Supporting Information

Experimental Section

Materials: Sodium citrate tribasic dihydrate ($HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$), NaF, Urea ($NH_2CONH_2$), $Yb(NO_3)_3$, $Er(NO_3)_3 \cdot 6H_2O$, $Tm(NO_3)_3 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were purchased from Shanghai Titan Scientific Co., Ltd. $Y(NO_3)_3 \cdot 6H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol absolute was taken from Shanghai Lingfeng Chemical Reagent Co., Ltd. Deionized water was obtained from a Milli-Q system (Tondino Scientific (Shanghai) Co., Ltd). All chemicals are analytical grade and were used as received without any further purification.

Synthesis of Co^{2+} doped $NaYF_4$: Yb/Er/Tm particles: Co^{2+} doped $NaYF_4$: Yb/Er/Tm particles were synthesized by the previous reported hydrothermal method.[1] Typically, (0.8-x) mmol $Y(NO_3)_3 \cdot 6H_2O$, 0.18 mmol $Yb(NO_3)_3$, 0.02 mmol $Er(NO_3)_3 \cdot 6H_2O$, 0.02 mmol $Tm(NO_3)_3 \cdot 6H_2O$, and x mmol $Co(NO_3)_2 \cdot 6H_2O$ (x=0, 0.05, 0.15, 0.25) were added to an aqueous solution of Sodium citrate tribasic dihydrate (0.5 mmol in 15 mL deionized water) under thorough stirring. The mixed solution was kept stirring for 1 h. Then, 4 mmol NaF and 20 mmol NH_2CONH_2 were slowly added into the solution. The mixed solution was kept stirring for another 1 h. After stirred evenly, the mixture solution was transferred to a 100 mL Teflon-lined stainless autoclave, thermally heated at 453 K for 12 h, and then cooled to room temperature. The obtained products were washed and centrifuged with deionized water and ethanol three times to remove

impurities and then dried at 353 K for 12 h in a vacuum drying oven. The final products obtained were named $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25).

Preparation of upconversion luminescent coating: The prepared $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) samples were mixed with ethanol according to the ratio of solid to liquid 1:100, and ultrasonic for 1 h to disperse evenly. The upconversion luminescent coating was obtained by dipping the evenly mixed solution with a non-woven cloth and coating it on a clean and highly transparent glass substrate (transmittance greater than 95%).

Characterizations: The crystalline phases were characterized by X-ray diffraction (XRD) using a high-resolution powder X-ray diffractometer (D8 Advance) with Cu Kα radiation. The morphologies of the samples were obtained by a high-resolution field emission scanning electron microscope (SEM). The upconversion emission analysis was measured by a low temperature absorption spectrometer (FLS-980). X-ray photoelectron spectroscopy (XPS) was measured by a ESCAlab250 spectroscopy instrument. The optical absorption performance was measured by a UV-Vis-IR diffuse reflectance spectroscopy (Perkin Elmer, model LAMBDA 1050). The chemical structures were measured by an infrared (IR) spectroscopy (Spotlight400). The light transmittance was tested by a transmissivity test apparatus (SDR851). The J-V curves of photovoltaic cell were measured by a solar simulator (ProMoSim evo3, standard solar radiation AM 1.5G, 100 mW/cm^2).

