

Supplementary Information

Hofmeister Effect Induced Hydrogel Electrolyte-Electrode Interfacial Adhesion Enhancement Strategy For Energy-Efficient and Mechanically Robust Redoxcapacitors

Yuehui Du,^a Funian Mo,^{*b} Chengbing Qin,^c Derek Ho,^d and Haibo Hu^{*a}

^a*School of Materials Science and Engineering, Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Ministry of education, Anhui University, Hefei 230601, China. Email: haibohu@ahu.edu.cn*

^b*School of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen, 518055, China. Email: mofunian@hit.edu.cn*

^c*State Key Laboratory of Quantum Optics and Quantum Optics Devices, Institute of Laser Spectroscopy, Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China.*

^d*Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong 999077, China; Hong Kong Center for Cerebro-Cardiovascular Health Engineering, Hong Kong 999077, China.*

Keywords: Hofmeister effect, Zn ions, MXene, redoxcapacitor, hydrogel electrolyte

Experimental

Materials

Ti₃AlC₂ MAX powder (Purity: 98%, Particle size: 200 mesh, ~74 μm) was purchased from 11 Technology Co., Ltd. (China). Silver nitrate (AgNO₃), hydrochloric acid (HCl), zinc sulfate heptahydrate (ZnSO₄·7H₂O), ferric chloride hexahydrate (FeCl₃·6H₂O), ammonium chloride (NH₄Cl), zinc chloride (ZnCl₂), acrylic acid, ammonium persulfate (APS, (NH₄)₂S₂O₈), N, N'-methylene-bisacrylamide, short-chain chitosan, N, N, N', N'-tetramethyl ethylenediamine, polyvinylpyrrolidone K30 (mol wt. 55,000), polyvinylpyrrolidone (mol wt. 360,000) were of analytic grade from Aladdin Reagent Co., Ltd. (Shanghai, China). Bacterial cellulose (BC) was purchased from Guilin Qihong Technology Co., Ltd. Ethylene glycol (EG) was obtained from Sinopharm Chemical Reagent Co., Ltd. Carbon cloth is WOS1011 carbon energy carbon cloth which purchased from CeTech Co.,Ltd, treated by nitric acid soaking. Deionized water was used in all the experiments.

Preparation of multilayered Ti₃C₂T_x powder:

First, 1.0 g LiF was added to 20 mL (9 M) HCl to prepare an etching solution. Then, 0.45 g Ti₃AlC₂ was added to the etching solution and stirred at 40 °C for 48 h. After reaction, the sediment after vacuum suction filtration was repeatedly washed with deionized water until the pH value of the filtrate turned to approaching six. After a freeze-drying treatment, the multilayer Ti₃C₂T_x powder was obtained.

Preparation of few-layered MXene nanosheets:

The multilayer Ti₃C₂T_x powder (0.3 g) was dispersed in deionized water (150 mL). Then the dispersion was sonicated in an ice bath for 1 h. After that, the mixture was centrifuged (4000 r, 5 min) to remove the unetched solid residue. The upper green colloid solution was the target product, which contained few-layered MXene nanosheets with a concentration of about 2.0 mg/mL.

Synthesis of silver nanowires

Silver nanowires were synthesized using a polyol method as follow. First, we weighed 0.421 g PVP (mol wt. 55,000) and 0.406 g PVP (mol wt. 360,000), which dissolved into 115 mL ethylene glycol at 130 °C. Then, the solution was transferred to a three-necked flask, when the temperature approached 140 °C, iron chloride solution (1.1 mmol/L, 12.5 mL), silver nitrate solution (0.26 mol/L, 20 mL), was slowly added to the above solution in sequence and held at 140 °C for 50 min. After the mixed solution was cooled to room temperature, the silver nanowires can be obtained by

centrifugation (2 min, 5000 r) and wash treatment, which were further dispersed in water to form a colloid solution with a concentration of 1 mg/mL for further usage.

Preparation of MXene/AgNWs&BC hybrid film

15 mL AgNW_s colloidal dispersion (1 mg/mL) was first mixed with 15 mL BC dispersion (2.0 mg/mL). Then, 25 mL MXene colloidal dispersion (2.0 mg/mL) was added to the above mixed suspension under continuously stirring. After that, a membrane was obtained via the vacuum filtration of the suspension. After being dried for 5 hours, a free-standing hybrid film of MXene/AgNW_s&BC was torn off from the filter and directly used as the flexible cathode.

