Supporting Information

3D Ordered Hierarchical Porous Non-Carbon Electrode for Highly Effective

and Efficient Capacitive Deionization

Yuchen Wu,^{‡ab} Gaopeng Jiang,^{‡a} Guihua Liu,^a Gregory Lui,^a Zachary Paul Cano,^a Qian Li,^a Zhen Zhang,^a Aiping Yu*a Zisheng Zhang*^b and Zhongwei Chen*^a

[‡]*These authors are contributed equally to this work.*

^{a.} Department of Chemical Engineering. Waterloo Institute for Nanotechnology, University of Waterloo. Waterloo, Ontario N2L3G1, Canada. E-mail: <u>zhwchen@uwaterloo.ca</u>, <u>aipingyu@uwaterloo.ca</u>

^{b.} Department of Chemical and Biological Engineering. University of Ottawa. Ottawa, Ontario K1N 6N5, Canada. Email: <u>Jason.zhang@uottawa.ca</u>

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Experimental Section

Synthesis of polystyrene (PS) template

The synthesis procedure of the PS template is adapted from the literature.^{1, 2} First, 2.5g polyvinylpyrrolidone (PVP, M.W. 10,000) was charged in a three-neck flask that contains 200 mL boiled distilled deionized water (oxygen-free DDI). After PVP was fully dissolved, the flask was placed in an oil bath with N₂ gas purging under the surface of the solution to expel the oxygen in the system. As the temperature was elevated to 70 °C for 15 min, styrene monomer (24 mL) was gradually added into the flask for 20 min with vigorous stirring and refluxing. Then, the potassium persulfate (40 mL, 5 mg mL⁻¹) was added dropwise into the mixture, and the emulsion polymerization was continued under an air-free atmosphere at 70°C for 24 h. The obtained PS template solution was centrifuged at 3000 rpm for 12 h to form ordered micro PS spheres and washed with DDI water. The ordered PS template was obtained after fully drying at 40°C overnight.

Synthesis of 3D Ordered Mesoporous Titanium Nitride (3DOM-TiN)

Titanium (IV) butoxide (TBOT, 97%, 10 mL), ethanol (>99%, 10 mL), and hydrochloric acid (37%, 2 mL) were mixed together with a volume ratio of 5:5:1-and stirred for at least 30 mins. The PS templates (2 g) were then immersed in the solution for 1 hour, and the excess solution was filtered out through vacuum

filtration. After drying in ambient conditions overnight, the composite sample was loaded into a Lindberg tube furnace and subjected to sequential heat treatments at 300°C for 1 h and 540°C for 30 min under Ar atmosphere followed by 800°C for 1.5 h under NH₃ atmosphere. The ramp rate in between each stage was 1 °C min⁻¹. The 3DOM-TiN was obtained after the sample was cooled down to room temperature in Ar gas. For comparison, bulk-TiN was also synthesized following the above procedure without the addition of the PS template.

Physicochemical Characterization

X-ray diffraction (XRD) patterns were obtained using a MiniFlex600 diffractometer (Rigaku, Japan) equipped with Cu-K α radiation ($\lambda = 0.154$ nm) source at a scanning speed of 2° min⁻¹ in the range of 5-90°. X-ray photoelectron spectroscopy (XPS) was measured using a Thermo Scientific K-Alpha spectrometer. The morphologies of the obtained samples was characterized by a LEO 1350 field emission scanning electron microscope (SEM). Transmission electron microscope (60 to 100kV). The nitrogen adsorption-desorption isotherm was obtained using an ASAP 2020 accelerated surface area and porosity system to analyze the surface area and pore structure.

Electrochemical Characterization

Cyclic voltammetry measurements were carried out using NaCl solutions with concentrations of 0.1, 0.5, 0.8 and 1M. The sweep potential ranged from -0.6 to 0.6 V and the sweep rate ranged from 5 to 50 mV s⁻¹ in an electrochemical cell with a three-electrode system including a graphite rod counter electrode, a saturated calomel reference electrode (SCE) and a glass carbon electrode coated with active materials as the working electrode. To further study and simulate the cathode and anode ion adsorption, the sweep potential range of -0.6 - 0 V and 0 - 0.6 V were adapted respectively, under the sweep rate range of 5 - 50 mV s⁻¹ in 1 mol L⁻¹ NaCl solution. The experiment was conducted using an EC-lab SP-300 working station. The specific capacity of the prepared materials was calculated by integrating the area of the CV curve to determine the value using the following equation:

$$C_s = \frac{\int IdV}{2\nu\Delta Vm} \#(1)$$

Where *Cs* is the specific capacitance (F g⁻¹), I is the current (A), v is the scan rate (mV s⁻¹), ΔV is the applied potential window (mV), and *m* is the electrode material mass (g). Electrochemical impedance spectroscopy (EIS) measurements were carried out at frequencies ranging from 100kHz to 1Hz. The amplitude of the alternating voltage was 10 mV and the direct current potential was 0 V vs open circuit potential.

