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Discovery of non-reversible thermally enhanced upconversion luminescence behavior in rare-earth doped nanoparticles

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Experimental section

Materials

$Gd(OOCCH_3)_3 \cdot 4H_2O$ (99.99%), $Yb(OOCCH_3)_3 \cdot xH_2O$ (99.9%), $Tm(OOCCH_3)_3 \cdot 4H_2O$ (99.9%) were purchased from Alfa Aesar. NaOH (97%) was purchased from Aladdin. NH_4F (≥99.99%), 1-octadecene (ODE, 90%), and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. All materials were used as-received without further purification.

Characterization

Transmission electron microscopy (TEM) measurements were carried out on a JEM-2100F (Japan) system operating at a voltage of 200 kV. Fourier-transform infrared (FTIR) spectra of the oleate acid (OA)-coated UCNPs and hydroxyl (OH)-coated UCNPs were measured on a Bruker Tensor FTIR spectrometer using the KBr method. The spectra in transmission mode were recorded in a wavenumber range of 4000-1000 cm^{-1}. The absorption spectra were measured on UV-VIS spectrophotometer (UV-2600). Upconversion emission spectra at both room temperature and high temperatures were recorded with an FLS-920 spectrometer (Edinburgh Instruments). A continuous-wave 980 nm diode laser was employed as the excitation source. The decay curves were measured on the same spectrometer with a plus modulator controlled 980 nm diode laser. The lifetime values were determined by fitting the decay curves with a monoexponential decay function. The decay curves were measured on the same spectrometer using a mechanically chopped 980 nm diode laser as the excitation source. The following equation was used to fit the decay curves:

$$I = I_0 + A_1 e^{-t/\tau_1} \tag{1}$$

where A_1 is a pre-exponential factor and τ_1 is the lifetime.

Synthesis of OA coated nanoparticles

In a typical process, 16 mL of aqueous solution of $Re(OOCCH_3)_3$ (0.2 M, Re = Gd, Yb, Tm) was added to a 250 mL three-neck flask containing 24 mL of OA and 36 mL of ODE. The mixture was heated to 150 °C and dwelled for 30 min under vigorous magnetic stirring and then cooled down to 50 °C naturally. Afterward, a mixture of NaOH (0.24 g) and NH_4F (0.293 g) dissolved in methanol(13 ml) was added and stirred for 60 min. The resultant solution was heated at 90 °C for 20 min to remove methanol. Afterwards, the solution was heated to 290 °C and kept for 1.5 h under nitrogen. After that the solution was cooled down to room temperature, the obtained UCNPs were precipitated by addition of ethanol, collected by centrifugation, washed with ethanol for several times and dried in vacuum for optical characterizations.

Synthesis of OH coated nanoparticles

OA-coated core-shell nanoparticles were added into a water solution with a pH value of 4. Then the mixture was placed in an ultrasonic bath and sonicated for 120 min. When the reaction was finished the aqueous solution was mixed with diethyl ether to remove the oleic acid by extraction with diethyl ether three times and the water layers were combined and re-extracted with diethyl ether. The nanoparticles in the water dispersible fraction were collected by centrifugation after precipitation with acetone. Afterwards, the product was dispersed in acetone again, and the final products were obtained by centrifugation. The resultant UCNPs were dried for characterizations.

Preparation of the nanoparticle/PDMS composite materials.

For OA-coated samples, in a typical procedure, 160 μL of cyclohexane solution (OH coated UCNPs are dispersed in ethyl alcohol) containing lanthanide-doped $NaGdF_4$ UCNPs (0.16 mmol), 0.8 g of SYLGARD silicone elastomer 184 and 40 μL of curing agent (Dow Corning) were thoroughly blended in a glass container. Then, the mixture was heated to 80 ^{o}C within 1 h in an oven and allowed for aging overnight. The composite materials with different types of nanoparticles can easily be cut into slices. We put the slice into a mixture of SYLGARD silicone elastomer (2.4 g) and curing agent (120 μL) in a glass container and quickly move the container into an oven that had been heated to 80 ^{o}C and allowed for aging overnight. Finally, the nanoparticle/PDMS composite sample was obtained.

