

Facile EG/Ionic Liquid Interfacial Synthesis of Uniform RE³⁺ Doped NaYF₄ Nanocubes

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Supporting Information

Experimental Section

Preparation of [C₈mim]PF₆. 1-Chlorooctane, 1-methylimidazole and KPF₆ were used to synthesize the IL via the reference method,¹⁻² and they were examined by ¹H NMR, ¹³C NMR, and IR. Their water contents after synthesis were measured by the Karl Fischer technique.

Preparation of RE³⁺ doped NaYF₄ nanocubes. In a typical synthesis, 0.10 mmol RE nitrate and 0.10 mmol sodium nitrate were dissolved in 1.5 mL of ethylene glycol solution under ultrasonic conditions. Then the above solution was transferred into a 15mL polytetra-fluoroethylene (PTFE) vial that containing 9 mL of [C₈mim]PF₆ to form a biphasic system. Finally, the vial was sealed and kept at 80°C for 24 h. After cooling to the room temperature naturally, transparent plate-like ionogels can be found on the bottom of the vial. Then they were washed by ethanol and deionized water several times under ultrasonic conditions, collected by centrifugation and dried under vacuum at 70 °C for 12h.

Characterizations. ¹H and ¹³C NMR spectra were collected on a Bruker Advance DRX400 spectrometer. Fourier transform infrared (FT-IR) spectra were collected at room temperature with a Bruker IFS 66 V instrument. The morphology and size of the as-synthesized products were observed under a scanning electron microscope (Hitachi S-4800). High resolution transmission electron microscopy (HRTEM) images were recorded using a FEI Tecnai G2 F20 at 200 kV. The structure and phase purity of the as-synthesized samples were determined using X-ray diffraction (XRD) analysis on a Bruker AXS D8 Advance Powder X-ray diffractometer (using CuK α radiation: $\lambda=1.5418\text{\AA}$). The upconversion emission spectra were obtained using a 980 nm laser from an OPO (optical parametric oscillator, Continuum Sunlite, USA) as the excitation source and detected by R955 (HAMAMATSU).

References:

1. Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; McCleskey, T. M.; Baker, G. A., The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids. *Green Chem.* 2007, **9**, 449.
2. Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D., Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation *Green Chem.* 2001, **3**, 156.

Table S1. NMR data of $[\text{C}_8\text{mim}]\text{PF}_6$

	^1H NMR	^{13}C NMR
	(400MHz, CDCl_3)	(400MHz, CDCl_3)
$[\text{C}_8\text{mim}]\text{PF}_6$	δ (ppm) = 8.56(s), 7.26(s), 7.22(s), 4.14(t), 3.91(s), 1.86(m), 1.27(m), 0.86(t)	δ (ppm) = 135.53, 123.54, 122.04, 49.93, 35.95, 31.51, 29.75, 28.82, 28.70, 25.97, 22.42, 13.89

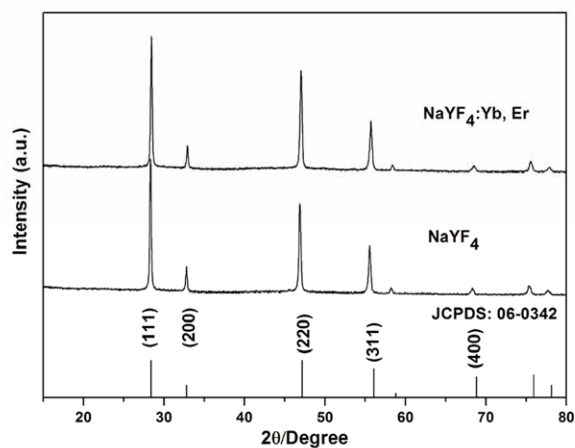


Fig. S1. XRD pattern of the nanocubes of NaYF_4 and $\text{NaYF}_4:18\%\text{Yb}^{3+}, 2\%\text{Er}^{3+}$.

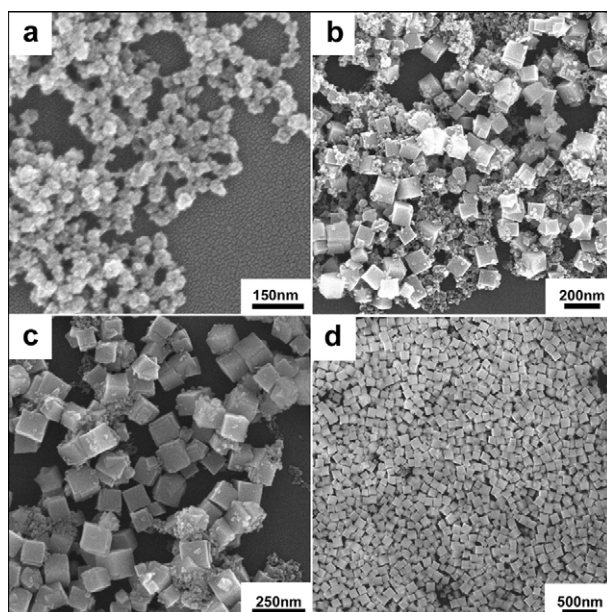


Fig. S2. SEM images of NaYF_4 nanocrystals under different reaction time a) 2h, b) 6h, c) 12h, d) 24h

