Supplementary Materials

1 *Materials and methods*

1.1 Chemicals

Indium nitrate ($In(NO_3)_3 \cdot xH_2O$), 2-amino-phthalic acid (NH_2-BDC), N,N-Dimethylformamide (DMF), potassium dichromate ($K_2Cr_2O_7$), ethanol, and 1,5-Diphenylcarbohydrazide (DPC) were acquired from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Disodium ethylene diamine tetra acetate (EDTA-2Na), Tert-butanol (TBA), p-benzoquinone (BQ), and Potassium bromate ($KBrO_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents and solvents were of analytical grade and did not require additional purification. Copper Wire Cloth (copper mesh) (60 mesh, McMaster-Carr) was employed.

1.2 Synthesis of MIL-68(In)-NH_2 and MIL-68(In)-NH_2/Cu

Synthesis of MIL-68(In)-NH_2

The synthesis of MIL-68(In)-NH_2 followed a relevant literature[1] with slight modification (Scheme S1). Typically, $In(NO_3)_3 \cdot xH_2O$ (3.170 g, 8.1 mmol) and NH_2-BDC (0.48 g, 2.7 mmol) were added to 25.8 mL DMF and stirred for 30 minutes. The mixture was then sealed into a 50 mL Teflon-lined autoclave and heated at 125 °C for 10 h. Subsequently, the obtained products were collected by centrifugation after cooling to room temperature. The powder product was washed three times with DMF and methanol in turn, and dried under vacuum at 60 ℃ for 24 h.

Synthesis of MIL-68(In)-NH_2/Cu

The precursor ratios need to be adjusted due to the need to control the growth state and growth thickness of the crystals so that the MOF grows uniformly on the copper mesh. To remove oil and impurities from the surface of the copper mesh, a copper mesh with the dimension of 3 cm × 3 cm was sequentially placed in 100 mL of acetone (C_3H_6O), ethanol (C_2H_5OH), and deionized water for ultrasonic cleaning for 20 minutes. It was then soaked in 100 mL HCl (1mol·L-1) for 10 minutes to remove the oxide layer, rinsed several times with deionized water, and finally dried under 80℃ for 6 hours before use[2].

The Synthesis method of MIL-68(In)-NH_2/Cu was similar to that of MIL-68(In)-NH_2. Briefly, $In(NO3)_3 \cdot xH_2O$ (1.056 g, 2.7 mmol), NH_2-BDC (1.44 g, 8.1 mmol) and copper mesh were added to 25.8mL DMF and stirred for 30 minutes. After that, the mixture was sealed in a Teflon-lined autoclave and heated at 125 ℃ for 10 hours. The mesh was then cooled down to room temperature and ultrasonically washed three times with DMF and methanol. Finally, the mesh was dried under vacuum circumstances at 60 ℃ for 24 h.

1.3 Analysis and Characterization

Using X-ray diffraction (XRD, Smart Lab SE) with Cu Kα radiation (40kV, 100mA), the crystal phase structures of each sample were determined. Morphologies and structures were analyzed via scanning electron microscopy (SEM, JEOL JSM-7500F). Surface functional groups were examined using Fourier transform infrared spectroscopy (FT-IR, FTIR-650) after uniform dispersion in potassium bromide. UV-visible diffuse reflectance spectra (UV-vis DRS, SolidSpec-3700) were recorded from

200 to 800 nm using barium sulfate as a reference. Specific surface areas and pore volumes were determined by Brunauer-Emmett-Teller (BET, ASAP 2460 2 02) analysis at 77 K. Surface chemical composition and electronic states were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB). Mott-Schottky analysis, electrochemical impedance spectroscopy (EIS), and photocurrent spectroscopy (PC) were conducted with an electrochemical workstation (CHI660E) using a 0.5 M sodium sulfate aqueous solution and a 300 W Xe-lamp (PLS-SXE300D) with the emitting wavelength in the range of 320~760 nm as the electrolyte and light source, respectively. Zeta potential versus pH on the sample surface was measured using a zeta potential analyzer (ZETASIZER Nano series).

1.4 Photocatalytic experiment

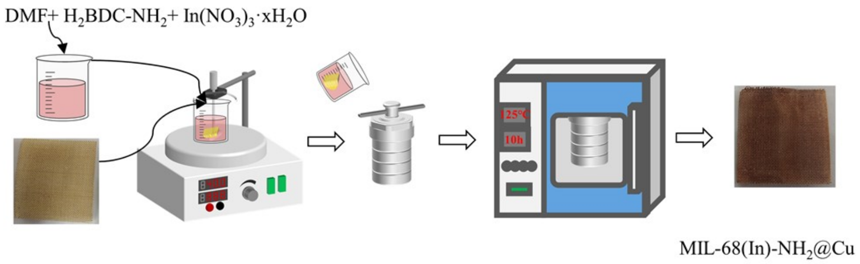
Using a cyclic reactor, the photocatalytic efficiency of MIL-68(In)-NH_2 and MIL-68(In)-NH_2/Cu was assessed for the reduction of Cr(VI) (Scheme S2). Operational parameters were set as follows: current intensity of 15 A (with a preferred operating range of 15±1 A) and peristaltic pump speed at 80 rpm/min.

