

A highly selective and energy efficient approach to boron removal overcomes the Achilles heel of seawater desalination

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1	Table-of-Contents	
2	Supplementary Texts	3
3	Supplementary Text 1. Electrode functionalization methods.....	3
4	Supplementary Text 2. Boron versus chloride (B/Cl) selectivity calculation	6
5	Supplementary Text 3. Materials and chemical reagents	7
6	Supplementary Text 4. Electrode characterization	8
7	Supplementary Text 5. Bipolar membrane (BPM) assisted electrosorption cell fabrication ..	10
8	Supplementary Text 6. Boron detection method.....	11
9	Supplementary Tables	12
10	Supplementary Table 1. BET data for the pristine and functionalized electrodes.....	12
11	Supplementary Table 2. Elemental analysis of functionalized electrodes from survey XPS.	13
12	Supplementary Table 3. Kendall rank correlation coefficients of different properties.	14
13	Supplementary Figures	15
14	Supplementary Figure 1. TGA analysis of functionalized electrodes	15
15	Supplementary Figure 2. SEM image of the pristine electrode.	16
16	Supplementary Figure 3. SEM images of functionalized electrodes	17
17	Supplementary Figure 4. Low vacuum SEM images and elements mapping of functionalized	
18	electrodes	18
19	Supplementary Figure 5. Pore size distribution of functionalized electrodes.....	19
20	Supplementary Figure 6. Electrochemically active surface area determination.....	20
21	Supplementary Figure 7. Cyclic voltammetry curves of all functionalized carbon cloth	21
22	Supplementary Figure 8. Current differences at the midpoint of the potential window of the	
23	CV curves versus the scan rates	22
24	Supplementary Figure 9. XPS spectra of functionalized electrodes.....	23
25	Supplementary Figure 10. Overview of the bipolar membrane electrosorption cell.....	24
26	Supplementary Figure 11. pH profiles of functionalized electrodes during testing	25

27	Supplementary Figure 12. Chloride removal capacity of each electrode after functionalization.	
28		26
29	Supplementary Figure 13. Effect of flow rates and applied potentials on the performance of	
30	the electrode functionalized with 1 M HNO ₃ for 20 hours.....	27
31	Supplementary Figure 14. 100-cycle stability test with the electrode treated with 1 M HNO ₃ for	
32	20 hours.	28
33	Supplementary Figure 15. Simulated electrosorption systems with different hydroxyl group	
34	densities.....	29
35	Supplementary Figure 16. Functionalized slit-pore systems and their corresponding number	
36	density profiles of B(OH) ₄ ⁻ and Cl ⁻	30
37	Supplementary Figure 17. Recovery efficiency of functionalized electrodes.....	31
38	Supplementary Figure 18. Calibration curve of boron using the azomethine-H method.....	32
39	References	33
40		
41		

Supplementary Texts

Supplementary Text 1. Electrode functionalization methods

The pristine carbon cloths were blown with compressed air to remove any loosely bound powder on the surface and interstices prior to subsequent treatment. Five different surface functionalization techniques were then applied to these electrodes, as described below. Throughout the rest of this Supplementary Information, the term ‘electrode’ refers specifically to the carbon cloth electrode, unless otherwise specified.

1. Functionalization that introduces basic oxygen-containing groups

UV Irradiation. The UV irradiation of the pristine carbon cloth (dimensions: $8 \times 8 \text{ cm}^2$, approx.) was carried out using a UV-light source (wavelength: 365 nm, XL-1000 UV Crosslinker, Spectro-UV, NY), with power of $4900 \mu\text{W cm}^{-2}$ for a specified duration (i.e., 10 min, 20 min, and 60 min) on each side. After the UV treatment, the functionalized electrodes were stored in plastic petri dishes at ambient conditions for future use.

Acid Treatment. The pristine carbon cloths (dimensions: $8 \times 8 \text{ cm}^2$, approx.) were soaked without stirring in 500 ml of 1 M concentrated acid solutions (i.e., HCl, HNO₃, and H₂SO₄) for a specified duration (i.e., 3 h, 20 h, and 2 weeks). After the soaking period, the functionalized electrodes were removed from the acid solution, washed with DI water, and dried at 90 °C overnight in a convection oven (Heratherm OMS60, Thermo Scientific). The dried and functionalized electrodes were stored in plastic petri dishes at ambient conditions for future use. We note that H₂SO₄ has two pK_a values (-3.00 and 1.99), whereas HCl and HNO₃ each have only one pK_a value (-8.00 and -1.3, respectively)¹. Under our functionalization conditions (i.e., $\text{pH} \approx 0$), they all donate the same amount of protons.

Thermal Treatment. The pristine carbon cloths were heated in an air-furnace (Lindberg Blue M, Thermo-Fisher Scientific, USA) at different specified temperatures (100, 200, and 300 °C). The temperature was raised from ambient to the desired higher value (100-300 °C) within 1.5 h and it was maintained constant for 2 h to complete the surface-oxidation process. Once completed, the furnace was allowed to cool to ambient temperature, and the functionalized electrodes were stored in plastic petri dishes at ambient conditions for future use.

2. Functionalization that introduces boron-selective groups

Direct Surface Grafting Using EDC-Dopamine. For this method, partially oxidized carbon cloths (30 mins UV treated on both sides), containing carboxyl groups on the surface, were used as substrates. Initially, the UV-treated carbon cloths (dimensions: $8 \times 8 \text{ cm}^2$, approx.) were soaked in 150 ml aqueous solution containing 0.1 M 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), under constant magnetic stirring (150 rpm). Then, a specified amount of dopamine chloride (monomer) was added in the mixture, to maintain its concentration to 0.1 M. This heterogeneous mixture was stirred overnight at ambient conditions to functionalize the electrodes with EDC-dopamine. After the reaction, the functionalized electrodes were removed from the solution, rinsed thoroughly with DI water, and dried at 90°C overnight in a convection oven. The dried electrodes were collected and stored in plastic petri dishes for further use.

Direct Surface Grafting Using NMDG and MAPD. For this method, N-methyl-D-glucamine (NMDG) and 3-methylamino-1,2-propanediol (MAPD) were used as the direct surface-grafting agents, respectively. The detailed step-by-step procedure is given below:

Initially, pristine carbon cloths were treated using UV-irradiation for 30 min to introduce hydroxyl and carboxyl groups on their surface through partial oxidation. These partially oxidized carbon cloths were treated using thionyl chloride (SOCl_2) to introduce acyl chloride groups on the surface. The functionalization reaction was carried out under inert conditions using Ar gas flow. Specifically, a mixture of 1.7 mL of dimethylformamide (DMF) and 25 mL of tetrahydrofuran were charged to a round bottom Schlenk flask (volume: 100 mL), and the UV-treated carbon cloths were subsequently added. In this heterogeneous mixture, 25 mL of SOCl_2 was carefully added dropwise to the flask via a syringe while maintaining the flask in an ice bath ($\sim 4^\circ\text{C}$). The reaction started immediately (with slight formation of vapor), and the mixture was continuously stirred with a magnetic stir bar. After 1 h, the ice bath was removed, and the reaction mixture was stirred overnight at ambient temperature.

After completion of the reaction ($\sim 24 \text{ h}$, with slight fading of the electrodes), the solvent- SOCl_2 mixture was carefully decanted in ice bath and the SOCl_2 -functionalized carbon cloths were rinsed quickly using DI water. The electrodes were then dried at 100°C overnight in a convection oven.

For the functionalization using NMDG, 80 mL of DMF and 24 g (0.123 mol) of NMDG powder were charged into a high-pressure vessel (volume: 150 mL). The molar concentration of the reaction mixture was 1.54 M NMDG in DMF. Then, the SOCl₂-functionalized carbon cloths were added into this mixture. The whole mixture was then heated at 90 °C for 3 days in an oil-bath under constant magnetic stirring. After completion of the reaction, the NMDG-functionalized electrodes were removed from the mixture, washed with methanol, and dried at 100 °C overnight in a convection oven to remove any residual solvent.

For the functionalization using MAPD, 80 mL of DMF and 9.533 mL of MAPD (density: 1.17 g mL⁻¹ at 25 °C) were charged into a high-pressure vessel (volume: 150 mL) to form a uniform, transparent mixture. The final molar concentration of the reaction medium was 1.54 M MAPD in DMF. Next, the SOCl₂-functionalized carbon cloths were added in this solution, and the heterogeneous reaction mixture was maintained at 90 °C for 3 days in an oil-bath under constant magnetic stirring. After completion of the reaction, the MAPD-functionalized electrodes were removed from the mixture, washed with methanol, and dried at 100 °C overnight to remove any residual solvent.

115 **Supplementary Text 2.** Boron versus chloride (B/Cl) selectivity calculation

116 Selectivity between boron (B) and chloride (Cl) is quantified by Eq. 1 below, where the numerator
117 and denominator represent, respectively, the ratio of boron electrosorbed during the charging
118 session to the total boron in the influent during that session, and the ratio of chloride electrosorbed
119 during the charging session to the total chloride in the influent during that session:

$$Selectivity = \frac{Q \int_0^{t_c} (C_{B,0} - C_B) dt / \int_0^{t_c} C_{B,0} dt}{Q \int_0^{t_c} (C_{Cl,0} - C_{Cl}) dt / \int_0^{t_c} C_{Cl,0} dt} \quad (1)$$

120 where $C_{B,0}$, $C_{Cl,0}$, C_B , and C_{Cl} is the initial boron, initial chloride, effluent boron, and effluent
121 chloride concentrations (mM), respectively, Q denotes the volumetric feed flow rate (mL min^{-1}),
122 and t_c represents the charging time (min).

