Electronic Supplementary Information

Well-dispersed Co_3O_4/Co_2MnO_4 nanocomposites as a synergistic bifunctional catalyst for oxygen reduction and oxygen evolution reactions

Dengdeng Wang, Xu Chen*, David G. Evans, and Wensheng Yang*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China
E-mail: chenxu@mail.buct.edu.cn

Experimental

Synthesis of CoMn-LDH Precursor and Co_3O_4/Co_2MnO_4 Nanocomposites CoMn-LDH precursors were prepared by using the SNAS method in a modified colloid mill reactor.[1,2] A salt solution was obtained by dissolving $Co(NO_3)_2 \cdot 6H_2O$ and $Mn(NO_3)_2$ (50 wt.%) with a Co/Mn molar ratio of 3:1 or 4:1 in freshly deionized water with a total cation concentration of 0.2 M. An aqueous base solution of NaOH and Na_2CO_3 was also prepared, in which the concentrations of the base were related to those of the metal ions as follows: $[CO_3^{2-}] = 2.0\ [Mn^{2+}]$, $[OH^-] = 1.6\ ([Co^{2+}] + [Mn^{2+}])$. Equal volumes of salt and base solutions were simultaneously added to a modified colloid mill reactor with a rotor speed of 3000 rpm and mixed for 2 min. The resulting suspension was aged at 30 °C for 5 h, then washed thoroughly with deionized water by centrifugation, and finally dried at 60 °C overnight. The Co_3O_4/Co_2MnO_4 nanocomposites were prepared by calcination of the as-synthesized

CoMn-LDH precursors in air at 500 °C for 4 h, and then cooled to ambient temperature.

Preparation of Samples for Comparison Experiments The pure Co_3O_4 powder and Co_2MnO_4 powder were prepared using conventional methods[3] by thermal treatment of metal nitrate precursors at 500 °C. Stoichiometric Co_3O_4 and Co_2MnO_4 samples with the same $[Co_3O_4]/[Co_2MnO_4]$ ratio as the $Co_3O_4/2.7Co_2MnO_4$ nanocomposite derived from the CoMn-LDH precursor were physically mixed and then ground well before characterization; this material is denoted $Co_3O_4 + Co_2MnO_4$.

Characterization Powder XRD data were collected on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (40 kV, 30 mA, and λ = 0.154 nm). SEM images and Energy dispersive X-ray spectroscopy (EDS) elemental analysis were obtained using a Zeiss Supra 55 scanning electron microscope. TEM images and EDS elemental analysis were obtained with a JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. The specific surface area was determined by nitrogen adsorption at 77 K using a Quantachrome Autosorb-1C-VP Analyzer. Elemental analysis for metal ions was performed using a Shimadzu ICPS-7500 inductively coupled plasma emission spectrometer (ICP–ES).

Electrochemical measurements were carried out at 25 °C on a PARSTAT 2273 potentiostat/galvanostat with a three-electrode electrochemical cell in a RDE configuration (Pine Research Instrumentation). A glassy carbon disk electrode (5 mm in diameter) with coated catalysts was used as the working electrode. The catalyst was composed of well-mixed 30 wt.% Co_3O_4/Co_2MnO_4 nanocomposite or control samples and 70 wt.% carbon powder (Vulcan XC-72). For electrode preparation, a 4 mg sample of this mixture and 100 μL of 5 wt.% Nafion solution were dispersed in 1 mL of 1:3 v/v water/isopropanol mixed solvent by sonication for at least 1 hour to form a homogeneous ink. Then 5.0 μL of the catalyst ink was loaded onto a glassy carbon disk electrode. The control sample Pt/C (20 wt.% Pt on Vulcan Xc-72, Etek) on a GC substrate was prepared in the same way and had a metal concentration of 28 μg cm^{-2}. An Ag/AgCl electrode in saturated KCl aqueous solution and a platinum wire were

used as the reference and counter electrodes, respectively. The potential scale was calibrated to a reversible hydrogen electrode (RHE). The electrolyte was saturated with oxygen by bubbling high-purity O_2 for 30 min prior to the start of each experiment and a flow of O_2 was maintained over the electrolyte during the measurements.

