Supporting Information for

Hierarchical porous Co_3O_4@$Co_xFe_{3-x}O_4$ film as an advanced electrocatalyst for oxygen evolution reaction

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1. Experimental Section:

All of the materials were analytical grade and used without further purification. Nickel foams (kunshan Desi electronic Technology Co., Ltd., purity>99.5%, thickness: 1mm) with a size of ca. 20mm*20mm were cleaned ultrasonically in a concentrated HCl solution (36-38 wt%) for 5 min to remove the surface NiO layer, then washed with deionized water and absolute ethanol, respectively, and then dried at 60 ℃ for 10h.

The fabrication of Co_3O_4@$Co_xFe_{3-x}O_4$ core/shell nanowires film was adopting two-step hydrothermal method, which was growing the nanoflakes @ nanowire arrays structure on the nickel foam. In the first step, the $Co_2(OH)_2CO_3$ nanowires film was grown on the substrates by in-situ growth. In a typical procedure, $Co(NO_3)_2$•$6H_2O$(0.58g, 2mmol), urea(0.6g, 10mmol) and NH_4F(0.30g, 8mmol) were dissolved and stirred in 40 ml of deionzed water to form a clear solution. The as-prepared nickel foam(2cm*2cm) and the aqueous solution was transferred to 50ml Teflon-lined stainless-steel autoclaves, which was sealed, maintained at 120 ℃ for 9h. The thin film material was washed with distilled water and ethanol with the ultrasonication, and dried at 80 ℃ for 6h. Then the cobalt nanowires film was obtained. In the second step, the process of growing nanoflakes on the nanowire was carried out. $FeCl_3$•$6H_2O$ (0.405g 1.5mmol) $NaNO_3$(0.85g 10mmol) were dissolved and stired in 36ml distilled wate. When the solution became clearly, 20 μL hydrochloric acid (36%-38%) was added. Then we transferred the thin film material and the solution together into the Teflon-lined stainless-steel autoclaves, which was sealed, maintained at 100 ℃ for 24h. The thin film material was washed with distilled water and ethanol with the ultrasonication, and dried at 80 ℃ for 6h. The precursor of hierarchical porous $Co_2(OH)_2CO_3$@ CoFe-LDH thin film material was obtained. At last, after the precursor was calcined at 450 ℃ under N_2 atmosphere for 2h, we got the hierarchical porous Co_3O_4@$Co_xFe_{3-x}O_4$ thin film material.

For comparison, the bare Co_3O_4 NWAs thin film material was synthesized. After the first step, we transferred the cobalt nanowires film to the atmosphere furnace. It was also calcined at 450℃ under N_2 atmosphere for 2h. Besides Co_3O_4 nanowires thin film, the $Co_xFe_{3-x}O_4$ nanoplates film was also prepared using a modified method reported before.[1] 1mmol $Co(NO_3)_2•6H_2O$, 0.5mmol $Fe(NO_3)_3•9H_2O$ and 10mmol urea was dissolved into 36mL distilled water, and then we transferred the as-prepared nickel foam and the solution to 50mL Teflon-lined stainless-steel autoclaves, which was sealed, maintained at 100 ℃ for 8h. At last, the precursor thin film material was calcined at 450 ℃ under N_2 atmosphere for 2h.

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max 2500 diffractometer (Cu Kα radiation, scan speed of $10°/min^{-1}$) in the 2θ range from 5° to 80°. The size and morphology was analyzed using a field-emission scanning electron microscope (FESEM) (HITACHI H-800) which was operated at 20 kV. Energy dispersive X-ray spectroscopy (EDS) mapping of the film samples were performed using a HORIBA 7593-H EDS attachment. High-resolution transmission electron microscopy (HRTEM) measurements were carried out using a JEOL JEM 2010 system operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out using a Perkin–Elmer PHI-5300 spectrometer. Brunner Emmet Teller (BET) measurements were carried out using a Micromeritics 3Flex surface characterization analyzer.

