

## Electronic Supplementary Information

### Experimental section

#### Materials

NF was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd. Cobaltous chloride hexahydrate,  $\text{NaBH}_4$  was bought from Tianjing Fuchen Chemical Reagent Factory. Nafion(5wt%) and Se powder were purchased from Sigma–Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and ethanol were purchased from Aladdin Ltd. (Shanghai, China). All the reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

#### Preparation of NiSe NWs/NF:

The NiSe NWs/NF was prepared according to previous reported method.<sup>1</sup> A piece of NF ( $1 \times 3 \text{ cm}^2$ ) was washed with HCl, ethanol and deionized water for several times to ensure the surface of the NF was well cleaned before use. For the preparation of NaHSe solution, Se powder (0.059 g) was added into deionized water (3 mL) containing  $\text{NaBH}_4$  (0.065 g). After gentle stirring for several minutes, a clear NaHSe solution was obtained. The freshly prepared NaHSe solution was added into ethanol (17 mL) under  $\text{N}_2$  flow. Then the solution was transferred into 25 mL Teflon-lined stainless steel autoclave with a piece of pretreated NF maintained at  $140 \text{ }^\circ\text{C}$  for 12 h in an electric oven. After the autoclave cooled down slowly at room temperature, the sample was collected and washed with water and ethanol for several times and then dried at  $60 \text{ }^\circ\text{C}$  for 8 h.

#### Preparation of Co-doped NiSe<sub>2</sub> NWs/NF:

For the preparation of the Co-doped NiSe<sub>2</sub> NWs/NF, 0.75 mmol cobaltous chloride hexahydrate (178.45 mg) was dissolved in ethanol (20 mL). After that, the NiSe NWs/NF as precursor template was put into the suspension carefully and then the solution was transferred into Teflon-lined stainless steel autoclave maintained at  $140 \text{ }^\circ\text{C}$  for 12 h in an electric oven. After the autoclave cooled down slowly at room temperature, the final products were washed with water and ethanol for several times and then was dried under vacuum dried at  $60 \text{ }^\circ\text{C}$  for 8 h. The real contents of Co of the Co-doped NiSe NWs/NF were measured by ICP-AES and determined to be 2.74 wt%.

A series of parallel experiments with different amounts of Co was conducted to investigate the displacement process. The samples of Co-doped NiSe NWs/NF made by replacing Ni cation using different amounts of cobaltous chloride hexahydrate (0.25, 0.5, 1.0, 1.25 mmol) were labeled as samples S1, S2, S3, S4. The real contents of Co were measured by ICP-AES and determined to be 0.62, 1.32, 3.01, and 4.07 wt%, respectively.

#### Preparation of RuO<sub>2</sub>:

RuO<sub>2</sub> catalyst was prepared according to reported method.<sup>2</sup> For the preparation of the RuO<sub>2</sub>, 0.01 mol of RuCl<sub>3</sub>•3H<sub>2</sub>O was dissolved in 100 mL water and stirred for 15 min at 100°C. After that, 1mL KOH solution (1.0 M) was added to the solution and stirring for 45 min at 100°C. The solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with water and then dried for 5 h at 80°C. The dry product was calcined in air at 300°C for 3 h to obtain RuO<sub>2</sub>.

## Characterization

The content of cobalt element in the samples was measured by using an ICP-AES (Optima 7300 DV). The samples were characterized by different analytic techniques. Scanning electron microscope (SEM) was operated on a field emission scanning electron microanalyzer (Zeiss Supra 40) at the acceleration voltage of 5 kV. Transmission electron microscope (TEM) images were obtained on a Hitachi H7650 transmission electron microscope with CCD imaging system on the acceleration voltage of 120 kV. High resolution TEM (HRTEM), selected area electron diffraction (SAED), the Energy disperse X-ray spectrum (EDS), and elemental mapping, were conducted on a JEM-ARM 200F Atomic Resolution Analytical Microscope on an acceleration voltage of 200 kV. X-Ray powder diffraction patterns (XRD) of the products were carried out on a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatism Cu-Kα radiation ( λ = 1.54178 Å ). The BET surface area was measured on a Quantachrome NOVA 1000 system at liquid N<sub>2</sub> temperature.

