Electronic Supplementary Material (ESI) for RSC Advances.


# Multi-color luminescence and anticounterfeiting application of upconversion nanoparticle

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## Materials

The rare-earth oxide Ln2O3 (99.99%) (Ln = Y, Tm Yb, Er, Nd) was obtained from Sinopharm Chemical Reagent Co., Ltd (China). Cyclohexane, methanol, sodium hydroxide, absolute ethanol and ammonium fluoride were purchased from Shanghai Reagent Chemicals Co., Ltd (China). Oleic acid (OA, 90%) and 1-octadecene (ODE, > 90%) were obtained from Alfa Aesar.

## synthesis

### synthesis of the $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ UCNPs

$\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ UCNPs were synthesized according to the previously report methods [27-28]. Firstly, 12 mL of OA along with 30 mL of ODE were added into a 100 mL necked flask which

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containing 2 mmol $Ln_2Cl_3 \cdot 6H_2O$ (Ln= 73mol%Y, 1mol% Tm, 1mol% Er, 5mol% Nd, 20mol% Yb). Then the mixture was heated to 150℃ and held at that temperature until the solution was clear. Later, a 10 mL of methanol solution containing NaOH (5 mmol) and $NH_2F$ (5 mmol) was added dropwise before it cooled down to room-temperature (RT). After 20 min attiring, the mixture solution was heated to 100℃ and held for 1 h to evaporate the methanol under the $N_2$ atmosphere. At last, the mixture solution was heated to 310℃ quickly and held at this temperature for 1 h. The nanoparticles were collected by adding ethanol and separated by centrifugation after the flask cooled down to room-temperature. The obtained OA- capped $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ UCNPs were dissolved in cyclohexane for further experiments.

**synthesis of the $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ @$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ UCNPs**

For monodispersed core/shell OA-capped $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$@$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ UCNPs were synthesized via the similar procedures described above. Typically, 2 mmol $Ln_2Cl_3 \cdot 6H_2O$ (Ln= 79.5mol%Y, 0.5mol% Tm, 20mol% Yb) as precursor were added into a 100 mL necked flask with 12 mL of OA along with 30 mL of ODE. Then the mixture solution was heated to 150℃ and held at that temperature until the solution was clear. After cooling down the solution to RT, the as-prepared OA-capped $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ cyclohexane

solution was dropwised into above solution before the injection of the NaOH and $NH_2F$ methanol solution and the cyclohexane was removed under the $N_2$ atmosphere. After following methanol removal, core/shell UCNPs were nucleated and grown, washing and centrifugation, the core/shell structured OA-capped $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$@$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ UCNPs were obtained and dissolved into cyclohexane for further experiments.

**synthesis of the $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ @$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ @$NaYF_4$ UCNPs**

Monodispersed core/shell/shell OA-capped $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ @$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ @$NaYF_4$ UCNPs were synthesized via similar procedures to those described above. Typically, $YCl_3 \cdot 6H_2O$, which replaced rare-earth $Ln_2Cl_3 \cdot 6H_2O$ as precursor solution, was synthesized. Then, the as-prepared core/shell-structured OA-capped of $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ @$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ cyclohexane solution was dropwise added to the above solution before the injection of the NaOH and $NH_2F$ methanol solution, and the cyclohexane was removed under a $N_2$ atmosphere. After methanol removal, core/shell/shell UCNPs were nucleated, grown, washed and centrifuged, and the core/shell/shell-structured OA-capped $\beta$-$NaYF_4$: $Yb^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Nd^{3+}$ @$NaYF_4$: $Yb^{3+}$, $Tm^{3+}$ @$NaYF_4$ UCNPs were obtained and dissolved into cyclohexane for further experiments.

The $\beta$-$NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 0.5% $Tm^{3+}$ @ $NaYF_4$ UCNPs, $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 30% $Yb^{3+}$, 0.5% $Tm^{3+}$ @ $NaYF_4$ UCNPs and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 1% $Tm^{3+}$ @ $NaYF_4$ UCNPs were synthesized via the similar procedures described above.

**Characterization**

The samples were checked via a Shimadzu XRD-6000 diffractometer with the CuKα1 radiation (λ=0.15406 nm). The scanning rate was 2° ·$min^{-1}$ in the 2$\theta$ range from 10° to 70°. The samples' size and morphology were observed by a transmission electron microscope (TEM, JEM-2100, JOEL, Japan), which was operated at an acceleration voltage of 200KV. The UC emission spectra were obtained from a FS5 luminescence spectrometer (Edinburgh, UK), which equipped with 980 nm laser and 1550 nm laser (BWT DS2-11312-105, China).

