Enhanced Electrocatalytic Reduction of Hexavalent Chromium with Reduced pH Dependance via Alternating Potential Polarization Using Polyaniline-Chitosan Composite Electrode

Huihui Zheng,[a] Weitong Xian,[a] Ye Xiao,*[a, b] Yetao Tang,[a,b] and Ronglinag Qiu [a, c, d]

[a] *School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China.*

[b] *Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou, China.*

[c] *Guangdong Provincial Key Laboratory of Agricultural and Rural Pollution Abatement and Environmental Safety, College of Natural Resources and Environment, South China Agricultural University, Guangzhou, PR China.*

[d] *Guangdong Laboratory for Lingnan Modern Agriculture, Guangzhou, PR China*

* Corresponding author:

Associate Professor, +86 15521052029, xiaoy299@mail.sysu.edu.cn

Polyaniline/chitosan (PANI/CS) composite synthesis

The PANI/CS composite was synthesized via in-situ oxidative polymerization [1, 2]. Firstly, 2.4 g of chitosan was weighed and dissolved in 400 mL of 1 mol/L HCl solution. After complete dissolution through ultrasonic-assisted stirring, 3.7 mL of aniline was added to the solution, followed by continuous stirring for 0.5 h to ensure homogeneous distribution. Subsequently, 9.128 g of ammonium peroxydisulfate was dissolved in 400 mL of 1 mol/L HCl solution under identical sonication conditions. The prepared ammonium peroxydisulfate solution was then introduced dropwise into the chitosan/aniline mixture via a peristaltic pump, with the reaction system maintained under continuous stirring for 24 h at ambient temperature (~25°C). The resultant dark green precipitate was obtained through vacuum filtration using a Buchner funnel. Subsequent purification involved repeated washing with 10% ethanol aqueous solution until the filtrate exhibited optical transparency. The purified polyaniline/chitosan composite was subjected to thermal drying in an oven at 60°C for 48 h, followed by mechanical pulverization using a planetary ball mill and subsequent sieving through a 100-mesh sieve to achieve uniform particle size.

Electrode preparation

The working electrodes were prepared according to the following three steps: slurry preparation, slurry coating, and electrode drying. First, the active material, conductive carbon black, and binder polyvinylidene difluoride (PVDF) were mixed with a mass ratio of 8:1:1, and an appropriate amount of N-methyl-2-pyrrolidone (NMP) was added. The slurry was then ground and stirred until a homogeneous solid-liquid dispersion was achieved. A predetermined amount of slurry was uniformly coated onto 2.5 × 2.5 cm^2 carbon paper, which was cleaned and dried before use. The coated electrode was then dried in a vacuum oven at 60°C. The mass of the loaded active material was determined by the mass difference of the carbon paper before and after coating. Typically, approximately 4.2 mg of active material was loaded on the electrode, corresponding to a loading of 0.67 mg/cm^2.

Cr(VI) electrochemical removal

All the Cr(VI) electrochemical removal experiments were carried out using a electrochemical workstation (CHI760E, Shanghai Chenhua). A platinum plate was employed as the counter electrode and an Ag/AgCl (+0.199 V vs. Standard hydrogen electrode, SHE) electrode as the reference electrode. Unless otherwise specified, all potentials reported in this work are referenced against the Ag/AgCl electrode.

To investigate the impact of active material on Cr(VI) electroreduction, chitosan electrode, PANI/CS electrode, and blank carbon paper were used as the working electrodes, respectively, to treat 50 mL of 50 mg/L Cr(VI) solution at pH of 2.9 with 20 mmol/L Na_2SO_4 as the electrolyte. The working electrode potential was set to +0.8 V for 0.5 s, followed by −1.5 V for 2 s, repeated for multiple cycles.

Since the density of loaded active material influences the quantity and distribution of active sites on the electrode surface, PANI/CS electrodes with active material mass of 2.2, 4.2, 6.2, and 8.2 mg, corresponding to loading of 0.35, 0.67, 0.99, and 1.31 mg/cm^2, were employed to treat 50 mL of a 50 mg/L Cr(VI) solution at pH 2.9 with 20 mmol/L Na_2SO_4 as the electrolyte. The working electrode potential was programmed as follows: +0.8 V applied for 0.5 s, followed by −1.5 V for 2 s, with this cycle repeated multiple times.

