

Supporting Information for

Hierarchical Ni-Co-O@Ni-Co-S Nanoarray as Advanced Oxygen Evolution Reaction Electrode

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1. Experimental Section:

The Ni-doped $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire array on Ni foam was synthesized by a simple hydrothermal method. In a typical procedure, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol), NH_4F (8 mmol) and $\text{CO}(\text{NH}_2)_2$ (10 mmol) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Nickel foam (about 3 cm × 2 cm) was carefully cleaned with concentrated HCl solution (37 wt%) in an ultrasound bath for several minutes in order to remove the surface NiO layer, and then deionized water and absolute ethanol were used for 5 min each to ensure the surface of the Ni foam was well cleaned. The aqueous solution and the Ni foam were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 120 °C for 12 h, and then allowed to cool to room temperature naturally. The red thin film on the metal substrate was obtained and subsequently rinsed with distilled water, ethanol each for 5 minutes with the assistance of ultrasonication, and dried at 80 °C for 6 h. The hierarchical Ni-Co-O@Ni-Co-S nanoarray were obtained by immersing the as-prepared Ni-doped $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire array in 1 mol L⁻¹ Na_2S solution with vigorous agitation overnight. And then the samples were rinsed several times by distilled water, dried at 80 °C for 6 h, and further annealed at 350 °C for 3 h to completely convert to Ni-Co-O@Ni-Co-S hierarchical structure.

X-ray powder diffraction patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10 °/min in the range from 10 to 90°. XPS spectrums were carried out by using a model of ESCALAB 250. The size and the morphology of the samples were characterized using a field-emission SEM (JEOL JSM6335) operating at 20 kV and a TEM system (H800) operating at 200 kV. The Energy Dispersive Spectrometer (EDS) was used to examine the composition of the samples scratched from substrate.

The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.) Prior to

the test measurements, H₂ was bubbled through the electrolyte solution to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H⁺/H₂ redox couple. Linear sweep voltammetry with scan rates of 1 mV s⁻¹ were conducted in 0.1 M and 1 M KOH solution. Pt was used as the counter electrode. AC impedance measurements were carried out in the same configuration at open circuit voltage from 10⁵-0.1 Hz with an AC voltage of 5 mV to measure the system resistance. In all measurements, we used saturated calomel electrode (SCE) as the reference. It was calibrated with respect to reversible hydrogen electrode (RHE) by using Pt electrode as standard electrode. 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 0.1 M KOH, $E(\text{RHE}) = E(\text{SCE}) + 1.00 \text{ V}$

