand-based functionalization are necessary, so as to control their physical properties and interactions with their surroundings. Tailored ligand peripheries lead to a variety of potential nanoparticle-based hybrid materials, which range from simple particle dispersion in polymer matrices, to highly ordered structures formed by directed- or self-assembly. At the simplest level, the uniform dispersion of nanoparticles in a continuous phase is critical to maintaining uniform properties in a composite material. In addition, such dispersion maintains the nanoscale integrity of the particles and thus their unique properties. Versatile routes to nanoparticle functionalization allow for straightforward variation of this ligand environment for their incorporation into polymer materials, fluids, and interfaces.[15–20]

A typical synthesis of high quality CdSe nanoparticles gives the core semiconductor stabilized by an aliphatic ligand periphery composed primarily of tri-*n*-octylphosphine oxide (TOPO). This ligand periphery affords nanoparticle dispersion in hydrophobic solvents, but does not provide for uniform integration into most polymer materials. Thus, effective chemistries that provide successful functionalization of the nanoparticle surface for later use in polymerization, while simultaneously protecting the nanoparticles from oxidation and aggregation, are key steps in the development of nanoparticle-based composite materials. In prior work, Bawendi and co-workers[5] reported a procedure for the integration of CdSe nanoparticles into polymers with long aliphatic side chains that resemble the aliphatic chains of TOPO. Alternatively, Schrock and Thomas[21] employed polymers with coordinating functionalities on the backbone to stabilize the nanoparticles and prevent their aggregation. These approaches are without question effective, but they require the use of specially designed monomers. Thus, general methods are needed for integration of nanoparticles into high-volume commodity polymers. Our previous studies showed two methods of functionalizing CdSe nanoparticles with polymers. The first was a “grafting-from” approach, where a phosphine oxide that contained a catalyst was used as the nanoparticle ligand and as the initiator of ring-opening metathesis polymerization (ROMP) of cyclic olefins from the surface of CdSe nanoparticles.[16] The second was a “grafting-to” technique by using pyridine-terminated poly(ethylene glycol), which was attached to the nanoparticle by ligand-exchange chemistry.[22] Both of these functionalization techniques allow for versatile modification of the CdSe nanoparticles as well as the dispersion and assembly of the CdSe nanoparticles in a number of polymer matrices and organic and aqueous solutions. However, neither approach affords nanoparticles suitable for integration into most conventional chain-growth polymers. In contrast, the approach described here is general and adaptable to many vinyl monomers to give uniform dispersion of CdSe nanoparticles in the resulting polymers. This straightforward and versatile method uses reversible addition fragmentation chain-transfer[23] (RAFT) polymerization as a controlled free-radical method to grow polymers radially outward from the nanoparticle surface. RAFT was chosen for its ability to polymerize a wide range of monomers in a controlled fashion, without the need for transition-metal catalysis.[24,25]

The application of RAFT-polymerization methodology to a polymer-grafting strategy requires appropriately tailored nanoparticles. Thus, compound **3** was prepared, which integrates two key features into the same molecule: 1) a phosphine oxide ligand capable of binding to the CdSe nanoparticle surface and 2) a trithiocarbonate moiety amenable to RAFT polymerization. Hydroxy-*n*-propyl substituted phosphine oxide **1** was synthesized by hydrophosphorylation of allyl alcohol with di-*n*-octylphosphine oxide (DOPO)[26] by using 2,2′-azobisisobutyronitrile (AIBN) as the radical source (Scheme 1). Trithiocarbonate **2** was prepared according to a literature procedure,[27] and used to prepare **3** by 1,1′-carbonyldiimidazole mediated coupling with phosphine oxide **1**. The structure of **3** was confirmed by ^{1}H and ^{31}P NMR spectroscopy. The characteristic methylene resonance α to the ester ($\delta = 4.14$ ppm) was observed in the

