Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Pyridine-based conjugated imprinted polymer as an adsorptive photocatalyst for efficient removal of aqueous Cr(VI)

Zhipeng Guo,[a] Wei Wei,*[a] Yihang Li,[a] Jin Li,[ab] Xiaoke Zhang,[a] Fengming Hou [ac] and Ang Wei*[a]

[a] State Key Laboratory of Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Jiangsu Key Laboratory for Biosensors, Nanjing University of Posts & Telecommunications, Nanjing, 210023, China

[b] Nantong Institute of Nanjing University of Posts and Telecommunications Co. Ltd., Nantong, 226001, China

[c] Kunshan Innovation Institute of Xidian University, Suzhou, 215316, China

* Correspondence author

E-mail: weiwei523@njupt.edu.cn (W. Wei), wei1177@126.com (A. Wei).

Experimental Section

Materials

4-vinylpyridine, ethylene glycol dimethacrylate, 2-hydroxyethyl methacrylate, methanol, p-benzoquinone, silver nitrate and azobisisobutyronitrile were purchased from Aladdin Biochemical Technology Co., Ltd. Poly-4-vinylpyridine with an average molecular weight of ~160, 000 was purchased from Macklin Biochemical Co., Ltd. Potassium dichromate, chromic nitrate nonahydrate, sodium hydroxide, ethanol, acetone, and acetonitrile were obtained from Shanghai Wokai chemical reagent Co., Ltd. All chemicals were used as received.

Synthesis of pyridine-based conjugated imprinted polymer

The pyridine-based conjugated imprinted polymer was synthesized via precipitation polymerization with the Cr(VI) target species. 4-vinylpyridine, ethylene glycol dimethacrylate, 2-hydroxyethyl methacrylate and azobisisobutyronitrile were used as functional monomer, crosslinker, copolymerized monomer and initiator agent, respectively. Initially, 160 mg of potassium dichromate was dissolved in 10 mL of acetone with ultrasound treatment. Then, 4-vinylpyridine was added and stirred for 1 h at room temperature to form a metal-monomer complex. After that, 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate were added into the resulting mixture. Finally, 60 mg of azobisisobutyronitrile was added. After 15 min, the mixture was purged with nitrogen for 10 min to remove dissolved oxygen, and then the mixture was transferred into a round bottom flask and sealed. Under the condition of nitrogen, the polymerization was carried out for 90 min at 65 °C. After the reaction, the product was washed with ethanol/water (70/30, V/V) for several times to remove the unreacted monomer and ingredient. In order to obtain the selective cavity of Cr(VI), the product was washed with acetonitrile/0.1 M NaOH (1/1, V/V) until the Cr(VI) ion could not be detected in the washing solution. After washed the remaining NaOH, the product was dried in an oven at 65 °C for 12 h. the obtained powder named Cr(VI)-IP-xVP ($x = 1.5$, 3 and 6), wherein x denoted the added molar mass of 4-vinylpyridine in the precipitation polymerization. For comparison, two samples without adding 4-vinylpyridine and potassium dichromate were prepared as the reference samples and named Cr(VI)-IP-0VP and NIP, respectively. NIP was the template-free non ion imprinted polymer.

Characterization

The valence states and crystal structures of the samples were studied by X-ray photoelectron spectroscopy (XPS, KRATOS Axis Supra) using monochromatic Al Kα radiation as the excitation source under vacuum at 2×10^{-6} Pa. All the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The diffuse reflectance spectra were performed on a UV-visible spectrophotometer (UV-vis DRS, UV-3600Plus, Shimadzu, Japan), $BaSO_4$ was used as the reflectance sample. Fourier transform infrared spectra (FTIR) were recorded with a Fourier transform infrared spectrometer (PerkinElmer Spectrum Two) with 2 cm^{-1} resolution in the range 400 ~ 4000 cm^{-1}, using KBr method at room temperature. The electron spin resonance (ESR) was measured on a Bruker EMXplus-6/1 spectrometer ($\lambda > 420$ nm). The free radical capturer was 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO), respectively. The concentration of Cr(III) in the suspension was determined by inductively coupled plasma mass spectrometer (ICP-MS, NEXION 2000, PerkinElmer).

