

Electronic Supplementary Information


NaYF₄:Yb,Er/MoS₂: from synthesis, surface ligands-stripping, to negative infrared photoresponse

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Experimental Section:

Synthesis of NaYF₄:Yb/Er UCNPs: NaYF₄:Yb/Er UCNPs were synthesized in a recent reported thermolysis method. For a typical procedure, 1.0 mL of YCl₃ (0.78 mol/L), 1.0 mL of YbCl₃ (0.20 mol/L), 0.5 mL of ErCl₃ (0.04 mol/L), 6 mL oleic acid and 15 mL octadecene were added into a 100 mL flask. The solution was heated to 120 °C for 10 min and then to 160 °C for 30 min. After the solution cooled to 60 °C, 8 mL methanol solution containing NH₄F (0.148 g) and NaOH (0.1 g) was added into the flask, and the solution was maintained at 50 °C for 30 min. Then the resulting solution was heated to 300 °C and maintained for 1.5 h under nitrogen atmosphere. After heating was stopped, the reaction solution was cooled to room temperature and absolute ethanol was added to precipitate the fluorides UCNPs. The products were isolated by centrifugation.


Synthesis of MoS₂ nanosheets: Firstly, 1 mmol of (NH₄)₂MoS₄ was mixed with 8 mL oleylamine (OM) and 8 mL of oleic acid (OA) under a N₂ flow at 80 °C for 30 min with continuous stirring. Then the temperature was raised to 330 °C and kept constant for 40 min. The reactor was cooled to room temperature with the N₂ supply on. After which, ethanol was added to precipitate the products and remove excess OA and OM. Finally, the black MoS₂ nanosheets were obtained by centrifugation and repeatedly washed with ethanol.



Synthesis of NaYF₄:Yb/Er UCNPs-MoS₂ composites: Firstly, varying amounts of (NH₄)₂MoS₄ was mixed with 8 mL OM and 8 mL of OA under a N₂ flow at 80 °C for 30 min with continuous stirring. 1 mmol of NaYF₄:Yb/Er UCNPs prepared previously (dispersed in hexane) was added to the mixture. It is then heated until all the hexane has evaporated, and the temperature was raised to 330 °C and maintained for 30 min. The product was cooled down to room temperature. The nanocomposites were then precipitated by adding ethanol and centrifuged to remove surfactants.

Surface ligand-stripping of nanomaterials: In a typical procedure, three drops of thionyl chloride (SOCl₂) were added into 5 mL hexane dispersion of nanomaterials (2 mg/mL) to form a homogeneous solution at room temperature. Then, 2 drops of DMF was added as catalyst to accelerate the removal of surface ligands. The resulting solution was gently shaken until nanocrystals were precipitated, typically within 2 min. The product was separated by centrifugation, and washed with additional portions of hexane for two times to remove excess SOCl₂ and byproducts before redispersing the solid residue in DMF.

Fabrication of infrared photoresponse device: The photoresponse devices were prepared by depositing the prepared nanomaterials on glass substrate, surface ligand stripping, and subsequent electrodes deposition. Specifically, 50 μL of hexane solution containing prepared nanomaterials (1 mg/mL) was drop-casted onto the surface of cleaned glass substrate (1x1 cm) and dried at 50 °C. This procedure was repeated for four times to ensure the thickness of film for subsequent device fabrication. For ligand removal, the prepared films were immersed in 10 mL hexane solution containing 0.2 mL SOCl₂ and 0.1 mL DMF for 30 s, followed by washing in hexane for 15 s to remove organic residues. Finally, gold electrodes (80-100 nm thick) were evaporated on the samples through a metal mask to form a 200 μm gap where light is illuminated.



Characterization: Field-emission scanning electron microscopy micrographs were taken using a JEOL JSM-7600 instrument. TEM images were recorded using JEOL-2010 with 200 kV accelerating voltage. The absorption spectra were measured in a spectrophotometer (Varian, Cary 5000). Upconversion spectra and lifetimes were determined at room temperature under excitation of 980 nm CW diode laser. XRD data was measured in Bruker Powder D8 diffractometer. FT-IR spectra were taken in a Frontier Spectrometers using KBr pellets. Electrical properties were monitored with a Keithley semiconductor parameter analyser, model 4200-SCS. The power density of 980 nm laser source used for photoresponse measurements was 18 W/cm².