CDI Cell Assembly and Electrosorption Experiment

The TiN electrode slurry were prepared with the following mass ratio, 3DOM-TiN: carbon (super P): polytetrafluoroethylene (PTFE) = 8:1:1. The working electrode was prepared by pressing the dried slurry into a 4 cm diameter, 3.0 mm thick round electrode and pressed onto the same size round stainless-steel metal mesh. A small piece of copper foil was wrapped around or attached to the end of the stainless-steel mesh to enhance the connection between the current collector and electrode clip and strengthen the resistance to yielding. The copper foil was not directly contacted with the active electrode material or saline water. The two electrodes were separated by glass fibers (Whatman, binder-free, Grade GF/C) to assemble a CDI cell. The CDI performance of the batch mode test (Fig. 5a & b) was obtained by measuring the conductivity of desalinated water using an Oakton CON 6+ conductivity meter. The calibration curve of conductivity to real-time salinity can be found in Fig. S12. During the continuous mode of CDI testing (Fig. 5c, d & e), the working conditions including potential voltages applied on the CDI cell, the concentration of the salt water, and flowrate were adjusted to reveal detailed desalination performance and behavior. The continuous salt concentration was measured by a VeraStat 3 electrochemical workstation and recalibrated with the results obtained by the Oakton CON 6+ conductivity meter.

Typically, two identical electrodes consisting of 0.4 g active material, 0.05 g super P, 0.05 g PTFE are used as anode and cathode in the symmetric CDI cell. The salt adsorption capacity (SAC) of the active material is calculated according to the following equation:

$$SAC = \frac{\left(C_0 - C_e\right) \times V}{m} \#(2)$$

where the C_0 is the initial concentration of the pumped in salt water, and C_e is the real-time concentration of the desalinated water, V is the real-time total volume of the desalinated water, and m is the total mass of active material at both the anode and cathode. The salt adsorption rate, SAR, is calculated using the following equation:

SAR = SAC/t#(3)

where *t* is the time corresponding to the SAC during the CDI desalination process.

Supplemental Figures



Fig. S1 Synthesis process of 3DOM-TiN.



Fig. S2 (a) SEM and (b) TEM images of 3DOM-TiN at low magnification.



Fig. S3 N₂ adsorption-desorption isotherm and associated pore volume distribution of bulk-TiN.



Fig. S4 (a) SEM image and (b) EDX spectrum of 3DOM-TiN as well as associated elemental mapping: (c) Ti, (d) C, (e) N, and (f) O.



Fig. S5 (a) XPS survey and HR-spectra of (b) O 1s and (c) C1 s for 3DOM-TiN.



Fig. S6 CV curves of (a) AC and (b) bulk-TiN electrode in 1 mol L^{-1} NaCl solution with scan rates of 50, 40, 30, 20, 10, and 5 mV·s⁻¹.



Fig. S7 (a) CV curves and (b) associated specific capacitance of 3DOM-TiN in 1.0, 0.8, 0.5, and 0.1 mol·L⁻¹ NaCl aqueous solutions.



Fig. S8 (a) high-resolution C1s XPS of 3DOM-TiN after 5000 cycles of stability test in half-cell and associated (b) comparison of the carbon species before and after cycling.

According to the high-resolution C 1s XPS after 5000 cycles of stability test in halfcell (**Figure S8a**), the sp² hybridized carbon still accounts the most in the 3DOM-TiN. Although the oxidization of NCR-coating was observed according to the increase in oxygenated carbon species and sp³ hybridized carbon (**Figure S8b**), the insignificant decease of the sp² hybridized carbon (~ 4 %) shows sufficient stability and resistivity to oxidation of NCR-coating for CDI application.



