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# Electronic Supplementary Information (ESI) for $CoMn_2O_4$ embedded in MnOOH nanorod as a bifunctional catalyst for oxygen reduction and oxygen evolution reactions

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## Experimental

### *1. Chemicals and materials*

Potassium permanganate (≥ 99.5%, $KMnO_4$) and ammonium hydroxide solution(25%-28%, $NH_4OH$) were purchased from Sinopharm Chemical Reagents Co., Ltd. (China). Cobalt nitrate hexahydrate (≥ 99.9%, $Co(NO_3)_2 \cdot 6H_2O$), Manganese acetate tetrahydrate (≥ 99.0%, $Mn(OAc)_2 \cdot 4H_2O$), Poly(Nvinyl-2-pyrrolidone) (PVP) and $RuO_2$ were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). Vulcan carbon powder XC-72 was purchased from Cabot Co. (USA). Nafion solution (5%) was purchased from Dupont Co. (USA). 20wt.% Pt/C were purchased from Johnson Matthey Company. All the chemicals were of analytical grade and used as received. Ultrapure water (resistivity: $\rho \geq 18$ MΩ cm) was used to prepare the solutions.

### *2. Synthesis of $CoMn_2O_4$-MnOOH NRs nanocomposites*

The $CoMn_2O_4$-MnOOH NRs was synthesized via a two-step hydrothermal process. In the first step, the MnOOH nanorods were prepared by the hydrothermal method as described by Yang et al.[1] Briefly, 0.474 g $KMnO_4$, 0.240 g Poly(Nvinyl-2-pyrrolidone) (PVP) and 1.103 g $Mn(OAc)_2 \cdot H_2O$ was dispersed in 80 mL deionized water with magnetic stirring for 10 minutes. Then, 10 mL ethylene glycol was dropwised slowly into the mixture. After stirring for 10 min. the prepared solution was transferred to an autoclave and maintained at 140 °C for 24 h. After cooled down to room temperature naturally, the product was centrifuged and washed with ethanol absolute and deionized water repeatedly, and dried at 60°C in an oven overnight.

Secondly, 0.125 g MnOOH was fully dispersed in 10 mL deionized water under ultrasonication. Then 0.145 g $Co(NO_3)_2·6H_2O$ dissolved in 10 mL of deionized water was added into the MnOOH suspension. Afterwards, 0.7 mL aqueous ammonia (25 wt.%) was added into the solution. The mixture was transferred into an autoclave and hydrothermally treated at 150 °C for 5 h. Finally, the product was filtered and washed with deionized water, and dried at 60°C. Based on the contents of Co and Mn in the $CoMn_2O_4$-MnOOH NRs, as measured by ICP-MS, the molar ratio ($CoMn_2O_4$ : MnOOH) was calculated to be 1 : 1, and the obtained sample was denoted as $CoMn_2O_4$-MnOOH NRs. Another two types of $CoMn_2O_4$-MnOOH NRs were prepared just by changing the amount of the $Co(NO_3)_2·6H_2O$. Based on the contents of Co and Mn in the $CoMn_2O_4$-MnOOH NRs, as measured by ICP-MS, the molar ratio ($CoMn_2O_4$ : MnOOH) was calculated to be 1 : 0.6 and 1 : 1.7, respectively. The obtained sample were denoted as $CoMn_2O_4$-MnOOH NRs (1 : 0.6) and $CoMn_2O_4$-MnOOH NRs (1 : 1.7), respectively. The pure $CoMn_2O_4$ nanoparticles was prepared as discussed in the above method with the addition of $Co(NO_3)_2·6H_2O$, $Mn(OAc)_2·4H_2O$ without MnOOH.

### *3. Characterization*

The crystal structure of samples was examined by X-ray diffractiion (XRD) using a Rigaku ultima Ⅳ diffractometer with Cu *Kα* radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JFC1600 microscope at 10 kV. Transmission electron microscopy (TEM) characterization was completed by using a JEOL JEM-2100 instrument with operating voltage at 200 kV. The exact compositions of the products were examined by inductively coupled plasma-optical emission spectrometry (ICP-OES, X Series 2, Thermo Scientific USA).

