

Supplementary Materials for

Exceptional capacitive deionization rate and capacity by block copolymer–based porous carbon fibers

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1. Supplementary Methods

1.1 Desalination capacity

The desalination capacity, Γ (in $\text{mg}_{\text{salt}} \text{g}^{-1}_{\text{electrode}}$), was determined by the change in salt concentration before and after desalination, according to the following equation,

$$\Gamma = \frac{(C_0 - C_t) \cdot V}{m} \quad (\text{S1})$$

where C_0 and C_t represent the initial and final solution concentrations, respectively, and are converted from electrical conductivities using the calibration curves (Supplementary Figure 8); V is the volume of salt solutions (20 mL); m is the total mass of the active materials loaded on two electrodes (~15 mg).

1.2 Average desalination rate

The average desalination rate, v (in $\text{mg}_{\text{salt}} \text{g}^{-1}_{\text{electrode}} \text{min}^{-1}$), was evaluated by the following equation,

$$v = \frac{\Gamma}{t} \quad (\text{S2})$$

where t is the charging time (min).

1.3 Electrical conductivity

The electrical conductivity (S , in S cm^{-1}) was derived from sheet resistance (R_s , in Ω/\square) measured by a four-point probe conductivity meter according to the following equation,

$$S = \frac{1}{R_s \cdot d} \quad (\text{S3})$$

where d is film thickness (cm).

1.4 Surface area

The effective surface area (A_{eff}) for desalination was estimated according to Equation S4, assuming that Na^+ ions form a monolayer on electrode surfaces and the desalination capacity is exclusively contributed by electrical double layers,

$$A_{\text{eff}} = \frac{\pi r_{\text{Na}^+}^2 \cdot \Gamma \cdot N_{\text{A}}}{M_{\text{NaCl}}} \quad (\text{S4})$$

where r_{Na^+} is the radius of hydrated Na^+ (360 nm); N_{A} is Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$); M_{NaCl} is the molecular weight of NaCl (58.4 g mol^{-1}).

1.5 Diffusion coefficient

According to Qu *et al.*(49), the Na^+ diffusion coefficient (D_{Na^+} , in $\text{cm}^2 \text{ s}^{-1}$) was estimated by the following Warburg impedance equation of electrolyte-flooded (electrodes immersed in a large amount of electrolyte) electrochemical systems (*e.g.*, CDI cells),

$$D_{\text{Na}^+} = \frac{1}{2} \left(\frac{RT}{F^2 c \sigma A} \right)^2 \quad (\text{S5})$$

where R is gas constant (8.314 J $\text{K}^{-1} \text{ mol}^{-1}$); T is temperature (298.15 K); F is Faraday constant (96485 C mol^{-1}); c is Na^+ concentration in bulk electrolytes ($8.56 \times 10^{-6} \text{ mol cm}^{-3}$); σ is diffusion resistance (in $\Omega \text{ s}^{-0.5}$) obtained by fitting Nyquist plots (fig. S3, B-D); A is the electrode geometric area (9.5 cm^2).

1.6 Coulombic efficiency

Coulombic efficiency (CE%) equals the ratio of charges used for ion adsorption to the total charges flowed into CDI cells,

$$D_{\text{Na}^+} = \frac{1}{2} \left(\frac{RT}{F^2 c \sigma A} \right)^2 \quad (\text{S5})$$

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1.6 Coulombic efficiency

Coulombic efficiency (CE%) equals the ratio of charges used for ion adsorption to the total charges flowed into CDI cells,

$$CE\% = \left(\frac{\Gamma F}{M_{\text{NaCl}}} \right) / \left(\int_0^t I dt \right) \quad (\text{S6})$$

where I and t represent the charging current (in A g^{-1}) and charging time (in s), respectively. Typical CE% of a CDI cell without any ion-exchange membranes is in the range of 0.5 – 0.8 (50).

1.7 Energy normalized adsorbed salt (ENAS)

For constant-voltage CDI (zero discharge voltage), the energy normalized adsorbed salt (ENAS) is calculated according to the following equation:

$$ENAS = \frac{\Gamma}{E_{\text{in}}} = \frac{\Gamma}{U \int_0^{t_C} I_C dt} \quad (\text{S7})$$

where Γ , E_{in} , U , t_C , and I_C represent desalination capacity (in $\text{mg}_{\text{NaCl}} \text{g}_{\text{PCF}}^{-1}$), energy input during charging (in $\text{J g}_{\text{PCF}}^{-1}$), applied voltage (in V), charging time (in s), and charging current density (in $\text{A g}_{\text{PCF}}^{-1}$), respectively.