Additional discussions

Sintering of particles: The fusion of small NPs to form larger NPs during sintering can be explained by Kelvin equation shown below:[1]

$$ln\frac{P_r}{P\infty}=\frac{2M\sigma}{\rho RT}\cdot\frac{1}{r} \tag{2}$$

where P_r is the actual vapour pressure, $P\infty$ is the saturated vapor pressure, M is the molecular weight, σ is the surface tension, ρ is the density, R is the universal gas constant, r is the radius of the particle and T is the temperature. Accordingly, particles with a smaller size exhibit a higher vapor pressure such that they are dissolved and contributed to the growth of larger particles, as can be inferred by the sharpening of the diffraction peaks for samples after heated to 565 K.

Interplay of energy transfer, radiative transition and nonradiative transition: As we know, the lifetime of the excited state of luminescence center (τ) can be related with the radiative transition rate (W_R), the non-radiative transition rate (W_{NR}) and the energy transfer rate (W_{ET}) by:[2]

$$\tau = 1/(W_R+W_{NR}+W_{ET}) \tag{3}$$

For the 475 nm emission, the decrease of lifetime with the rise of sample temperature is not unusual as the non-radiative decay rate (W_{NR}) is enhanced at elevated temperatures due to stronger coupling to lattice phonons. The accelerated decay from the $^1G_4$ level thus favors the population of lower levels and therefore increase the lifetime of the $^2F_{5/2}$ levels possibly by an energy back transfer process from Tm^{3+} to Yb^{3+}.

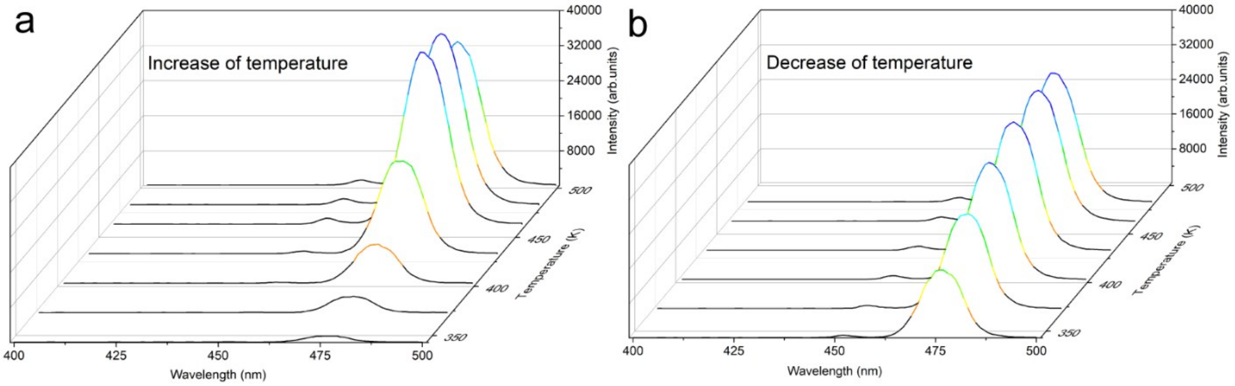


Fig. S1 The stability of upconversion luminescence of the Tm^{3+}:$^1G_4 \rightarrow ^3H_6$ emission for OA-coated samples in a heating-cooling circle (343 K → 500 K → 343 K). The dwelling time at each tempearture (for recording the spectra) is 1 min.