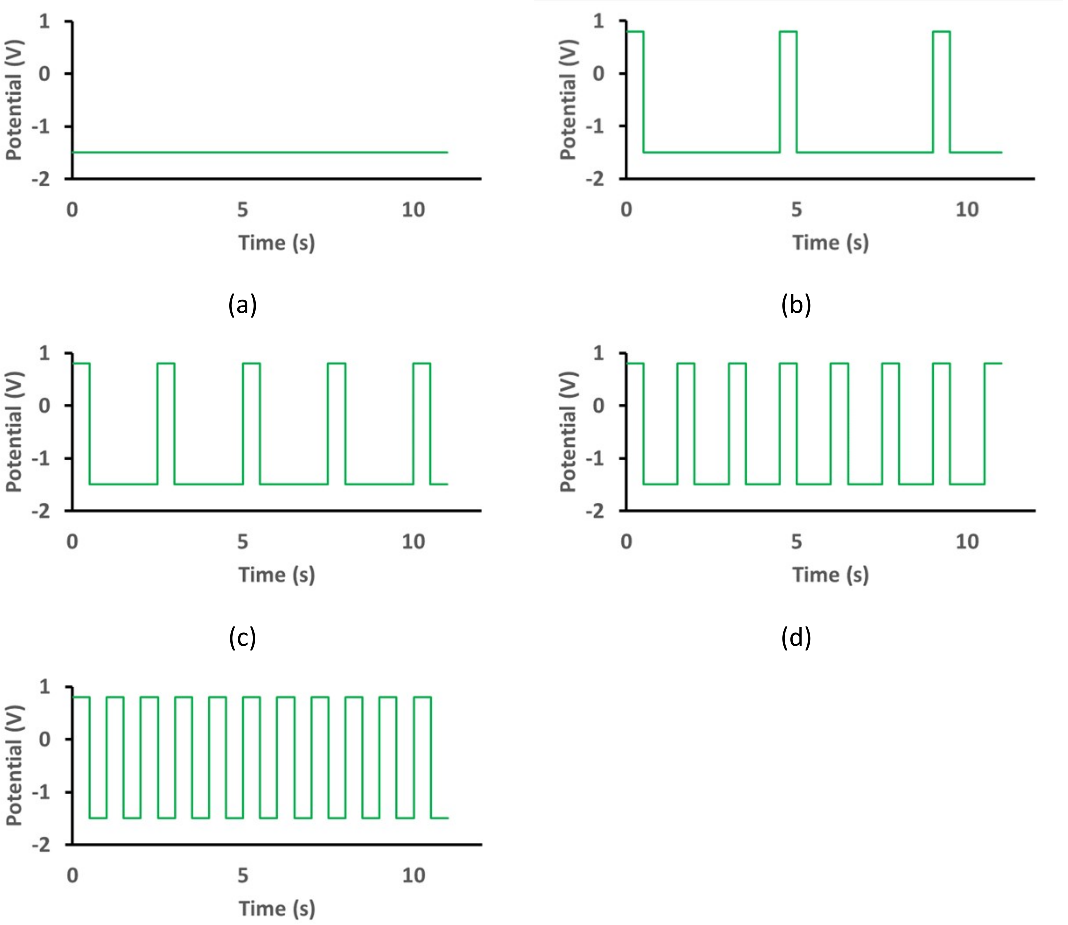
To investigate the impact of pH on Cr(VI) electroreduction, the pH of solutions was adjusted to 1.9, 2.9, 3.9, and 4.9 using 0.1 mmol/L sulfuric acid solution. A PANI/CS electrode with a loading density of 0.67 mg/cm^2 was employed as the working electrode to treat 50 mL of 50 mg/L Cr(VI) solution, with 20 mmol/L Na_2SO_4 serving as the electrolyte. The working electrode potential was programmed as follows: +0.8 V applied for 0.5 s, followed by −1.5 V for 2 s, with this cycle repeated multiple times.

