

Electronic Supplementary Material (ESI) for nanoscale.  
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## Supplementary Information (ESI) for

### **Enhanced Energy Transfer in Heterogeneous Nanocrystals for Near Infrared Upconversion Photocurrent Generation**

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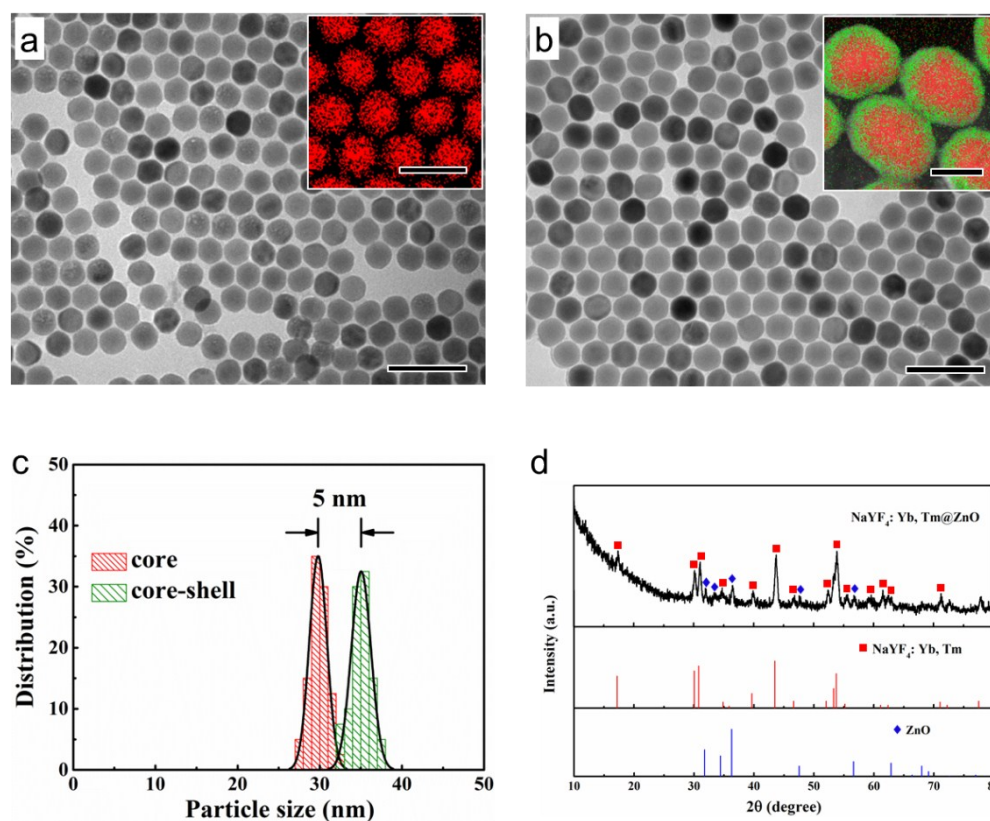
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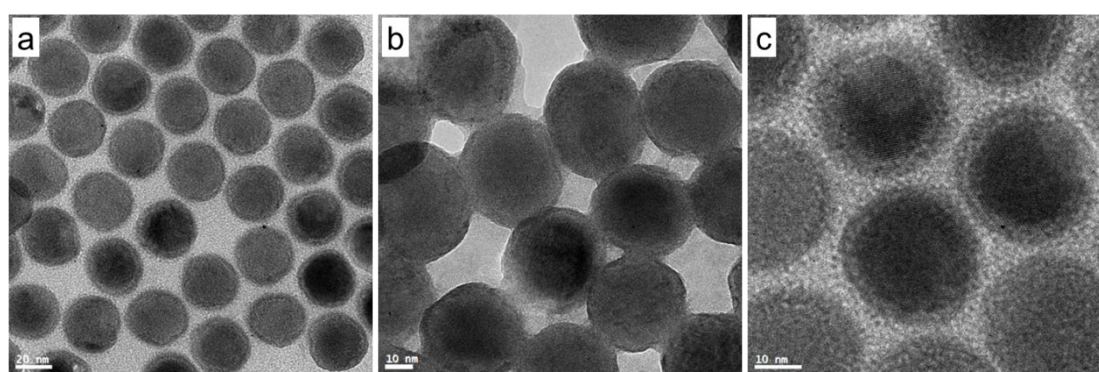
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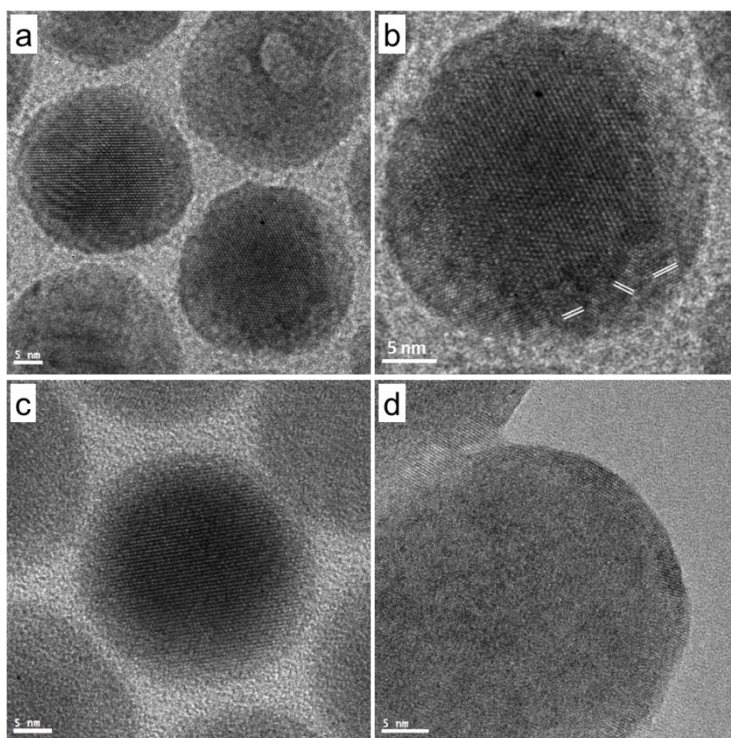
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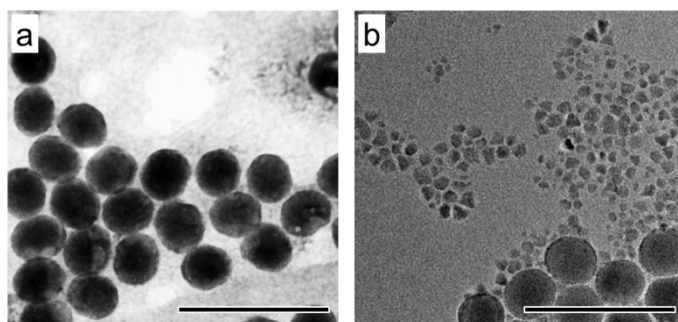
**Fig. S1** (a) and (b) are the typical TEM images of as-prepared NaYF<sub>4</sub>: Yb, Tm and NaYF<sub>4</sub>: Yb, Tm@ZnO nanoparticles, respectively, with the inserts showing the phase mapping results. The colors of the phases are ZnO in green and NaYF<sub>4</sub>: Yb, Tm in red. (c) The corresponding size distributions of nanoparticles shown in (a) and (b). (d) The XRD pattern for NaYF<sub>4</sub>: Yb, Tm@ZnO, and the standard PDF card for NaYF<sub>4</sub>: Yb, Tm and ZnO. The scale bars for (a) and (b) are 100 nm. The scale bars for the inserted images are 50 nm in (a) and 25 nm in (b).



