Supporting Information for

Tuning the size and upconversion emission of $NaYF_4$: Yb^{3+}/Pr^{3+} nanoparticles through Yb^{3+} doping

Shuwei Hao,[a] Wei Shao ,[a] Hailong Qiu, [a] Yunfei Shang , [a] Rongwei Fan , [c] Xuyun Guo, [d] Lili Zhao, [a,e] Guanying Chen*, [a,b] and Chunhui Yang*[a]

[a] School of Chemical Engineering and Technology, Harbin Institute of Technology, 150001 Harbin, People's Republic of China.

[b] Institute for Lasers, Photonics and Biophotonics, Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA.

[c] National Key Laboratory of Tunable Lasers, Institute of Optical-Electronics, Harbin Institute of Technology, 150001 Harbin, People's Republic of China

[d] Department of Chemistry, the Hong Kong University of Scienece and Technology, Clear water Bay, Hong Kong SPA.

[e]Harbin Huigong Technology Co., Ltd.

E-mails: guanying@buffalo.edu

yangchh@hit.edu.cn

Experimental Section

Materials

All chemicals were of analytical grade and used without further purification. $YCl_3 \cdot 6H_2O$ (99.99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $PrCl_3 \cdot 6H_2O$ (99.99%) were supplied by Beijing Founde Star Science and Technology Co., Ltd China. NaOH (98%), NH_4F (98%), 1-octadecene (ODE, 90%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich.

Synthesis of $NaYF_4$: Yb^{3+}/Pr^{3+} nanoparticles: $NaYF_4$: Yb^{3+}/Pr^{3+} nanoparticles codoped with 0.5 mol% Pr^{3+} and 10, 30, 50 and 70 mol% Yb^{3+} were synthesized using a solvothermal method adapted from our recent work. A typical procedure is as follows: a 100 mL three-necked flask containing 6 mL oleic acid (OA) and 15 mL 1-octadecene (ODE) were added given amounts of $YCl_3 \cdot 6H_2O$ (x mmol), $YbCl_3 \cdot 6H_2O$ ((0.995- x) mmol) and $PrCl_3 \cdot 6H_2O$ (0.005 mmol). The mixture was heated to 150 ℃ to form a pellucid solution and remove residual water and oxygen, and then cooled down to room temperature. 10 mL of methanol solution containing NaOH (2.5 mmol) and NH_4F (4 mmol) was slowly dropped into the flask and stirred for 30 min to ensure that all fluoride was completely consumed. Then the solution was heated to 70-80℃ for evaporating methanol completely from the reaction mixture. Subsequently, the solution was heated to 300℃ at a rate of about 18 °C/min, and then maintained for 1 h under argon atmosphere. After cooling down to room temperature, the resulting products were precipitated by ethanol and collected by centrifugation at 5000 rpm for 5 min. The precipitate was then purified with ethanol three times, and finally dispersed in cyclohexane for further uses.

Characterization

X-ray Diffraction. The powder X-Ray diffraction (XRD) pattern was carried out on a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Kα source (λ=0.15418 nm). The 2θ angle of the XRD spectra was recorded at a scanning rate of 5 °/min from 20° to 80°.

Transmission Electron Microscopy. The morphology and size of the resulting nanoparticles were investigated by means of transmission electron microscope (TEM, Tecnai G2 Spirit Twin 12) operating at 80 kV. High resolution transmission electron microscopic (HRTEM) images were obtained on the microscope of Spirit Twin Tecnai G2 D339 operating at 300 kV. One drop of diluted colloidal $NaYF_4$ solution dispersed in cyclohexane was allowed to be dried on the surface of the carbon-coated copper grid.

Upconversion Spectra. Upconversion spectra were recorded using a lens-coupled monochromator (Zolix Instruments Co. Ltd., Beijing) with a slit width defining spectral resolution of 2 nm. The emissions were excited at 980 nm using a fiber-coupled laser diode (Hi-Tech Optoelectronics Co. Ltd., Beijing). All measurements were performed at room temperature, preserving the same geometry for the upconversion luminescence recording. Photographic images of colloidal nanocrystals $NaYF_4$: Yb^{3+}/Pr^{3+} were taken by a digital camera (Canon Power Shot SX100 IS) without adding any filter.