To investigate the influence of time ratios of anodic and cathodic potentials applied on the working electrode, PANI/CS electrode with a loading density of 0.67 mg/cm^2 was employed. For only cathodic potential application, i.e., direct potential experiment, the working electrode potential was set to −1.5 V constantly during the reaction period. The working electrode was applied with +0.8 V for 0.5 s and followed by −1.5 V for 0.5 s, cyclically repeated, for the anodic:cathodic (+/−) time ratio of 1:1 experiment. Similarly, +/− time ratio experiments of 1:2, 1:4, and 1:8 were carried out by fixing the anodic potential time of 0.5 s with cathodic potential time of 1 s, 2 s, and 4 s respectively in each cycle. All the experiments were carried out in a 50 mL solution of 50 mg/L Cr(VI) at pH of 2.9 using 20 mmol/L Na_2SO_4 as the electrolyte.

The concentration of Cr(VI) was measured by the standard diphenylcarbazide UV-Vis spectrophotometry at wavelength of 540 nm. The determination of total chromium concentration involves oxidizing Cr(III) to Cr(VI), followed by measurement via the diphenylcarbazide UV-Vis spectrophotometric method. The procedure is detailed as follows: Accurately measure an appropriate volume of chromium-containing solution and dilute to approximately 50 mL with ultrapure water. Adjust the pH of the diluted solution to above 10 using NaOH solution, then add excess 30% H_2O_2 and mix. The solution is boiled on a hot plate to facilitate the reaction. Evaporate the solution to ~5 mL, then cool to room temperature. After cooling, replenish the volume to ~50 mL with deionized water and repeat the above steps (pH adjustment and H_2O_2 addition) to ensure complete oxidation of Cr(III). Add MnO_2 to decompose residual H_2O_2. Allow the mixture to stand for 6 hours, then filter to remove precipitates. Measure the Cr(VI) concentration in the treated solution using the diphenylcarbazide method and calculate the total chromium concentration. Validation tests on Cr(III) samples with known total chromium concentrations demonstrated an accuracy of 98 ± 0.5% for this method.

Characterization methods

The functional groups of the prepared PANI/CS composite and raw chitosan were analysed with a Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet Corporation, USA) with a wavenumber range of 400~4000 cm^{-1}. The surface morphology and structure of the electrodes before and after Cr(VI) electroreduction were observed using a scanning electron microscope (SEM, Zeiss, Germany) at an accelerating voltage of 15.0 kV. Additionally, the elemental distribution on the sample surface was analysed by energy-dispersive spectroscopy (EDS). Prior to characterization, the electrode samples were coated with a thin layer of gold. The surface elemental composition and valence state of the electrode samples before and after Cr(VI) electroreduction were characterized using an X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa, USA) with Al Kα radiation as the excitation source. Before XPS peak fitting, the binding energies were calibrated using the C1s of adventitious carbon at 284.8 eV. The PANI/CS electrode and chitosan electrode were characterized by cyclic voltammetry in an electrolyte of 20 mmol/L Na_2SO_4 solution containing 100 mg/L Cr(VI) at pH 2.9 with a scanning potential range of +0.8 V to −0.8 V and a scan rate of 5 mV/s.



(a)

