Electronic Supporting Information

Strong Upconverting and Downshifting Emission of Mn²⁺ ions in Yb,Tm:NaYF₄@NaLuF₄/Mn:CsPbCl₃ core/shell Heterostructure towards Dual-model Anti-counterfeiting

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Experimental section

Materials: Y_2O_3, Lu_2O_3, Yb_2O_3, and Tm_2O_3 are the same purity (99.99%), Cs_2CO_3 (99.9%), $PbCl_2$ (99.99%), $MnCl_2·H_2O$, 2-ME (98%), TOPO (95%) and TEOS (99%) was purchased from Aladdin, China. The NaOH (AR), NH4F (AR), methanol (AR), ethanol (AR), oleic acid (OA, AR), and 1-octadecene (ODE, AR) was purchased from Sinopharm Chemical Reagent Co.,Ltd, China. The rare earth chlorides required for the synthesis of UCNPs are obtained by reacting rare earth oxides with hydrochloric acid.

Synthesis of nanomaterial

Synthesis of NaYF₄:Yb/Tm@NaLuF₄ UCNPs:

The NaYF₄:Yb/Tm nonaparticles were synthesized by using a procedure to that of NaYF₄ cores[27]. Typically, 0.795ml aqueous solution of YCl_3 (1M) , 0.2ml $YbCl_3$ (1M), 0.005ml $TmCl_3$ (1M) was mixed with 7 ml OA and 15 ml ODE under persistently stirring for 10 minutes in a 50 ml three-necked flask. The mixture was gradually heated to 160℃, and kept at 160℃ for 10 minutes, the solution became golden, and then cooled down to room temperature. Afterward, 10 ml methanol solution containing 2.5mmol NaOH and 4mmol NH₄F was added to the three-necked flask, and the solution turned turbid yellow. Next, the mixture was heated to 80℃ and held for 20 minutes to ensure complete evaporation of cyclohexane and methanol, and then rapidly increased to 280℃ and maintained for 1 h under stirring violently(1100r/min). At last, the mixture was cooled to room temperature. The whole experiment was carried out in a nitrogen environment. Samples were collected by centrifugation, that is, the mixture was washed with ethanol/cyclohexane mixture three times to remove the excess residue, and finally the samples were dispersed in 4 ml cyclohexane.

The preparation method of NaYF₄:Yb/Tm@NaLuF₄ core/shell NPs is similar to the NaYF₄:Yb/Tm NPs, except that the content of aqueous solution is 1ml $LuCl_3$ (1M) and the pre-prepared cores NPs in 4 ml cyclohexane was added to the solution and kept at room temperature for 10 min before 10 ml methanol solution. The last samples were dispersed in 4 ml cyclohexane.

Synthesis of CsPbCl₃ :Mn perovskite QDs:

$PbCl_2$ (0.105g), $MnCl_2$ (0.0768g) OAm (1 mL), OA (1 mL),and ODE (10 mL) were added to a 50-mL 3-neck round-bottom flask and were stirred and refilled with N2 followed by heating the solution to 120 °C for 1 hour. The solution was then increased to 180 °C and maintained for 10 minutes. Then the required temperature increased, the Cs-oleate (0.8 mL) was swiftly injected and after 30 s the solution was cooled with an ice bath. The QDs were precipitated with acetone and the centrifuged followed by dissolution in 4 ml toluene.

Synthesis of UCNPs/QDs@SiO₂ composites:

First, 1ml TOPO, 0.5 ml 2-ME and 0.5 ml UCNPs were added into 4 ml of the CsPbCl₃:Mn QDs solution in a beaker, then the mixture solution was stirred for 30 min under room temperature. Then 0.3 ml TEOS was added without sealing and stirred for another 30 min in the room temperature. Finally, the obtained composites solution was centrifuged for 5 min at 9000 rpm and the precipitate were redispersion in 4ml cyclohexane.

Preparement of anti-counterfeiting patterns:

The anti-counterfeiting patterns were prepared by screen printing method, which low-cost and easy to operate. First, 0.5 ml above redispersion cyclohexane solution of composites, which the concentration of UCNPs and PQDs are 0.125 and 0.47 mmol/ml, respectively., was added to 2 ml of glycerol and sufficiently sonicated stirring to form a homogeneous mixed solution. Next, dropped the mixed solution onto the screen with the pattern model, and then gently paint the pattern on paper or banknotes. Finally, the pattern was photographed with a SLR

camera under the irradiation of 365 nm xenon lamp and 980 nm laser (power intensity of 23 mw cm^{-2}) excitation.

