## **Supporting Information**

# A Novel Integrated Cr(VI) Adsorption-Photoreduction System using MOF@Polymer Composite Beads

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#### **Experimental section**

*Materials and characterization methods:* All chemicals, solvents and polymers used for the synthesis are commercially available and were used without any further purification unless specified otherwise.

The powder X-ray diffraction (PXRD) patterns were collected at the room temperature in a varying 20 range between 5–50 using a multipurpose Bruker D8 Advance diffractometer using Cu K $\alpha$  ( $\lambda$ = 1.54187 Å) radiation while rotating about their central axis during data collection in order to improve the measurement statistics. The X-ray diffraction patterns for beads were collected at Bruker D8 Venture diffractometer using the Mo K $\alpha$  ( $\lambda$ = 0.71075 Å) radiation. The bead samples were loaded on the tip of a glass fiber rod.

The Scanning Electron Microscopy (SEM) images were collected using the FEI Teneo SEM instrument at an acceleration voltage of 5-20 kV. All samples were deposited on a carbon tape and were coated with a 7 nm thick Iridium layer prior imaging.

The N<sub>2</sub> isotherms were recorded at 77 K by BELSORP mini system and the Brunauer-Emmett-Teller (BET) model in the relative pressure range of 0.05-0.30 were applied to determine the BET surface area. All samples were activated by firstly solvent exchange with ethanol and then heating to 140 °C under vacuum (10<sup>-3</sup> mbar) prior to the measurement.

A PerkinElmer LAMBDA 950S UV/Vis Spectrophotometer with a Tungsten source was used to collect absorbance spectrum of the solutions. A PerkinElmer Thermogravimetry Analyzer (TGA) was used to measure MOF content in the polymeric beads.

A NeXIon 350D Perkin Elmer ICP-MS instrument with KED option was used to measure total amount of Cr in the solutions. The Cr oxidation state in samples was measured by a VersaProbe II (Physical Electronics Inc) X-ray photoelectron spectroscopy (XPS) using the monochromated Ka X-ray line of an Aluminium anode. The pass energy was set to 46.95eV with a step size of 0.2eV. The samples were electrically isolated from the sample holder and charges were compensated. The spectrum were referenced at 284.8eV using the C-C bound component of the C1s transition.

An Agilent 5110 ICP-OES instrument was used to measure Zr content. The elemental analysis were performed on a Thermo Scientific Flash 2000 Organic Elemental Analyzer to provide C/H/N combustion analyses of compounds.

### $BDC-(NH_2)_2$ ligand synthesis:



Step 1: 20 g of 2,5-dimethyl-1,4-phenylenediamine and 34 ml of acetic anhydride are added into 300 ml acetic acid and the resulting solution is stirred for 3 hours at room temperature. The white precipitate is filtered, washed copiously with deionized water, and dried at 70 °C to give N,N'-(2,5-dimethyl-1,4-phenylene)diacetamide. Yield:  $\sim$  31 g.

Step 2: Without further purification, 9 g of N,N'-(2,5-dimethyl-1,4phenylene)diacetamide is added into 300 ml H<sub>2</sub>O at 90 °C, to which a solution containing 39 g of KMnO<sub>4</sub> in 450 ml is added dropwise. The reaction mixture is further stirred for 5 hours at 90 °C. After cooling down to room temperature, the solution is filtered, and the filtrate is acidized with HCl to pH = 5. The precipitate is filtered, washed copiously with deionized and recrystallized in DMSO to give yellow needle crystals water. of 2.5diacetamidoterephthalic acid. Yield: ~ 6 g. <sup>1</sup>H NMR (DMSO-*d6*, 400 MHz):  $\delta$  (ppm) 10.69 (s, 2H, -N-H), 8.91 (s, 2H, -C-H), 2.11 (s, 6H, -CH<sub>3</sub>).