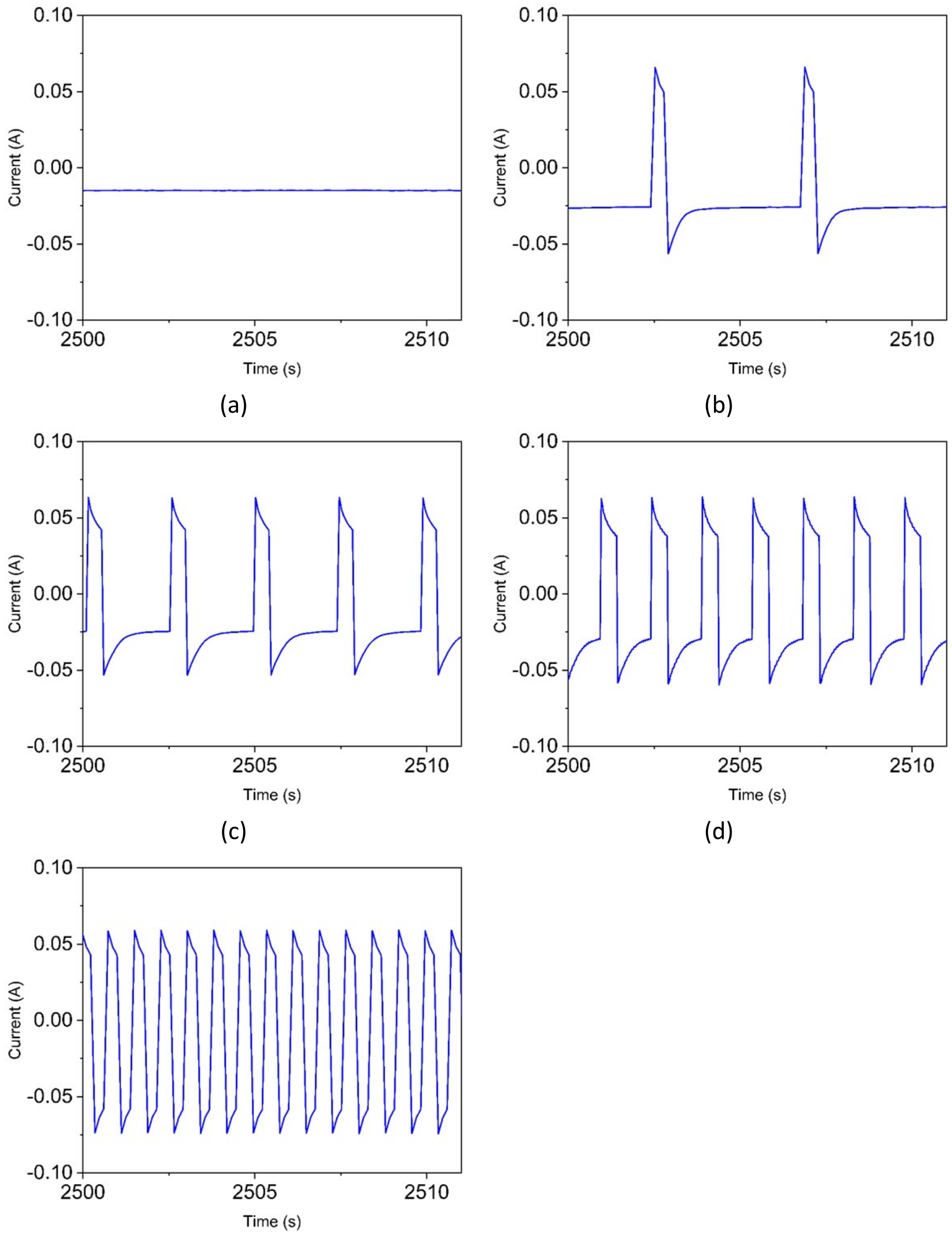
(b)

(c)

(d)

(e)

Fig. S1 Working electrode potential profile when using direct potential (a) and alternating potential (b, c, d, and e). The potentials are versus Ag/AgCl electrode. The figures only show the first 11 s, which is repeated until the end of the experiments. The (b), (c), (d), and (e) is designated as anodic/cathodic (+/−) time ratio of 1:8, 1:4, 1:2, and 1:1, respectively.



(a) (b) (c) (d) (e)

Fig. S2 Current-time profile during Cr(VI) removal when using direct potential (a) and alternating potential (b, c, d, and e). 50 mL solution of 50 mg/L Cr(VI) at pH of 2.9 using 20 mmol/L Na_2SO_4 as the electrolyte.