Supplementary Text 3. Materials and chemical reagents

The knitted pristine activated carbon cloth was purchased from Charcoal House LLC., Crawford, NE, USA. The pristine carbon cloth did not undergo any polymer treatment during manufacturing. Granular boric acid (> 99.5%) and sodium chloride (> 99%) were purchased from J.T. Baker and Sigma-Aldrich, respectively. Azomethine-H (~ 95%), ammonium acetate ($\geq$ 98%), ethylenediaminetetraacetic acid disodium salt dehydrates (EDTA), thioglycolic acid (98%). L(+) Ascorbic acid (99%) was purchased from Acros. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC, MW: 191.7 g mol⁻¹), N-methyl-D-glucamine (NMDG, 99%, MW: 195.21 g mol⁻¹), 3-methylamino-1,2-propanediol (MAPD, 98-99%, MW: 105.18 g mol⁻¹), thionyl chloride (SOCl₂, > 99%, MW: 118.97 g mol⁻¹), tetrahydrofuran (THF, 99%, MW: 72.11 g mol⁻¹, laboratory grade), dimethylformamide (DMF, anhydrous, 99.8%, MW: 73.1 g mol⁻¹), methanol (MeOH, MW: 32.04 g mol⁻¹, laboratory grade), hydrochloric acid (HCl, certified ACS grade), nitric acid (HNO₃, trace metal grade), sulfuric acid (H₂SO₄, certified ACS grade) were purchased from Thermo-Fisher Scientific (Waltham, MA). Deionized (DI) water (resistivity: 18.2 M Ω $\times$ cm, TOC < 5.0 μ g L⁻¹) was generated via a Milli-Q Water Purification System (Burlington, MA). All reagents were used as obtained, without any further purification.

Supplementary Text 4. Electrode characterization

Scanning Electron Microscopy (SEM). The surface morphology of the pristine and functionalized electrodes was analyzed using a scanning electron microscope (Nova-200 nanolab SEM/FIB, FEI Company, USA) at 5 kV with 0.4 nA beam current. The completely dried electrodes were carefully mounted on horizontal SEM stubs with conductive graphite paint (Electrodag 502). The outer surface morphology and microstructure of each sample were characterized at low and high magnifications.

X-ray Photoelectron Spectroscopy (XPS). The atomic composition and surface functionalization of the pristine and functionalized electrodes were determined using an XPS analyzer (Kratos axis ultra, Kratos analytical). The XPS system was operated at room temperature under 3×10^{-8} Pa using monochromatic Al-K α X-ray source (8 mA and 14 kV). An electron gun was used to maintain charge neutrality on the surface of each sample. Survey scans (pass energy: 160 eV) were used to quantify the atomic composition of the various samples. Core scans (pass energy: 20 eV) were used to investigate the binding environment of the elements in each sample. Binding energies of all the elements were calibrated relative to C1s at 284.8 eV. Collected data were analyzed using CasaXPS software (version 2.3.25PR1.0).

Thermogravimetric Analysis (TGA). Thermogravimetric analyses of pristine and functionalized electrodes were performed with a TA Instruments TGA Q550 instrument. Approximately 10-20 mg of dried sample were loaded onto Platinum pans, and the temperature was increased to 700 °C at a ramp rate of 5 °C min⁻¹ under flowing N₂ gas. The mass of the electrode at 110 °C was considered as the initial mass of the dried electrodes, and the mass loss data at higher temperatures were normalized to this value to determine the extent of mass variation with temperature.

Brunauer-Emmett-Teller (BET) Surface Area Analysis. The porosity, pore volume, and pore-radius of the functionalized electrodes were determined through the N₂ adsorption-desorption method using a surface area and porosity analyzer (ASAP 2020 Plus, Micrometrics). Approximately 150 mg of the dried electrodes were activated at 110 °C under vacuum overnight, followed by N₂ adsorption-desorption measurements.

Magic angle spinning nuclear magnetic resonance (MAS NMR). The interaction between boron and MAPD-functionalized electrode was investigated by using ¹¹B solid-state MAS NMR. Before

analysis, the MAPD-functionalized electrode underwent three charging/discharging cycles in the electrosorption system under the same conditions as previous experiments. Subsequently, the used electrode was vacuum-dried, milled into powders, and prepared for MAS NMR analysis. ^{11}B solid-state MAS NMR spectra were acquired at room temperature using a Bruker Avance NEO 500 MHz NMR spectrometer equipped with a Bruker 3.2 mm cross-polarization MAS (CPMAS) probe. A MAS frequency of 20 kHz was employed for all ^{11}B signal acquisitions. Spectra were obtained using a Hahn-echo pulse sequence featuring a 90° pulse of 6 μs and a recycle delay of 5 s. Calibration of the ^{11}B chemical shifts was performed using 0.1 M boric acid solution as an external reference^{2, 3}.

Electrochemically active surface area (EASA) determination. The EASA was estimated from the double-layer capacitance (C_{dl}) via cyclic voltammetry measurements. Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (CHI 660E) with a three-electrode setup, consisting of a functionalized carbon cloth electrode as the working electrode, a platinum (Pt) wire as the counter electrode, and an Ag/AgCl electrode (in 4 M KCl with AgCl solution) as the reference electrode (Supplementary Fig. 6a). The electrolyte used was a 0.5 M aqueous Na_2SO_4 solution. CV measurements were conducted in the non-faradaic region (-0.1 to 0.1 V) with scan rates ranging from 20 to 100 mV s^{-1} . Each functionalized electrode underwent 10 repetitions of the CV measurement. The electrolyte was replaced between measurements for each functionalized electrode. The EASA was estimated according to

$$EASA = \frac{C_{\text{dl}}}{C_s} \quad (2)$$

where C_{dl} is the double-layer capacitance, and C_s represents the specific capacitance of standard electrode materials per unit surface area. Based on literature-reported C_s values for carbon electrode materials, a value of 0.02 mF cm^{-2} was used for the EASA calculation⁴. C_{dl} was determined from the slope of the linear regression between the current differences ($\Delta i/2 = (i_a - i_c)/2$) at the midpoint of the potential window (i.e., $E = 0 \text{ V}$) of the CV curves versus the scan rates, divided by the area of the functionalized electrode immersed in the electrolyte (i.e., 4 cm^2). The i_a and i_c are the anodic and cathodic currents, respectively.

Supplementary Text 5. Bipolar membrane (BPM) assisted electrosorption cell fabrication

We built the BPM-electrosorption cell based on our previous work⁵. We used an ultra-corrosion-resistant grade 2 titanium sheet (0.02 inches thick, McMaster Carr) for the current collectors and flow path (Supplementary Fig. 10). Acrylic plates (0.5 inches thick, McMaster Carr) served as the endplates. For the membrane gasket material, we used ultra-thin silicone (0.01 inches thick, McMaster Carr). Fabrication of the anode material was described in Supplementary Text 1. We used the pristine electrode as the cathode material. Throughout the study, we utilized a commercially available bipolar membrane (Fumasep FBM with PEEK reinforcement, Fuel Cell Store).

Supplementary Text 6. Boron detection method

Information regarding the preparation of azomethine-H solution, buffer solution, boron standard solutions, and its analysis is briefly described as follows^{6, 7}: (1) azomethine-H solution was prepared from dissolving 3.8 g azomethine-H and 8 g L-ascorbic acid with 1 L deionized water; (2) buffer solution was made by adding 500 g ammonium acetate to 1 L deionized water; (3) boron standard solutions were prepared by diluting from 100 mg L⁻¹ boric acid solutions with deionized water into six boron standard solutions (0, 0.1, 0.5, 1, 2, and 5 mg L⁻¹); and (4) analyzed solutions in polypropylene tubes (capacity = 15 mL) were filled with 3.5 mL boron standard solutions or samples, followed by 0.5 mL 0.0025 M Ethylenediaminetetraacetic acid (EDTA) solution, 2.5 mL azomethine-H solution, and 1 mL buffer solution and allowed to stand for 1 h.

Boron concentrations were analyzed in triplicate by the UV/vis spectrophotometer (Hitachi U-2900, Hitachi High-Technologies Co., Kyoto, Japan) with the absorbance at 410 nm. Mean boron concentrations were determined by averaging triplicate measurements for each collected sample. The triplicate variability of one sample was < 5% of the mean. All reagents above were analytical grade and purchased from Sigma Aldrich (St. Louis, MO, USA). Calibration curves (Supplementary Fig. 18) were constructed throughout each day of testing using six boron standard solutions (0, 0.1, 0.5, 1, 2, and 5 mg L⁻¹) with an average $R^2 \geq 0.999$.

Supplementary Tables

Supplementary Table 1. BET data for the pristine and functionalized electrodes.

	Items	BET surface area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (cm ³ g ⁻¹)
Pristine		1127.06	1.72	0.48
	3 h	1421.10	1.74	0.62
HNO ₃	20 h	1325.12	1.75	0.58
	2 w	1598.24	1.71	0.68
H ₂ SO ₄	3 h	1477.95	1.71	0.63
	20 h	1218.81	1.72	0.52
	2 w	1095.39	1.71	0.47
HCl	3 h	1252.47	1.74	0.55
	20 h	1650.49	1.77	0.73
	2 w	1164.73	1.70	0.50
Thermal annealing	100 °C	1475.47	1.79	0.66
	200 °C	1940.02	1.76	0.85
	300 °C	944.99	1.74	0.41
UV irradiation	10 min	1609.83	1.76	0.71
	20 min	1333.70	1.71	0.57
	60 min	1280.64	1.77	0.57
Functional groups	DP*	189.79	1.6	0.08
	NMDG*	834.04	1.79	0.37
	MAPD*	918.81	1.75	0.40

*DP: Dopamine; NMDG: *N*-methyl-D-glucamine; MAPD: 3-methylamino-1,2-propanediol.

224 **Supplementary Table 2.** Elemental analysis of functionalized electrodes from survey XPS.