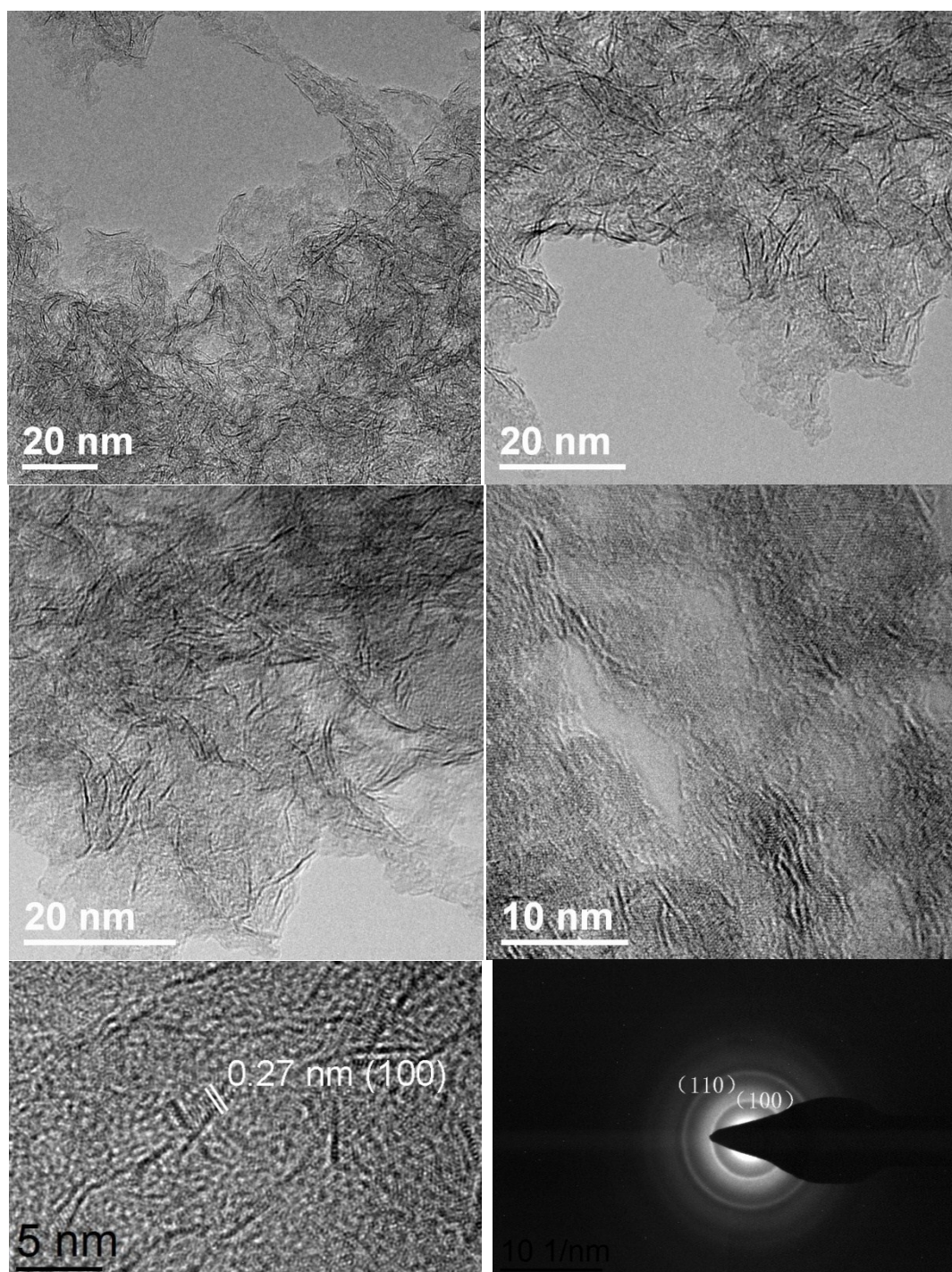


Figure S1. TEM,HRTEM images and the corresponding SAED pattern of MoS₂ nanosheets.