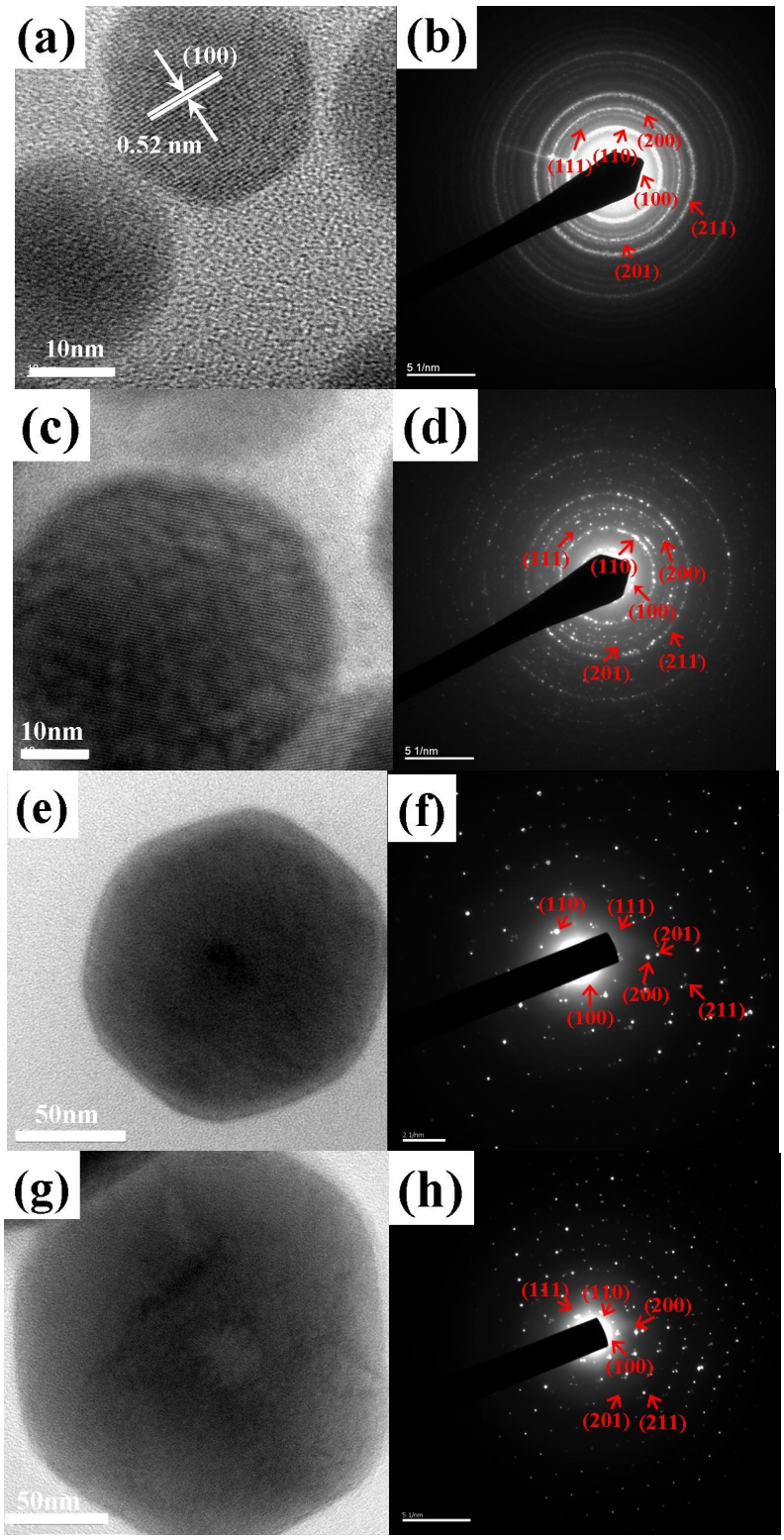

Fig. S1 HRTEM images of $NaYF_4$: Yb^{3+}/Pr^{3+} nanocrystals doped with (a) 10%, (c) 30%, (e) 50% and (g) 70%Yb^{3+} ions concentrations, respectively. Selected area electron diffraction pattern of (b) $NaYF_4$:10%Yb^{3+}/0.5%Pr^{3+}, (d) $NaYF_4$:30%Yb^{3+}/0.5%Pr^{3+}, (f) $NaYF_4$:50%Yb^{3+}/0.5%$Pr^{3+}$and (h) $NaYF_4$:70%Yb^{3+}/0.5%Pr^{3+} nanoparticles, respectively.