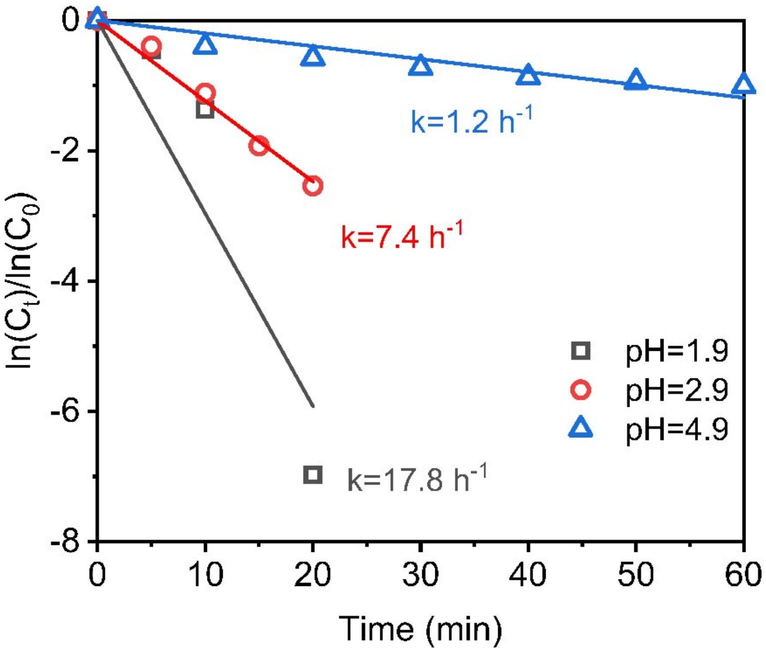


Fig. S3 Pseudo-first order fitting of the kinetics data at various initial solution pH.

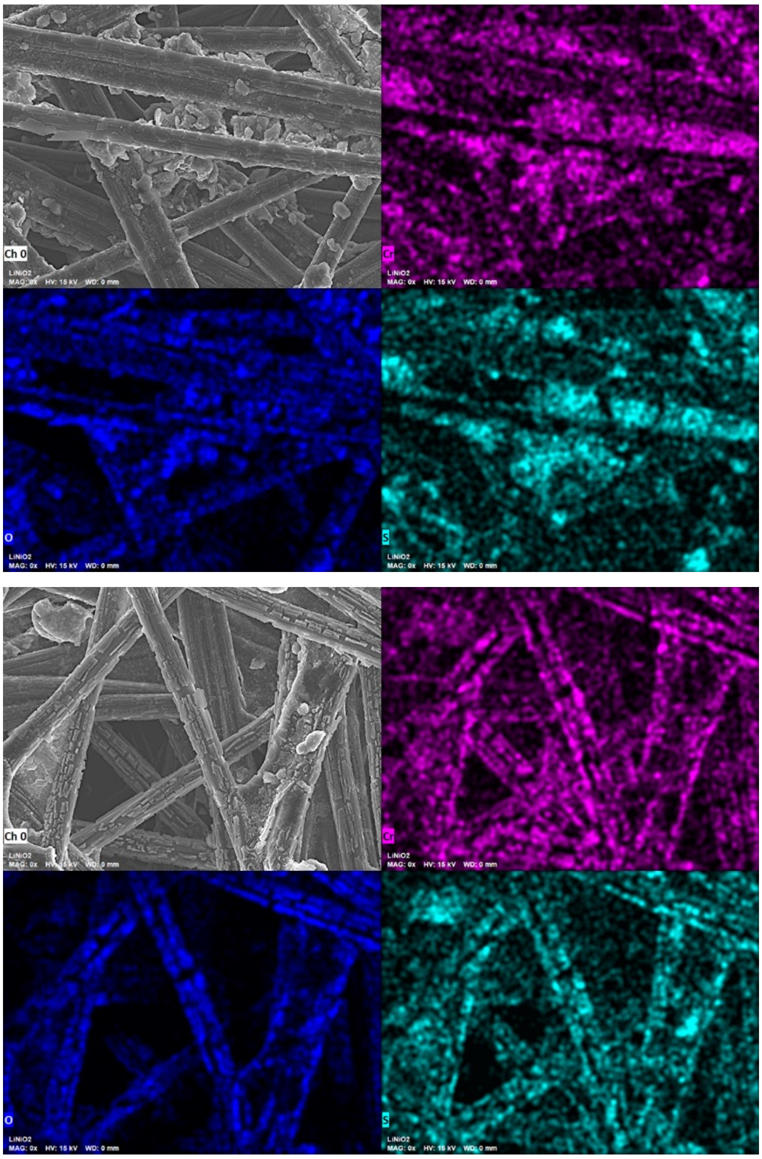


Fig. S4 SEM image and EDS mapping of Cr, O, and S for the PANI/CS electrode after Cr(VI) removal using direct (upper) and alternating (bottom) potentials.