Preparation of flexible Zn anode

Flexible Zn anode was prepared by simply electrodepositing Zn on the carbon cloth substrate. Firstly, the carbon cloth was soaked in nitric acid for 48 h and then rinsed with deionized water, which was further dried at 80 °C for 1 h to improve its hydrophilicity. Secondly, the electrochemical deposition was conducted on a LAND 2001A battery test system with the carbon cloth as the working electrode and a zinc foil as the reference electrode in a ZnSO₄·7H₂O plating solution (1 M). After electrodepositing at a constant current density of 5 mA/cm² for 5 h, the carbon cloth with uniform and conformal Zn coating serving as the flexible Zn anode was obtained.

Synthesis of polyacrylic acid-Fe³⁺-chitosan hydrogel

The polyacrylic acid-Fe³⁺-chitosan hydrogel (PF-C) was synthesized by a radical polymerization. Firstly, 10 mL AA monomer, 0.75 g of chitosan (CS), 7 mg N, N-methylenebisacrylamide and 0.1 g FeCl₃·6H₂O were dissolved into 30 mL deionized water, and stirred for 2 min at ambient temperature under N₂ atmosphere to obtain a precursor solution. Secondly, the ammonium persulfate (APS) 0.07 g and 15 μL N, N, N', N'-tetramethyl ethylenediamine were then added to the mixed solution as initiator and catalyst, respectively. After being stirred for 20 min, the resulting solution was then poured into mold, and subsequently placed into an oven at 70 °C for 2 h to obtain the PF-C hydrogel. With the same method, a series of PF-C_x (X=0, 0.25, 0.5, 0.75, 1) were synthesized by varying the CS content, and PF hydrogel was also prepared as the control group without adding CS.

Preparation of flexible solid-state MXene-based Zn-ion redoxcapacitor

The flexible MXene-based Zn-ion redoxcapacitor was assembled by sandwiching the as-prepared PF-C hydrogel between the MXene/AgNW_s&BC cathode and CC@Zn anode. Subsequently, the Hofmeister effect was triggered by immersing the assembly

into a mixed salt solution of 2.5 M NH₄Cl+0.5 M ZnCl₂, which enabled all the components to tightly bonded with each other by the improved interfacial adhesion between the electrodes and the obtained hydrogel electrolyte, finally realizing the fabrication of the flexible solid-state MXene-based Zn-ion redoxcapacitor.

Assembly of self-powered wearable systems.

An electronic watch was applied for wearable demonstration. Before the operations, the original battery was removed from the electronic watch and the booster module was connected to the watch with solder. The flexible solid-state MXene-based Zn-ion redoxcapacitor was assembled into 1 cm x 7 cm size as in the previous steps, so that it could form a free-standing power wristband. The wristband was then attached to the electronic watch to form a self-powered wearable system.

Electrochemical measurements

CV, GCD, and EIS (open circuit voltage with ±10 mV amplitude) measurements were conducted using an electrochemical workstation (CHI 660E, Chenhua). The areal capacitance (C_s , mF cm⁻²), areal energy density (W_s , μWh cm⁻²), mass specific capacitance ($C_{m_{cathode}}$, F g⁻¹) and mass energy density ($W_{m_{cathode}}$, Wh kg⁻¹) were calculated based on the GCD curves according to the following equations:

$$C = \frac{Q}{\Delta E} = \frac{I\Delta t}{\Delta E} \quad (1)$$

$$C_s = \frac{C}{S} = \frac{I\Delta t}{S\Delta E} \quad (2)$$

$$W_s = \frac{0.5C(\Delta E)^2}{3600s} \quad (3)$$

$$C_{m_{cathode}} = \frac{C}{m_{cathode}} = \frac{I\Delta t}{m_{cathode}\Delta E} \quad (4)$$

$$W_{m_{cathode}} = \frac{0.5C(\Delta E)^2}{3600m_{cathode}} \quad (5)$$

where C , Q , I , Δt represents the total capacitance, total charge, discharge current, and discharge time, respectively. ΔE is the potential window during the discharge process after IR drop, and S is the total area of the positive and negative electrodes, $m_{cathode}$ is the total mass of active materials (MXene and AgNWs) used in the cathode.

The ionic conductivity of the hydrogel electrolyte was evaluated by the AC impedance method in the range from 100 kHz to 0.01 Hz, in which the hydrogel (sized: 10 mm×5 mm×2 mm) was sandwiched between two carbon cloths so that it was in close contact with them. The ionic conductivity of the gel electrolyte was calculated

using the following equation:

$$\sigma = \frac{L}{R S}$$

L is the thickness of the gel electrolyte, R is the impedance of the gel electrolyte obtained from the low frequency intercept of the semicircle, S is the area of the gel electrolyte.

