Facile Fabrication of Transparent and Upconversion Photoluminescent Nanofiber Mats with Tunable Optical Properties

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ABSTRACT: A facile fabrication strategy of transparent and upconversion photoluminescent nylon 6 (PA6) nanofiber mats was developed based on PA6 nanofiber mats, carboxylic acid-functionalized upconversion nanoparticles (UCNP-COOH), and poly(methyl methacrylate) (PMMA) solution. UCNP-COOH were prepared by a solvothermal method, followed by the ligand exchange process. The electrosprinning method and the spin-coating process were employed to combine PA6 nanofiber mats with UCNP-COOH and PMMA to introduce upconversion photoluminescent properties and transparency into the nanocomposite mats, respectively. The prepared UCNP-COOH/PA6/PMMA nanofiber mats are transparent and exhibit green emission, which are similar to UCNP-COOH when they were excited under 980 nm laser. The upconversion luminescent intensity of the functional nanofiber mats can be tailored by adjusting the weight fraction of UCNP-COOH as fillers. This facile strategy can be readily used to other types of intriguing nanocomposites for diverse applications.

INTRODUCTION

Owing to their distinctive photoluminescent properties of turning near-infrared light to shorter wavelength radiation,1,2 upconversion nanoparticles (UCNP) have drawn growing attention in the fields of bioimaging,3,4 photodynamic therapy,5,6 three-dimensional display technologies,7,8 and photovoltaics,9 to name but a few.10 Polymer nanocomposite materials with photoluminescence and transparent properties are promising for many technological applications because of the advantage of polymers,12,13 including excellent process-ability, lightweight, flexibility, and excellent impact resistance.14,15 Recently, UCNPs were introduced into polymer matrices [such as polystyrene,16,17 poly(methyl methacrylate) (PMMA),18,19 polydimethylsiloxane,20 etc.] to prepare bulk polymer nanocomposites or thin film which may be used in various fields.21

Currently, the electrosprinning technology offers a direct way to produce nanofibers with diameters ranging from tens to hundreds of nanometers.22,23 Moreover, a variety of functional nanomaterials can be incorporated into electrospun nanofibers by the co-electrospinning method.24,25 The co-electrospinning process was performed by simply mixing functional nanoparticles and polymeric solution in the same solvent environment and then electrosprinning to fabricate functional nanofibers with special properties.26 For example, flexible and freestanding UCNP/PMMA nanofiber mats with upconversion photoluminescent properties were fabricated by combining oleic acid (OA)-capped UCNP with PMMA nanofibers.25 UCNP/PVP nanofibers were also prepared by the electro-spinning strategy.28 However, all these thin composite nanofiber mats combined with UCNPs are not transparent, and so, they are limited when used in some areas, such as optical devices, sensors, and so on.29

Combined with PMMA,30 polycaprolactone, and polyamide, respectively, photoluminescent nylon 6 (PA6) nanofibers have been used to prepare polymer nanocomposites owing to their outstanding mechanical properties.31,32 Meanwhile, the nanocomposites can show the function of the nanoparticles embedded into the nanofibers.33 However, with the introduction of functional nanoparticles into the nanofiber mats, transmittance properties of the samples prepared by electrosprinning got poorer.34 To improve the transparency of the nanofiber mats, various techniques were developed to prepare transparent composites, such as casting, melt mixing, and hot-press method;35 some transparent polymer matrices were used to combine with the nanofiber mats to produce the composite mats. However, no reports concerning the introduction of UCNPs into transparent nanofiber mats have appeared so far. Thus, in this work, carboxylic acid-functionalized upconversion nanoparticles (UCNP-COOH), PA6, and PMMA were combined to prepare transparent and upconversion photoluminescent UCNP-COOH/PA6/PMMA nanofiber mats.