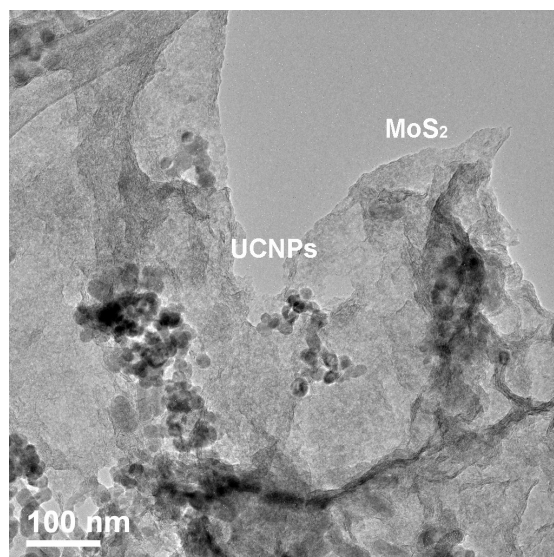


Figure S2. TEM images of UCNPs-MoS₂ nanocomposites.

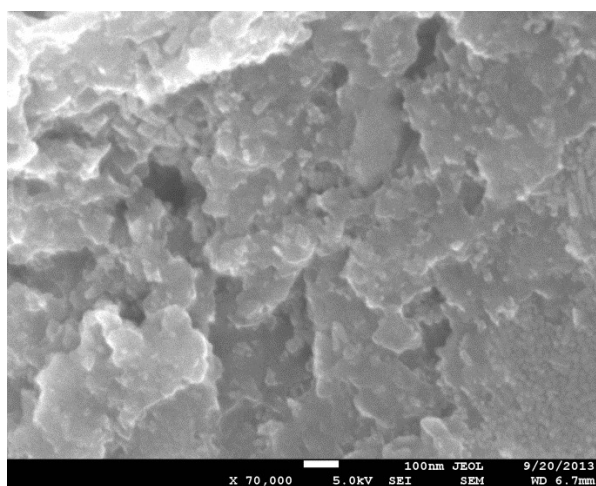


Figure S3. FESEM images of NaYF₄:Yb,Er UCNPs-MoS₂ hybrid nanocomposites (1/0.2).

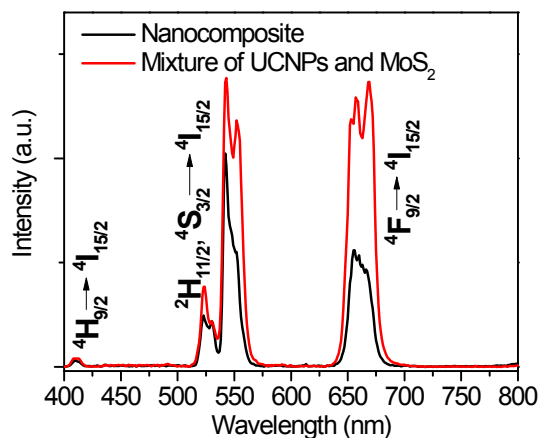


Figure S4. Upconversion spectra of UCNPs-MoS₂ nanocomposites (1/0.2) and the mixture of NaYF₄:Yb,Er UCNPs and MoS₂ nanosheets in a molar ratio of 1/0.2.

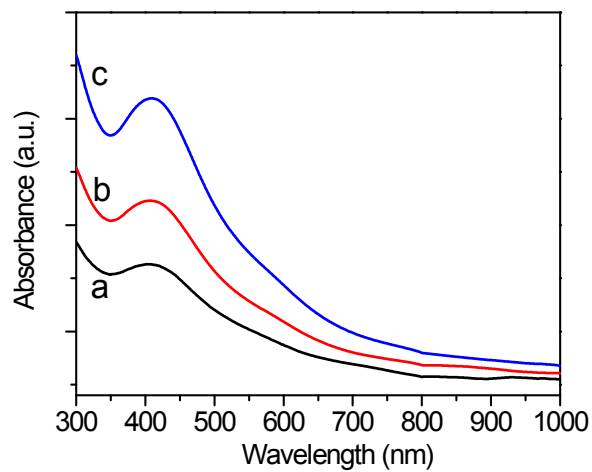


Figure S5. Absorbance spectra of UCNPs-MoS₂ nanocomposites prepared with various molar ratios of UCNPs/MoS₂, a): 1/0.1, b): 1/0.2, c): 1/0.4 (at the concentration of 1 mg/ml).

