

## Supporting Information

### **MOFs as electron-transfer-bridge for dye photosensitizer and low cost Ni<sub>2</sub>P co-catalyst to increased photocatalytic H<sub>2</sub> generation**

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## 1. Synthesis of UiO-66 octahedrons

The catalyst UiO-66 was prepared following the previous protocols with slight modification.[1] In a typical synthesis, 200 mL DMF solution containing  $ZrCl_4$  (204.0 mg, 8.75 mM) and 1,4-benzenedicarboxylic acid (BDC) (145.0 mg, 8.75 mM) were added by acetic acid (24 mL) to obtain the homogeneous solution. The as-made solution was sealed and then put into an oven for reaction at 120 °C for 24 h. The resultant product was collected by centrifugation, washed with DMF for three times, and then immersed in methanol for three 24 h periods to replace the DMF within MOFs. Finally, UiO-66 was activated by removing the methanol solvent under vacuum for 12 h at 150 °C.

## 2. Synthesis of UiO-66/Ni(OH)<sub>2</sub> composites

$Ni(OH)_2$  was hydrothermally grown upon the surface of UiO-66 octahedrons to obtain UiO-66/ $Ni(OH)_2$  composite. In a typical experiment, 100 mg of UiO-66 was ultrasonically dispersed into a mixed solution of ethanol (30 mL) and water (0.625 mL) for 0.5 h. The  $Ni(OAc)_2 \cdot 4H_2O$  with desirable amount (1.75mg, 3.5mg, 7.0mg and 13.8mg) and 0.625 mL of  $NH_4OH$  are then added at room temperature. After 30 min stirring, the suspension was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated to 180 °C for 8 h. The resultant product was centrifugally separated, washed with water and ethanol, and finally dried at 80 °C in oven to obtain UiO-66/ $Ni(OH)_2$  composite.

## 3. Synthesis of UiO-66/ $Ni_2P$ hybrid photocatalysts

UiO-66/ $Ni_2P$  hybrid photocatalysts were prepared by phosphating the UiO-66/ $Ni(OH)_2$  composites at 300 °C for 2 h. Typically, 100 mg of UiO-66/ $Ni(OH)_2$  composite and 50 mg of sodium hypophosphite were mixed and grinded by using a mortar and pestle. The mixture was then thermally treated at 300 °C for 2 h in Ar atmosphere. The obtained product was washed with water and ethanol, and dried at 80 °C overnight in oven to the final UiO-66/ $Ni_2P$ -xwt% ( $x=0.35, 0.69, 1.38, \text{ and } 2.76$ , respectively), where  $x$  is the mass content of  $Ni_2P$  in UiO-66/ $Ni_2P$ .

## 4. Characterization

X-ray powder diffraction (XRD) analysis was carried out on a DX-2700X-ray diffractometer using  $Cu K\alpha_1$  radiation. The voltage and current were 40 kV and 40 mA, respectively. Morphology and microstructure were observed by field emission scanning electron microscopy (SEM: Hitachi S-4800) and transmission electron microscopy (TEM:JEM-2100). FT-IR spectra were collected on an Vertex80+Hyperion2000 spectrometer. UV-vis diffuse reflectance spectra (DRS) were recorded on HITACHI3900 UV-Vis spectrophotometer.  $BaSO_4$  was used as a reflectance standard. Photoluminescence (PL) measurements were performed on a HITACHI F-4600 fluorometer. X-ray photoelectron spectra (XPS) were recorded on ESCALAB250Xi spectrometer (Thermo-VG Scientific) using Mg  $K\alpha$  radiation (1253.6 eV).

## 5. Photocatalytic measurements

Photocatalytic H<sub>2</sub> generation was tested in a 70-mL closed Pyrex reactor with a quartz window for passing visible light. In a typical photocatalytic reaction, UiO-66/Ni<sub>2</sub>P photocatalysts (10 mg) and Erythrosin B dye (30 mg) was dispersed in 10 mL TEOA solution (10 vol%). Prior photocatalytic H<sub>2</sub> generation reaction, the suspension was bubbled with argon for 30 min to drive off residual air inside the reactor. A 300 W Xe lamp was used to evoke the photocatalytic H<sub>2</sub> generation. A 420 nm cutoff filter was equipped to offer the visible light. The generated gases were sampled intermittently and analyzed by a gas chromatography (GC-1690, Kexiao, China) with a TCD detector.