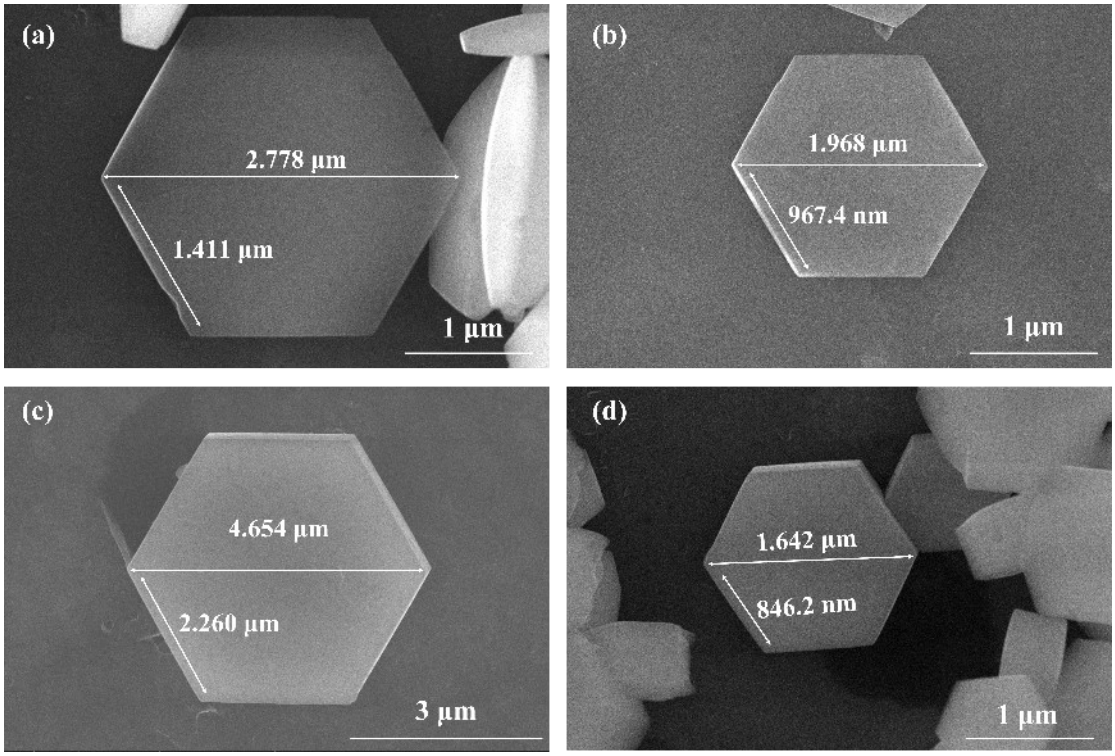


Figure S1. SEM images of diameter and side length of $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) hexagonal crystals: (a) x=0, (b) x=5, (c) x=15 and (d) x=25.

