

## Supporting Information

### **Performance enhancement in up-conversion nanoparticles-embedded perovskite solar cells by harvesting near-infrared sunlight**

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# 1 Experimental

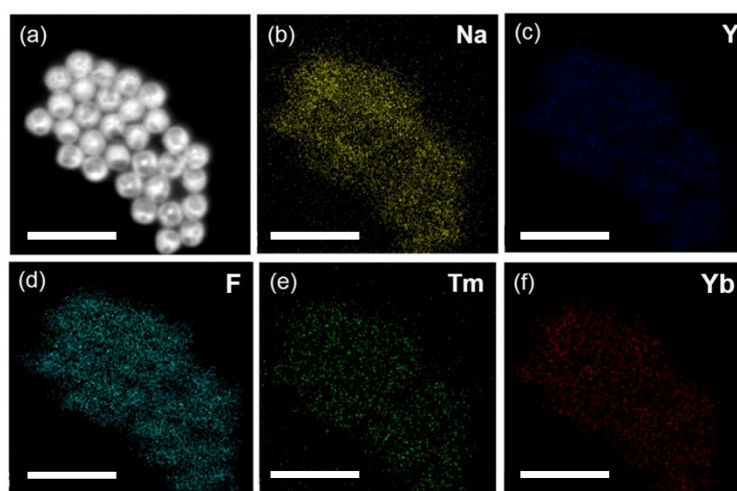
## 1.1 Device fabrication

The patterned fluorine-doped tin oxide (FTO) substrates with a sheet resistance of  $7 \Omega \text{ sq}^{-1}$  were cleaned by sonication sequentially with acetone, detergent, deionized water and isopropyl alcohol for 15 min respectively. The substrates were further treated with oxygen plasma to remove organic impurities. A compact-TiO<sub>2</sub> (c-TiO<sub>2</sub>) layer was deposited on the clean pre-heated FTO substrates by spray pyrolysis from a precursor solution of titanium diisopropoxide bis (acetylacetonate) solution, followed by sintering at 500 °C for 50 min. The UCNP layer was spin-coated on the layer of c-TiO<sub>2</sub> at 5000 rpm for 20 s. The samples were annealed at 80 °C for 30 min in the glovebox. For one-step method, PbI<sub>2</sub>, FAI, MABr, and PbBr<sub>2</sub> were dissolved together in a mixed solvent of DMF and DMSO (DMF: DMSO = 4:1 in volume ratio) to form a 1 M precursor solution. The MABr and PbBr<sub>2</sub> (1:1 molar ratio) had 10 mol% in total perovskite precursor solution. Meanwhile, CsI was dissolved in 1 mL DMSO solution. The CsI solution was added into the perovskite precursor solution (1:20 volume ratio) and then the mixed solution was stirred overnight under a temperature of 60 °C. In one-step method, 45  $\mu\text{L}$  of mixed perovskite precursor solution was first dropped on the UCNP layer and followed by spin coating. The spin rate was 1000 rpm for 10 s in the step one and then increased to 6000 rpm for 20 s in the step two. 100  $\mu\text{L}$  of chlorobenzene was dropped onto the spinning-film 5 s prior to the end of the second step. The as-prepared films were dried at 70 °C for 10 min and then thermally annealed at 100 °C for 60 min, resulting in mixed-cation perovskite Cs<sub>0.05</sub>(MA<sub>0.17</sub>FA<sub>0.83</sub>)<sub>99.5</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> film. Spiro-OMeTAD was used as the hole-transporting layer and was spin coated on the perovskite layer by using 45  $\mu\text{L}$  solution (85.7 mg, 33.84  $\mu\text{L}$  4-tert-butylpyridine, 10.05 mg lithium bis(trifluoromethyl sulphonyl) imide and 3.16 mg FK209 dissolved in 1 mL chlorobenzene) at 4000 rpm for 20 s. All the film deposition processes were performed in an N<sub>2</sub>-filled glovebox. Finally, the devices were finished by thermally evaporating a 100-nm Au electrode layer. The active area of the solar cells was defined to be 0.07 cm<sup>2</sup> by using metal masks.

