*Supporting information for*

# A Novel Mn/Co dual nanoparticle decorated hierarchical carbon structure derived from biopolymer hydrogel as highly efficient electro-catalyst for oxygen reduction reaction

Lujie Cao[#a,b], Zhenyu Wang[#a], Jinlong Liu[#a], Bingxue Wang[a], Zhiqiang Wang[a], Mingyang Yang[a,b], Hui Pan*[b,c], and Zhouguang Lu*[a]

[a] *L. Cao, Z. Wang, J. Liu, B. Wang, Z. Wang, S. Gu, M. Yang, Prof. Z. Lu Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, P. R. China, E-mail: luzg@sustc.edu.cn*

[b] *L. Cao, M. Yang, Prof. H. Pan, Joint Key Laboratory of the Ministry of Education Institute of Applied Physics and Materials Engineering, University of Macau Macao SAR, P. R. China , E-mail: huipan@um.edu.mo*

[c] *Prof. H. Pan, Department of Physics and Chemistry, Faculty of Science and Technology, University of Macau, Macao SAR, P. R. China*

## Experiment section

Firstly, 100 ml Chitosan solution (40 mg mL$^{-1}$ in 1% aqueous acetic acid) was poured into a 500 mL beaker, and then the CS solution would form a plane with certain thickness automatically. Then the mixed $Zn(NO_3)_2$ (5 M), $Co(NO_3)_2$ (0.05 M) and $MnAc_2$ (0.05 M) aqueous solution was poured on the surface of the CS solution. Within 1 minute, the hydrogel was formed. Then the hydrogel surface was washed by water thoroughly. After that, it was put in a refrigerator for 2 h and put in a freeze-drying machine for 10 h. At last, the freeze dried ZnMnCo-chitosan hydrogel was obtained. To anneal the sample, the furnace temperature was increased gradually from room temperature to 800/900/1000 °C with a ramping rate of 5 °C min$^{-1}$ and held for 2 h under argon gas (Ar) flow. The sample was subsequently cooled down to room temperature, and it was used for testing without further treatment.

## Characterizations

Field emission scanning electron microscopy (FESEM) was performed on ZEISS-Merlin. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) were tested on FEI Tecnai G2 F30 Super-Twin TEM. X-ray diffraction (XRD) curves were collected on Rigaku at 40 kV and 40 mA. A Micromeritics ASAP 2020 was used for the $N_2$ adsorption-desorption analysis; prior to analysis, all of the samples were degassed at 150 °C for over 5 h under vacuum. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed by Agilent inductively coupled plasma atomic emission spectroscopy (ICP-AES) 720.

## Electrochemical measurements

All the electrochemical measurements were carried out in a conventional three-electrode cell using a Bio-logic electrochemical work station at 25 °C. A glassy carbon (GC) electrode (5.0 mm diameter) was used as the working electrode. A Hg/HgO for KOH (0.1 M) were used as the reference electrode. A carbon rod was used as the counter electrode. The electrochemical experiments were conducted in $O_2$-saturated 0.1 M KOH for the oxygen reduction reaction (ORR). All potentials appeared were referred to reversible hydrogen electrode ($E_{RHE} = E_{Hg/HgO} + 0.059 \times pH$ for 0.1 M KOH and $E_{RHE} = E_{SCE} + 0.2415 + 0.059 \times pH$ for 0.5M $H_2SO_4$). The catalyst ink was prepared by ultrasonically dispersing a mixture of 3 mg catalyst, 360 uL ethanol, 120 uL isopropanol and 20 uL of 5 wt% Nafion solutions. Then 10 uL of the catalyst ink was pipetted and spread onto the glassy carbon (GC) electrode. Then, the loadings of the catalyst would be 60 μg. The polarization curves were recorded with different rotation speed at a 10 mV $s^{-1}$ scan rate. Before the polarization test, the voltammograms were recorded at a 50 mV $s^{-1}$ scan rate. The electrolyte was saturated with $O_2$ before the ORR activity test. The long-term durability test was conducted by the i–t chronoamperometric response by applying a -0.467 V and 0.073 V potential in 0.1 M KOH and 0.5 M $H_2SO_4$, respectively. To remove the capacitive current of the working electrode, the background current was measured by running the above electrodes without rotation in Ar-saturated 0.1 M KOH. For the methanol tolerance test, 3M methanol was added to the electrolyte. The reported ORR polarization curves had been subtracted by the background current from the capacitive current in the manuscript.