The corresponding time-resolved upconversion spectra of Er ion were also measured. Results show that the lifetimes of UCNPs decreased from 704 μs in UCNPs to 590 μs in UCNPs-MoS₂ nanocomposites. Such a reduced lifetime indicates the existence of fluorescence resonance energy transfer (FRET) in nanocomposites, that is, the upconverted energy could be transferred from excited energy levels of Er³⁺ ion in UCNPs to MoS₂.

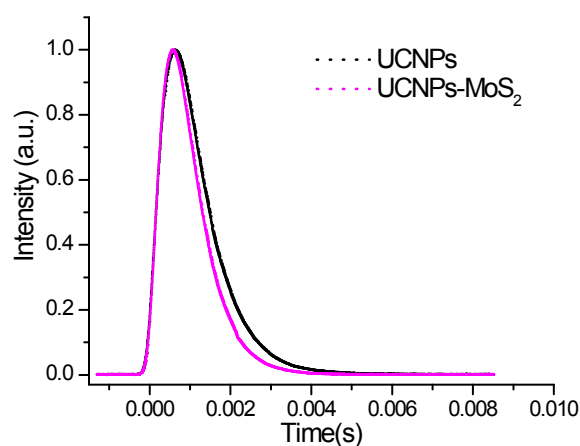


Figure S6. Time-resolved 550 nm upconversion emission of Er ion of NaYF₄:Yb,Er UCNPs, NaYF₄:Yb,Er UCNPs-MoS₂ nanocomposites under 980 nm excitation.

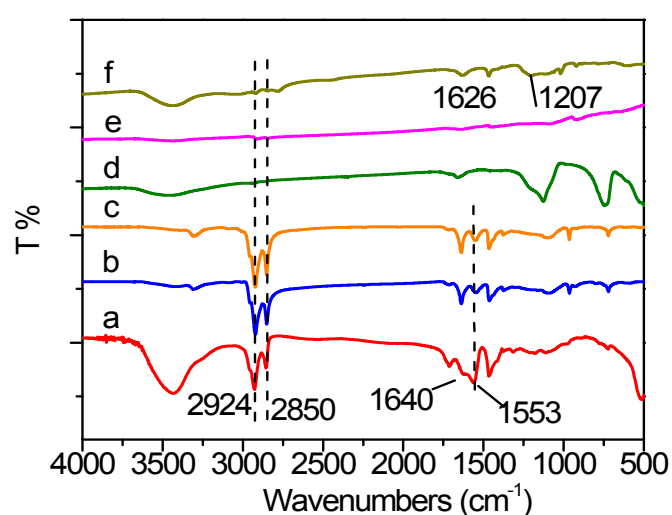


Figure S7. FT-IR spectra of ligands-capped NaYF₄:Yb,Er, MoS₂, and NaYF₄:Yb,Er-MoS₂ composites before (a, b and c) and after (d, e and f) SOCl₂/DMF treatment, respectively.