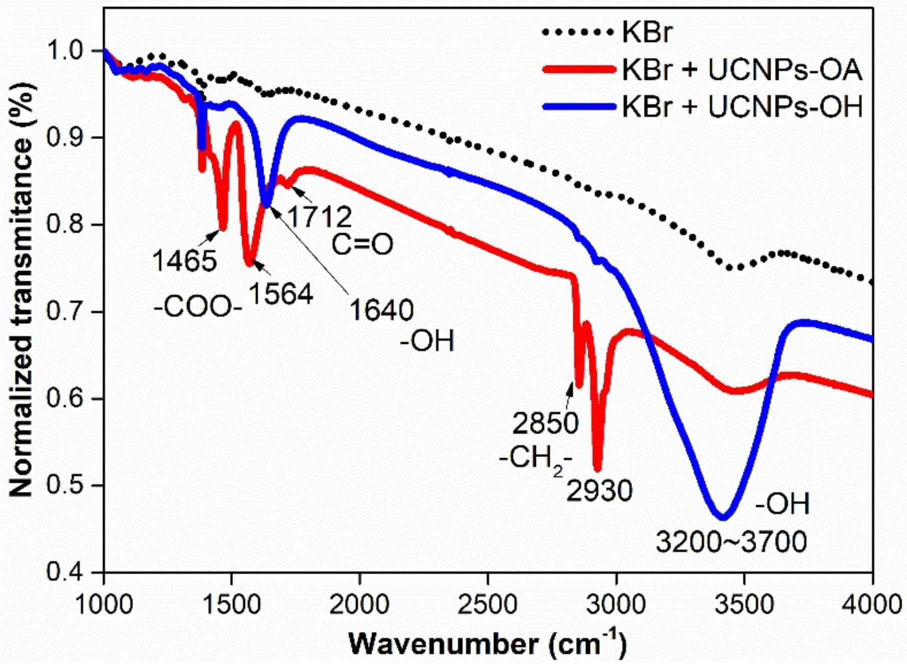
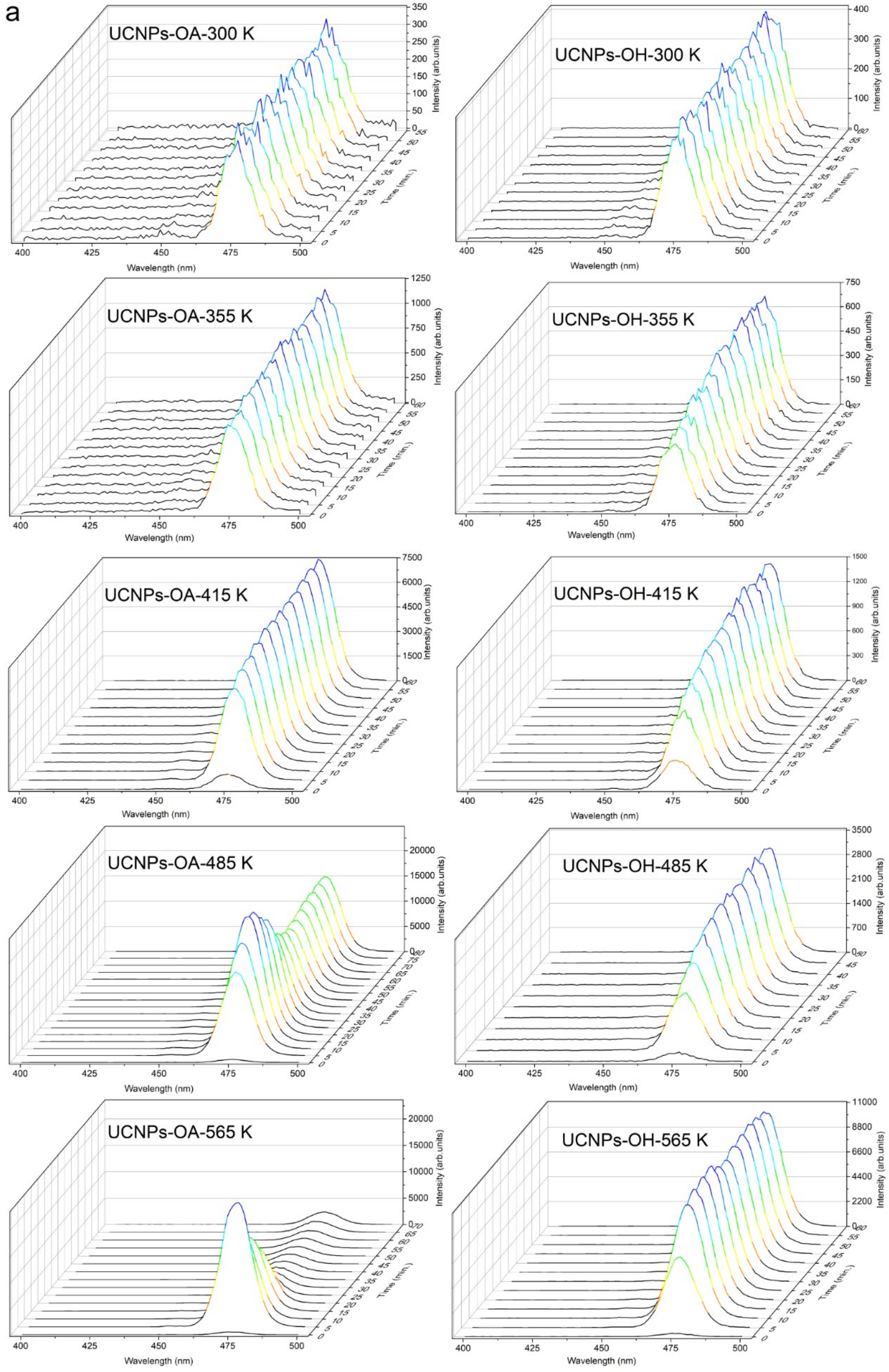


