Supplementary Materials for

Enhancing Capacitive Deionization Performance of NaMnO$_2$ by Interlayer Engineering and Redox-reaction

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1. Experimental Section

1.1 Synthesis of Colloidal MnO$_2$ Nanosheets

The colloidal MnO$_2$ Nanosheets were prepared by a previously reported with some modifications$^1$. Briefly, 2.375 g of manganese nitrate was dissolved in 40 mL deionized water. Then, a mixture containing 6.9 mL of H$_2$O$_2$, 17.2 mL of tetramethylammonium hydroxide and 55.9 mL of deionized water was added into above solution under vigorous stirring. The mixture was stirred at room temperature overnight. The obtained suspension was dialyzed in deionized water for 48 h and further washed by using a centrifuge to remove the large precipitations.

1.2 Self-assembly preparation of NaMnO$_2$ and CNT/NaMnO$_2$ samples

Typically, 50 mL of deionized water containing 50 mg of NaNO$_3$ was added into 200 mL of the manganese oxide colloidal suspension (0.5 mg mL$^{-1}$) under vigorous stirring at 60 °C for 6 h. Then NaMnO$_2$ obtained was washed three times with water and then dried at 60 °C before measurements were performed. CNT/NaMnO$_2$ was also prepared through the same process as applied in the synthesis of NaMnO$_2$ except with adding 20 mg CNT.

1.3 Materials characterization

The morphologies and structures of the samples were characterized through field emission scanning electron microscopy (FE-SEM, FEI Sirion200) and transmission
electron microscopy (TEM, JEM-2010F). The crystal structure and phase composition of the composites were investigated using powder X-ray diffraction (XRD, Bruker D8). Nitrogen adsorption–desorption isotherms were collected at 77 K by using an Autosorb 6B instrument to determine the texture properties of the samples. Thermogravimetric analysis (TGA) was performed with TG209 (NETZSCH Co.). XPS measurements were performed with an ESCALAB 250 (Thermo Scientific, USA) by using Al Kα (hv = 1486.6 eV) X-ray radiation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to analyze the chemical composition of the NaMnO₂ samples and concentration of Mn in the tank after the cyclic test of AC//NaMnO₂.

1.4 Electrochemical Measurements

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) were conducted by using a CHI 660E electrochemical workstation in 1 M NaCl solution. A three-electrode system consisting of a platinum foil as the counter electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and the sample was used as the working electrode. To prepare the working electrodes, a homogeneous slurry of sample, polytetrafluoroethylene (PTFE), and carbon black with the mass ratio of 8:1:1 in ethanol was pressed by a rolling mill into a film and dried at 80 °C overnight. The obtained electrodes were pushed onto a titanium mesh which used as current collectors. The specific capacitance (C, F g⁻¹) was calculated from the CV curves as

\[
C = \frac{1}{2} \times \frac{I}{v} \times \Delta V \times m
\]

Where \(C\) is the specific capacitance (F g⁻¹), \(I\) is the response current density(A), \(v\) is the potential scanning rate (V s⁻¹), \(\Delta V\) is the voltage change (V), and \(m\) is the active material mass (g).

1.5 HCDI experiments

To prepare the membrane-free HCDI electrodes, 82.5 wt% active materials (AC, MnO₂, NaMnO₂ and CNT/NaMnO₂), 10 wt% carbon black, 6 wt% polyvinyl butyral (PVB), and 1.5 wt% polyvinylpyrrolidone (PVP) were mixed together to obtain a homogeneous slurry. Subsequently, the resulting slurry with about 100 mg of solids was cast on a graphite paper (5×7 cm²) and then dried at 80 °C overnight. The thickness of AC, MnO₂, NaMnO₂ and CNT/NaMnO₂ are 120, 100, 100 and 100 μm, respectively. The HCDI cell consisting of an activated carbon (AC) electrode, a
NaMnO₂ electrode (or CNT/NaMnO₂) and a piece of anion exchange membrane (200 μm, Hangzhou Iontech Environmental Technology Co., Ltd. Zhejiang, China) was denoted as NaMnO₂//AC (or CNT/NaMnO₂//AC) (Figure S5), whereas that consisting of an AC electrode, a MnO₂ electrode and a piece of anion exchange membrane was denoted as MnO₂//AC. An ~1.5 mm thick silicon gasket and two pieces of ~120 μm thick nonwoven fabric were used as the spacer and separator of the HCDI cells, respectively. Different concentrations of NaCl and voltages were employed to investigate the desalination performance of the HCDI system in various operation conditions. Ion removal step was conducted by applying a voltage (0.4 V to 1.2 V) for a certain time, while the captured ions were released by applying negative voltage (-0.4 V to -1.2 V) for a certain time. A tank (2.5L) of NaCl aqueous solution with different concentrations (100 to 20000 mg L⁻¹, or 1.7 mM to 341.9 mM) was pumped into the CDI setup by a peristaltic pump at a flow rate of 9 mL min⁻¹, and then flowed into another tank. An electrochemical workstation (CHI 660E) was used to supply the needed voltage. The changes of effluent conductivity and pH were recorded by an ion conductivity meter and pH monitor systems. The NaCl solution concentration was calculated by a calibration curve according to the conductivity profiles. The ion removal capacity (IRC, Γ, mg g⁻¹), charge consumed (Σ, C g⁻¹) and charge efficiency (Λ) were defined as Equation 2, Equation 3 and Equation 4, respectively:

\[
\Gamma = \frac{\Phi \times \int (C_0 - C_t) \cdot dt}{m} \\
\Sigma = \frac{\int i \cdot dt}{m} \\
\Lambda = \frac{\Gamma \times F}{M \times \Sigma}
\]