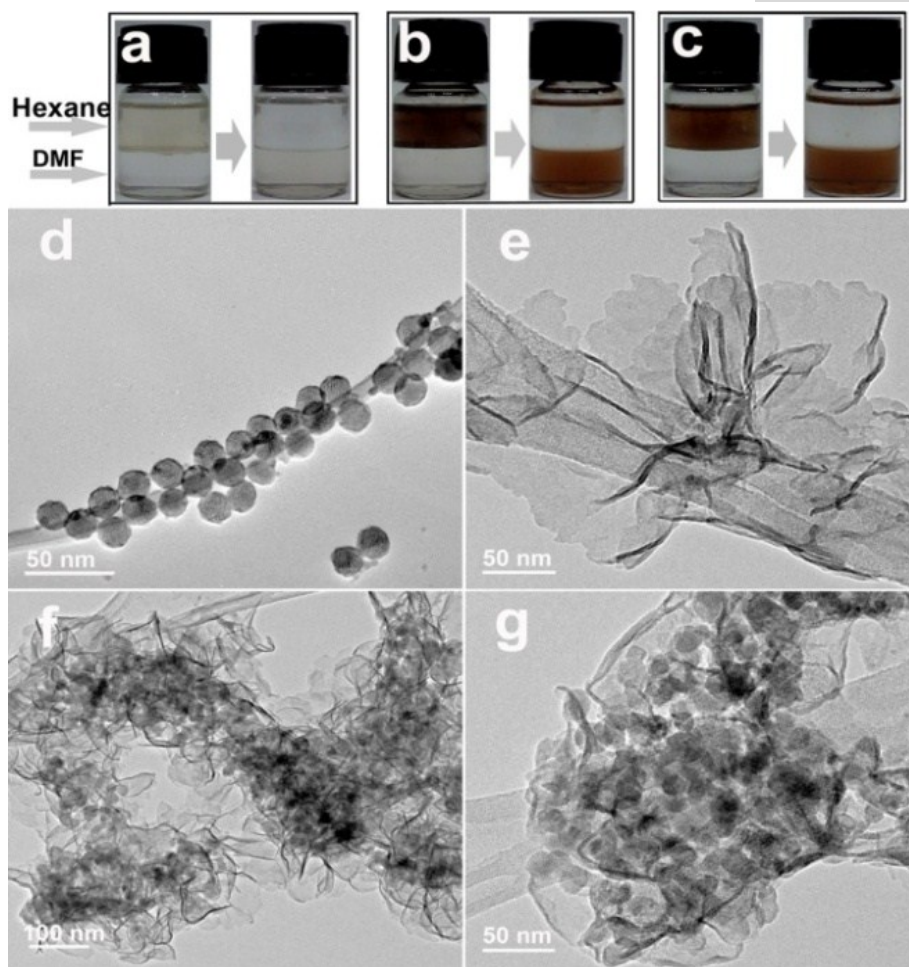


Figure S8. Illustration of the phase-transfer of (a) NaYF₄:Yb,Er, (b) MoS₂, and (c) NaYF₄:Yb,Er-MoS₂ composites (1/0.2) from nonpolar solvent (hexane) to polar solvent (DMF) before and after SOCl₂/DMF treatment, and the corresponding TEM images of (d) NaYF₄:Yb,Er, (e) MoS₂ and (f, g) NaYF₄:Yb,Er-MoS₂ composites (1/0.2) dispersed in DMF after surface ligands removal.