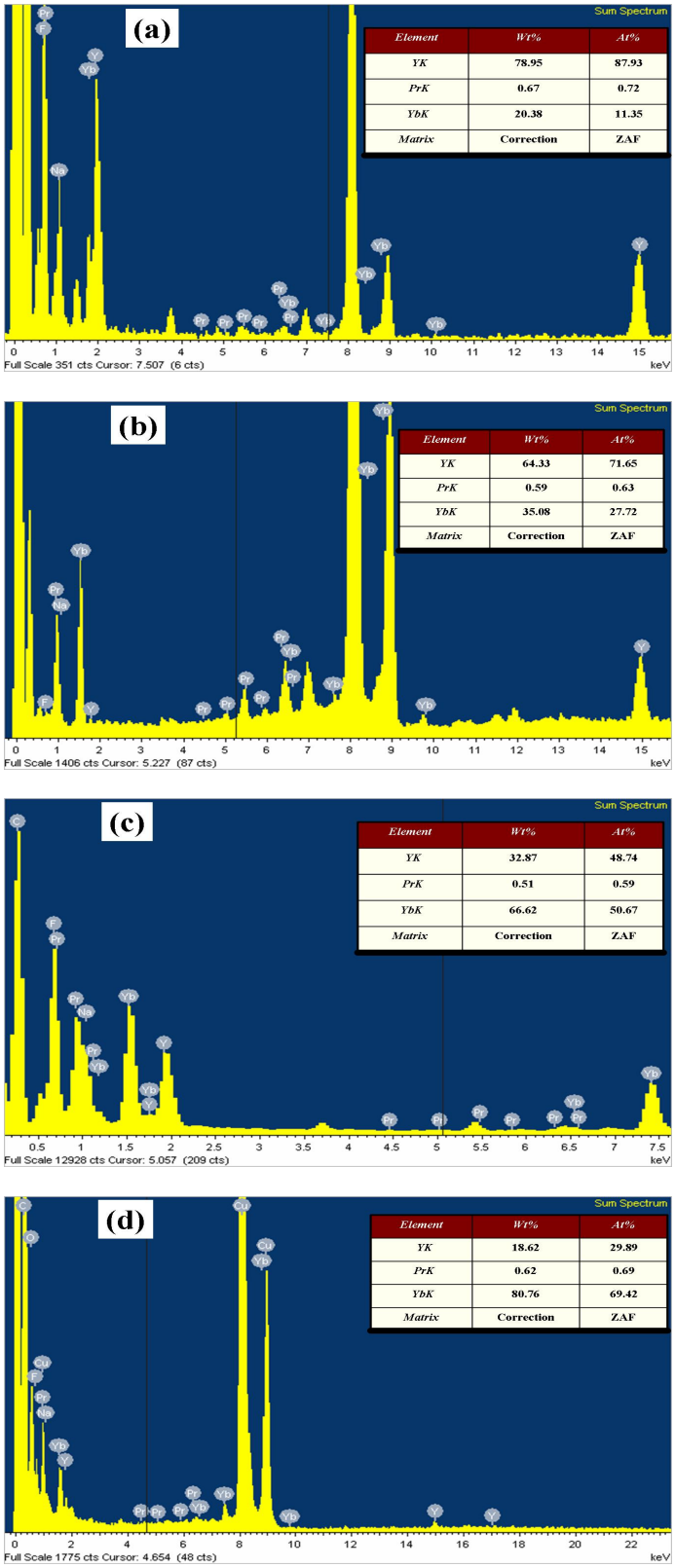

Fig. S2. The energy dispersive x-ray analysis (EDAX) of the 10, 30, 50, 70 mol% Yb^{3+} doped $NaYF_4$ nanocrystals. As one can see, the results here in Figure S2(a)-(d) give clear evidence that the evolution of size in Fig. 1 (a)-(d) indeed is induced by the doping of Yb^{3+} ions. Quantitatively, the practical percentage of catonic content of Yb^{3+} ions (conunted on cations displayed in Figure S2) was calculated to be about 11.35, 27.72, 50.67 and 69.42 mol%, which generally is in good agreement with $NaYF_4$ nanoparticles doped with 10, 30, 50, 70 mol% Yb^{3+} ions counted on cationic precursors..