Supporting Information

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Herein, nanofiber mats with tunable upconversion luminescent and transparent properties were fabricated by a combination of co-electrospinning and spin-coating methods by combining electrospun PA6 fibers, UCNP-COOH, and PMMA. The procedure includes the preparation of UCNP-COOH, which is prepared by the solvothermal method, followed by the ligand exchange method, then co-electrospinning of UCNP-COOH/PA6 nanofiber mats by using the mixed solution of PA6 and UCNP-COOH in formic acid solution as raw materials, and then spin-coating of nanofiber mats with PMMA solution. The obtained nanofiber mats with tailorable optical properties are transparent and show strong green upconversion emission under 980 nm laser excitation. We developed a suitable method for large scale production to prepare upconversion photoluminescent, low-cost, flexible, and optically transparent nanofiber mats. This facile strategy can be readily used to other types of intriguing nanocomposites for diverse applications.

**RESULTS AND DISCUSSION**

Owing to the hydrophobicity of the surface of OA-coated UCNPs, it is difficult to disperse in formic acid solution. The nanoparticles may precipitate quickly from the nylon 6/formic acid solution, and thus, the nanoparticles are hardly dispersed into nylon nanofiber nanocomposites as the matrix with high uniformity during the co-electrospinning process. Therefore, the modification of nanoparticles to improve their dispersity in formic acid solution is essential. Water-soluble UCNP-COOH capped with polyacrylic acid (PAA) as the ligand were prepared by the solvothermal method and the ligand exchange method. The as-prepared UCNP-OA and UCNP-COOH could be easily dispersed in cyclohexane and ethanol, respectively. The transmission electron microscopy (TEM) images of the as-prepared UCNP-OA and UCNP-COOH samples are shown in Figure 1. The TEM images showed that the as-prepared UCNP-OA and UCNP-COOH nanoparticles are all spherical and their average sizes are 10.4 ± 1.5 and 10.5 ± 1.3 nm, respectively. The size distribution of these nanoparticles is shown in Figure S1. The nanoparticles dispersed in the solvent can emit strong green light under 980 nm laser excitation [Figure 1a (inset) and Figure 1b (inset)].

X-ray diffraction (XRD) was used to characterize the crystalline phase structures of nanoparticles, and diffraction patterns are illustrated in Figure S2 (UCNP-OA and UCNP-COOH and the standard pattern for hexagonal β-NaYF₄). Strong diffraction peaks can be clearly observed in XRD patterns, and these peaks are characteristic of β-NaYF₄ (JCPDS: 16-0334) with almost 100% crystallinity. In addition, there are no other peaks existed in the patterns, which illustrate that a pure crystalline phase of β-NaYF₄ was synthesized via the solvothermal method and the ligand exchange method.

The successful preparation of UCNP-COOH samples by the ligand exchange method was confirmed by Fourier transform infrared (FT-IR) spectra (Figure S3). According to Figure S3, the existence of PAA capping ligand after the ligand exchange process was confirmed by the disappearance of alkene stretchings (=C–H) at 3007 cm⁻¹, which corresponded to OA. Furthermore, a band at 1564 cm⁻¹ appeared in the spectrum of the UCNP-OA (Figure S3a) associated with the asymmetric (νas) stretching vibrations of the carboxylic group of the OA. After the ligand exchange process, bands corresponding to the carboxylic group are observed at 1640 cm⁻¹.

The corresponding upconversion spectra of the UCNP-OA and UCNP-COOH samples are shown in Figure S4. The upconversion spectra of the UCNP-OA and UCNP-COOH samples were the same with the previously reported spectra of the UCNPs. The spectra of UCNP-OA and UCNP-COOH both feature three different Er³⁺ emission bands. The green emission is associated with the transitions ⁴I_{15/2}−⁴I_{11/2} (521 nm) and ⁴S_{3/2}−⁴I_{15/2} (539 nm) and red emission is associated with the transitions ⁴F_{9/2}−⁴I_{15/2} (654 nm) for the Er³⁺ ions.