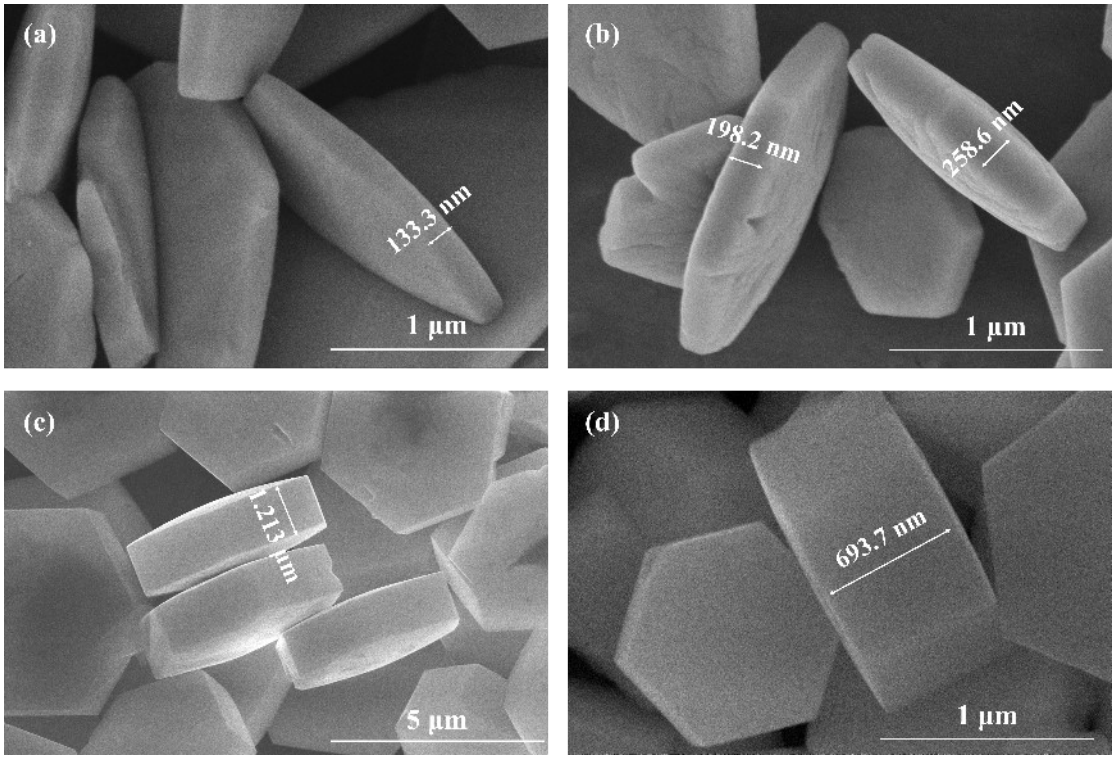


Figure S2. SEM images of thickness of $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) hexagonal crystals: (a) x=0, (b) x=5, (c) x=15 and (d) x=25.