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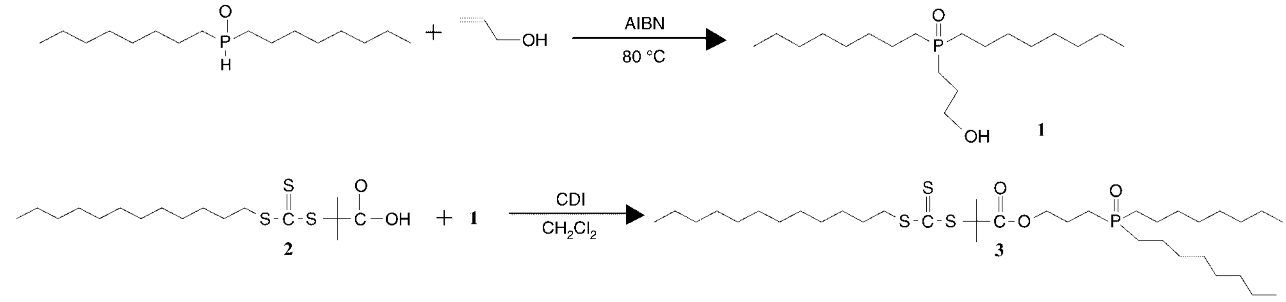

Scheme 1. Synthesis of **1** and **3**.

^{1}H NMR spectrum of **3**, and a single resonance at $\delta = 49.1$ ppm, characteristic of a trialkylphosphine oxide, was seen in ^{31}P NMR spectrum. High-resolution mass spectrometry of **3** was consistent with calculated values (calculated 678.4303, found 678.4333).

Conventional TOPO-covered CdSe nanoparticles were prepared following known procedures.[28–30] Ligand **3** was then attached to the nanoparticle through ligand-exchange chemistry, by standard washing with pyridine of TOPO-covered CdSe, followed by stirring the pyridine-capped nanoparticles in a solution of **3** in THF at 50 °C for several hours. Nanoparticles functionalized with ligand **3** were isolated by using a centrifuge device,[31] and the dissolution and centrifugation process was repeated until no appreciable excess ligand was present. The absence of appreciable unbound ligand could be observed visually by a loss of the original yellow color, indicative of trithiocarbonate **3**, in the supernatant. This new surface coverage on the CdSe nanoparticles was confirmed by recovery of an optically clear hexane solution of nanoparticles, and in the corresponding ^{1}H and ^{31}P NMR spectra resonances characteristic of **3** were observed, whereas TOPO resonances were not.

Graft-from polymerizations were performed by the addition of monomer or monomers to a benzene or toluene solution of **3**-covered nanoparticles that contained a free-radical initiator. These solutions were subjected to three freeze–pump–thaw cycles, and polymerizations were performed under a nitrogen atmosphere at 70 °C. Several initial experiments led to our ultimate use of di-*tert*-butylperoxide as the preferred free-radical initiator. Common free-radical initiators such as azobisisobutyronitrile (AIBN) and benzoyl peroxide were observed to induce nanoparticle degradation quickly at 70 °C. This is in accord with the known susceptibility of CdSe nanoparticles to free radical degradation.[32] However, the lower concentration of radicals inherent to *tert*-butylperoxide-initiated chemistry allows polymerization to proceed from the surface of the CdSe nanoparticle with a greatly reduced concern for nanoparticle degradation. In addition, the polymerization generates an encapsulating shell around the nanoparticles, which must function as a steric barrier that helps maintain the original high quality of the nanoparticles used at the outset.

Functionalization of CdSe nanoparticles with trithiocarbonate **3** allowed successful polymerization of a wide variety of monomers, to give homopolymers, random copolymers, and block copolymers emanating from the CdSe nanoparticle surface (Table 1). Verification of polymer growth from the nanoparticle surface was confirmed by gel permeation chromatography (GPC) and NMR spectroscopy after the polymer had been removed from the surface. Homopolymers of styrene, methyl acrylate, and butyl acrylate of significant molecular weight with low polydispersity indexes (PDIs) were grown from the nanoparticle surface. Similarly, a number of polystyrene-based random copolymers were prepared, including poly(styrene-*r*-methyl acrylate), poly(styrene-*r*-acrylic acid), and poly(styrene-*r*-isoprene), with the number-average molecular weights ($\bar{M}_n$) ranging from 9000 to 49000 g mol^{-1} and PDIs from 1.2 to 1.3. Monomer incorporation into random copolymers grown from the nanoparticle surface was generally found to be tunable and consistent with feed ratios. One exception was found in the case of acrylic acid. Homopolymerization was not possible, but copolymerization of acrylic acid and styrene could be performed when acrylic acid feed ratios were kept under 30 %. In general, the relatively low PDIs shown in Table 1 indicate that this controlled free-radical RAFT polymerization can be performed successfully from the surface of CdSe nanoparticles.

