Electronic Supplementary Information

In situ Synthesis of NiSe@CoP Core-Shell Nanowires Array on Nickel Foam as a Highly Efficient and Robust Electrode for Electrochemical Hydrogen Generation in Both Alkaline and Acidic Media

Yuan-Zi Xu[a]*, Cheng-Zong Yuan[b], Zi-wei Liu[a] and Xue-Ping Chen[a]*

[a.] *Department of Chemistry, University of Science and Technology of China. Hefei, Anhui, 230026, P. R. China . E-mail: chenxp08@ustc.edu.cn; xuyuanzi@mail.ustc.edu.cn*

[b.] *Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China. Hefei, Anhui, 230026, P. R. China*

Experimental section

Materials

All reagents were of analytical grade and used without further purification. NF was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd. $NaBH_4$, potassium hydroxide (KOH, 85.0%), aqueous cobalt nitrate ($Co(NO_3)_2$) and selenium powder (Se) were bought from Tianjin Fuchen Chemical Reagent Factory. Hydrochloric acid (HCl), sodium hypophosphite (NaH_2PO_2, 99.0%), sulfuric acid (H_2SO_4, 98.0%), ethanol and Nafion solution (5%) were purchased from Aladdin Ltd. (Shanghai, China). 20 wt% Pt/C was purchased from Alfa Aesar. 0.5 M H2SO 4 solution was prepared by diluting the concentrated sulfuric acid. 1 M KOH solution was prepared by potassium hydroxide and deionized water and the final pH was ~14. The water used throughout all experiments was purified through a Millipore system (resistivity: 18 MΩ·cm).

Preparation of NiSe/NF:

A piece of NF (1 × 3 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 (0.055 g) was added into deionized water (3 mL) containing $NaBH_4$ (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 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 °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 °C for 8 h.

Preparation of NiSe@CoOOHNWs/NF:

For the preparation of the NiSe@CoOOH NWs/NF, 0.45 mmol cobalt nitrate hexahydrate (95 mg) was dissolved in ethanol (20mL). 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 °C for 12 h in an electric oven. After the autoclave cooled down slowly at room temperature, the final product was washed with water and ethanol for several times and then was dried under vacuum dried at 60 °C for 8 h.

Preparation of NiSe@CoP NWs/NF:

The NiSe@CoOOH NWs/NF and NaH_2PO_2 (150 mg) were put at two separate positions in a porcelain boat and charged into a tube furnace with NaH_2PO_2 at the upstream side of the furnace. The furnace was allowed to heat to 300 °C for 1 h with a heating speed of 2 °C min^{-1}.

Characterization

X-Ray powder diffraction patterns (XRD) of the products were characterized using a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ=1.54178Å). Scanning electron microscope (SEM) was operated on a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5kV). The transmission electron microscopy (TEM) images were acquired on a JEOL-2100F with an electron acceleration energy of 200kV. High-resolution transmission electron microscopy (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and corresponding energy dispersive spectroscopic EDS) mapping analyses were performed on a on a JEM-ARM 200F Atomic Resolution Analytical Microscope on an acceleration voltage of 200 kV. The chemical composition of the samples was analyzed by Raman spectroscopy performed with a Renishaw InVia confocal microprobe Raman system using a laser with an excitation wavelength of 532 nm. X-ray photoelectron spectra (XPS) were acquired on a Thermo ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-Kα X-ray as the excitation source.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a typical three-electrode setup with a Pt counter electrode and Ag/AgCl reference electrodes. Electrochemical characterization of the catalysts was carried out in KOH and H_2SO_4 electrolytes, respectively. LSV measurements were conducted with a scan rate of 2mV s^{-1}. All of the potentials in the LSV polarization curves were presented without iR compensation. To prepare the Pt/C loaded electrode, Pt/C (20 mg) and Nafion solution (10 mL 5wt%) were dispersed in water/ethanol solvent mixture (1 mL, 1:1 v/v) by 30 min sonication to form an ink. Then catalyst ink (140 mL) was loaded on a NF with a catalyst loading of 2.8 mg cm^{-2}. Electrochemical impedance spectroscopy (EIS) was conducted at various overpotentials with a 10 mV AC potential from 100 000 to 0.01 Hz. Accelerated degradation measurements were conducted for 1000 cyclic voltammetry (CV) cycles in 1 M KOH solution at a scan rate of 50 mV s^{-1} and linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 2 mV s^{-1}. The long-term durability test was performed using chronopotentiometric measurements. All electrolytes were saturated by N_2 bubbles before and during the experiments. All potentials reported in this paper were converted from vs. Ag/AgCl to vs. RHE by adding a value of 0.197 V + 0.059*pH. Only the Tafel data in this paper were iR corrected.