References

1. Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater.*, 2002, **14**, 4286.
2. S. L. Xu, Z. R. Chen, B. W. Zhang, J. H. Yu, F. Z. Zhang and D. G. Evans, *Chem. Eng. J.*, 2009, **155**, 881.
3. T. Nissinen, T. Valo, M. Gasik, J. Rantanen and M. Lampinen, *J. Power Sources*, 2002, **106**, 109.

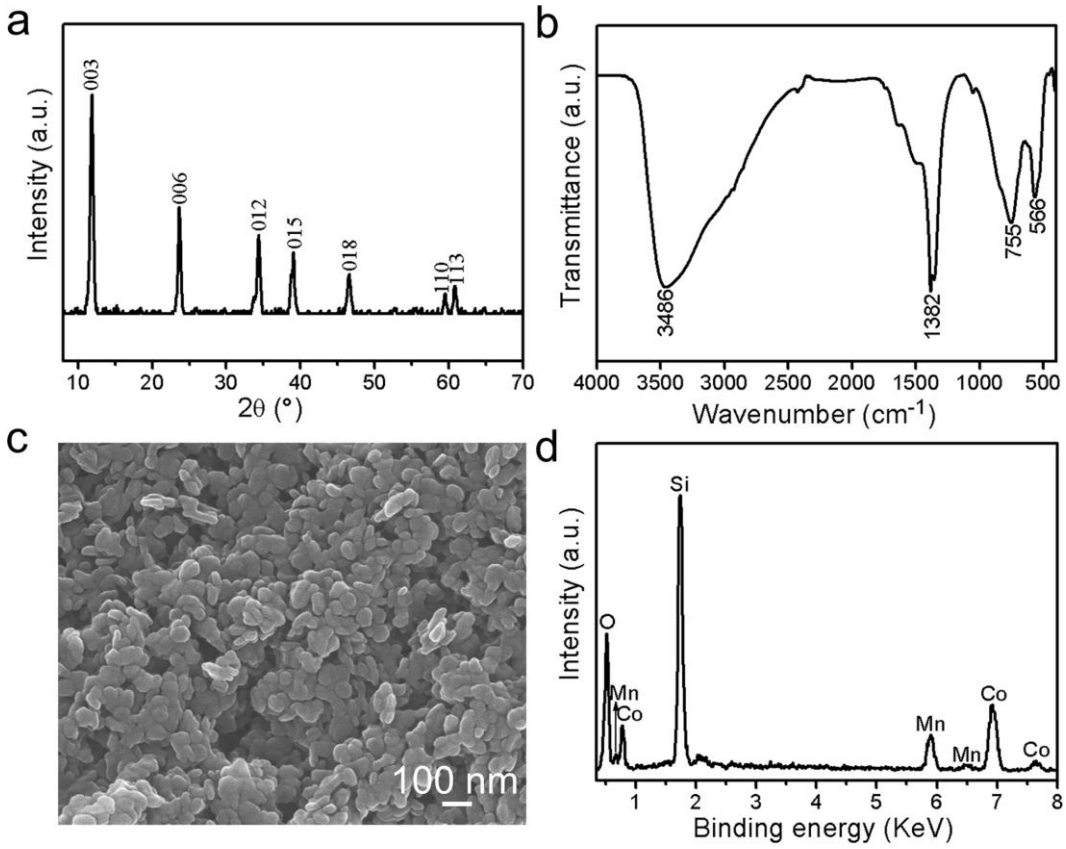

Fig. S1 (a) XRD pattern of the CoMn-LDH precursor with a Co/Mn molar ratio of 3:1. (b) FT-IR spectrum of the CoMn-LDH precursor. The FT-IR spectrum was recorded in the range 4000 to 400 cm^{-1} with 1 cm^{-1} resolution on a Bruker Vector-22 spectrometer using the KBr pellet technique. (c) SEM image and (d) EDS spectrum of the CoMn-LDH precursor.

