Electronic Supplementary Information

Active-Core/Active-Shell Structure with Enhanced Quantum-cutting Luminescence in Pr-Yb Co-Doped Monodisperse Nanoparticles

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Experimental Section

Materials

All chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout. $LnCl_3 \cdot 6H_2O$ (Ln=Gd, Pr, Yb, Y), NaOH, NH_4F, 1-octadecene (ODE), oleic acid (OA), cyclohexane and ethanol were all supplied by Sinopharm Chemical Reagent Company.

Synthesis of the Pr^{3+}/Yb^{3+}: $NaGdF_4$ core nanoparticles

$YbCl_3 \cdot 6H_2O$ (0.8mmol*x (x=0, 1, 2, 4, 6, 10 mol%)), $PrCl_3 \cdot 6H_2O$ (0.8mmol*0.1 mol%), $GdCl_3 \cdot 6H_2O$ (0.8mmol* (1 – 0.1– x) mol%) were added to a 50 ml flask containing 8ml OA. In order to remove water from the solution, the mixture was heated at 150℃ for 30min. Afterwards, 12ml ODE was added and the mixture were stirred for another 30min to get a clear solution, and then cooled down to room temperature. Then 10ml methanol solution containing 2mmol NaOH and 3mmol NH_4F was slowly added to the flask, and the solution was heated at 50℃ for 30min to remove methanol. Afterwards, the mixture was heated at 150℃ for 10min and then was heated up to 280℃ rapidly. After heating preservation for 90 min, the solution cooled down to room temperature. The products were washed with ethanol several times, precipitated by addition of ethanol, collected by centrifugation, and finally re-dispersed in 6 ml cyclohexane. The whole reaction process was under protection of N_2.

Synthesis of the Pr^{3+}/Yb^{3+}: $NaGdF_4$@Yb^{3+}: $NaYF_4$ core-shell nanoparticles

$YbCl_3 \cdot 6H_2O$ (0.8mmol*x (x=0, 1, 2, 6, 10 mol%) and $YCl_3 \cdot 6H_2O$ (3.2mmol- 0.8mmol*x) were added to a 50ml flask containing 8ml OA. And the mixture was heated at 150 ℃ for 30min to remove water from the solution. Then 12ml ODE was added and the solution was heated for another 30 min at 150 ℃ to receive a clear solution and then cooled down to 70℃. Afterwards, the pre-prepared core nanoparticles in 6ml cyclohexane were added to the above solution and kept at 100℃ for 40min. After the removal of cyclohexane, 16ml methanol containing 4mmol NaOH and 12mmol NH_4F was slowly added and the mixture was heated at 50℃ for 1h. Thereafter, the solution was heated at 150℃ for 10min, and further heated at 280 ℃ for 90min, and finally cooled down to room temperature. The products were washed with ethanol several times,

precipitated by addition of ethanol, collected by centrifugation and finally be baked in 60℃. The whole reaction process was under protection of N_2.

Characterization

X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu-K_α radiation (λ=0.154 nm). The size and shape of the samples were studied using a transmission electron microscope (TEM, JEM-2010). The high-angle annual dark field (HAADF) TEM observations were performed on an FEI aberration-corrected transmission electron microscope (Titan Cubed S-Twin) operated at 200 kV. TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon coated copper grid. Photoluminescence (PL), PL excitation (PLE) spectra and luminescence decay curves in both the visible and near-infrared regions were recorded by an Edinburgh Instruments spectrofluoremeter (FLS920) equipped with both continuous (450W) and pulsed xenon lamps or hydrogen lamps. Using the Hamamatsu PMT detectors (R928 and R5509-72), the visible and near-infrared luminescence signals were detected. All the measurements were carried out at room temperature.

Figure S1-S4

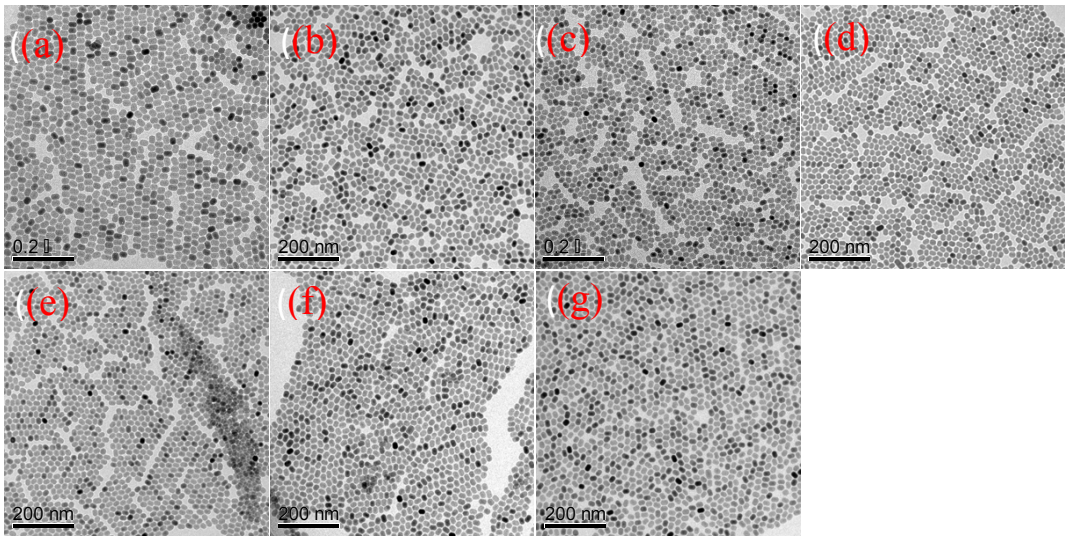

Fig. S1 TEM images of 0.1% Pr^{3+}/x% Yb^{3+}: $NaGdF_4$@ y% Yb^{3+}: $NaYF_4$: (a) x=0, y=0; (b) x=1, y=0; (c) x=2, y=0; (d) x=4, y=0; (e) x=6, y=0; (f) x=4, y=1; (g) x=4, y=2.

