## Efficient Oxygen Reduction Reaction Using Mesoporous Ni-doped Co<sub>3</sub>O<sub>4</sub> Nanowire Array Electrocatalysts

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#### 1, Spinel structure of Co<sub>3</sub>O<sub>4</sub> crystal



Figure S1 Ball-and-stick model of the unit cell of Co<sub>3</sub>O<sub>4</sub><sup>[1]</sup>

# 2. Mechanism of mesoporous Ni-doped Co<sub>3</sub>O<sub>4</sub> nanowires in hydrothermal reaction The reactions involved may be illustrated as follows.<sup>[2]</sup>

$$Co^{2+} + xF^{-} \rightarrow [CoF_x]^{2-x} \tag{1}$$

$$H_2NCoNH_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{2}$$

$$CO_2 + H_2 O \to CO_3^{2^-} + 2H^+$$
 (3)

$$NH_3 + H_2 O \rightarrow NH_4^+ + OH^- \tag{4}$$

$$2[CoF_{x}]^{2-x} + CO_{3}^{2-} + 2OH^{-} + nH_{2}O \rightarrow Co_{2}(OH)_{2}CO_{3}nH_{2}O + 2xF^{-}$$
(5)

During the annealing process:

$$3Co(0H)_2CO_3nH_2O + O_2 \rightarrow Co_3O_4 + (3n+3)H_2O + 3CO_2$$
(6)

3. Structural characterization of the Ni-doped Co<sub>3</sub>O<sub>4</sub> NW arrays



Figure S2 (A) XRD pattern and (B) Raman spectrum of  $Co_3O_4$  NW arrays on Ni foam.



Figure S3 FTIR spectrum of Ni-doped Co<sub>3</sub>O<sub>4</sub> NW arrays

XRD pattern in Figure S2A shows that the sample only contain spinel  $Co_3O_4$  phase (JCPDS 42-1467) and Ni phase (JCPDS 04-0850) from the Ni foam substrate. In the Raman spectrum, the  $Co_3O_4$  nanowire arrays exhibit four obvious peaks at 476, 519, 616, and 686 cm<sup>-1</sup>, which are assigned to the E<sub>g</sub>, F<sub>2g</sub>, F<sub>2g</sub> and A<sub>1g</sub> modes of  $Co_3O_4$ .<sup>[3]</sup> In the FTIR spectrum, the peaks at 3435 and 1630 cm<sup>-1</sup> are attributed to the bending and stretching vibration modes of the absorbed water molecules. Two distinct bands at 573 and 665 cm<sup>-1</sup> belong to the typical stretching vibrations of Co–O bonds in

 $Co_3O_4.^{[4]}$ 

4. TG-MS masurement



**Figure S4** Analysis of the outlet gases from the decomposition of by TG-MS (heating rate 5°Cmin<sup>-1</sup> under Ar/O<sub>2</sub> (9:1) atmosphere): H<sub>2</sub>O (blue) and CO<sub>2</sub> (red). The main weight loss around 325 °C is ascribed to the crystal transition of Co(OH)<sub>2</sub>CO<sub>3</sub> to Co<sub>3</sub>O<sub>4</sub> judging from the evolution of CO<sub>2</sub> (M =44) and H<sub>2</sub>O (M =18).

#### 5. Characterization of 3D graphene foam



Figure S5 (A) SEM image and (B) Raman spectrum of 3D-graphene foam

The obtained graphene foam exhibits a continuous and interconnected 3D network with branches of  $30-50 \ \mu\text{m}$  and macropores of  $150-500 \ \mu\text{m}$ , and no evident cracks are observed (Fig. S5A). Closer inspection reveals a smooth surface at the thin graphene skeleton which appears to assume a similar surface topology and

architecture of the nickel substrate utilised during synthesis owing to conformal CVD growth.<sup>[5]</sup> As seen from Fig. S5B, the Raman spectrum reveals two characteristic peaks at ca. 1581 and 2684 cm<sup>-1</sup> which are due to the G and 2D bands respectively. Note that the highly symmetrical 2D band peak indicates that the surface is comprised of mono- to few-layer graphene sheets. Furthermore, the intensity ratio of the G and 2D bands also indicates that the graphene foam is comprised of single and few layer graphene domains.<sup>[6]</sup>



6. Characterization of pure Co<sub>3</sub>O<sub>4</sub> NW arrays on graphene foam

**Figure S6** (A, B) SEM images of free-standing pure  $Co_3O_4$  NWs array on 3D graphene foam (C) TEM image and (D)EDS spectrum of the mesoporous  $Co_3O_4$  NW. (E-F) Elemental mapping of O and Co, respectively.

7. Measurements for cycling stability



**Figure S7** ORR polarization plots of Pt/C (A) and Ni-doped  $Co_3O_4$  NW array after 4000 cycles in  $O_2$ - saturated electrolyte. Potential cycling was carried out between 0.5 and 1.1 V vs. RHE at 50 mVs<sup>-1</sup>.