**Fig. S2** TEM images of PCS synthesized at 180 °C (a), and ES synthesized at 210 °C (b) and (c).

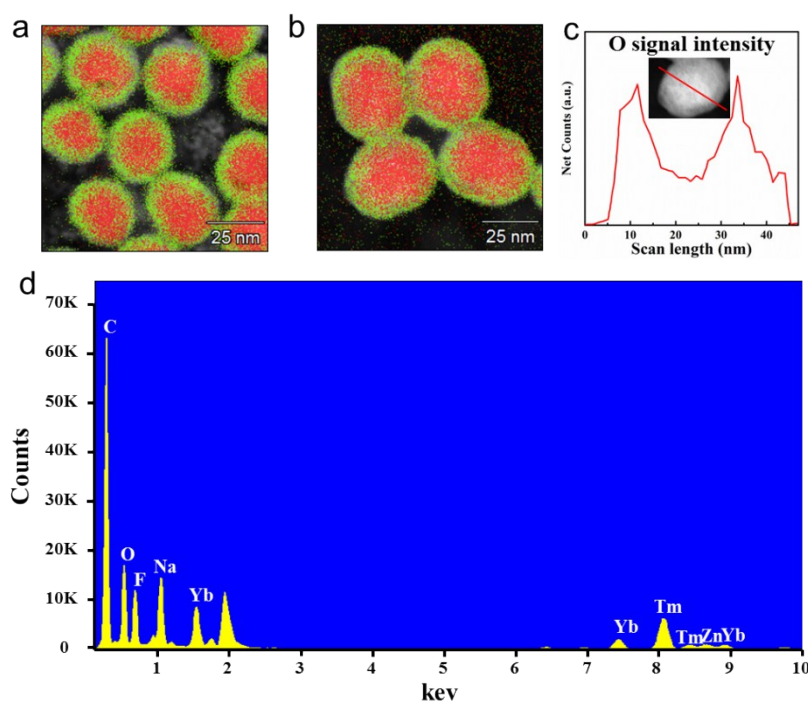


**Fig. S3** High-resolution TEM images of PCS synthesized at 180 °C (a) and (b), and of ES synthesized at 210 °C (c) and (d).