Characterization

XRD analysis was used to show the crystalline characteristics of the prepared UCNPs, QDs and composites nanoparticles using a diffractometer (DX-2700). The morphology is characterized by transmission electron microscopy (TEM) (JEOLJEM-2100., JP). UV-vis–NIR absorption spectra of the sample (solid powder) were measured with a UV-Vis-NIR spectrophotometer (Varian Cary 5000). The UCL spectra and UCL decay curves are measured via the FLS980E spectrometer (Edinburgh Instruments Ltd., UK). The DSL spectra and DSL decay curves are measured via the FLS1000E spectrometer (Edinburgh Instruments Ltd., UK).
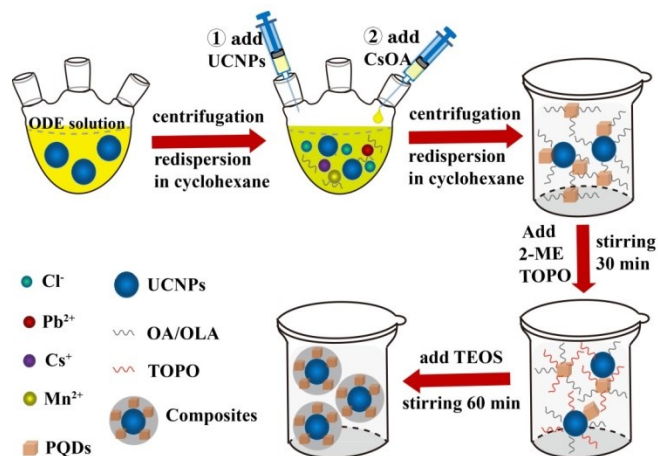
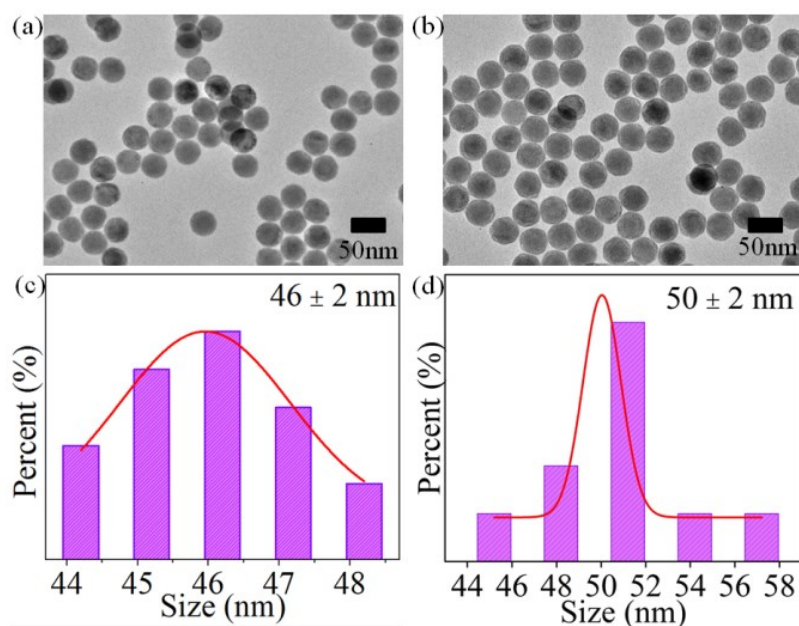Scheme S1. Schematic illustration of the preparation process of UCNPs/PQDs@SiO$_2$

Figure S1. TEM images of (a) Yb,Tm:NaYF4 and (b)Yb,Tm:NaYF4@NaLuF4 UCNPs; (c) and (d) are the corresponding particle size statistics.