Static adsorption experiments

Adsorption experiments were carried out by mixing 10 mg of sample into a conical flask with 10 mL of Cr(VI) aqueous solution ($K_2Cr_2O_7$ was dissolved in deionized water). The pH was adjusted using HCl and NaOH. The conical flask was placed on a shaking table, the temperature was 25 °C, and the rotating speed was 200 r/min. After a scheduled time interval, the concentration of Cr(VI) was determined by a diphenylcarbazide colorimetric (DPCI) method at 540 nm in a UV-vis spectrophotometer. The adsorption capacity of Cr(VI) was calculated by the following equation:

$$q_t = \frac{(C_0 - C) \times V}{m}$$

Wherein, q_t (mg/g) represented the adsorption capacity, C_0 (mg/L) and C (mg/L) were the initial concentration and the timely concentration of Cr(VI), V (L) was the volume of the Cr(VI) solution, and m (g) was the weight of the prepared material (dry) added into the solution.

Selective adsorption

The adsorption selectivity of Cr(VI)-IP-6VP for Cr(VI) ion was quantified using the distribution coefficient (K_d) and selectivity coefficient (k). The concentration of each ion was 50 mg/L, and the mixture was shaken at pH = 2.5, 25 °C, and 200 rpm for 30 min.

$$K_d = \frac{(C_0 - C) \times V}{C \times m}$$

$$k = \frac{K_d(Cr(VI))}{K_d(M)}$$

where C_0 (mg/L) and C (mg/L) represented the initial and final solution concentrations, V (L) was the volume of the Cr(VI) solution, and m (g) was the weight of the prepared material added into the solution. M represented the competitive ion, as Cu^{2+}, Cr^{3+}, and SO_4^{2-}.

Photoreduction of Cr(VI) and photostability

The photocatalytic performance of the as-prepared Cr(VI)-IP-xVP was determined by photoreduction of Cr(VI). A 300 W xenon lamp (light intensity: 58 mW/cm^2) was used as the light source equipped with a cutoff filter ($\lambda > 420$ nm), which was purchased from Beijing Education Au-light Co., Ltd. (CEL-HXF 300F3). The distance between the light source and the liquid level was about 10 cm. The temperature was controlled at 25 °C by a flowing water bath. Firstly, 5 mg of photocatalyst was added into 20 mL of Cr(VI) solution, and then the pH was adjust to 2.5 by 0.5 mol/L HCl. Secondly, the suspension was magnetically stirred in the darkness for 30 min to achieve an adsorption-desorption equilibrium. Then, the visible light source was turned on. After a given time interval, 0.5 mL of the suspension was taken out and centrifuged to remove the photocatalyst. The concentration of Cr(VI) was determined by a DPCI method. The photoreduction performance of Cr(VI) was estimated by C/C_0, and the photocatalytic reaction kinetics was analysed by the Langmuir-Hinshelwood model.

The stability and repeatability of Cr(VI)-IP-6VP were investigated. After each cycle, the photocatalyst was separated from water. And then, the photocatalyst was soaked in a mixture of acetonitrile/0.1 M NaOH (1/1, V/V) aqueous solution to remove the Cr(VI) adsorbed on the surface of the photocatalyst. Finally, the cleaned photocatalyst was added in a fresh Cr(VI) aqueous solution for a new cycle.

Table S1. Selective adsorption of Cr(VI) with competitive ions.

Ions	**Cr(VI)-IP-6VP**		
	K_d(Cr(VI))	**K_d(M)**	**k**
$Cr_2O_7^{2-}/Cu^{2+}$	6.526	0.186	35.07
$Cr_2O_7^{2-}/Cr^{3+}$	7.637	0.271	28.19
$Cr_2O_7^{2-}/SO_4^{2-}$	5.172	1.425	3.63

Table S2. Kinetic constants of the adsorption of Cr(VI) onto the adsorbents.

