

Upconverting Lanthanide-Doped NaYF₄–PMMA Polymer Composites Prepared by in Situ Polymerization

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The incorporation of nanoparticles (NPs) in polymer matrixes to obtain transparent polymer composites has been a challenge undertaken by several research groups in the literature recently.^{1–6} In situ polymerization of NPs in polymer matrixes to obtain bulk polymer–NP composites often results in the loss of transparency in the final product. In large bulk polymerization of nanocomposites a phase separation of the NPs during the polymerization process regularly occurs which leads to agglomeration of the NPs and a turbid final product because of scatter. Several techniques have been developed to incorporate various nanoparticles in transparent polymer composite materials which prevent agglomeration of the NPs during the polymerization process.^{1–6} These procedures revolve around either ligand exchange of the NPs' original stabilizing ligands or the selection of appropriate polymeric hosts that inhibit agglomeration of the NPs during polymerization.

In this communication we present a general technique to synthesize oleic acid stabilized NP/poly(methyl methacrylate) (PMMA) bulk polymer composites via in situ polymerization in the presence of a poly(ethylene glycol) (PEG)–monooleate ligand. The miscibility of PEG and PMMA is well-known and has been extensively studied in the literature.⁷ In theory, the monooleate ligand could be tailored to a desired polymer matrix which would extend this technique even further. As a proof of principle we synthesized transparent upconverting NP/PMMA bulk polymer composites. Polymerization of PMMA in the presence of this commercially available PEG–monooleate results in clear bulk polymer–NP composite materials which, in principle, can be extended for other types of NPs such as iron oxide and semiconducting quantum dots (QDs). These composite materials have potential ap-

plications in light emitting diodes (LEDs),⁶ security labeling,⁸ lasers,⁹ and displays.¹⁰

Several publications have reported the incorporation of upconverting NPs in thin films of PMMA or other polymers. In these cases, the transparency of these thin films is due to their small thickness.^{11,12} To our knowledge, no examples of upconversion in bulk polymer–NP composites have been reported in the literature. We chose to employ hexagonal phase NaYF₄:0.5% Tm³⁺, 30% Yb³⁺ and NaYF₄:2.0% Er³⁺, 20% Yb³⁺ upconverting NPs when synthesizing the nanocomposites.¹³ The bulk versions of these materials are some of the most efficient upconverters known to date.¹⁴ Transparent composites with loadings as high as 3 wt % of NPs are attained. We also demonstrate that it is possible to tune the nanocomposites to emit different colors by mixing or choosing appropriate upconverting NPs. Taking advantage of this fact, we prepared a clear nanocomposite that emits white light under 980 nm laser diode excitation.

The ability to synthesize transparent upconverting polymer nanocomposites can facilitate the manufacture of a three-dimensional (3D) volumetric optical display. In this type of three-dimensional display, the overlap of two infrared (IR) lasers induces the upconversion process and produces the desired color.¹⁰ The point of intersection of the two lasers was termed a “voxel”, or volumetric pixel, by previous researchers.¹⁰ The movement of this “voxel” around the optical transparent display medium allowed the researchers to draw 3D images. The transparent medium used previously was heavy metal fluoride glasses doped with lanthanide (Ln³⁺) ions. By demonstrating the ability to synthesize transparent NP–polymer composites, we hope to combine the ease of polymer processing with the upconversion properties of the Ln³⁺-doped NaYF₄ NPs. These nanocomposites are easier and less expensive to manufacture than conventional heavy metal fluoride glasses and can readily be molded into various shapes. In addition, doping several Ln³⁺ ions into a single monolithic bulk medium can lead to a detrimental cross-relaxation processes between the ions which quenches the upconversion luminescence.¹⁰ The use of NPs eliminates this problem as the phosphors are spatially isolated from each other in the polymer matrix. Thus, it is possible to mix several nanocrystals with different upconversion emissions without worrying about cross-relaxation occurring.