## Electrochemical measurements

Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using the Co-doped NiSe NWs/NFs as the working electrode, a graphite plate as the counter electrode and an Ag/AgCl electrode as the reference electrode. Electrochemical characterization of the Co-doped NiSe NWs/NF catalysts was carried out in KOH electrolytes. To prepare RuO<sub>2</sub> loaded electrodes, 20 mg RuO<sub>2</sub> and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30 min sonication to form an ink finally. Then 240 μL catalyst ink was loaded on a Ni foam with a catalyst loading of 4.8 mg cm<sup>-2</sup>. All potentials were measured and calibrated to RHE using the following equation: E (RHE) = E (Ag/AgCl) + 0.197 V + 0.059\*pH. All electrolytes were saturated by oxygen bubbles before and during the experiments. The long-term durability test was performed using chronopotentiometric measurements. Electrochemical data were corrected for the uncompensated series resistance R<sub>s</sub>, which was determined through fitting of AC impedance data to a modified Randles circuit. The value of R<sub>s</sub> was 1.8 Ω in 1.0 M KOH. The potential was determined by

$$E_{\text{corrected}} = E_{\text{uncorrected}} - iR_s$$

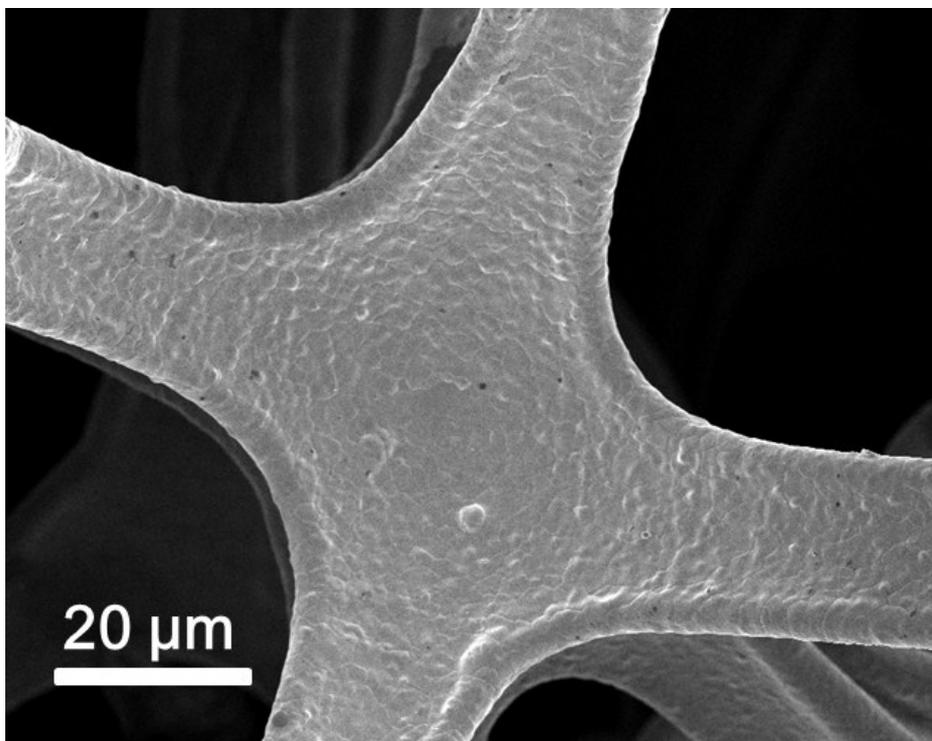


Fig.S1 SEM images the surface of the NF

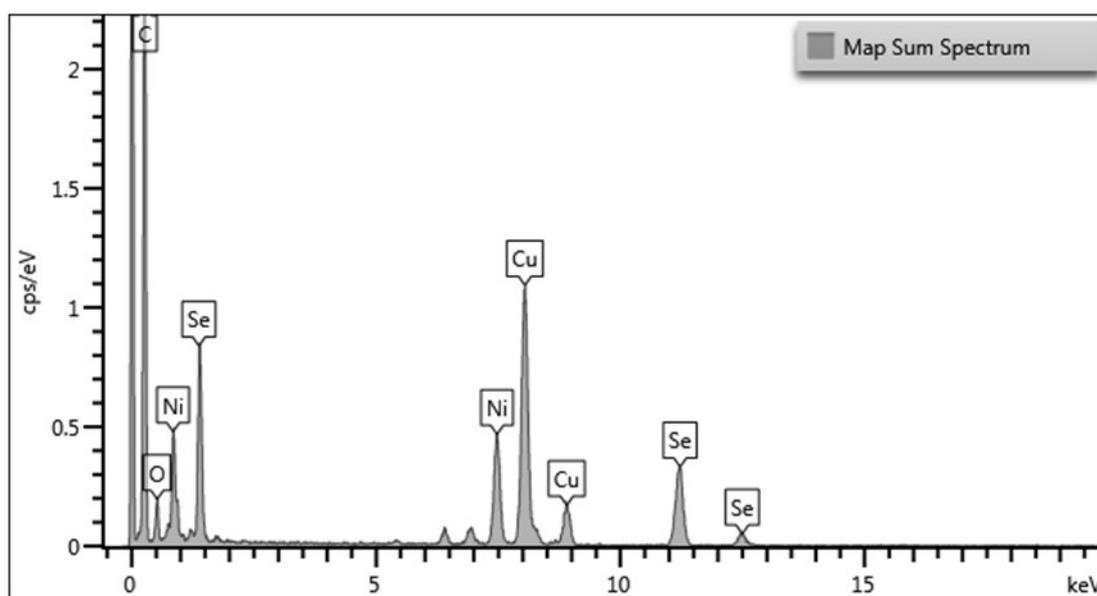


Fig.S2.EDX spectrum of the NiSe /NF, which was composed of the elements Ni and Se, the presence of C and Cu peaks were emanated from the TEM grid.