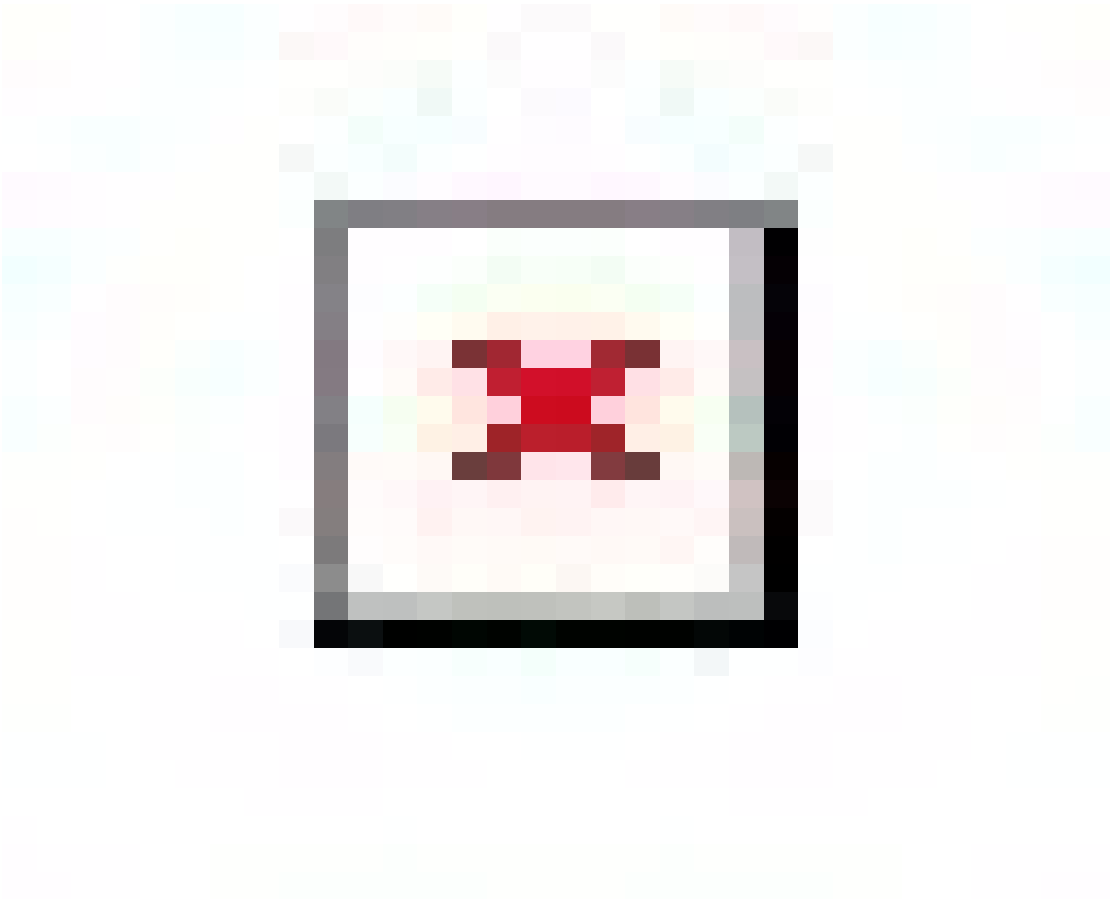


Figure S3. XPS spectra of $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) hexagonal crystals: (a) Co 2p, (b) Na 1s, (c) Y 3d and (d) F 1s.

Table S1

The XPS measured actual molar ratios of prepared $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) samples.

Element symbol	Atomic concentration percentage			
	0% Co^{2+}	5% Co^{2+}	15% Co^{2+}	25% Co^{2+}
C	16.1	14.13	19.3	22.17
O	9.02	8.23	9.02	10.03
Y	14.01	13.92	12.82	11.09
F	50.52	53.33	49.18	46.89
Na	9.8	9.75	8.55	8.26
Er	0.23	0.26	0.16	0.17
Tm	0.02	0.01	0.03	0.03
Yb	0.29	0.32	0.32	0.32
Co	——	0.05	0.63	1.03

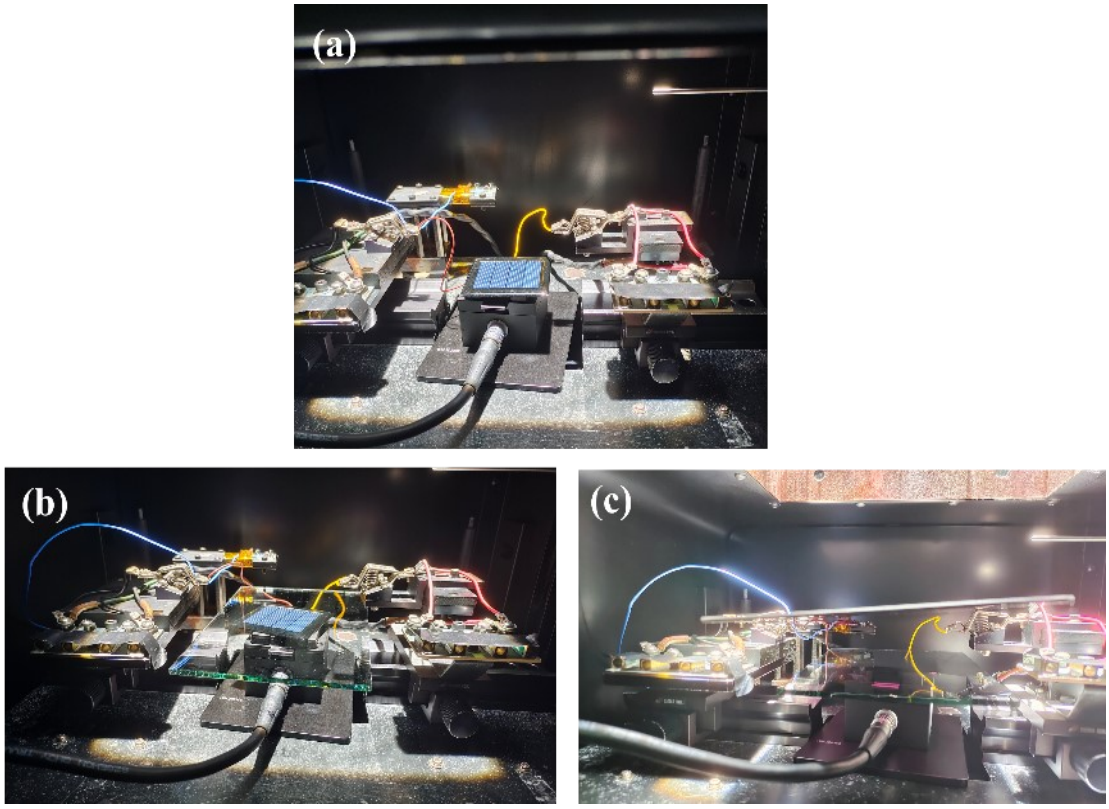
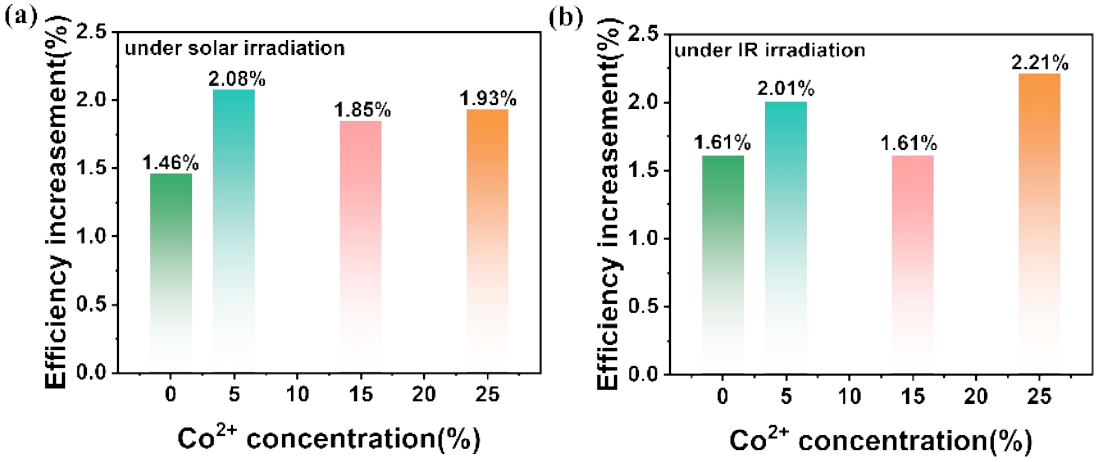


