Facile Fabrication of Upconversion Photoluminescent Transparent Semiaromatic Polyamide Nanocomposites Through Interfacial Chemistry Modification

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ABSTRACT: Transparent upconversion photoluminescent polyamide nanocomposites were fabricated via a facile in situ polycondensation method with interfacial chemistry modification employing polyacrylic acid-functionalized upconversion nanoparticles (UCNP-PAA) as fillers and transparent semiaromatic polyamides (SAPA) as host materials. The as-prepared UCNP-PAA could be dispersed uniformly in the polyamide salt solution and the SAPA chains can be grafted to the UCNP-PAA through condensation reactions. The grafted SAPA ligand on the surface of UCNP increases the compatibility between SAPA and UCNP, thus causing uniform dispersion of the UCNP in the polyamide nanocomposites and improving the transmittance of the polyamide nanocomposites. The obtained polyamide nanocomposites are transparent and show strong green upconversion photoluminescence. This work solved the problem of the dispersity of incorporated nanoparticles and improving the transparency of nanocomposites and, more importantly, endowed the traditional engineering plastic with upconversion photoluminescent properties which can be applied in three-dimensional displays and the related solar cell field in the future.

1. INTRODUCTION

With the development of nanotechnology, plenty of functional nanoparticles have been incorporated into the polyamides to prepare polyamide nanocomposites with special properties, such as light and magnetic, to name but a few.1–4 Among these functional nanoparticles, upconversion nanoparticles (UCNPs) have been extensively applied in various fields because of their excellent photoluminescent properties of transferring long-wavelength near-infrared light to shorter wavelength UV or visible light.5–8 Recently, UCNPs were introduced into a polymer matrix (such as polystyrene,9 poly(methyl methacrylate),10,11 polydimethylsiloxane,12,13 etc.) for the synthesis of polymer nanocomposites which can be used in various fields such as three-dimensional (3D) display because of the polymer nanocomposites are of low cost, light weight, and easily processable properties.5,14–16 Transparent semiaromatic polyamides (SAPAs) are one of the promising type of engineering thermoplastics which have been widely used in diverse industrial fields, owing to their outstanding thermal, mechanical, and transparency properties.17–21 Most of the SAPA nanocomposites mainly focused on the fabrication of materials with improved mechanical, thermal, antiaging properties, and so forth.22–24 The advanced photoluminescent properties of the traditional polyamide nanocomposites, especially the transparent polyamide nanocomposites with optical properties is rarely demonstrated. So far, no reports concerning the combination of photoluminescent UCNP with the SAPA matrix have appeared.

It is crucial for bulk polymer nanocomposites which incorporated with luminescent nanomaterials to be transparent, therefore the application can be more extensively.25 However, light scattering on the interface between polymer and nanoparticles and the nanoparticles agglomerated in the polymer matrix will decrease the transparency of polymer nanocomposites.26 Thus, the key point to obtain transparent polymer nanocomposites was to prevent their agglomeration during the polymerization process.27,28 Several methods involve either the surface modification of nanoparticles or choosing appropriate polymer matrix to prevent the nanoparticles from agglomerating in the process of polymerization.29–31

Herein, a facile in situ melt polycondensation method was proposed to fabricate a series of upconversion luminescent transparent SAPA/UCNP-PAA bulk polymer nanocomposites. The chemistry interface properties of UCNP-PAA were modified by covalently grafting SAPA chains, thus the
compatibility between UCNP-PAA and SAPA were increased. The UCNP-PAA dispersed excellent in the polyamide nanocomposites leading to a good transparency of the nanocomposites. When excited by 980 nm laser, the obtained polyamide nanocomposites show strong green photoluminescent emission, thus, these nanocomposites have potential to be used in 3D display, and so forth. This work provides a general and robust strategy to fabricate polyamide nanocomposites through the interfacial chemistry modification.