Step 3: 5 g of 2,5-diacetamidoterephthalic acid is added into 200 ml NaOH solution (10%) and refluxed under N<sub>2</sub> gas for 10 hours. After cooling down to room temperature, the solution is acidized with HCl to pH = 5. The green precipitate is filtered, washed copiously with water, and dried at 70 °C to give 2,5-diaminoterephthalic acid. Yield: ~3 g. <sup>1</sup>H NMR (DMSO-*d6*, 400 MHz):  $\delta$  (ppm) 8.06 (s, 4H, -NH<sub>2</sub>), 7.22 (s, 2H, -C-H).

Zr-BDC-( $NH_2$ )<sub>2</sub> synthesis: In a typical reaction, 125 mg of  $ZrCl_4$  was dissolved in 1 ml HCl and 15 ml DMF and then 146 mg of diamino therephthalic acid was added and sonicated until complete dissolution. The solution was heated in the oven at 80°C for 12 hrs. The obtained crystals were isolated and washed with DMF and ethanol several times and dried at 85°C <sup>1</sup>.

*Polymer modification:* The polyethersulfone (PES) was chemically modified with carboxylic groups in bulk by controlled acetylating and oxidating reaction following previously reported procedure <sup>2</sup>.

Synthesis of composite beads: The composite beads were synthesized based on our previously reported method <sup>3</sup> with further modification. The corresponding amount of the MOF powder was dispersed in DMF by mechanical stirring for 10 h at room temperature. The temperature was raised to 60°C and the corresponding amount of polyethylene glycol for 100 g/L of solution was added as the pore-forming agent and the solution was stirred for 1 hr until complete dissolution. Then, the corresponding amount of PES/PES-COOH (75/25 wt%) blend for 100 g/L concentration was added gradually to the solution while stirring. The MOFpolymer dope solution was stirred for 24 h at 60 °C for complete dissolution of the polymer and dispersion of MOF into the polymer matrix. Then, the dope solution was added dropwise to an ethanol/water (1:1 v:v) coagulation bath at 5 °C to form the beads. The non-solvent in the coagulation bath was refreshed after the bead formation and the beads were left in the bath for additional 30 min to ensure complete polymer precipitation and separation of the solvent from polymer matrix. The beads were dried in air at room temperature. All beads were activated before use by heating to 140 °C under vacuum to remove the solvent molecules from the pores. The percentage of the MOF (filler) to polymer in beads is calculated based on the dope polymer solution by Eq-S1 and confirmed by TGA under air flow (Fig S3). The ZrO<sub>2</sub> content remaining after decomposition of the beads with 80 % wt loading of Zr-BDC- $(NH_2)_2$  is 29 wt% which is in good agreement with theoretical value of 32 wt%.

$$MOF \ loading \ (wt\%) = \frac{MOF \ wt}{MOF \ wt + polymer \ wt} \times 100$$
(Eq-S1)

*Synthesis of neat polymeric beads:* The PES neat beads were prepared according to the aforementioned procedure for composite beads, only without the addition of the MOF in the first step.

Table S1. Polymers used in this study





Fig S1. XRD pattern of (a) as-synthesized Zr-BDC-(NH<sub>2</sub>)<sub>2</sub> and (b) Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>@PB compared to simulated UiO-66 structure collected at  $\lambda$ = 1.54187 and 0.71075 Å, respectively. (c) Indexed PXRD of as-synthesized Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>. The determined domain size (Le Bail method) using an isotropic size model and the SRM1976 standard for the instrumental resolution is 10(2) nm. Unit cell a-axis is 20.8112(3) °A.



Fig S2. (a) UV–vis absorbance spectrum of the free BDC- $(NH_2)_2$  ligand and (b) Kubelka-Munk representation of the diffuse reflectance of the Zr-BDC- $(NH_2)_2$  MOF in comparison to UiO-66-NH<sub>2</sub> indicating a shift toward visible range absorption



Fig S3. (a) TGA analysis of Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>@PB with 80 wt% MOF loading and (b)  $N_2$  adsorption isotherm of Zr-BDC-(NH<sub>2</sub>)<sub>2</sub> and Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>@PB.

