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Liquid Crystalline Order and Electric Switching of Upconversion Luminescence in Colloidal Nanorod Suspensions

Sungoh Park, Haridas Mundoor, Blaise Fleury, Patrick Davidson, Jao van de Lagemaat,

order of the particles naturally arises from the interactions between nanorods in the isotropic solvent rather than from their confinement and aligning surface interactions in an anisotropic matrix. Moreover, dispersions of nanorods in a solvent usually show a strong response to the application of an alternating electric field.[13–16] In the nematic phase, the director aligns along or perpendicular to the electric field direction (depending on dielectric anisotropy), whereas, in the isotropic phase at a lower concentration, the electric field induces the orientational order of the nanorods.[11] In this article, we demonstrate the electric switching and polarization-dependent luminescence of nematically ordered suspensions of UCNR in an isotropic medium. Further, we demonstrate the electric switching of the nematic director and the emergence of orientational order in the low concentration isotropic dispersion of the nanorods induced by the external electric field. We also establish that the upconversion luminescence emission of the particles forming the nematic phase is strongly polarized. Finally, we show how the upconversion luminescence can easily be switched and modulated by applying an electric field and discuss potential applications. More generally, we demonstrate how tunable properties of mesostructured composite materials can be designed by combining properties of individual nanoparticles with the emergent soft matter behavior in the form of long-range orientational order and facile electric switching.

2. Results and Discussion

2.1. Upconversion Nanorods and Their Properties

The slender β-$NaYF_4$:Yb/Er nanorods used in this study have been designed to form a lyotropic liquid-crystalline phase when dispersed in a solvent at high concentrations. Transmission electron microscopy (TEM) images reveal their highly anisotropic shape (**Fig e 1**a). In addition, the particles were treated with hydrochloric acid (HCl) to improve the colloidal stability of the suspensions by electrostatic stabilization and to further increase the aspect ratio of these particles (Figure 1a,b). Indeed, the as-synthesized particles had a length L、1.6 m and diameter D、40 nm, whereas they were、1.6 m long and、20 nm in diameter after the acid treatment (Figure 1a,b). Stable colloidal suspensions were produced by dispersing the nanorods in ethanol. Moreover, when filled into capillaries, the suspensions spontaneously showed the coexistence of an isotropic phase at the top and a nematic phase at the bottom of a vertically oriented capillary, as expected for such slender nanorods.

The UCNR's photon upconverting properties are illustrated in Figure 1c, which shows a typical Er^{3+} emission spectrum. A drop of a very dilute dispersion was deposited on a substrate and dried to probe the polarization of the emission at the single particle level with an analyzer **A**. A single nanorod was excited, and its upconversion luminescence was collected while the angle between the nanorod's long axis and **A** was varied. The

