

## Electronic Supplementary Information

### **Heterostructures NaGdF<sub>4</sub>:Yb,Er anchored on MIL-101 for promoting photoelectronic response and photocatalytic activity**

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#### **1. Materials and Methods**

##### **Materials**

GdCl<sub>3</sub>·6H<sub>2</sub>O (99%), YbCl<sub>3</sub>·6H<sub>2</sub>O (99.9%), ErCl<sub>3</sub>·6H<sub>2</sub>O (99.9%) were purchased from Sigma-Aldrich. Oleic acid (90%), 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC) acid (99%) was bought from Aladdin. 1-octadecene (90%) were from Macklin. Ammonium fluoride (NH<sub>4</sub>F), sodium hydroxide (NaOH), cyclohexane, Chromicnitrate nonahydrate (99.9%), methanol, N,N-Dimethylformamide (DMF) and ethanol were purchased from Sinopharm chemical reagent Beijing Co., Ltd. Doubly distilled water was used in all experiments. All chemicals company without further purification.

##### **Experimental method synthesis of NaGdF<sub>4</sub>:Yb,Er upconversion nanoparticles**

GdCl<sub>3</sub>·6H<sub>2</sub>O (0.78 mmol), YbCl<sub>3</sub>·6H<sub>2</sub>O (0.2 mmol) and ErCl<sub>3</sub>·6H<sub>2</sub>O (0.02 mmol) were mixed with 8 mL oleic acid and 12 mL octadecene (ODE) in a 100 mL flask. The solution was heated to 150 °C to form a clear and homogeneous solution, and then cooled down to 50 °C, 9 mL methanol solution containing NaOH (2.5 mmol) and NH<sub>4</sub>F (4 mmol) was added into the flask and stirred for 30 min. Subsequently, the system was slowly heated to 110 °C to evaporate off the methanol and residual

moisture, degassed at 110 °C for 20 min. Then it heated to 300 °C and maintained for 1.5 h under nitrogen protection. After naturally cooling down, the solution was washed with ethanol for three times, and dissolved in 10 mL cyclohexane before further treatment.

### **Synthesis of MIL-101**

2.0 g  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.83 g  $\text{H}_2\text{BDC}$  were added to 100 mL of water. The mixture was stirred for 30 min, then poured into a 100 mL Teflon-lined stainless steel autoclave and heated at 260 °C for 16 h. After being naturally cooled to room temperature, the resulting dark green mixture was filtered using a sand core funnel to remove unreacted terephthalic acid. The obtained MIL-101 was washed three times with ethanol and DMF, and the obtained product was dissolved in 50 mL of DMF.

### **Synthesis of MIL-101(Cr)/ $\text{NaGdF}_4\text{:Yb, Er}$ Composites**

In a general procedure, firstly, various quantity (1mL, 2mL, 3mL, 4 mL) of UCNPs (0.1mmol/mL) were dissolved in 10 mL of ethanol. And then above solution was mixed the UCNPs obtained with 15mL of MOF (0.01 mol/mL). The solution was stirred for 30 min for mixed fully. The resulting suspension was stirred for 24 h at 40 °C to make the full combination of MOF and UCNP, then centrifuged and washed three times to obtain the product. Finally, the obtained product was dried at 100 °C for 8 h under vacuum.

### **Photocurrent test**

Photocurrent measurements were performed on CHI660E electrochemical work station (Chenhua Instrument, China) in a conventional three electrode configuration with a Pt foil as the counter electrode and a Ag/AgCl (saturated KCl) as the reference electrode. A 500W xenon lamp served as a light source, 0.1 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. The working electrodes were prepared as follows:

10 mL of the prepared photocatalyst (MIL-101/UCNPs) powder was added to the trenol, ground for ten minutes, and then the slurry was evenly spread on a 1.0 cm × 1.0 cm conductive glass, and dried in air. The photoresponse of the samples as light on and off were measured at 0.0 V.

### **Photocatalytic Measurement**

In a typical experiment, 25 mL of the dye solution was loaded into a 100 mL breaker placed in a circulating water system. Next, 25 mg of UCNPs, MIL-101 and MIL-101/UCNPs were separately added to the solution and stirred in the dark for 30 minutes to achieve an adsorption-desorption balance. Thereafter, the solution was exposed to an ultraviolet lamp (300 W) for 5 hours, the real-time concentration of the dye molecules was monitored by UV-Vis spectrometer every hour.