Supplementary figures

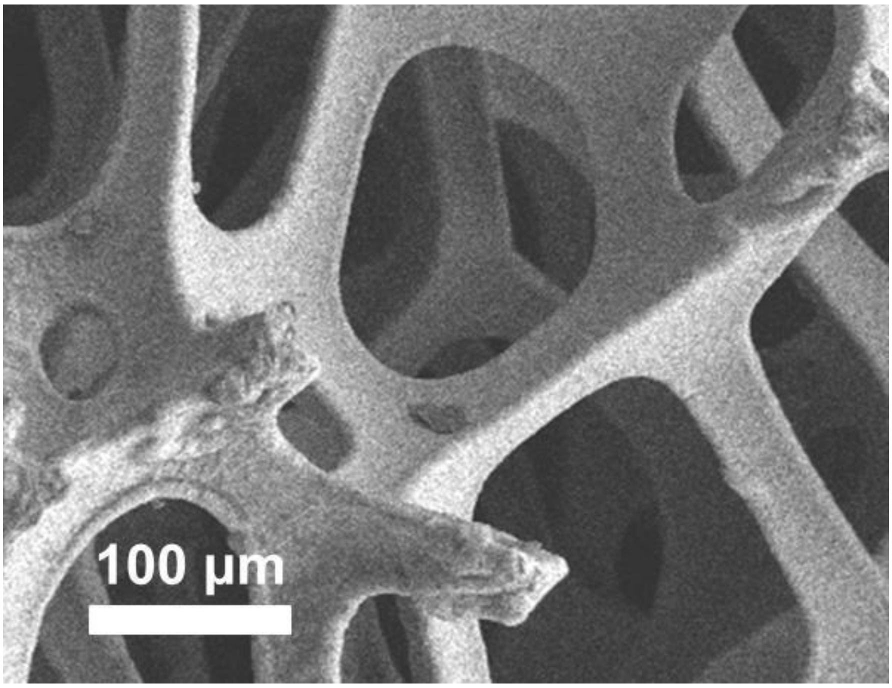

Figure S1. SEM images the surface of the NF.

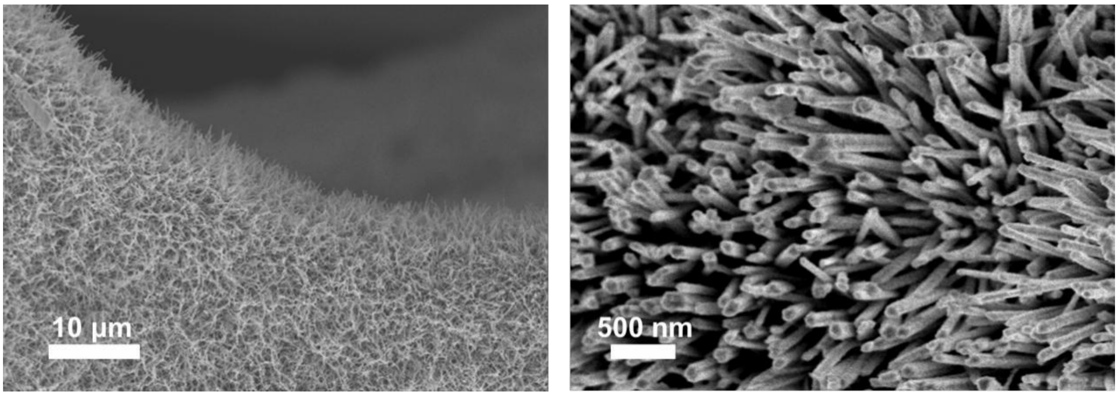

Figure S2. SEM images the surface of the NiSe NWs/NF.