Samples	**k_{obs} (min^{-1})**	**q_e (mg/g)**	**R^2 (pseudo-first-order model)**	**R^2 (pseudo-second-order model)**
Cr(VI)-IP-0VP	/	/	/	/
Cr(VI)-IP-1.5VP	0.032	60.7	0.91	0.96
Cr(VI)-IP-3VP	0.056	102.0	0.94	0.97
Cr(VI)-IP-6VP	0.080	141.7	0.96	0.99
NIP	0.067	109.4	/	/

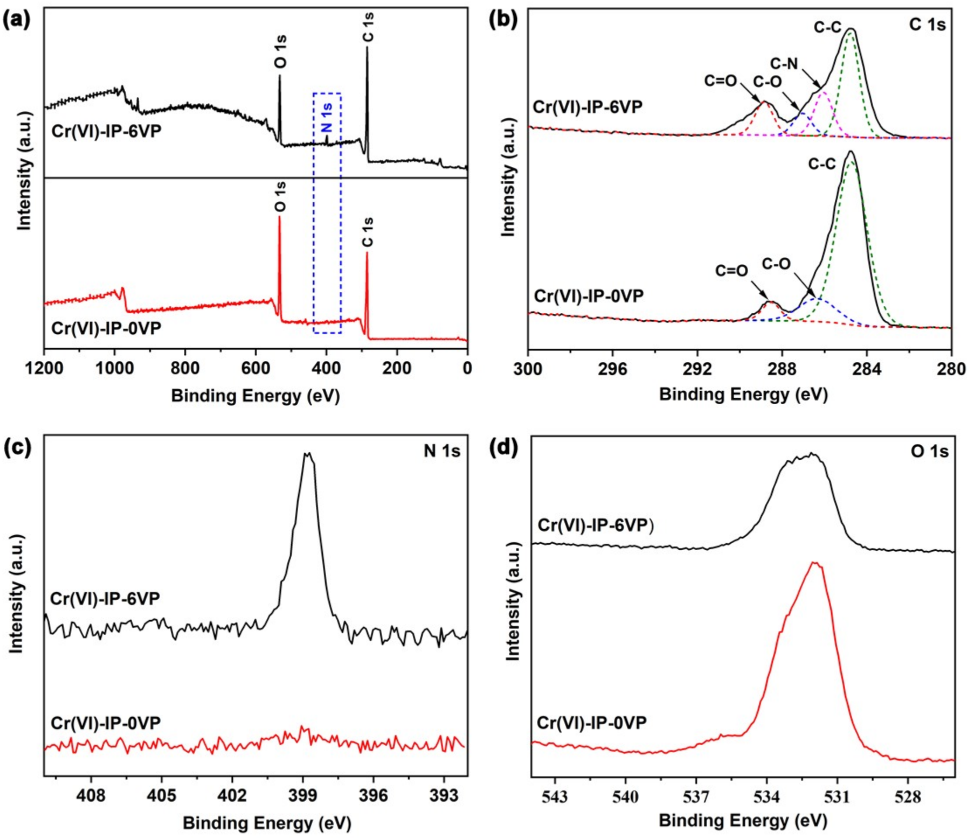

Fig. S1. XPS spectra of Cr(VI)-IP-0VP and Cr(VI)-IP-6VP: (a) Survey, (b) C 1s, (c) N 1s, and (d) O 1s.

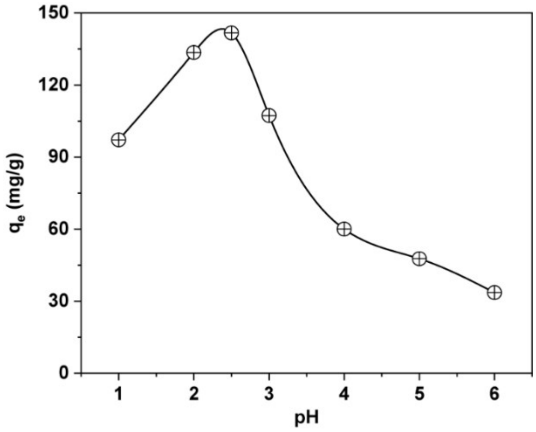

Fig. S2. Effect of pH in aqueous solution on the adsorption (25 °C).