In 1 M KOH, $E(\text{RHE}) = E(\text{SCE}) + 1.06 \text{ V}$

2. Supplementary Figures

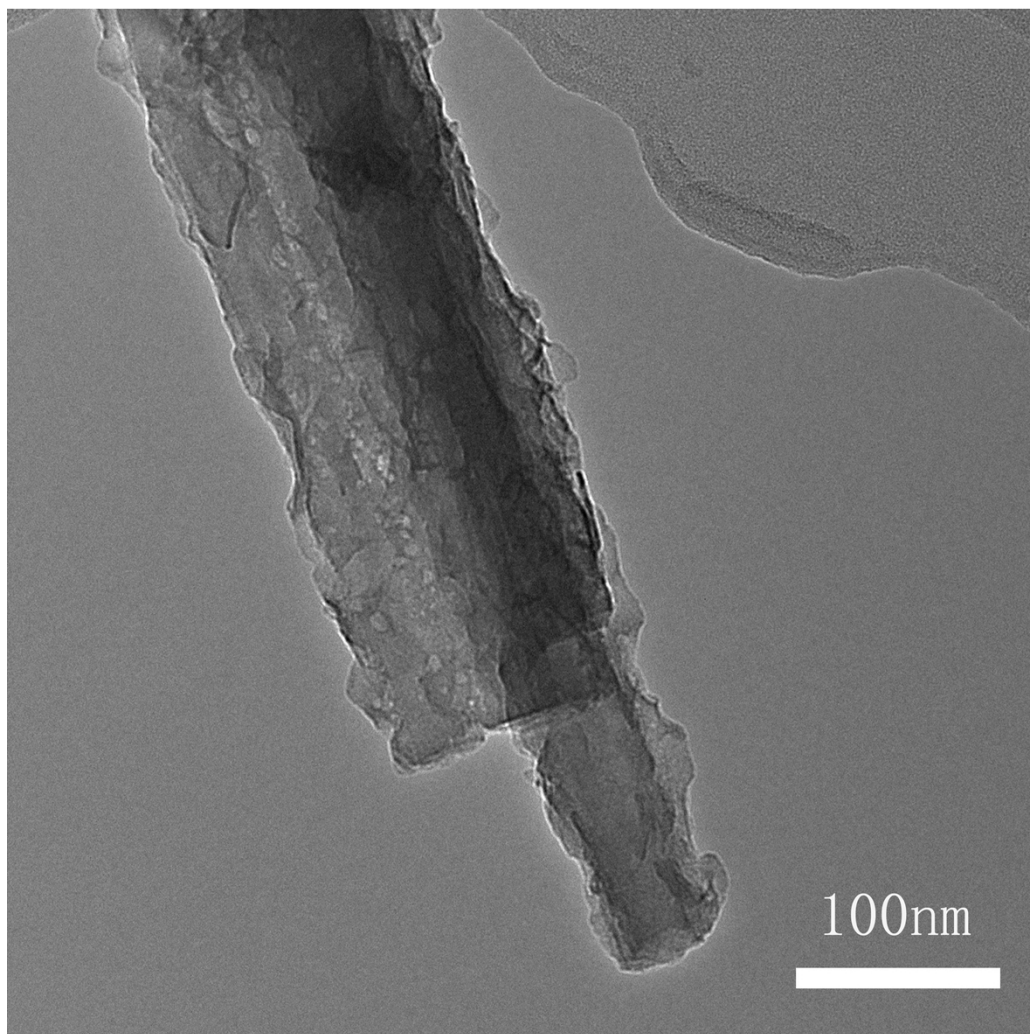


Figure S1. TEM image of an individual hierarchical Ni-Co-O@Ni-Co-S nanostructure.

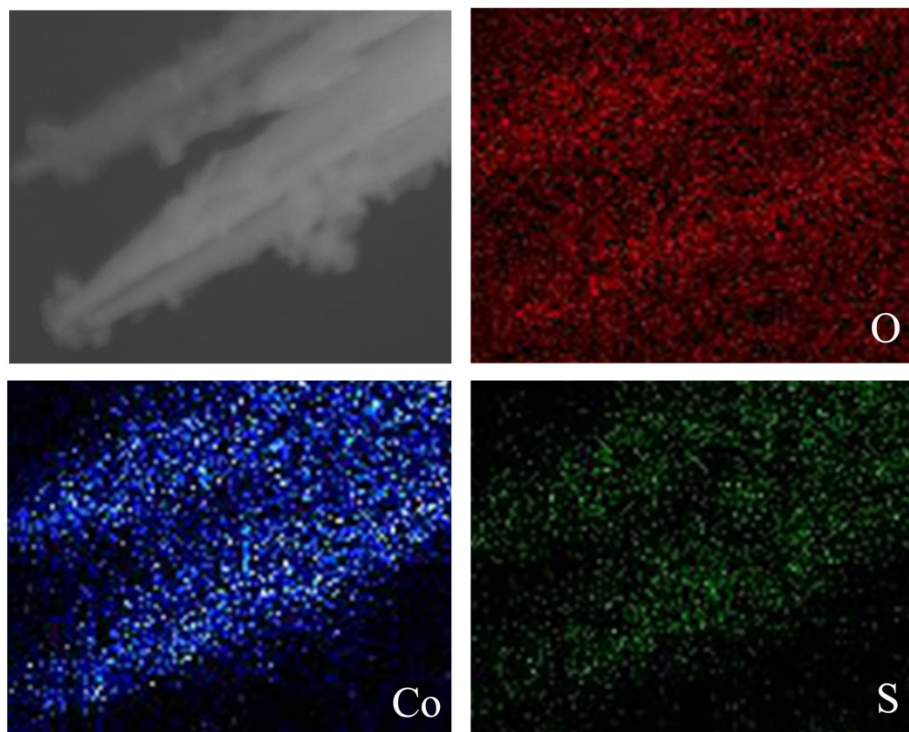


Figure S2. EDS mapping results of hierarchical Ni-Co-O@Ni-Co-S nanostructure.