The nanofiber mats were prepared by co-electrospinning and then spin-coating of nanofiber mats with PMMA solution; the process is shown in Scheme 1. The morphologies of the as-prepared UCNP-OA and UCNP-COOH were characterized by scanning electron microscopy (SEM), and the results are shown in Figure 2. Electrospun UCNP-COOH/PA6 nanofiber mats were uniform and smooth with no beads on the surface of the nanofiber. When the weight fraction of nanoparticles increased to 2 wt%, few beads appeared. The morphology was not changed seriously with the weight fraction of UCNP-COOH increasing as shown in Figure 2a−d. According to SEM images, the UCNP-COOH/PA6 nanofiber (Figure 2a−d) showed a range of diameters ranging from 100 to 250 nm. The diameter distributions of these nanofibers are shown in Figure S5. The thin coating layer of PMMA can be observed on the surface of functional nanofiber mats after spin-coating of PMMA solution onto the surface of nanofiber mats as shown in Figure 2e−h. The coating layer of PMMA was so thin that we can see the nanofiber on the surface of the mats.

Another important feature of the nanofiber mats was the transparency against visible light. The transparency of all the nanofiber mats samples were measured through UV–Vis spectra as presented in Figure 3. According to the spectra, the UCNP-COOH/PA6/PMMA nanofiber mats exhibited transparency in the range of 79–86% in the visible wavelength range from 380 to 760 nm. The transparency of the nanofiber mats was found to be reduced, when the content of UCNP-COOH increased in the mats.

The results were supported by digital images illustrated in Figure 4 for UCNP-COOH/PA6/PMMA nanofiber mats with different nanoparticle contents, respectively. Figure 4a−h shows digital images of UCNP-COOH/PA6/PMMA nanofiber mats under visible light and 980 nm laser irradiation, with nanoparticle contents of 0.5, 1, 1.5, and 2 wt%, respectively. PMMA-coated UCNP-COOH/PA6/PMMA nanocomposite fiber mats emitted green color when they were placed under
980 nm laser irradiation. From these images, we can clearly see the text under the nano fiber mats, and this indicates that the nano fiber mats have a high degree of transparency. According to the previous reported work, the transparency of the nano fibers and polymer nanocomposites relies on the diameter of nano fibers and the refractive index difference between the nano fibers and the polymers matrix. The nano fiber mats have a high degree of transparency, and this is because the refractive index between PA6 nano fiber and PMMA polymer matrix was similar. The diameter of the UCNP-COOH/PA6 nano fibers is in the range of 100–250 nm, and so, the PA6 nano fibers were thin enough for light transmission.18

Upconversion fluorescence spectra of UCNP-COOH/PA6/PMMA nano fiber mats are shown in Figure 5. The spectra of UCNP-COOH/PA6/PMMA nano fiber mats are similar to the
respectively. Nanoparticle contents of 0.5 (a), 1 (b), 1.5 (c), and 2 wt % (d), PMMA nano fibers also compared the upconversion properties of the successfully incorporated into PA6 nano fibers and the PMMA polymer matrix has negative effects on the upconversion photoluminescent intensity of the UCNP-COOH/PA6/PMMA nano fibers. These results showed that the UCNP-COOH were successfully incorporated into PA6 nano fibers and the properties of the filler nanoparticles are well preserved. We also compared the upconversion fluorescence spectra of UCNP-COOH/PA6 with UCNP-COOH/PA6/PMMA nano fiber mats (Figure S6) with the same loading of nanoparticles of 2 wt %. The spectra of UCNP-COOH/PA6/PMMA nano fiber mats are similar to the UCNP-COOH/PA6 nano fiber mats, which means that they have the same kind of emission centers. However, the upconversion photoluminescent intensity was decreased slightly, which is because the PMMA polymer matrix has negative effects on the upconversion photoluminescent of the nano fiber.