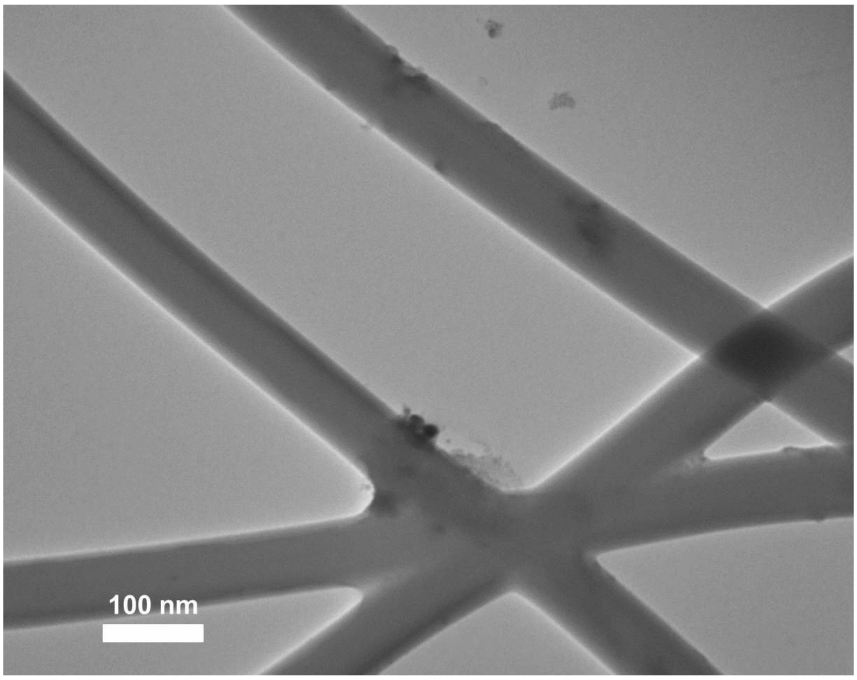

Figure S3. SEM images the surface of the NF.

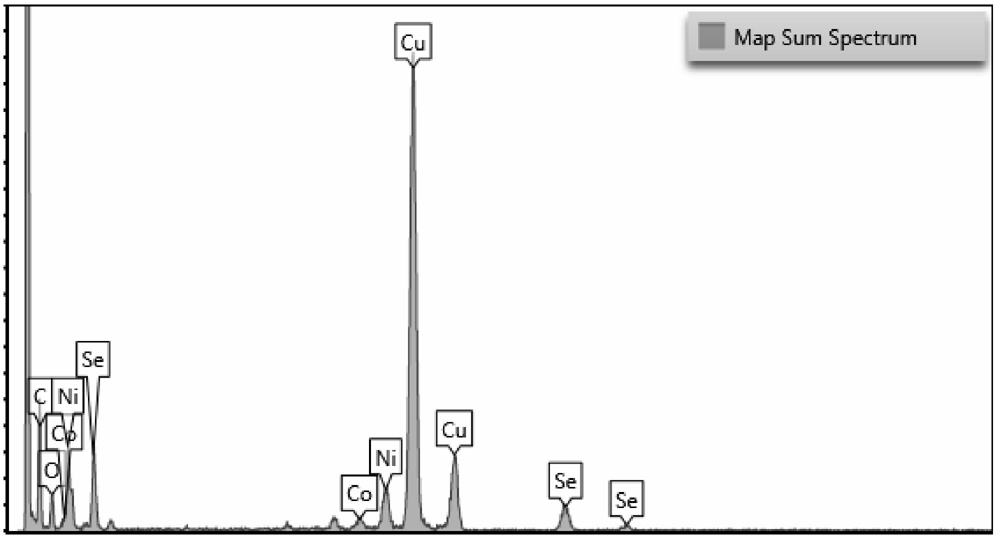

Figure S4. EDX spectrum of the NiSe /NF, which was composed of the elements Ni and Se, the presence of C and O peaks were emanated from the TEM grid.