Fig. S9 (a) System resistance (R_s) and charge transfer resistance (R_{ct}) of the 3DOM-TiN and bulk-TiN electrodes; (b) Linear fitting to the real part of impedance (Z') versus the -1/2 power of the angular frequency ($\omega^{-0.5}$) plots.

The Warburg coefficient σ (ohm·s^{-0.5}) was extracted by fitting the real part of impedance (*Z'*) versus the -1/2 power of the angular frequency ($\omega^{-0.5}$) plots in a frequency range of 1 to 10 Hz. The steeper linear line and smaller diffusion Warburg coefficient σ indicated the higher efficiency of ion diffusion of 3DOM-TiN compared with bulk-TiN.^{3,4}



Fig. S10 CV curves of 3DOM-TiN in 1M NaCl solution with varying scan rates and associated linear fitting of $i/v^{1/2}$ vs $v^{1/2}$ in (a, b) cathodic range (-0.6 ~ 0V) and (c, d) anodic range (0 – 0.6 V); (e) Linear fitting of $i/v^{1/2}$ vs $v^{1/2}$ of 3DOM-TiN in 1M NaCl solution with varying scan rates in the full range (-0.6 ~ 0.6V) and (f) associated Dunn method analysis of capacitance contribution of 3DOM-TiN at scan rate of 10 mV·s⁻¹ in the same potential range. The shaded regions show the current contributions from the electrical double-layer capacitive processes.

Dunn's method is generally described as follows. The quantity analysis of the capacitance contributions from the surface capacitive effects (C_{EDL}) and diffusion-controlled process (pseudo capacitance) is enabled by Dunn's method.⁵ The current density (*i*) from the CVs can be expressed as the following two parts, k_1v and $k_2v^{0.5}$, at a fixed potential:

$$i = k_1 v + k_2 v^{0.5} \#(4)$$

Where the first part, k_1v accounts for the current density contributed from the EDL capacitive, while $k_2v^{0.5}$ accounts for the current density contributed from the pseudo-capacitance. The equation can be rearranged by dividing the $v^{0.5}$ on both sides:

$$iv^{-0.5} = k_1 v^{0.5} + k_2 \#(5)$$

Thus, by extracting the *i* from the CVs at each scan rates *v* and plotting the *iv*^{-0.5} vs. $v^{0.5}$, a linear fitted line with the slope of k_1 and y-intercept of k_2 can be obtained. Fig. S10 displays the contributions of C_{EDL} and pseudocapacitance of the 3DOM-TiN electrode as cathode, anode and a full-scan CV from both cathode and anode, together with the *iv*^{-0.5} vs. $v^{0.5}$ and their linear fitting process. Using the k_1 and k_2 obtained from the linear fitting, the contribution of C_{EDL} and pseudo capacitance can be calculated at specific potential *V* and scan rate, *v*.



Fig. S11 Conductivity profile of saline water during batch-mode CDI process using 3DOM-TiN, Bulk-TiN and AC electrodes with applied potential of 1.2 V and initial salinity of 100 mg L⁻¹.

All three electrodes reached their lowest conductivity at around 25 minutes, which is the maximum salt adsorption capacity moment. After 25 minutes, although the electrodes kept absorbing salt, the capacity declined rapidly, which is not energy and cost effective. Thus, the salt adsorption capacity of the electrode was determined at the lowest conductivity moment. The salinity of the water is based on a series calibration with a series of standard NaCl solutions.



Fig. S12 Calibration of the Conductivity to NaCl Concentration. The inserted graph is the enlarged part from 0-300 μ S/cm².

The calibrated equation of Conductivity-Concentration is:

Concentration $(mg/L) = 0.04699 * Conductivity(\mu S) + 2.33873$

Where $R^2=0.99998$, indicating that the salinity of the solution can be considered as linearly dependent on the conductivity.



Fig. S13 Ragone plots of SAR vs. SAC for 3DOM-TiN electrode in continuous symmetric CDI cell obtained under different flow rates; the inset plots illustrate the maximum SAR and SAC at 25 min;



Fig. S14 Regeneration cycling stability test of AC electrode in continuous symmetric CDI cell with saline water (100 mg L⁻¹ NaCl) flow through at 5 ml min⁻¹ at applied voltage of 1.2 V.

Supplemental Tables

	BET Surface Area	BET Pore Volume
	$m^2 \cdot g^{-1}$	cm ³ ·g ⁻¹
3DOM-TiN	141.61	0.291
Bulk-TiN	31.65	0.030

 Table S1 BET surface area and pore volume of 3DOM-TiN and bulk-TiN.