Contact Angle measurement



Fig S4. Water contact angle at the surface of (a) neat PES polymer, (b) carboxylic modified PES and (c) modified PES blend (25/75 wt%)

Cr(VI) Batch experiments: The Cr(VI) solutions were prepared by dissolving the corresponding amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water and the pH of the solution was adjusted to 3 using HCl. All samples were activated by immersing in 4M HCl solution for 4 h and then were washed with water before the capture experiment. In a typical batch experiment, 50 mg of the adsorbent were immersed in 5 ml of Cr(VI) solution and left under mild stirring until equilibrium reached. The Cr(VI) uptake was calculated from the difference between the total amount of Cr in initial and final solution measured by ICP-MS.

The photocatalytic regeneration experiments were performed in a 25 mL Pyrex glass reactor, at room temperature under continuously visible light irradiation from a 300 W Xe lamp equipped with a UV cut-off filter ( $\lambda > 420$  nm) (Scheme S1). In a typical experiment, 50 mg of the Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>@PB was suspended in 10 ml of 4M HCl solution. Then, the solution was purged with nitrogen for 20 min under gentle stirring, in order to remove dissolved oxygen. The beads were irradiated for 4 hr under mild stirring and the total amount of Cr in the solution was measured by ICP-MS.



Scheme 1. Schematic illustration of the photocatalytic set up.

Sorbent	Cr (VI) Capacity (mg/g adsorbent)	Equilibrium time	Recyclability (% in # cycles)	Ref.
Commercial Activated	101.4	> 3 days	-	4
Carbon (GA-3)		-		
Lab-made Activated	182.8	-	53.6% in 1 cycle	4
Carbon (CK-22)				
Ambersep 900 Resin	451.3	-	98% in 10 cycle	5
Chemically-modified	625	16 h	65% in 10 cycle	6
Chitosan Beads				
Chitosan Chelating Resin	58.48	2 h	88% in 5 cycle	7
Phosphonium-enhanced	180	30 min	23.7%	8
Chitosan				
PANI@NC-600	198.04	8 h	85% in 5 cycle	9
Waste slurry	640	-	92%	10

Table S2. Sorption capacities for chromium species by conventional sorbents in the literature.

$MOF^+$	796	50 min	-	11
Zr-BDC-(NH <sub>2</sub> ) <sub>2</sub>	146	16 min	5 cycles	This work
Zr-BDC-(NH <sub>2</sub> ) <sub>2</sub> @PB	208	35 min	5 cycles	This work





Fig S5. (a) PXRD pattern of Zr-BDC- $(NH_2)_2$  crystals after a Cr adsorption and a photoregeneration cycles. (b) TGA analysis and (c) FT-IR spectrum of as-synthesized Zr-BDC- $(NH_2)_2$  crystals and after 24 h exposure to HCl. PXRD of this sample indicates the sample is amourphous. (d) Cl 2p XPS analysis of Zr-BDC- $(NH_2)_2$  for as-synthesized, activated and upon Cr(VI) capture showing the Cl<sup>-</sup> exchange mechanism.



Fig S6. SEM image of (a) surface and (b) cross section of Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>@PB and Zr-BDC-(NH<sub>2</sub>)<sub>2</sub> (c) as synthesized (d) after three Cr capture/regeneration cycles



Fig S7. EDX spectrum analysis of (top) Activated Zr-BDC- $(NH_2)_2$ @PB and (bottom) Cr loaded Zr-BDC- $(NH_2)_2$ @PB. (Insets) elemental analysis of the spectrums. Ir is used for coating of the sample during sample preparation hence is removed from the elemental analysis.



Fig S8. (a) Cr(VI) adsorption performance of Zr-BDC- $(NH_2)_2$ @PB treated under different conditions (initial concentration of 5 ppm) (b) Regeneration of Zr-BDC- $(NH_2)_2$ @PB, the percentage corresponds to the ratio of adsorbed Cr that is released during the regeneration (c) Total Cr and Cr(VI) concentration released in photoregenerated solution.