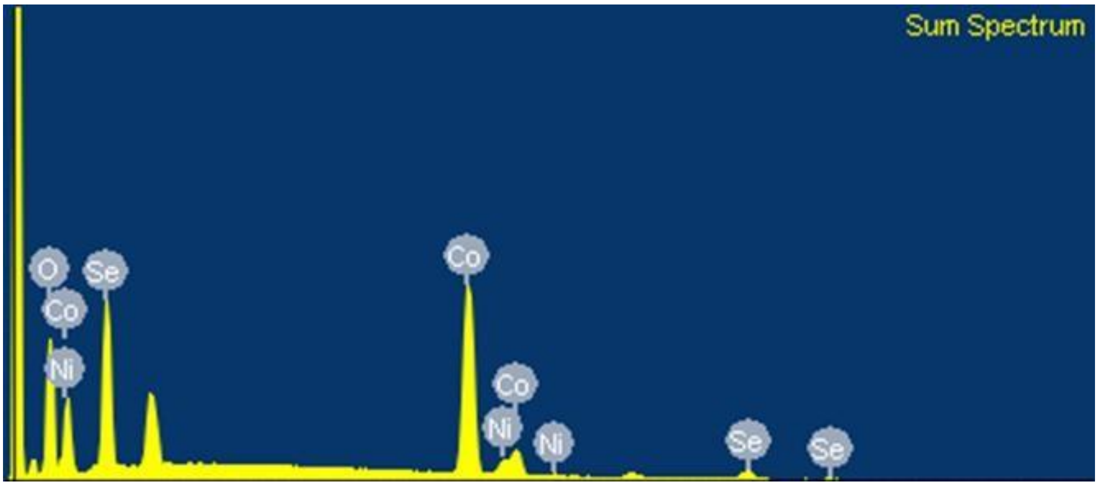

Figure S5. EDX spectrum of the NiSe@CoOOH/NF, which was composed of the elements Ni , Se , Co and O.

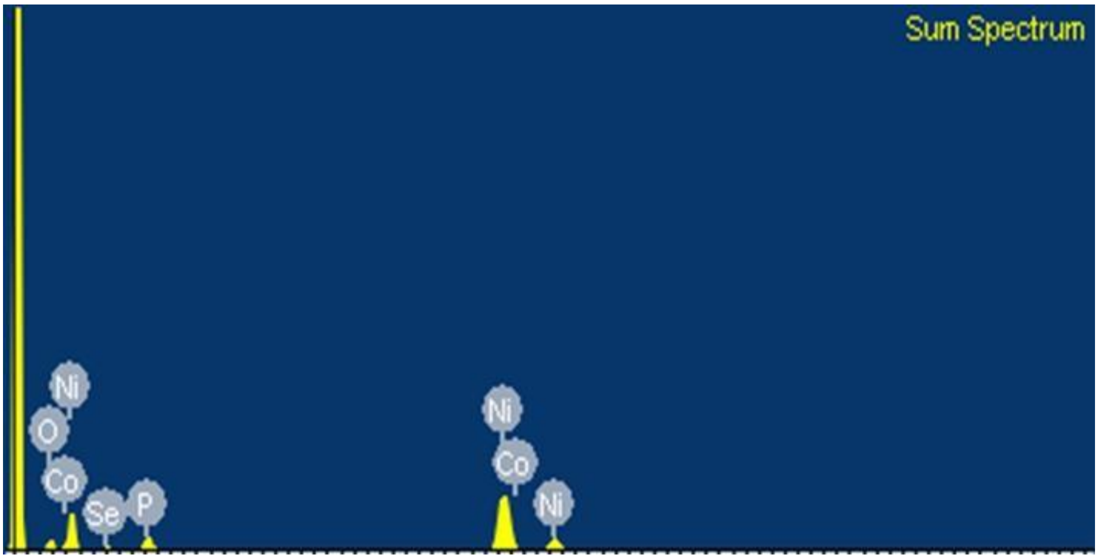

Figure S6. EDX spectrum of the NiSe@CoP NWs/NF, which was composed of the elements Ni, Se, Co and P the presence of O peak were emanated from the TEM grid.