Table 1: All reactions were performed at 70 °C in benzene or toluene in a N$_2$ atmosphere by using *tert*-butyl peroxide as the initiator.

Polymer	$\bar{M}_n$ [g mol^{-1}]	PDI
polystyrene	27000	1.17
poly(methyl acrylate)	31000	1.17
poly(butyl acrylate)	42000	1.32
poly(styrene-*r*-methyl acrylate)	49000	1.29
poly(styrene-*r*-acrylic acid)[a]	37000	1.19
poly(styrene-*r*-isoprene)	9000	1.30
poly(styrene-*b*-methyl acrylate)[a]	21000	1.18
poly(styrene-*b*-butyl acrylate)[a]	38000	1.32

[a] Nanoparticle degradation was observed in the form of a blue shift in the fluorescence emission and UV/Vis absorption spectra.

The preparation of surface-grafted poly(styrene-*b*-methyl acrylate) was accomplished in two steps. First, styrene was polymerized from the nanoparticle surface, and the polystyrene-grafted nanoparticle composite was isolated by precipitation into methanol. In a second step, the polystyrene-functionalized nanoparticles with an active chain end were heated in a toluene solution of methyl acrylate and *tert*-butyl peroxide to 70 °C for 22 h, and the block copolymer–CdSe nanoparticle composite was precipitated into methanol.

Block copolymer formation was confirmed by an increase in molecular weight from the original homopolymer composite, as observed by GPC, and in the corresponding ^{1}H NMR spectrum, in which resonances of both polystyrene and poly(methyl acrylate) were observed. The polydispersity indices were narrow ($\mathrm{PDI} < 1.3$), as expected with the RAFT technique, for all polymer architectures including block copolymers. Due to the slow initiation kinetics inherent to *tert*-butyl peroxide, polymerizations usually required 24 h; in the cases of butyl acrylate and block copolymers, longer reaction times were required (ca. 32–48 h).

A key result of this study is the retention of the unique optical properties of the CdSe nanoparticles after polymer grafting by the controlled RAFT process. This is observed clearly in the photoluminescence and UV/Vis spectra of the composite materials (Figure 1). The band-edge absorption peak of the CdSe nanoparticle is centered at about 525 nm in the starting **3**-covered nanoparticles, as well as in both the polystyrene and poly(methyl acrylate)–nanoparticle composites. From the fluorescence spectra, it is also evident that the nanoparticle integrity remains intact, with emission maxima centered around 545 nm both before and after polymerization.[33] The combination of these optical-characterization methods with transmission electron micrographs confirms that the nanoparticle integrity is maintained throughout the polymerization process. This is in direct contrast to the use of conventional free-radical initiators with quantum dots, in which the optical properties are lost irreversibly. In addition, the method does not require the use of an inorganic coating over the original quantum dots, thus providing a simple approach to these composite materials.

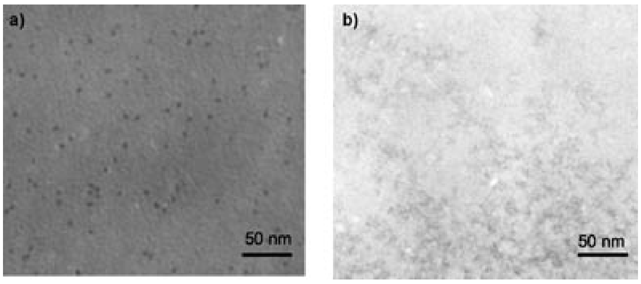

Figure 1. Transmission electron micrographs of a) poly(styrene)–covered CdSe nanoparticles in poly(styrene), b) TOPO-covered CdSe nanoparticles in poly(styrene).