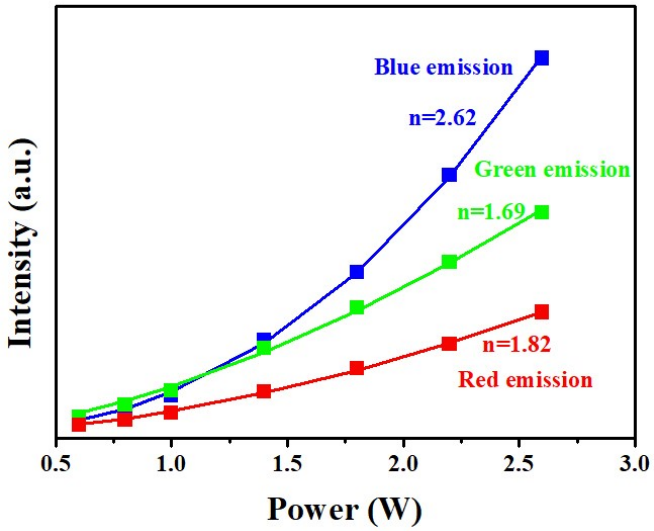


**Figure S1** The mechanism of the photon excitation process based on laser power vs emission intensity under 980 nm excitation.

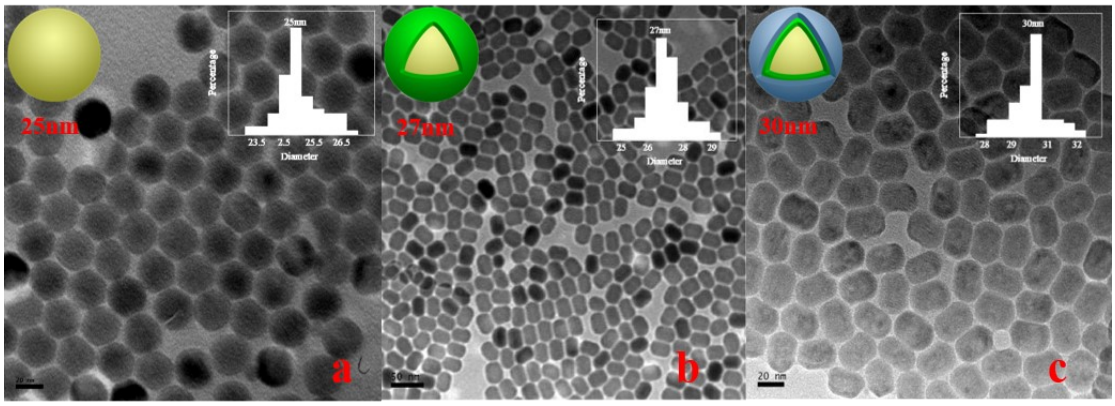


**Figure S2** The TEM images of $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ (a), $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 0.5% $Tm^{3+}$ (b) and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 0.5% $Tm^{3+}$ @ $NaYF_4$ (c)

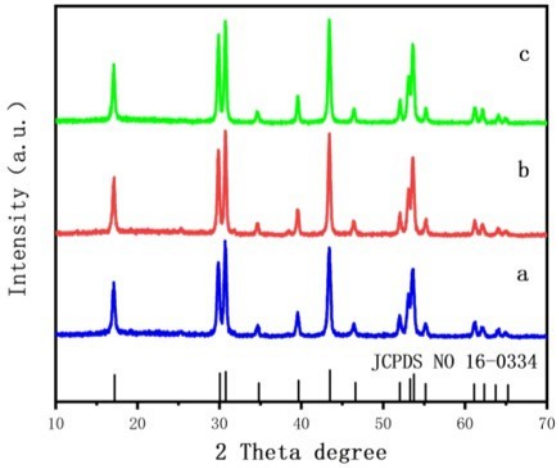


**Figure S3** XRD patterns of $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ (a), $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 0.5% $Tm^{3+}$ (b) and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 0.5% $Tm^{3+}$ @ $NaYF_4$ (c).

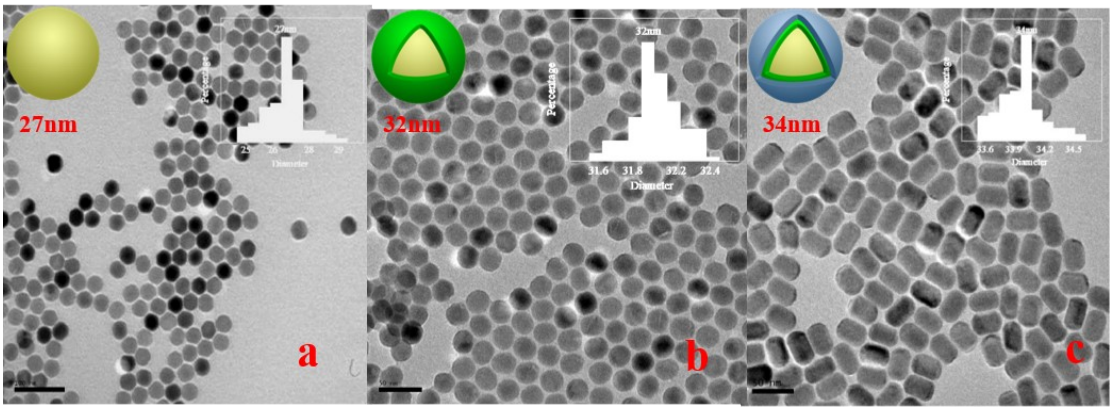


**Figure S4** The TEM images of $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ (a), $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 30% $Yb^{3+}$, 0.5% $Tm^{3+}$ (b) and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 30% $Yb^{3+}$, 0.5% $Tm^{3+}$ @ $NaYF_4$ (c)