8. SEM characterization of Ni-doped Co<sub>3</sub>O<sub>4</sub> NW arrays



Figure S8 SEM of Ni-doped Co<sub>3</sub>O<sub>4</sub> NW array initial state (B) after stability testing

9. TEM characterization of commercial Pt/C catalysts



Figure S9 TEM images of commercial Pt/C (A) initial state (B) after stability testing

10. Table S1 Summary of reported half-wave potential  $(E_{1/2})$  and diffusion-limited

Catalyst	Catalyst loading	E <sub>1/2</sub> vs RHE	Diffusion- limited current	Reference
Co <sub>3</sub> O <sub>4</sub> /rGO	0.17 mg/cm <sup>2</sup>	~0.84 V	~5.10 mA cm <sup>-2</sup>	[7]
Fe <sub>3</sub> O <sub>4</sub> /N-GAs	0.01mg	~0.68 V	~4.4 8 mA cm <sup>-2</sup>	[8]
Co <sub>0.5</sub> Mo <sub>0.5</sub> OyN <sub>z</sub> /C(823K)	0.7 mg/cm <sup>2</sup>	~0.80 V	~4.1 0 mA cm <sup>-2</sup>	[9]
PN-ACNT	0.08 mg/cm <sup>2</sup>	~0.80 V	~6.7 8 mA cm <sup>-2</sup>	[10]
Porous N-doped carbon	0.128 mg/cm <sup>2</sup>	~0.83V	~4.54 mA cm <sup>-2</sup>	[11]
Co <sub>3</sub> O <sub>4</sub> nano-rod/carbon	0.20 mg/cm <sup>2</sup>	~0.78 V	$\sim 2.82 \text{ mA cm}^{-2}$	[12]
N-Fe-CNT/CNP	1.0 mg /cm <sup>2</sup>	~0.93 V	> 3.4 mA cm <sup>-2</sup>	[13]
Co <sub>3</sub> O <sub>4</sub> /C NWs Array	$0.2 \text{ mg}/\text{cm}^2$	~0.78 V	unknown	[14]
N-doped Carbon nanosheets	0.6 mg/cm <sup>2</sup>	~0.87 V	~5.8 mA cm <sup>-2</sup>	[15]
Ni-Co <sub>3</sub> O <sub>4</sub> NW array	0.08 mg/cm <sup>2</sup>	~0.86 V	5.76 mA cm <sup>-2</sup>	This work

current at 1600 rpm for non-precious metal electrocatalysts

## 11. Electrochemical impedance spectroscopy (EIS)



Figure S10 EIS in O<sub>2</sub>-saturated electrolyte at 0.765 V.

Fig.S10 presents Nyquist plots measured by electrochemicalimpedance spectroscopy (EIS). Both of the  $Co_3O_4$  NWs electrodes show two semicircles. Usually, the semicircle at the high-frequency zone presents the diffusion of ions into pores, which is a typical EIS characteristic of the embedded electrode, and the low-frequency semicircle which is equal to the charge transfer resistance (Rct) is the characteristic of the charge transfer process.<sup>[16]</sup>The Ni-doped  $Co_3O_4$  NW array showed a lower Rct value than  $Co_3O_4$  NW array.

12. XPS full scan survey for different Co<sub>3</sub>O<sub>4</sub> NWs samples



Figure S11 XPS spectra of (A) pure Co<sub>3</sub>O<sub>4</sub> NWs, (B) Ni-doped Co<sub>3</sub>O<sub>4</sub> NWs

 $(n_{Ni}/n_{Co}=5:95)$ , (C) Ni-doped Co<sub>3</sub>O<sub>4</sub> NWs $(n_{Ni}/n_{Co}=1:9)$ , and (D) Ni-doped Co<sub>3</sub>O<sub>4</sub> NWs $(n_{Ni}/n_{Co}=1:4)$ 

13. XPS spectra for different Co<sub>3</sub>O<sub>4</sub> NWs samples



**Figure S12** XPS spectra of Ni element in (A) Ni-doped  $Co_3O_4$  NWs $(n_{Ni}/n_{Co}=5:95)$ , (B) Ni-doped  $Co_3O_4$  NWs $(n_{Ni}/n_{Co}=1:9)$ , and (C) Ni-doped  $Co_3O_4$   $(n_{Ni}/n_{Co}=1:4)$ NWs. The main peak at *ca.* 855.2 and 872.6 eV together with their satellite are characteristic XPS feature of Ni<sup>2+</sup>.<sup>[17]</sup>



**Figure S13** XPS spectra of O element in (A) pure  $Co_3O_4$  NWs, (B) Ni-doped  $Co_3O_4$  NWs ( $n_{Ni}/n_{Co}=5:95$ ), (C) Ni-doped  $Co_3O_4$  NWs ( $n_{Ni}/n_{Co}=1:9$ ), and (D) Ni-doped  $Co_3O_4$  NWs ( $n_{Ni}/n_{Co}=1:4$ ). The O 1s spectrum is deconvoluted into three main peaks: The peaks at 530.1, 531.8, and 533.0 eV are ascribed to the oxygen atoms of the spinel structure lattice, physisorbed and chemisorbed water at or near the surface, and the hydroxide species, respectively.<sup>[18]</sup> The higher intensity of the 531.8 eV peak in the Ni-doped  $Co_3O_4$  NWs ( $n_{Ni}/n_{Co}=1:9$ ) sample indicates a stronger absorption capacity of hydroxide species.

14. Morphology changes with the ratio of  $n_{Ni}/n_{Co}$  in Co<sub>3</sub>O<sub>4</sub> NW array



Figure S14 SEM images of (A) pure (B)  $n_{Ni}/n_{Co}=5:95$ ) (C)  $n_{Ni}/n_{Co}=1:9$ , and (D)  $n_{Ni}/n_{Co}=1:4$  in Co<sub>3</sub>O<sub>4</sub> NW array,

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