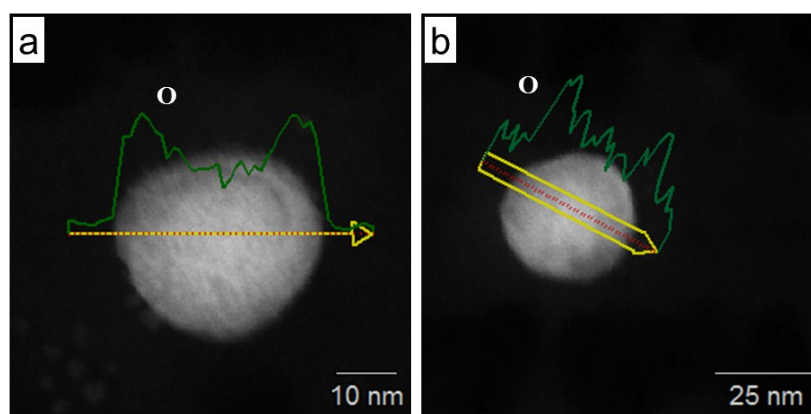


**Fig. S4** TEM images for PCS synthesized at 180 °C (a), and NC synthesized at 240 °C (b).

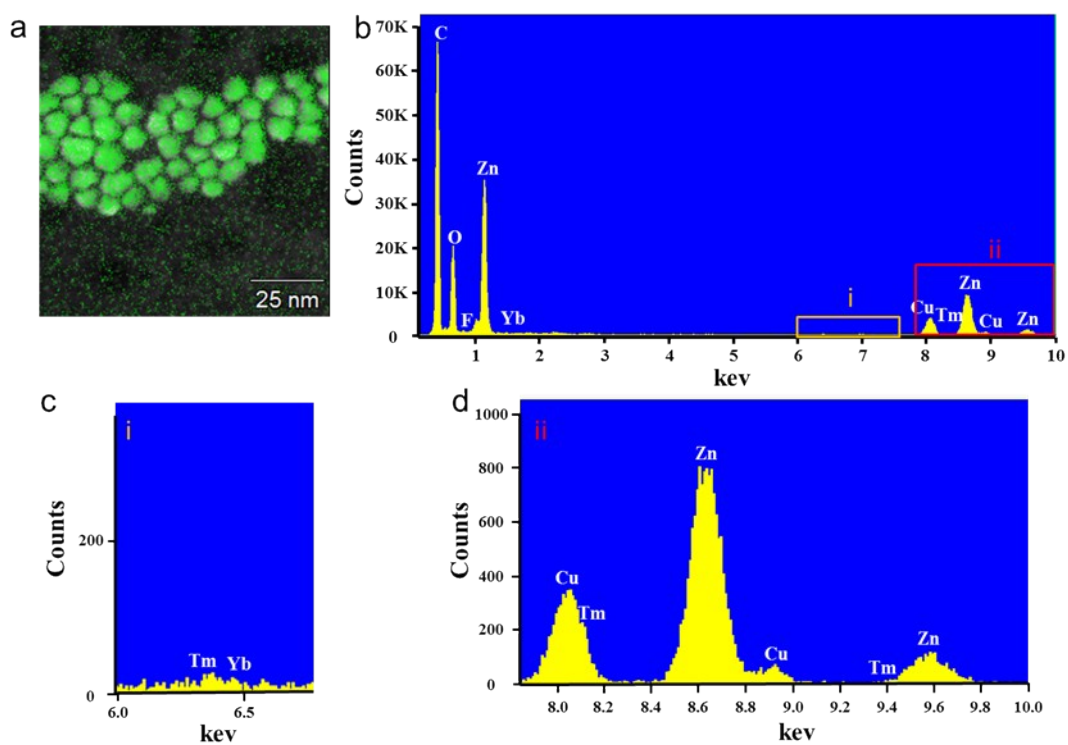
The scale bars are 100 nm.



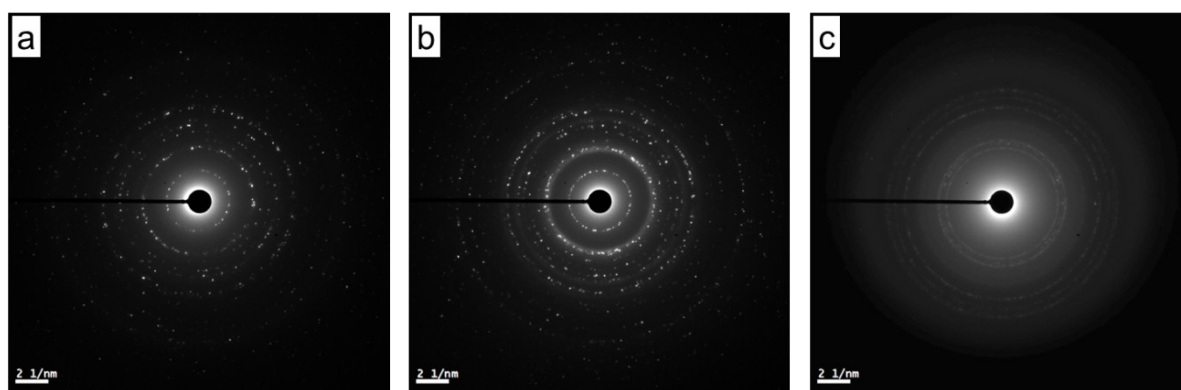
**Fig. S5** (a) and (b) are the phase mapping results for PCS and ES, respectively. The colors of the phases are ZnO in green and NaYF<sub>4</sub>: Yb, Tm in red. (c) EDS line profile of O elemental distribution for ES. (d) EDS spectrum of NaYF<sub>4</sub>: Yb, Tm@ZnO nanoparticles. The core-shell nanoparticles are composed of NaYF<sub>4</sub>: Yb, Tm and ZnO. The shell phase is the ZnO material, and the core phase is the NaYF<sub>4</sub>: Yb, Tm UCNP material.