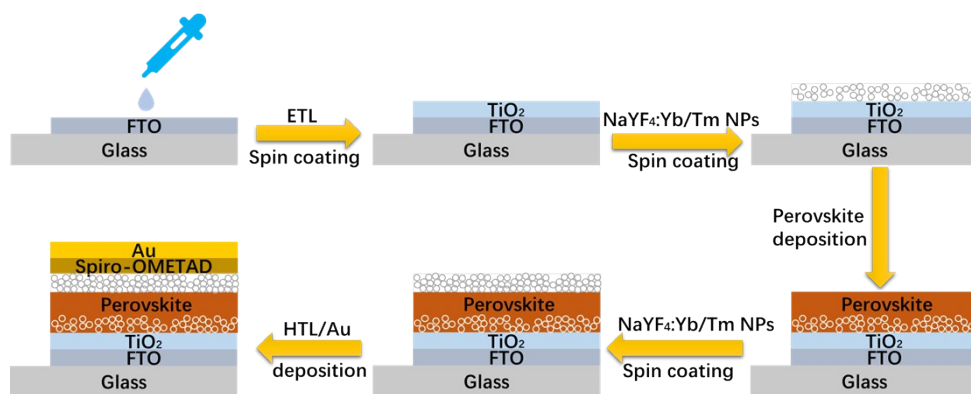
## 1.2 Device characterizations

The photocurrent density–voltage ( $J$ – $V$ ) curves were measured using the solar simulator (ABET Sun 3000 solar simulator) with Keithely model 2400 as a digital source meter under illumination of AM 1.5G solar light ( $100 \text{ mW cm}^{-2}$ ). The incident photon to current efficiency (IPCE) as a function of wavelength of the PSCs was measured by a PV measurements QEXL from 300 to 900 nm. The devices stability measurements were performed in ambient environment at  $25 \text{ }^\circ\text{C}$  and with relative humidity of 20%. The NIR response of the PSC devices was tested using a 980 nm laser ( $3 \text{ W cm}^{-2}$ ) with an 800 nm high-pass optical filter on the light path. Time-resolved PL (TRPL) spectra were examined by using a fluorescence spectrophotometer RF-5301PC under excitation of a 470 nm pulsed laser.

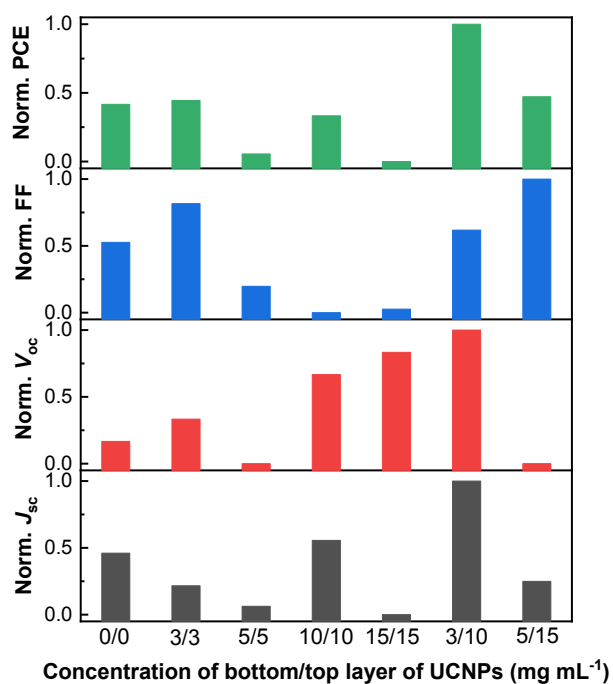
## 2. Supplementary figures



**Figure S1.** (a) STEM image and (b-f) EDX elemental mapping of  $\beta$ - $\text{NaYF}_4$ :18%Yb,0.5%Tm UCNPs and line-profile analysis of  $\beta$ - $\text{NaYF}_4$ :18%Yb,0.5%Tm UCNPs with different elements (Na, Y, F, Tm and Yb). All of the scale bars are 100 nm.



**Figure S2.** Fabrication processes for the double-UC PSCs.



**Figure S3.** Normalized photovoltaic parameters of double-UC PSCs with different concentrations of UCNP (bottom layer/top layer).

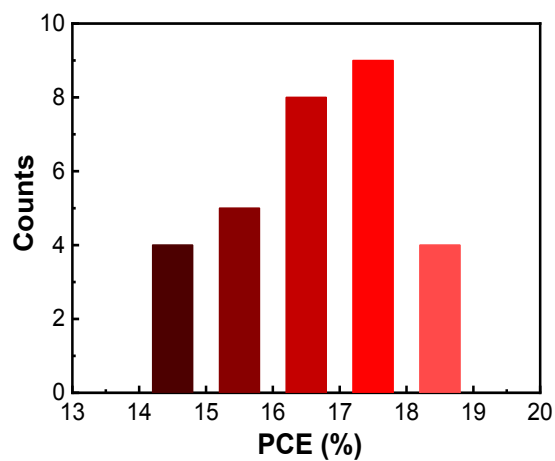


Figure S4. Statistical histogram of the double-UC PSCs.