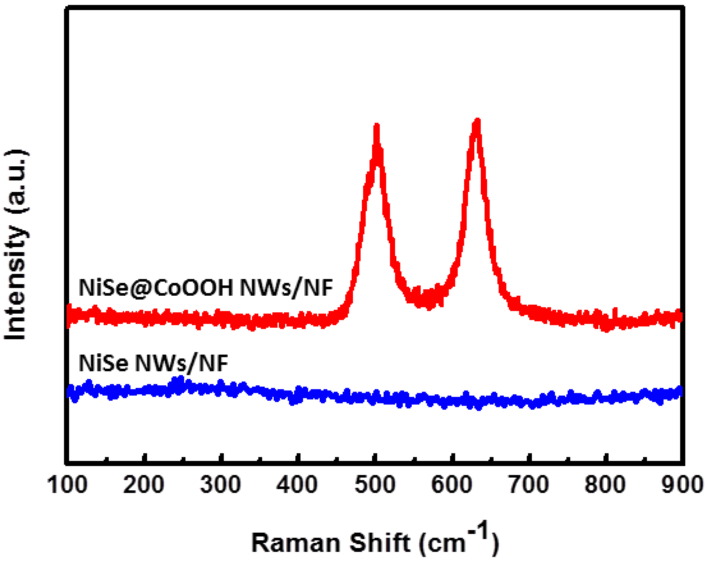

Figure S7. Raman spectra of the NiSe NWs/NF and NiSe@CoOOH NWs/NF.

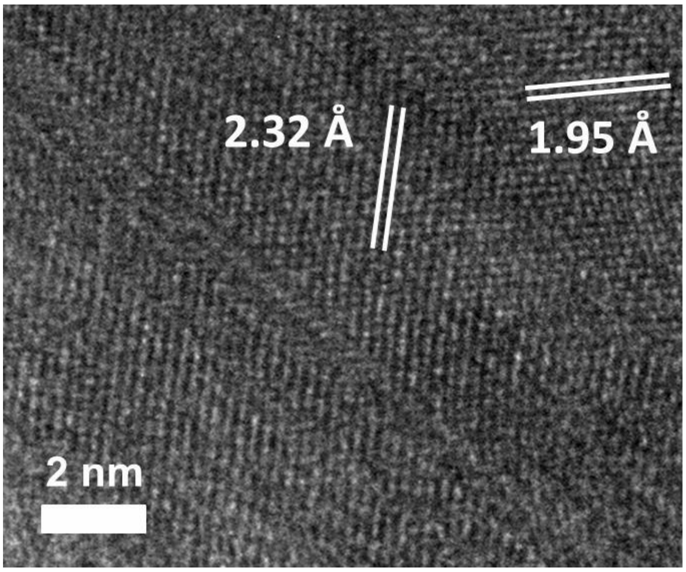

Figure S8. HRTEM image for NiSe@CoP NWs/NF.

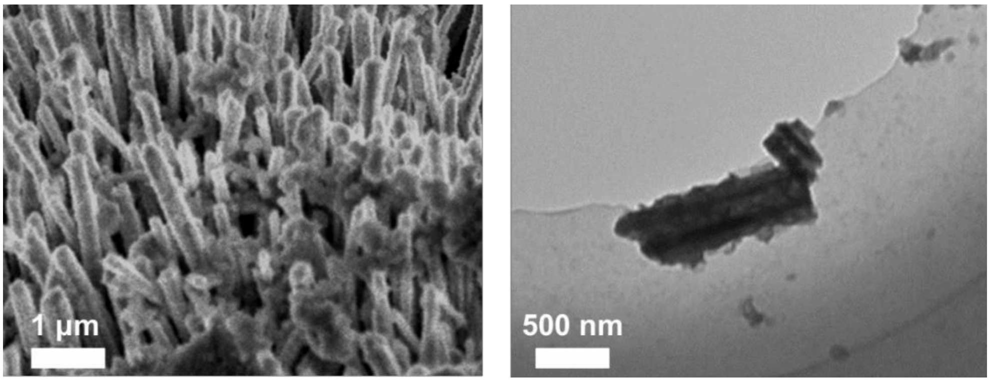

Figure S9. SEM image TEM image of NiSe@CoP $\mathrm{NW_S}$/NF after the long-term electrochemical stability in 1.0 M KOH solutions.

