$Cu/Cu_2O/NH_2$-MIL-88B (Fe) heterojunction as the photocatalyst to remove hexavalent chromium heavy metal ions in water

Chemicals

2-aminoterephthalic acid (NH_2-BDC), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), Copper nitrate ($Cu(NO_3)_2$), potassium dichromate ($K_2Cr_2O_7$), diphenylcarbazide (DPC), N,N-dimethylformamide (DMF), ethanol (CH_3CH_2OH), and methanol (CH_3OH), hydrochloric acid (HCl) were supplied by Sinopharm Chemical Reagents Limited Company and used as original form without further purification.

Characterization

The X-ray diffraction (XRD, Germany) was recorded with a LabX-6000 X-ray diffractometer. The infrared spectra were obtained by Nicolets50 Fourier transform infrared spectrometer (FT-IR, America). The morphology and microstructure of the samples were analyzed via a scanning electron microscope (SEM, S-4800, Japan) and energy dispersive X-ray (EDX) spectrometer. Also, it was characterized by a transmission electron microscope (TEM) and a high-resolution TEM (HR-TEM) using a JEM2100 transmission electron microscope (TEM, JEOL) operating at 200 kV. The N_2 adsorption-desorption isotherm and Brunauer-Emmett-Teller (BET, America) method were used to test the porous nature and surface area with Autosorb-IQ-XR. The X-ray photoelectron spectroscopy measurements were investigated, using an ESCALAB250 X-ray electron spectrometer with Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) (XPS, America). The UV-vis absorption spectra of samples were recorded by the Lambda35 UV-visible spectrophotometer (DRS, America). The photocatalytic experiments were carried out under 300W Xe lamps (CeauLight CEL-S500) with a cutoff filter of 420nm.

