Supporting Information

Scavenger-Free and High-Efficiency Photoreduction of Concentrated Cr(VI) via MOF@COF Heterojunctions: The Role of Interfacial Charge Transfer

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Test S1. Characterizations

This study analyzed the phases of the materials using an powder x-ray diffraction (PXRD, SmartLab SE), investigated the surface chemical properties with Fourier-transform infrared spectroscopy (FT-IR, IRTracer-100), characterized the morphology and structure of the samples with scanning electron microscopy (SEM, Hitachi SU8600; Energy Spectra: Oxford Ultimax 40), determined the elemental composition and valence states with an X-ray photoelectron spectroscopy (XPS, Thermofisher escalab 250xi) spectrometer, Nitrogen adsorption and desorption measurements were done at 77 K using an TriStar II analyzer. The UV-vis diffuse reflectance spectra (DRS, Shimadzu UV-2700) were obtained by the $BaSO_4$ as a reflectance standard at room temperature. All the photoelectrochemical tests were performed on an electrochemical workstation (Chenhua CHI E660) with a standard three-electrode system. Electron spin resonance (ESR) signals were recorded with a Bruker ESR A300 spectrometer. The zeta potential of the samples was determined by a zeta potential analyzer (Zetasizer Nano ZSE). The photocatalytic chamber (CEL-LB70) and the xenon light source system (CEL-HXF300-T3) were provided by CEAULIGHT.

Test S2. Experimental Section

Synthesis of UiO-66-NH_2: UiO-66-NH_2 was synthesized following a previous report.[1] A mixture of amino terephthalic acid (NH_2-BDC, 1.242 g) and zirconium tetrachloride ($ZrCl_4$, 1.6 g) in N, N-dimethylformamide (DMF, 400 mL) was prepared. Acetic acid (HAC, 14 mL) was added to the mixture, which was then sonicated to ensure homogeneity. The resulting solution was transferred to a reactor and heated at 120 °C for 24 h. After cooling to room temperature, the solution was washed several times with fresh DMF and methanol by filtration and dried under vacuum at 70 °C for 24 hours. The pink product obtained was UiO-66-NH_2.

Synthesis of HDU-105: HDU-105 was synthesized following a previous report.[2] First, 1,3,5-Tris-(4-formylphenyl)benzene (TF) (23.42 mg, 0.06 mmol) and 2,2′-

benzothiadiene4,7-(dimethylbenzene) acetonitrile (BD) (32.97 mg, 0.09 mmol), n-BuOH (0.25 mL), o-DCB (2.25 mL) and DBU (0.5 mL) were gradually added to a 25 mL Pyrex tube. Then, the prepared mixture underwent three freeze–pump–thaw cycles followed by sealing under vacuum. Subsequently, after heating at 120 ◦C for 3 days. Finally, after drying at 100 ◦C under vacuum for 8 h, the yellowish powder, i.e., HDU-105, was successfully generated.

Synthesis of UiO-66-NH_2@HDU-105： UiO-66-NH_2@HDU-105 was synthesized via solvothermal synthesis. TF (23.42 mg, 0.06 mmol) was dissolved in a mixed solution of n-BuOH (1 mL), and UiO-66-NH_2 (56.39 ~ 563.9 mg) was added. HAC (6 M, 0.1 mL) was added and stirred for 3 hours. Afterward, BD (32.97 mg, 0.09 mmol) and 1 mL o-DCB, 0.5 mL DBU was added, and the solution was sonicated for 15 minutes to obtain a uniform suspension. The mixture was then heated at 120 °C for 72 hours, washed alternately with DMF, acetone, and methanol, and vacuum dried at 80 °C overnight to produce various composite ratios.

Photocatalytic chromium Extraction Experiment.

The whole photocatalytic reaction was carried out in a photo-catalytic reactor (CELLB70) equipped with a 300 W xenon lamp fitted with a UV cut-off filter ($\lambda > 420$ nm, with an optical power density of 397 mW/cm^2.) as a source of visible light to evaluate the photocatalyst activity. 10 mg UiO-66-NH_2, HDU-105, UiO-66-NH_2@HDU-105 powder was dispersed in 50 mL uranium solution to create a suspension. The suspension was stirred in the dark for an hour to achieve adsorption-desorption equilibrium. Afterward, experiments were conducted to reduce chromium under light conditions. During the investigation, samples were taken from the suspension at varying intervals and passed through a filter membrane with a pore size of 0.22 μm to obtain the supernatant. Using a UV-Vis spectrophotometer, the supernatant was tested for absorbance at 540 nm was measured using dibenzoyl hydrazine colorimetry (DPC).[3] Furthermore, the photocatalysis experiments required

adjusting initial pH levels in the chromium solution using hydrochloric acid and sodium hydroxide solutions. The photocatalytic reduction efficiency was calculated according to Eq. 1 to obtain:

$$Photocatalytic\ reduction\ efficiency = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) were the instantaneous concentrations of Cr(VI) remaining in solution at initial and reaction t (min), respectively.