Fig. S2 FTIR spectra of pure KBr (black dots), mixtures of KBr and OA and OH coated nanoparticles (UCNPs).


a
UCNPs-OA-300 K
UCNPs-OH-300 K
UCNPs-OA-355 K
UCNPs-OH-355 K
UCNPs-OA-415 K
UCNPs-OH-415 K
UCNPs-OA-485 K
UCNPs-OH-485 K
UCNPs-OA-565 K
UCNPs-OH-565 K
Wavelength (nm)
Time (min.)
Intensity (arb.units)

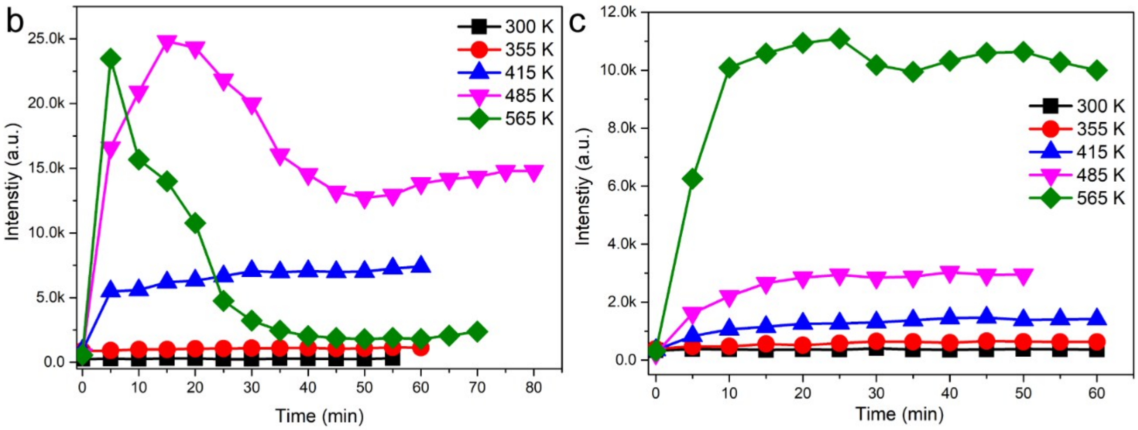


Fig. S3 a) The stability of upconversion luminescence of the Tm^{3+}:$^1G_4 \rightarrow ^3H_6$ emission for OA-coated samples and OH coated samples. b, c)The emission intensity at 475 nm vs. time for b) OA- and c) OH- coated samples recorded from 300 K to 565 K.