Material characterization

The morphology of the samples was characterized by utilizing the scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (JEM-2100, JEOL, Japan). The composition characterizations were performed by using the X-ray powder diffractometer (XRD-SmartLab 9KW). The Infrared spectra was tested by the FTIR spectrometer (VERTEX 801HYPERION2000, Bruker Optics, Germany) in the wavelength range from 4000 to 400 cm^{-1} .

The adhesion force was evaluated by the 90° peel force measurement. First, the CC@Zn and MXene/AgNWS&BC films were rinsed with deionized water and ethanol in sequence, and then allowed to dry naturally. The previously prepared hydrogel samples were cut to standard size (100 mm x 10 mm x 2 mm) and pressed onto the CC@Zn or MXene/AgNWS&BC films for 1 h to bring them into close contact. After that, the assemblies were soaked in an electrolyte of 2.5 M NH_4Cl + 0.5 M ZnCl_2 for 5 h. The other side of the CC@Zn or MXene/AgNWS&BC films was glued to the acrylic plate using double-sided adhesive. Moreover, a commercial polyimide (PI) film (thickness: 0.05 mm) was bonded to the top of the hydrogel with Krazy glue (cyanoacrylate) as a rigid backing for the peeling process. Finally, a 90° peel test was carried out on an Instron 5967 tensile & compression tester to measure the peel force at a constant peel rate of 50 mm min^{-1} .

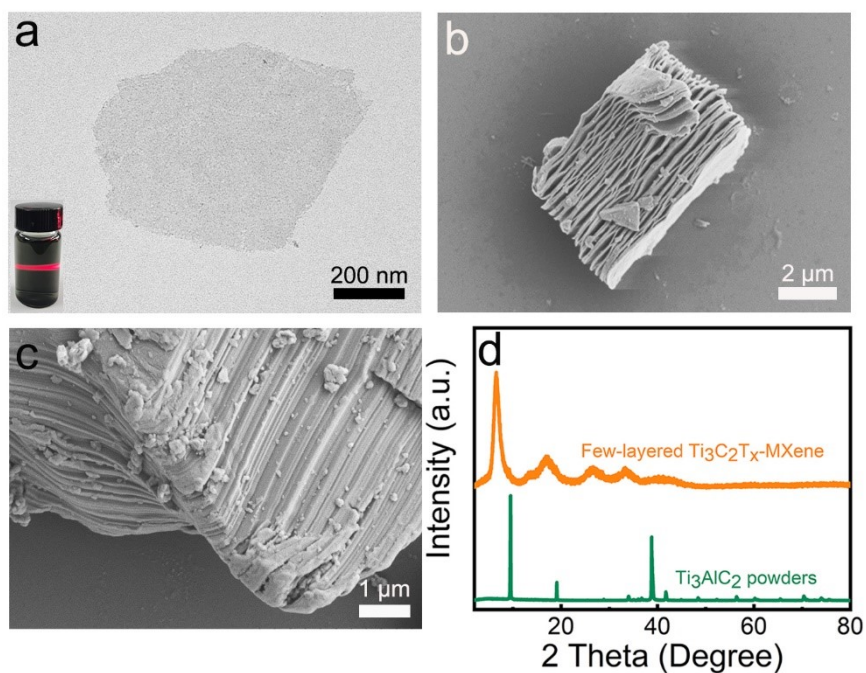


Figure S1. a) TEM image of the obtained few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanoflakes, dispersed in aqueous solution (inset). b) SEM image of the multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene obtained after etching. c) SEM image of the MAX phase precursor. d) The comparison of XRD patterns of the MAX phase precursor and the obtained few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanoflakes.