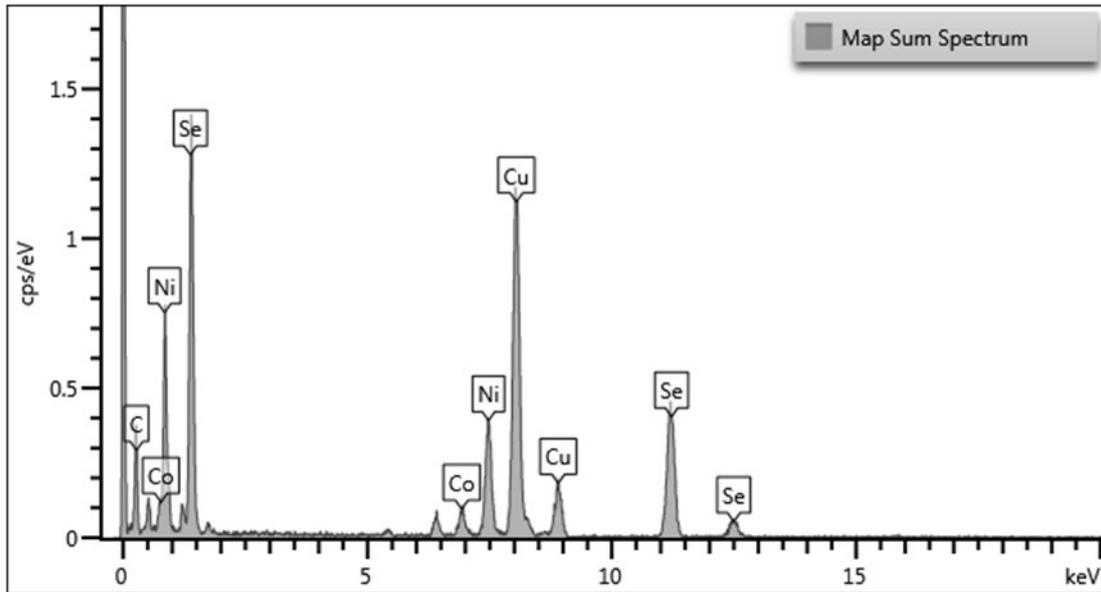


Fig.S3. EDX spectrum of the Co-doped NiSe<sub>2</sub> NWs/NF, which was composed of the elements Ni, Co, and Se, the presence of C and Cu peaks were emanated from the TEM grid.