*Fitting of Cr(VI) batch sorption isotherms:* Both Zr-BDC-(NH<sub>2</sub>)<sub>2</sub> and Zr-BDC-(NH<sub>2</sub>)<sub>2</sub>@PB data sets are L2 type isotherms and were fitted to Langmuir isotherm:

$$q = q_m \left( \frac{b \ C_e}{1 + b \ C_e} \right) \tag{Eq-S2}$$

where q (mg/g) is the amount of Cr(VI) adsorbed at the equilibrium concentration  $C_e$  (ppm),  $q_m$  is the maximum sorption capacity of the sorbent and b (L/mg) is the Langmuir constant related to the free energy of the sorption. The fitting of the data for two samples are given in Table S3.

Table S3.	Fitting	of the	isotherm	data	with	Langmuir	model
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Compound	$q_m (mg/g)$	b (L/mg)
Zr-BDC-(NH <sub>2</sub> ) <sub>2</sub>	152.1269	0.0597
Zr-BDC-(NH <sub>2</sub> ) <sub>2</sub> @PB	216.4120	0.0305

*Defect Analysis:* CHN analysis and ICP-OES of Zr content activated Zr-BDC-(NH<sub>2</sub>)<sub>2</sub> samples were performed to confirm the formula. The results shows slight deviation from theoretical formula, which suggests that there are some defects in the structure. The elemental calculation shows there are approx. 2.1 ligands missing per unit cell for activated MOF. This is also matches with the same calculation from TGA result of the activated MOF which shows approx. 1.9 missing ligand (Fig S5(b)). The missing ligand can be due to the etching effect of the acti on MOF structure <sup>12, 13</sup>.

Table S4. CHN analysis of Zr-BDC-(NH<sub>2</sub>)<sub>2</sub> samples after activation with HCl

Compound	Formula	Zr%	С%	Н%	N%
Theoretical structure	$[Zr_6O_6][C_8H_8O_4N_2Cl_2]_6$	24.37	25.67	2.15	7.48
Theoretical defect	$[Zr_6O_6][C_8H_8O_4N_2Cl_2]_4[H_2O]_{0.2}$	31.32	21.99	2.08	6.41
Experimental		33.70	23.24	2.44	5.88

Integrated adsorption-photoreduction system: The system was comprised of two identical glass columns (ID: 15 mm, L: 100 mm) connected in sequence. The columns were sparged with co-current N<sub>2</sub> stream through the gas line connected to the inlet. The gas flow rate was controlled by a flowmeter enabling us to achieve different two-phase flow regimes. The flow rate of liquid feed stream was carefully adjusted by a variable flow peristaltic pump. A Cr(VI) solution of 5 ppm in water (pH~3) with flow rate of 0.4 mL/min was fed to the system and the gas flow rate was adjusted to achieve a two-phase slug flow regime (Fig S10). The samples were collected regularly at the outlet of each column and were characterized by ICP-MS. After each experiment, the Cr solution was drained and the columns were flushed with water. Each column were regenerated by a 4 M HCl solution while being gas-sparged and irradiated with visible light for 4 h. The system was equipped with a 300 W Xe lamp equipped with a UV cut-off filter ( $\lambda$ >420nm) for visible light irradiation. The design of the system and the moving nature of the adsorbent beads in the columns allows the light to reach all the particles in the column. To confirm total reduction of Cr(VI) to Cr(III), all Cr(III) species were precipitated by adding NaOH to the solution and the supernatant was analyzed by ICP-MS. After regeneration, the columns were flushed with water again and became ready for the next cycle.



Fig S9. Cr(VI) content of the regeneration solutions.



Fig S10. (a) As-synthesized Zr-BDC- $(NH_2)_2$  powder and (b) Zr-BDC- $(NH_2)_2$ @PB (c) gas-sparged column during adsorption and (d) during photoregeneration



Fig S11. Cr(VI) adsorption test on a single column with composite beads after 80 hr fluidization, the 5ppm Cr(VI) solution was fed to the column at hour 80, Zr content in the outlet tank 1.72 ppb.

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