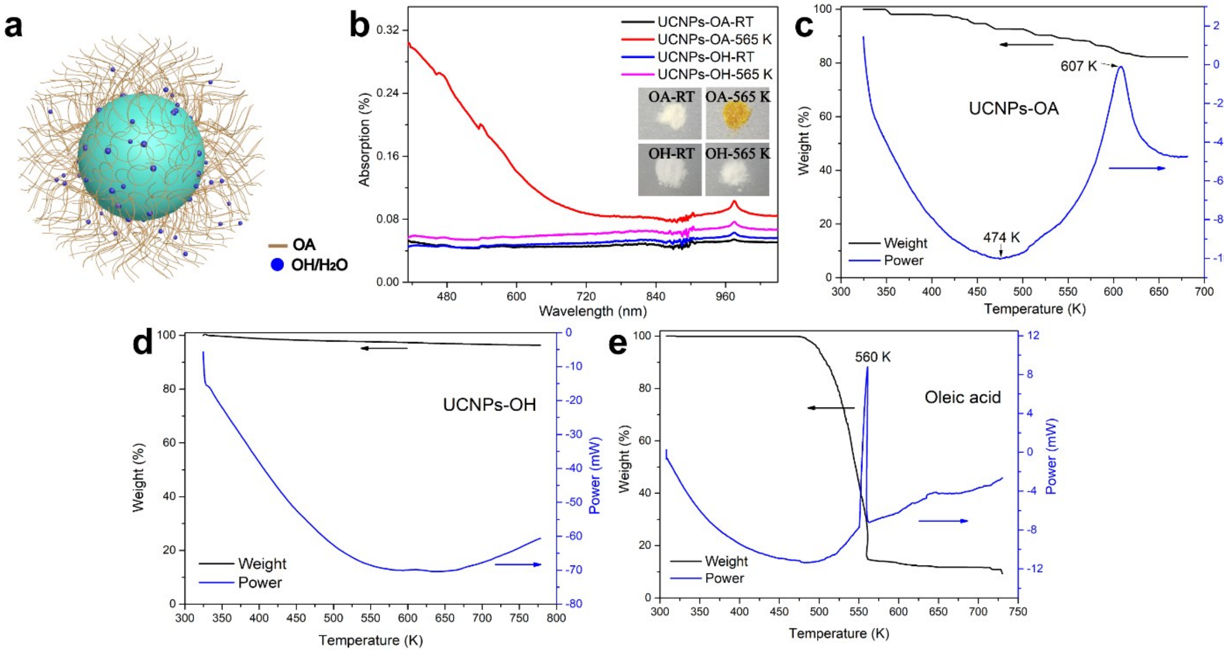


Fig. S4 a) Schematic diagram of a signle NP coated by a thick layer of OA. Water molecules are also trapped by the long alkyl chains of OA. b) Absorption spectra of preliminary OA coated samples (UCNPs-OA-RT) and OH coated samples (UCNPs-OH-RT) and corresponding samples (UCNPs-OA-565K) and (UCNPs-OH-565K) after measurements (being heated at 565 K), optical images are corresponding samples are inserted. c,d) DSC and TG curves of OA coated and OH coated UCNPs. e) DSC and TG curves of pure OA.

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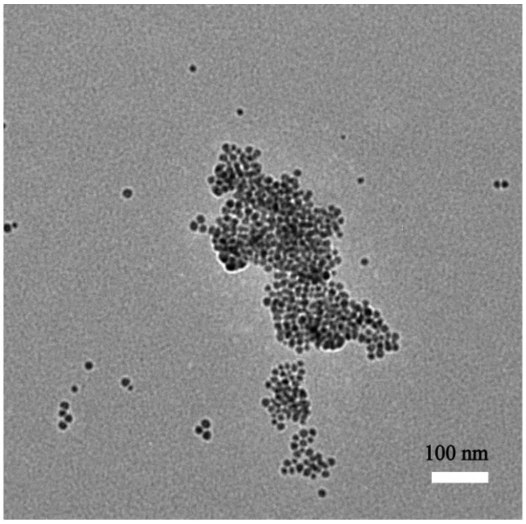

Fig.S5 TEM pictures of OH coated nanoparticles (after acid treatment)