The X-ray diffraction (XRD) pattern for the CoMn-LDH precursor (Fig. S1a) exhibits the characteristic diffraction peaks of a well-crystallized LDH structure with a series of (00*l*) harmonics at low angle corresponding to a basal spacing of 7.55 Å. The presence of the interlayer CO_3^{2-} anions was confirmed by the peak at 1382 cm^{-1} in the Fourier transform infrared (FT-IR) spectrum of the precursor (Fig. S1b). Scanning electron microscopy (SEM) (Fig. S1c) revealed the characteristic platelet-like nanoparticulate morphology of the CoMn-LDH precursor with the particle diameter ranging from 50 to 100 nm. The energy-dispersive spectrum (EDS)

(Fig. S1d) confirmed the elemental composition of the CoMn-LDH precursor. The Co/Mn ratio obtained from EDS was ~3, which is consistent with the ratio in the precursor solution.

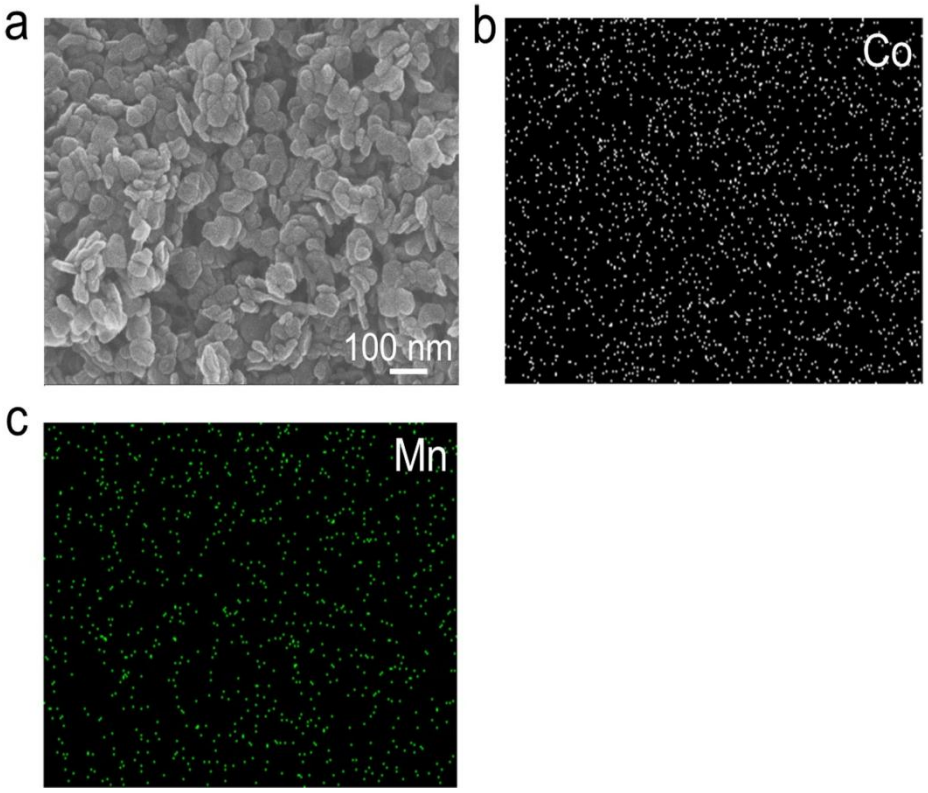

Fig. S2 (a) SEM image and (b, c) elemental mapping of $Co_3O_4/2.7Co_2MnO_4$.