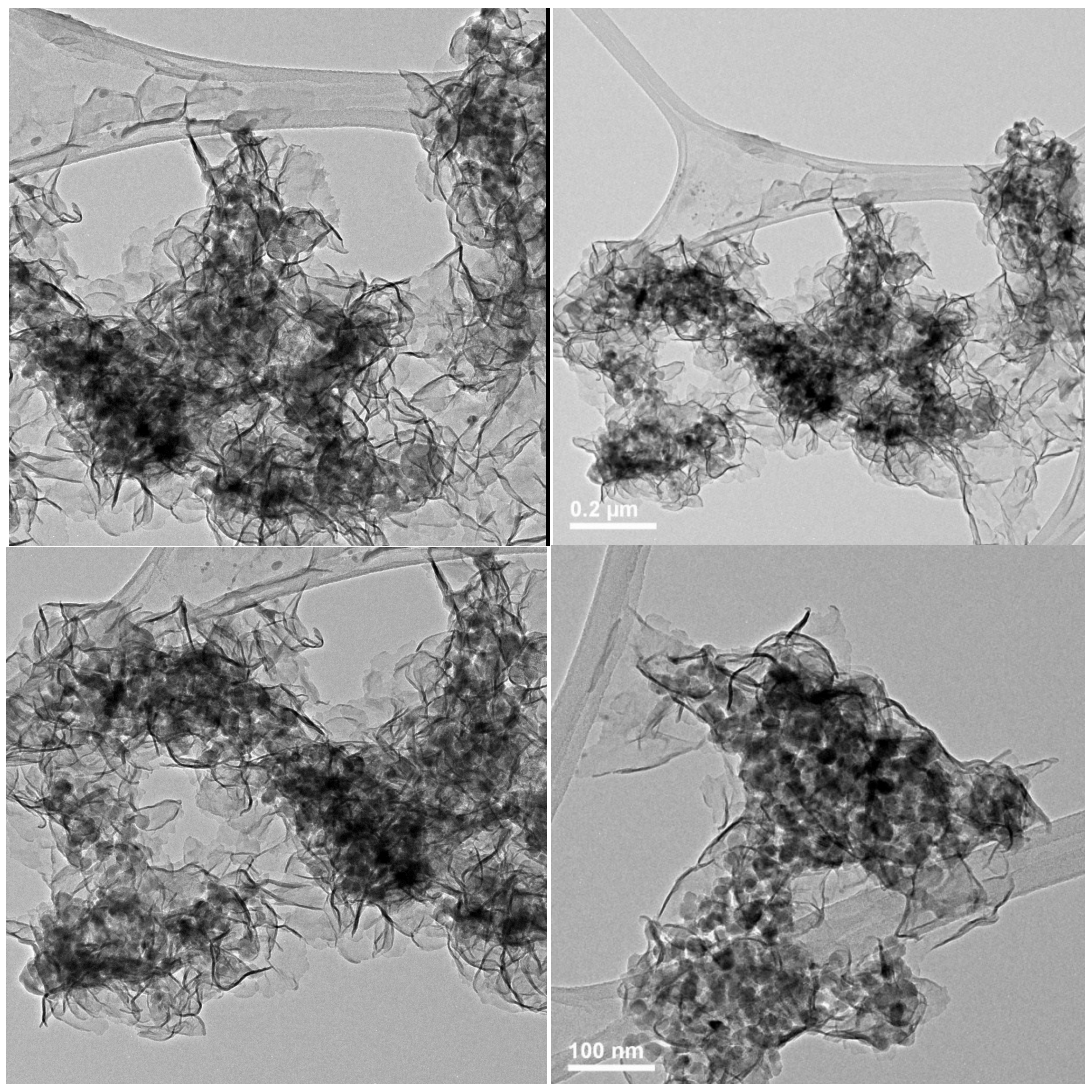


Figure S9. TEM images of NaYF₄:Yb,Er UCNPs-MoS₂ nanocomposites after surface ligands-stripping.

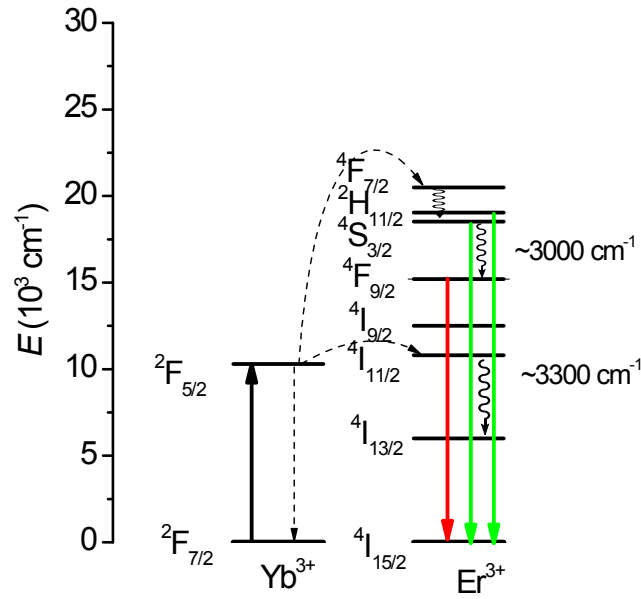


Figure S10. The energy level diagrams of the Er^{3+} and Yb^{3+} dopant ions and upconversion mechanisms under excitation of 980 nm. The full, dotted, and curly arrows represent emission, energy transfer and multiphonon relaxation processes, respectively.

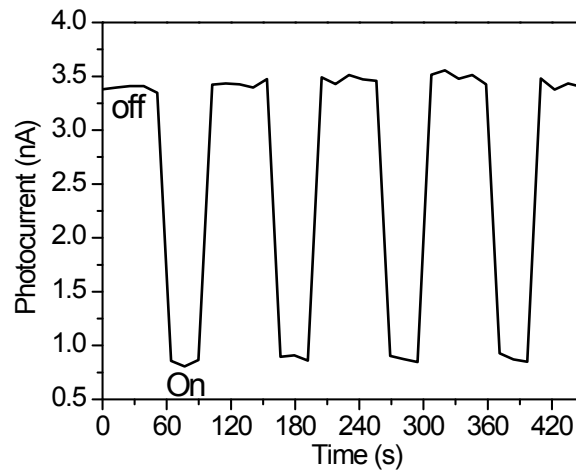


Figure S11. Real-time measurement of drain current of infrared photoresponse device prepared with $\text{NaYF}_4:\text{Yb},\text{Er}$ UCNPs- MoS_2 composite (1/0.2) films treated with hexane solution of SOCl_2/DMF , while the 980 nm infrared light is switched on and off with V_{DS} 10 mV in the absence of gate bias.