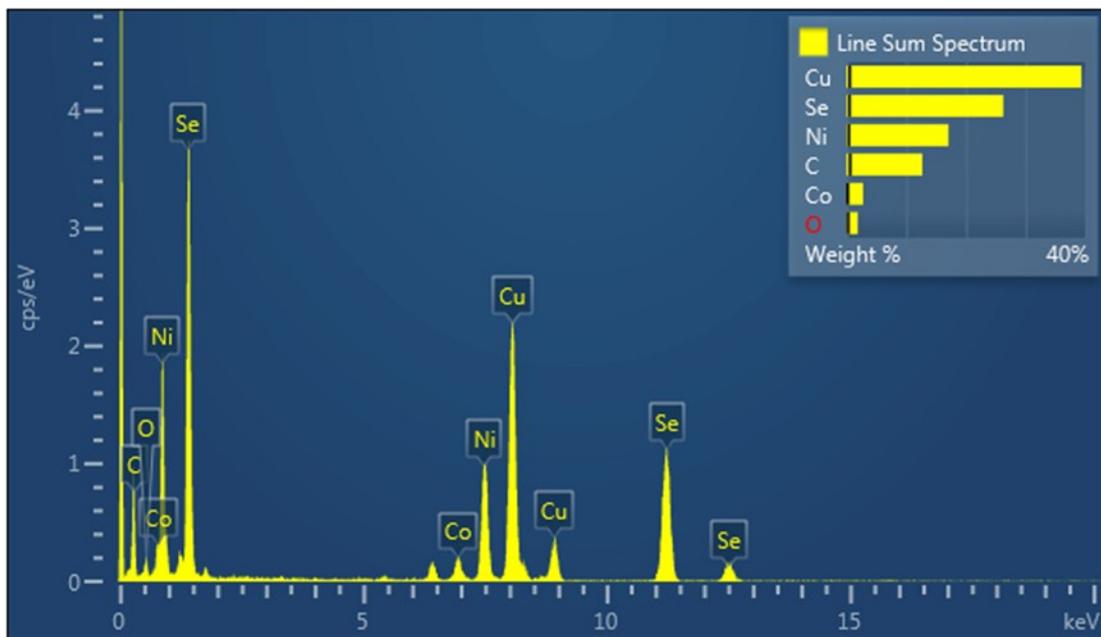


Fig.S4. Point-scan EDX spectrum of the Co-doped NiSe<sub>2</sub> NW, the presence of C and Cu peaks were emanated from the TEM grid.

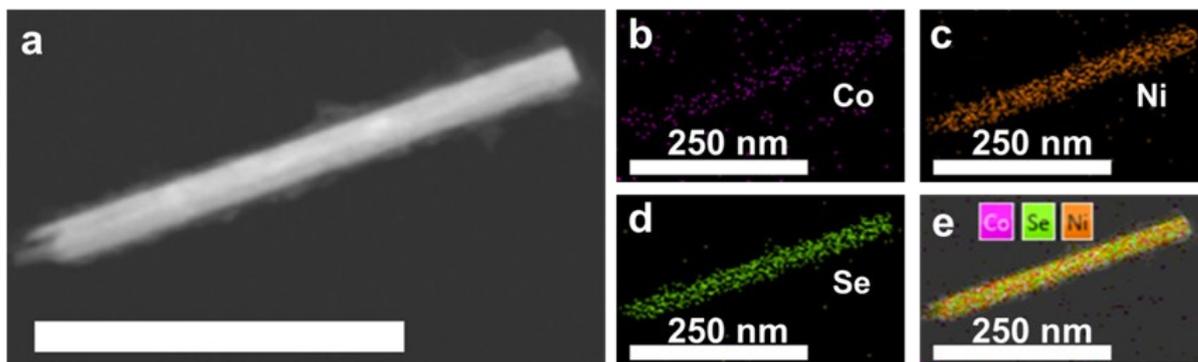


Fig.S5. EDX mapping of sample S2: (a) bright field image, (b) Co element mapping, (c) Ni element mapping, and (d) Se element mapping.