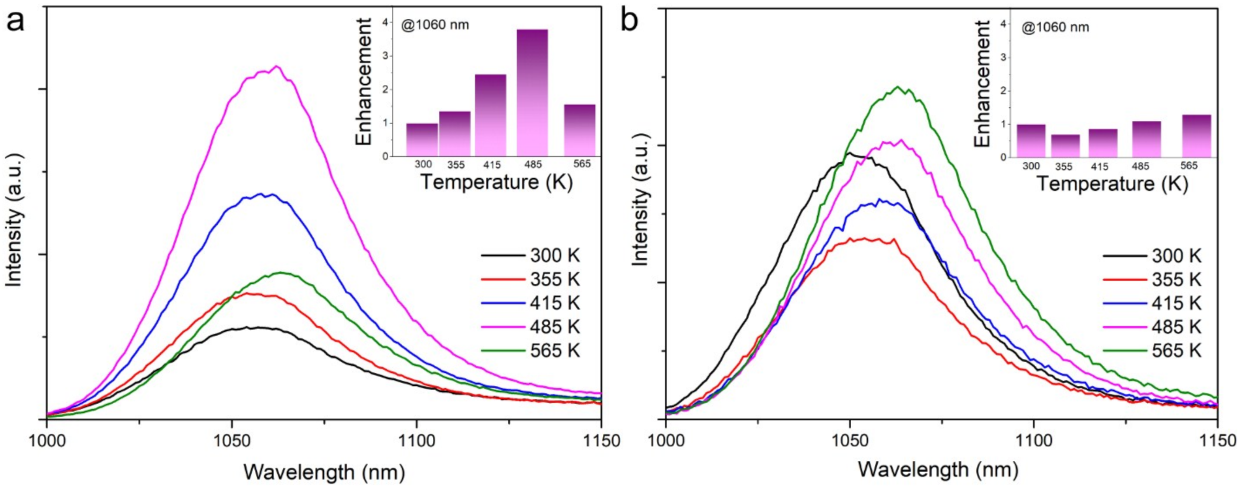

Fig. S6 NIR luminescence of Yb^{3+} at different temperatures of a) OA-coated samples and b) OH-coated samples (inserts are emission enhancement factor at 1060 nm).

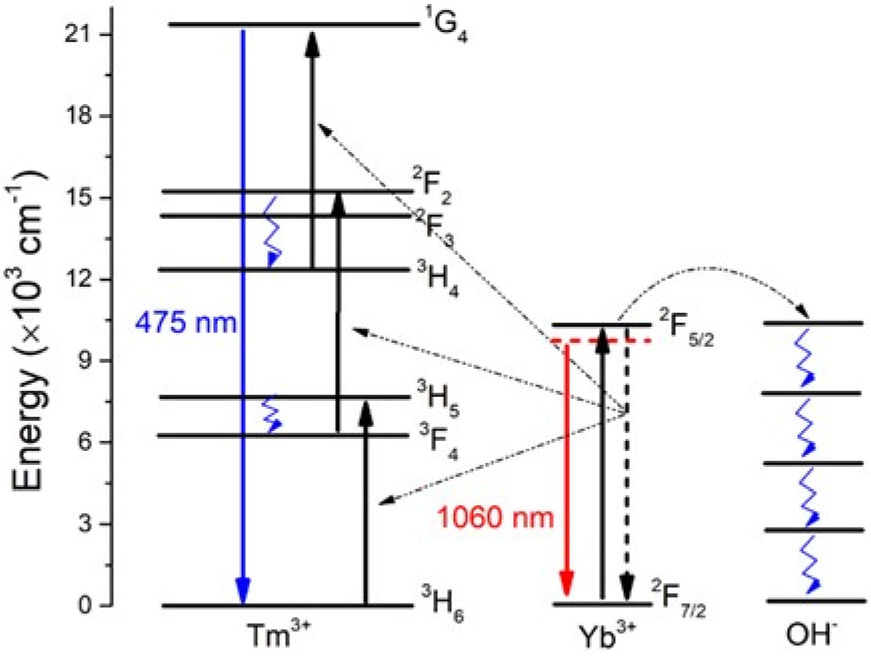

Fig. S7 Schematic energy-level diagram of Tm^{3+}/Yb^{3+} co-doped NaGdF$_4$ nanoparticles and energy transfor process involving surface quenchers in a UCNP.