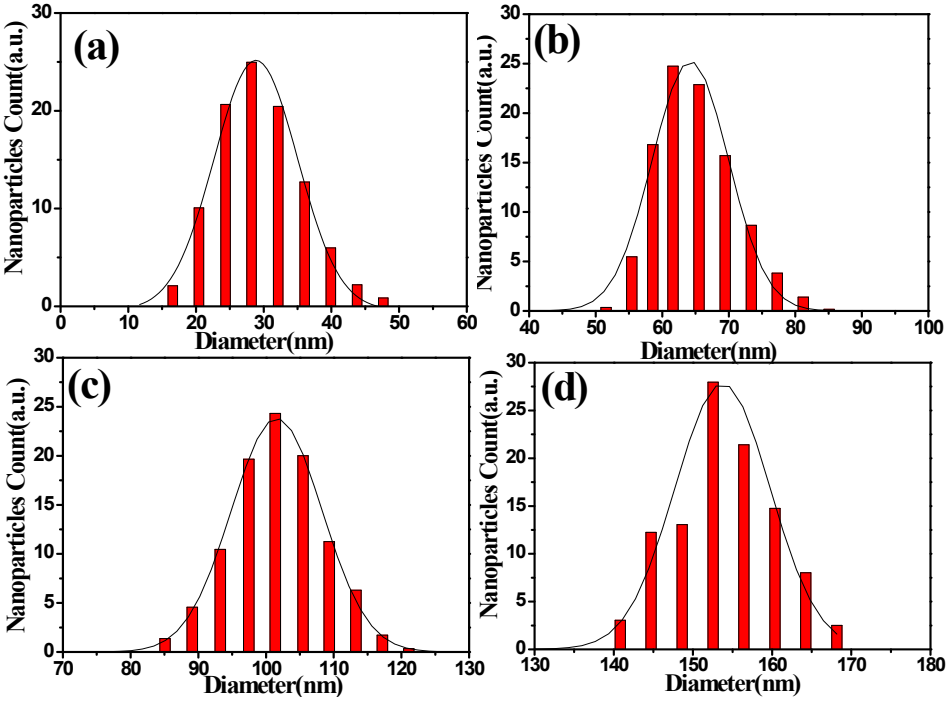

Fig. S3. Size distribution of $NaYF_4$: Yb^{3+}/Pr^{3+} and various concentration of Yb^{3+} ions. (a)10% Yb^{3+}, (b) 30% Yb^{3+}, (c) 50% Yb^{3+}, (d) 70% Yb^{3+}, respectively. These data were obtained from the TEM images of more than 200 $NaYF_4$: Yb^{3+}/Pr^{3+} nanocrystals, which dispalys the increase in the size of the $NaYF_4$:Yb^{3+}/Pr^{3+} nanoparticles with the increment of Yb^{3+} ions doping. The average sizes for nanoparticles with relative content of Yb^{3+} ions of 10, 30, 50 and 70 mol% were found to be about 29, 62, 103 and 153 nm, respectively.

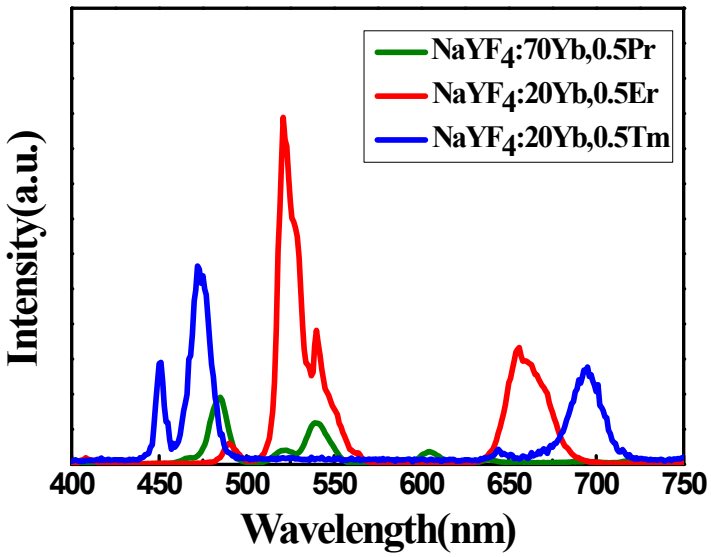

Fig. S4 The upconversion luminescence spectra of hexagonal $NaYF_4$:70%Yb^{3+}/0.5%Pr^{3+} (green line), hexagonal $NaYF_4$:20%Yb^{3+}/0.5%Er^{3+} (red line) and hexagonal $NaYF_4$: 20%Yb^{3+}/0.5%Tm^{3+} (blue line) UCNPs dispersed in hexane (1 wt%). These three samples were excited by a 980 nm laser diode (500 mW).