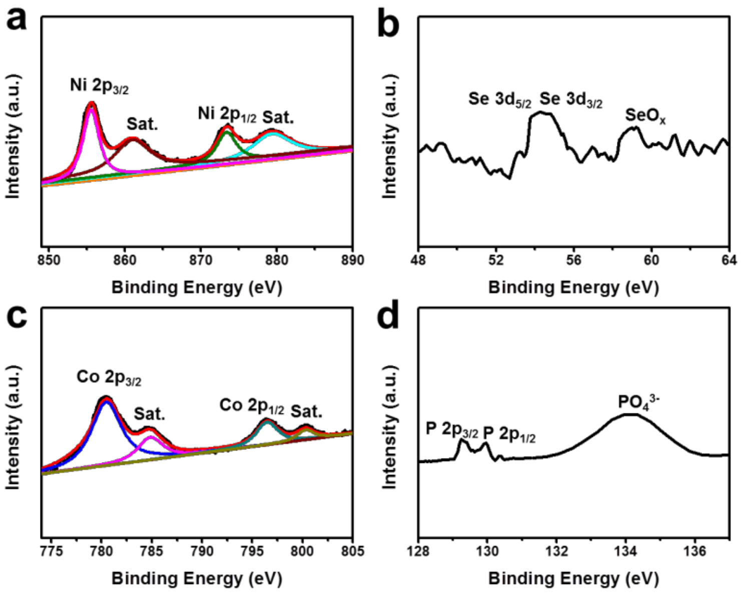

Figure S10. XPS spectra for the NiSe@CoP NWs/NF in the (a) Ni 2p, (Se) Se 3d, (c) Co 2p and (d) P 2p regions after HER electrolysis in 1.0 M KOH solutions.

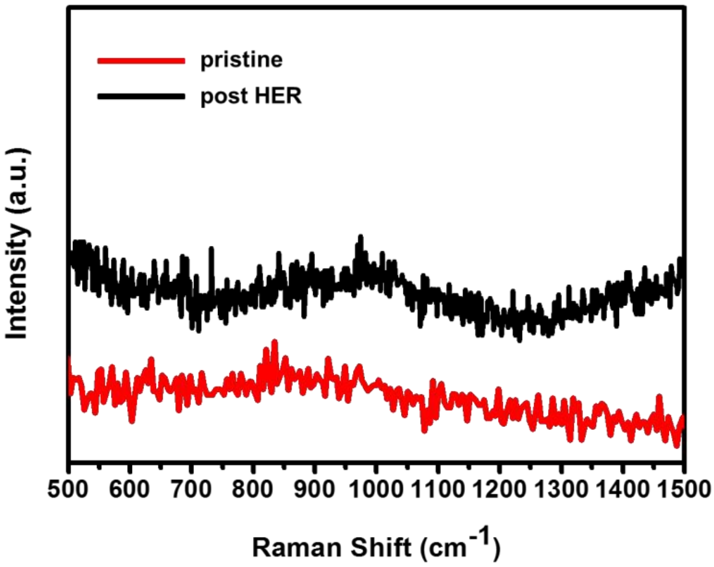

Figure S11. Raman spectra for NiSe@CoP NWs/NF before and after HER electrolysis in 1.0M KOH solutions.