Where \(\Phi\) is the flow rate (mL min⁻¹), \(C_0\) and \(C_t\) are the influent and the effluent NaCl concentration (mg L⁻¹), respectively; \(m\) is the total mass of the two electrodes (g); \(i\) is the current during the adsorption process (A); \(F\) is the Faraday constant (96 485 C mol⁻¹); and \(M\) is the molar mass of NaCl (58.5 g mol⁻¹).
**Figure S1** Raman spectra of the CNT/NaMnO$_2$. 
Figure S2 Elemental mapping of NaMnO$_2$. 
Figure S3 Water contact angle measurements of samples
Figure S4 CV curves of (a) NaMnO$_2$, (b) MnO$_2$ and (c) CNT/NaMnO$_2$ at different scan rate.
Figure S5 The schematic cell configuration of the HCDI consisting of the MnO$_2$-based and AC electrodes.
A HCDI mode of NaMnO$_2$/AC-1 without anion exchange membrane was conducted at -1.2 V. As displayed in Figure S6, the NaMnO$_2$/AC-1 cell did not exhibit any reduction in concentration and current due to its operation principle depending on the polarity of bias, whereas the AC//AC cell showed the conductivity of effluent kept decreasing as same as when the applied voltage is +1.2 V.
Figure S7 (a) XRD patterns and (b) IRC at various voltages of NaMnO$_2$ before and after thermal treatment.
Figure S8 Kim-Yoon plots of (a) NaMnO$_2$/AC, (b) CNT/NaMnO$_2$ and (c) MnO$_2$/AC in NaCl solution with an initial concentration of 500 mg L$^{-1}$ by varying the cell voltage.
Figure S9 pH changes of the effluent during charge-discharge process when tested with 500 mg L\(^{-1}\) NaCl solution: (a) MnO\(_2\)/AC, (b) NaMnO\(_2\)/AC and (c) CNT/NaMnO\(_2\)/AC.
Figure S10 Representative EDS spectra of AC electrodes of NaMnO$_2$/AC after ion removal experiments.

EDS spectra are shown (a) before and (b) after washing of the electrode with copious amounts of deionized water, indicating Cl$^-$ ions are physisorbed on the carbon surface.
Figure S11 (a) atomic ratio of C, N, and O on the surface of AC after 100 cycles; (b) C1s XPS spectra of AC before cycles; (c) C1s XPS spectra of AC after 100 cycles.
Table S1 The compositions and the interlayer spacing of samples

<table>
<thead>
<tr>
<th></th>
<th>Chemical compositions measured by the ICP-AES method</th>
<th>Interlayer spacing (Å) calculated from the (001) peaks</th>
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<tr>
<td>NaMnO$_2$</td>
<td>Na$_{0.2}$MnO$_2$</td>
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<td>Na$_{0.26}$MnO$_2$</td>
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<td>Na$_{0.17}$MnO$_2$</td>
<td>7.15</td>
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<tr>
<td>CNT/NaMnO$_2$</td>
<td>CNT/Na$_{0.19}$MnO$_2$</td>
<td>7.18</td>
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<tr>
<td>CNT/NaMnO$_2$-IAS</td>
<td>CNT/Na$_{0.24}$MnO$_2$</td>
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<tr>
<td>CNT/NaMnO$_2$-IRS</td>
<td>CNT/Na$_{0.16}$MnO$_2$</td>
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**Table S2** Comparison of desalination performance among different deionization systems

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cell configuration</th>
<th>voltage (V)</th>
<th>Exchange membrane</th>
<th>NaCl (mg L(^{-1}))</th>
<th>SAC (mg g(^{-1}))</th>
<th>Ion removal rate (mg g(^{-1}) min(^{-1}))</th>
<th>Reference</th>
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<tr>
<td>NC800-PEDOT</td>
<td>CDI</td>
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<td>GSSNA-11</td>
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<td>None</td>
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<td>MnO(_2)/CNT–CS)</td>
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<td>10.07</td>
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<td>⁶</td>
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<tr>
<td>Na(_{0.43})MnO(_2)//AC</td>
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<td>Anion</td>
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<td>3.96</td>
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<td>Na-birnessite//AC</td>
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<td>Anion</td>
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<td>6.66</td>
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<td>¹¹</td>
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<td>Anion</td>
<td>500</td>
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<td>5.1</td>
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</tr>
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<td>Anion</td>
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<td>5.7</td>
<td>this work</td>
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<td>1.2</td>
<td>Anion</td>
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<td>42.6</td>
<td>7.3</td>
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Reference