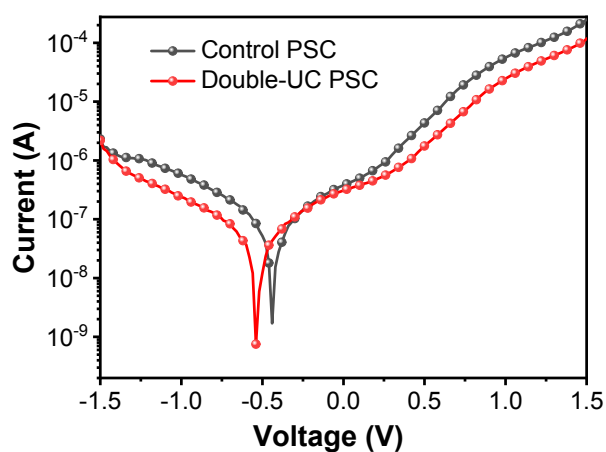
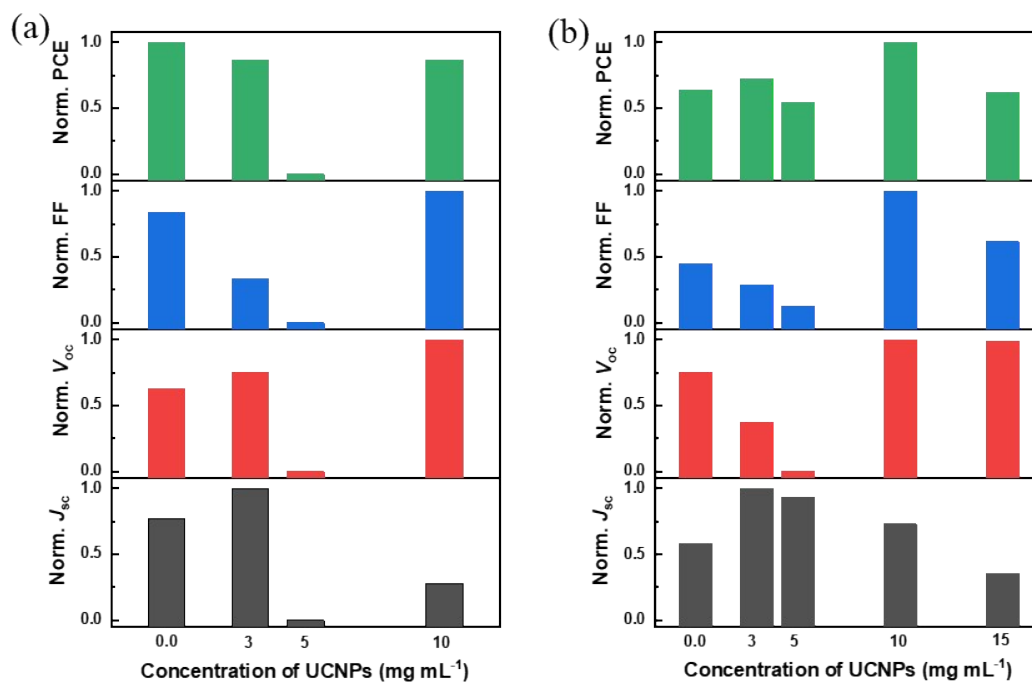


Figure S5. Dark I-V curves of the control and the double-UC PSCs.



**Figure S6.** Normalized photovoltaic parameters of (a) B-UC PSCs and (b) T-UC PSCs with different concentrations of UCNPs.

**Table S1** Comparison of photovoltaic performance in PSCs incorporated with up-conversion nanomaterials.

UCNPs	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	Ref.
$\beta$ -NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Tm <sup>3+</sup>	25.46	1.06	67.50	18.20	This work
$\beta$ -NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Er <sup>3+</sup>	22.71	1.15	75.39	19.70	[1]
NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Er <sup>3+</sup>	22.60	1.06	73.90	17.80	[2]
$\beta$ -NaYF <sub>4</sub> :Yb <sup>3+</sup> , Er <sup>3+</sup>	20.23	1.10	72.00	15.98	[3]
$\beta$ -NaYF <sub>4</sub> :Yb <sup>3+</sup> ,Tm <sup>3+</sup>	21.70	1.10	70.60	16.90	[4]

## References

- [1] F.-L. Meng, J.-J. Wu, E.-F. Zhao, Y.-Z. Zheng, M.-L. Huang, L.-M. Dai, X. Tao, J.-F. Chen, *Nanoscale*, **2017**, 9, 18535–18545.
- [2] M. He, X. Pang, X. Liu, B. Jiang, Y. He, H. Snaith, Z. Lin, *Angew. Chem. Int. Ed.*, **2016**, 55, 4280–4284.
- [3] J. Roh, H. Yu, J. Jang, *ACS Appl. Mater. Interfaces*, **2016**, 8, 19847–19852.
- [4] M. Que, W. Que, X. Yin, P. Chen, Y. Yang, J. Hu, B. Yu, Y. Du, *Nanoscale*, **2016**, 8, 14432.