Item		Atomic % C	Atomic % N	Atomic % O
Thermal annealing	100°C	65.36	2.36	32.28
	200°C	81.21	2.44	16.34
	300°C	60.66	2.56	36.78
UV irradiation	10 min	74.64	2.97	22.39
	20 min	74.53	2.82	22.65
	60 min	65.19	2.37	32.44
HCl	3h	50.44	2.76	46.81
	20h	51.87	2.05	46.07
	2 weeks	78.73	1.54	19.73
HNO ₃	3h	64.42	3.11	32.47
	20h	61.65	3.58	34.77
	2 weeks	64.37	3.86	31.77
H ₂ SO ₄	3h	58.74	2.71	38.56
	20h	72.2	2.21	25.59
	2 weeks	71.4	4.48	24.12
Functional groups	DP*	75.63	5.05	19.33
	MAPD*	54.99	3.59	41.41
	NMDG*	75.89	5.05	19.06

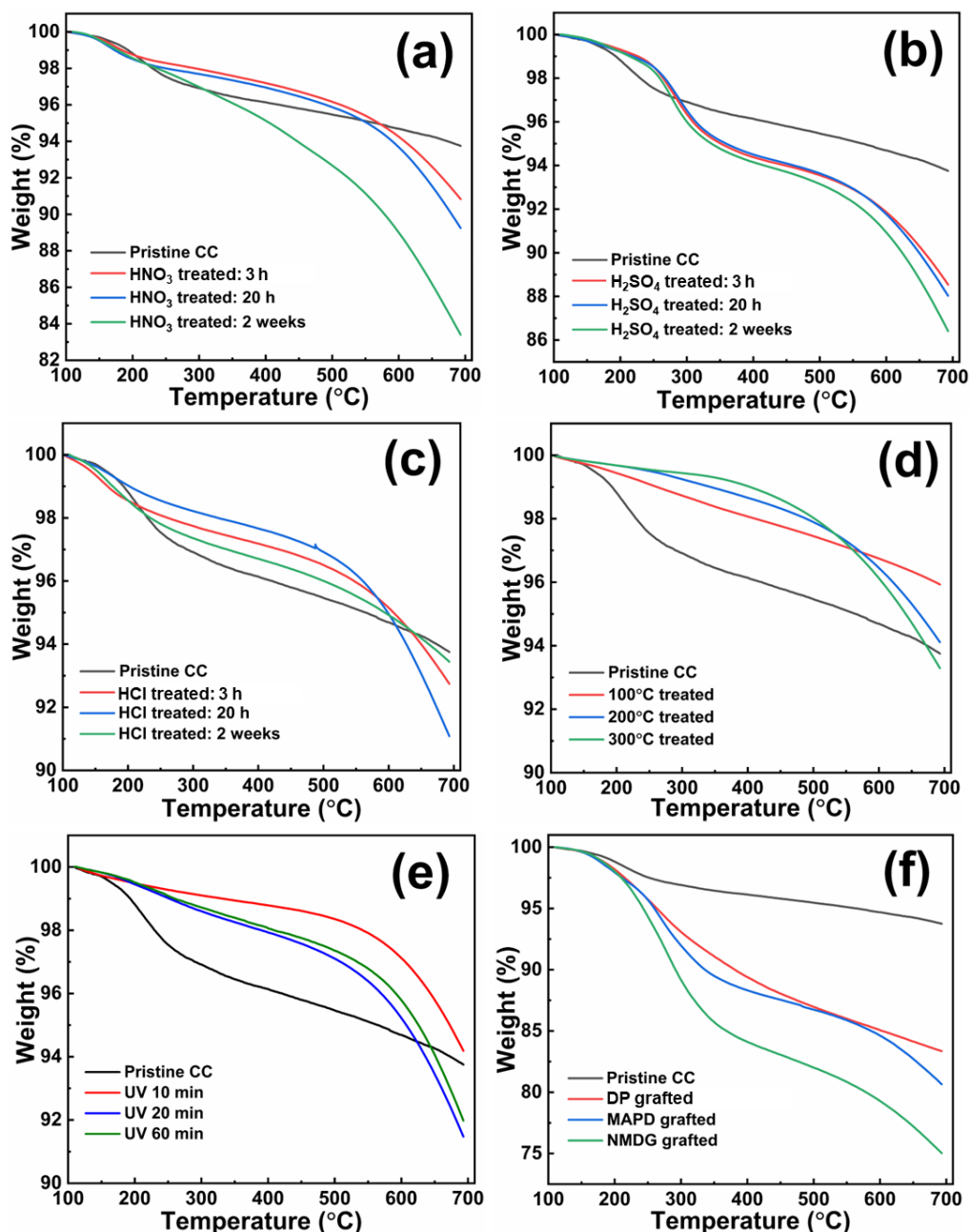
225 *DP: Dopamine; NMDG: *N*-methyl-D-glucamine; MAPD: 3-methylamino-1,2-propanediol.

226 **Supplementary Table 3.** Kendall rank correlation coefficients of different properties.

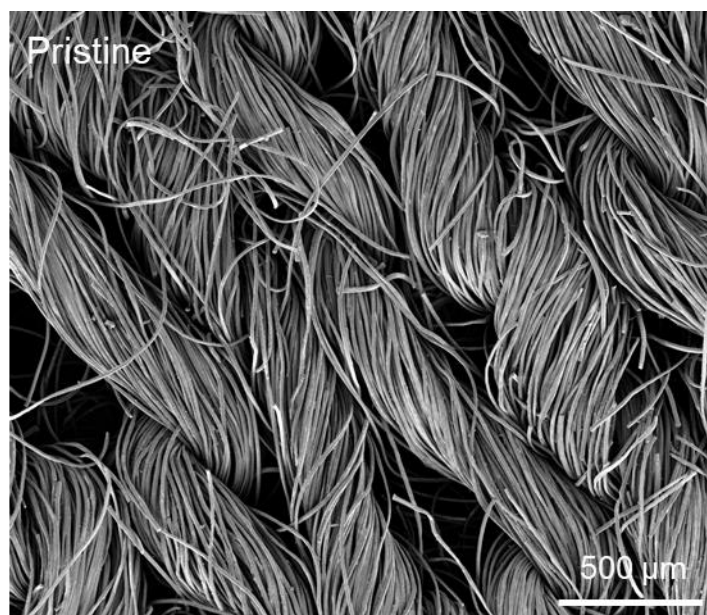
Kendall rank correlation	Selectivity	Hydroxyl	Lactone	Carboxyl	BET	Pore volume	Pore size	EASA
Selectivity	1.000	0.190	0.163	0.033	-0.033	-0.026	-0.150	-0.307
Hydroxyl	0.190	1.000	-0.020	0.556	-0.216	-0.223	-0.068	-0.046
Lactone	0.163	-0.020	1.000	0.190	0.020	0.026	-0.041	-0.412
Carboxyl	0.033	0.556	0.190	1.000	0.020	0.013	0.014	0.216
BET	-0.033	-0.216	0.020	0.020	1.000	0.970	0.191	0.203
Pore volume	-0.026	-0.223	0.026	0.013	0.970	1.000	0.226	0.197
Pore size	-0.150	-0.068	-0.041	0.014	0.191	0.226	1.000	0.178
EASA	-0.307	-0.046	-0.412	0.216	0.203	0.197	0.178	1.000

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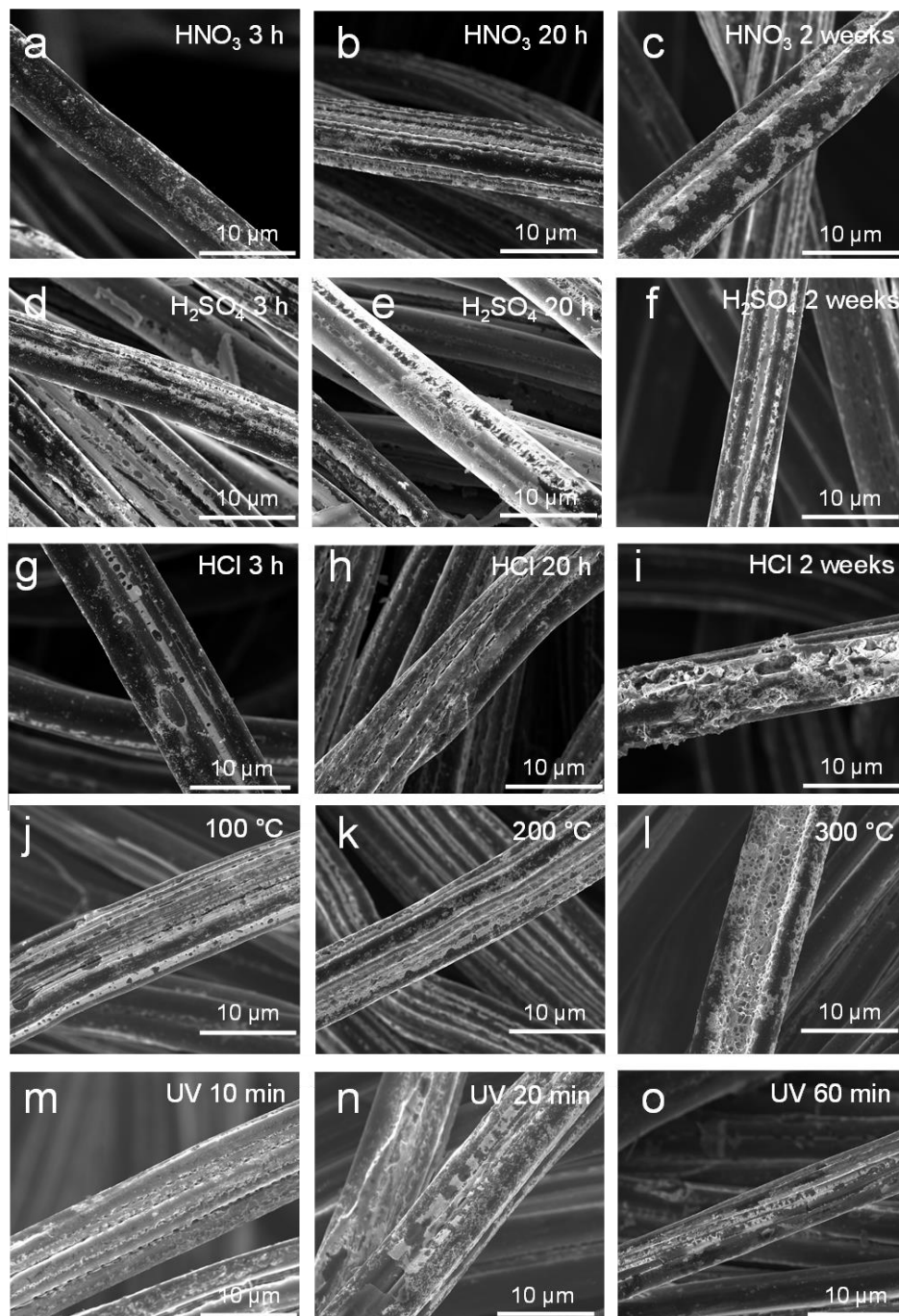
Supplementary Figures



