Supporting Information for

Egg-Box Structure in Cobalt Alginate: A New Approach to Multifunctional Hierarchical Mesoporous N-Doped Carbon Nanofibers for Efficient Catalysis and Energy Storage

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Supplementary Figures S1-S12 and Supplementary Table S1.
**Experimental materials and methods**

**Materials.** Sodium alginate was provided by the Bright Moon Seaweed Group (Qingdao, China). Dimethyl sulfoxide (DMSO), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) and ethanol were purchased from Sinopharm Chemical Reagent (Shanghai, China). Triton X-100™ (biochemical grade) and Polyethylene oxide (PEO) (M$_{w}$=900kDa) were purchased from Aladdin. Nafion® perfluorinated resin solution containing 5% Nafion® were purchased from Sigma-Aldrich. Hydrochloric acid was purchased from the Shuangshuang Chemistry Company (Yantai, China).

**Preparation of N-doped porous carbon nanofibers (N-PCNFs).** PEO and sodium alginate with a weight ratio of alginate to PEO at 8:2 in a 50 mL solution were mixed with 1.0 wt% of Triton XU100™ (0.5 mL) and 5 wt% of DMSO (5 mL) to generate the precursor. A high voltage power supply (Dongwen High Voltage, China) was employed to generate the electric field of 0-30 kV. The applied voltage was fixed at 20 kV in this study. The typical distance between the syringe tip and the collector was 20 cm. After 6 hours of electrospinning, the A-NFs fibrous membranes were dried in a vacuum oven at a temperature of 80 °C overnight to dry any remaining solvent. Then, the A-NFs were immersed in a Co$^{2+}$ (0.1 M) alcohol solution to form the CoA-NFs. The obtained CoA-NFs were pyrolyzed at different temperature (600, 700, and 800 °C) at the heating rate of 2 °C min$^{-1}$ for 1 h in NH$_3$ atmosphere to form the N-PCNFs-600, N-CoA-CNFs-700 and N-CoA-CNFs-800. As a comparison, the CoA-NFs were pyrolyzed at different temperature (600, 700, and 800 °C) for 1 h in Ar atmosphere to form the CoA-CNFs-600, CoA-CNFs-700 and CoA-CNFs-800. Then, all the samples were soaked into a 2 M hydrochloric acid solution for 10 h to remove the metal and leave the porous structure in the nanofibers to obtain the NUPCNFs-600, N-PCNFs-700, N-PCNFs-800, PCNFs-600, PCNFs-700 and PCNFs-800.

**Characterizations.** The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM; JSM-7001F, JEOL, Tokyo, Japan). The phase structures were characterized with X-ray diffraction (XRD, DX2700, China) operating with Cu Kα radiation (l=1.5418 Å) at a scan rate (2θ) of 1° min$^{-1}$ with the accelerating voltage of 40 kV. Raman spectroscopy were obtained on a Renishaw 1000 Raman spectrometer with the 514.5 nm excitation line of an Ar ion laser. TEM and high-resolution TEM (HRTEM) images were obtained using a JEMU2100F with an accelerating voltage of 200 kV. The chemical composition was investigated by X-ray photoelectron spectroscopy (XPS) using an ESCALab250 electron spectrometer (Thermo Scientific Corporation) with monochromatic 150 W Al Kα radiation. Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a relative pressure (P/P$_0$) range between 0.05 and 0.20, pore size distribution plots were derived from the adsorption branch of the isotherms based on the BJH model. Thermogravimetric analysis (TGA) measurement was carried out on an EXSTAR TG/DTA 6300 instrument (Seiko Instruments, Japan) in air.

**Electrochemical Measurements.**

**ORR.** The electrocatalytic activities of N-PCNFs catalysts towards ORR were measured in 0.1 M KOH solution using CV at room temperature. An ink of the catalyst was prepared by mixing 2.5 mg of catalyst powder with 25 µl of a 5 wt% Nafion solution and 500 µl of ethanol, and further placed in an ultrasonic bath. The RDE measurements were performed in a three-electrode, one-compartment cell at room temperature, equipped with a Pt wire counter electrode and a Ag/AgCl reference electrode. Cyclic voltammograms with a sweep rate of 50 mV s$^{-1}$ are recorded in the potential range of 0 to -1.2 V versus a Ag/AgCl reference electrode. Linear sweep voltammetry (LSV) was performed in N$_2$-saturated or O$_2$-saturated 0.1 M KOH. ORR polarization curves were recorded at a scan rate of 10 mV s$^{-1}$ under various electrode rotation rates (625, 900, 1025, 1600, 2025 and 2500 rpm, respectively).

The RRDE test in alkaline media was conducted using a Ag/AgCl as the reference electrode and a platinum rod as the counter electrode. Before each measurement, 0.1 M KOH electrolyte was bubbled with O$_2$ for more than 30 min. The RRDE measurements were carried out at 1600 rpm using on a CHI 760 E electrochemical workstation with a RRDE-3A rotator (ALS Co., Ltd).