2. Supplementary Figures

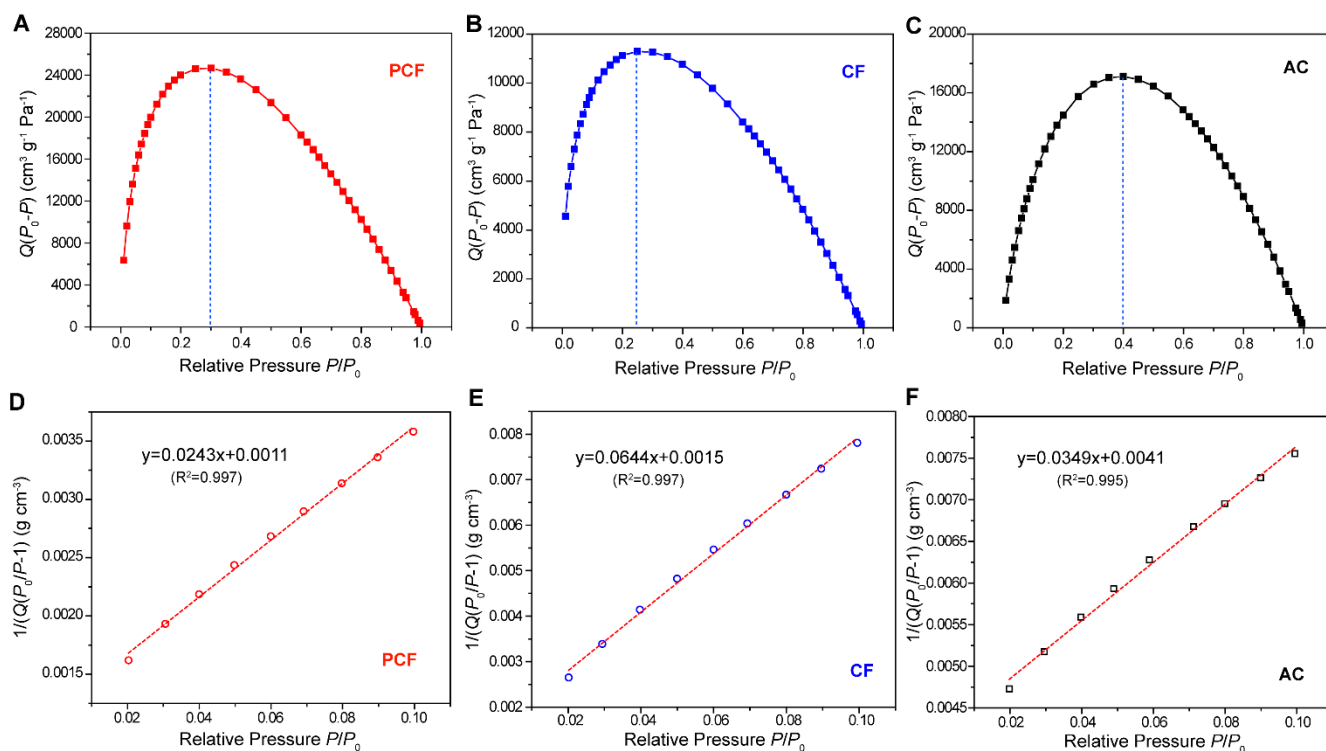


Fig. S1. Validation of the CO₂ BET Surface Areas. (A-C) $Q(P_0-P)$ versus relative pressure of CO₂ during the sorption on (A) PCF, (B) CF and (C) AC. The dashed lines mark the peak positions. (D-F) BET plots of (D) PCF, (E) CF and (F) AC. Q , P_0 , and P are gas adsorption quantity ($\text{cm}^3 \text{g}^{-1}$), saturation pressure (760 mmHg), and gas pressure (mmHg), respectively.

The CO₂-based BET surface areas were lower than the N₂-based BET surface areas, because a higher operating temperature (273 K for CO₂ vs. 77 K for N₂) leads to a smaller quantity of adsorbed gas molecules at adsorption-desorption equilibria (51). By analyzing the relationships between gas adsorption quantity and relative pressure (fig. S1), as proposed by Kim *et al.* (52), the CO₂-based BET surface areas were validated, because the following conditions are met:

- 1) The linear relative pressure range in the BET plots (fig. S1, D-F) must correspond to positive slope in the $Q(P_0-P)$ vs. relative pressure plots (fig. S1, A-C, the section to the left of the dashed lines);
- 2) The y-intercepts of the linear lines in the BET plots (fig. S1, D-F) must be positive.