2. RESULTS AND DISCUSSION

2.1. Preparation of UCNP-PAA Nanoparticles. In the present work, to incorporate UCNP into SAPA bulk polymers, water-soluble UCNP-PAA was fabricated via the sequential solvothermal method and then the ligand exchange process. The UCNP-oleic acid (OA) and UCNP-PAA samples have high solubility in cyclohexane and water, respectively. According to the transmission electron microscopy (TEM) images (Figure 1b,c), the UCNPs are spherical with a regular morphology and the average sizes are 15 ± 1.6 nm. From the photographs (inset), the UCNP-OA and UCNP-PAA solutions all emit strong green luminescent, which means that the nanoparticles prepared have the ability to emit upconversion luminescent light under the irradiation of 980 nm laser. X-ray diffraction (XRD) patterns (Figure S1) show that the prepared UCNPs were well-crystallized, and the characteristic peaks could match with the β-NaYF₄ phase (JCPDS: 16-0334) very well.

According to Fourier transform infrared (FT-IR) spectra (Figure S2), the disappearance of the carboxylate stretching (∆s-COO⁻) at 1564 cm⁻¹, (∆s-COO⁻) at 1463 cm⁻¹, and the alkene stretching (∆-CH=) at 3007 cm⁻¹ which correspond to OA proves the existence of PAA on the surface of nanoparticles after the ligand exchange process. Furthermore, the peak at 1734 cm⁻¹ and the peak at 1639 cm⁻¹ also suggest the existence of the −COOH groups. Based on these results, we can firmly draw the conclusion that hydrophilic PAA chains connected on the surface of UCNP instead of OA. The corresponding UV–vis absorption spectra of UCNP-OA and UCNP-PAA were almost the same (Figure S3) and upconversion photoluminescent spectrum of OA-capped UCNP and PAA-capped UCNP both possess three Er³⁺ distinct emission bands (Figure S4). The green light emission was ascribed to the transitions of 2H₁₁/₂→4I₁₅/₂ (521 nm), 4S₃/₂→4I₁₅/₂ (539 nm), and red emission were connected with the transitions of 4Fl₂→4I₁₅/₂ (654 nm) of the Er³⁺ ions.

2.2. Fabrication of SAPA/UCNP-PAA Nanocomposites via the Melt Polycondensation Process. After the modification of UCNP with PAA, we incorporated UCNP-PAA into the bulk transparent SAPAs with various UCNP-PAA loadings through the melt polycondensation process, the process was shown in Scheme 1. Figure 2a–h shows photographs of SAPA/UCNP-PAA nanocomposites with various UCNP-PAA loadings under 980 nm laser excitation (bottom) and ambient light (top). These photos showed that with the increasing of the loading of UCNP-PAA incorporated into the polyamides matrix (UCNP-PAA loadings: 0.2, 0.4, 0.6, and 0.8 wt %), the transmittance of SAPAs nanocomposites decreases gradually (transmittance: 90, 88, 85, 82%). The decrease of transmittance with the increasing of UCNP-PAA loadings is attributed to the scattering of the nanoparticles. From these digital photographs, we can conclude that even with the loading of 0.8 wt % nanoparticles, the polyamide nanocomposites still have high degree of transparency (82%). Under 980 nm laser excitation, SAPA/UCNP-PAA nanocomposites show green upconversion emission, respectively. Also when the loadings weight was as low as 0.2 wt %, the polyamide nanocomposites still exhibit upconversion luminescent properties and showed high transparency (90%). The strong upconversion fluorescence is owing to the highly dispersed UCNP-PAA in polyamide nanocomposites not being affected by the melt polycondensation process.

To investigate the dispersion of the UCNP in nanocomposites, the nanocomposites samples were ultramicrocuted to result in ultrathin section samples that had 200 nm thickness for TEM characterization. TEM images of the SAPA/UCNP-PAA nanocomposites with different loadings of UCNP-PAA are shown in Figure 3a–d. With various loadings of UCNP-PAA in the polyamide nanocomposites samples, the UCNP are dispersed as individual particles in the polyamide matrix. From these photographs we can see that the UCNP-PAA are...
uniformly dispersed in the polyamide nanocomposites without obvious agglomeration.