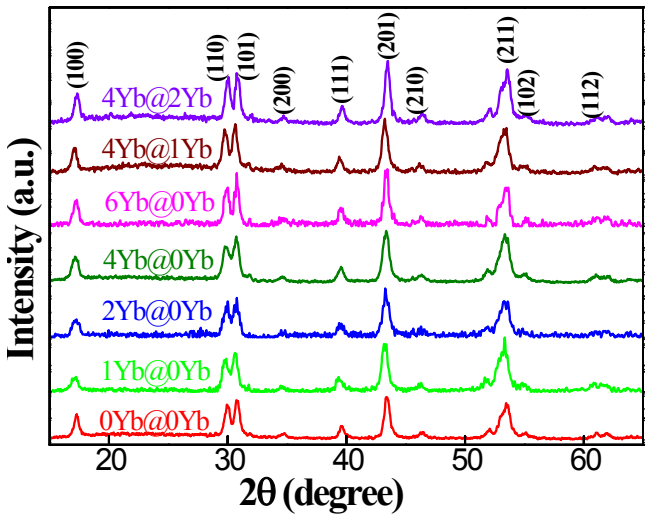

Fig. S2 XRD patterns of 0.1% Pr^{3+}/x% Yb^{3+}: $NaGdF_4$@ y% Yb^{3+}: $NaYF_4$: (a) x=0, y=0; (b) x=1, y=0; (c) x=2, y=0; (d) x=4, y=0; (e) x=6, y=0; (f) x=4, y=1; (g) x=4, y=2., showing that the prepared products are pure hexagonal phase (JCPDS 27—0699).

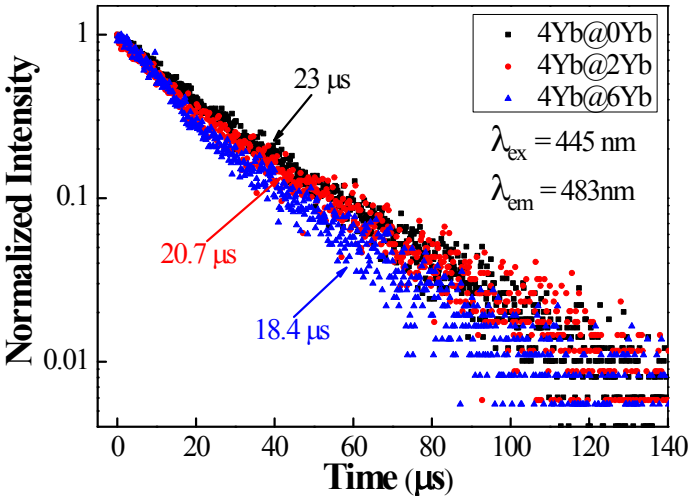

Figure S3. Normalized decay curves of $^3P_0$ level in the 0.1Pr^{3+}/4Yb^{3+}: $NaGdF_4$@xYb^{3+}: $NaYF_4$ (x=0, 2, 6 mol%) samples under excitation at 445 nm.

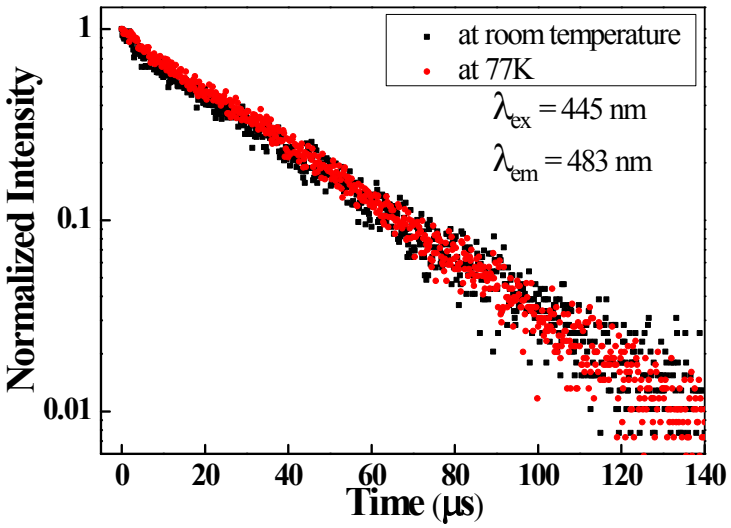

Figure S4. Normalized decay curves of Pr^{3+}: $^3P_0 \rightarrow {}^3H_4$ transition in the 0.1Pr^{3+}: $NaGdF_4$@$NaYF_4$ sample under 445 nm excitation, measured at 77K and room temperature respectively.