The electrochemical measurements were carried out at 298 K in a three-electrode glass cell connected to an electrochemical workstation (a CHI 660D, Chen Hua, Shang Hai). Before the electrochemical tests, H_2 was given to the electrolyte to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H_2/H^+ couple. The hierarchical nanostructured film on nickel foam substrate (1 cm^2) was used as the working electrodes. In all tests, the platinum electrode (1 cm^2) and saturated calomel electrode was used as the counter and reference electrodes respectively. The saturated calomel electrode (SCE) was calibrated with respect to reversible hydrogen electrode (RHE) by using Pt electrode as standard electrode. And the prepared 1 mol L^{-1} KOH aqueous solution was used as the electrolyte. All the potentials reported in our manuscript are against RHE. The stability testing of the sample was operated at a constant overpotential for achieving a high initial current density.

In 1 M KOH, E(RHE) = E(SCE) + 1.06 V

2. Supplementary Figures

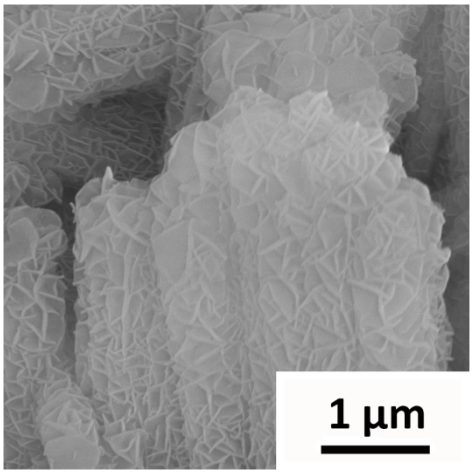

Figure S1. SEM image of hierarchical porous $Co_2(OH)_2CO_3$@ CoFe-LDH without calcinations process.

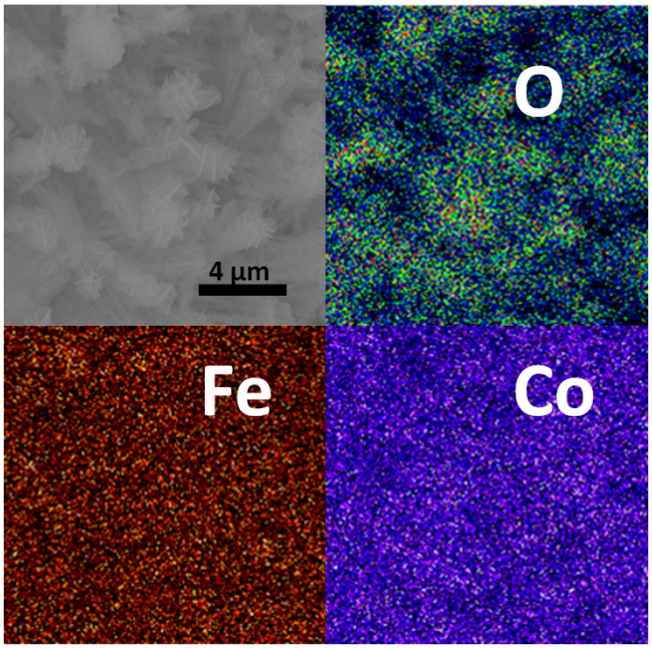

Figure S2. EDS mapping results of hierarchical porous Co_3O_4@$Co_xFe_{3-x}O_4$ film.

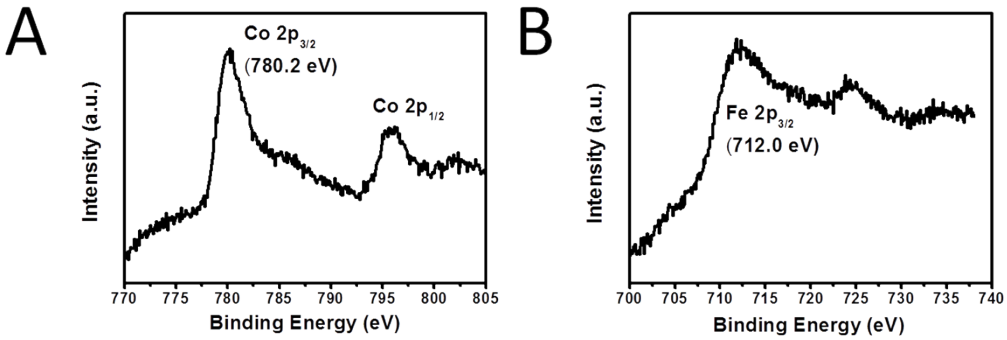

Figure S3. (A), the binding energy of Co 2p and (B), the binding energy of Fe 2p in hierarchical porous Co_3O_4@$Co_xFe_{3-x}O_4$ film.