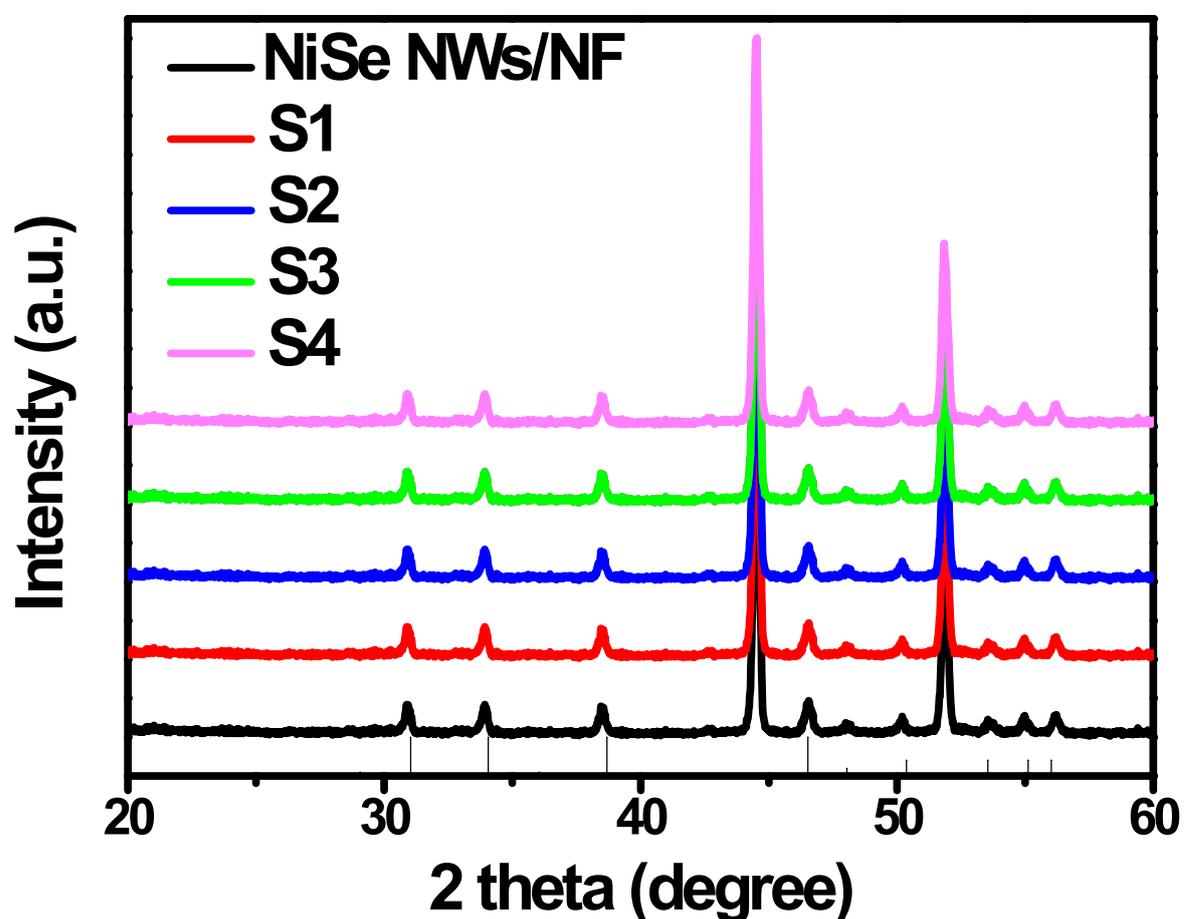


Fig.S6. XRD patterns of sample 1,2,3,4 and the NiSe NWs/NF

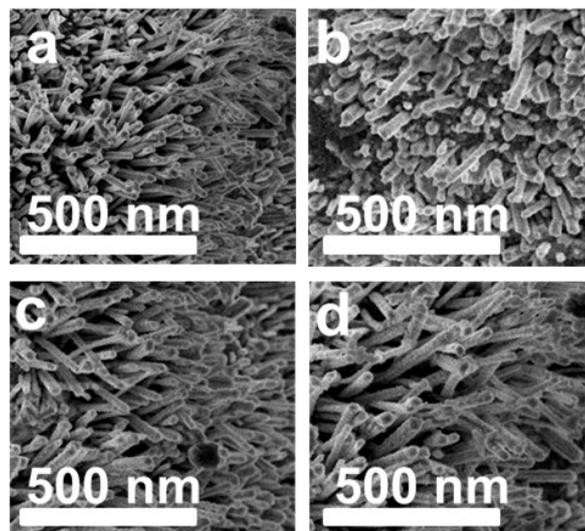


Fig.S7 (a) SEM image of sample 1.(b) SEM image of sample 2.(c) SEM image of sample 3.(d) SEM image of sample 4.

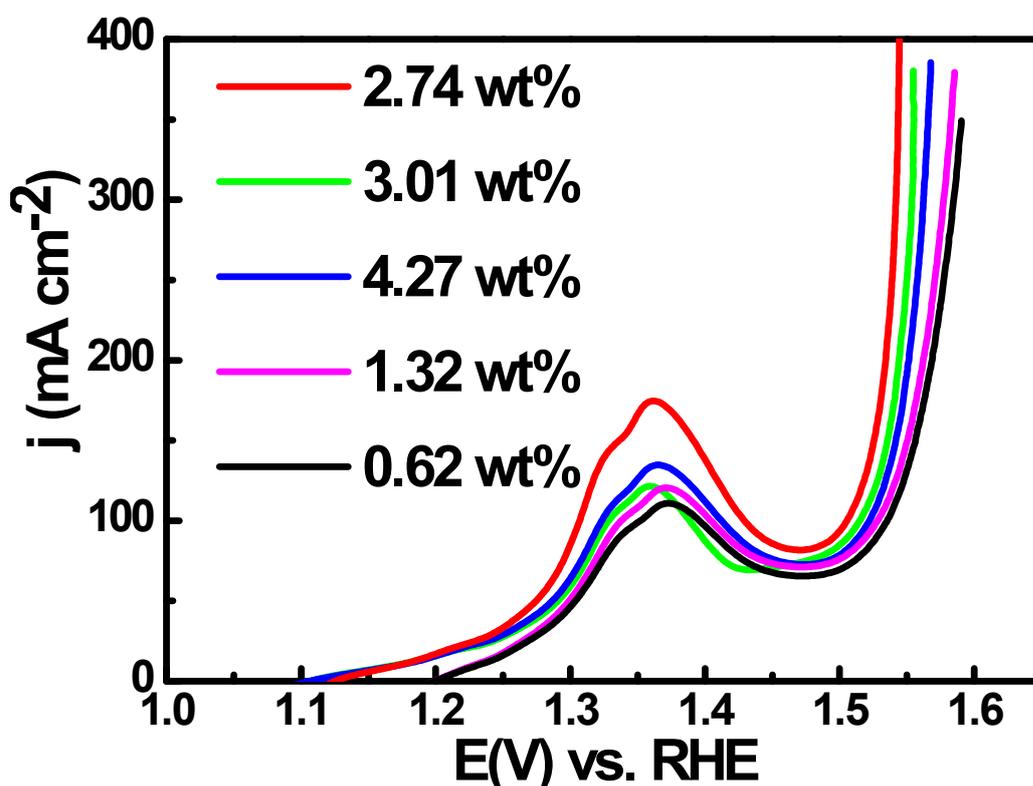


Fig.S8 IR-corrected polarization curves for OER for different contents of Co of the Co-doped NiSe NWs/NFelectrodes, suggest that the amount of 2.74 wt% is the optimal in this system.