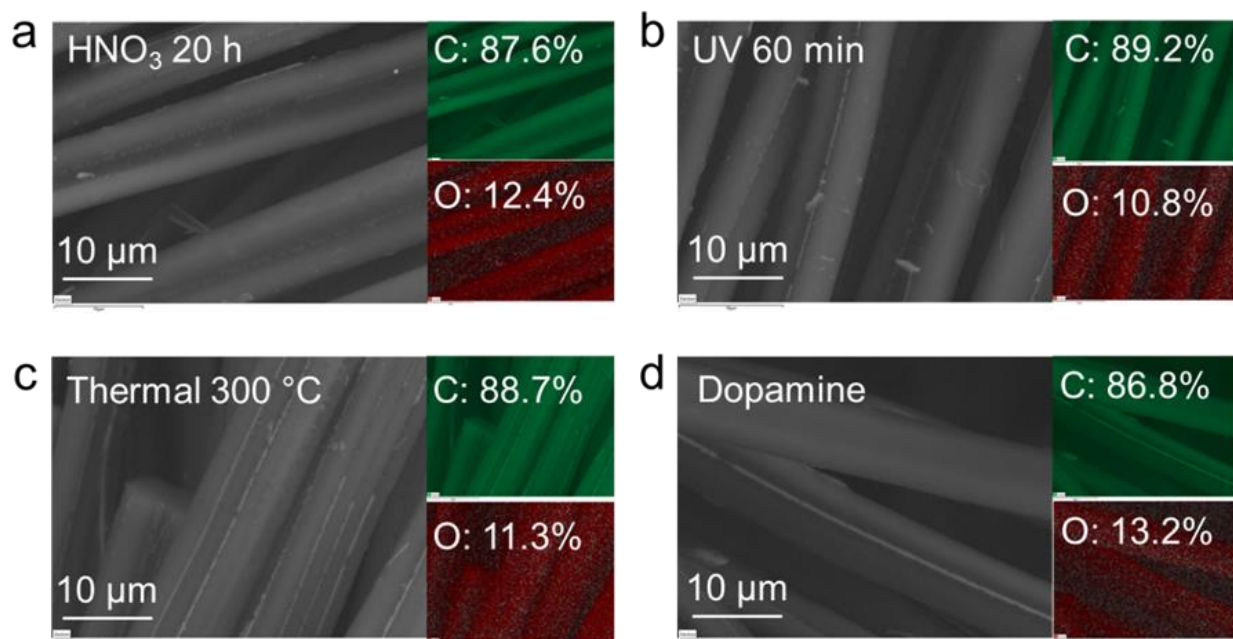
Supplementary Figure 1. TGA analysis of functionalized electrodes: (a) HNO₃ treated, (b) H₂SO₄ treated, (c) HCl treated, (d) thermally annealed, (e) UV irradiated, and (f) boron-selective groups functionalized electrodes. The results for each sample were normalized by the mass of the sample at 110 °C. DP, NMDG, and MAPD represent dopamine, *N*-methyl-D-glucamine, and 3-methylamino-1,2-propanediol.



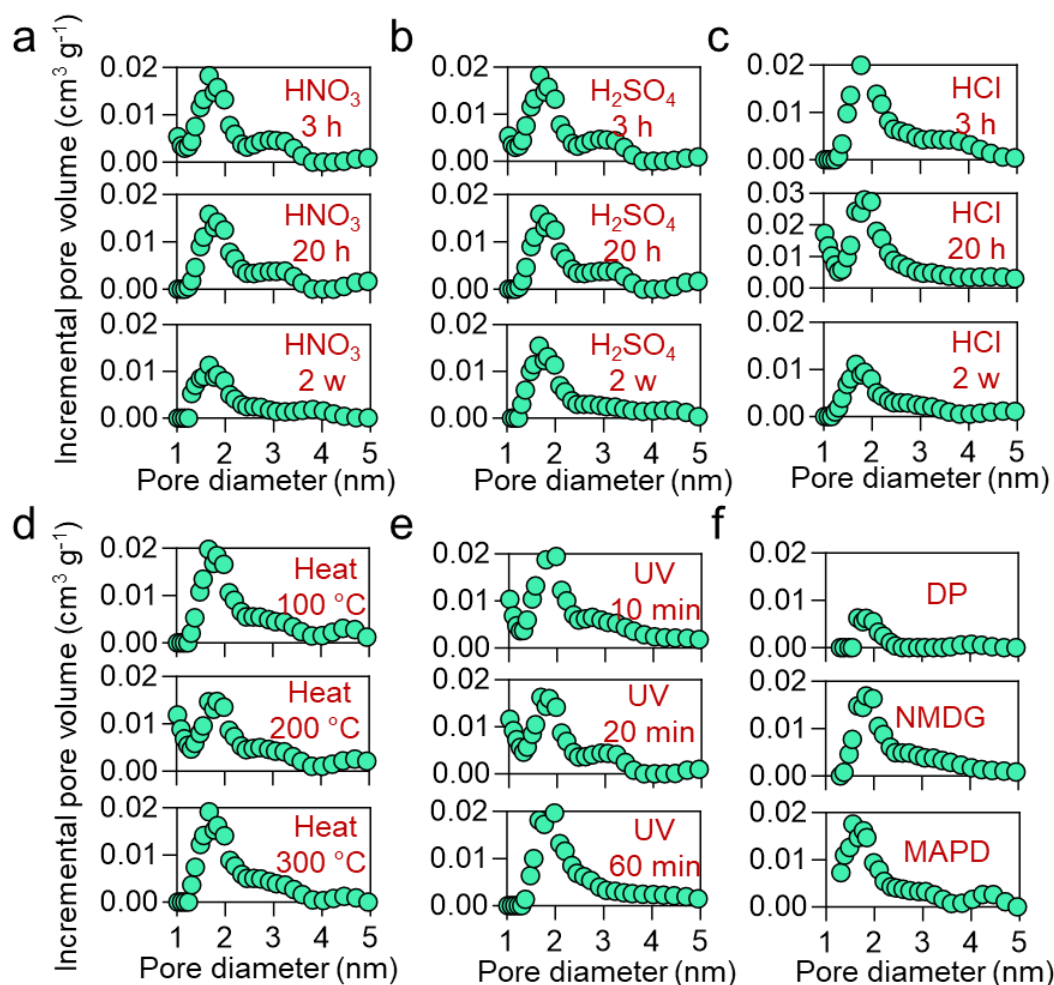
Supplementary Figure 2. SEM image of the pristine electrode.



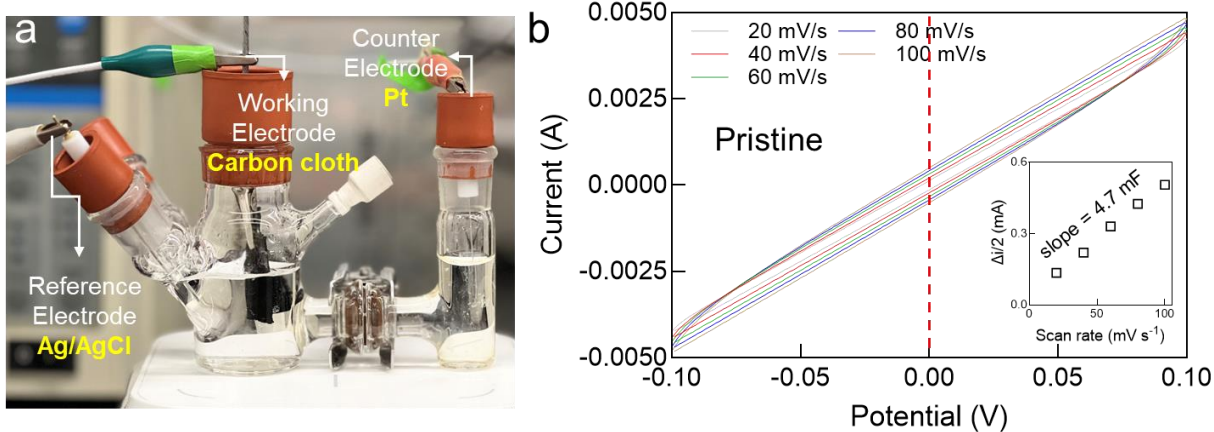
Supplementary Figure 3. SEM images of functionalized electrodes: HNO_3 treated electrodes with duration of (a) 3 h, (b) 20 h, and (c) 2 weeks; H_2SO_4 treated electrodes with duration of (d) 3 h, (e) 20 h, and (f) 2 weeks; HCl treated electrodes with duration of (g) 3 h, (h) 20 h, and (i) 2 weeks; Thermally annealed electrodes at temperature of (j) 100, (k) 200, and (l) 300 °C; UV irradiated electrodes with duration of (m) 10, (n) 20, and (o) 60 min.