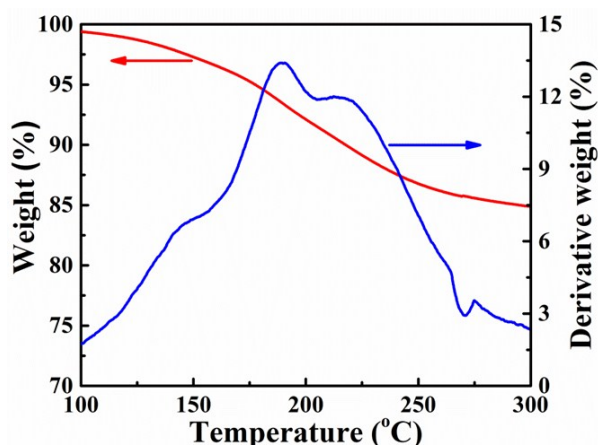
**Fig. S6** EDS line scans of O on different NaYF<sub>4</sub>: Yb, Tm@ZnO nanoparticles.



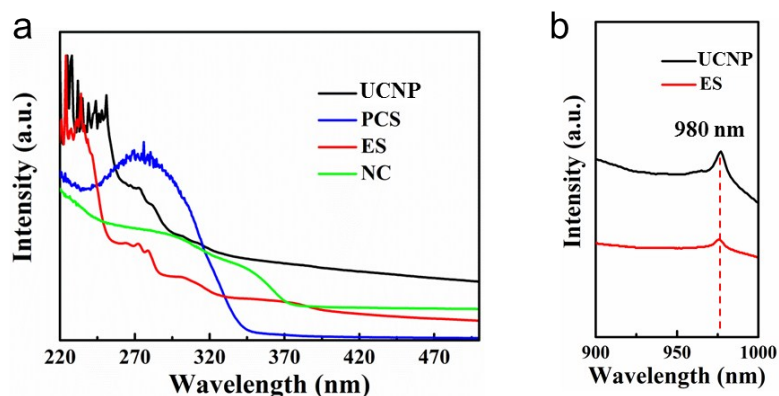
**Fig. S7** Phase mapping image for NC. The color of the phase is ZnO in green. (b) The full EDS spectrum of NC synthesized at 240 °C. (c) and (d) are selected ranges of the EDS spectrum marked in (b).



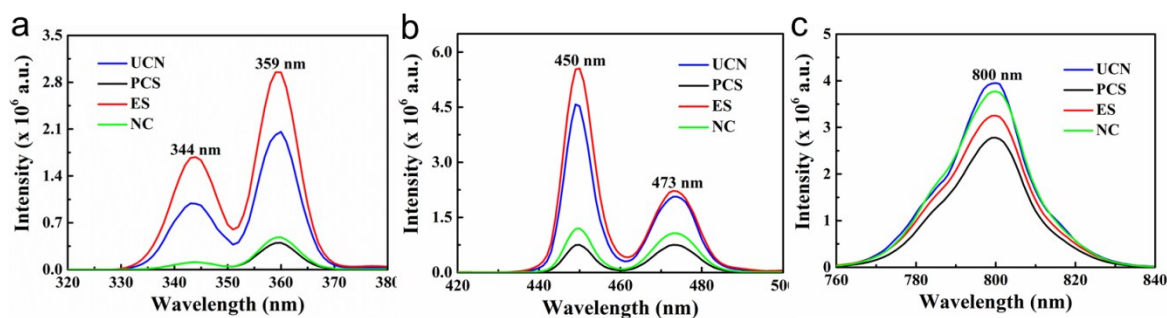
**Fig. S8** SAED images for PCS (a), ES (b) and NC (c).