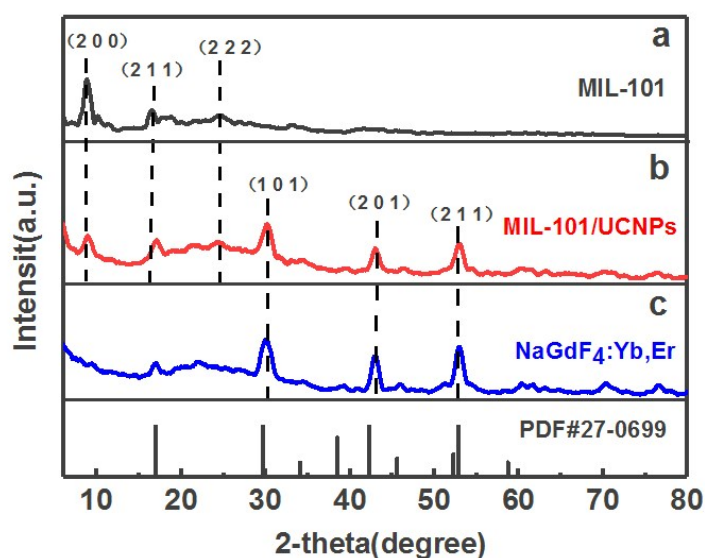
## **2. Characterization**

The X-ray diffraction (XRD) pattern was recorded on a D8 (Bruker, Germany) X-ray diffractometer with graphite monochromator Cu Ka radiation ( $\lambda=1.54178$ ). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) image and electron diffraction X-ray (EDX) mapping patterns were performed on a JEM-2010HR field emission transmission electron microscope (JEOL, Japan). A diode laser 980 nm was used as the pump source, upconversion emission spectra were recorded by CARY Eclipse fluorescence spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-2450 UV-vis spectrometer. The photocurrent measurements were performed on a CHI660D electrochemical workstation (Chenhua Instrument, China). All the measurements were performed at room temperature.

## **3. Analysis**

### **XRD analysis of UCNPs, MIL-101 and heterostructure composites**

Fig. 1 shows the XRD patterns of nanosheets prepared before and after the combination of MOF and UCNPs. All of the diffraction peaks from primitive UCNPs nanoplates (Fig. S1c) can be clearly indexed to pure  $\beta$ -phase UCNPs crystal (PDF#27-0699). The peaks at  $30.1^\circ$ ,  $42.7^\circ$ , and  $52.8^\circ$  ( $2\theta$  degree) are consistent with the (101), (201), and (211) planes of UCNPs crystal. After the combination of MOF and UCNPs, the sample exhibits another set of XRD peaks in addition to those from the UCNPs nanoplates (Fig. S1b). The peaks at  $9.2^\circ$ ,  $16.3^\circ$  and  $26.5^\circ$  agreed well with the XRD patterns of MIL-101 documented in the literature (Fig. S1a). Accompanied by the XRD results, the results suggest that the introduction of UCNPs in the MIL-101 affects neither their morphology nor the phase.

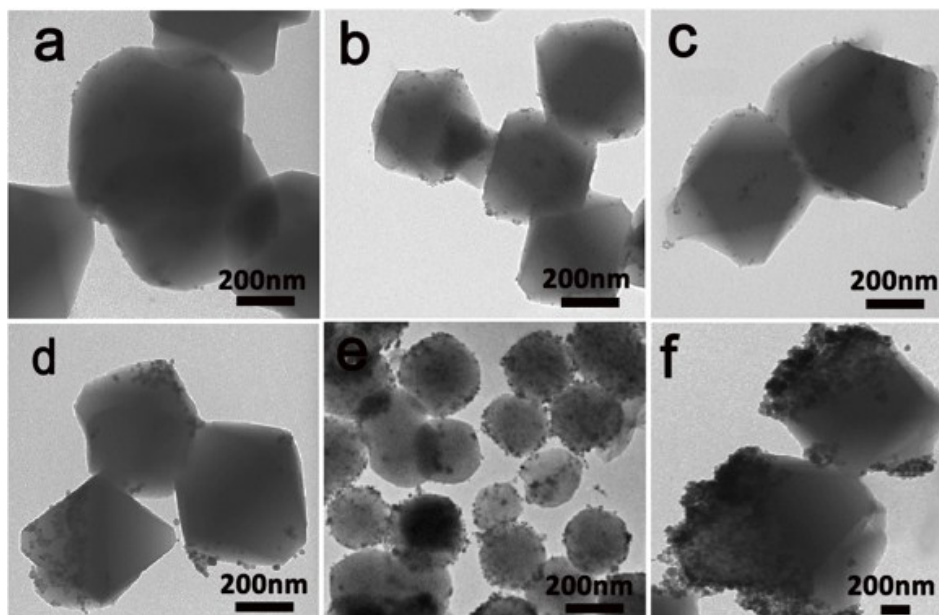


**Fig. S1** XRD patterns of the prepared (a) MIL-101, (b) MIL-101/UCNPs, (c) UCNPs.

### TEM images of composites with different amounts of UCNPs

Fig. S2 shows a TEM image of a heterogeneous composite with different amounts of UCNPs. It can be seen that when the doping amount is 1 mL and 2 mL, the loading of UCNPs is too low and the distribution is not uniform. When the doping amount of UCNPs is 4mL, UCNPs agglomerate on the surface of MOF, and the dye molecules cannot fully contact with the surface of MIL-101, which affects the subsequent catalytic reaction. Therefore, the doping amount of 3 mL is the best doping amount in