Chromium extraction from natural water

To evaluate the photocatalytic performance of the material in real-world environments, groundwater and surface water samples were collected from a deep well in Huanyan (Miyun District, Beijing) and the Wuling Mountain region (Hebei Province), respectively. To simulate a pollution scenario, the collected water samples were spiked with 30 mg L^{-1} Cr(VI), and the initial pH was adjusted to 3.0 using diluted HCl or NaOH solutions. Subsequently, 10 mg of UiO-66-NH_2@HDU-105 was dispersed into the reaction system to initiate the photocatalytic reduction of Cr(VI).

Test S3. Experimental Section

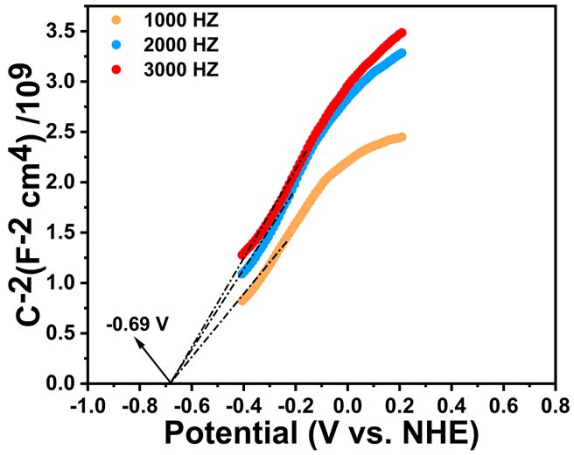

Figure S1. Mott-Schottky plots of HDU-105.

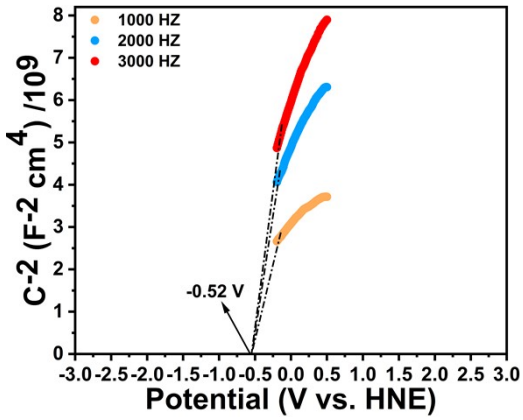

Figure S2. Mott-Schottky plots of UiO-66-NH_2.

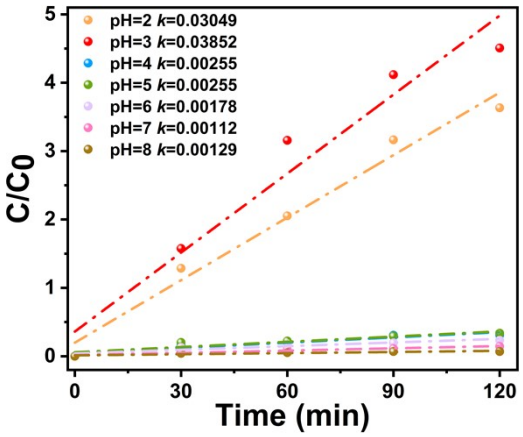

Figure S3. Pseudo-first-order kinetics curves of the photocatalytic Cr(VI) reduction reaction under different pH.

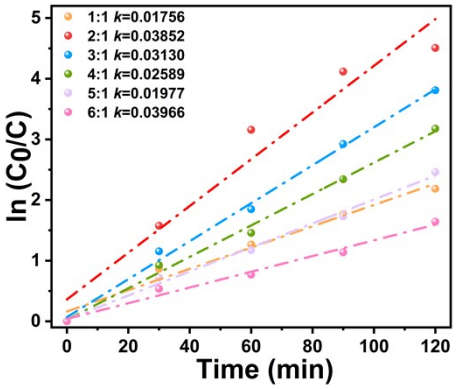

Figure S4. Pseudo-first-order kinetics curves of the photocatalytic Cr(VI) reduction reaction under different ratios.