To investigate the interface connection between UCNP with the polyamide bulk matrix, we hypothesis that SAPA ligands were chemically bonded on the surface of UCNP by condensation reactions between the functional group of SAPA (−NH₂) and UCNP-PAA (−COOH). To confirm the grafting copolymerization between UCNP-PAA and SAPA chains, UCNP needed to be separated by removing the physically absorbed polyamides chains. The polyamide nanocomposites were dissolved in formic acid, then the nanoparticles were washed six times with formic acid. The SAPA chains can be dissolved in formic acid, and thus only the UCNP which are chemically grafted by SAPA chains can be left after several washing step. Thus, we can characterize the separated UCNP with FTIR to confirm the existence of the chemically bonded SAPA on the surface of UCNP. The SAPA chains on the UCNP after polymerization was also characterized by FTIR (Figure 4a). The bands at 1636 cm⁻¹ is assigned to the stretching vibration of C=O groups of the polyamides. The broad band at 3300 cm⁻¹ corresponds to the hydrogen bonded −NH− and −COOH groups of the polyamides, and the C−H stretching vibrations appeared at 2854 and 2933 cm⁻¹. Consequently, the existence of SAPA chains which are chemically grafted to the UCNP was confirmed by the FTIR results.

Upconversion fluorescence spectra of SAPA/UCNP-PAA bulk polymer nanocomposites with various loadings of hydrophilic UCNP-PAA are presented in Figure 4b. The photoluminescent spectra of bulk nanocomposites were similar to the incorporated UCNP, which shows that the nanoparticles and the nanocomposites possess the same emission centers. For the SAPA/UCNP-PAA bulk polymer nano-
composites, the red emission is associated with the transitions of $^{4}S_{3/2}→^{4}I_{15/2}$ (654 nm) and the green emission are connected with the transitions of $^{5}S_{2}→^{5}I_{15/2}$ (539 nm), $^{3}H_{4}→^{3}I_{15/2}$ (521 nm) of the Er$^{3+}$ ions. From Figure 4b, we can conclude that with the improvement of UCNP content, the intensity of upconversion photoluminescent increased gradually.

3. CONCLUSIONS

In this work, a facile in situ melt polycondensation strategy was reported to prepare a series of transparent upconversion photoluminescent SAPA/UCNP-PAA bulk nanocomposites in the presence of UCNP-PAA uniformly dispersed in polyamide salts solution. The interface chemistry between the nanoparticles and the polyamide matrix was also investigated. The grafted SAPA on the surface of nanoparticles increased the compatibility between SAPA and UCNP, and thus a series of uniformly dispersed and transparent SAPA/UCNP-PAA nanocomposites were prepared. When excited by 980 nm laser, the obtained polyamide nanocomposites show strong green photoluminescent emission, thus these nanocomposites have great potential to be used in 3D display, and so forth.

4. EXPERIMENTAL SECTION

4.1. Materials. All of the chemicals used were of analytical purity without further purification. Diethylene glycol (DEG), hydrochloric solution, NaOH, toluene, NH$_{3}$F, ethanol, methanol, cyclohexane, and OA were bought from Sinopharm Chemical Reagent Co. Polyacrylic acid (PAA), rare earth oxide [Y$_{2}$O$_{3}$, Yb$_{2}$O$_{3}$, Er$_{2}$O$_{3}$ are all of the same purity grade (99.999%)], 1-octadecene (ODE), terephthalic acid, and isophthalic acid were bought from Aladin Chemical Reagent Co. Rare earth chlorides (LnCl$_{3}$, Ln: Y, Yb, Er) were fabricated by dissolving rare earth oxide in hydrochloric acid, then evaporating to remove the reductant HCl.