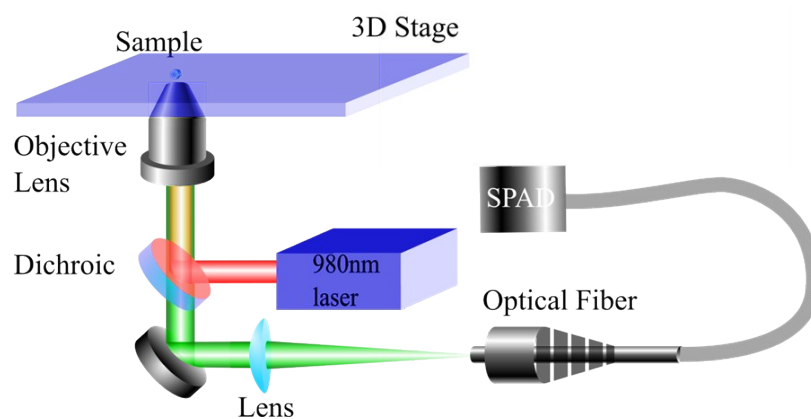
**Fig. S9** TGA results for UCNP. According to the previous reports,<sup>[1]</sup> the weight loss at the temperature from 150 °C to 300 °C can be ascribed to the desorption of OA<sup>-</sup>. It can be observed that the desorption of OA<sup>-</sup> from the surface of UCNP starts from 160 °C and arrives at the maximum at about 190 °C to 230 °C.



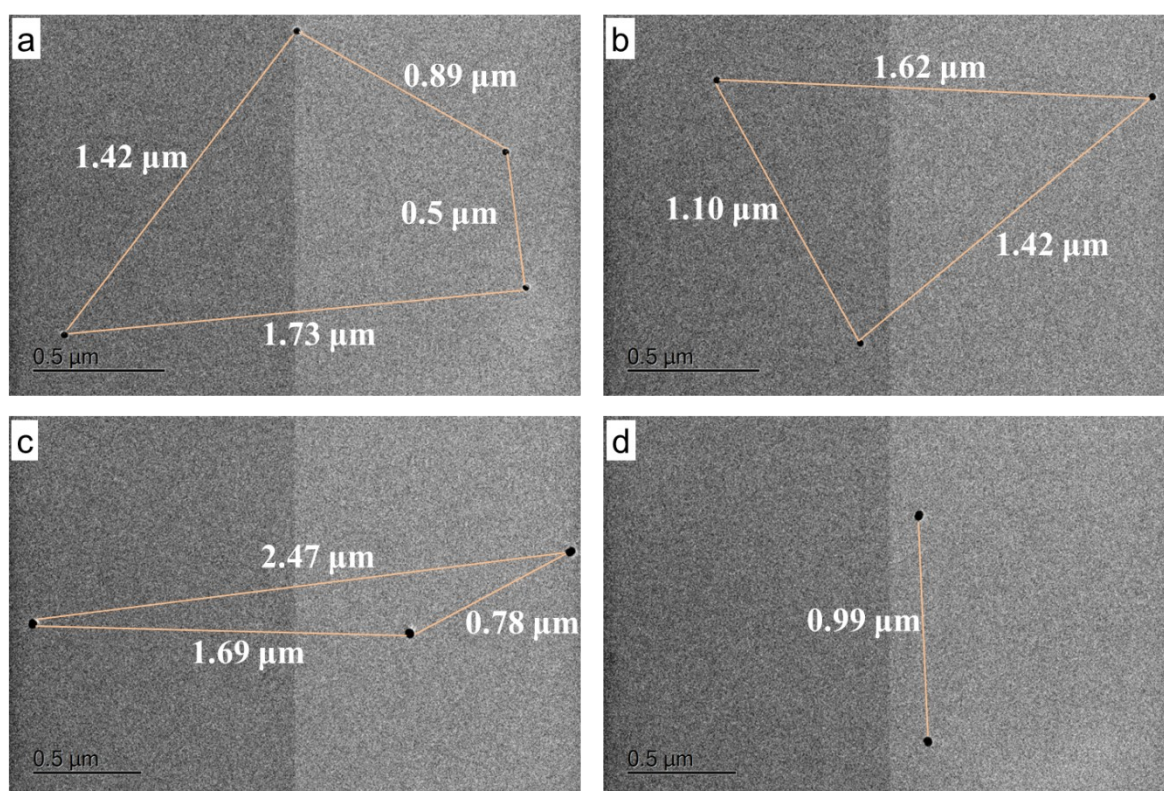
**Fig. S10** UV-vis spectrum for nanoparticles synthesized at different temperatures.



**Fig. S11** The PL spectrum in different ranges of NaYF<sub>4</sub>: Yb, Tm-ZnO nanoparticles synthesized at different temperatures.



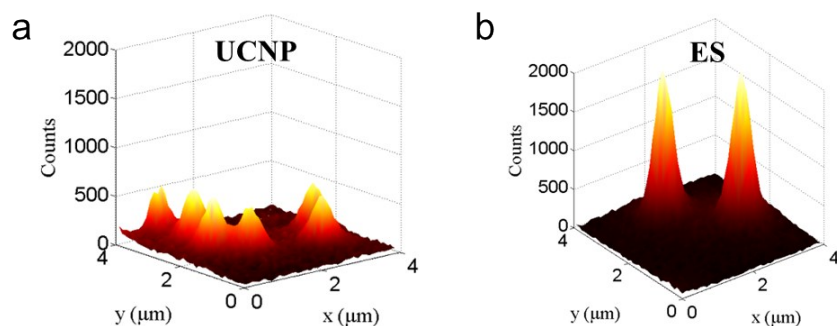
**Fig. S12** System setup for customized scanning confocal microscope.