CONCLUSIONS

In summary, we developed a viable strategy based on co-electrospinning and spin-coating methods for the fabrication of the transparent and upconversion photoluminescent nano fiber mats with tunable upconversion luminescent intensity. PA6 nano fiber mats were decorated by UCNP-COOH and PMMA to introduce upconversion photoluminescent properties and transparency into the nano fiber mats, respectively. The UCNP-COOH/PA6/PMMA nano fiber mats exhibited green upconversion luminescent and transparent properties. The upconversion luminescent intensity of the functional nano fiber mats can be tailored by adjusting the weight fraction of UCNP-COOH as fillers. This facile strategy can be readily used to other types of intriguing nanocomposites for diverse applications. As such, by minimizing the enthalpic interaction between functional nanoparticles and polymer matrix, functional polymer-based nano fiber composites can be readily crafted by the co-electrospinning method, thereby facilitating the fundamental investigation of their structure–property relationships. The transparent and upconversion photoluminescent nano fiber mats with tunable upconversion luminescent intensity may find diverse potential applications, such as optical devices, sensors and so on.

EXPERIMENTAL SECTION

Materials. All the chemicals used were of analytical purity without further purification. Diethylene glycol (DEG), hydrochloric solution, NaOH, toluene, NH₄F, ethanol, methanol, cyclohexane, OA, and formic acid were bought from Sinopharm Chemical Reagent Co. PAA, rare earth oxides [Y₂O₃, Yb₂O₃, and Er₂O₃] are all of the same purity grade (99.999%), and 1-octadecene (ODE) were bought from Aladdin. Rare earth chlorides (LaCl₃, Ln: Y, Yb, Er) were synthesized according to the literature. PMMA (M₉ = 20 000 000 g/mol) was purchased from Asahi Kasei. PA6 (M₉ = 40 000 g/mol) was purchased from DuPont.

Characterization. JEOL TEM 100CX high-resolution transmission electron microscopy was conducted to characterize UCNP-OA and UCNP-COOH. Samples of the UCNP-OA and UCNP-COOH for TEM characterization were fabricated by drop-coating dilute dispersions onto the copper grid, respectively. SEM micrographs were measured on a field emission scanning electron microscope (JSM7500F). XRD patterns were conducted on a Y2000 X-ray diffractometer by using Cu Ka radiation (40 kV, 40 mA). FT-IR spectra were collected by using a Nicolet 460 spectrometer. Upconversion fluorescence spectra were recorded on an Edinburgh FSS fluorescence spectrometer excited by 980 nm laser (0–2500 mW, Beijing Hi-Tech Optoelectronic Co.). Transmittance of the nanocomposite fiber mats was measured on a Cary 5000 UV–vis–NIR spectrophotometer (Varian, USA).

Preparation of OA-Capped NaYF₄: 20% Yb³⁺, 2% Er³⁺ Nanoparticles (UCNP-OA). Sphere-like UCNP-OA was prepared by a typical method. YCl₃ (152.3 mg, 0.78 mmol), YbCl₃ (55.9 mg, 0.2 mmol), and ErCl₃ (5.5 mg, 0.02 mmol) were dissolved in 10 mL of methanol in a flask, and then, 15 mL of OA and 35 mL of ODE were added and kept at 160 °C for 30 min and then cooled down to 50 °C. NH₄F (0.2964 g) and NaOH (0.2 g) were dissolved in 25 mL of methanol and then was added to the solution 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 were dispersed in cyclohexane.

Preparation of Hydrophilic NaYF₄: 20% Yb³⁺, 2% Er³⁺ Nanoparticles (UCNP-COOH). The ligand exchange process was applied by using a previously reported experimental procedure but modified as follows: DEG (10 mL) and PAA (0.5 g) were added into a flask and then heated to 110 °C under N₂. Subsequently, 2 mL of toluene containing 30 mg of UCNP-OA was added into the solution at 110 °C, then heated to 240 °C, and kept for 3 h. After cooling to room temperature, UCNP-COOH were washed three times with ethanol.