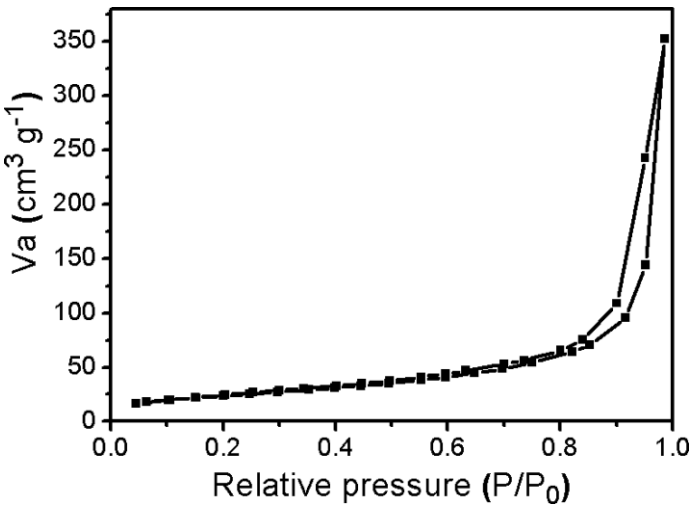

Fig. S3 N_2-sorption isotherms of $Co_3O_4/2.7Co_2MnO_4$.

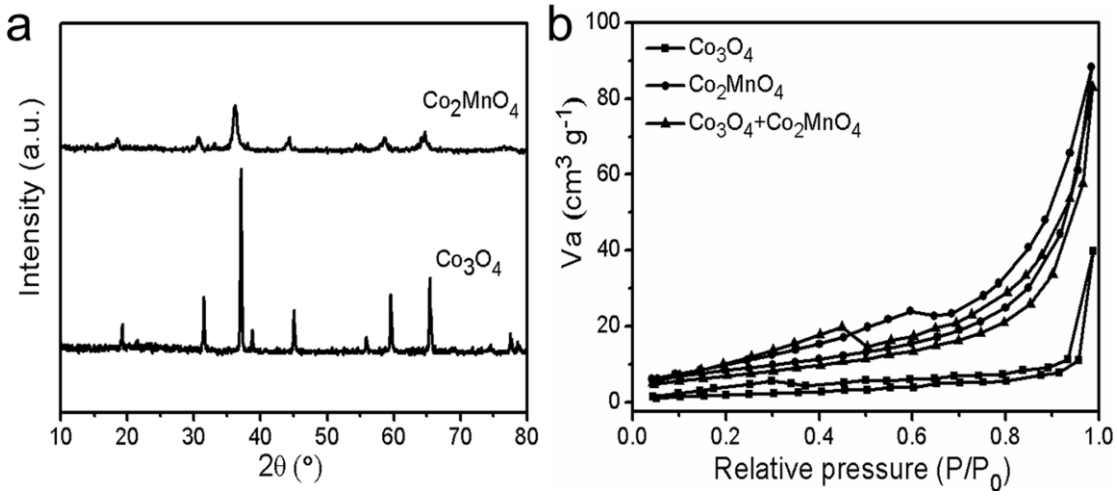

Fig. S4 (a) XRD patterns of Co_3O_4 and Co_2MnO_4 prepared by traditional calcination methods. All diffraction peaks can be indexed to cubic structured Co_3O_4 (JCPDS No. 42-1467) and Co_2MnO_4 (JCPDS No. 23-1237), respectively. (b) N_2-sorption isotherms of Co_3O_4, Co_2MnO_4, and their physical mixture Co_3O_4+Co_2MnO_4. The BET specific surface areas of Co_3O_4, Co_2MnO_4, and Co_3O_4+Co_2MnO_4 were 7.7, 30.9, and 26.1 m^2/g, respectively.