## 6. Photoelectrochemical measurements

Photoelectrochemical measurements were tested using a three-electrode configuration in mixed solution of 10% (v/v) TEOA and 0.1 mol/L Na<sub>2</sub>SO<sub>4</sub> at pH = 10 by an electrochemical analyzer (CHI-660D, Chen hua, China). The electrodes were prepared by dropping the sample suspension (100 μL) onto the surface of ITO glass. The suspension was prepared as follows: samples (5 mg) were added into ErB solution (1 mL, 3.4 × 10<sup>-3</sup> M), and then 50 μL Nafion (5 vol%) solution was added under the ultrasonication for 30 min. The as-made electrodes, Hg/Hg<sub>2</sub>Cl<sub>2</sub>, and Pt were working, reference, and counter electrode, respectively. Photocurrent densities were measured using under the visible light irradiation, and the photoresponse were measured with chopped light at 0.5 V bias. The electrochemical impedance spectroscopy (EIS) was performed with a bias potential of -0.2 V at frequency range from 10<sup>-2</sup> to 10<sup>6</sup> Hz. The cathodic polarization curves were obtained using the linear sweep voltammetry (LSV) technique with a scan rate of 5 mV<sup>-1</sup>.

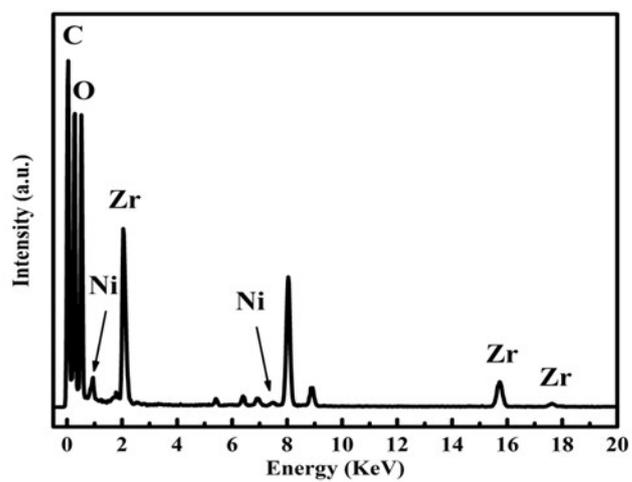


Fig. S1 EDS spectrum of UiO-66/Ni(OH)<sub>2</sub>

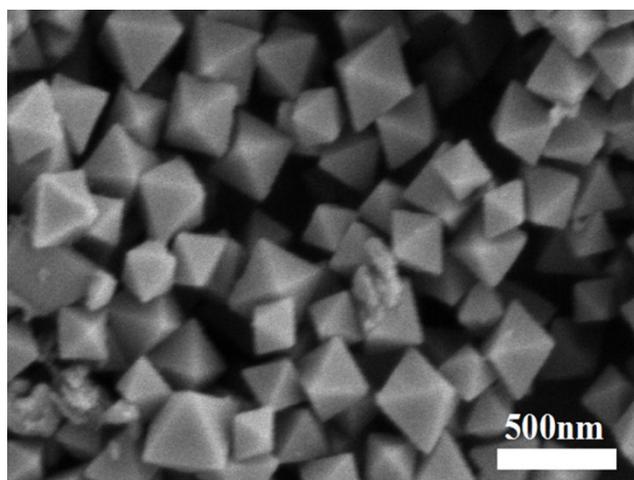
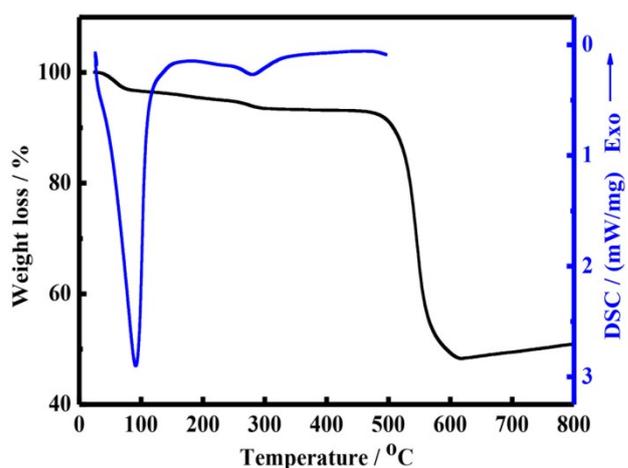
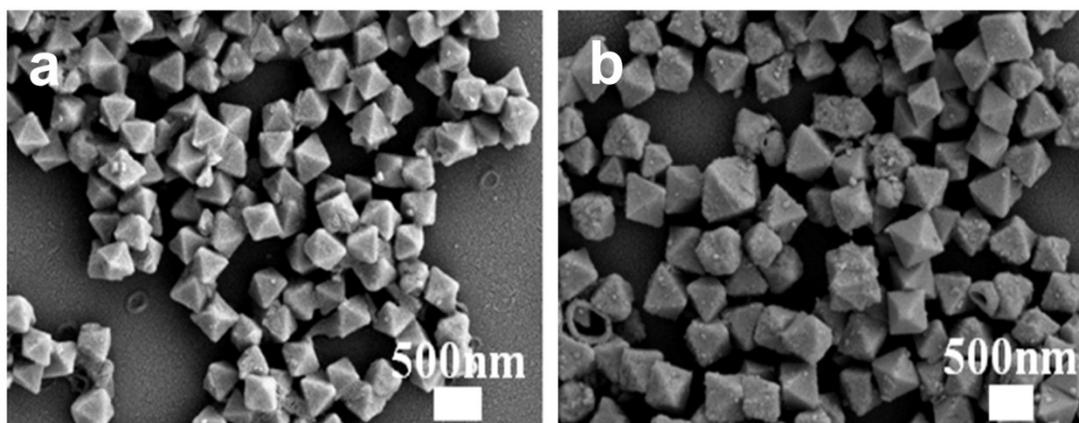