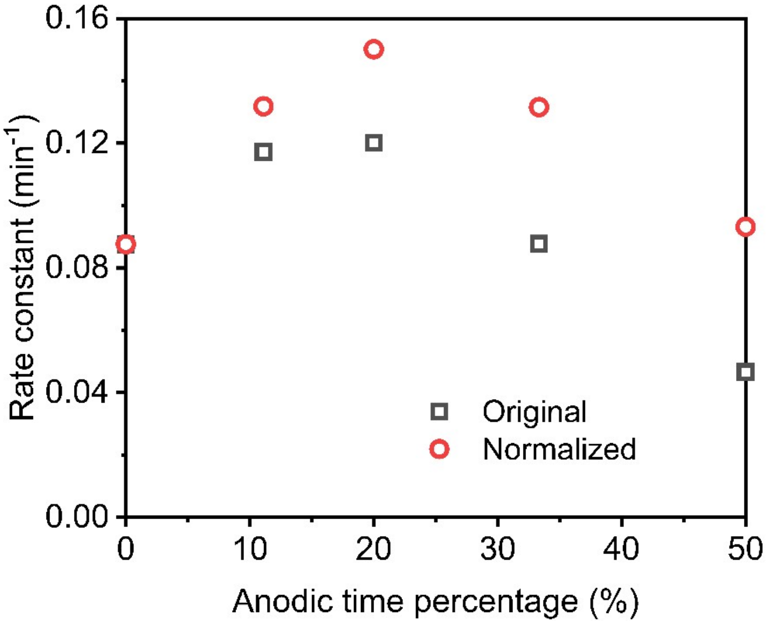


Fig. S5 Influence of anodic time percentage on the Cr(VI) removal rate constant. The rate constant was normalized based on the time percentage of cathodic potential applied on the working electrode. At anodic time percentage of 0, 11.1%, 20%, 33.3%, and 50%, +/− time ratio was 1:8, 1:4, 1:2, and 1:1, respectively.

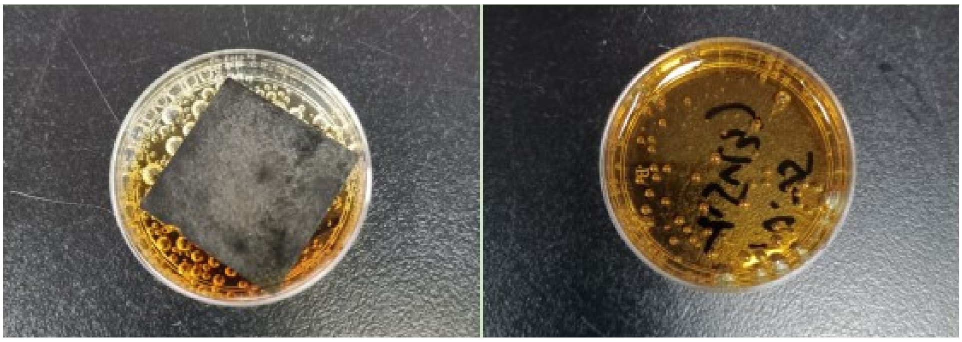


Fig. S6 Pictures show the regeneration of electrode after Cr(VI) removal.