Within the photocatalytic reaction vessel, a piece of MIL-68(In)-NH_2/Cu measuring 15 mm × 15 mm was fixed. A solution of $K_2Cr_2O_7$ (300 mL, 50 mg/L) was added to the reflux vessel. By adjusting peristaltic pump speeds, the solution circulated from the lower to upper parts of the reactor and back, ensuring continuous flow. To achieve adsorption-desorption equilibrium, the system was allowed to equilibrate for one hour in complete darkness. Subsequently, the xenon lamp illuminated the system, and 3 mL of suspension was collected at various time intervals from the reflux vessel.

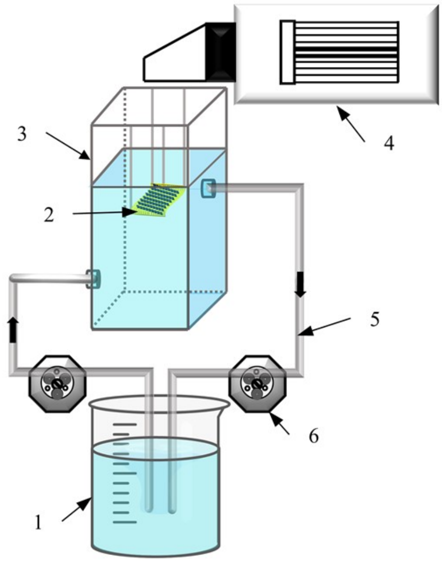
After filtering the suspension through a 0.22 μm needle filter, the concentration of Cr(VI) was determined using a UV–vis spectrophotometer (DPC colorimetric method) at the maximum absorption wavelength of 540 nm. The removal rate of Cr(VI) was calculated using the formula:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

where $R(\%)$ represents the removal rate, C_0 is the initial concentration of Cr(VI), and C_t is the concentration of Cr(VI) at time t.



Scheme S1 Schematic of the preparation of MIL-68(In)-NH_2/Cu



Scheme S2 Photocatalytic cycle reaction system: (1) reflux vessel, (2) the photocatalytic material, (3) photocatalytic reaction vessel, (4) xenon lamp light source, (5) connecting pipes, (6) peristaltic pumps