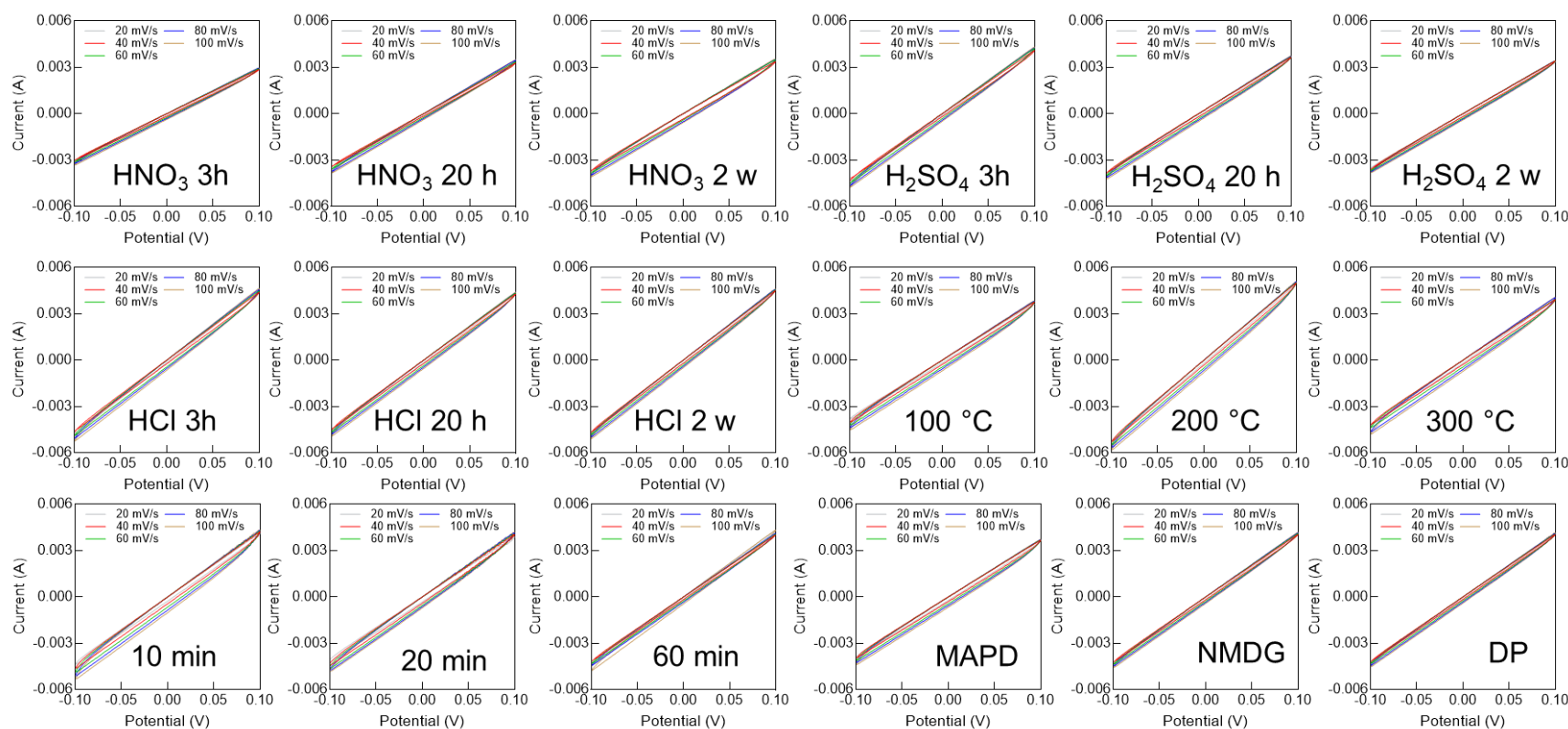
Supplementary Figure 4. Low vacuum SEM images and elements mapping of functionalized electrodes (a-d). The green and red overlays represent the elemental mappings of carbon and oxygen atoms, respectively. The SEM chamber pressure was increased to 60 Pa using nitrogen.



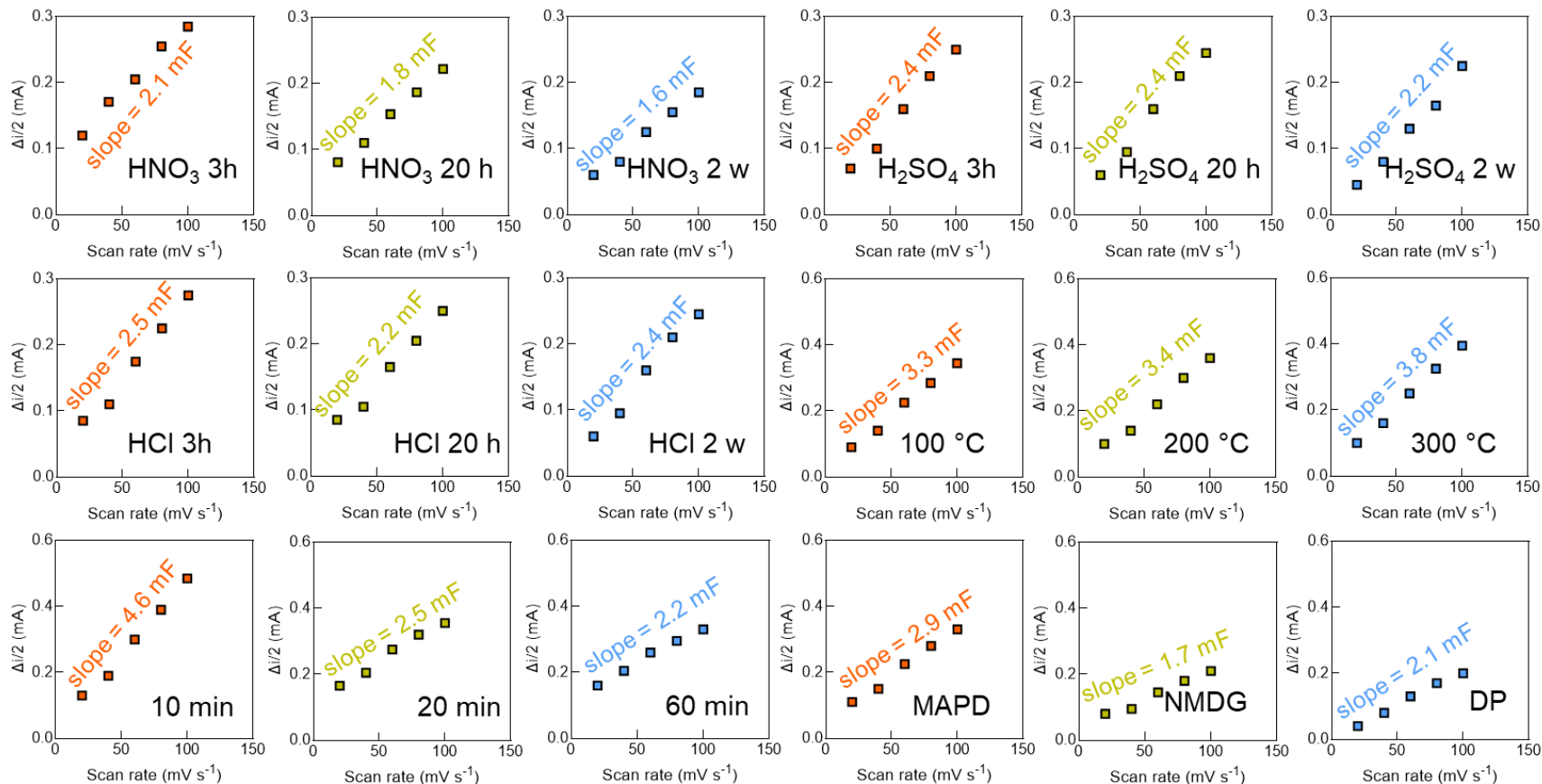
Supplementary Figure 5. Pore size distribution of functionalized electrodes. **(a)** HNO_3 treated, **(b)** H_2SO_4 treated, **(c)** HCl treated, **(d)** thermally annealed, **(e)** UV irradiated, and **(f)** boron-selective groups functionalized electrodes. The results for each sample were normalized by the mass of the sample at 110 °C. DP, NMDG, and MAPD represent dopamine, *N*-methyl-D-glucamine, and 3-methylamino-1,2-propanediol, respectively.



Supplementary Figure 6. Electrochemically active surface area determination. (a) Experimental setup. (b) Cyclic voltammetry curves of the pristine carbon cloth in the non-faradaic region (-0.1 to 0.1 V vs. Ag/AgCl) at scan rates of 20, 40, 60, 80, and 100 mV s⁻¹. The inset figure is current differences ($\Delta i/2 = (i_a - i_c)/2$) as a function of scan rate for the pristine electrode. The i_a and i_c are the anodic and cathodic currents at $E = 0$ V, respectively.

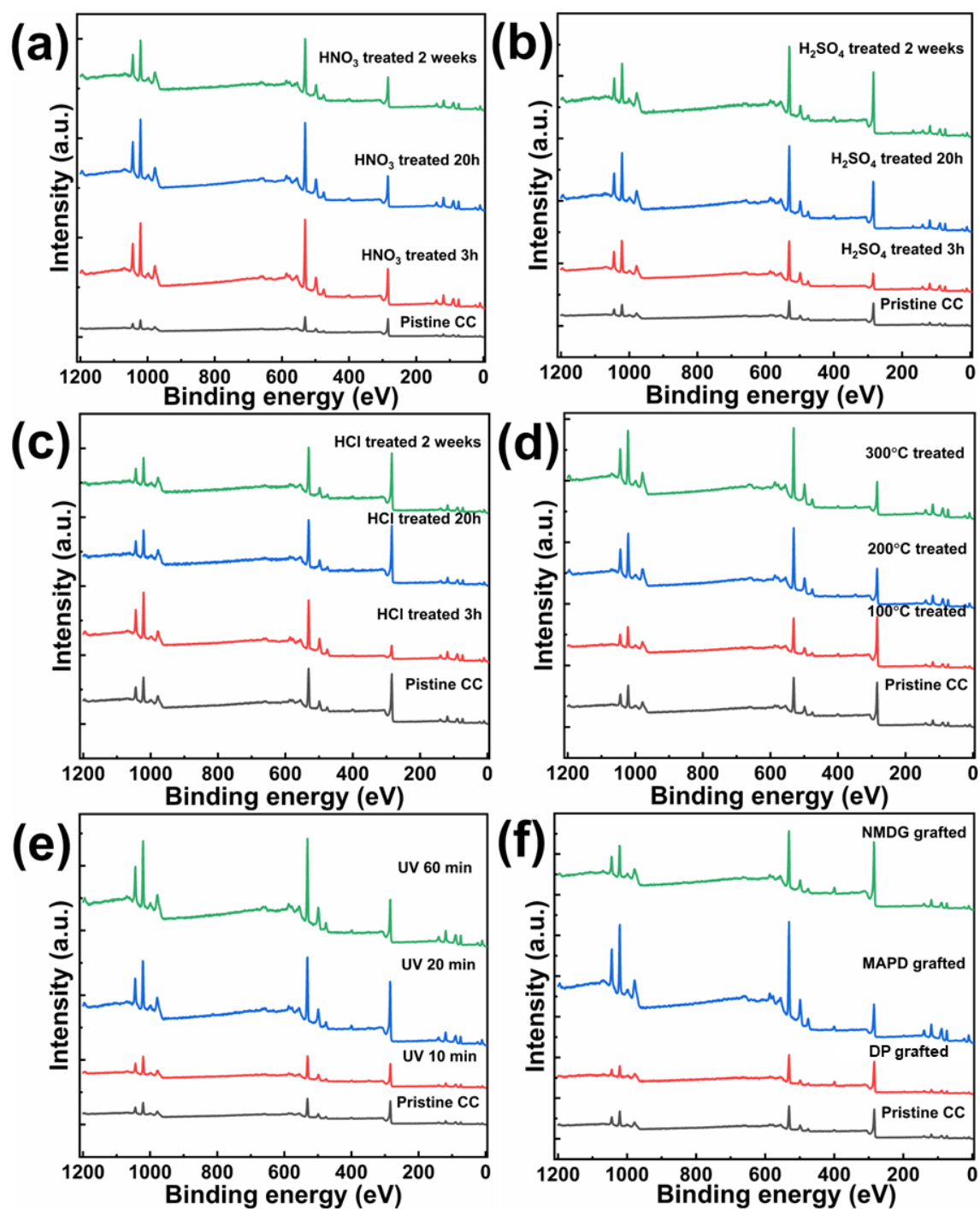


Supplementary Figure 7. Cyclic voltammetry curves of all functionalized carbon cloth (HNO₃, H₂SO₄, HCl, thermally annealed, UV irradiated, and boron-selective groups) in a non-faradaic region (-0.1 to 0.1 V vs. Ag/AgCl) at scan rates of 20, 40, 60, 80, and 100 mV s⁻¹. DP, NMDG, and MAPD represent dopamine, *N*-methyl-D-glucamine, and 3-methylamino-1,2-propanediol, respectively.