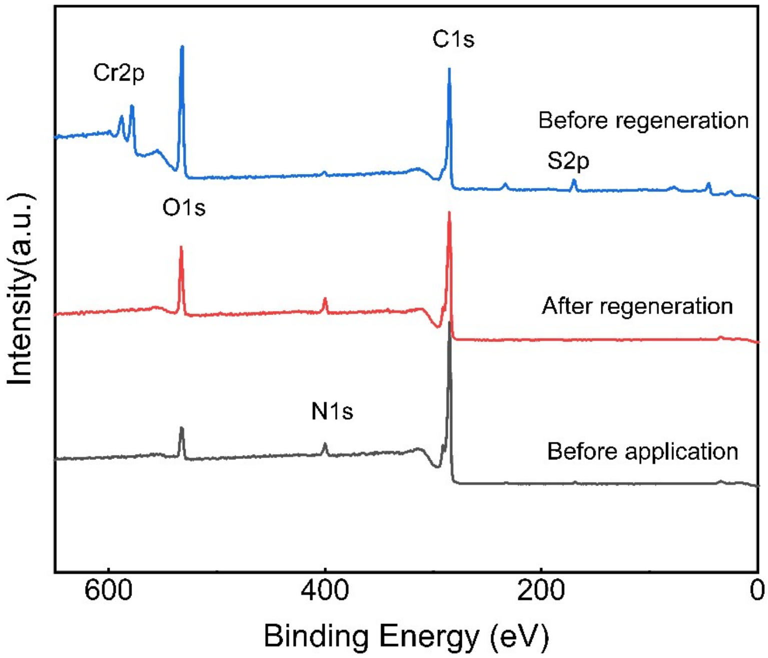


Fig. S7 XPS survey spectra of the PANI/CS electrode before and after Cr(VI) removal and regeneration.

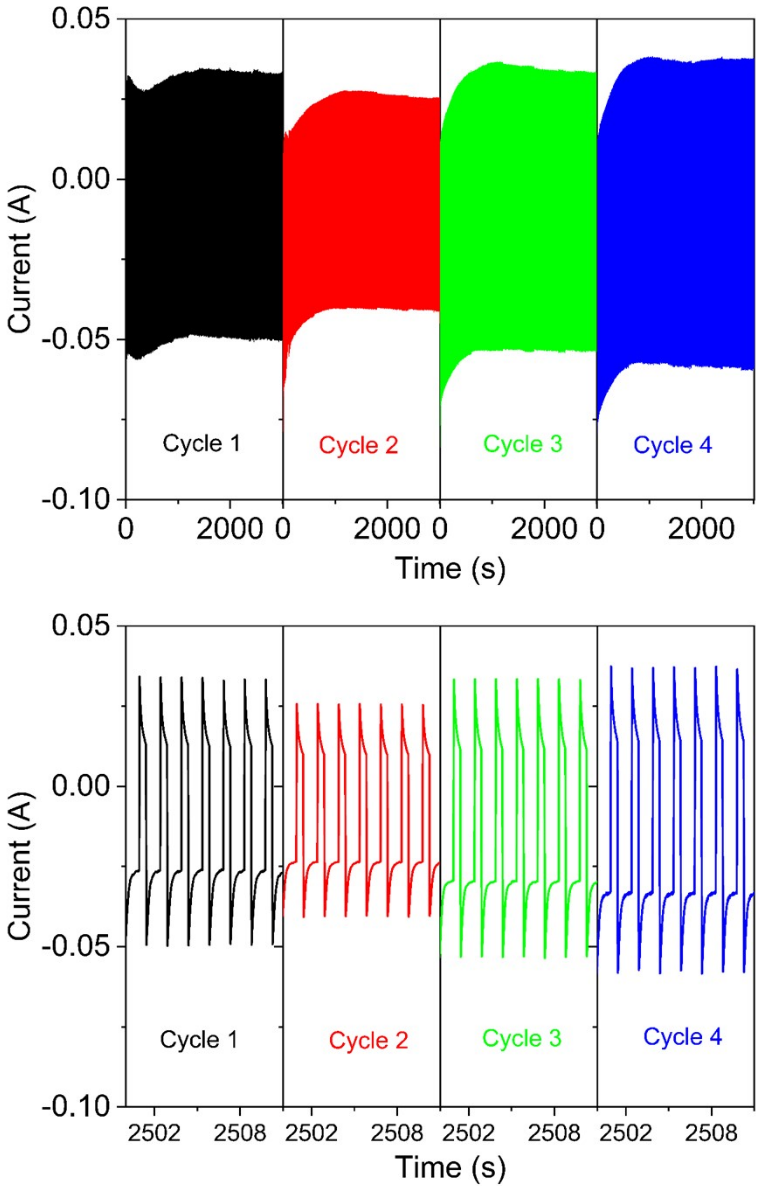


Fig. S8 Current-time profile during Cr(VI) electrochemical removal at different application cycles. The upper figure shows the overall profile, and the bottom figure shows the enlarged profile at treatment time range of 2500~2511 s during each application/reuse cycle.