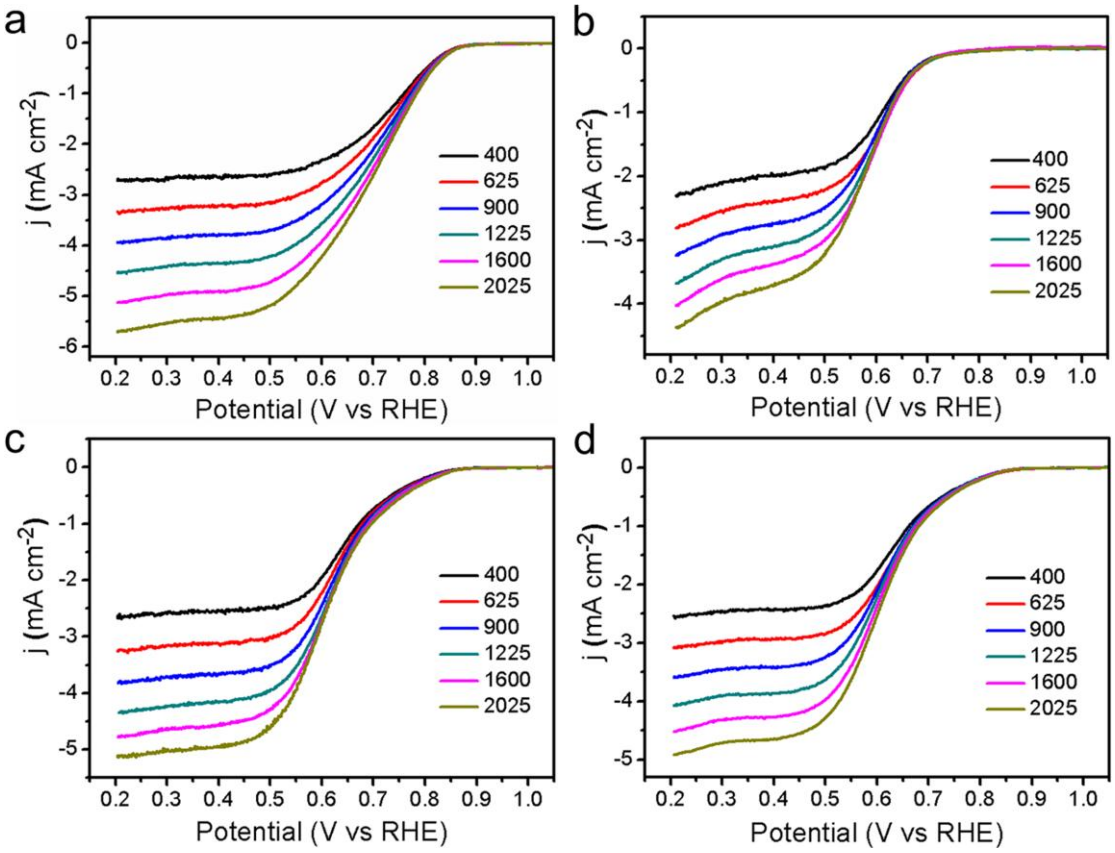

Fig. S5 Rotating-disk voltammograms recorded on different catalyst-modified electrodes in O_2-saturated 0.1 M KOH solution at different rotation rates as indicated. (a) $Co_3O_4/2.7Co_2MnO_4$, (b) Co_3O_4, (c) Co_2MnO_4 and (d) Co_3O_4 + Co_2MnO_4.

The working electrodes were scanned at a sweep rate of 5 mVs^{-1} with varying rotation speed from 400 rpm to 2025 rpm. The RDE current–potential data can be applied to construct Koutecky–Levich (*K–L*) curves according to the equations [Eqs. (1) and (2)] that have been widely used to analyze the ORR reaction kinetics.

$$1/j = 1/j_k + 1/j_l \quad (1)$$

$$j_l = 0.62nFC_0D^{2/3}\nu^{-1/6}\omega^{1/2} \quad (2)$$

where j is the measured current density, j_k and j_l are the kinetic- and limiting current densities, respectively, ω is the angular frequency of the rotation (rad s^{-1}), n is the overall number of electrons transferred during oxygen reduction, F is the Faraday constant (96 500 C mol^{-1}), C_0 is the saturated oxygen concentration in 0.1 M KOH