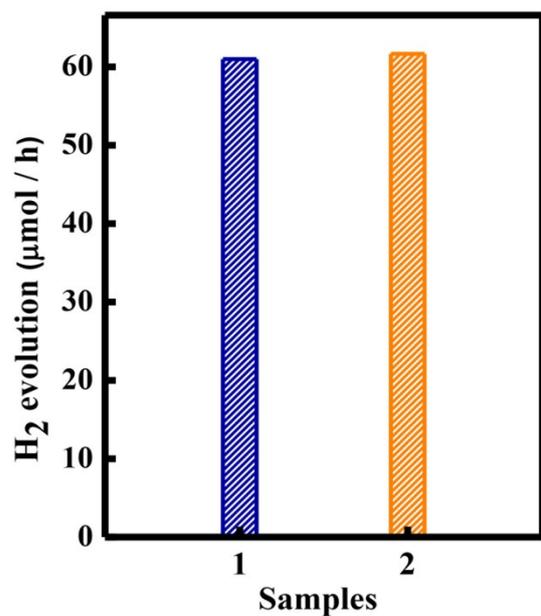
Fig. S2 SEM image of UiO-66 after thermally treated at 300 °C for 2 h in Ar atmosphere.



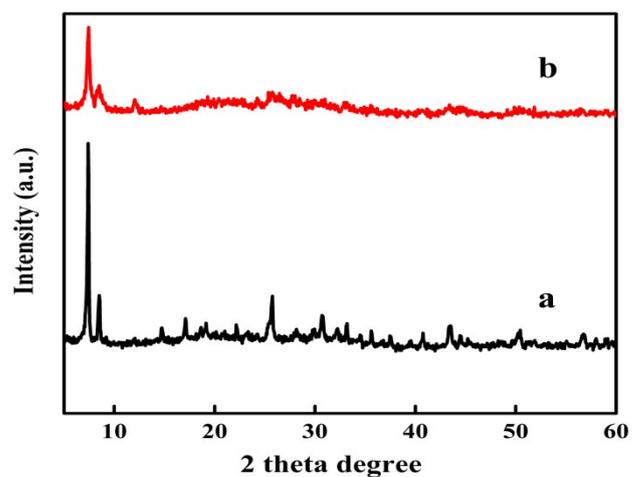
**Fig. S3** TG-DSC thermograms of UiO-66, showing the weight loss and corresponding enthalpic change during heating up UiO-66 in N<sub>2</sub> atmosphere. The ~ 8 wt% loss less than 100 °C should be caused by the adsorbed water loss, as evidenced by the very distinct endothermic peak shown in Fig. R1. The ~5 wt% loss at 300 °C results from the removal of guest methanol molecules as methanol was used to replace DMF in the synthesis of UiO-66 MOFs, as signified by the small endothermic peak in DSC curve.