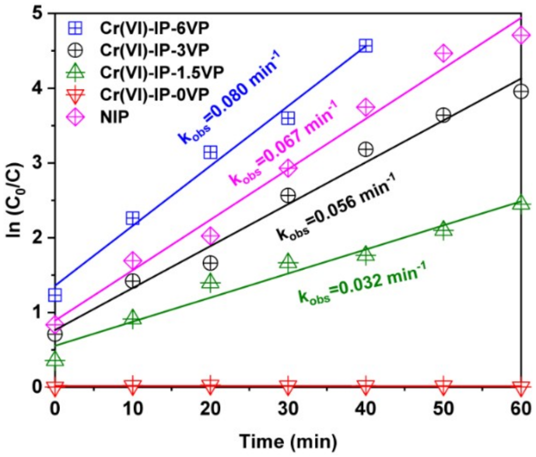

Fig. S3. Kinetic curves of photocatalytic Cr(VI) reduction.

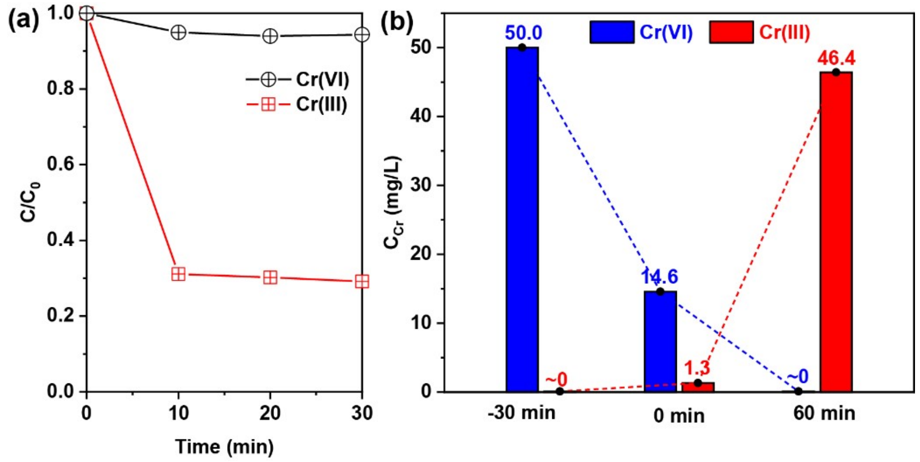

Fig. S4 (a) Absorption of Cr(VI) and Cr(III) with Cr(VI)-IP-6VP (catalyst dosage = 0.25 g/L, Cr(VI) = 50 mg/L, Cr(III) = 50 mg/L). (b) The concentrations of Cr(VI) and Cr(III) in the suspension during the absorption and photoreduction (catalyst dosage = 0.25 g/L, Cr(VI) = 50 mg/L).