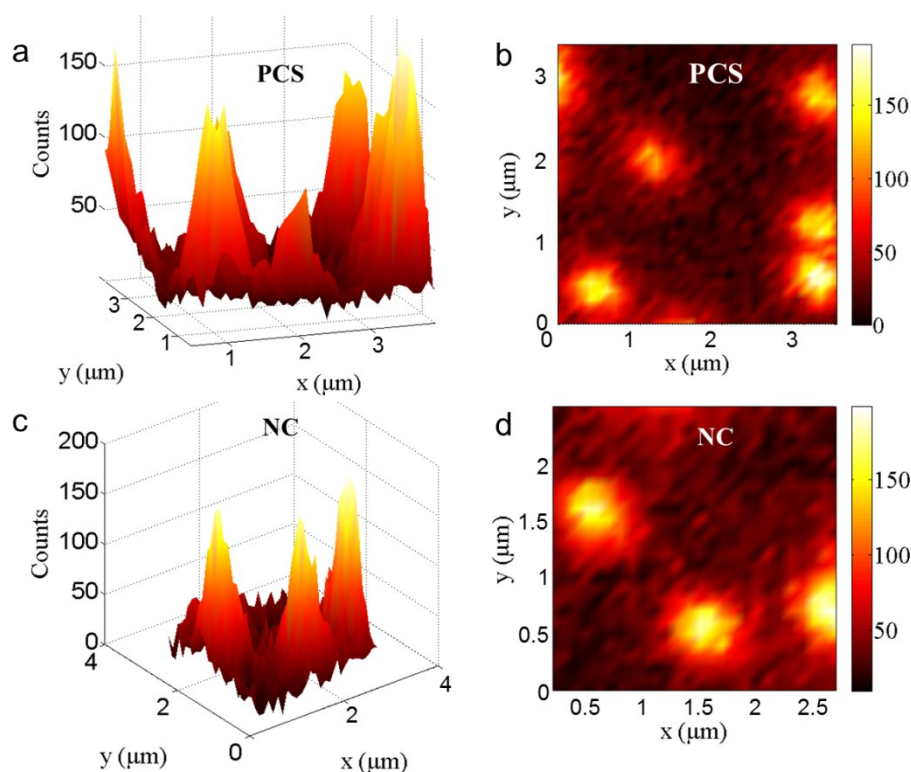
**Fig. S13** (a) and (b) are TEM images of UCNP nanoparticles using for confocal microscopy quantitative measurements. (c) and (d) are TEM images of ES using for confocal microscopy quantitative measurements.

Due to the limitation of laser spot size, the distance between different particles should be at least larger than 0.5 μm in order to obtain clear single particle emission. Fig. S13 shows that the distance between different particles in all images are all larger than 0.5 μm, hence,

concentration of the nanoparticles are suitable for confocal microscopy quantitative measurements.

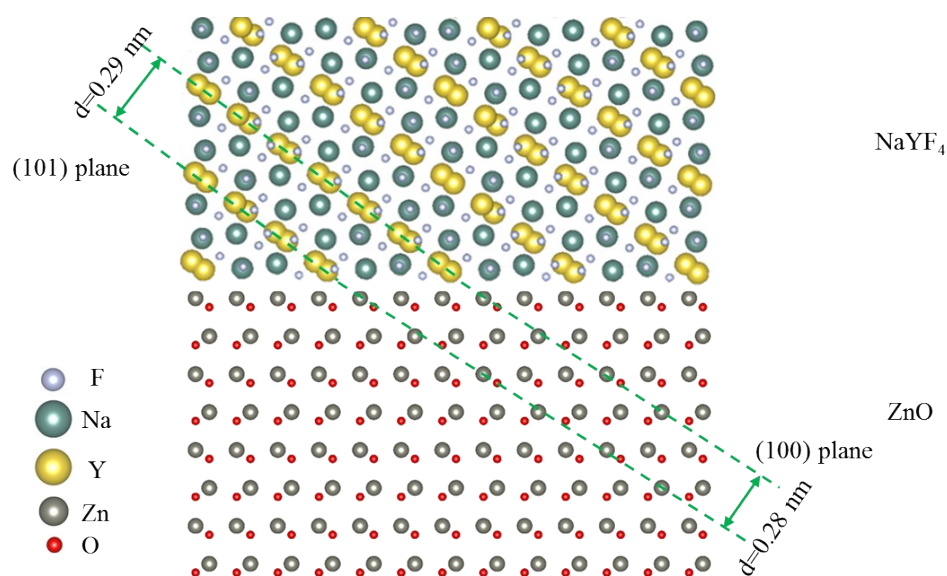


**Fig. S14** (a) and (b) are the 3-D confocal microscopy quantitative measurement of single UCNPs and ES nanoparticles, respectively.