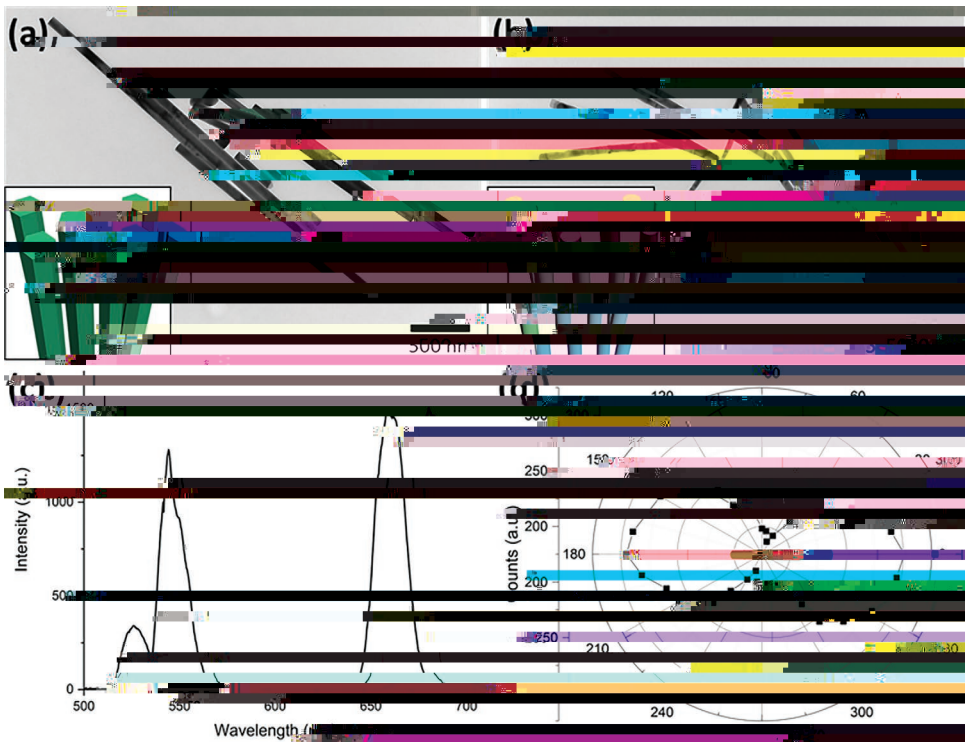

Figure 1. a,b) TEM micrograph of $NaYF_4$:Yb, Er colloidal UCNR before the acid treatment (a) and after the acid treatment (b). The insets in (a) and (b) are the schematics depicting the shapes of the rods before and after the acid treatment. c) Typical photon-upconversion luminescence spectrum of the UCNRs, where a 980 nm diode laser was used as excitation source. d) The polarization of upconversion luminescence from a single particle at 658 nm emission where the analyzer is rotated from 0 to 360 . The angle is measured between the long axis of the UCNR and the analyzer. Schematic at the center of the polar plot shows the nanorod direction.

polar plot of the emission peak at 658 nm demonstrates that the upconversion luminescence is strongly polarized (Figure 1d).

2.2. Electro-Optic Effects in the Isotropic Phase of UCNR Suspensions

We now discuss the influence of an electric field **E** on the isotropic phase of UCNR suspensions in ethanol. In the absence of

in the absence of field). The nematic phase causes no optical transmission when the sample is placed between crossed polarizers, and the nematic director ( ) is initially parallel to **P** as shown in **Fig e 4**a. However, applying **E** at 45 with respect to **P** or **A** results in the reorientation of the director This gives rise to a strong optical transmission through the sample placed between crossed polarizers (Figure 4b).

Furthermore, by adding a 530 nm full-wavelength ( ) retardation plate, the reorientation of can be characterized through probing the change in the polarized interference colors. We set the initial orientation of the director (at 45 to **P** or **A**) by applying a weak magnetic field (100–200 mT), as the nanorods tend to align perpendicular to the magnetic field (Figure 4c). As **E** was applied in the direction perpendicular to , we observed that the rods realigned along the field in about 15 s (Figure 4c–f). The time evolution of the optical transmission measured with the photodiode in this geometry is shown in **Fig e**

To conclude, we have developed a new breed of photon-upconverting liquid-crystalline materials with facile responses to external electric and magnetic fields. Polarization-dependent photon-upconversion-based luminescence in these materials can be tuned by low-voltage electric fields and is of interest for a large variety of applications, ranging from electro-optic and photonic devices to dynamic smart windows and solar cells.

4. Experimental Section

Materials Used: The chemicals used for synthesis, ytterbium nitrate hexahydrate [$Yb(NO_3)_3$, $6H_2O$], yttrium nitrate hexahydrate [$Y(NO_3)_3$, $6H_2O$], erbium nitrate pentahydrate [$Er(NO_3)_3$, $5H_2O$], sodium fluoride (NaF), and oleic acid were all purchased from Sigma Aldrich. Sodium hydroxide (NaOH) was purchased from Alfa Aesar. HCl, which was used for acid treatment, was purchased from Fisher Scientific.

Synthesis and Acid Treatment: The particles used in this study were β-$NaYF_4$:Yb/Er nanorods designed to exhibit efficient photon-upconversion luminescence when excited with infrared light at 980 nm. They were synthesized following a hydrothermal method reported earlier.[36] Briefly, NaOH (1.2 g) was dissolved in deionized (5 mL) water and mixed with ethanol (7 mL). Oleic acid (20 mL) was mixed with the solution. Next, NaF solution (8 mL, 1 M) was added and mixed. Then, yttrium nitrate hexahydrate (950 L, 0.5 M), ytterbium nitrate hexahydrate (225 L, 0.2 M), and erbium nitrate pentahydrate (50 L, 0.2 M) solutions were added. The mixture was transferred to a 50 mL Teflon-lined autoclave, kept under vigorous stirring for 20 min, and then heated to 190 C in an oven (OGH60, Heratherm). After 24 h, the mixture was allowed to cool down to room temperature. Subsequently, the particles deposited at the bottom of the Teflon chamber were collected and washed with deionized water and ethanol three times, and then redispersed in cyclohexane. The quantum yield of the acid-treated UCNR particles was estimated to be、0.1%.[33]

The UCNR nanoparticles were treated with HCl to improve the quality of the dispersion through surface charging and to further increase their aspect ratio.[6] During the acid treatment, the oleic acid ligands were removed from the particles by protonation, leaving the surfaces of the particles positively charged. In the first step, UCNR dispersions (4 mL) in cyclohexane and HCl (2 mL, 3.8 wt%) aqueous solutions were typically transferred to 20