Table S1. Current efficiency of electrochemical removal of Cr(VI) using PANI/CS electrode under various conditions

Cathodic potential (V)	Anodic potential (V)	Cathodic time (s)	Anodic time (s)	Time (min)	Negative charge (C)	Positive charge (C)	Net Charge (C)	Cr(VI) Concentration (mg/L)	Theoretical charge (C)	Current efficiency (%)
-1.5	-	Direct	-	10	-15.66	0.00	-15.66	18.08	8.89	56.72
-1.5	-	Direct	-	15	-20.92	0.00	-20.92	15.09	9.72	46.43
-1.5	-	Direct	-	20	-25.81	0.00	-25.81	14.58	9.86	38.20
-1.5	-	Direct	-	30	-35.58	0.00	-35.58	11.55	10.70	30.08
-1.5	-	Direct	-	40	-44.70	0.00	-44.70	11.62	10.68	23.89
-1.5	+0.8	4	0.5	10	-18.50	2.82	-15.69	15.70	9.55	60.85
-1.5	+0.8	4	0.5	15	-26.94	4.23	-22.71	8.06	11.67	51.41
-1.5	+0.8	4	0.5	20	-34.76	5.64	-29.12	5.43	12.40	42.59
-1.5	+0.8	4	0.5	30	-49.99	8.63	-41.37	4.38	12.70	30.69
-1.5	+0.8	4	0.5	40	-65.70	11.68	-54.02	4.23	12.74	23.58
-1.5	+0.8	2	0.5	10	-20.18	5.33	-14.85	16.38	9.36	63.01
-1.5	+0.8	2	0.5	15	-28.90	8.04	-20.86	7.29	11.89	56.98
-1.5	+0.8	2	0.5	20	-37.02	10.87	-26.14	3.95	12.82	49.02
-1.5	+0.8	2	0.5	30	-51.69	16.32	-35.37	1.95	13.37	37.81
-1.5	+0.8	2	0.5	40	-66.35	21.74	-44.61	1.61	13.47	30.19
-1.5	+0.8	1	0.5	10	-19.88	9.43	-10.45	25.03	6.95	66.50
-1.5	+0.8	1	0.5	15	-29.99	14.34	-15.64	12.81	10.35	66.18
-1.5	+0.8	1	0.5	20	-39.25	19.25	-20.00	6.76	12.03	60.17
-1.5	+0.8	1	0.5	30	-56.76	29.25	-27.51	2.30	13.27	48.26
-1.5	+0.8	1	0.5	40	-73.75	39.37	-34.38	1.25	13.57	39.47

Cathodic potential (V)	Anodic potential (V)	Cathodic time (s)	Anodic time (s)	Time (min)	Negative charge (C)	Positive charge (C)	Net Charge (C)	Cr(VI) Concentration (mg/L)	Theoretical charge (C)	Current efficiency (%)
-1.5	+0.8	0.5	0.5	10	-18.30	12.44	-5.86	35.99	3.90	66.58
-1.5	+0.8	0.5	0.5	15	-27.15	18.71	-8.45	27.31	6.31	74.73
-1.5	+0.8	0.5	0.5	20	-36.27	25.53	-10.75	22.58	7.63	71.02
-1.5	+0.8	0.5	0.5	30	-54.80	40.04	-14.76	14.97	9.75	66.04
-1.5	+0.8	0.5	0.5	40	-73.96	55.03	-18.92	8.64	11.51	60.84
-1.5	+0	1	0.5	10	-19.81	4.43	-15.38	14.94	9.76	63.44
-1.5	+0	1	0.5	15	-28.93	6.63	-22.30	5.65	12.34	55.34
-1.5	+0	1	0.5	20	-37.15	8.97	-28.18	2.10	13.33	47.30
-1.5	+0	1	0.5	30	-53.14	13.65	-39.49	0.70	13.72	34.75
-1.5	+0	1	0.5	40	-69.27	18.51	-50.76	0.45	13.79	27.17

References

1. S. Sahnoun and M. Boutahala, *Int. J. Biol. Macromol.*, 2018, **114**, 1345-1353.
2. C. C. Sun, B. W. Xiong, Y. Pan and H. Cui, *J. Colloid Interface Sci.*, 2017, **487**, 175-181.