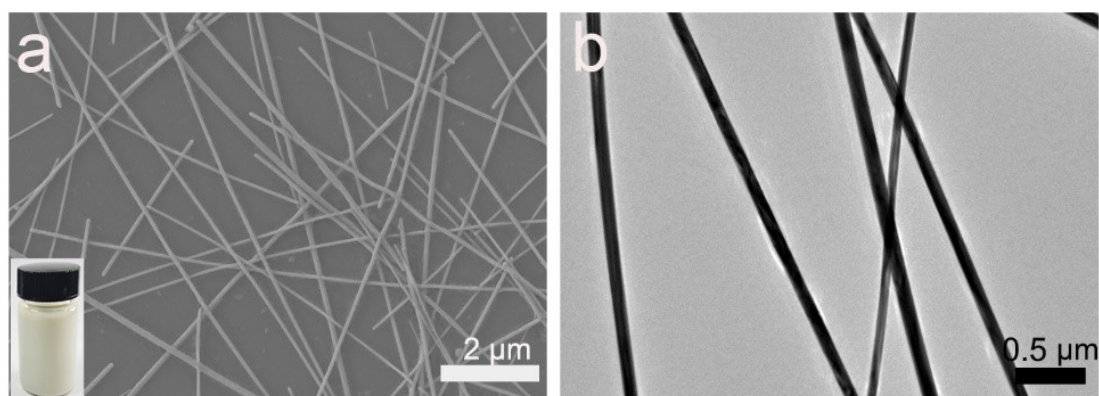


Figure S2. a) SEM image and b) TEM image of the prepared AgNWs, dispersed in aqueous solution (inset in a).

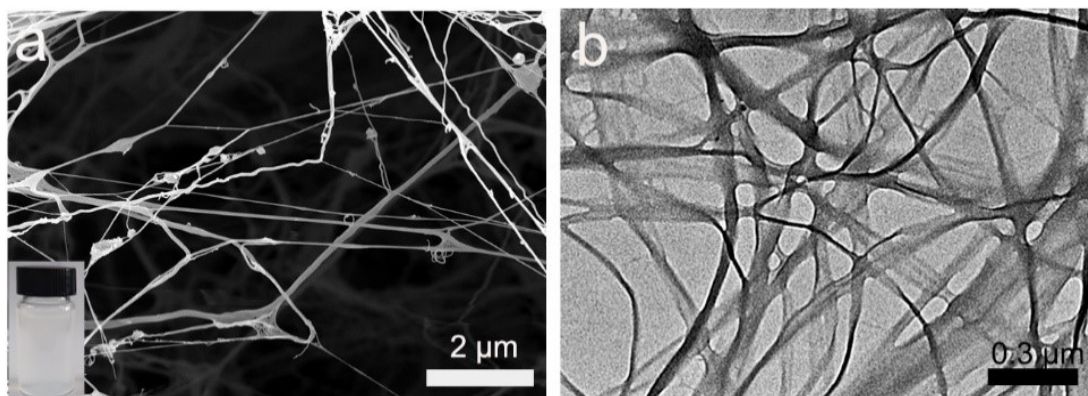


Figure S3. a) SEM image and b) TEM image of BC.