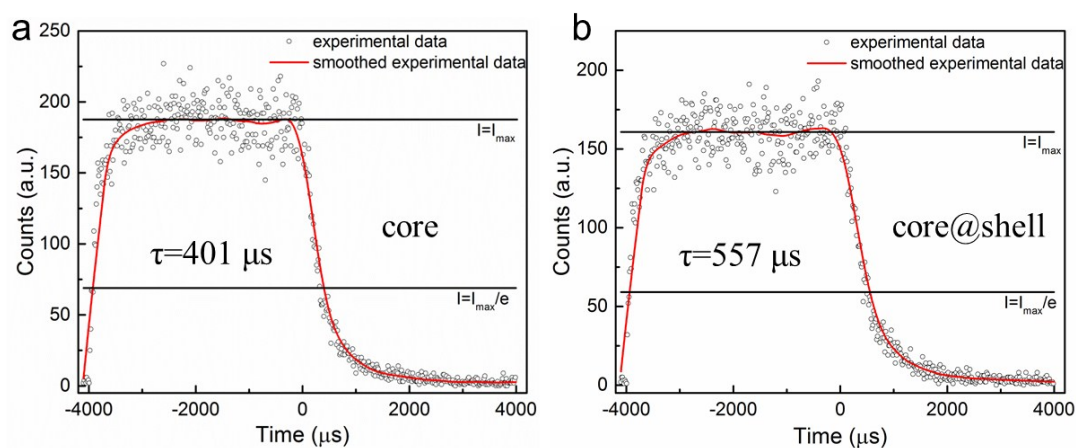


**Fig. S15** Confocal microscopy quantitative measurements of (a, b) single PCS particles, and (c, d) NC particles.

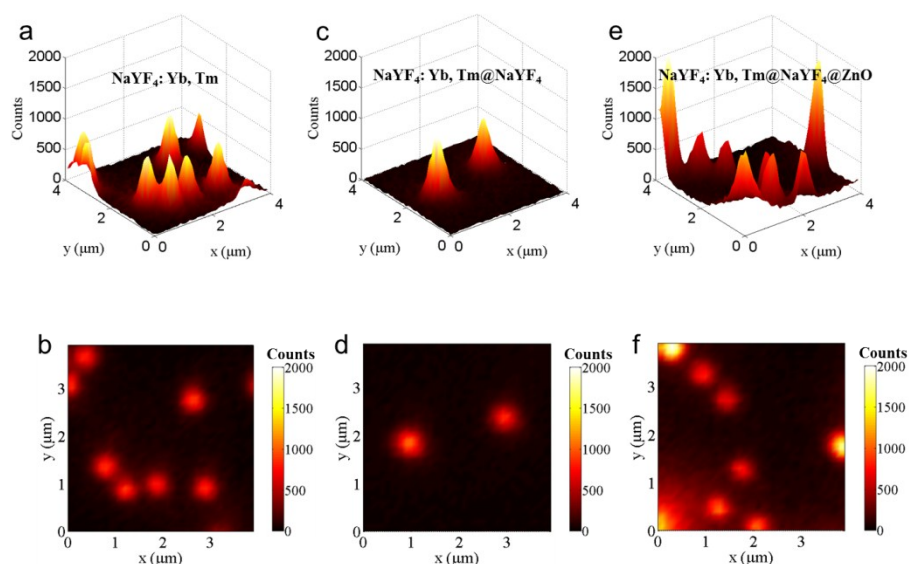




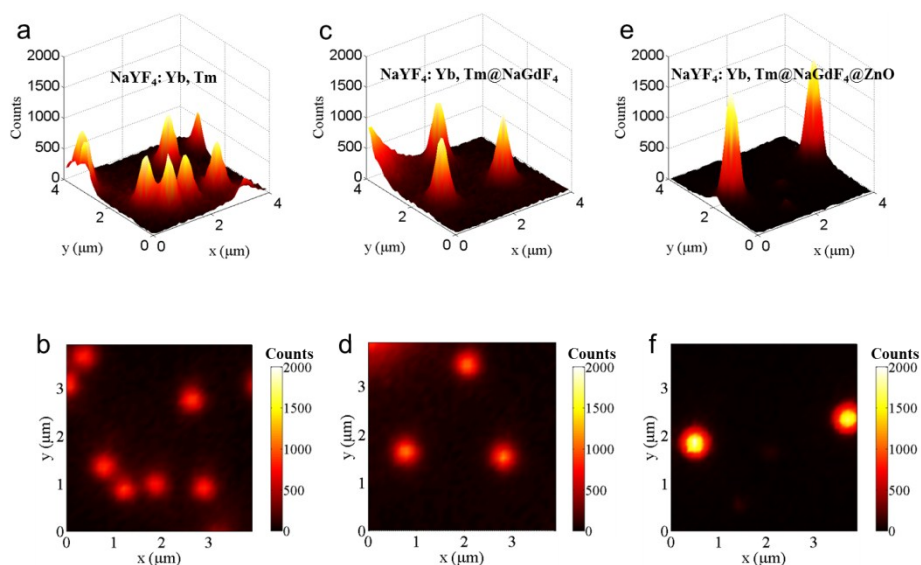
**Fig. S16** Schematic modelling of the interface of NaYF<sub>4</sub> (010) plane and ZnO (001) plane, in which the in-plane lattice constant of NaYF<sub>4</sub> (010) is  $d_{(101)}=0.29$  nm and the in-plane lattice constant of ZnO (001) is  $d_{(100)}=0.28$  nm.