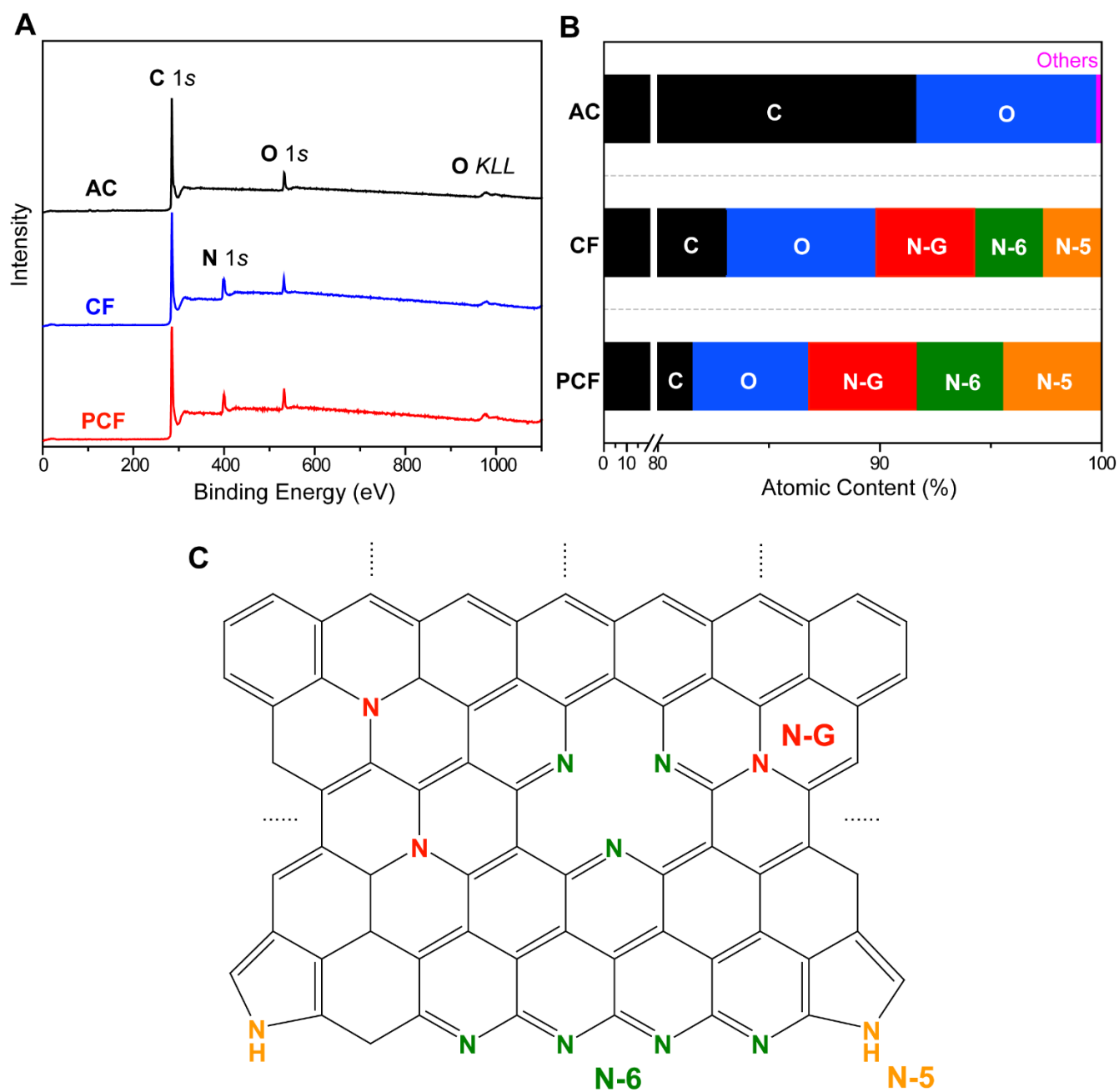


Fig. S2. Elemental compositions of PCF, CF, and AC. (A) XPS survey spectra. (B) Atomic contents. In AC, “Others” include Mg and Si. (C) Schematic of a possible configuration of nitrogen dopants. N-G: graphitic-N; N-6: pyridinic-N; N-5: pyrrolic-N.

