# Experience

## Experimental reagent

All reagents were of analytical grade and could be used without further purification.

#### Instrument required for experiment

Chinese Academy of Sciences; electric thermostat blast oven (DHG-9071A), purchased from Shanghai Shenguang Instrument Co., Ltd; electronic analytical balance (FA1004B), purchased from Shanghai Youke Instrument Co., Ltd; ultra-pure water machine (Advance-I-GL), purchased from Chengdu Tangshi Kangning Technology Development Co., Ltd. Peristalticpump (YZ1515X-A), purchased from Boading longer Precision Pump Co., Ltd. Conductivity i trument (DDSJ-308F), purchased from Shanghai Lei Magnetic Brand Professional Supplier. Electrochemical workstation (CHI-760E), purchased from CH Instruments, USA.

X-ray diffraction (XRD) patterns were examined on a Bruker D8 Advanced X-ray Diffractometer (Cu-K $\alpha$  radiation:  $\lambda = 0.15406$  nm). Raman spectroscopy obtained by using Renishaw inVia Reflex (514 nm laser). The chemical states were measured using an Axis Ultra X-ray photoelectron spectroscope (XPS, Kratos Analytical Ltd., UK) equipped with a standard monochromatic Al-K $\alpha$  source (hv = 1486.6 eV).

## Materials synthesis

*Preparation of ZIF-9*: Initially, a solution of 0.14g cobalt nitrate hexahydrate in 25mL methanol (referred to as Solution 1) was prepared. Subsequently, a solution containing 0.001 mol of benzimidazole in 15mL methanol, supplemented with 30µL of triethylamine (defined as Solution 2), was meticulously prepared. The amalgamation of Solution 1 into Solution 2 ensued, followed by a rigorous stirring process at 30°C for 8 hours. The resultant mixture was then subjected to purification using methanol and subsequently dried under vacuum conditions at 50°C for the final product isolation.

*Preparation of 2-Carboxyl-ZIF-9:* Replace benzimidazole with benzimidazole-2-carboxylic acid, other steps are the same.

*Preparation of 5-Carboxyl-ZIF-9:* Replace benzimidazole with benzimidazole-5carboxylic acid, other steps are the same. The synthesized series of ZIF precursors were heated in a Muffle furnace. Calcined at 400°C for 2 hours and 600°C for 2 hours, the obtained carbon materials are labeled Bulk-Co<sub>3</sub>O<sub>4</sub>, 2D-Co<sub>3</sub>O<sub>4</sub> and Pseudo-2D-Co<sub>3</sub>O<sub>4</sub>, respectively.

## Electrochemical performance measurements

The electrode ink was prepared by mixing active material (80 wt%) with active carbon (10 wt%) and PVDF (10 wt%) in NMP solvent under ultrasonication for 30 min. A certain volume of the ink was dropped onto the graphite paper with a thickness of 0.5 mm (area of  $1 \times 1$  cm<sup>2</sup>) and dried at 60 °C for 12 h. The potential sweep cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted by using an electrochemical workstation (CHI-660E) with three-electrode conFigure duration in NaCl electrolyte (1.0 M). The Ag/AgCl electrode and platinum (Pt) wire were used as reference and counter electrodes, respectively. CV curve and galvanostatic charge/discharge (GCD) measurements were carried out in the potential range of -0.1 to 1.0 V. Specific capacitances (C, F g<sup>-1</sup>) were calculated by **Equation S1**.

$$C = \frac{\int I dv}{2vm\Delta V} \tag{1}$$

where C is the specific capacitance, I is the current, V is the potential, v is the scan rate, m is the electrode mass, and  $\Delta V$  is the potential window.

$$logi = blogv + a \tag{2}$$

where i is the current, v is the scan rate.

$$\frac{i}{v^{1/2}} = k_1 v^{1/2} + k_2 \tag{3}$$

where i is the current, v is the scan rate.