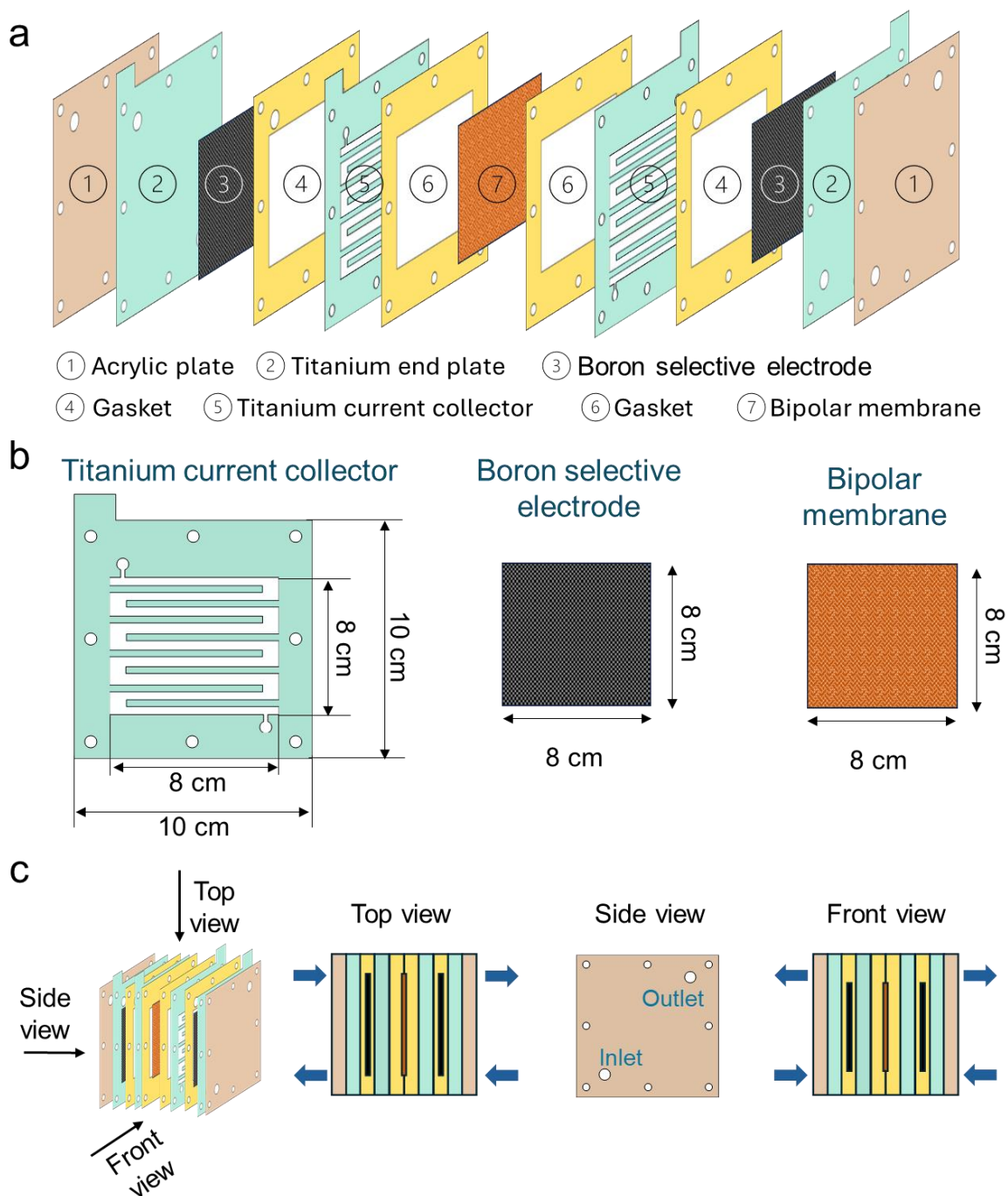


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9 **Supplementary Figure 8.** Current differences ($\Delta i/2 = (i_a - i_c)/2$) at the midpoint of the potential window (i.e., $E = 0$ V) of the CV
 10 curves versus the scan rates. The i_a and i_c are the anodic and cathodic currents at $E = 0$ V, respectively. DP, NMDG, and MAPD
 11 represent dopamine, *N*-methyl-D-glucamine, and 3-methylamino-1,2-propanediol, respectively.



Supplementary Figure 9. XPS spectra of functionalized electrodes: (a) HNO₃ treated, (b) H₂SO₄ treated, (c) HCl treated, (d) thermally annealed, (e) UV irradiated, and (f) boron-selective groups functionalized electrodes. DP, NMDG, and MAPD represent dopamine, *N*-methyl-D-glucamine, and 3-methylamino-1,2-propanediol, respectively.

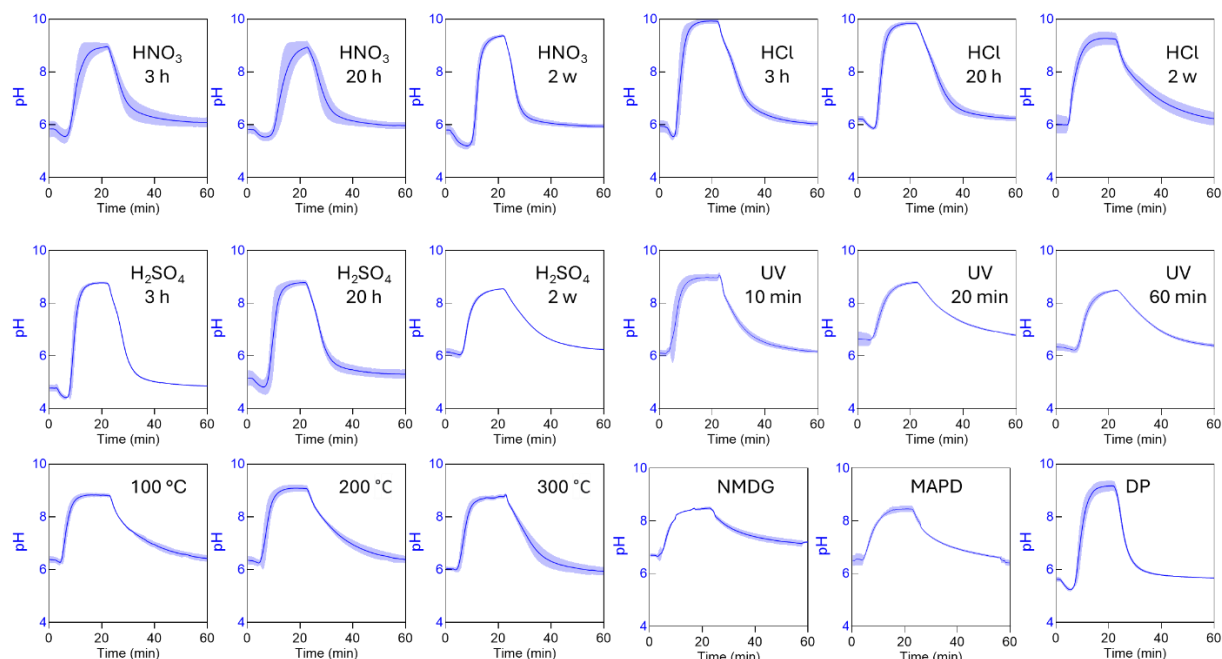


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19 **Supplementary Figure 10.** Overview of the bipolar membrane electrosorption cell. (a) Cell
20 structure and components. (b) Cell size specifications. (c) Top, side, and front views of the
21 assembled cell.