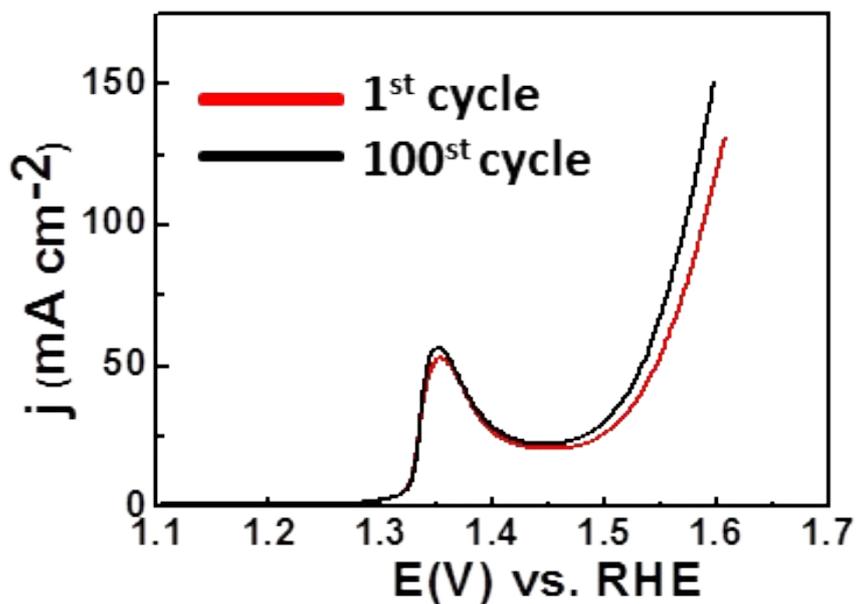


Fig. S9 LSV Polarization curves at a scan rate of  $2 \text{ mV s}^{-1}$  for NiSe NWs /NF before and after 100 CV cycles between +1.1 and +1.7 V.

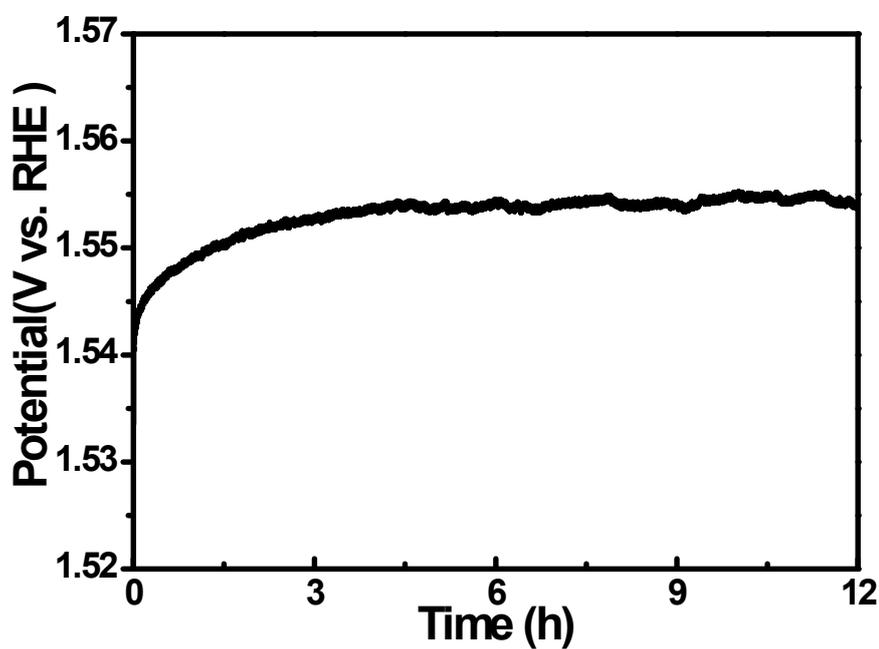


Fig. S10 Chronopotentiometric curve of NiSe NWs/NF with constant current density of  $100 \text{ mA cm}^{-1}$ . All experiments were carried out in  $1.0 \text{ m KOH}$ .