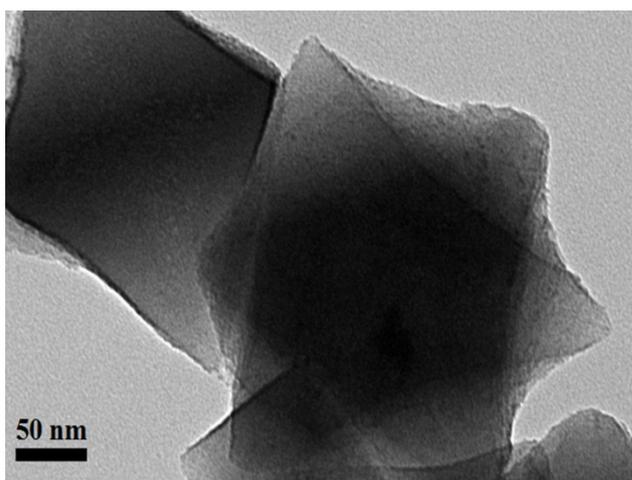
**Fig. S4** SEM image of (a) UiO-66/Ni<sub>2</sub>P-0.35 and (b) UiO-66/Ni<sub>2</sub>P-2.76 samples.



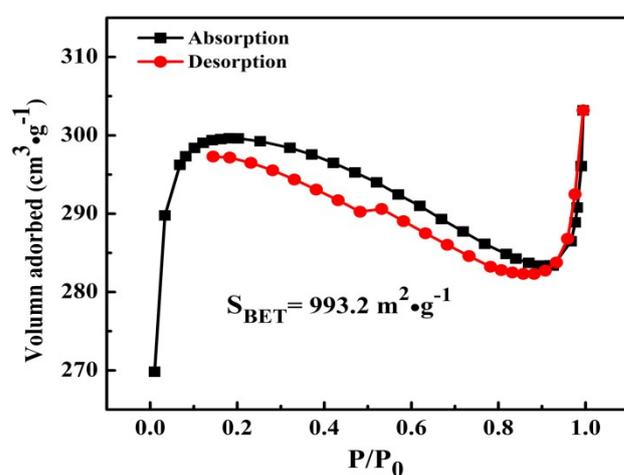
**Fig. S5** Effect of  $\text{NaH}_2\text{PO}_2$  on photocatalytic  $\text{H}_2$  generation on UiO-66/ $\text{Ni}_2\text{P}$ -0.69 hybrid. Sample 1: addition of 25 mg  $\text{NaH}_2\text{PO}_2$ . Sample 2: no  $\text{NaH}_2\text{PO}_2$  addition.



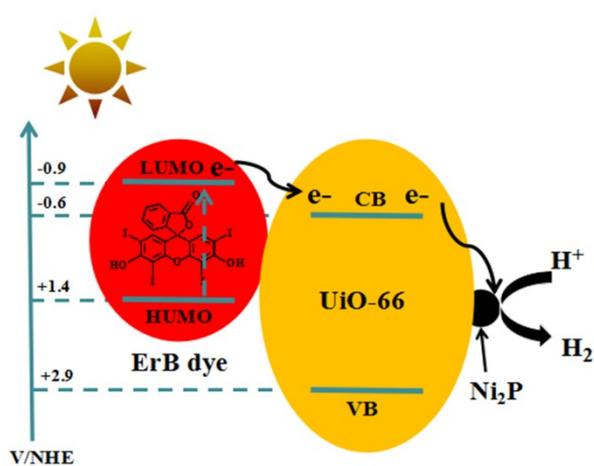
**Fig. S6** XRD patterns of UiO-66/ $\text{Ni}_2\text{P}$   $x=0.69\%$  hybrid (a) before and (b) after  $\text{H}_2$  generation for 12 h.



**Fig. S7** TEM images of after H<sub>2</sub> production for 12 h. No aggregation, phase and morphology change for Ni<sub>2</sub>P were detected after 12 h long-term H<sub>2</sub> generation reactions.



**Fig. S8** N<sub>2</sub> adsorption–desorption isotherms of produced UiO-66 octahedrons.



**Fig. S9** Schematic illustration of the charge transfer route in the system of ErB/UiO-66/Ni<sub>2</sub>P.

**Reference:**

[1] J.D. Xiao, Q. Shang, Y. Xiong, Q. Zhang, Y. Luo, S.H. Yu, H.L. Jiang, Boosting Photocatalytic Hydrogen Production of a Metal-Organic Framework Decorated with Platinum Nanoparticles: The Platinum Location Matters, *Angewandte Chemie*, 128 (2016) 9535-9539.