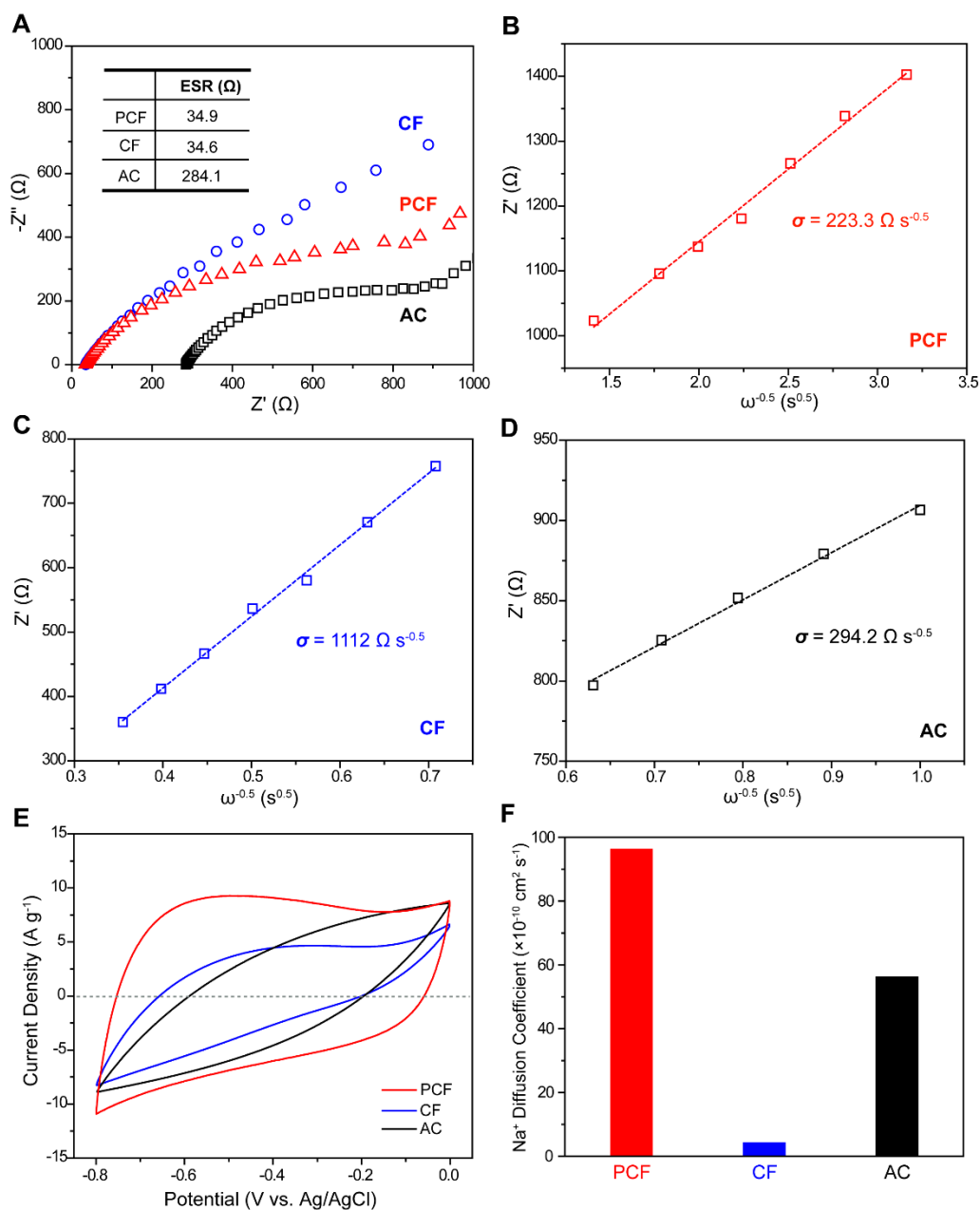


Fig. S3. Additional electrochemical performances. (A) Nyquist plots of the PCF, CF, and AC desalination cells containing 500 mg L^{-1} of NaCl solutions. The inset table lists the electrical series resistance (ESR) values. (B-D) Z' vs. reciprocal of the square root of frequency (ω) for (B) PCF, (C) CF, and (D) AC. The dashed lines are the linear best fittings, the slopes of which equal to the diffusion resistances (σ) of the ions in the carbon materials. (E) Cyclic voltammograms of PCF, CF, and AC at 100 mV s^{-1} in 2000 mg L^{-1} NaCl aqueous solutions. (F) Diffusion coefficients of Na^+ in PCF, CF, and AC probed by EIS in 500 mg L^{-1} NaCl solutions.

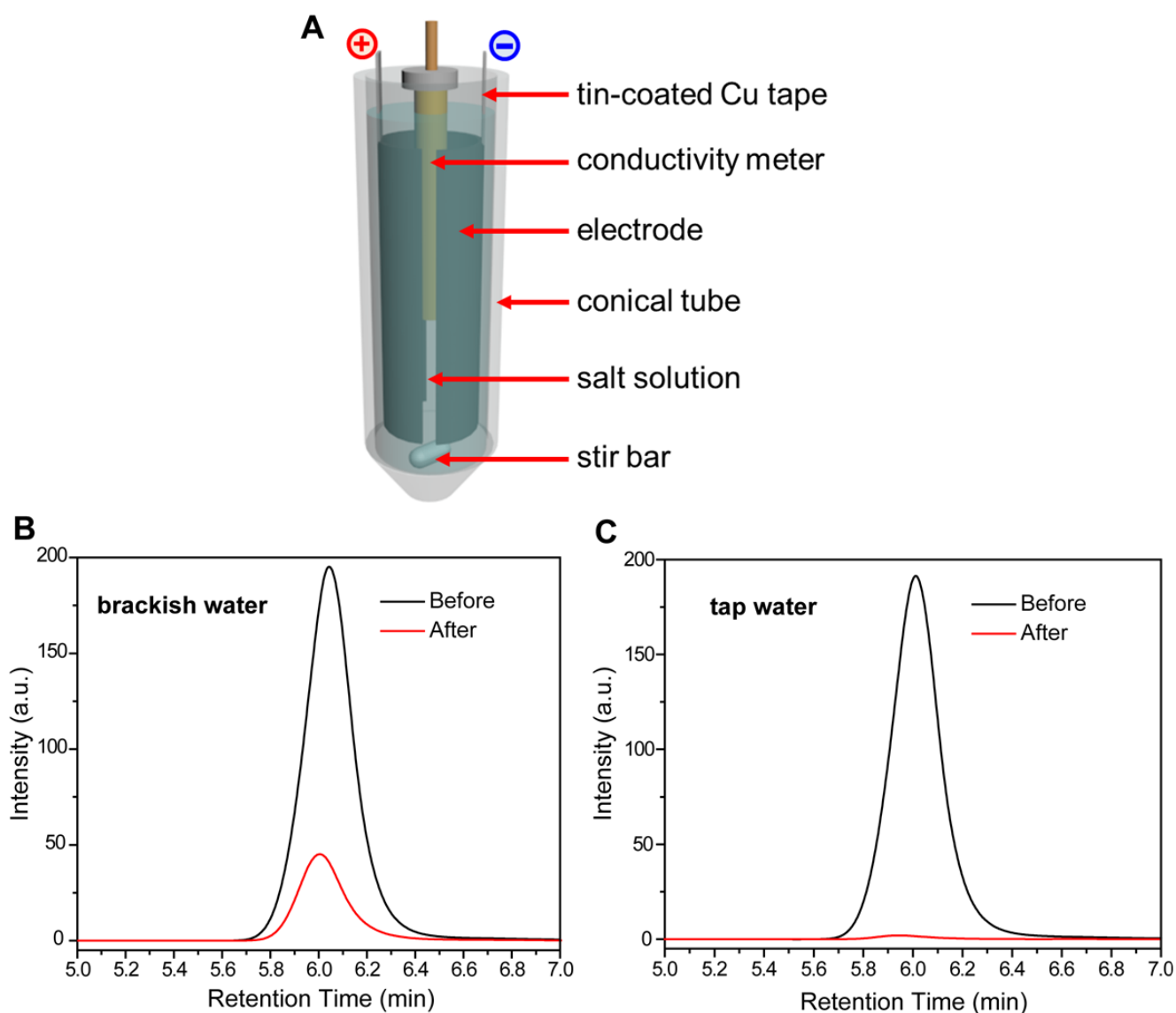


Fig. S4. Cell configuration and ion chromatography. (A) Schematic illustration of a deionization cell composed of two carbon electrodes adhered to Sn tapes and a conductivity meter enclosed in a conical tube. A stir bar was used to keep the salt concentration homogenous in the solution for measurement purposes. The cell contained an excess of NaCl solution to probe the intrinsic deionization properties of PCF. (B and C) Representative Cl^- ion chromatograms of (B) brackish water and (C) tap water before and after deionization.