### *4. Electrochemical measurements*

The electrochemical measurements of catalysts were conducted on a electrochemical workstation (CHI 660E) with a three-electrode electrochemical system in a rotating disk electrode (RDE) configuration. A glassy carbon disk electrode (4 mm in diameter) modified with catalyst was used as the working electrode. Hg/HgO electrode and a Platinum wire were used as reference and counter electrode, respectively. To increase the electronic conductivity, the catalyst was mixed with carbon black (Vulcan XC-72R) at a 3:7 mass ratio. As for catalyst ink, 10 mg well-mixed sample was ultrasonically dispersed in 1mL ethanol absolute with 50 μL 5 wt.% Nafion solution for 30 min. Then 6 μL homogeneous catalyst ink was dropped onto the glassy carbon disk electrode with catalyst loading of 0.455 mg·cm$^{-2}$.

The electrocatalytic properties of catalysts were investigated by testing cyclic voltammetry (CV), linear sweep voltammograms (LSV) and current-time (i-t) chronoamperometry in 0.1 M KOH aqueous solution. The ORR activity was measured in $O_2$-saturated electrolyte solution at a scan rate of 0.01 V·s$^{-1}$ with rotating speed from 400 to 2500 rpm. For the OER test, the working electrode was scanned at a scan rate of 10 mV s$^{-1}$ in $O_2$-saturated 0.1 M KOH with the electrode rotated at 1600 rpm.

The electron transfer number (n) was calculated by the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_{\mathrm{k}}} + \frac{1}{J_{\mathrm{d}}} = \frac{1}{J_{\mathrm{k}}} + \frac{1}{B\omega^{1/2}}$$

$$B = 0.62nFC_{\mathrm{o}}D_{\mathrm{o}}^{2/3}v^{-1/6}$$

Where $J$ is the measured current density, $J_{\mathrm{k}}$ and $J_{\mathrm{d}}$ are the kinetic and diffusion limited current densities, respectively; $F$ is the Faraday constant (96485 C mol$^{-1}$), n is transferred electron number, $C_{\mathrm{o}}$ is the saturated concentration of oxygen ($1.2 \times 10^{-6}$ mol cm$^{-3}$), $D_{\mathrm{o}}$ is the diffusion coefficient of oxygen ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$) and ν is kinematic viscosity of the electrolyte (0.01 cm$^2$ s$^{-1}$) in 0.1 M KOH at 25 $^{\mathrm{o}}$C..

Electrochemically active surface area (ECSA) was calculated by the measurement of double layer capacitance.[2] The double layer current $I$ is linearly proportional to the scan rate (ν), and the capacitance C is given by the equation: $I$ = Cν. The ECSA was obtained using the equation: ECSA = C/$C_{\mathrm{s}}$, where $C_{\mathrm{s}}$ is the specific capacitance of sample or the capacitance of an atomically smooth surface of the material per unit area. For our calculation, we use the specific capacitance value of 60 μF cm$^{-2}$ in 0.1 M KOH.[2, 3]