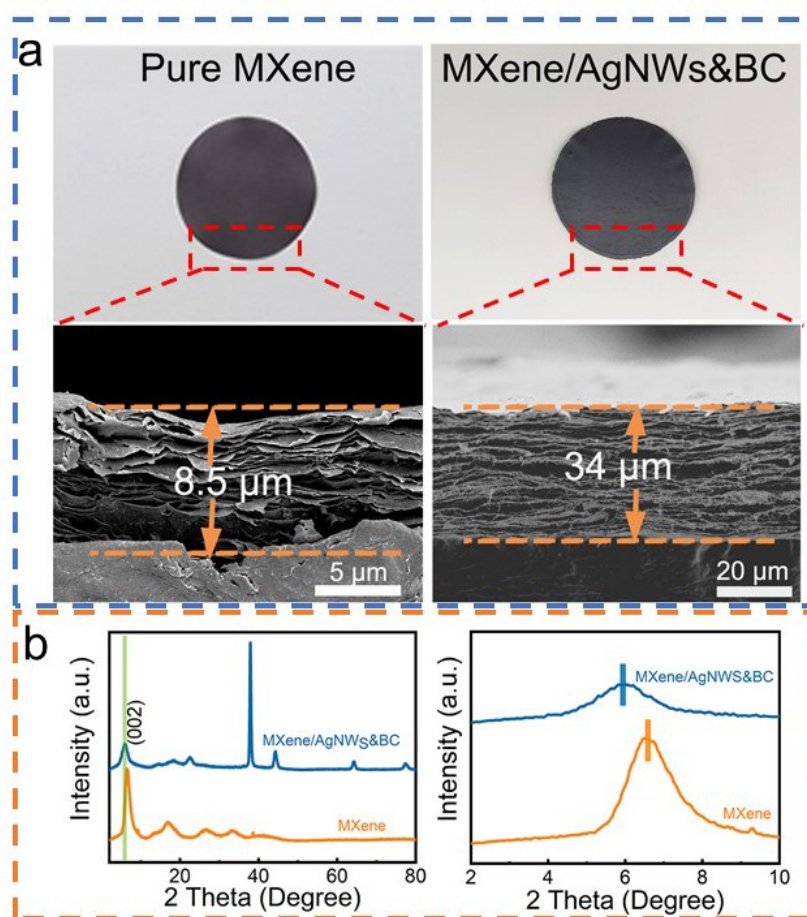


Figure S4. a) Photographs of pure MXene and MXene/AgNWs&BC hybrid films, as well as the corresponding cross-sectional SEM images. b) The comparison of XRD patterns of pure MXene and MXene/AgNWs&BC hybrid films, and the (002) peak in a selected 2 Theta range.

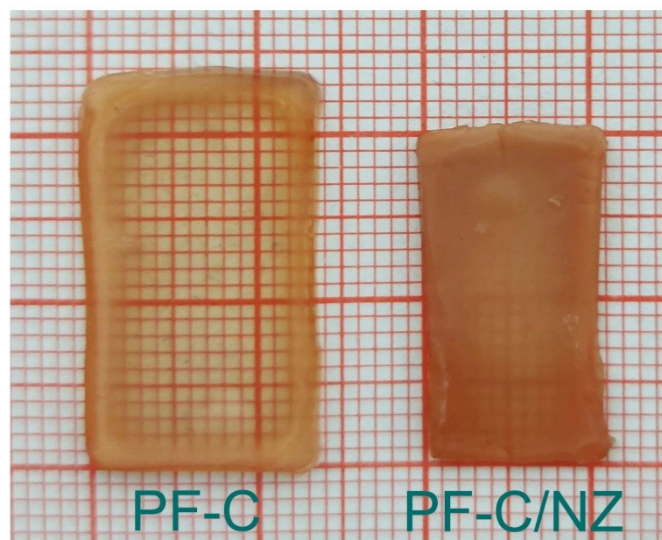


Figure S5. Optical photographs of the PF-C_{0.75} hydrogel before and after immersing in a mixed solution of 2.5 M NH₄Cl+0.5 M ZnCl₂, where significant volume shrinkage can be observed in PF-C_{0.75} hydrogel after immersion.

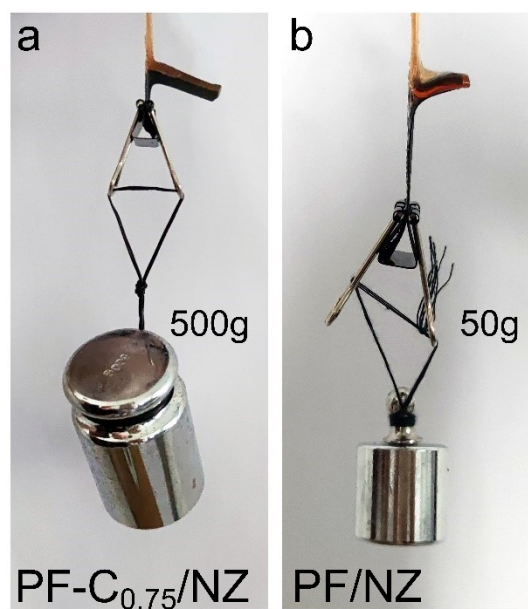


Figure S6. Load-bearing capacity test of the a) CC@Zn//PF-C_{0.75}/NZ and b) CC@Zn//PF/NZ interface structures.

Table S1. Components and characteristics of the synthesized PF-C_x/NZ hydrogels.

Sample name	AA (mL)	Cross linker s(mg)	CS (g)	Electrolyte solution (NH ₄ Cl+ZnCl ₂)	Water (mL)	Ionic conductivity (mS cm ⁻¹)	Adhesion energy (J m ⁻²)
PF-C	10	7	0	2.5 M +0.5 M	30	57.4	89.3
PF-C _{0.25} /NZ	10	7	0.25	2.5 M +0.5 M	30	86.8	517.9
PF-C _{0.5} /NZ	10	7	0.5	2.5 M +0.5 M	30	95.5	759.9
PF-C _{0.75} /NZ	10	7	0.75	2.5 M +0.5 M	30	117.6	1018.7
PF-C ₁ /NZ	10	7	1	2.5 M +0.5 M	30	103.4	889.8