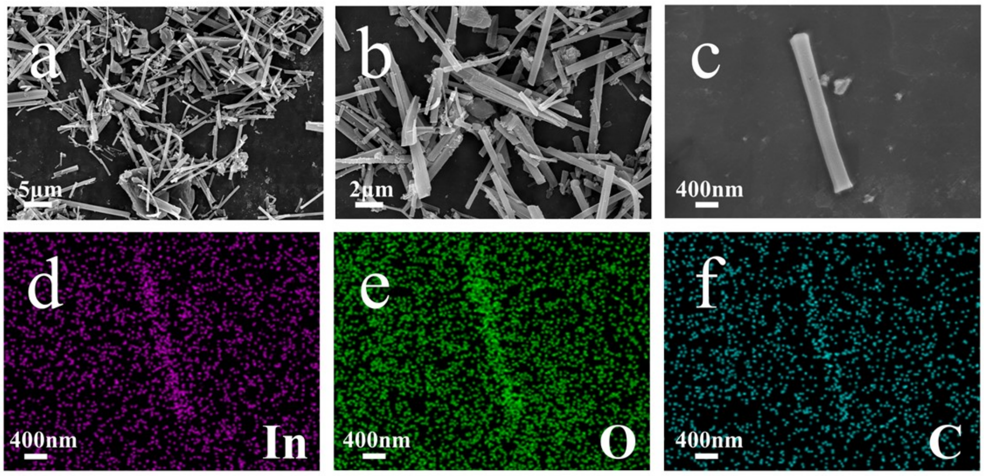


Fig. S1 SEM images of (a~c) MIL-68(In)-NH_2, (d~f) EDS images of MIL-68(In)-NH_2

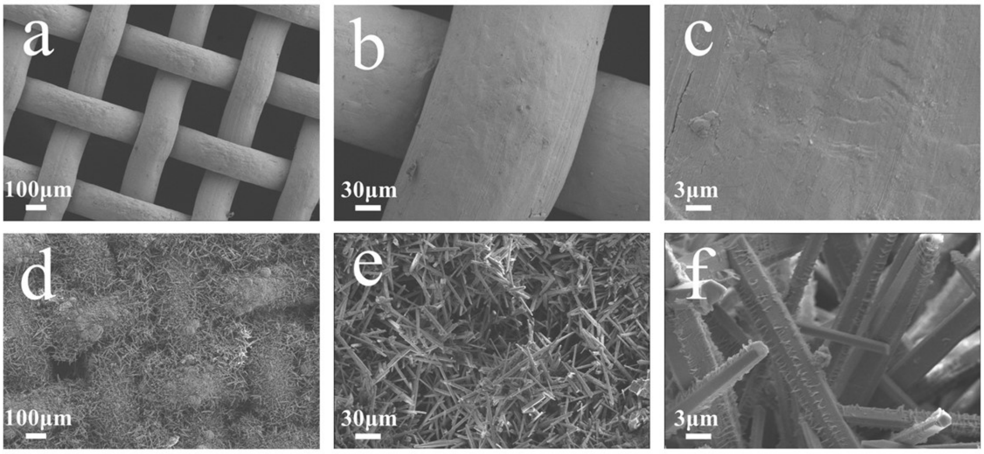


Fig. S2 SEM images of copper mesh (a~c) and MIL-68(In)-NH$_2$/Cu (d~f)

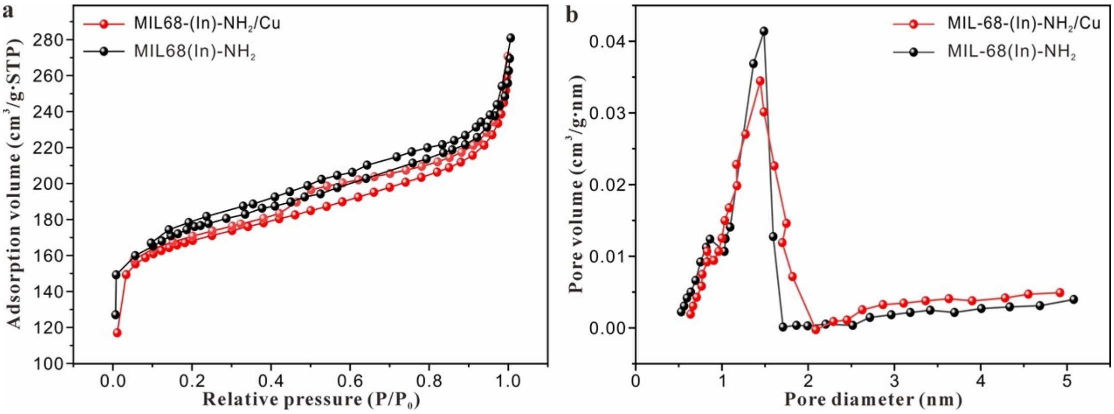


Fig. S3 Nitrogen absorption-desorption isotherms(a) and Pore size distribution profiles(b) of the samples