Preparation of UCNP-COOH/PA6/PMMA Nano Fiber Mats by the Combination of the Co-electrospinning Method and the Spin-Coating Process. The co-electrospinning method and spin-coating process were used to prepare UCNP-COOH/PA6/PMMA nano fiber mats. UCNP-COOH were prepared by using the previously reported experimental procedure, and the details are shown in Supporting Information. First, PA6 (1.5 g) and UCNP-COOH (15 mg) were dissolved in 5 mL of formic acid to form the mixture solution before the electrosprinning process. The
voltage used was 30 kV, and the distance between the polymer solution and the collection screen (tin foil) was 16 cm. The feeding rate was kept at 1 mL/h. The co-electrospinning method was performed for 6 h with the relative humidity of 75%. The nanofiber mats were dried in vacuum for 24 h. The spin-coating method was used to combine PAni nanofiber mats with PMMA thin layers. Pieces of PAni nanofiber mats were cut and the mats were laid on the glass, followed by dripping anhydrous ethanol evenly on the mats and then spinning at 1000 rpm for 0.5 min; this procedure was repeated until the mats have no wrinkle. Then, 10 wt % PMMA chloroform solution was dripped evenly on the mats, followed by spinning at 1000 rpm for 1 min; then, the mats were immersed in water, and the membranes were removed with a pair of tweezers. The samples were dried in vacuum at 45 °C for 1 h.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00648.

Diameter size distribution, XRD patterns, FT-IR spectra, and emission spectra of the UCNPs (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Auzel, F. Upconversion and anti-Stokes processes with f and d ions in solids. *Chem. Rev.* 2004, 104, 139–174.

(2) Cheng, Z.; Lin, J. Synthesis and application of nanohybrids based on upconverting nanoparticles and polymers. *Macromol. Rapid Commun.* 2015, 36, 790–827.

(3) Vetrone, F.; Naccache, R.; Juarranz de la Fuente, A.; Sanz-Rodriguez, F.; Blazquez-Castro, A.; Rodriguez, E. M.; Jaque, D.; Solé, J. G.; Capobianco, J. A. Intracellular imaging of HeLa cells by non-functionalized NaYF4:Er3+, Yb3+ upconverting nanoparticles. *Nanoscale* 2010, 2, 495–498.

(4) Yan, C.; Zhao, H.; Perepichka, D. F.; Rosei, F. Lanthanide-Doped Upconverting Nanoparticles: Synthesis, Structure and Properties. *Small* 2016, 12, 3888–3907.

(5) Zhang, P.; Steelant, W.; Kumar, M.; Scholfield, M. Versatile photosensitizers for photodynamic therapy at infrared excitation. *J. Am. Chem. Soc.* 2007, 129, 4526–4527.

(6) Barreto, J. A.; O’Malley, W.; Kubel, M.; Graham, B.; Stephan, H.; Spiccia, L. Nanomaterials: Applications in Cancer Imaging and Therapy. *Adv. Mater.* 2011, 23, H18–H40.

(7) Deng, R.; Qin, F.; Chen, R.; Huang, W.; Hong, M.; Liu, X. Temporal full-color tuning through non-steady-state upconversion. *Nat. Nanotechnol.* 2015, 10, 237–242.

(8) Sang, X.; Chen, W.; Chen, P.; Liu, X.; Qi, J. Transparent organic/inorganic nanocomposites for tunable full-color upconversion. *J. Mater. Chem. C* 2015, 3, 9089–9094.

(9) He, M.; Pang, X.; Liu, X.; Jiang, B.; He, Y.; Snaitl, H.; Lin, Z. Inside Back Cover: Monodisperse Dual-Functional Upconversion Nanoparticles Enabled Near-Infrared Organolead Halide Perovskite Solar Cells (Angew. Chem. Int. Ed. 13/2016). *Angew. Chem., Int. Ed.* 2016, 55, 4367.

(10) Chen, G.; Qi, H.; Prasad, P. N.; Chen, X. Upconversion Nanoparticles: Design, Nanochemistry, and Applications in Theranostics. *Chem. Rev.* 2014, 114, 5161–5214.

(11) Wilhelm, S. Perspectives for Upconverting Nanoparticles. *ACS Nano* 2017, 11, 10644–10653.

(12) Caseri, W. Nanocomposites of polymers and metals or semiconductors: Historical background and optical properties. *Macromol. Rapid Commun.* 2000, 21, 705–722.