4.2. Characterization. High-resolution transmission electron microscopy (TEM, JEOL TEM 100CX) were conducted to character UCNP-OA, UCNP-PAA, and SAPA/UCNP-PAA nanocomposites. Samples of the UCNP-OA and UCNP-PAA for TEM characterization were fabricated by drop-coating dilute dispersions onto the copper grid, respectively. The samples of nanocomposites were prepared for TEM by using microtome (ULTRACUTE, Reichert-Jung) resulting in samples that had 200 nm thickness. The ultrathin cross sections were characterized by TEM (100 kV). XRD patterns were conducted on a Y2000 diffractometer by using Cu Kα radiation (40 kV, 40 mA). FT-IR spectra were collected by using a Nicolet 460 spectrometer. The transmittance of the nanocomposites was conducted on a photoelectric mist meter (WGW, Shanghai Yidian Physical Optical Instrument Co. LTD). Upconversion fluorescence spectra were recorded on an Edinburgh F5S fluorescence spectrometer excited by 980 nm laser (0–2500 mW, Beijing Hi-Tech Optoelectro Co.).

4.3. Preparation of OA-Capped NaYF$_{4}$: 20%Yb$^{3+}$, 2% Er$^{3+}$ Nanoparticles (UCNP-OA). Sphere-like UCNP-OA was prepared by a typical method. YCl$_{3}$ (152.3 mg, 0.78 mmol), YbCl$_{3}$ (55.9 mg, 0.2 mmol), and ErCl$_{3}$ (5.5 mg, 0.02 mmol) were dissolved in 10 mL of methanol in a flask, then 15 mL of OA and 35 mL of ODE were added and kept at 160 °C for 30 min, then cooled down to 50 °C. NH$_{3}$F (0.2964 g) and NaOH (0.2 g) were dissolved in 25 mL of methanol, then was added and degassed at 110 °C and then kept at 300 °C for 1 h. After cooling to room temperature, UCNP-OA was precipitated out and washed three times with ethanol and cyclohexane. Finally, UCNP-OA was dispersed in cyclohexane.

4.4. Synthesis of Hydrophilic PAA-Capped UCNPs (UCNP-PAA). The general ligand exchange procedure was proceeded according to a previously literature with little modification as the followings: DEG (20 mL) and PAA (1 g) were added into a 50 mL Schlenk flask, then the temperature was increased to 110 °C under N$_{2}$. Then, 4 mL of toluene containing 60 mg of UCNP-OA was added into the flask with stirring, the solution was continued to react for 3 h at 240 °C. When the ligand exchange process was finished, the solution was cooled to room temperature. The final UCNP-PAA products were collected by centrifugation (10,000 rpm), and then washed with ethanol three times. Finally, the product was dried in the vacuum oven at 40 °C for 12 h.

4.5. Preparation of SAPA/UCNP-PAA Bulk Nanocomposites. The bulk polymer nanocomposites in this work were prepared with different loadings of UCNP-PAA. The synthetic process of the transparent polyamide nanocomposites is shown in Scheme 1. In a typical procedure, 1 g of PA6T salts, 4 g of PA6I salts, and 10 g of water solution containing 30 mg of UCNP-PAA were loaded into a test glass tube. The mixtures were stirred and sonicated for 30 min. The test tube was then transferred to an autoclave. The suspension was heated to 280 °C with an elevated temperature (3 °C/ min) and the pressure was kept at 1 MPa for 3 h, then the pressure was decreased to normal pressure by release the vapor in 1 h. The system was kept at normal pressure and 280 °C, and 1 h later, the sample was cooled to room temperature and then the test tubes were broken and the products were obtained.

ASSOCIATED CONTENT

Supporting Information The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03894.

- XRD patterns, FT-IR spectra, UV–vis absorption spectra, and emission spectra of the UCNP-OA and UCNP-PAA (PDF)

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Notes

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