The diameter of Yb,Tm:NaYF4 and Yb,Tm:NaYF4@NaLuF4 nanoparticles are about 46 nm and 50 nm, respectively. Therefore, the thickness of NaLuF4 shell is about 2 nm. It is well known that nonradiative resonance energy transfer is effective in a range of less than 10 nm.
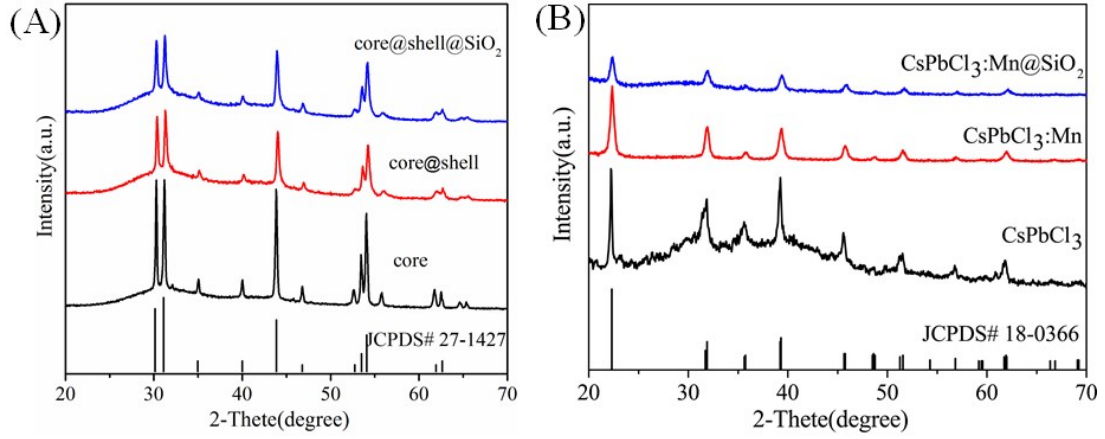
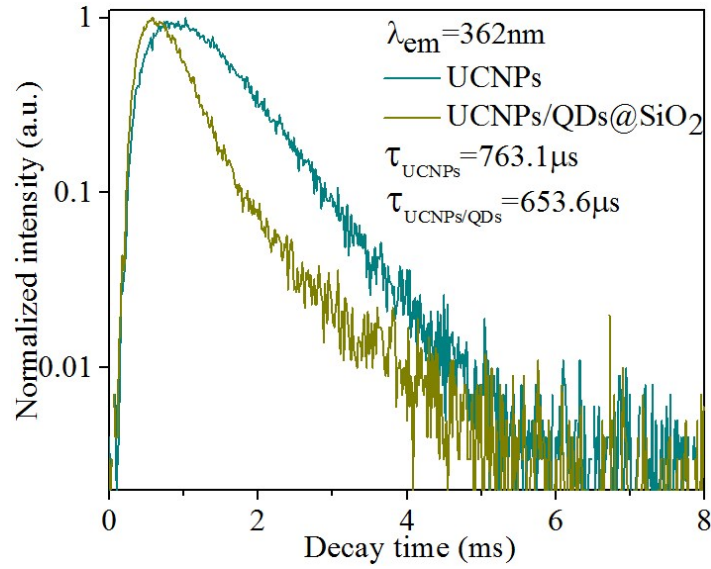Figure S2. (a) and (b) are XRD patterns of UCNPs and PQDs, respectively.

Figure S3. Fluorescence decay dynamics of UCNPs and UCNPs/QDs at 362 nm under the excitation of 980 nm pulse laser.

The lifetimes the composites were calculated with the equation :

$$I(t) = I_0 + A_{1\mathrm{exp}}(-t/\tau_1) + A_{2\mathrm{exp}}(-t/\tau_2) \quad (1)$$

Where I_t and I_0 represent the luminescence intensity at t and 0 μs, τ_1 and τ_2 are the short and long lifetime, A_1 and A_2 are the decay amplitudes of the component, respectively. The average lifetimes of the composites were

calculated by the formula:
$$\tau = \frac{A_1\tau_1{}^2 + A_2\tau_2{}^2}{A_1\tau_1 + A_2\tau_2} .$$

In view of the lifetime of donor were only affected by the FRET, while photon emission reabsorption will not. We define FRER efficiency (η) can be estimated based on the corresponding decay lifetimes:

$$\eta = 1 - \frac{\tau_a}{\tau_p} \quad (1)$$

where τ_a and τ_p are the luminescence lifetimes of the donor in the absence and presence of the acceptor, respectively. The FRET efficiency of UCNPs/PQDs@SiO$_2$ is 14% by taking the lifetimes value into the above formula.

Table s1. The atomic ratio of the composites from EDS .

Element	Weight %	Atomic %
O K	8.54	21.36
F K	5.30	11.16
Na K	2.40	4.18
Si K	19.1	33.67
Y L	7.32	3.29
Pb M	19.37	3.74
Cl K	13.14	14.83
Cs L	13.57	4.09
Mn K	2.15	1.62
Tm L	0.68	0.16
Yb L	0.73	0.17
Lu L	7.68	1.73