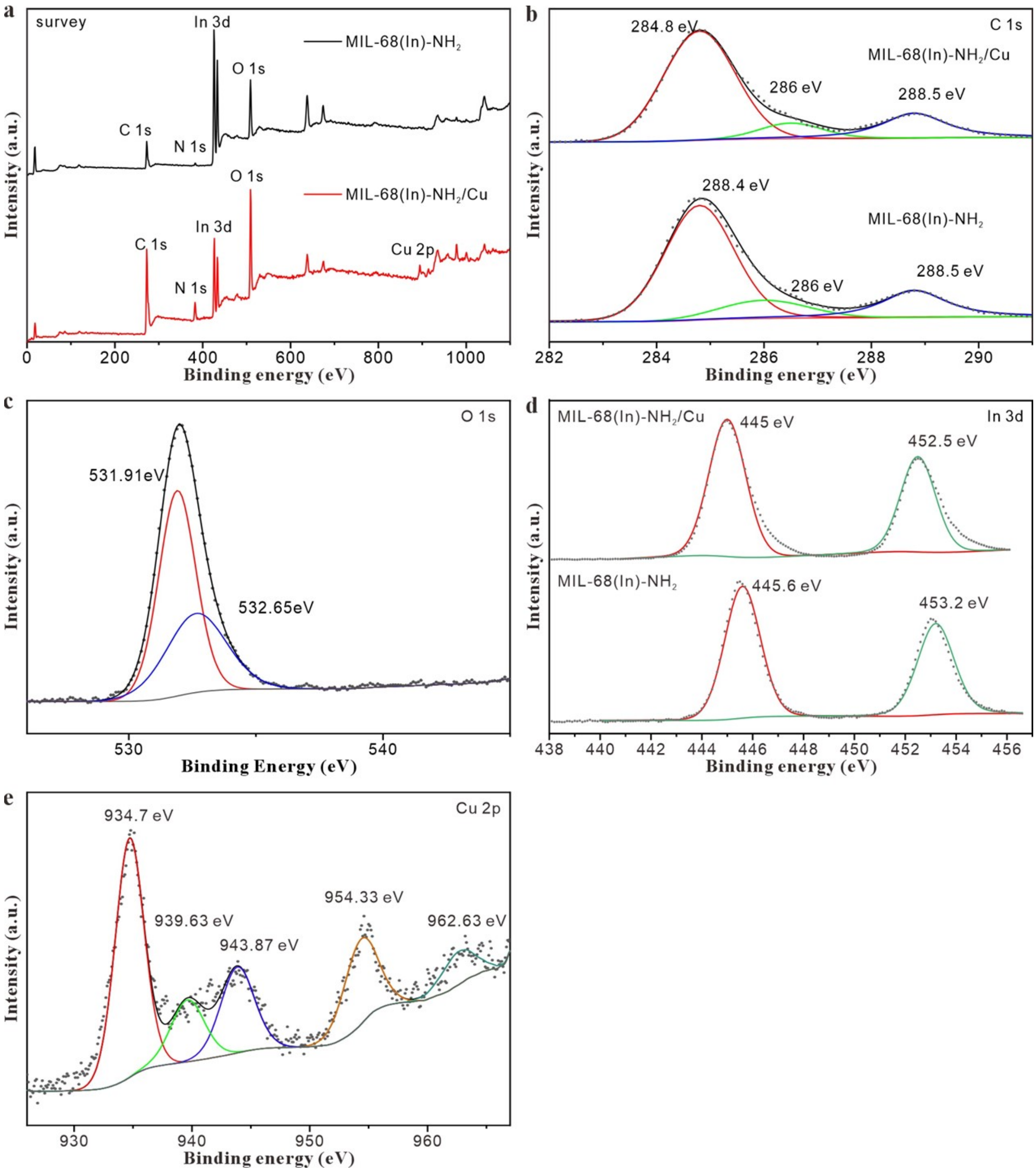


Fig. S4 XPS spectra of samples: (a) XPS fully scanned spectrum; (b) C 1s spectra; (c) O 1s spectra; (d) In 3d spectra; (e) Cu 2p spectra.

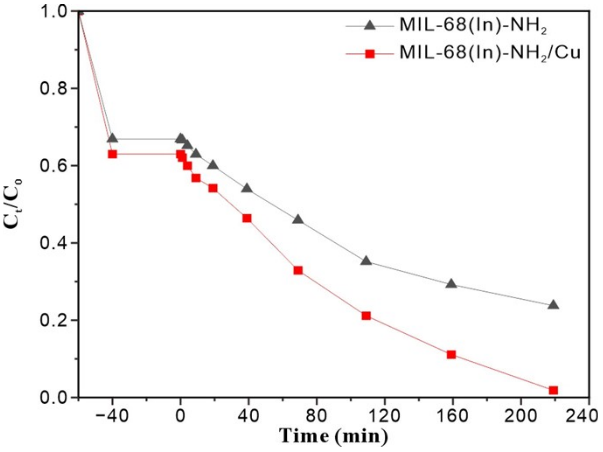


Fig. S5 The photocatalytic efficiency of MIL-68(In)-NH2 and MIL-68(In)-NH2/Cu on Cr (VI).

Table. S1 Specific surface area and pore volume of MIL-68(In)-NH_2 and MIL-68(In)-NH_2/Cu

photocatalytic material	specific surface （m^2/g）	pore volume （cm^3/g）	
		total pore volume	micropore
MIL-68(In)-NH_2	642.4255	0.436127	0.23501
MIL-68(In)-NH_2/Cu	550.9214	0.410507	0.18892

Table S2. Comparison of reported photocatalytic materials for reduction of Cr(VI)

Photocatalyst	Form	Time	Light source	Reduction efficiency	Reference
Acid-HTCC	powder	100min	300 W xenon lamp (λ >420nm)	90%	3
$CuNb_2O_6$/g-C_3N_4	powder	150min	500W xenon lamp (250< λ <2500)	92.80%	4
Bi_2S_3-ZnS/$MoSe_2$	powder	180min	500W xenon lamp (λ >420nm)	95.4%	5
$SnIn_4S_8$/$Cd_{0.5}Zn_{0.5}S$	powder	30min	300W xenon lamp	91.1%	6
MIL-68(In)-NH_2/Cu	reticulate	160min	300W xenon lamp	98.28%	This work

References

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