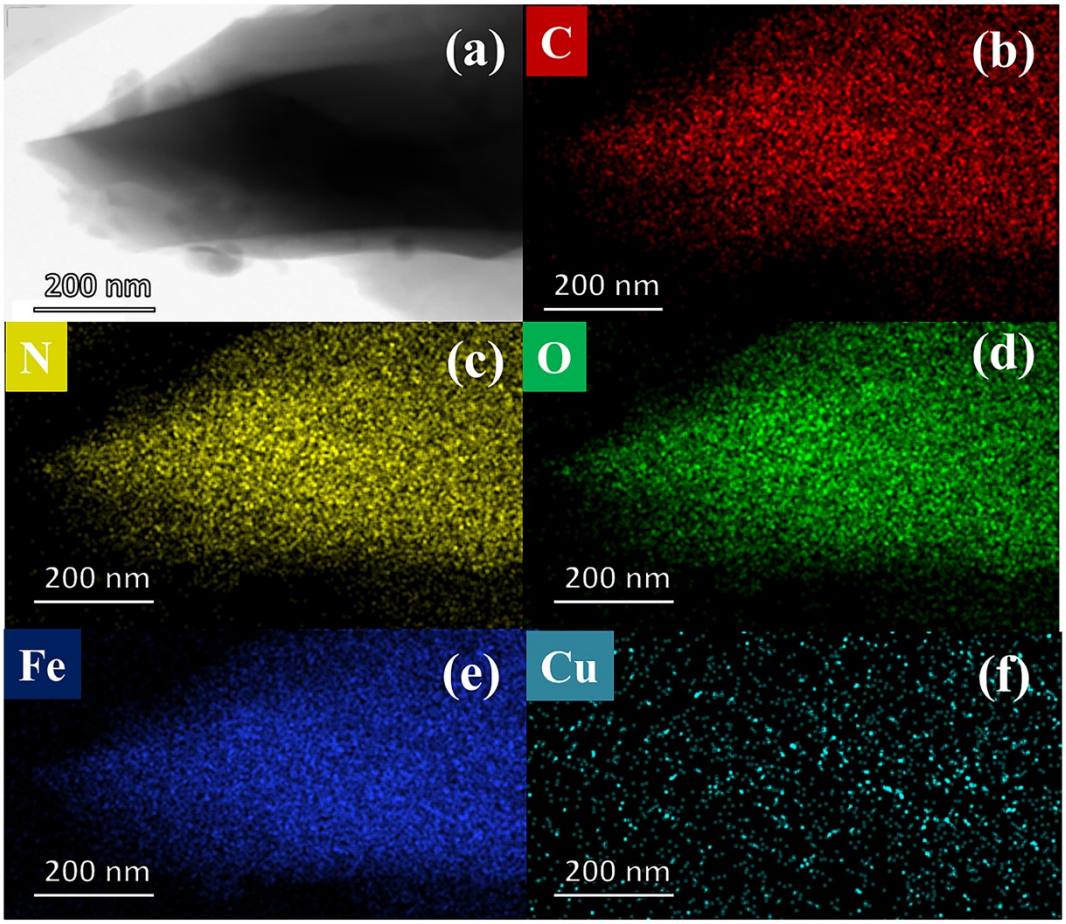
Photocatalytic activity test

At room temperature, 10 mg of catalyst was added to 50 mL of Cr(VI) (20 $mg \cdot mL^{-1}$) aqueous solution to study the photocatalytic activity, ethanol was added to the solution as hole trapping agent and the pH value was varied to 2 by adding HCl solution.The pH of the solution was adjusted to the desired value with diluted aqueous HCl and NaOH. Firstly, the mixed solution was stirred in the darkness. Take a certain amount of solution to centrifuge at regular intervals. The supernatant was filtered with a 0.22 μm syringe filter to remove suspended catalyst particles. After a certain period, it is proved that adsorption-desorption equilibrium was reached when the concentration of Cr (VI) solution did not change with time in the darkness. Then, the suspension was irradiated with a 300w Xe lamp with a UV-cutoff filter ($\lambda > 420nm$), and a certain amount of solution was taken at intervals for centrifugation, filtration, and detection. The filtered solution was measured with a UV-vis spectrophotometer for the absorbance of the DPC-Cr (VI) complex at 540 nm. At the same wavelength, the concentration of Cr (VI) was calculated according to Beer-Lambert Law. And the corresponding adsorption-reduction efficiency of Cr (VI) was calculated following the formula:

$$\text{Adsorption - reduction efficiency (\%)} = C/C_0 \times 100\%$$

Here, C: concentration of Cr (VI). C_0: initial concentration of Cr (VI). And the concentration of total Cr was determined by inductively coupled plasma (ICP).

Fig. S1 TEM and Mapping images of $Cu/Cu_2O/NH_2$-MIL-88B (Fe) (15 wt.%)



Tab. S1 BET table of $Cu/Cu_2O/NH_2$-MIL-88B (Fe) (15 wt.%) and NH_2-MIL-88B (Fe)

Samples	Surface area ($m^2 \cdot g^{-1}$)
NH_2-MIL-88B (Fe)	556.49
$Cu/Cu_2O/NH_2$-MIL-88B (Fe) (15 wt.%)	461.84

Fig. S2 XPS spectra of N 1s (a) and O 1s (b) of $Cu/Cu_2O/NH_2$-MIL-88B (Fe) (15 wt.%) samples