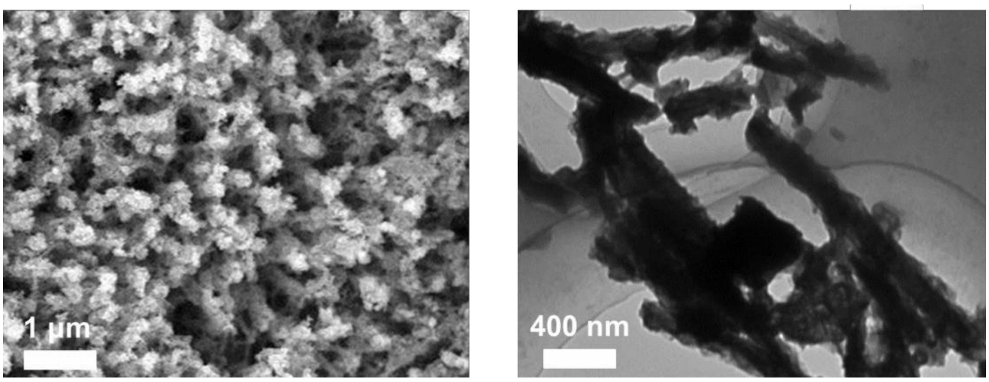

Figure S12. SEM image TEM image of NiSe@CoP NW$_S$/NF after the long-term electrochemical stability in 1.0 M H_2SO_4 solutions.

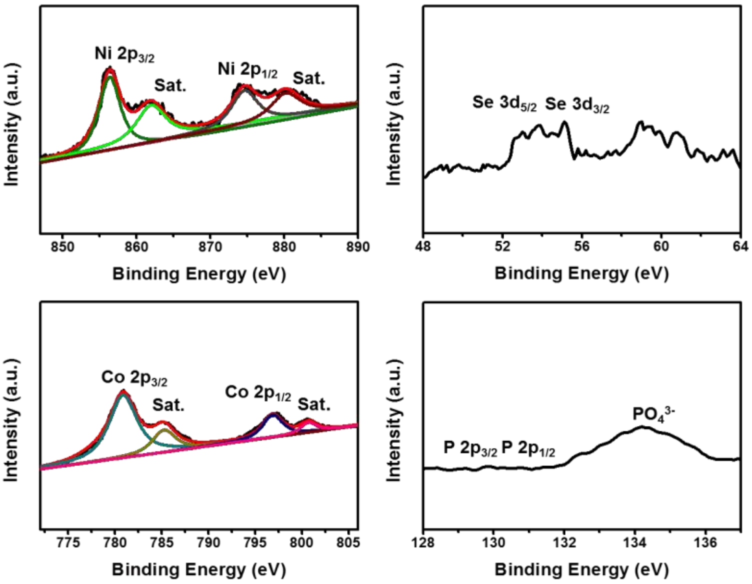

Figure S13. XPS spectra for the NiSe@CoP NWs/NF in the (a) Ni 2p, (b) Se 3d, (c) Co 2p and (d) P 2p regions after HER electrolysis in 0.5 M H_2SO_4 solutions.

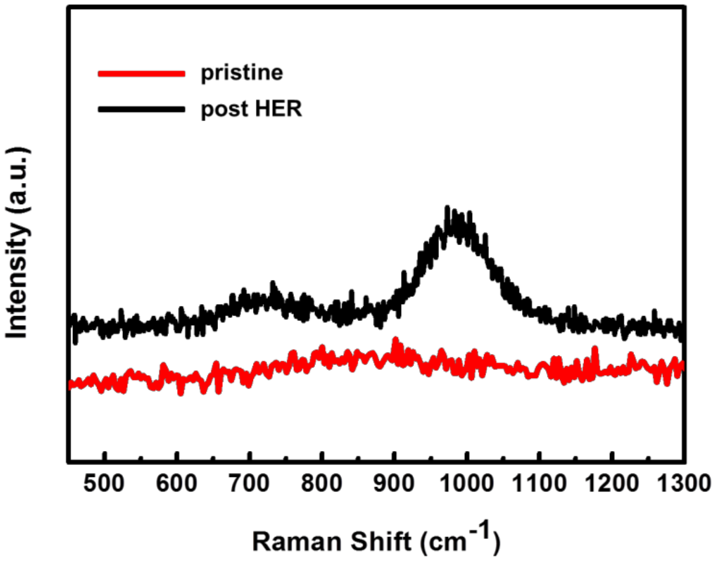

Figure S14. Raman spectra for NiSe@CoP NWs/NF before and after HER electrolysis in 0.5 M H_2SO_4 solutions.