	20	d (220)	а	Х
	0	Å	Å	(TiN _x)
3DOM-TiN	61.945	1.4986	4.2386	0.9872
Bulk-TiN	62.332	1.4931	4.2232	0.6574

Table S2 Lattice constants and N/Ti ratio of 3DOM-TiN and bulk-TiN.

The d_{220} is determined according to Bragg's law:

$$d_{220} = \frac{n\lambda}{2sin\theta}$$

 TiN_x lattice parameter is then calculated:

$$a_{TiN_{\chi}} = d_{220}\sqrt{h^2 + k^2 + l^2}$$

From the obtained values of lattice parameters, the N/Ti ratio of 3DOM-TiN and bulk-TiN were calculated⁶:

 $a_{TiN_x} = 4.1925 + 0.0467x$

	Ti	С	Ν	0
XPS survey (wt%)	65.95	9.96	12.87	11.22
EDX spectrum (wt%)	64.35	10.80	11.32	13.53

Table S3 Elemental composition of 3DOM-TiN via XPS survey and EDX spectrum.

Electrode	Cell Voltage V	Salinity mg·l ⁻¹	SAC mg·g ⁻¹	References
Commercial Activated Carbon	1.2	292-1170	10.9~13.0	7
Commercial Carbon Aerogel	1.2	50~500	1.4~2.9	8
Commercial Activated Carbon	1.2	292	10.5	9
rGO-Ti	1.2	300	9.2~13.2	10
CNT-Ti	1.2	500	~4.3	11
Ti-AC	1.2	500	~2.7	12
Ti NPs/AC	1.2	100	~8.04	13
3D-GA/TiO ₂	1.2	100	~23	14
Ti ₃ C ₂ -Mxene	1.2	100	13	15
Activated Carbon	1.2	100	~13.7	This Work
Bulk-TiN	1.2	100	~4.5	This Work
3DOM-TiN	1.2	100	~22.1	This Work
3DOM-TiN	1.2	500	23.6	This work

Table S4 Salt adsorption capacity comparison of several commercial and titaniumbased CDI electrodes

	Working Condition		SAR		
Electrode	Voltage V	Flow rate ml·min ⁻¹	Salinity mg·L ⁻¹	mg·g ⁻¹ ·min ⁻¹	References
3DOM-TiN	1.2	5	500	~3.2	This work
Bulk-TiN	1.2	5	100	0.09	This work
Activated Carbon	1.2	5	100	0.4	This work
N-doped mesoporous Carbon	1.2	5	500	0.2~1.2	16
Porous Carbon membrane	1.2	60	1000	0.2~0.3	9
N, P, S co-doped hollow carbon polyhedra	1.2	50	500	0.5	17
Surface-treated carbon	1.2~1.4	8.6	500	1.2	18
High- performance activated carbon	1.2~1.4	26	600	0.2	19
Macro/Micropore Carbon	1.2	50~500	500	1.2	20
Graphene sheet	1.2	20~80	500	0.8	21
Nitrogen-doped graphene composites	1.4	N/A	300	~2.0	22
Porous carbon nanosheet	1.2	66.9	1000	1.0	23

Table S5 Comparison of salt adsorption rate of this work with several carbon-based

 electrode materials for capacitive deionization

	W	Working Condition		SAD	
Electrode	Voltage V	Flow rate ml·min ⁻¹	Salinity mg·L ⁻¹	mg·g ⁻¹ ·min ⁻¹	References
3DOM-TiN	1.2	5	500	~3.2	This work
Bulk-TiN	1.2	5	100	0.09	This work
Activated Carbon	1.2	5	100	0.4	This work
Na ₃ V ₂ (PO ₄) ₃ @C	1.0	15	585	2.4	24
$Na_4Mn_9O_{18}$	1.2	10	500	~0.4	25
Na ₂ FeP ₂ O ₇	0.9~1.5	2	584.4	0.48	26
MnO ₂ electroless deposition	1.2	5	100	3.0	22
Ti ₃ C ₂ -Mexene	1.2	22	500	1.0	15
TiO ₂ -coated AC	1.0	N/A	500~1000	2~3	27

Table S6 Comparison of salt adsorption rate of this work with several metal-based

 electrode materials for capacitive deionization

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