- (1) Guan, C.; Lue, C.; Cheng, Y.; Song, S.; Yang, B. *J. Mater. Chem.* **2009**, *19*, 617–621.
- (2) Sun, H.; Zhang, H.; Ju, J.; Zhang, J.; Qian, G.; Wang, C.; Yang, B.; Wang, Z. Y. *Chem. Mater.* **2008**, *20*, 6764–6769.
- (3) Althues, H.; Simon, P.; Kaskel, S. *J. Mater. Chem.* **2007**, *17*, 758–765.
- (4) Althues, H.; Palkovits, R.; Rumpelcker, A.; Simon, P.; Sigle, W.; Bredol, M.; Kynast, U.; Kaskel, S. *Chem. Mater.* **2006**, *18*, 1068–1072.
- (5) Zhang, H.; Wang, C.; Li, M.; Zhang, J.; Lu, G.; Yang, B. *Adv. Mater.* **2005**, *17*, 853–857.
- (6) Lee, J.; Sundar, V. C.; Heine, J. R.; Bawendi, M. G.; Jensen, K. F. *Adv. Mater.* **2000**, *12*, 1102–1105.
- (7) Silvestre, C.; Cimmino, S.; Martuscelli, E.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1987**, *28*, 1190–1199.

- (8) Cheng, K. H.; Aijmo, J.; Ma, L.; Yao, M.; Zhang, X.; Como, J.; Hope-Weeks, L. J.; Huang, J.; Chen, W. *J. Phys. Chem. C* **2008**, *112*, 17931–17939.
- (9) Scheife, H.; Huber, G.; Heumann, E.; Bar, S.; Osiaç, E. *Opt. Mater.* **2004**, *26*, 365–374.
- (10) Downing, E.; Hesselink, L.; Ralston, J.; Macfarlane, R. *Science* **1996**, *273*, 1185–1189.
- (11) Zhou, Z.; Hu, H.; Yang, H.; Yi, T.; Huang, K.; Yu, M.; Li, F.; Huang, C. *Chem. Commun.* **2008**, 4786–4788.
- (12) Wang, J.; Hu, J.; Tang, D.; Liu, X.; Zhen, Z. *J. Mater. Chem.* **2007**, *17*, 1597–1601.
- (13) Li, Z.; Zhang, Y. *Nanotechnology* **2008**, *19*, 345606/1–345606/5.
- (14) Kraemer, K. W.; Biner, D.; Frei, G.; Guedel, H. U.; Hehlen, M. P.; Luethi, S. R. *Chem. Mater.* **2004**, *16*, 1244–1251.

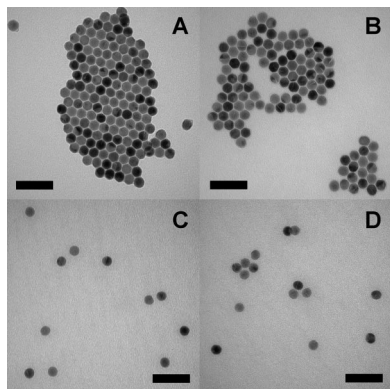


Figure 1. Low-resolution transmission electron micrographs of (A) NaYF₄:2% Er³⁺, 20% Yb³⁺ NP colloid (THF), (B) NaYF₄:2% Er³⁺, 20% Yb³⁺ NP colloid (MMA), and (C) 1 wt % and (D) 2 wt % NaYF₄:2% Er³⁺, 20% Yb³⁺ NP-PMMA composite materials. The scale bars in all TEM images are equal to 100 nm.

The NaYF₄:0.5% Tm³⁺, 30% Yb³⁺ and NaYF₄:2.0% Er³⁺, 20% Yb³⁺ NPs utilized in this study were synthesized via a procedure previously reported in the literature.¹³ Powder X-ray diffraction of the synthesized NPs (Figure S1, Supporting Information) indicate they have the hexagonal phase and are highly crystalline with an average crystallite size of 24 nm (Scherrer equation). The transmission electron micrograph (TEM) of the NaYF₄:2.0% Er³⁺, 20% Yb³⁺ NPs shows that they are hexagonal in shape with an average diameter of 27 nm ± 1.3 nm (Figure 1). The original upconverting NaYF₄ NPs are highly processable as a result of the presence of the oleic acid capping ligand on their surface and can be dispersed with ease in nonpolar organic solvents to yield clear colloids. It is the presence of these oleic acid ligands on the surface of the NPs that does not allow for their dispersal as clear colloids in the MMA monomer.