The electron transfer number ($n$) was determined from RRDE measurement on the basis of the disk current ($I_D$) and ring current ($I_R$) via the following equation:

$$n = \frac{4NI_D}{NI_D + I_R};$$

the peroxide percentage (H$_2$O$_2$ %) was calculated based on the following equation:
where N=0.43 is the current collection efficiency of Pt ring.

**LIBs.** The samples were mixed with acetylene black and poly (vinylidene fluoride) (PVDF) at a weight ratio of 8:1:1 in N-methyl-2-pyrolidone (NMP) solvent to form the slurry. Then, the resultant slurry was uniformly pasted on Cu foil substrate. The as-prepared electrode sheet was dried in a vacuum oven at 120 °C for 10 h and then pressed. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt%). CR2016-type coin cells were assembled in a glove box for electrochemical characterization. Lithium metal foil was used as both the counter and reference electrodes. The charge-discharge measurements were conducted using a cell testing instrument (LAND CT2001A) over the potential range from 0.01 to 3.00 V. Cyclic voltammetry (CV) (0.01 V to 3.0 V, 0.1 mV s⁻¹) was performed using on a CHI 760 E electrochemical workstation (CH Instruments, Inc.).

**SCs.** Two-electrode symmetric supercapacitor systems were used to measure the performance of all the samples as SCs electrodes with 6.0 M KOH solution as the electrolyte. The electrodes were prepared by mixing 85 wt% active material, 10 wt% carbon black, and 5 wt% poly-(vinylidene fluoride) (PVDF) and dried at 80 °C for 5 h under vacuum. The CVs were carried out on a CH1 760 E electrochemical workstation at room temperature and the galvanostatic charge-discharge measurements were made using a cell testing instrument (LAND CT2001A) over the potential range from 0 to 0.8 V. In the two-electrode system, the specific capacity was calculated according to the equation:

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

in which I (A) is the discharge current, \(\Delta t\) (s) is the discharge time, \(m\) (g) is the total mass of anode and cathode materials, and \(\Delta V\) (V) is the potential window.
Figure S1. (A) XRD patterns of A-NFs and CoA-NFs. (B) TGA measurement of CoA-NFs in air.

Figure S2. SEM images of (A) A-NFs, (B) CoA-NFs, (D) N-PCNFs-700, (E) N-PCNFs-800, (F) PCNFs-600, (G) PCNFs-700 and (H) PCNFs-800. (C) TEM image of N-CoA-CNFs-600.
Figure S3. (A) Low-magnification TEM image and (B) High-magnification TEM image of PCNFs-600.

Figure S4. SEM images of (A) N-PCNFs-600 (Fe) and (B) N-PCNFs-600 (Ni).

Figure S5. (A) Nitrogen adsorption-desorption isotherm and (B) the corresponding pore size distribution curve of N-PCNFs-600, N-PCNFs-700 and N-PCNFs-800.
Figure S6. CV curves of (A) N-PCNFs-700, (B) N-PCNFs-800 and (C) PCNFs-600 in N$_2$- and O$_2$-saturated 0.1 M KOH aqueous solution.

Figure S7. LSV curves of (A) N-PCNFs-700, (B) N-PCNFs-800 and (C) PCNFs-600 at various rotation speeds.

Figure S8. XPS spectra of N-PCNFs-600, (A) full survey scan spectrum, (B) N 1s, (C) C 1s and (D) O 1s peak
Figure S9. (A) RDE curves of N-PCNFs-600 (Ca) and N-PCNFs-600 at 1600 rpm. (B) SEM image of N-PCNFs-600 (Ca).

Figure S10. CVs of (A) N-PCNFs-700, (B) N-PCNFs-800, (C) PCNFs-600 and (D) PCNFs-700 SCs in 6.0 M KOH solution between 0 and 0.8 V at different scan rates.
**Figure S11.** Galvanostatic charge-discharge curves of (A) N-PCNFs-700 and (B) N-PCNFs-800 at different current densities.

**Figure S12.** Nyquist plots of N-PCNFs-600, PCNFs-600, N-PCNFs-700 and N-PCNFs-800 (inset, high-frequency region Nyquist plots).

**Table S1.** The atomic percentages of C, N and O for N-PCNFs-600, N-PCNFs-700 and N-PCNFs-800.

| Item            | N-PCNFs-600 | N-PCNFs-700 | N-PCNFs-800 |
|-----------------|-------------|-------------|-------------|
| C-contents (at%)| 92.0        | 92.9        | 94.3        |
| N-contents (at%)| 1.2         | 0.8         | 0.5         |
| O-contents (at%)| 6.8         | 6.3         | 5.2         |