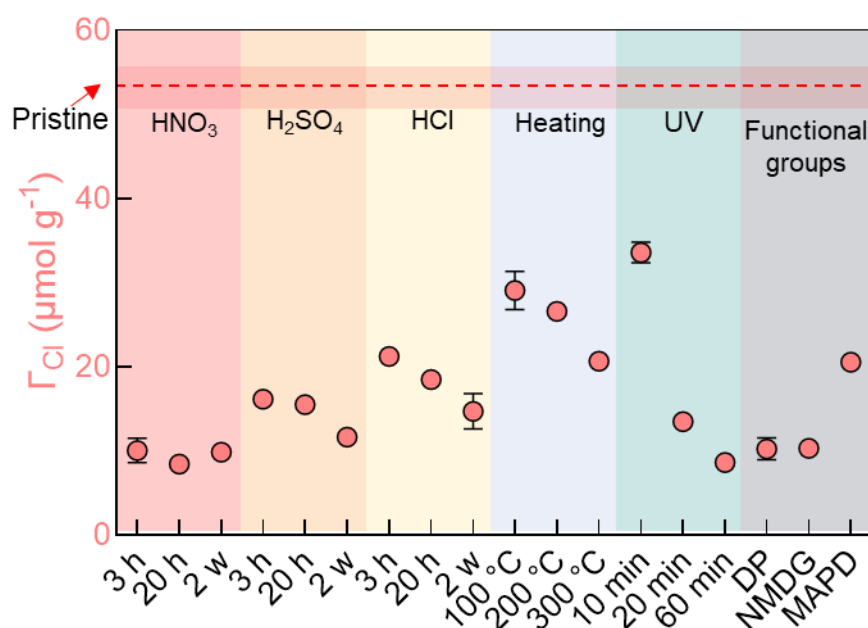
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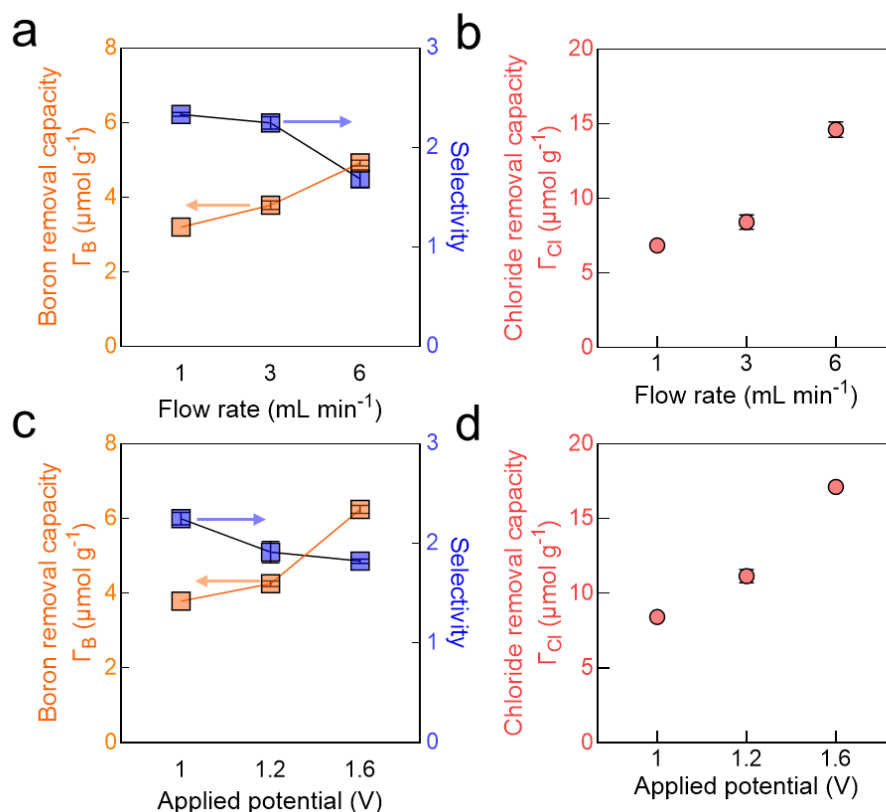


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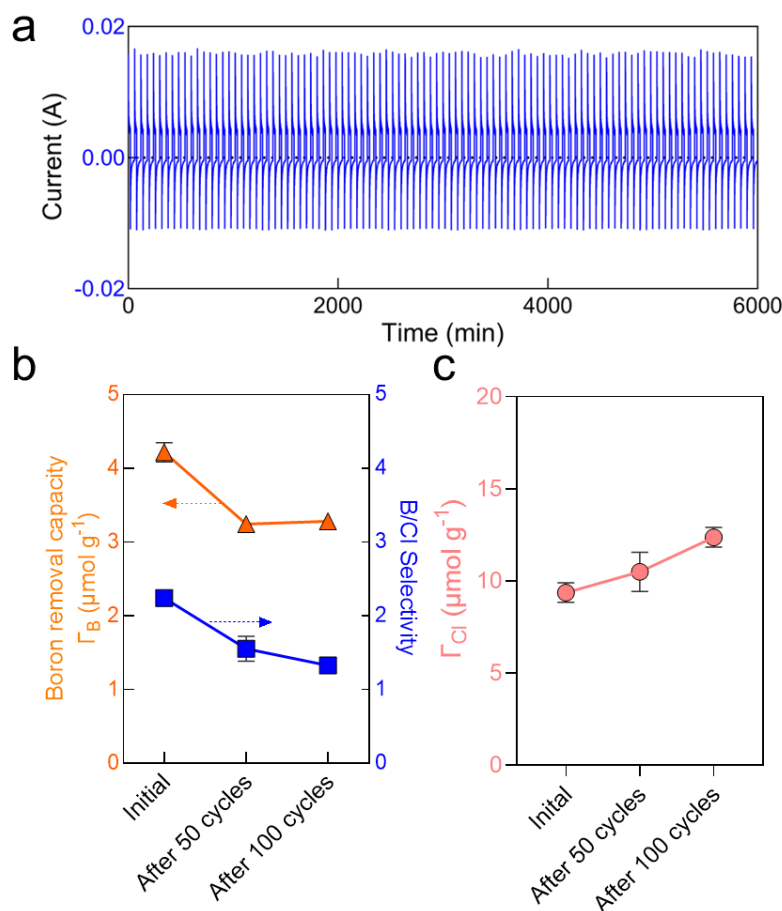
25 **Supplementary Figure 11.** pH profiles of functionalized electrodes during testing. Blue curves
 26 present the mean value of three consecutive cycles during charging, and the shaded areas are the
 27 standard deviations from three consecutive cycles. The BPM assisted electrosorption system was
 28 operated with a feedwater containing 5 mM NaCl and 1 mM B(OH)₃ at a flow rate of 3.0 mL min⁻¹
 29 in a single-pass configuration. The anode and cathode sides received identical feedwater without
 30 pH adjustment (pH 6.0 ± 0.2). Each cycle consists of applying 1.0 V for 20 minutes (charging
 31 period), followed by 0 V for 40 minutes (discharging period). Before collecting samples, the
 32 system was allowed to operate overnight (> 12 h) to exclude the effect of pure adsorption. DP,
 33 MAPD, and NMDG represent dopamine, 3-methylamino-1,2-propanediol, and *N*-methyl-D-
 34 glucamine, respectively.



Supplementary Figure 12. Chloride removal capacity (Γ_{Cl}) of each electrode after functionalization. The pink dashed line represents the mean chloride removal capacity of the pristine electrode over three consecutive cycles, while the corresponding shaded area represents the standard deviation from these cycles ($n=3$). The BPM assisted electrosorption system operated with a feedwater containing 5 mM NaCl and 1 mM B(OH)₃ at a flow rate of 3.0 mL min⁻¹ in a single-pass configuration. The anode and cathode sides received identical feedwater without pH adjustment (pH 6.0 $\pm$ 0.2). Each cycle consists of applying 1.0 V for 20 minutes (charging period) followed by 0 V for 40 minutes (discharging period). Before collecting samples, the system was allowed to operate overnight (> 12 h) to exclude the effect of pure adsorption. DP, MAPD, and NMDG represent dopamine, 3-methylamino-1,2-propanediol, and *N*-methyl-D-glucamine, respectively. Data are presented as mean $\pm$ standard deviation derived from three consecutive cycles ($n=3$).

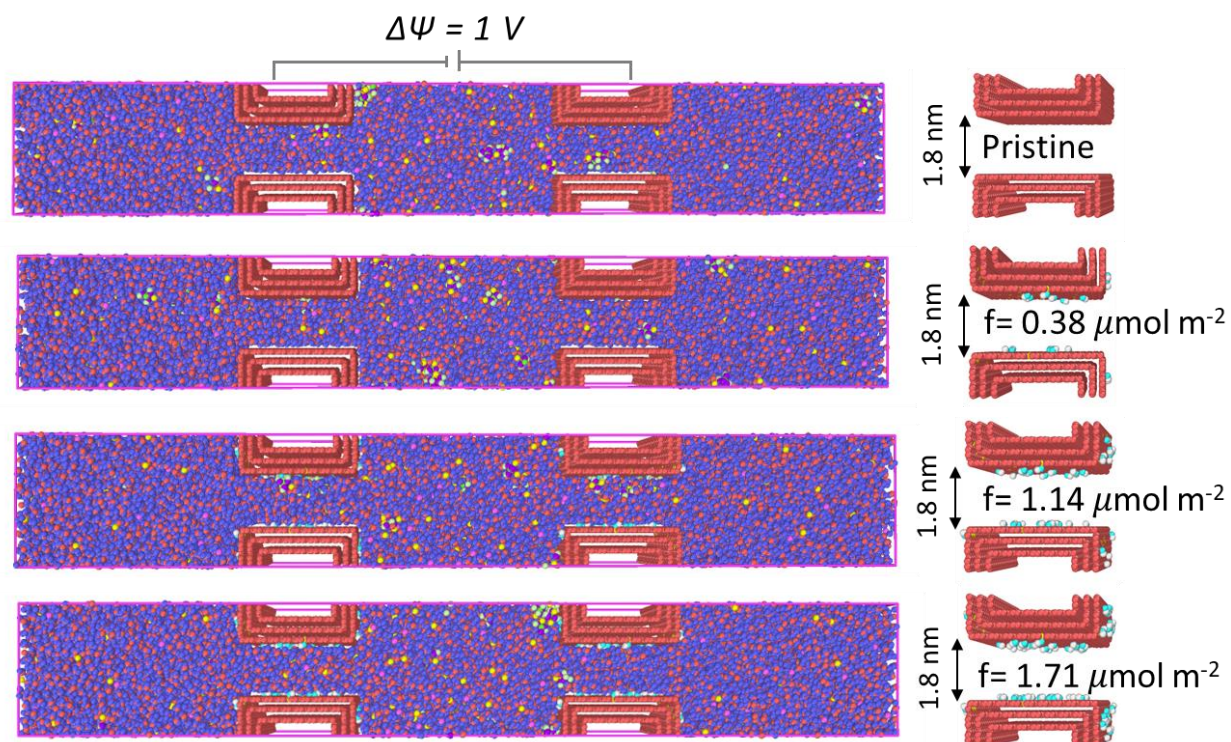


Supplementary Figure 13. Effect of flow rates and applied potentials on the performance of the electrode functionalized with 1 M HNO₃ for 20 hours. (a) Boron electrosorption capacity (orange square) and B/Cl selectivity (blue square) at different flow rates (1-6 mL min⁻¹). (b) Chloride removal capacity at different flow rates. (c) Boron electrosorption capacity (orange square) and B/Cl selectivity (blue square) at different applied potentials (1.0-1.6 V). (d) Chloride removal capacity at different applied potentials. The anode and cathode sides received identical feedwater without pH adjustment (pH 6.0 ± 0.2). Boron/chloride removal capacities were calculated by the amount of boron/chloride removed during the charging cycle. Each cycle consists of applying 1.0 V (unless stated otherwise) for 20 minutes (charging period) followed by 0 V for 40 minutes (discharging period). The flow rate is 3 mL min⁻¹ (unless stated otherwise). Before collecting samples, the system was allowed to operate overnight (> 12 h) to exclude the effect of pure adsorption. Data are presented as mean ± standard deviation derived from three consecutive cycles (n=3).