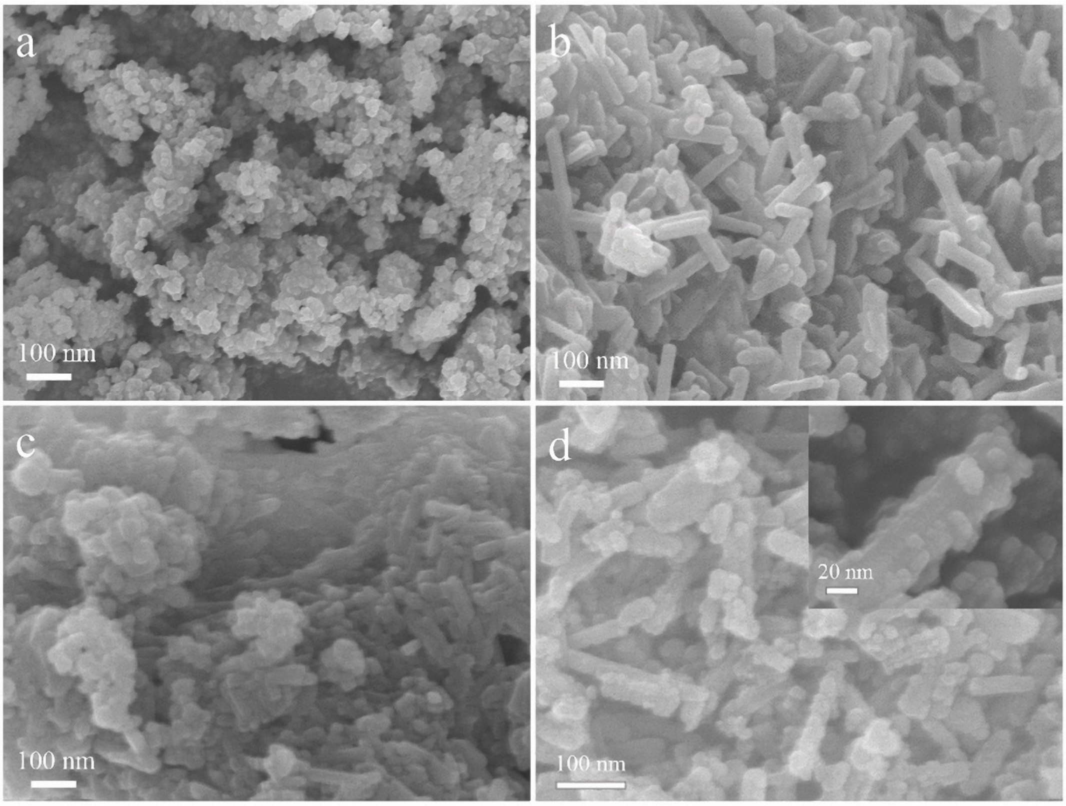

**Fig. S1** SEM image of $CoMn_2O_4$ (a), MnOOH (b), $CoMn_2O_4$+MnOOH (c) $CoMn_2O_4$-MnOOH NRs (d).

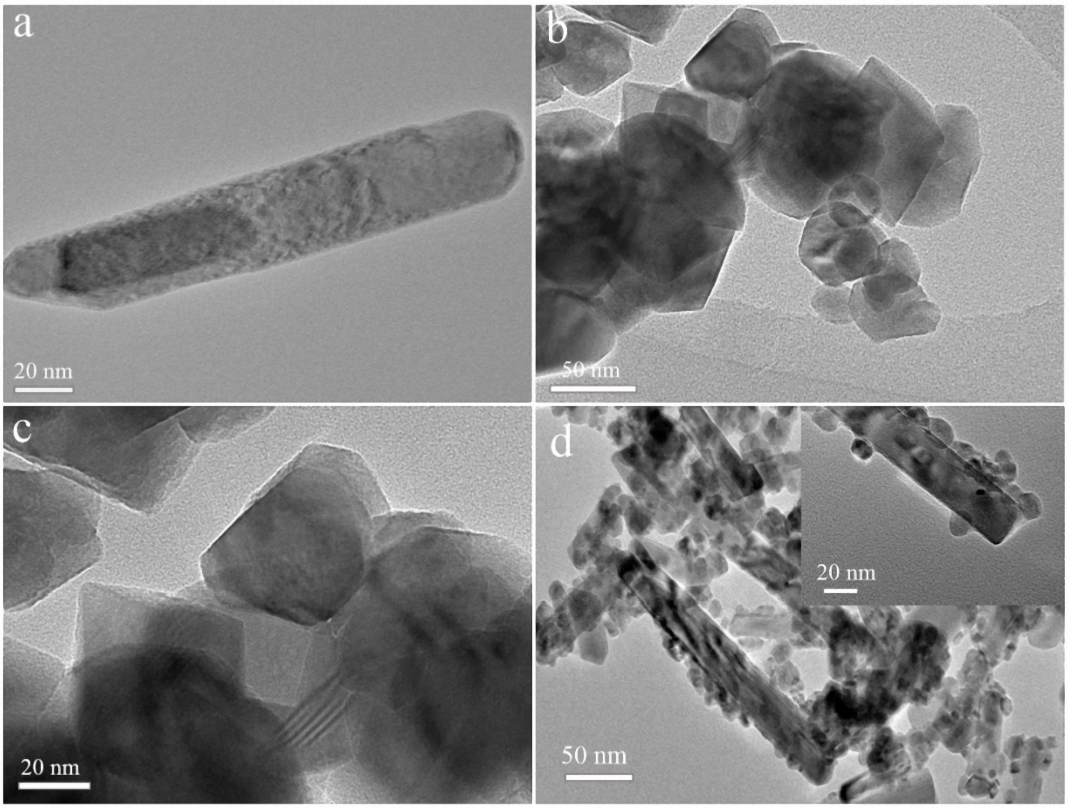

**Fig. S2** TEM image of MnOOH (a),$CoMn_2O_4$ (b-c), $CoMn_2O_4$-MnOOH NRs (d).

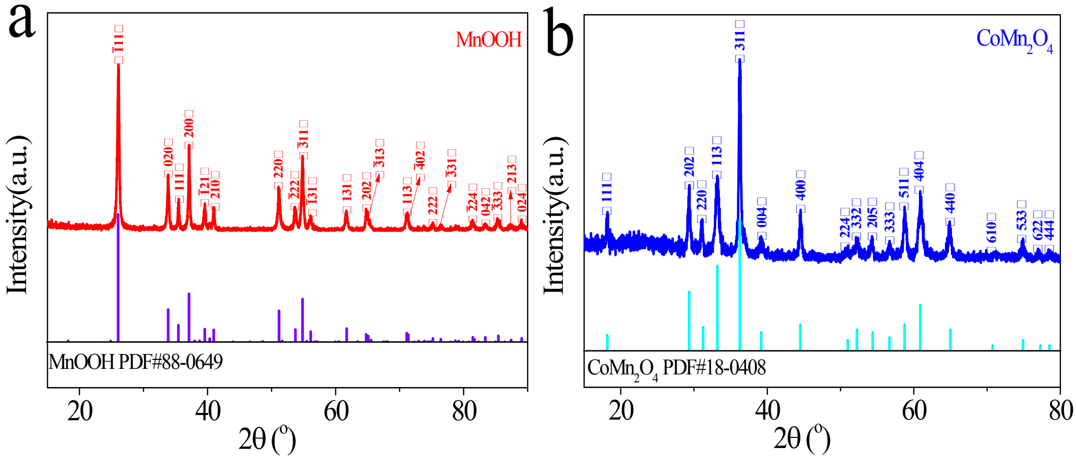