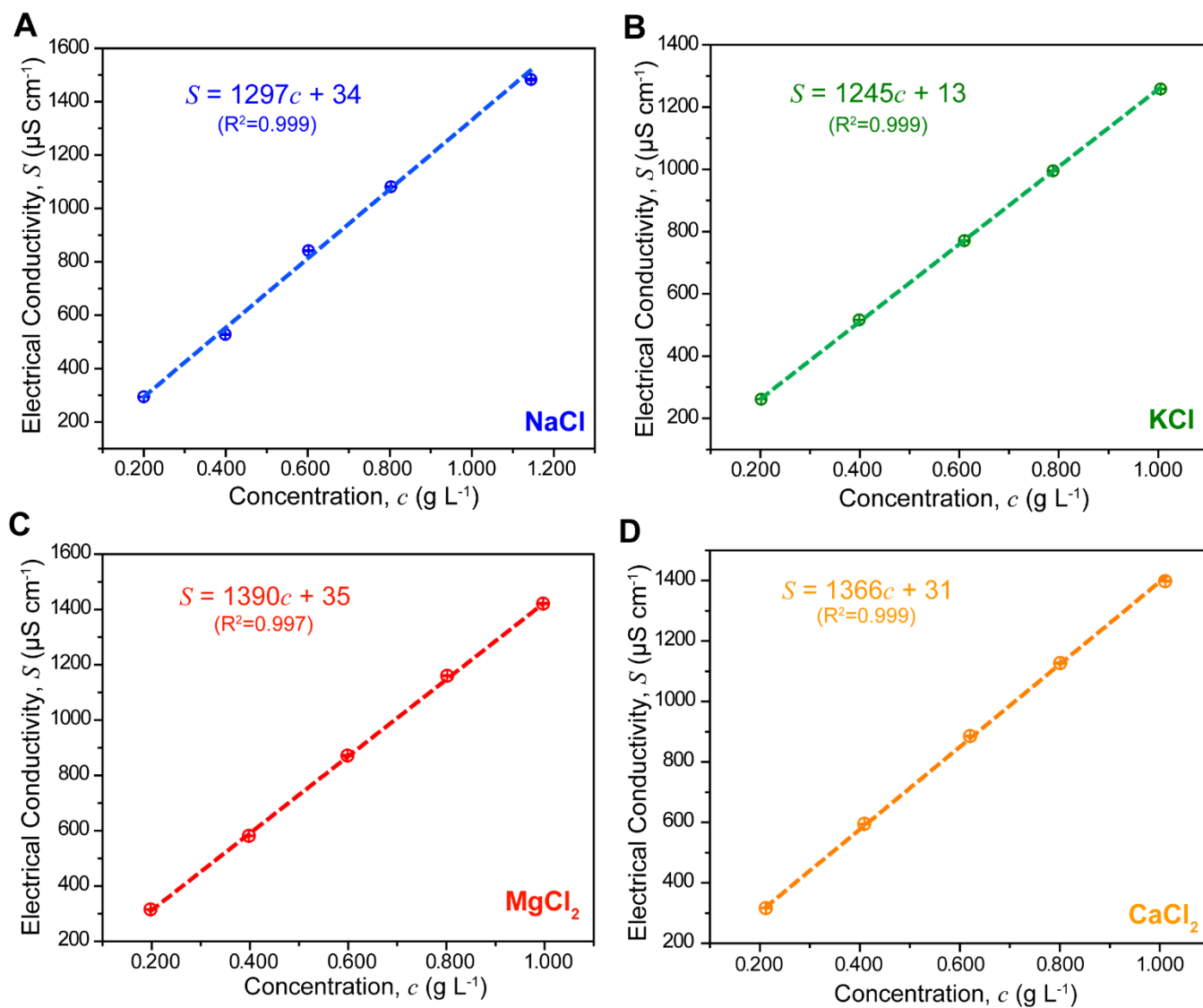


Fig. S5. Calibration curves of (A) NaCl, (B) KCl, (C) MgCl₂, and (D) CaCl₂ aqueous solutions. Each data point represents the average ionic conductivity of five independent measurements. The dashed lines are the best linear fittings.