It was observed that the oleic acid-coated NaYF₄ NPs could not be dispersed in MMA without severe agglomeration. The particles would settle out of solution within a matter of minutes. To combat this problem we included PEG-monooleate to help stabilize the NPs in the monomer mixture. The NPs dispersed in tetrahydrofuran (THF) were first mixed with the desired amount of PEG-monooleate. THF was evaporated gently using a rotovap. MMA was then added to the reaction vial, and the resulting solution was sonicated for 2 min to disperse the NPs. After the inclusion of the PEG-monooleate, the NPs were observed to be stable in the MMA monomer resulting in a clear NP-monomer dispersion with no discernible agglomeration or settling occurring. The interdigitation of the PEG-monooleate with the oleic acid on the surface of the NPs renders the NPs dispersible in MMA. The resulting NP-MMA monomer solution was then polymerized in bulk form to obtain clear composite materials in cylindrical glass vials 52 mm in length and with a diameter of 25 mm to give solid cylindrical blocks. Detailed synthetic procedures are given in the Supporting Information.

Transmission electron microscopy (TEM) measurements were performed on the PEG-coated particles to determine if any agglomeration had occurred in the monomer solution.

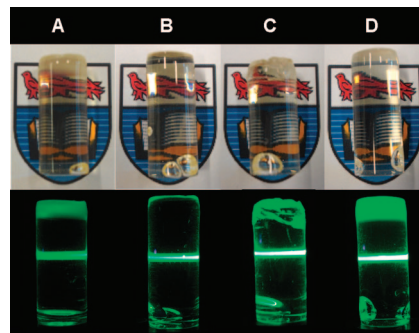


Figure 2. Photographs of NP-PMMA composites under ambient light (top) and 980 nm laser diode excitation (bottom) (A) 0.5 wt %, (B) 1 wt %, (C) 2 wt %, and (D) 3 wt % NaYF₄:2% Er³⁺, 20% Yb³⁺ NPs in PMMA.

As shown in Figure 1, the TEM images of the NPs stabilized with the PEG-monooleate dispersed in the MMA monomer solution are comparable to those of the original NP dispersed in THF. The NPs are well spaced, and no discernible agglomeration is observed. The interparticle spacing is noticed to increase slightly in the case of the PEG-monooleate coated NPs which can be attributed to PEG polymer chains coating the outside of the NPs.

The size of the PEG-monooleate coated NPs dispersed in MMA monomer was also investigated using dynamic light scattering. DLS measurements on the NPs dispersed in MMA returned an average diameter of 30 nm and a polydispersity index of 0.14. This corresponds well to the NP diameter determined from both the TEM and the XRD results and indicates that the NPs are well dispersed in the monomer solution.

Stability of the NPs in the monomer solution is not enough though, as a stable dispersion does not always lead to transparent nanocomposites. Polymerization of the monomer dispersion can lead to phase separation of the NPs and agglomeration.⁶ In our case the composites were observed to retain their transparent nature after the polymerization step was complete. The coordination of the PEG-monooleate on the surface of the NPs helps to stabilize them in the polymer matrix.⁷

TEMs of the nanocomposite (ultramicrotome cut, thickness < 100 nm) with different wt % loadings of NPs are shown in Figure 1 and in Figures S2 and S3 (Supporting Information). From these images it can be seen that the NPs are highly dispersed throughout the composite materials with a low degree of agglomeration. In the 0.5 wt % and 1 wt % composite samples (Figures 1C, S2, and S3, Supporting Information), the majority of the NPs are dispersed as individual particles throughout the polymer matrix. Some agglomerations consisting of only two to three NPs can be observed, but these are in the minority when compared to the isolated NPs. In samples with loadings of 2 wt % of NPs and higher (Figures 1D, S2, and S3, Supporting Information) some degree of NP assembly is observed. These agglomerations contain five to six nanoparticles at most but still demonstrate a clear degree of separation between the NPs.

Figure 2A-D shows photographs of NaYF₄:2% Er³⁺, 20% Yb³⁺ NP-PMMA nanocomposites of various NP loadings

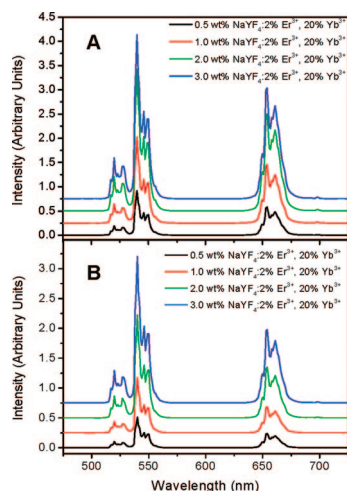


Figure 3. Upconversion luminescence spectra of (A) NP-PMMA composite materials and (B) colloidal solutions of NPs in THF with various wt % loadings excited with a 980 nm laser diode (power density = 150 W/cm²).

under ambient light (top) and 980 nm laser diode excitation (bottom) with a power density of 150 W/cm². From these photos it is clear that even the 3 wt % sample has a high degree of transparency. The upconversion photos also demonstrate the clarity of these samples as no scattering or divergence of the beam is observable as it passes through the samples. NP loadings higher than 3 wt % resulted in a gradual loss of transparency in the composite material.