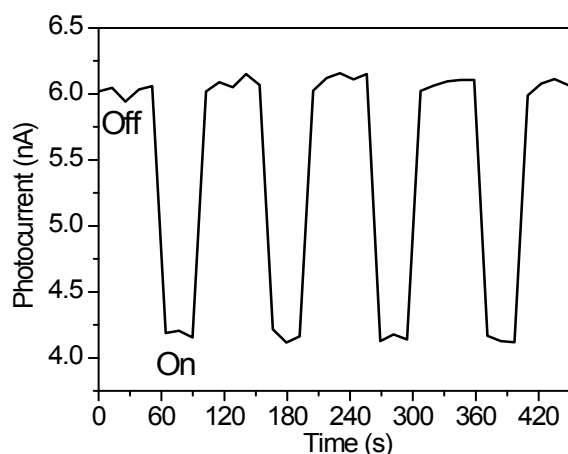


Figure S12. Real-time measurement of drain current of infrared photoresponse device prepared with NaYF₄:Yb,Er UCNPs films treated with hexane solution of SOCl₂/DMF, while the 980 nm infrared light is switched on and off with V_{DS} 10 mV in the absence of gate bias.

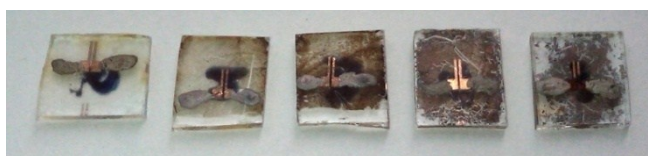



Figure S13. Images of device films of UCNPs, UCNPs-MoS₂ composites (1/0.1, 1/0.2, 1/0.4), and MoS₂ on glass substrate (from left to right) after SOCl₂/DMF treatment.

Proposed mechanism for negative photoresponse:

Recently, Talapin et al. proposed a model to explain the negative photoconductivity in the research of InAs nanocrystal film (W. Y. Liu, J. S. Lee and D. V. Talapin *J. Am. Chem. Soc.* 2013, **135**, 1349), in which donorlike surface defect state form a localized level (D_{ss}) presumably located above the mobility edge. Photo-induced trapping of mobile electrons on localized level (D_{ss}) resulted in negative photoconductivity. Such donorlike surface state has been observed in semiconductor nanocrystals (a) M. Shim and P. Guyot-Sionnest, *Nature* 2000, **407**, 981; b) D. Y. Petrovykh, M. J. Yang and L. Whitman, *J. Surf. Sci.* 2003, **523**, 231.). This model is also a reasonable explanation for the experimentally observed negative photoresponses in this work. We presume that such donorlike surface state is also formed in UCNPs and MoS₂ after



surface treatment and locate above the mobility edge (Figure 3b). Upon 980 nm irradiation, mobile electrons get energy and are excited. As the excitation energy exceeded the energy difference between the mobility edge and D_{ss} level, mobile electrons are promoted and trapped at D_{ss} level (k1). The electron trapped in D_{ss} states get released under thermal fluctuation and nonradiatively recombine with the hole in valence band (VB), which reduces the number of carriers of materials as k2 process shown in Fig. 3b (W. Y. Liu, J. S. Lee and D. V. Talapin *J. Am. Chem. Soc.* 2013, **135**, 1349), thus decreasing the conductivity. Excited energy is dissipated as heat in the lattice. The trapped excited-electron can also partially relax into the conduction band (k3, CB). For an upconversion involved process, Er^{3+} ion in $NaYF_4:Yb,Er$ UCNPs convert 980 nm infrared excitation into high-energy photons (UV and visible), which can also effectively excite mobile electrons and decrease conductivity *via* k1 and k2 processes. When infrared light is off, electrons are no longer trapped and the conductivity is restored. Increasing the ratio of MoS_2 in hybrid composites may increase D_{ss} surface state due to the large specific area of nanosheet structure, thus causing stronger negative photoresponse. The detailed mechanism is still under investigation.