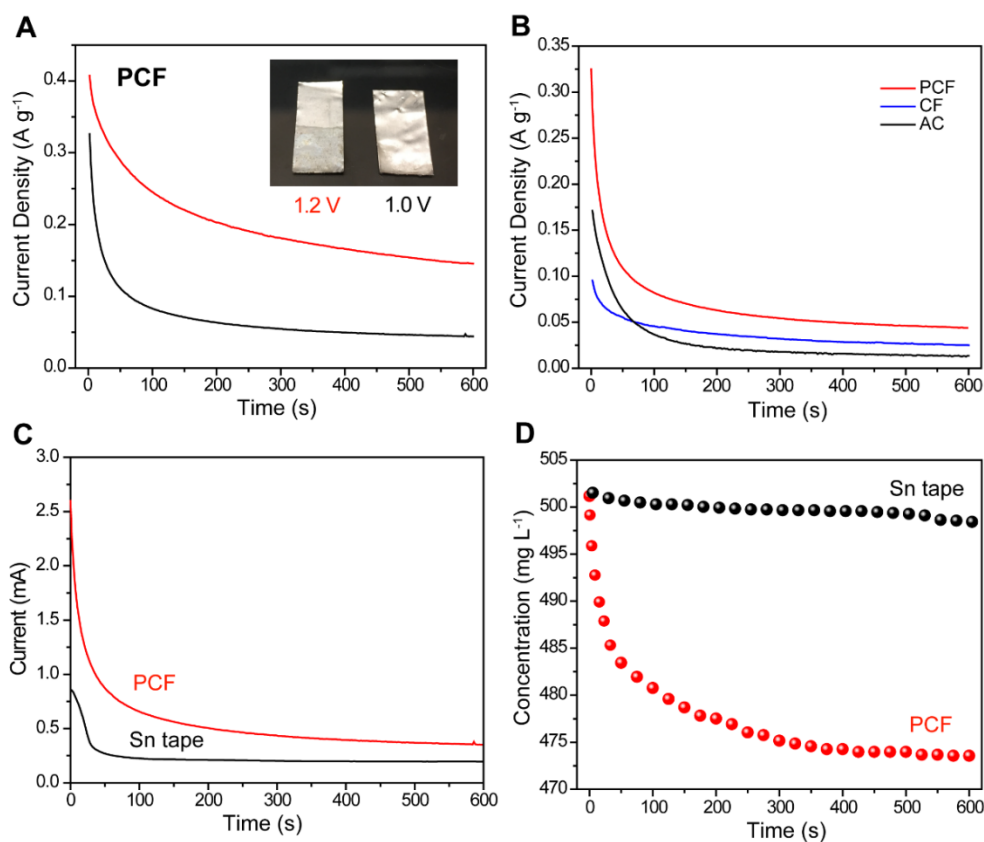


Fig. S6. Electrochemical properties. All materials were tested in 500 mg L⁻¹ NaCl aqueous solutions. (A) Constant-voltage charge-discharge profiles of PCF at 1.0 V (black) and 1.2 V (red). Inset: Photograph of bare tin tapes charged at 1.2 V and 1.0 V for 600 s. (B) Current density (normalized to the mass of active material) time-evolution profiles of PCF, CF, and AC during charging (1.0 V). (C) Current and (D) NaCl concentration vs. time for the desalination cells with two symmetric electrodes of PCF on Sn tapes (red) and bare Sn tapes (black). The applied bias was 1.0 V for both electrodes. The cells contained an excess of NaCl solution (500 mg L⁻¹) to probe the intrinsic deionization properties of the materials.

By integrating the areas below the charging curves (fig. S6B), we estimated the Coulombic efficiencies of PCF, CF, and AC to be 0.72, 0.85, and 0.47, respectively, using Equation S6. The appreciably lower Coulombic efficiency of AC could originate from its high internal resistance, as reflected by its limited electrical conductivity. The limited electrical conductivity induced charge dissipation and resulted in inefficient charge utilization.

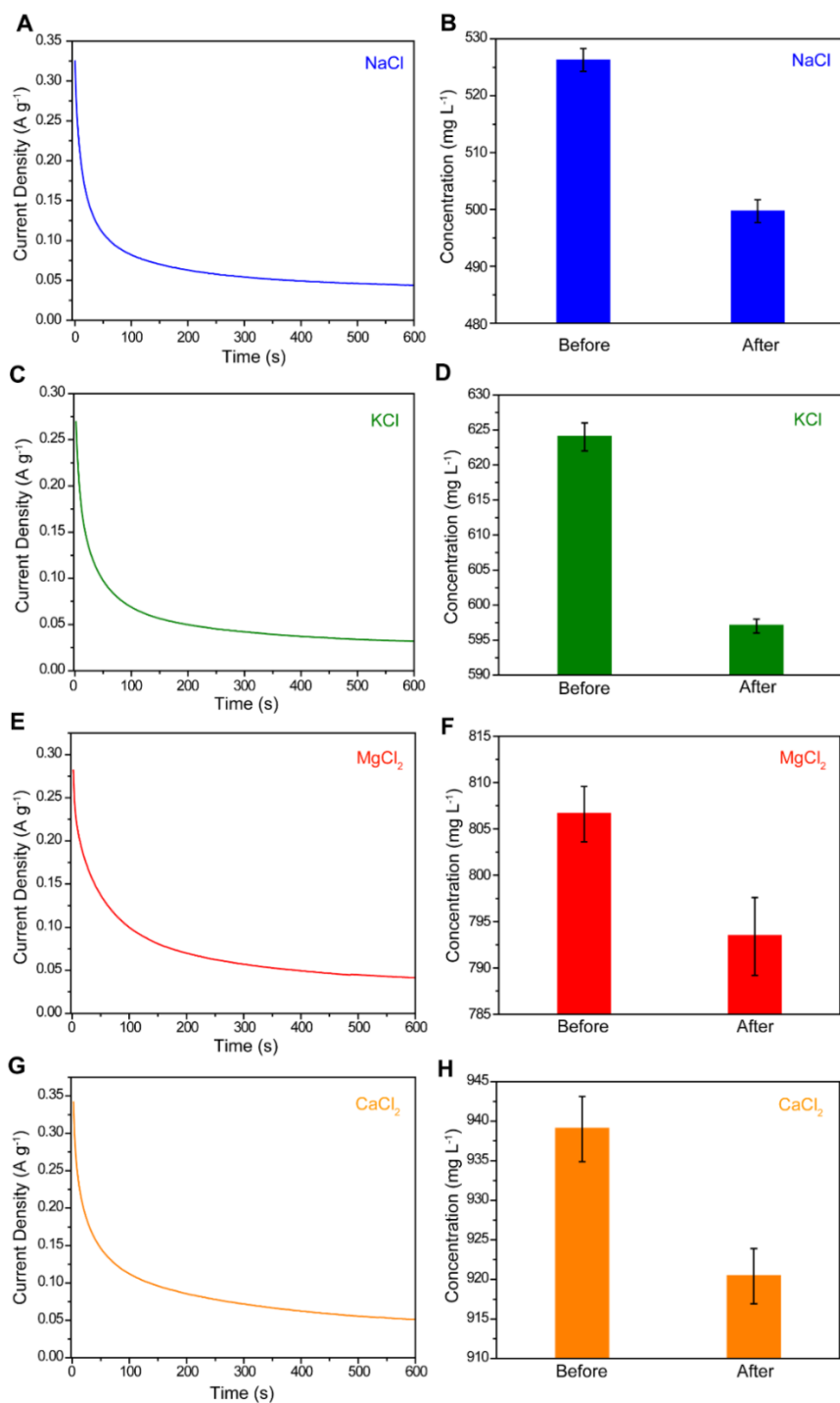


Fig. S7. Constant-voltage deionization performances of PCF. (A, C, E, and G) The current density (based on the mass of active material) time-evolution profiles of charging PCF in (A) NaCl, (C) KCl, (E) MgCl₂, and (G) CaCl₂ aqueous solutions. (B, D, F, H) Bar charts of (B) NaCl, (D) KCl, (E) MgCl₂ and (H) CaCl₂ concentrations before and after desalination. The error bars represent one standard deviation.