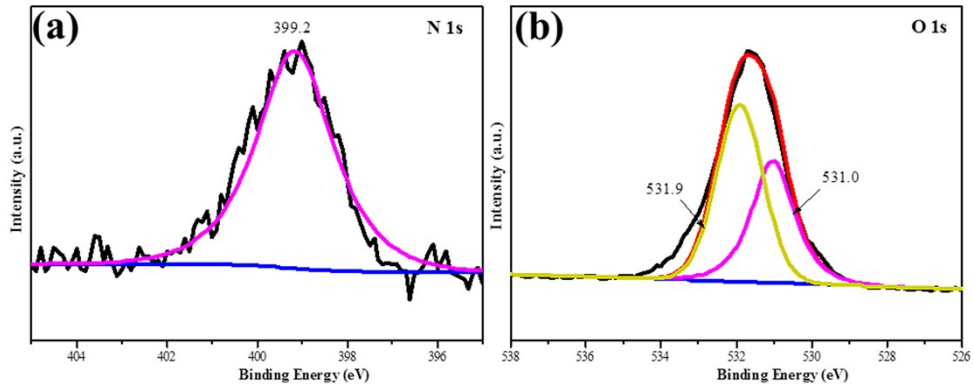


Fig. S3 XPS spectra of Fe 2p of $Cu/Cu_2O/NH_2$-MIL-88B (Fe) (15 wt.%) samples

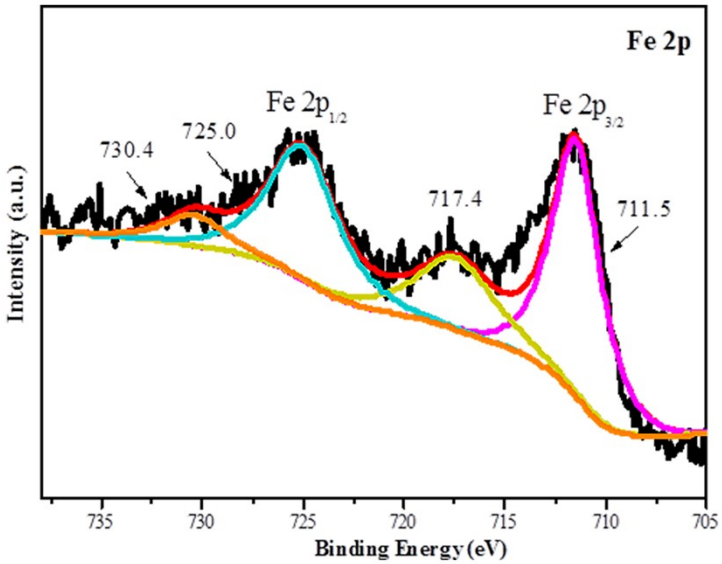
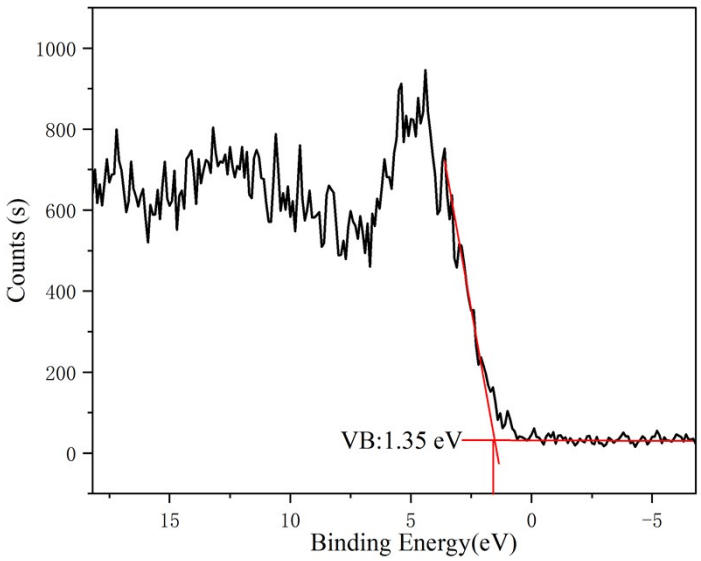


Fig. S4 XPS Valence band spectra of Cu/Cu2O/NH2-MIL-88B (Fe) (15 wt.%) samples



Tab. S2 Surface elemental and % distribution of $Cu/Cu_2O/NH_2$-MIL-88B (Fe) (15 wt.%) samples

Element	Core level	Position (eV)	Elem. comp. (At %)	Elem.distribution (wt.%)
C	1s	281.31	46.91	24.09
N	1s	395.97	4.66	2.79
O	1s	528.39	25.89	17.72
Fe	2p	708.30	18.49	44.31
Cu	2p	930.88	4.05	11.09

Tab. S3 k and R^2 of photocatalytic reduction of Cr (VI) under different conditions

Samples	k / min^{-1}	R^2
No Light	0.00202	0.80261
No Catalyst	-0.00018	0.94466
NH_2-MIL-88B (Fe)	0.00675	0.99541
Cu/Cu_2O/NH_2-MIL-88B (Fe) (15 wt.%)	0.01863	0.98479

Fig. S5 XRD spectra (a) and FT-IR spectra (b) of Cu/Cu2O/NH2-MIL-88B (Fe) samples after experiment

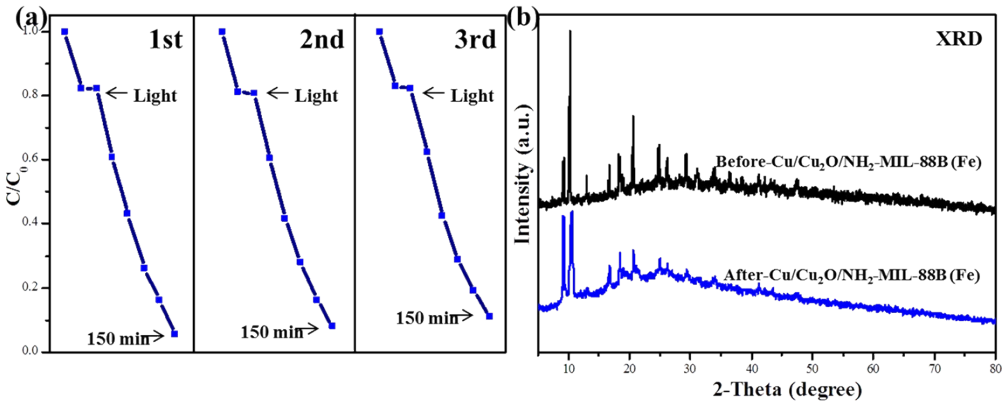


Fig. S6 Active species capture analysis