**Fig. S3** XRD patterns of MnOOH(a) and $CoMn_2O_4$ (b).

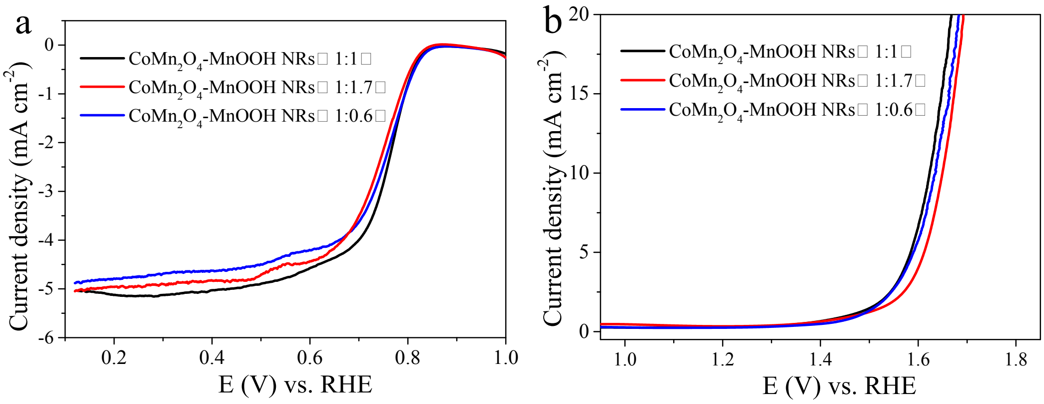

**Fig. S4** LSVs for ORR of samples in $O_2$-saturated 0.1 M KOH with a rotating speed of 1600 rpm (a), LSV of the OER on samples with a sweep rate of 10 mV $s^{-1}$ and a rotating speed of 1600 rpm (b).