Table S1. EDS data of Co/Fe ratios in hierarchical porous Co_3O_4@$Co_xFe_{3-x}O_4$ nanostructures.

Samples	Co (atomic %)	Fe (atomic %)	Co:Fe
Co_3O_4@$Co_xFe_{3-x}O_4$	22.27	23.87	1.07:1

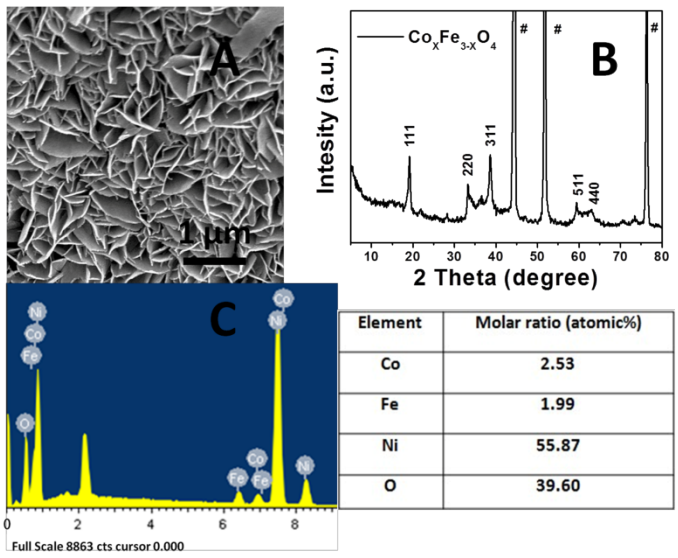

Figure S4. (A), SEM image of $Co_xFe_{3-x}O_4$ nanoplatelets film; (B), XRD pattern of $Co_xFe_{3-x}O_4$ nanoplates film; (C) EDS pattern of $Co_xFe_{3-x}O_4$ nanoplates film and the table showing the corresponding molar ratio among these elements.

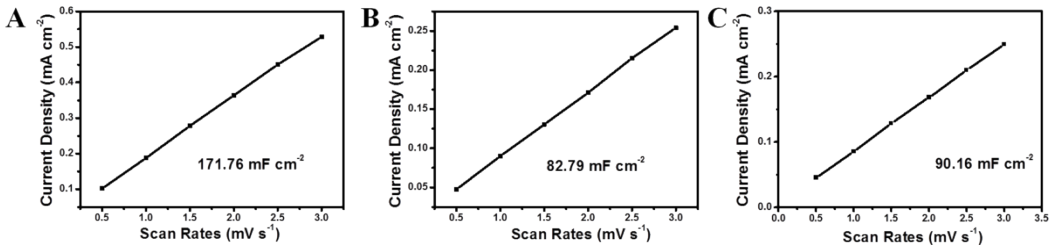

Figure S5. Plots of current densities vs. scan rates derived from the EDLC results for (A) hierarchical Co_3O_4@$Co_xFe_{3-x}O_4$ nanowires film, (B) $Co_xFe_{3-x}O_4$ nanosheet film and (C) Co_3O_4 nanowires film. The calculated EDLC values are 171.76, 82.79 and 90.16 mF cm^{-2} for Co_3O_4@$Co_xFe_{3-x}O_4$, Co_3O_4 and $Co_xFe_{3-x}O_4$, respectively.

Reference:

1. J. Sun, Y. Li, X. Liu, Q. Yang, J. Liu, X. Sun, D. G. Evans and X. Duan, *Chem. Commun.*, 2012, **48**, 3379-3381.