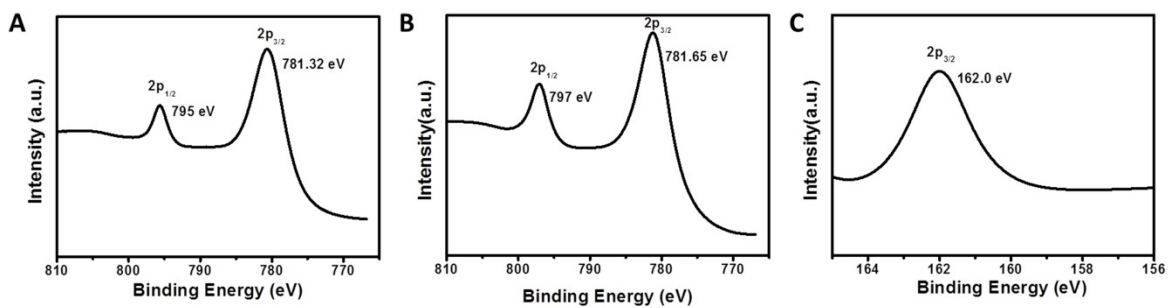


Figure S3. (A), the binding energy of Co 2p in CoO NWA; (B) and (C), the binding energy of Co 2p and S 2p in hierarchical Ni-Co-O@Ni-Co-S NA.

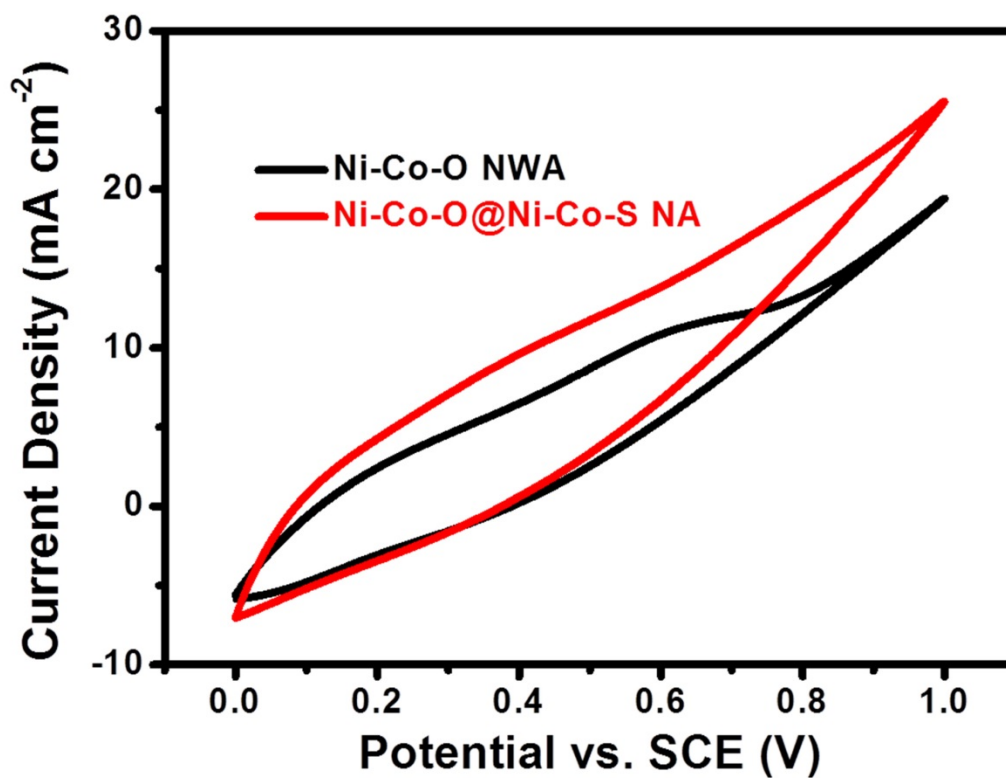


Figure S4. Cyclic voltammetry curves of Ni-Co-O NWA and hierarchical Ni-Co-O@Ni-Co-S NA at a scan rate of 5 mV s⁻¹.