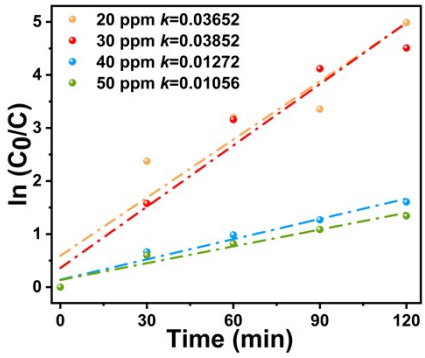

Figure S5. Pseudo-first-order kinetics curves of the photocatalytic Cr(VI) reduction reaction under different Cr(VI) concentrations.

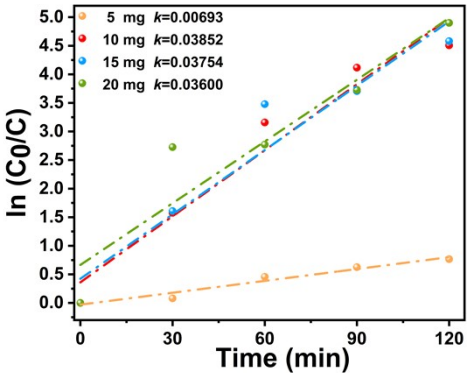

Figure S6. Pseudo-first-order kinetics curves of the photocatalytic Cr(VI) reduction reaction under different Catalyst dosages.

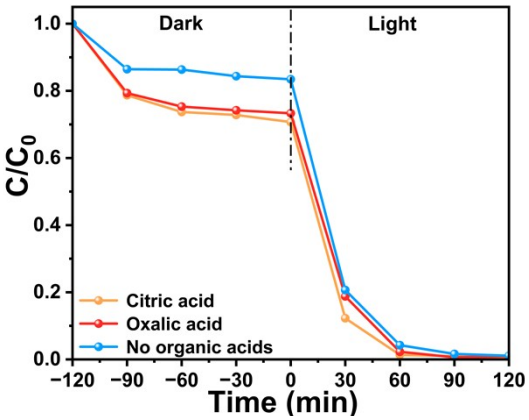

Figure S7. Effect of different organic acids on the photocatalytic reduction of Cr(VI). (Experimental conditions: initial Cr(VI) concentration = 30 mg L^{-1}, organic acid concentration = 0.5 mmol L^{-1}, pH = 3.0.)

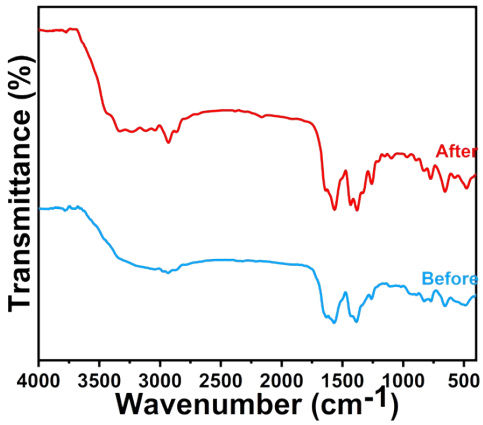

Figure S8. FT-IR spectra of UiO-66-NH_2@HDU-105 before (blue) and after cycling (red; identical to Figure 1c)

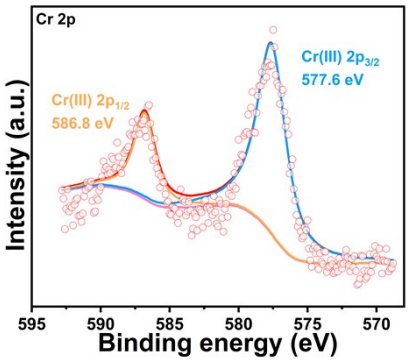

Figure S9. XPS survey spectra of Cr 2p.

References

1. N. Rabiee, A. M. Ghadiri, V. Alinezhad, A. Sedaghat, S. Ahmadi, Y. Fatahi, P. Makvandi, M. R. Saeb, M. Bagherzadeh, M. Asadnia, R. S. Varma and E. C. Lima, *Chemosphere*, 2022, **299**, 134359.
2. C. Wang, W. Lu, W. Song, Z. Zhang, C. Xie, Z. Ji, Y. Li and J. Wang, *Appl. Catal. A-Gen.*, 2023, **666**, 119433.
3. O. B. Nchoe, M. J. Klink, F. M. Mtunzi and V. E. Pakade, *J. Mol. Liq.*, 2020, **298**, 111991.