**Fig. S17** Upconversion luminescence decay curves of Tm<sup>3+</sup> for blue light. The collected emission wavelength is  $475 \pm 25$  nm. It is obvious that the lifetime of the epitaxially aligned core@shell nanoparticles is longer than the lifetime of upconversion nanoparticles, indicating that the epitaxially aligned shell layer is beneficial for reducing the non-radiative pathways.



**Fig. S18** (a) and (b) are confocal microscopy quantitative measurement of single  $\text{NaYF}_4:\text{Yb, Tm}$  particles. (c) and (d) are confocal microscopy quantitative measurements of single  $\text{NaYF}_4:\text{Yb, Tm}@NaYF_4$  particles. (e) and (f) are confocal microscopy quantitative measurements of single  $\text{NaYF}_4:\text{Yb, Tm}@NaYF_4@ZnO$  particles.



**Fig. S19** (a) and (b) are confocal microscopy quantitative measurements of single  $\text{NaYF}_4:\text{Yb, Tm}$  particles. (c) and (d) are confocal microscopy quantitative measurements of single  $\text{NaYF}_4:\text{Yb, Tm}@NaGdF_4$  particles. (e) and (f) are the confocal microscopy quantitative measurements of single  $\text{NaYF}_4:\text{Yb, Tm}@NaGdF_4@ZnO$  particles.

In our work, the epitaxially aligned buffer layer is proposed to play a significant role in enhancing the luminescence. As is well-documented, the epitaxially grown ZnO can minimise the non-radiative pathways, including scattering, photon-phonon coupling in the crystal, and quenching on crystal surface defects. In addition, the energy value of the bottom of the conduction band for ZnO is close to  $^1D_2$  of  $Tm^{3+}$ , and hence, the epitaxial alignment at the interface facilitates the energy absorbed by ZnO transferred back to  $Tm^{3+}$  to populate the  $^1D_2$  energy level. To verify this hypothesis, we prepared  $NaYF_4: Yb, Tm@NaYF_4$ ,  $NaYF_4: Yb, Tm@NaYF_4@ZnO$ ,  $NaYF_4: Yb, Tm@NaGdF_4$  and  $NaYF_4: Yb, Tm@NaGdF_4@ZnO$  samples, and tested the emissions of single particles, as shown in Fig. S18 and S19. As is well known, the energy state of  $Y^{3+}$  is significantly higher than those of  $Yb^{3+}$  and  $Tm^{3+}$ , and thus, the energy in the  $Yb^{3+}$  and  $Tm^{3+}$  cannot be transferred to  $Y^{3+}$  due to the large energy mismatch. In contrast, the energy level of  $^6P_{7/2}$  for  $Gd^{3+}$  is close to the energy levels of  $^1I_6$  and  $^1D_2$ , which enables the  $^6P_{7/2}$  energy level of  $Gd^{3+}$  to act as the energy transfer channel.<sup>[2,3]</sup> As a result, the emission of  $NaYF_4: Yb, Tm@NaGdF_4@ZnO$  is expected to be enhanced compared with  $NaYF_4: Yb, Tm$ , while the emission of  $NaYF_4: Yb, Tm@NaYF_4@ZnO$  is expected to not be enhanced compared with  $NaYF_4: Yb, Tm$ . This is consistent with our experimental observations. Thus, the epitaxially aligned buffer layer is proposed to contribute to the enhanced luminescence.

According to previous reports,<sup>[4]</sup> in which the formation of  $Yb^{3+}-Fe^{3+}$  dimers can populate the  $^1D_2$  and the subsequent  $^1I_6$  energy levels, and enhance the ultraviolet upconversion emission, there may be another mechanism for the lack of a decrease in the ultraviolet emission. Due to the formation of the buffer layer, the  $Yb^{3+}$  and  $Tm^{3+}$  diffuse into the crystal lattice of ZnO.<sup>[5]</sup> The  $3d$  electron configuration of Zn may couple with  $Yb^{3+}$ , and form the  $Yb^{3+}-Zn$  dimer. The mixed electron wavefunctions of  $Yb^{3+}$  and Zn may form some new energy levels, which can populate the  $^1D_2$  level of  $Tm^{3+}$  and suppress the decrease in the ultraviolet emission.

Even though the above confocal microscopy measurements of single particles and evidence from previous reports can help to explain the effects of the buffer layer towards enhanced luminescence, the details and the direct evidence are still absent. We will carry out deep investigations on this point in our following work.

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5. B. Chen, D. Peng, X. Chen, X. Qiao, X. Fan and F. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 12788.