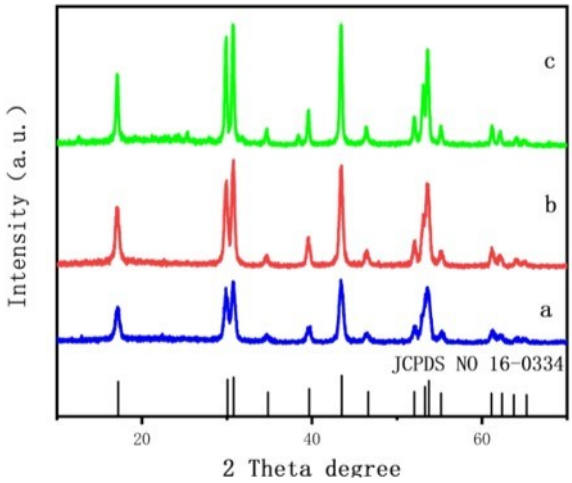


**Figure S5** XRD patterns of $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ (a), $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 30% $Yb^{3+}$, 0.5% $Tm^{3+}$ (b) and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 0.9% $Tm^{3+}$, 5% $Nd^{3+}$ @ $NaYF_4$: 30% $Yb^{3+}$, 0.5% $Tm^{3+}$ @ $NaYF_4$ (c)

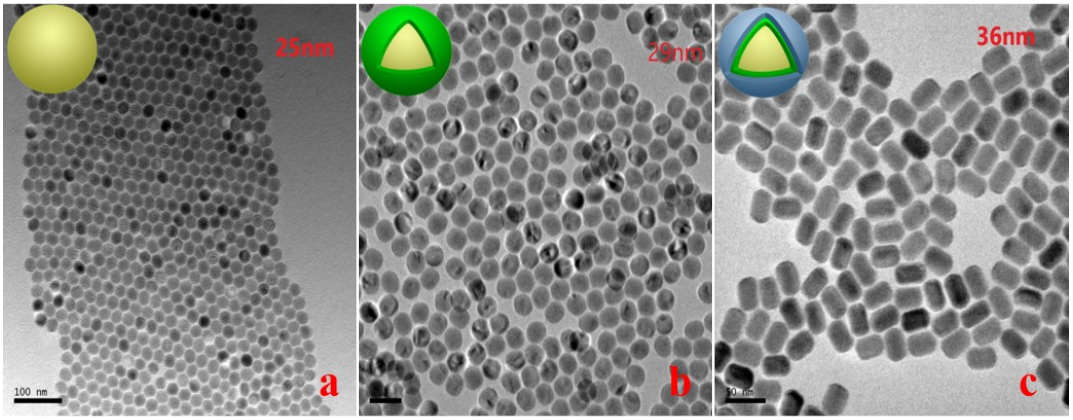


**Figure S6** The TEM images of $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ (a), $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 1% $Tm^{3+}$ (b) and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 1% $Tm^{3+}$ @ $NaYF_4$, (c)

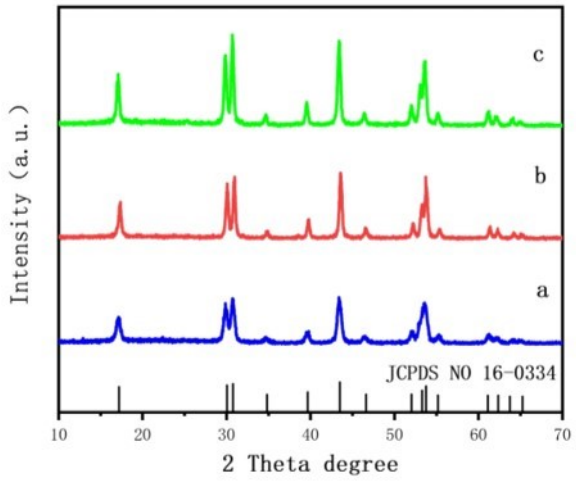


**Figure S7** XRD patterns of $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ (a), $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 1% $Tm^{3+}$ (b) and $NaYF_4$:30% $Yb^{3+}$, 0.1% $Er^{3+}$, 1% $Tm^{3+}$, 10% $Nd^{3+}$ @ $NaYF_4$: 20% $Yb^{3+}$, 1% $Tm^{3+}$ @ $NaYF_4$ (c).