(13) Hinklin, T. R.; Rand, S. C.; Laine, R. M. Transparent, Polycrystalline Upconverting Nanocrystals: Towards 3-D Displays. *Adv. Mater.* 2008, 20, 1270–1273.

(14) Kao, J.; Thorikelsson, K.; Bai, P.; Rancatore, B. J.; Xu, T. Toward functional nanocomposites: taking the best of nanoparticles, polymers, and small molecules. *Chem. Soc. Rev.* 2013, 42, 2654–2678.

(15) Downing, E.; Hesselink, L.; Ralston, J.; Macfarlane, R. A. Three-Color, Solid-State, Three-Dimensional Display. *Science* 1996, 273, 1185–1189.

(16) Chai, R.; Lian, H.; Cheng, Z.; Zhang, C.; Hou, Z.; Xu, Z.; Lin, J. Preparation and characterization of upconversion luminescent NaYF4:Yb, Er (Tm)/PS bulk transparent nanocomposites through in situ polymerization. *J. Colloid Interface Sci.* 2010, 345, 262–268.

(17) Qian, H.; Li, Z.; Zhang, Y. Multicolor polystyrene nanospheres tagged with up-conversion fluorescent nanocrystals. *Nanotechnology* 2008, 19, 255601.

(18) Boyer, J. C.; Johnson, N. J. J.; van Veggel, F. C. J. M. Upconverting Lanthanide-Doped NaYF4–PMMA Polymer Composites Prepared by in Situ Polymerization. *Chem. Mater.* 2009, 21, 2010–2012.

(19) Chai, R.; Lian, H.; Hou, Z.; Zhang, C.; Peng, C.; Lin, J. Preparation and Characterization of Upconversion Luminescent NaYF4:Yb3+, Er3+ (Tm3+)/PMMA Bulk Transparent Nanocomposites Through In Situ Photopolymerization. *J. Phys. Chem. C* 2010, 114, 610–616.

(20) Wang, F.; Han, Y.; Lim, C. S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping. *Nature* 2010, 463, 1061–1065.

(21) Ye, S.; Teng, Y.; Juan, A.; Wei, J.; Wang, L.; Guo, J. Modulated Visible Light Upconversion for Luminescence Patterns in Liquid Crystal Polymer Networks Loaded with Upconverting Nanoparticles. *Adv. Opt. Mater.* 2017, 5, 1600956.

(22) Liao, H.; Wu, Y.; Wu, M.; Zhan, X.; Liu, H. Aligned electroporous cellulose fibers reinforced epoxy resin composite films with high visible light transmittance. *Cellulose* 2012, 19, 111–119.

(23) Hou, Z.; Li, C.; Ma, P.; Cheng, Z.; Li, X.; Zhang, X.; Dai, Y.; Yang, D.; Lian, H.; Lin, J. Up-Conversion Luminescent and Porous NaYF4:Yb3+, Er3+@SiO2 Nanocomposite Fibers for Anti-Cancer Drug Delivery and Cell Imaging. *Adv. Funct. Mater.* 2012, 22, 2713–2722.

(24) Alam, A.-M.; Ghouri, Z. K.; Barakat, N. A. M.; Saud, P. S.; Park, M.; Kim, H. Y. Photoluminescent and transparent Nylono-6 nanofiber mat composed by CdSe@ZnS quantum dots and poly (methyl methacrylate). *Polymer* 2016, 85, 89–95.

(25) Barakat, N. A. M.; Abadir, M. F.; Sheikh, F. A.; Kanjwal, M. A.; Park, S. J.; Kim, H. Y. Polymeric nanofibers containing solid nanoparticles prepared by electrospinning and their applications. *Chem. Eng. J.* 2010, 156, 487–495.