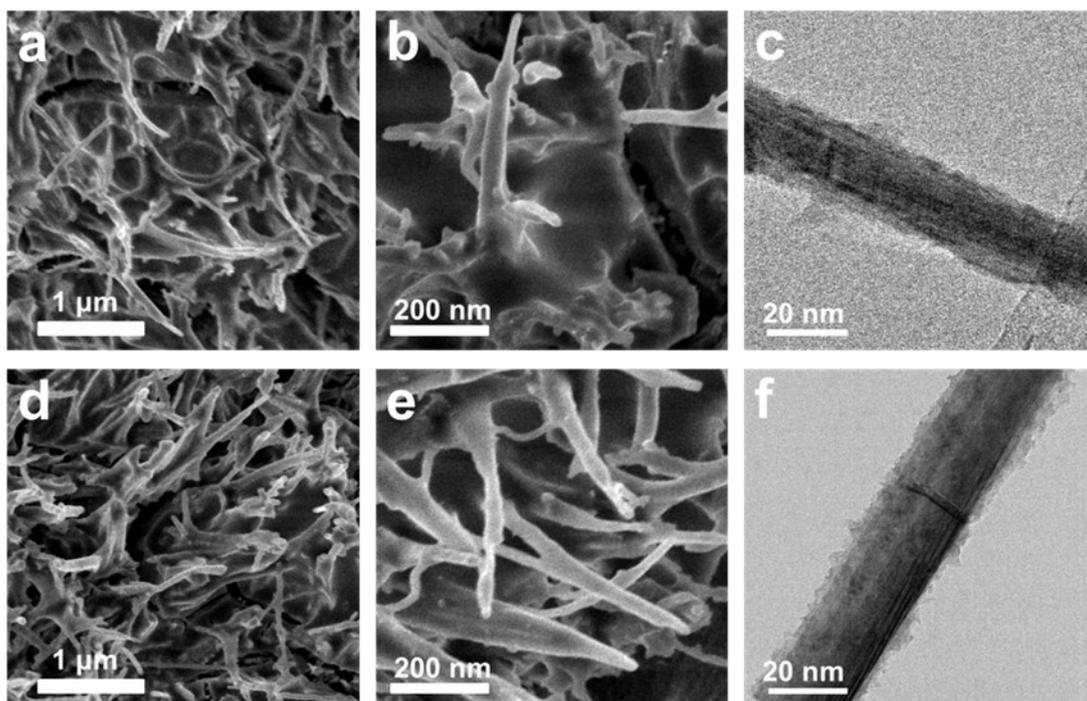


Fig. S11. (a and b) SEM images (c) TEM image of a NiSe NW after the long-term electrochemical stability. (e and f) SEM images, (g) TEM image of a post-Co-doped NiSe NWs/NF after the long-term electrochemical stability test.

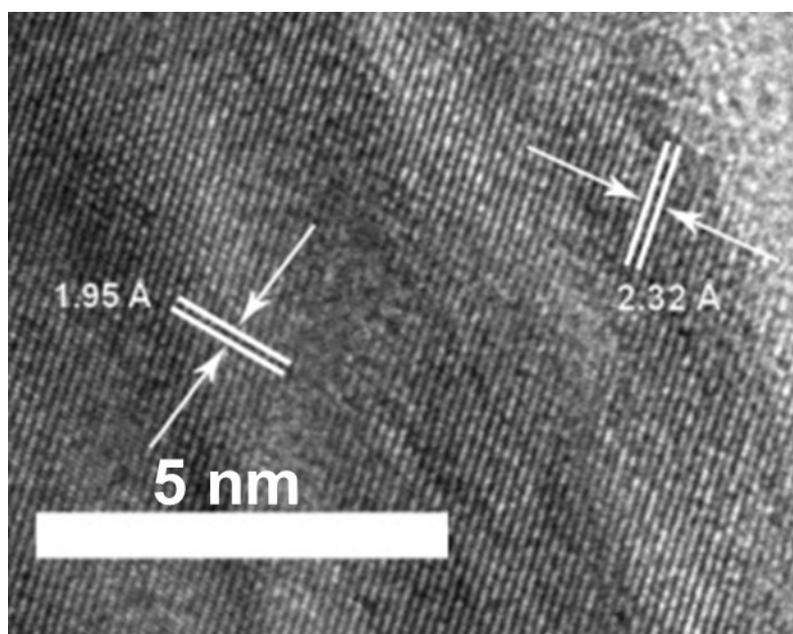


Fig. S12. HRTEM image taken from Co-doped NiSe NWs/NF after OER electrolysis in 1.0 M KOH.