To probe the influence of block copolymer molecular weight and composition, a new batch of PCF (PCF-n) from PMMA-*b*-PAN with a molecular weight of 63-*b*-107 kDa ($\phi_{\text{PAN}} \sim 0.61$, polydispersity=1.12) was prepared. The original PCF was from PMMA-*b*-PAN with a molecular weight of 48-*b*-52 kDa ($\phi_{\text{PAN}} \sim 0.52$, polydispersity=1.08). N₂- and CO₂-physisorption both revealed that the surface areas of PCF-n were appreciably lower than those of PCF (fig. S8, A-C). The lower surface areas corroborated with our recent finding that PCF from PMMA-*b*-PAN of $\phi_{\text{PAN}} \sim 0.5$ showed the highest surface areas (43). Due to the decreased surface area, the desalination capacity of PCF-n was $11.5 \pm 1.8 \text{ mg g}^{-1}$, $\sim 38\%$ of that of PCF measured in 500 mg L^{-1} NaCl aqueous solutions (fig. S8D). This result demonstrated a positive correlation between the desalination capacity and surface area of PCF. The latter depended strongly on the molecular weight and composition of PMMA-*b*-PAN.

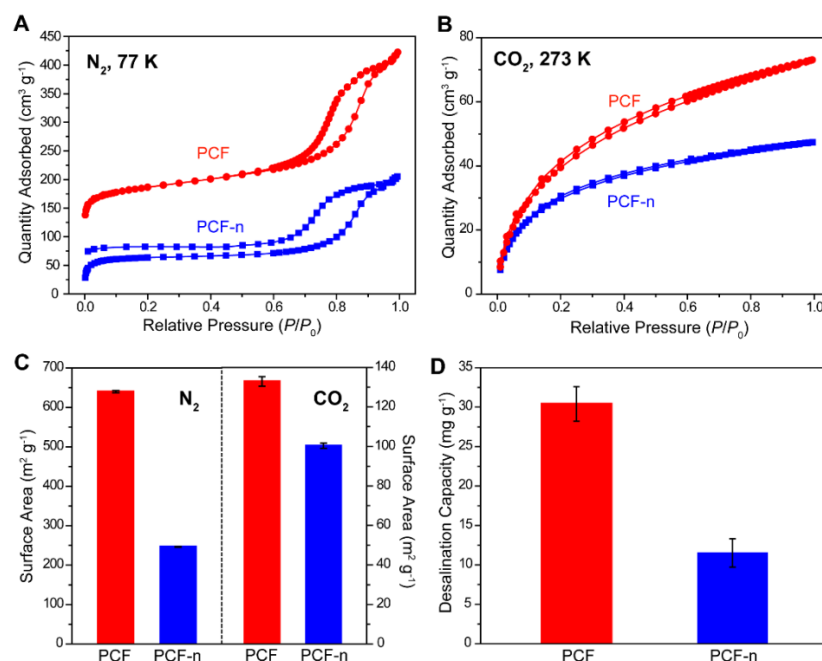


Fig. S8. Effects of block copolymer molecular weight and composition on PCF. (a) N₂ physisorption isotherm at 77 K and (b) CO₂ physisorption isotherms at 273 K. (C) Surface areas of PCF and PCF-n. The error bars are systematic errors of the instrument. (D) Desalination capacities of PCF and PCF-n (charging voltage: 1.0 V; 500 mg L^{-1} NaCl aqueous solutions). The error bars represent one standard deviation.

3. Supplementary Tables

Table S1. NaCl concentrations of brackish water (BW) and tap water (TW) before and after deionization.

Batch	Initial Concentration (mg L ⁻¹)		Final Concentration (mg L ⁻¹)	
	Cl ⁻	NaCl ^{a)}	Cl ⁻	NaCl ^{a)}
BW#1	60.1	990	13.5	223
BW#2	60.4	996	13.4	221
BW#3	60.6	999	13.0	214
BW#4	58.9	971	14.5	239
TW#1	57.6	475	0.61	5.0
TW#2	57.2	472	0.55	4.5
TW#3	57.4	473	0.63	5.2
TW#4	57.1	471	0.89	7.3

Note:

a) The NaCl concentrations (c_{NaCl}) were evaluated based on the Cl⁻ concentration (c_{Cl^-}) measured by ion chromatography,

$$c_{\text{NaCl}} = \text{DF} \times c_{\text{Cl}^-} \times \frac{M_{\text{NaCl}}}{M_{\text{Cl}^-}},$$

where M_{Cl^-} and M_{NaCl} are molar masses of Cl⁻ (35.45 g mol⁻¹) and NaCl (58.44 g mol⁻¹), respectively. DF is a diluting factor of the solutions injected into ion chromatograph columns to avoid detector saturation. For tap water, DF = 5; For brackish water, DF = 10.

Table S2. Capacitive desalination performances of selected state-of-the-art carbon-based electrodes.