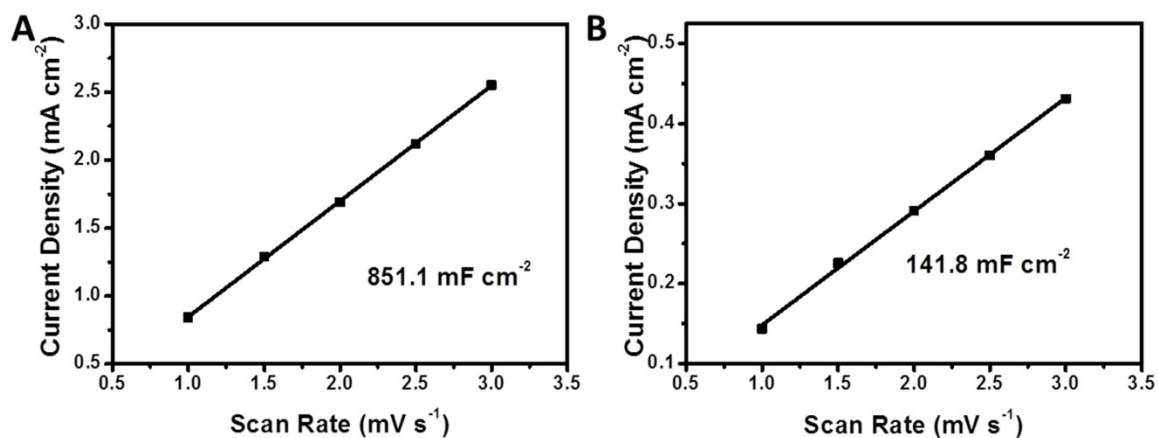


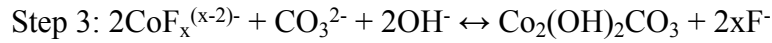
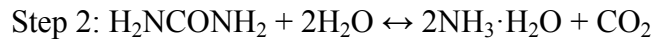
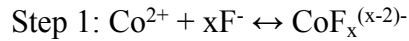
Figure S5. Plots of current densities versus scan rates of hierarchical Ni-Co-O@Ni-Co-S NA (A) and Ni-Co-O NWA (B) measured in the range without Faradic reaction. The double layer capacitances of both samples are calculated to be 851.1 mF cm⁻² and 141.8 mF cm⁻², respectively.

Table S1. EDS data of Ni/Co ratios in Ni-Co-O nanowires and hierarchical Ni-Co-O@Ni-Co-S nanostructures.

Samples	Ni (atomic %)	Co (atomic %)	Ni:Co
Ni-Co-O nanowires	7.14	30.07	1:4.21
Ni-Co-O@Ni-Co-S	6.91	29.44	1:4.26

Discussions of the growth of Ni-doped $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires.

The mechanism of the growth process can be explained by the following steps:



The increased concentration of anions (CO_3^{2-} , OH^-) in the as-prepared reactant solution would lead to the formation of a nucleus, which was prone to form on the substrate surface (i.e. nickel foam in this case) rather than in aqueous solution. Afterwards, the following growth process resulted in the formation of nanowire arrays. However, as the fresh growth solution containing $\text{Co}(\text{NO}_3)_2$ and urea showed a pH value of ~ 6 , the a small amount of metallic nickel would be dissolved in the solution. The subsequent hydrothermal process precipitated both the dissolved Ni and Co, resulting in the formation of Ni doped $\text{Co}_2(\text{OH})_2\text{CO}_3$.