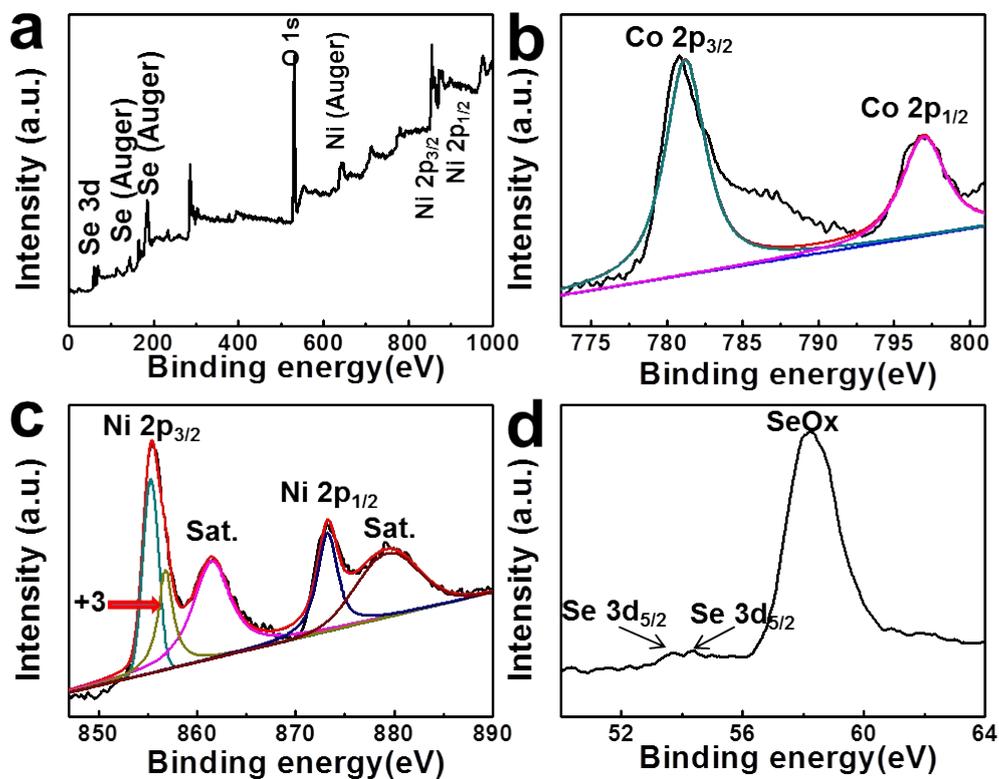


Fig. S13 (a) XPS survey spectrum for Co-doped NiSe NWs/NF after OER electrolysis. XPS spectra for the post-OER Co-doped NiSe NWs/NF in the (b) Co 2p, (c) Ni 2p and (d) Se 3d regions

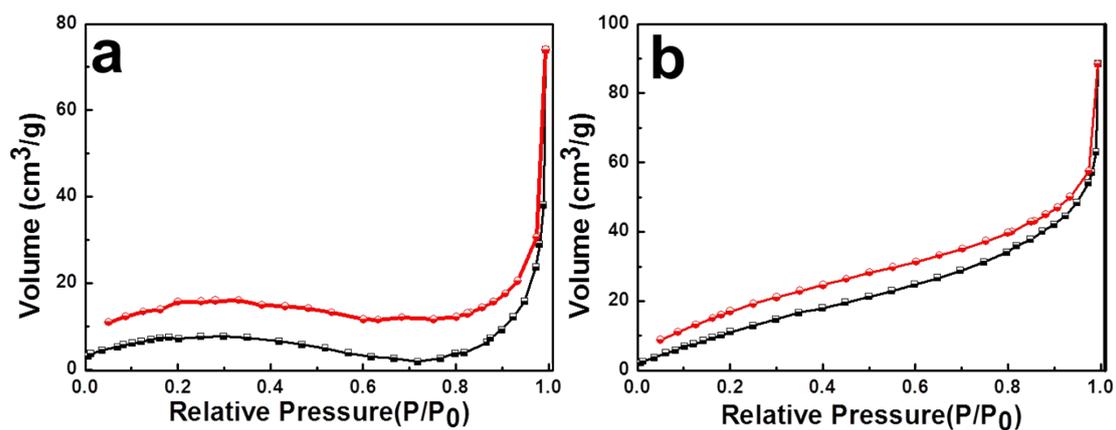


Fig.S14 Nitrogen adsorption/desorption isotherm of (a) NiSe NWs/NF and (b) Co-doped NiSe NWs/NF.

## Reference

1. Tang, C.; Cheng, N.; Pu, Z.; Xing, W.; Sun, X. P, *Angew. Chem., Int. Ed.*, 2015, 54, 9351–9355.
2. J. C. Cruz, V. Baglio, S. Siracusano, V. Antonucci, A. S. Aric, R. Ornelas, L. Ortiz-Frade, G. Osorio-Monreal, S. M. Durn-Torres and L. G. Arriaga, *Int. J. Electrochem.Sci.* 2011, 6, 6607.