Supporting Information for

A Bifunctional Oxygen Electrocatalyst from Monodisperse MnCo$_2$O$_4$ Nanoparticles to Nitrogen-enriched Carbon Nanofibers

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Experimental

Materials synthesis

Polypyrrole nanowires and nitrogen-enriched carbon nanofibers: Polypyrrole nanowires were synthesized by a previously reported method$^1$. In a typical synthesis, a solution of 0.75 g cetyltrimethylammonium bromide (CTAB) in 200 mL of 0.5 M HCl was cooled to 0–4 °C in an ice bath. 1.366 g of ammonium persulfate (APS) was then introduced under vigorous stirring. 5 min later, 1.76 mL of pyrrole was added to the solution. The solution was rested for 8-12 h to synthesize the polypyrrole nanowires. The resulting PPy nanowires were carbonized in nitrogen at 800 °C for 2 h to form nitrogen-enriched carbon nanofibers (denoted as NCF).

MnCo$_2$O$_4$-NCF composite: MnCo$_2$O$_4$-NCF composite was prepared by solvothermal method. Briefly, 40 mg of NCF was first dispersed in 40 mL ethanol. Then, 0.3 mL of 0.6 M Co (OAc)$_2$, 0.15 mL of Mn(OAc)$_2$ aqueous solutions and 0.5 mL NH$_4$OH (~28 wt.%) were added dropwise at 80 °C and aged for 3 h. The aged solution was transferred to a furnace and heated at 150 °C for 4-6 h. After cooling down to the room temperature, the reaction products were separated by filtration, followed by washing with ethanol and water several times, and then dried at 60 °C.

Characterization

The morphology and structure of the MnCo$_2$O$_4$-NCF composite was characterized by Transmission electron microscopy (TEM, JEOL JEM-2010F, 200 kV) and field-emission scanning electron microscopy (FESEM, JEOLJSM-6700F). X-Ray powder diffraction (XRD) patterns were recorded
on a Bruker D8 Advance spectrometer with a Cu Kα1 radiation source (λ = 0.15406 nm). X-Ray photoemission spectroscopy (XPS) was performed on a KRATOS AXIS DLD spectrometer. Thermogravimetric analysis (TGA) measurement was carried out in air on a Shimadzu DTG-60H from room temperature to 800 °C at a heating rate of 10 °C/min.

Electrochemical performance was evaluated in a standard three-electrode electrochemical cell with a glassy carbon rotating disk electrode (RDE, 5 mm diameter), a Pt foil counter electrode and a Ag/AgCl (3M) reference electrode. The working electrode was prepared by dispensing 5 μL of catalyst ink (5 mg sample dispersed in 1 mL of ethanol and water mixture (1:1 v/v) onto the rotation disk electrode, followed by drying in air at 50 °C for 30 min. 5 μL of 0.5 % Nafion solution was then dropped onto the electrode and dried at room temperature. OER stability is tested after 20 cycles at 50 mV/s, potential window is 0.5~0.9 V. We recorded the first cycle, 200 and 400 cycle for comparison at 900 rpm.

Supplementary Figures

Figure S1. TEM images of PPy nanowires.
Figure S2. TEM image of the nitrogen-enriched carbon nanofibers.

Figure S3. XRD patterns of nitrogen-enriched carbon nanofibers and MnCo$_2$O$_4$-NCF composite.

Figure S4. TGA analysis of the MnCo$_2$O$_4$-NCF composite.
Figure S5. (a) XPS spectra of NCF (red), MnCo$_2$O$_4$/NCF composite (black), and pure MnCo$_2$O$_4$ nanoparticle (blue). (b) O1s spectra of MnCo$_2$O$_4$/NCF composite and MnCo$_2$O$_4$ nanoparticle. (c) Mn2p and (d) Co2p spectra of MnCo$_2$O$_4$/NCF composite and MnCo$_2$O$_4$ nanoparticle.
Figure S6. (a) N1s spectra of MnCo$_2$O$_4$/NCF composite. (b) N1s spectra of NCF. (c) O1s spectra of MnCo$_2$O$_4$/NCF composite and (d) O1s spectra of MnCo$_2$O$_4$ nanoparticle.

Figure S7. (a) C1s spectra of MnCo$_2$O$_4$/NCF composite. (b) C1s spectra of NCF.

Figure S8. TEM image of pure MnCo$_2$O$_4$ nanoparticles.
Figure S9. RDE measurements and corresponding Koutecky-Levich plots at different rotation rates for various samples: (a-b) NCF; (c-d) MnCo$_2$O$_4$-NCF; (e-f) MnCo$_2$O$_4$-VC-72 mixtures and (g-h) pure VC-72.