(26) Yang, R.; Qin, G.; Zhao, D.; Zheng, K.; Qin, W. Synthesis and upconversion properties of Ln3+ doped YOF nanofibers. *J. Fluorine Chem.* 2012, 140, 38–42.
(27) Bao, Y.; Luu, Q. A. N.; Zhao, Y.; Fong, H.; May, P. S.; Jiang, C. Upconversion polymeric nanofibers containing lanthanide-doped nanoparticles via electrospinning. *Nanoscale* 2012, 4, 7369.

(28) Dong, B.; Song, H.; Yu, H.; Zhang, H.; Qin, R.; Bai, X.; Pan, G.; Lu, S.; Wang, F.; Fan, L. Upconversion Properties of Ln3+ Doped NaYF4/Polymer Composite Fibers Prepared by Electrospinning. *J. Phys. Chem. C* 2008, 112, 1435−1440.

(29) Zhao, J.; Chi, Z.; Yang, Z.; Chen, X.; Arnold, M. S.; Zhang, Y.; Xu, J.; Chi, Z.; Aldred, M. P. Recent developments of truly stretchable thin film electronic and optoelectronic devices. *Nanoscale* 2018, 10, 5764−5792.

(30) Li, B.; Yuan, H.; Zhang, Y. Transparent PMMA-based nanocomposite using electrospun graphene-incorporated PA-6 nanofibers as the reinforcement. *Compos. Sci. Technol.* 2013, 89, 134−141.

(31) Wang, J.; Zhou, S.; Huang, J.; Zhao, G.; Liu, Y. Interfacial modification of basalt fiber filling composites with graphene oxide and polydopamine for enhanced mechanical and tribological properties. *RSC Adv.* 2018, 8, 12222−12231.

(32) Heikkilä, P.; Harlin, A. Parameter study of electrospinning of polyamide-6. *Eur. Polym. J.* 2008, 44, 3067−3079.

(33) Cheng, S.; Xie, S.-J.; Carrillo, J.-M. Y.; Carroll, B.; Martin, H.; Cao, P.-F.; Dadmun, M. D.; Sumpter, B. G.; Novikov, V. N.; Schweizer, K. S.; Sokolov, A. P. Big Effect of Small Nanoparticles: A Shift in Paradigm for Polymer Nanocomposites. *ACS Nano* 2017, 11, 752−759.

(34) Yano, H.; Sugiyama, J.; Nakagaito, A. N.; Nogi, M.; Matsuura, T.; Hikita, M.; Handa, K. Optically Transparent Composites Reinforced with Networks of Bacterial Nanofibers. *Adv. Mater.* 2005, 17, 153−155.

(35) Bergshoef, M. M.; Vancso, G. J. Transparent Nanocomposites with Ultrathin, Electrospun Nylon-6,6 Fiber Reinforcement. *Adv. Mater.* 1999, 11, 1362−1365.

(36) Zhang, J.; Liu, F.; Li, T.; He, X.; Wang, Z. Surface charge effect on the cellular interaction and cytotoxicity of NaYF4:Yb3+,Er3+@SiO2 nanoparticles. *RSC Adv.* 2015, 5, 7773−7780.

(37) Chen, Z.; Chen, H.; Hu, H.; Yu, M.; Li, F.; Zhang, Q.; Zhou, Z.; Yi, T.; Huang, C. Versatile Synthesis Strategy for Carboxylic Acid−functionalized Upconverting Nanophosphors as Biological Labels. *J. Am. Chem. Soc.* 2008, 130, 3023−3029.

(38) Naccache, R.; Vetrone, F.; Mahalingam, V.; Cuccia, L. A.; Capobianco, J. A. Controlled Synthesis and Water Dispersibility of Hexagonal Phase NaGdF4:Ho3+/Yb3+Nanoparticles. *Chem. Mater.* 2009, 21, 717−723.

(39) Yang, J.; Shen, D.; Li, X.; Li, W.; Fang, Y.; Wei, Y.; Yao, C.; Tu, B.; Zhang, F.; Zhao, D. One-Step Hydrothermal Synthesis of Carboxyl-Functionalized Upconversion Phosphors for Bioapplications. *Chem.—Eur. J.* 2012, 18, 13642−13650.