The CdSe–polymer composite materials can be solution or spin cast into optically clear thin films. Analysis of the composite thin films by transmission electron microscopy (TEM) reveals the uniform nature of the material, as the nanoparticles are dispersed throughout the matrix in an non-aggregated fashion. Figure 2a shows an image of a polystyrene-encapsulated nanoparticle film prepared by the RAFT process, while Figure 2b shows the case where styrene was polymerized in the presence of TOPO-covered CdSe nanoparticles. In the latter case the micrographs show gross aggregation of the nanoparticles in the polymer matrix. Thus, growth of the matrix material radially outward from the nanoparticle surface provides compatibility of the two disparate materials into a single and uniform composite.

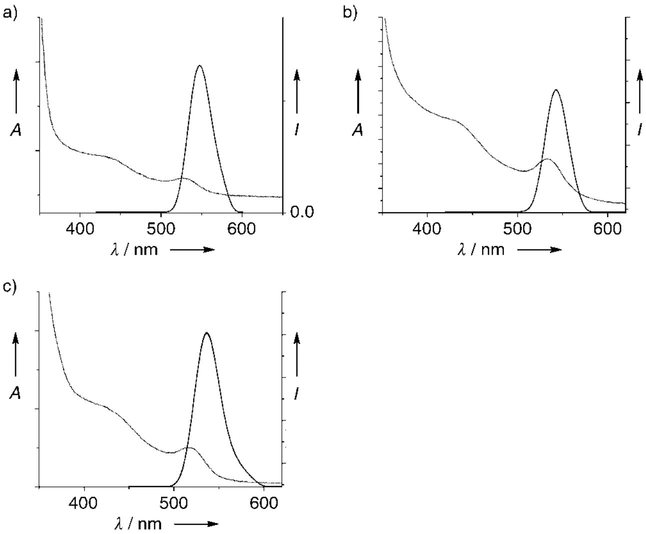

Figure 2. Absorption (*A*) and fluorescence spectra (*I* is intensity) on toluene solutions of a) **3**-covered CdSe nanoparticles, b) poly(methyl acrylate)-covered CdSe nanoparticles prepared by RAFT, and (**3**) poly-(styrene)-covered CdSe nanoparticles prepared by RAFT.

In summary, we have adapted the RAFT-method of controlled free-radical polymerization to CdSe nanoparticles, by tailoring the nanoparticles with trithiocarbonate moieties, followed by polymerization from the nanoparticle surface. This RAFT-enabled growth method provides a general procedure for tailoring CdSe nanoparticles with a variety of polymers, while maintaining the unique structural and optical properties of the nanoparticles, and without the requirement of a protective inorganic shell. Through this general functionalization procedure, novel composite materials can be produced rapidly, and the choice of materials into which nanoparticles can be dispersed is expanded considerably. This, in turn, opens new possibilities for self- and directed-assembly studies on quantum dots. The retention of the photophysical properties of the quantum dots following the polymerization considerably expands their potential application base.

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[31] The removal of excess ligands was found to be easier when a centrifuge device was employed. THF was removed from the ligand-exchange solution and the nanoparticles were redissolved in hexane. The hexane solution was then centrifuged. After centrifugation, the excess ligand was removed from the bottom of the centrifuge and discarded. The nanoparticles were isolated from the device, dissolved in hexane, and the procedure was repeated.

[32] W. H. Guo, J. J. Li, Y. A. Wang, X. G. Peng, *J. Am. Chem. Soc.* **2003**, *125*, 3901. In our experiments, rather high free-radical concentrations (ca. 0.25 M) resulted in nanoparticle degradation within minutes or less, whereas lower concentrations (ca. 0.02 M) resulted in observable degradation during the initial course of the polymerization (several hours).

[33] A small tail in the fluorescence emission spectrum of the poly(styrene)–CdSe composite is observed which is attributed to a small amount of degradation. It is hypothesized that this degradation is not observed in the poly(methyl acrylate)–CdSe composite because of the faster initiation and growth kinetics of methyl acrylate relative to styrene.