[The data listed in this table are mainly selected from performances obtained with desalination conditions similar to our work: two-electrode system, no ion-exchange membranes, and desalination potentials <1.5 V. The data here are mainly for comparison of materials performance rather than engineering of the device design. This table by no means is exhaustive but represents the state-of-the-art for comparison.]

Electrode ^{a)}	NaCl Concentration (mg L ⁻¹)	Voltage (V)	Desalination Capacity (mg g ⁻¹ _{electrode})	Average Desalination Rate (mg g ⁻¹ _{electrode} min ⁻¹)	Ref.
PCF	500	1.0	30.4	3.0-38	This work
CF	500	1.0	7.4	0.74	This work
AC	500	1.0	11.0	1.1	This work
Carbon Nanotubes					
CNT-CNF composite	500	1.2	16.3	0.51	(53)
CNT sponge	500	1.2	17.0	0.05	(54)
Single-walled CNT/porous reticulated vitreous carbon	75	1.1	3.2	0.64	(55)
Graphene/CNT hybrid sponge	500	1.2	18.7	0.62	(56)
CNT	500	1.2	2.5	~0.025	(57)
Carbon Fibers					
Electro-spun CNF	60	1.2	1.3	0.0013	(58)

ZnCl ₂ -activated CNF	500	1.2	10.5	0.17	(59)
Hollow CNFs	-	1.2	1.9	0.021	(60)
N-doped PAN-derived carbon nanofibers	585	1.2	19.9	3.98	(61)
Graphene coated, N-doped PAN-derived carbon nanofibers	585	1.2	27.6	1.84	(61)
N-doped porous carbon nanofiber aerogel	500	1.2	14.3	0.24	(62)
P-doped carbon nanofiber aerogel	1000	1.2	16.2	0.27	(63)
Cellulose-derived CNF	500	1.2	13.1	0.066	(64)

Graphene

N-doped nanoporous graphene aerogel	50	1.5	21	0.7	(24)
Nanoporous graphene aerogel	500	1.2	12.4	0.21	(65)
3D porous graphene aerogel	25	1.2	6.2	0.069	(66)
N-doped graphene powder	-	1.8	4.8	0.12	(67)

Graphene powder	-	1.8	3.9	0.098	(67)
N-doped graphene sponge	50	1.2	8.0	0.27	(24)
Graphene spheres	25	1.6	2.3	1.2	(68)
Graphene/mesoporous carbon	500	1.5	24.3	0.20	(69)
Graphene aerogel	500	1.2	9.9	0.99	(70)
Graphene sponge	500	1.5	14.9	0.50	(71)
Three-dimensional macroporous graphene	105 $\mu\text{S cm}^{-1}$	1.2	2.0	2.18	(12)
Holey graphene sheet	5000	1.2	26.8	0.45	(13)
Sandwich-like nitrogen-doped graphene composite	500	1.0	10.3	0.19	(72)
3D intercalated graphene sheet-sphere nanocomposite	500	1.2	22.1	0.35	(73)

Porous Carbon

Poly(sulfobetaine methacrylate)-coated porous carbon	245	1.2	16.5	3.3	(74)
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Basswood-derived hierarchically porous carbon monoliths	100	1.2	5.7	0.033	(23)
Mesoporous carbon film	23500	1.2	21.0	2.1	(75)
Carbon aerogel	2250	1.3	7.1	0.071	(76)
TiC-derived carbon powder	290	1.2	10.1	1.01	(31)
YP50-F activated carbon	290	1.2	9.1	0.91	(31)
Mesoporous templated carbon	290	1.2	12.8	1.28	(31)
CO ₂ -activated CF/carbon black	90	1.6	9.1	0.075	(47)
Carbide-derived microporous carbon	290	1.4	14.9	0.89	(9)
Carbon aerogel monolith	2922	1.5	9.6	0.96	(48)
Silica-templated ordered mesoporous carbon	500	1.2	10.8	0.06	(77)
N-doped hollow carbon sphere	500	1.4	13.0	0.22	(78)

Loofa-derived porous carbon monolith	585	1.0	22.5	0.38	(15)
Zwitterionic polymer coated porous carbon	245	1.2	16.5	3.3	(74)
N-doped porous carbon spheres	1000	1.2	14.9	0.50	(79)
Biomass-derived N-doped porous carbon	40	1.2	15.5	0.44	(14)
N-doped pollen-derived porous carbon powder	~260	1.4	18.0	0.30	(80)
N-doped mesoporous carbon spheres	584	1.2	20.6	0.67	(36)
Meso-, micro-porous activated carbon powder	584	1.0	20.9	0.35	(81)
N-doped carbon sheet/rGO composite	589	1.2	17.5	1.75	(82)
Ordered mesoporous carbon nano-polyhedra	584	1.2	14.6	0.49	(20)
Polypyrrole-derived nano-porous carbon sheet	1169	1.2	27.4	2.5	(83)

Activated carbon (MSP-20)	292	1.2	15.2	0.59	(84)
H ₂ -treated carbon beads	292	1.2	11.6	1.2	(84)
H ₂ -treated carbon beads	292	1.2	10.7	2.4	(84)
Activated carbon (YP-50)	1169	1.2	9.2	0.90	(50)
Activated carbon (YP-50)	1169	1.2	4.3	2.4	(50)
Metal organic framework-based carbon	584	1.2	6.9	5.4	(85)
Metal organic framework-based carbon	584	1.2	10.7	2.4	(85)
Activated luffa-derived biowaste porous carbon sponge	2500	1.0	25.0	0.42	(86)
N, P, S co-doped hollow carbon polyhedron	500	1.0	14.0	0.12	(87)

^{a)} Acronyms of materials: CNT – carbon nanotube; CNF – carbon nanofiber; PAN – poly(acrylonitrile); rGO – reduced graphene oxide.

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