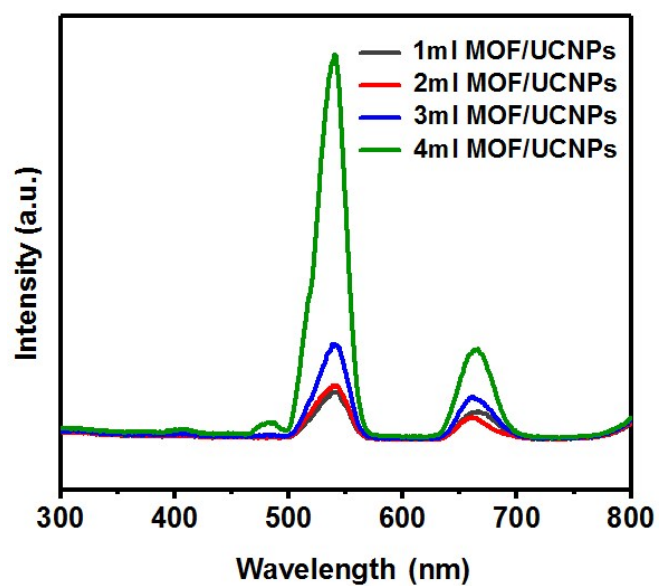
both morphology and performance.



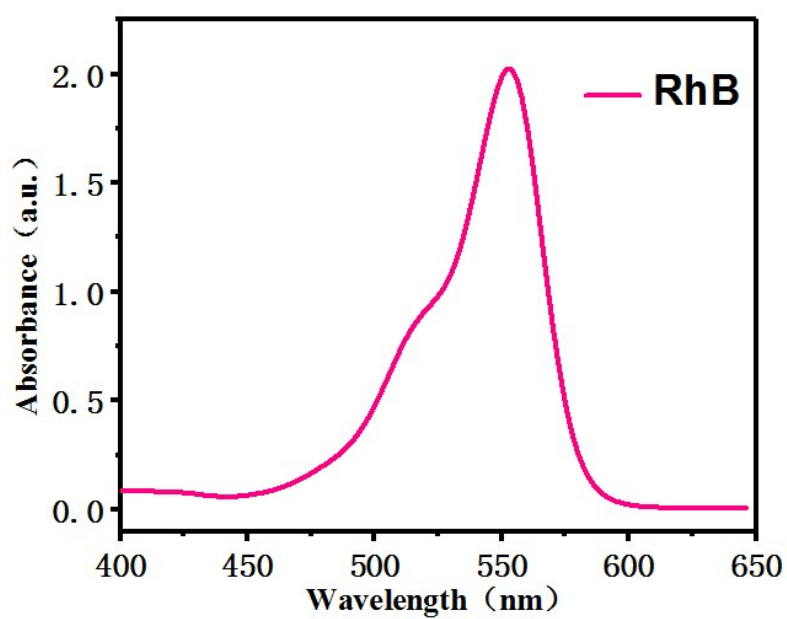
**Fig. S2** (a-f) TEM images of MIL-101/UCNPs samples, the doping amount of UCNPs: (a,b) 1mL; (c,d) 2mL; (e,f) 4mL.

### **UC fluorescence analysis of composites with different amounts of UCNPs.**

Fig. S3 shows the upconversion fluorescence intensity of heterogeneous composites with different amounts of UCNPs. It can be observed that as the UCNPs increase, the up-conversion fluorescence of the composite shows an increasing intensity. When the doping amount is 4 mL, the up-conversion fluorescence intensity is greatly improved. This is because the excessive amount of UCNPs causes polymerization on the surface of MIL-101, which exhibits strong fluorescence intensity and cannot be absorbed by MIL-101.



**Fig. S3** UC spectra of heterogeneous composites with different amounts of UCNPs.



**Fig. S4** UV-visible absorption spectrum of RhB.

## Reference

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- (2) D. K. Wang, R. K. Huang, W. J. Liu, D. R. Sun; and Z. H. Li, *ACS. Catal.*, 2014, **4**, 4254.