(1.2×10^{-6} mol cm^{-3}), D is the diffusion coefficient of oxygen (1.9×10^{-5} cm s^{-1}), and v is the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

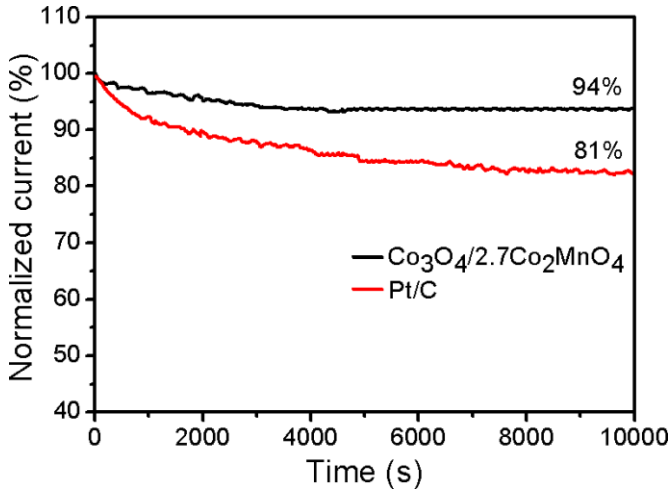

Fig. S6 Chronoamperometric curves of the $Co_3O_4/2.7Co_2MnO_4$ nanocomposite and Pt/C at 0.7 V vs. RHE in O_2-saturated 0.1 M KOH solution at 400 rpm.

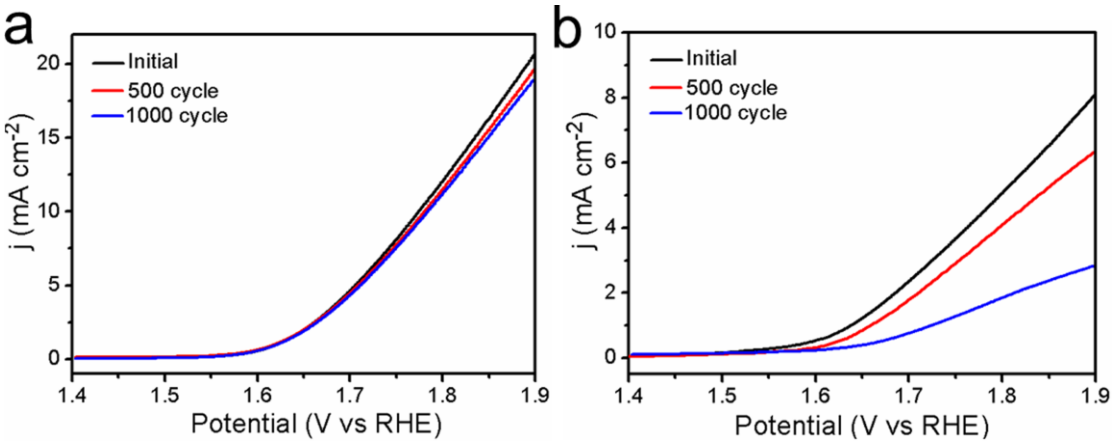

Fig. S7 LSVs of the OER for $Co_3O_4/2.7Co_2MnO_4$ (a) and Pt/C (b) catalyst-modified RDEs in O_2-saturated 0.1 M KOH solution at 1600 rpm with a sweep rate of 5 mV s^{-1} before, after 500 cycles and 1000 cycles.

The OER stability of the catalysts was evaluated by continuous cyclic sweeps between 1.4 V and 1.9 V vs. RHE at a sweep rate of 100 mV s^{-1} for given number of cycles. At the end of each cycling, the resulting electrode was used for LSV at 1600 rpm with a sweep rate of 5 mV s^{-1} (Fig. S7a). As seen from Fig. S7a, the $Co_3O_4/2.7Co_2MnO_4$ nanocomposite lost ~2% of the initial OER current density at 1.9 V vs. RHE after 500 cycles and decreased by ~3.2% after 1000 cycles. The Pt/C catalyst (Fig. S7b) maintained only ~78.3% of the initial OER current density after 500 cycles and ~ 35.1% after 1000 cycles. These results indicate that the $Co_3O_4/2.7Co_2MnO_4$ nanocomposite has good OER stability.