#### CDI performance measurements

Capacitive Deionization (CDI) unit-cell was constructed with two pairs of identical electrodes, ion exchange membrane for anion and cation, and spacer. Each individual CDI carbon electrode was composed of active material, active carbon, and PVDF with 8:1:1 ratio, and prepared on the graphite paper (thickness: 0.1 mm) as

current collector. The CDI tests were conducted using a batch-mode with a continuous recycling system, which includes a CDI unit-cell, a peristaltic pump, a power source, and a fluid reservoir. The ambient temperature and the total volume of the NaCl solution in the desalination experiment were maintained at 298 K and 80 mL, respectively. In the CDI desalination process, the saline water was desalinated through CDI unit-cell and recycled in a closed circuit. The real-time change of the brackish water concentration was measured with a conductivity probe which was connected to the CDI system. The correlation between conductivity and concentration was achieved based on a calibration table prepared before the test. The original concentration of NaCl aqueous solution used in the desalination system is 5.128 mM, 10.256 mM, and 17.094 mM (corresponding to 300 mg L<sup>-1</sup>, 600 mg L<sup>-1</sup>, and 1000 mg L<sup>-1</sup>), respectively. The applied voltage at both ends of the electrodes is 1.0 V, 1.2 V, and 1.4 V, respectively. The desalination capacity ( $\Gamma$ , mg g<sup>-1</sup>) and mean desalination capacity rate (v, mg g<sup>-1</sup> min<sup>-1</sup>) at t min were calculated as follows:

$$SAC = (C_0 - C_t) \times V/m$$
<sup>(4)</sup>

where  $C_0$  and  $C_t$  are the NaCl concentrations at initial stage and t min, respectively (mg L<sup>-1</sup>), V is the volume of the NaCl solution (L), and m is the total mass of the electrode materials (g).

$$SAR = SAC/t$$
 (5)

SAR is the desalination rate.



Figure S1. XRD plots of precursors ZIF-9, 2-Carboxyl-ZIF-9, and 5-Carboxyl-ZIF-9.



Figure S2. (a-c) TEM image and SAED of 2D-Co<sub>3</sub>O<sub>4</sub>.



**Figure S3.** (a) N<sub>2</sub> adsorption-desorption curve (inside illustration is pore size distribution curve); (b) Specific surface areas of the four materials.



**Figure S4.** (a) CV curves of Pseudo-2D-Co<sub>3</sub>O<sub>4</sub> at different sweep speeds; (b) CV curves of Bulk-Co<sub>3</sub>O<sub>4</sub> at different sweep speeds; (c) CV curves of commercial Co<sub>3</sub>O<sub>4</sub> at different sweep speeds; (d) GCD curves of 2D-Co<sub>3</sub>O<sub>4</sub> at different current densities; (e) b-value curves of 2D-Co<sub>3</sub>O<sub>4</sub>.



**Figure S5.** (a) capacitive contribution and diffusion contribution of  $2D-Co_3O_4$  electrode; (b) Na<sup>+</sup> diffusion coefficients calculated from a plot of Z' versus the inverse of the square root of the frequency ( $\omega^{-1/2}$ ).

The b-values of the 2D-Co3O4 material were calculated using Equation S2, and it was found that the b-values were all in the range of 0.5~1, which belongs to the pseudocapacitance range. The capacitance diffusion occupancy of the materials is

obtained according to Equation S3. It was found to be mainly controlled by diffusion at lower scan rates (<0.1 V/s) and by capacitance at higher sweep rates (**Figure S4a**). The plot of the percentage of capacitive contribution at different sweep speeds also shows that the percentage of capacitive contribution increases as the scan speed increases (**Figure S5**).



Figure S6. Capacitive contribution of 2D-Co<sub>3</sub>O<sub>4</sub> at different scan rate.



Figure S7. Capacitive contribution of 2D-Co<sub>3</sub>O<sub>4</sub> at different scan rate.



Figure S8. Cyclic desalinization diagram of 2D-Co<sub>3</sub>O<sub>4</sub>.



Figure S9. SAC comparison between different types of materials.



Figure S10. SAC of 2D-Co<sub>3</sub>O<sub>4</sub> in 600 mg/L various salt solutions at 1.2 V.