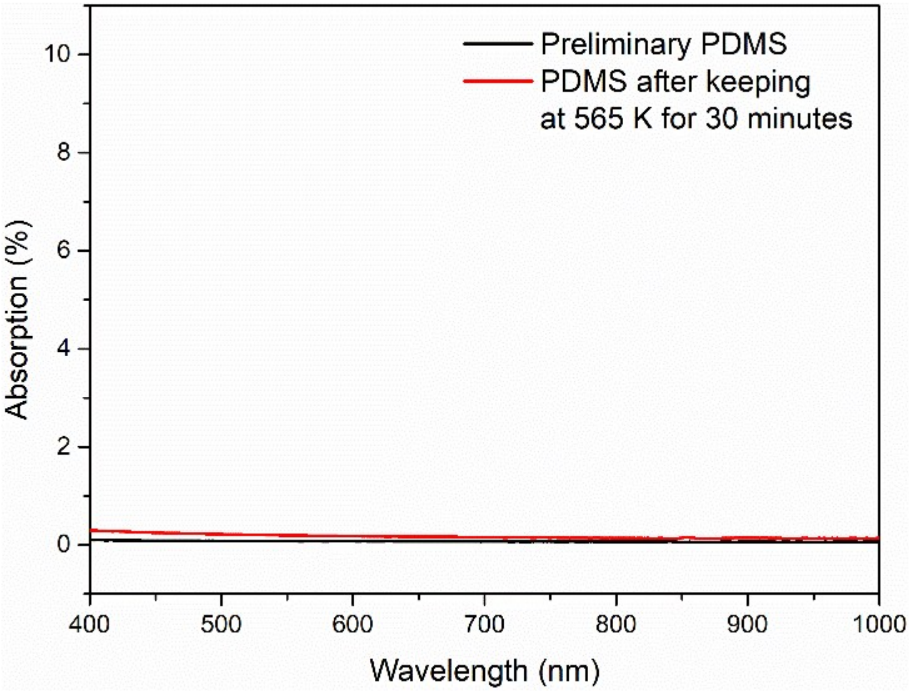

Fig. S8 Absorption spectra of pure PDMS (black line) and PDMS after being kept at 565 K for 30 minutes (red line).

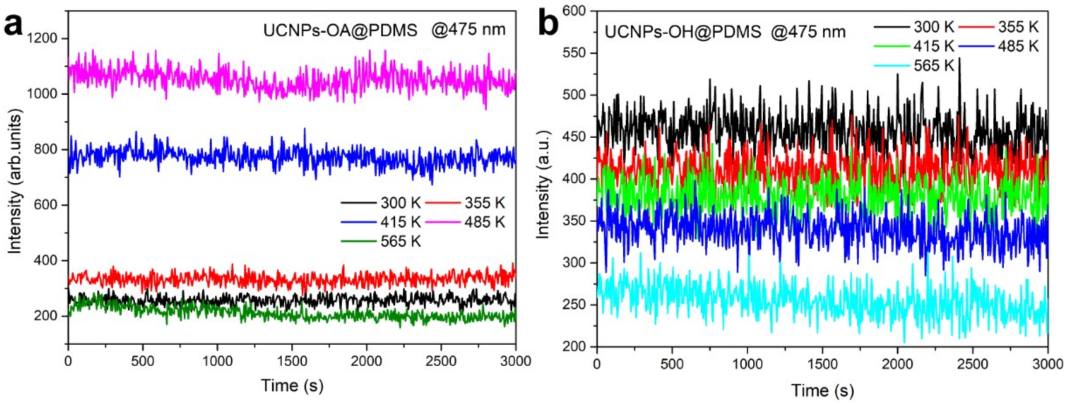

Fig. S9 Emission stability at 475 nm as a function of time from UCNPs coated by a) OA and b) OH that are entirely embedded in PDMS at different temperatures.

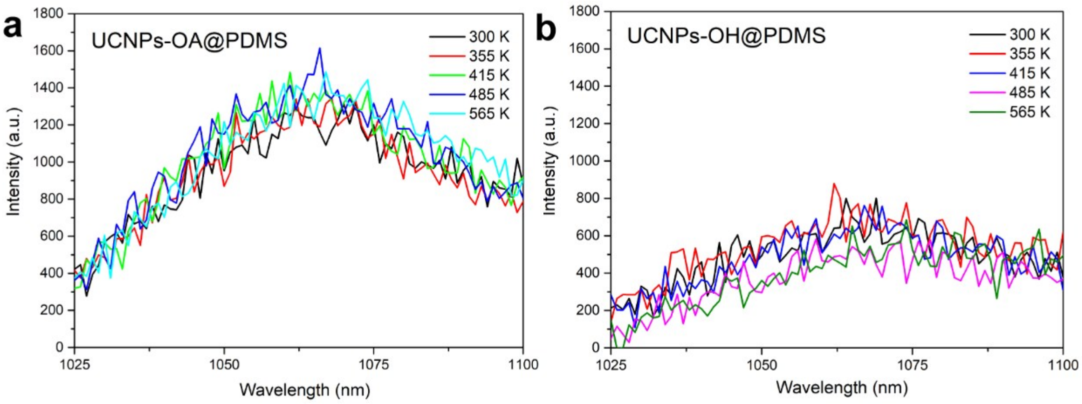

Fig. 10. NIR spectra for UCNPs coated by a) OA and b) OH that are entirely embedded in PDMS recorded at different temperatures. All samples were kept at coresponding temperatures for 30 minutes before measurement.

References

(1) J. R. QU, M. A. HU, J. Z. Chen, *Earth Science - Journal of China University of Geosciences,* 2005, **30**, 195-198.

(2) X. Y. Guo, W. Y. Song, C. F. Chen, W. H. Di and W. P. Qin, *Physical Chemistry Chemical Physics*, 2013, **15**, 14681-14688.