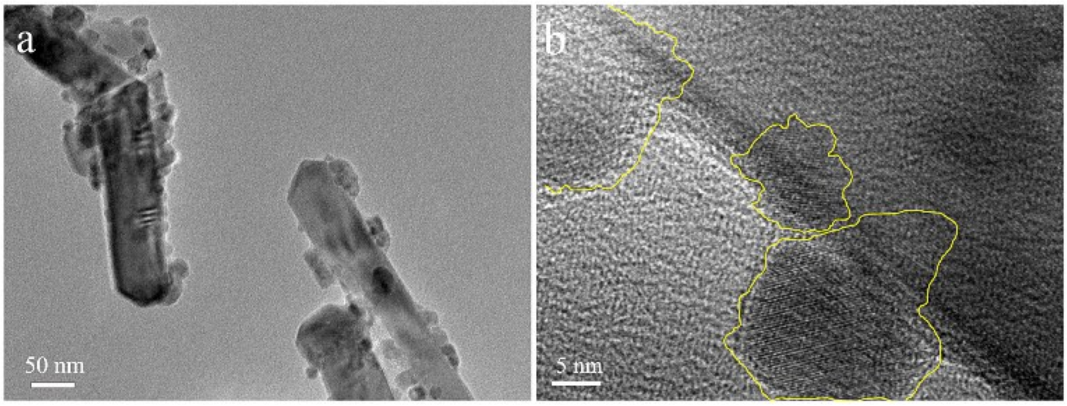

**Fig. S5** TEM image (a) and HRTEM image (b) of $CoMn_2O_4$-MnOOH NRs after electrocatalysis.

**Table S1** Comparison in the oxygen electrode activities

| Catalyst material | $E_{j=3}$ (V) | $E_{j=10}$ (V) | Δ$E$ (V) | Reference |
|---|---|---|---|---|
| $CoMn_2O_4$-MnOOH NRs | 0.74 | 1.62 | 0.88 | This work |
| $CoMn_2O_4$ | 0.70 | 1.69 | 0.99 | This work |
| MnOOH | 0.62 | - | - | This work |
| $CoMn_2O_4$+MnOOH | 0.63 | 1.72 | 1.09 | This work |
| $Co_3O_4/2.7Co_2MnO_4$ | 0.68 | 1.77 | 1.09 | 4 |
| $Mn_3O_4$@$CoMn_2O_4$-$Co_xO_y$ | 0.73 | 1.72 | 0.99 | 5 |
| $Co_2MnO_4$-3.9/CNT | 0.85 ($E_{1/2}$) | 1.61 | 0.76 | 6 |
| $H_2$-treated $CaMn_{0.75}Nb_{0.25}O_{3-\delta}$ | 0.66 | 1.79 | 1.13 | 7 |
| $MnO_2$-$CoFe_2O_4$/C | 0.77 | 1.70 | 0.93 | 8 |
| CoNiMn-LDH/RGO | 0.69 | 1.61 | 0.92 | 9 |
| $CoMn_2O_4$/NCNT | 0.76 | 1.72 | 0.96 | 10 |
| $MnCo_2O_4$@PPy | 0.75 | 1.79 | 1.04 | 11 |
| $MnCo_2O_4$-10 (vs Ag/AgCl) | -0.38 | 0.82 | 1.2 | 12 |
| $La_{0.8}Sr_{0.2}Co_{1-x}Mn_xO_3$-60 | 0.704 | 1.736 | 1.032 | 13 |
| $MnFe_2O_4$ | 0.715 | 1.82 | 1.105 | 14 |
| $0.21NiMnO_3/NiMn_2O_4$ | 0.73 | 1.61 | 0.88 | 15 |
| dandelion-like α-$MnO_2$ | 0.73 | 1.78 | 1.05 | 16 |
| urchin-like α-$MnO_2$ | 0.71 | 1.87 | 1.16 | 16 |
| Co-TA-800 | 0.81 | 1.69 | 0.88 | 17 |
| PCN–CFP | 0.67 ($E_{1/2}$) | 1.63 | 0.96 | 18 |
| Fe/N-CNTs | 0.81 | 1.75 | 0.94 | 19 |
| Co@$Co_3O_4$/NC-1 | 0.80 | 1.65 | 0.85 | 20 |
| $Ni_3Fe$/N-C sheets | 0.78 | 1.62 | 0.84 | 21 |

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