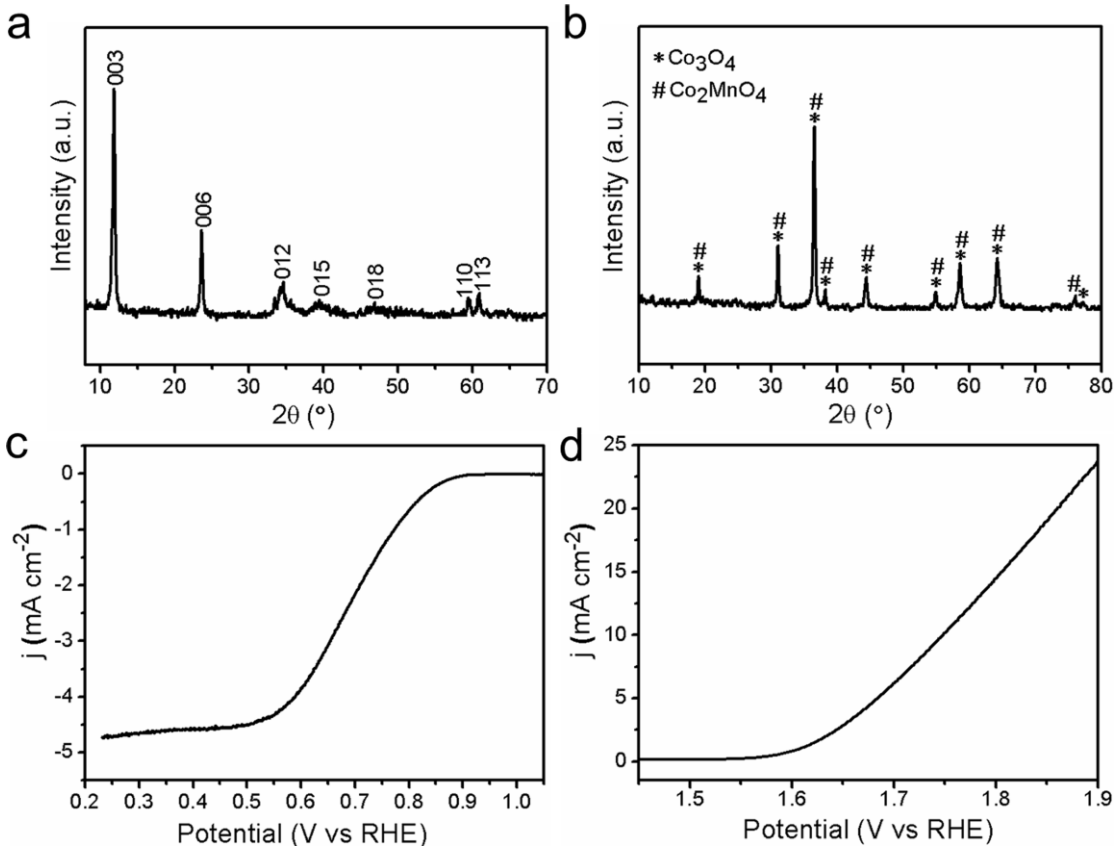

Fig. S8 (a) XRD pattern of the CoMn-LDH precursor with a Co/Mn molar ratio of 4:1. (b) XRD pattern of the $Co_3O_4/1.3Co_2MnO_4$ nanocomposite derived from calcination of the CoMn-LDH precursor with a Co/Mn molar ratio of 4:1. LSVs of the $Co_3O_4/1.3Co_2MnO_4$ nanocomposite for ORR (c) and OER (d) in O_2-saturated 0.1 M KOH solution at 1600 rpm with a sweep rate of 5 mV s^{-1}.