The Koutecky-Levich (K-L) plots were obtained by linear fitting of the reciprocal rotating speed versus reciprocal current density collected at different potentials from 0.2 V to 0.5 V. The overall electron transfer numbers per oxygen molecule involved in a typical ORR process were calculated from the slopes of K-L plots using the following equation: $1/J_d = 1/J_k + 1/J_{lim} = 1/J_k + 1/(B\omega^{1/2})$ (**equation S1**), where $J_d$ is the measured current at a special potential, $J_k$ is the kinetic current in amperes at a constant potential, ω is the electrode rotating speed in rpm, and B, the reciprocal of the slope, which was determined from the slope of Koutecky-Levich plots based on Levich equation as followed: $B=0.2nFv^{-1/6}C_{O2}D_{O2}^{2/3}$ (**equation S2**), in which n is the number of electrons transferred per $O_2$ molecule, F is the Faraday constant (96,485 C $mol^{-1}$), v is the kinetic viscosity, and $C_{O2}$ is the concentration of $O_2$ ($1.2 \times 10^{-3}$ mol $L^{-1}$). $D_{O2}$ is the diffusion coefficient of $O_2$ in 0.1 M KOH ($1.9\times 10^{-5}$ cm $s^{-1}$), the constant 0.2 is adopted when the rotating speed is in rpm.

**Figure S1 Photo images of freeze-dried hydrogel (left) and hydrogel after heat treatment (right).**

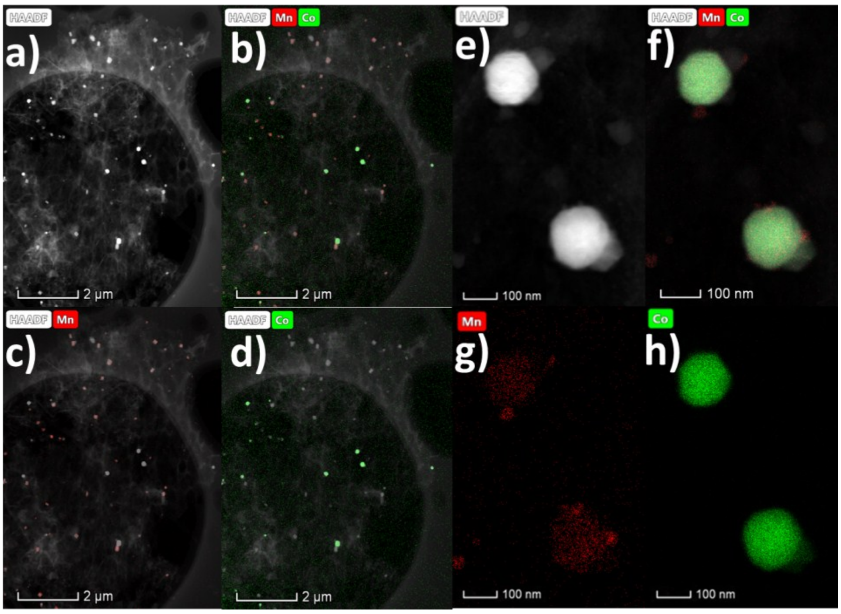

**Figure S2 EDS mapping images of Mn/Co-HCS-900 in low (a–d) and high (e–h) magnifications. It can be seen that the Mn/Co dual-metal exists both in top-down (g,h) and left-right (see Figure 3e in manuscript) way.**