It is important that the upconverting nanocrystals retain their original optical properties when dispersed in the nanocomposite. If any quenching of the excited states occurs in the polymer matrix, the efficiency of the upconversion process is compromised. To determine if this was the case the upconversion properties of the original particles versus the nanocomposites were investigated. The visible upconversion spectra of the NaYF₄:2% Er³⁺, 20% Yb³⁺ NPs in THF and the PMMA composites under 980 nm laser diode excitation (power density: 150 W/cm²) are shown in Figure 3A,B, respectively. The spectra correspond well to what has been reported previously for Er³⁺ upconversion in hexagonal NaYF₄ NPs. A dominant green upconversion luminescence was observed from the (²H_{11/2}, ⁴S_{3/2}) → ⁴I_{15/2} transitions and red from the ⁴F_{9/2} → ⁴I_{15/2} transition, respectively, in both sets of samples. As seen from these spectra, the upconversion properties of the synthesized composites are comparable to those of the original NP colloids. A slight increase in the luminescent intensity is observed in the case of the PMMA composite materials. This can be attributed to the larger density of the PMMA composite materials versus THF which leads to a higher concentration of NPs per volume in the composite samples. As one increases the concentration of the NPs from 0.5 wt % to 3 wt % the intensity of the upconversion emissions increases similarly in both the colloidal and the composite samples. This is a good indication that the optical properties of the NPs are not affected in the composite material.

To demonstrate the ability to mix NPs with different emissive properties to obtain various color combinations, we synthesized a white light upconversion NP-PMMA

composite material. The majority of previous attempts to obtain white light through upconversion in NPs revolve around codoping a material with both Tm³⁺ and Er³⁺ to get simultaneous blue, green, and red emissions.¹⁵ This method can lead to cross-relaxation mechanisms between the dopant ions that reduce the efficiency of the upconversion processes. By dispersing the NPs in an inorganic or organic matrix they are kept spatially separated, and cross-relaxations are avoided thus maintaining the efficiency of the upconversion process.¹⁶ The upconversion spectra of the NaYF₄:2% Er³⁺, 20% Yb³⁺ and NaYF₄:0.5% Tm³⁺, 30% Yb³⁺ doped PMMA composite material under different excitation densities are shown in Figure S4 (Supporting Information). Besides the above-reported Er³⁺ emissions, three Tm³⁺ upconversion emissions are also observed. The blue upconversion emission observed between 440 and 500 nm is assigned to the ¹D₂ → ³F₄ and ¹G₄ → ³H₆ transitions. The weak red emission between 630 and 670 nm is assigned to the ¹G₄ → ³F₄ transition. The inset of Figure S4 (Supporting Information) shows a digital photograph of the composite materials under the excitation conditions (power density = 630 W/cm²). The CIE color coordinates of the polymer composite for this power density are 0.28, 0.36. We observed a change in the color coordinates from green to an off white as the power density changed from 140 W/cm² to 630 W/cm² (Figure S5 and Table S1, Supporting Information). This is fully expected as the various emissions possess different power dependencies. Previous reports on upconverting white light materials report color coordinates over a very limited range of power densities which is not a true reflection on a materials performance.¹⁵

We have presented an efficient method for the generation of transparent upconverting NP-polymer composite materials. The inclusion of the PEG-monooleate ligand in the monomer solution stabilizes the NP throughout the polymerization step, preventing their phase separation. The luminescent properties of the NPs remain intact after the polymerization is complete. This method is cost efficient as it makes use of a relatively inexpensive, commercially available chemical (PEG-monooleate). Preliminary results on CdSe QDs indicate that the procedure outlined here is compatible with other types of NPs, such as iron oxide and semiconductor NPs.

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Supporting Information Available: Experimental details, powder XRDs, and TEM micrographs of the samples (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) Mahalingam, V.; Mangiarini, F.; Vetrono, F.; Venkatramu, V.; Bettinelli, M.; Speghini, A.; Capobianco, J. A. *J. Phys. Chem. C* **2008**, *112*, 17745–17749.
- (16) Sivakumar, S.; van Veggel, F. C. J. M.; Raudsepp, M. *J. Am. Chem. Soc.* **2005**, *127*, 12464–12465.