Figure S4. (a) Photovoltaic cell works under an intensity of sunlight; (b) Photovoltaic cell coated with the $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) samples works under 1 standard solar intensity radiation (AM1.5G, 100 mW/cm^2); (b) Photovoltaic cell coated with the $NaYF_4$: Yb/Er/Tm/Co (18/2/2/x mol%, x=0, 5, 15, 25) samples works under IR light (a filter was used to remove ultraviolet and visible light from solar radiation, photon wavelength ≥ 760nm).

Table S2

List of relevant studies on upconversion materials enhancing the efficiency of solar cell

Materials	Efficiency increase (%)	References
5% Co^{2+} doped $NaYF_4$: Yb/Er/Tm	2.08	This work
$NaYF_4$:Er^{3+}, Yb^{3+}@SiO_2@TiO_2	2.17	Liang et al.[2]
β-$NaYF_4$: Yb^{3+}, Er^{3+}	1.49	Roh et al.[3]
$NaYF_4$: Yb^{3+}, Tm^{3+}	1.24	Liang et al.[4]
TiO_2: (Er^{3+}, Yb^{3+})	1.72	Xie et al.[5]



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68 **Figure S5.** Efficiency increasement of different Co^{2+} doped $NaYF_4$: Yb/Er/Tm

69 upconversion luminescent coatings on photovoltaic cell under solar irradiation (a) and

70 under IR irradiation (b).

References

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2. L. Liang, Y. Liu, C. Bu, K. Guo, W. Sun, N. Huang, T. Peng, B. Sebo, M. Pan, W. Liu, S. Guo and X. Z. Zhao, *Adv Mater*, 2013, **25**, 2174-2180.
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