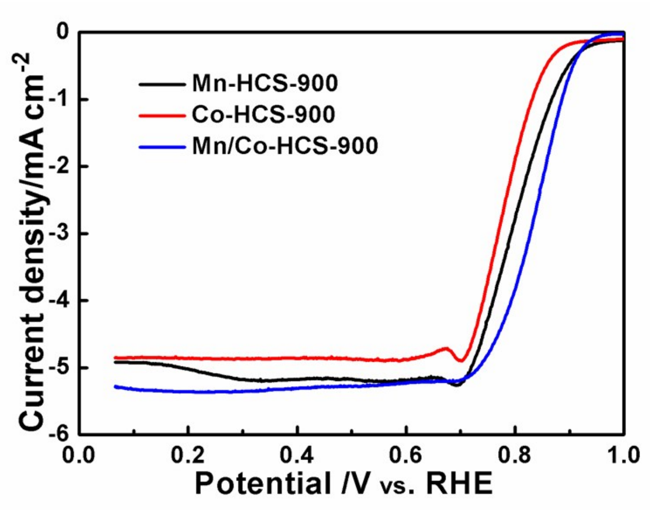

**Figure S3 Linear sweep voltammetry (LSV) of the Mn-HCS-900, Co-HCS-900 and Mn/Co-HCS-900 catalysts.**

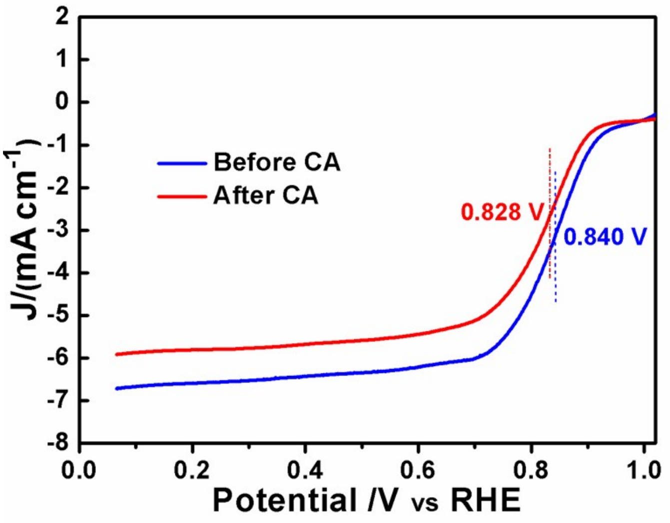

**Figure S4 Linear sweep voltammetry (LSV) of the Mn/Co-HCS-900 before and after CA test with the half-wave potential 0.840 V and 0.828 V, respectively.**

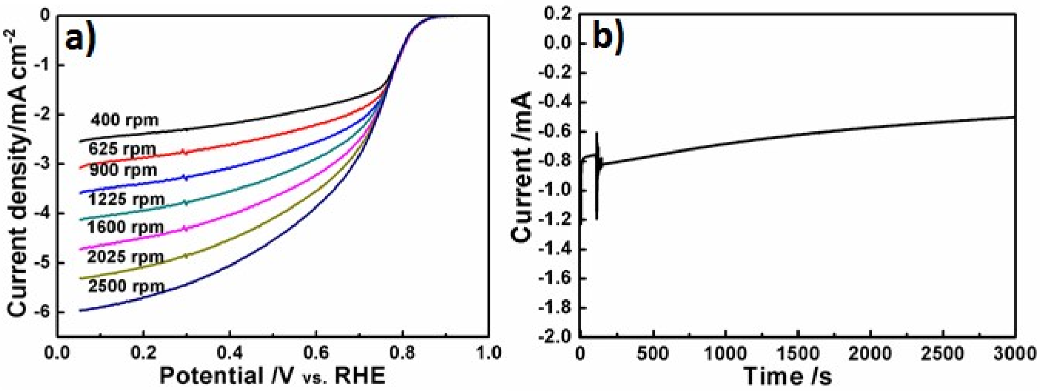

**Figure S5 LSV curves of Mn/Co-HCS-900 at different rotation speeds toward ORR (a) and i-t chronoamperometric response curves of Mn/Co-HCS-900 under 0.5 M $H_2SO_4$ (b). Mn/Co-HCS-900 shows a comparable 0.72 V half-wave, which is comparable to that of an iron-cobalt (FeCo) alloy nanoparticles (0.739 V) embedded on N-doped porous carbon nanofibers (Reference: Journal of Colloid and Interface Science, Volume 533, 1 January 2019, Pages 578-587). And it shows better methanol tolerance comparing with Pt/C without losing the current abruptly.**