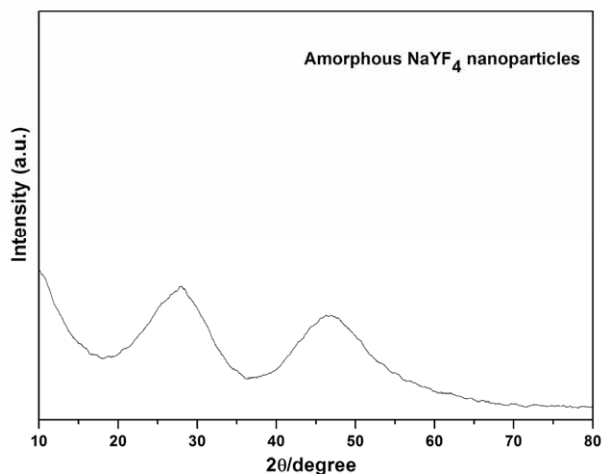


Fig. S3. XRD pattern of the amorphous NaYF₄ nanoparticles.

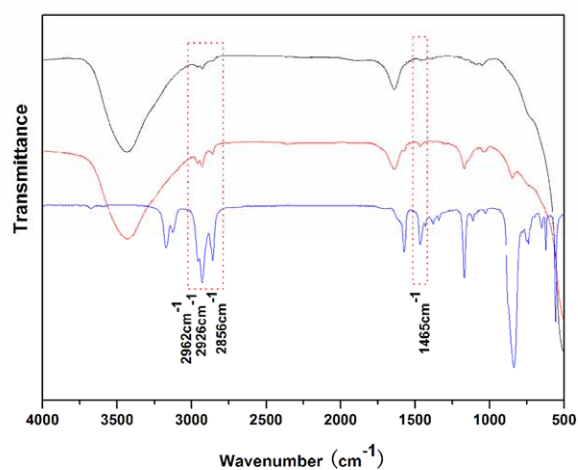


Fig. S4. FTIR spectra of the nanocubes, nanoparticles, and the pure [C₈mim]PF₆.

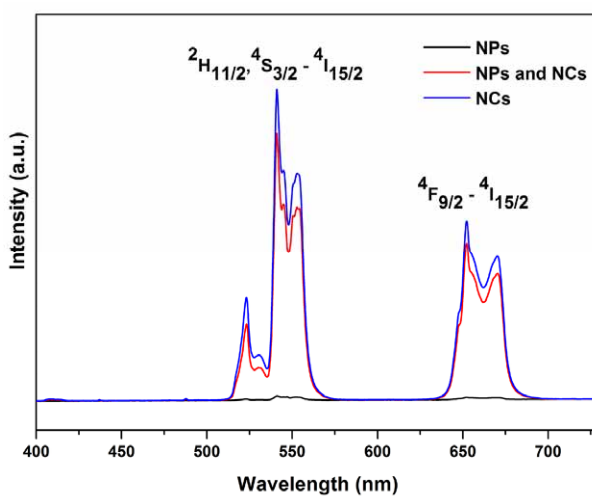


Fig. S5. Upconversion emission spectra of NaYF₄: 18%Yb³⁺, 2% Er³⁺ nanosystems obtained under different reaction time: nanoparticles (2h), nanoparticles and nanocubes (12h), and nanocubes (24h).

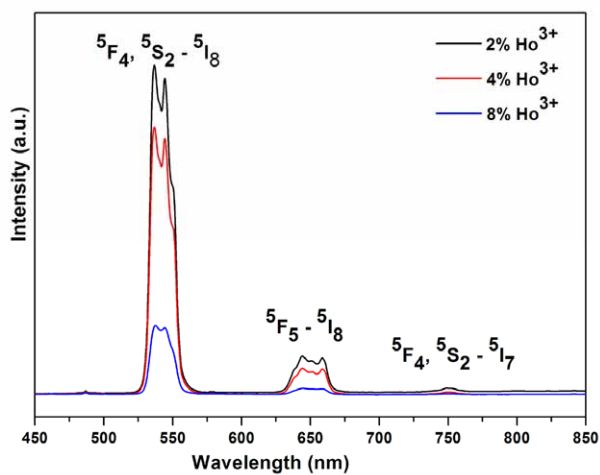


Fig. S6. Upconversion emission spectra of NaYF₄ nanocubes doped with 20%Yb³⁺ and 2, 4, 8% Ho³⁺, respectively.

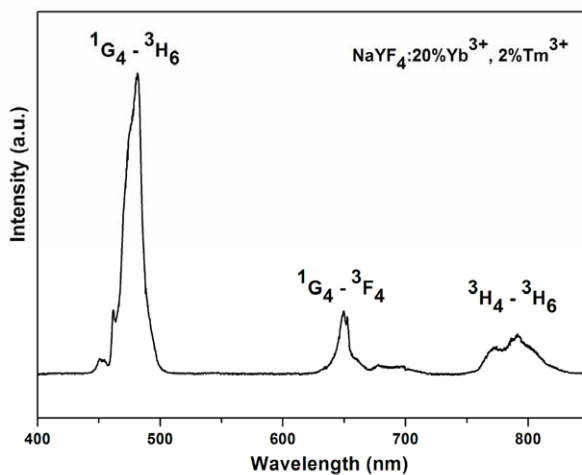


Fig. S7. Upconversion emission spectra of NaYF₄ nanocubes doped with 20%Yb³⁺ and 2%Tm³⁺.