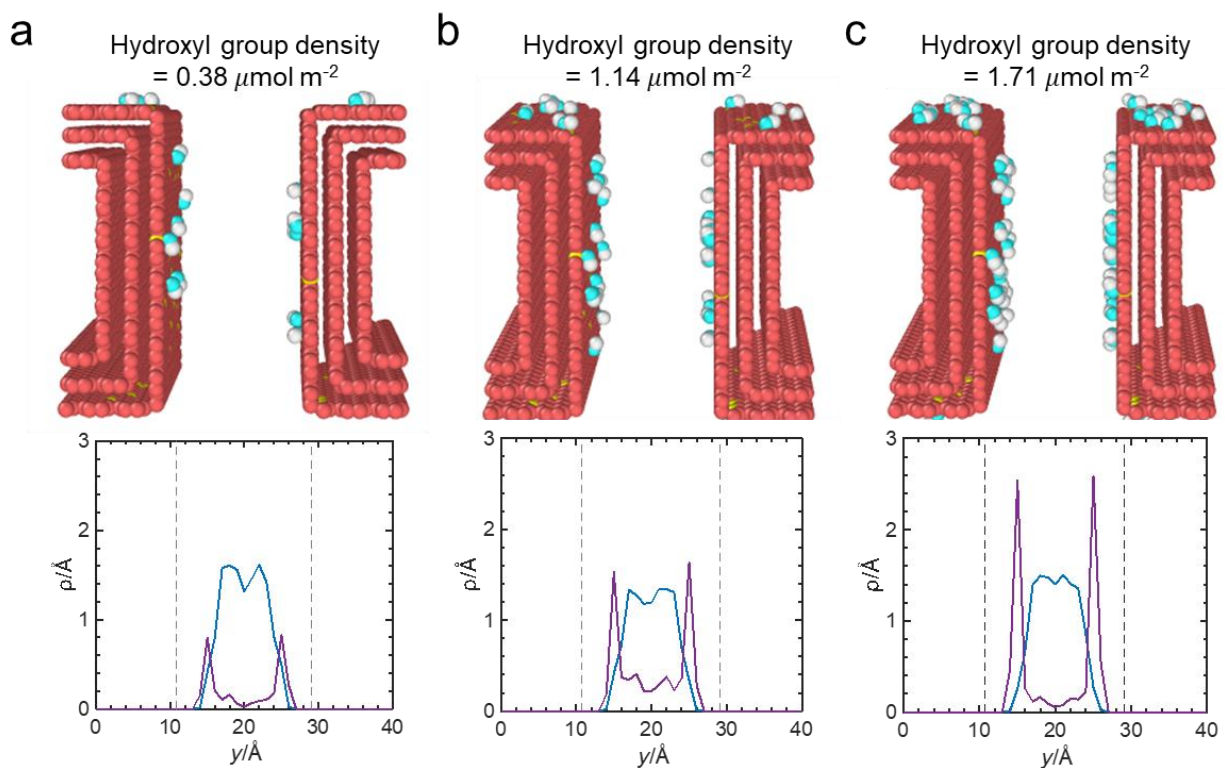


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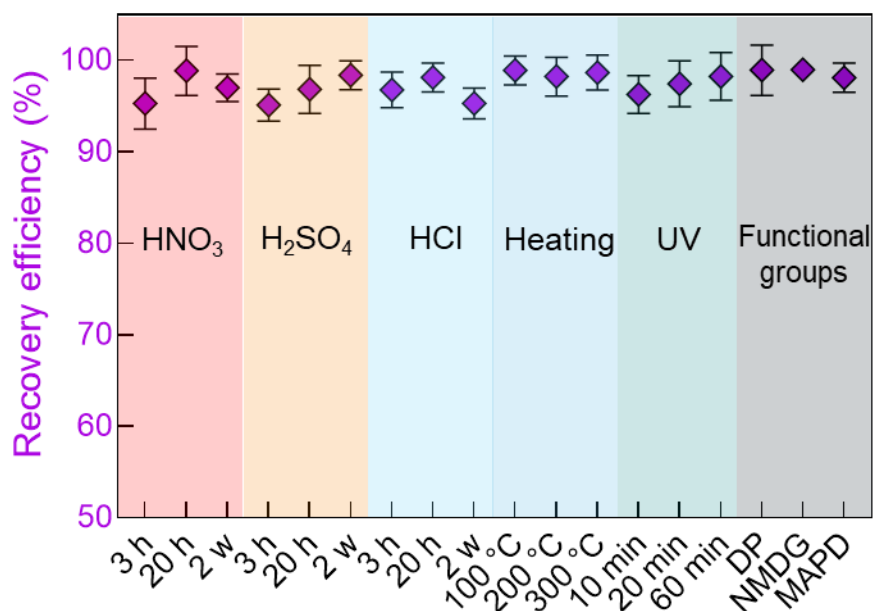
65 **Supplementary Figure 14.** 100-cycle stability test with the electrode treated with 1 M HNO₃ for
 66 20 hours. (a) Current data for the 100-cycle test. (b) Boron removal (orange triangle) and B/Cl
 67 selectivity (blue square) of the electrode during the test. (c) Chloride removal (pink circle) during
 68 the test. The BPM assisted electrosorption system was operated with a feedwater containing 5 mM
 69 NaCl and 1 mM B(OH)₃ at a flow rate of 3.0 mL min⁻¹ in a single-pass configuration. The anode
 70 and cathode sides received identical feedwater without pH adjustment (pH 6.0 ± 0.2). Recovery
 71 efficiency was calculated by the amount of boron released during discharging and the amount of
 72 boron removed during charging. Each cycle consists of applying 1.0 V for 20 minutes (charging
 73 period) followed by 0 V for 40 minutes (discharging period). Before collecting samples, the system
 74 was allowed to operate overnight (> 12 h) to exclude the effect of pure adsorption. Data in Panels
 75 b and c are presented as mean ± standard deviation derived from three consecutive cycles (n=3).



Supplementary Figure 15. Simulated electrosorption systems with different hydroxyl group densities (0-1.71 $\mu\text{mol m}^{-2}$).



Supplementary Figure 16. Functionalized slit-pore systems and their corresponding number density profiles of B(OH)_4^- (purple solid line) and Cl^- (blue solid line) with **(a)** 0.38, **(b)** 1.14, and **(c)** $1.71 \mu\text{mol m}^{-2}$ of hydroxyl groups. Gray dashed line represents the slit-pore surface.

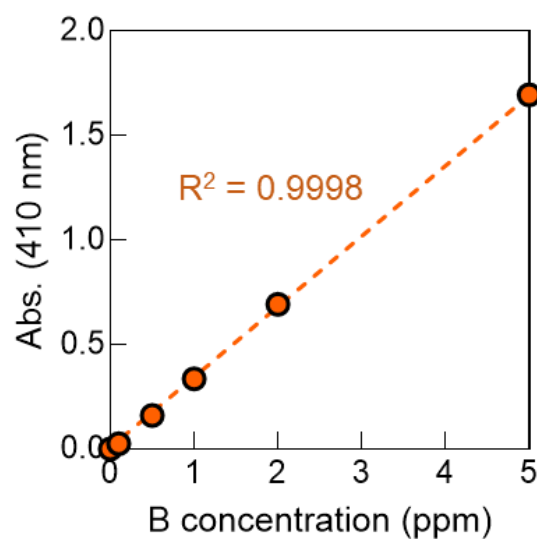


84

85 **Supplementary Figure 17.** Recovery efficiency of functionalized electrodes. The BPM assisted
 86 electrosorption system was operated with a feedwater containing 5 mM NaCl and 1 mM B(OH)₃
 87 at a flow rate of 3.0 mL min⁻¹ in a single-pass configuration. The anode and cathode sides received
 88 identical feedwater without pH adjustment (pH 6.0 ± 0.2). Recovery efficiency was calculated by
 89 comparing the amount of boron released during discharging to the amount of boron removed
 90 during charging. Each cycle consists of applying 1.0 V for 20 minutes (charging period) followed
 91 by 0 V for 40 minutes (discharging period). Before collecting samples, the system was allowed to
 92 operate overnight (> 12 h) to exclude the effect of pure adsorption. DP, MAPD, and NMDG
 93 represent dopamine, 3-methylamino-1,2-propanediol, and *N*-methyl-D-glucamine, respectively.
 94 Data are presented as mean ± standard deviation derived from three consecutive cycles (n=3).

95

96



Supplementary Figure 18. Calibration curve of boron using the azomethine-H method. The calibration standards consisted of six boron concentrations (0, 0.1, 0.5, 1, 2, and 5 mg L⁻¹), with detailed preparation methods provided in Supplementary Text 6. The R^2 obtained from the linear fitting of the data indicates excellent quantification of boron ions, even at concentrations below 0.1 mg L⁻¹.

References

1. Reich H, Bordwell F. Equilibrium pKa Table (DMSO Solvent and Reference). *ACS Division of Organic Chemistry*, (2021).
2. Kamcev J, Taylor MK, Shin D-M, Jarenwattananon NN, Colwell KA, Long JR. Functionalized Porous Aromatic Frameworks as High-Performance Adsorbents for the Rapid Removal of Boric Acid from Water. *Advanced Materials* **31**, 1808027 (2019).
3. Sanfeliu C, *et al.* 11B-MAS NMR approach to the boron adsorption mechanism on a glucose-functionalised mesoporous silica matrix. *Microporous and Mesoporous Materials* **266**, 232-241 (2018).
4. Valipour A, Hamnabard N, Meshkati SMH, Pakan M, Ahn Y-H. Effectiveness of phase- and morphology-controlled MnO₂ nanomaterials derived from flower-like δ -MnO₂ as alternative cathode catalyst in microbial fuel cells. *Dalton Transactions* **48**, 5429-5443 (2019).
5. Patel SK, Pan W, Shin Y-U, Kamcev J, Elimelech M. Electrosorption Integrated with Bipolar Membrane Water Dissociation: A Coupled Approach to Chemical-free Boron Removal. *Environmental Science & Technology* **57**, 4578-4590 (2023).
6. Spencer RR, Erdmann DE. Azomethine H colorimetric method for determining dissolved boron in water. *Environmental Science & Technology* **13**, 954-956 (1979).
7. López F, Giménez E, Hernández F. Analytical study on the determination of boron in environmental water samples. *Fresenius' journal of analytical chemistry* **346**, 984-987 (1993).