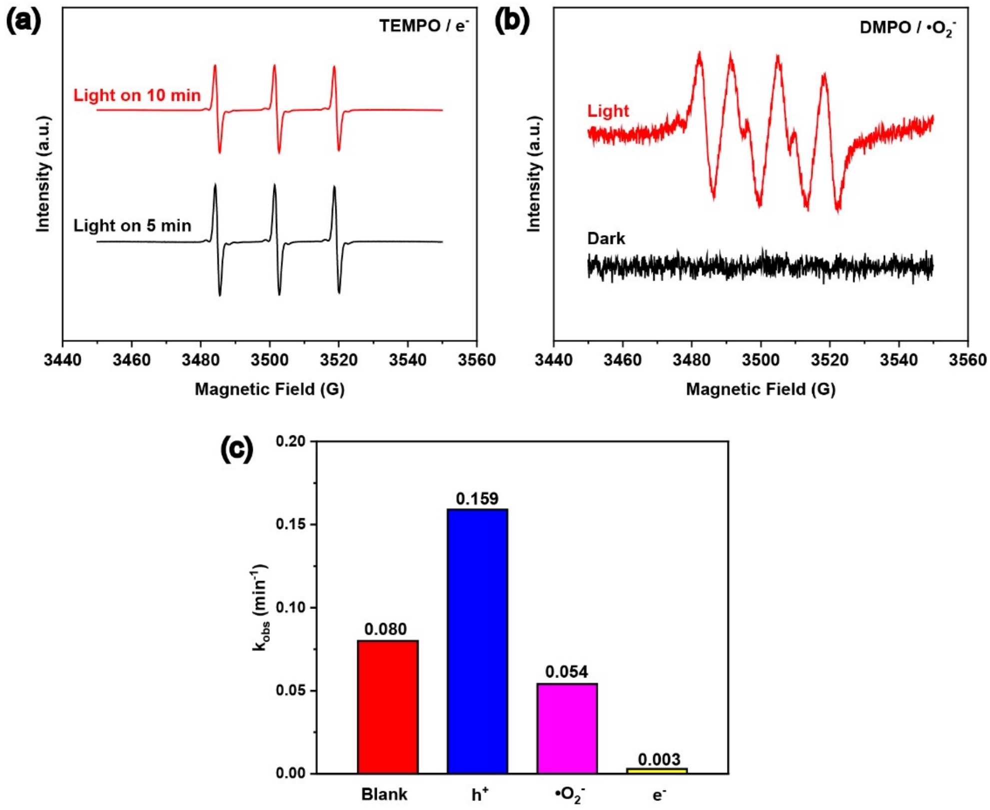

Fig. S5. ESR spectra of e^- (a) and $\cdot O_2^-$ (b). (c) Effect of different scavengers on photoreduction of Cr(VI). Methanol, p-benzoquinone, and silver nitrate were the scavengers of h^+, $\cdot O_2^-$, and e^-, respectively.

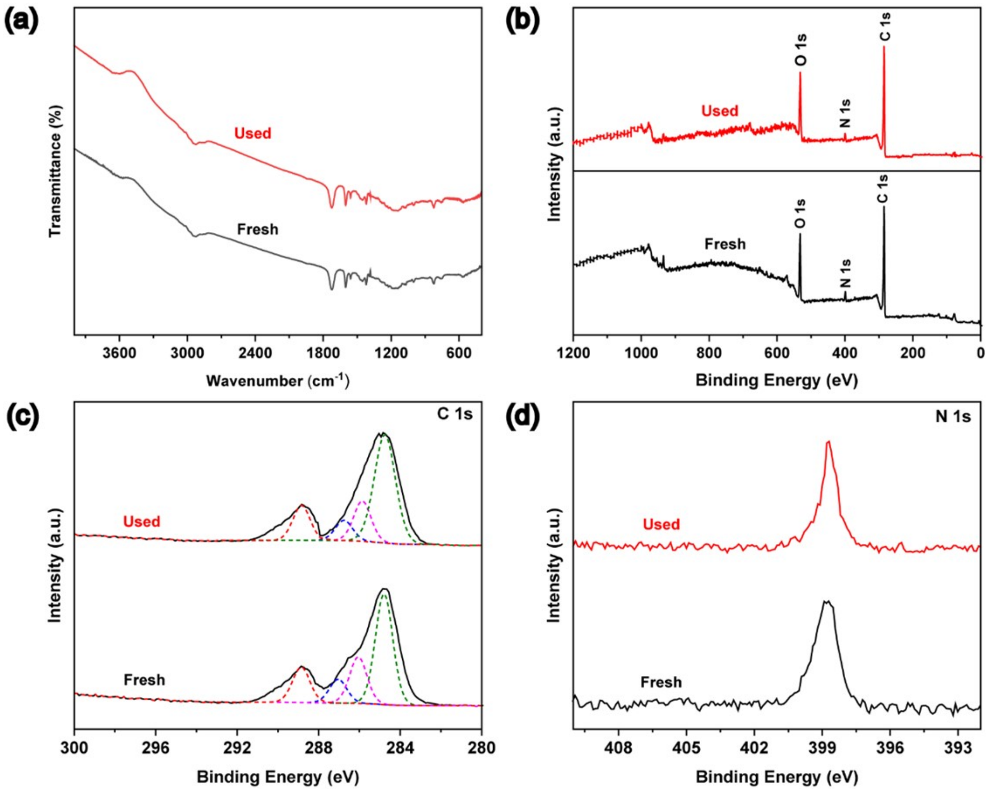

Fig. S6. (a) FTIR spectra of Cr(VI)-IP-6VP after photoreduction of Cr(VI). XPS spectra of the used Cr(VI)-IP-6VP: (b) Survey, (c) C 1s and (d) N 1s.