

Electronic Supplementary Information

Improving the intrinsic electrocatalytic hydrogen evolution activity of few-layer NiPS₃ by cobalt doping

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Experimental Section

Synthesis of $Ni_{1-x}Co_xPS_3$ NSs. Bulk $Ni_{1-x}Co_xPS_3$ ($x=0, 0.03, 0.05, 0.07$ and 0.09) samples were prepared by solid state reaction with stoichiometric amounts (total of 2 gram) of Ni, Co, P and S powders. The elemental powders were mixed thoroughly using a mechanical mixer for at least 2 h. The mixture was then sealed into quartz tube under vacuum of 2.5×10^{-3} bar. After that, the sealed samples were heated from room temperature to 700 °C with a heating rate of 1 °C/min. After maintained at 700 °C for 5 d, the tubes were cooled down to room temperature, and the synthesized $Ni_{1-x}Co_xPS_3$ bulk black powders were obtained. $Ni_{1-x}Co_xPS_3$ NSs were obtained from an ultrasonication-assisted exfoliation process. In a typical procedure, 0.8 g bulk $Ni_{1-x}Co_xPS_3$ was added to a 20 mL glass vial containing 15 mL N,N-dimethyl formamide (DMF). The above solution was subject to ultrasonication for 48 h to get the exfoliated $Ni_{1-x}Co_xPS_3$ NSs.

Characterization. XRD measurements were performed on a Rigaku D/max 2500 X-ray diffractometer using Cu K α radiation. A JEOL ARM 200F transmission electron microscope (JEOL, Tokyo) and field-emission gun (FEG) scanning electron microscope (JEOL 6500 SEM) were used to characterize the morphology of the synthesized materials. The point resolution of the HRTEM was ~ 0.19 nm. The thickness of $Ni_{1-x}Fe_xPS_3$ NSs was analyzed by atomic force microscopy (AFM) on a Bruker DI MultiMode-8 system. X-ray photoelectron spectra were recorded on an ESCALAB MKII using an Al K α excitation source. Raman spectra were collected on a Renishaw inVia confocal micro-Raman spectroscopy system using a TE air-cooled 576×400 CCD array with a 532 nm excitation laser. The resolution of the Raman spectrometer was ~ 0.9 cm^{-1} , and the diameter of the incident light spot was ~ 1 μm . For electrical conductivity measurement, $Ni_{1-x}Co_xPS_3$ bulk materials were compressed into a disc with a diameter of 5 mm and a thickness of 1.5 mm, under a pressure of 3 MPa and a pressure time of 3 min. Then I - V curves were collected using a semiconductor analyzer (Keithley 4200 SCS) in the range of -1 to 1 V.

Electrochemical measurements. The exfoliated solution was centrifuged and washed with absolute ethyl alcohol to get the solid $Ni_{1-x}Co_xPS_3$ NSs. 10 mg of $Ni_{1-x}Co_xPS_3$ NSs were dispersed in absolute ethyl alcohol (0.5 mL) and then 10 μL of Nafion were added. Then the solution was sonicated for about 30 min to get a uniform ink solution. 5 μL of catalyst ink were dropcasted onto a polished glassy carbon electrode (GCE, 5 mm in diameter) for a catalyst loading of 0.51 ± 0.01 mg/cm^2 and dried in the air. All of the electrochemical measurements were performed in 100 mL of 1M KOH aqueous solution employing a three-electrode configuration using a rotating disk electrode (RDE) operating at 1,200 RPM. A platinum wire was used as a counter electrode and an Ag/AgCl (in 3.5 M KCl solution) electrode was used as a reference electrode. All of the linear sweep scan rate were measured at 5 mV/s. Cyclic voltammograms at various scan rates (20, 40, 60, 80, 100, 120, 140, 160, and 180 mV/s) were collected in the range of 0.224–0.324 V vs. RHE. The electrochemical impedance spectroscopy (EIS) were tested at 200 mV overpotential with the frequency ranging from 10^6 to 0.1 Hz. To better compare the true catalytic activity of different catalysts, we used the series resistance determined from EIS experiments to correct the polarization measurements and subsequent Tafel analysis for the iR losses. All of the potentials were referenced to a reversible hydrogen electrode (RHE).

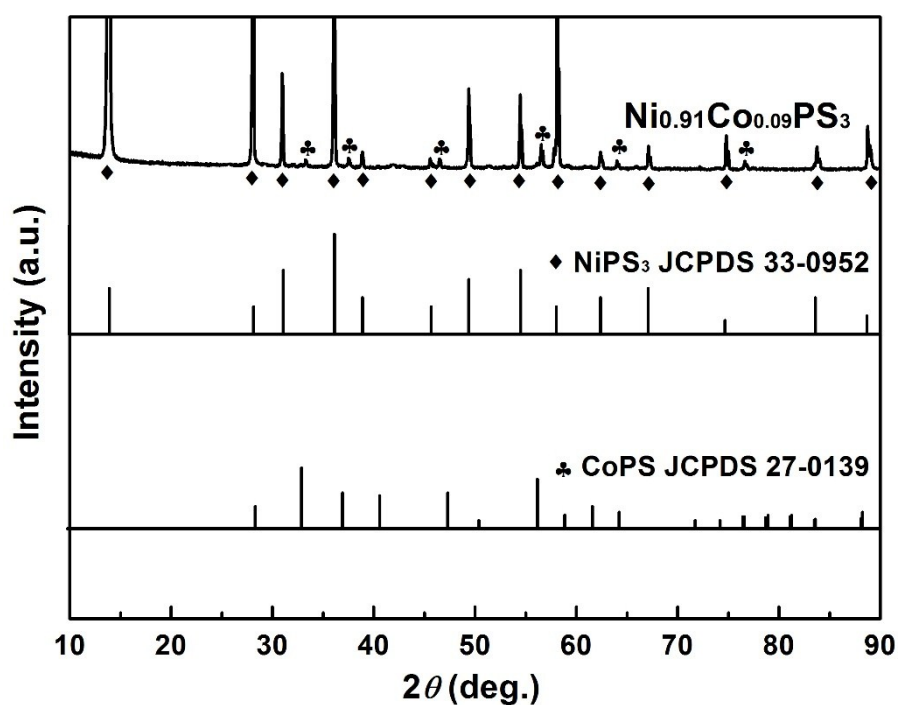


Fig. S1. Magnified XRD pattern of $\text{Ni}_{0.91}\text{Co}_{0.09}\text{PS}_3$ sample. It can be seen that with high doping content of Co, a small amount of CoPS can be produced.

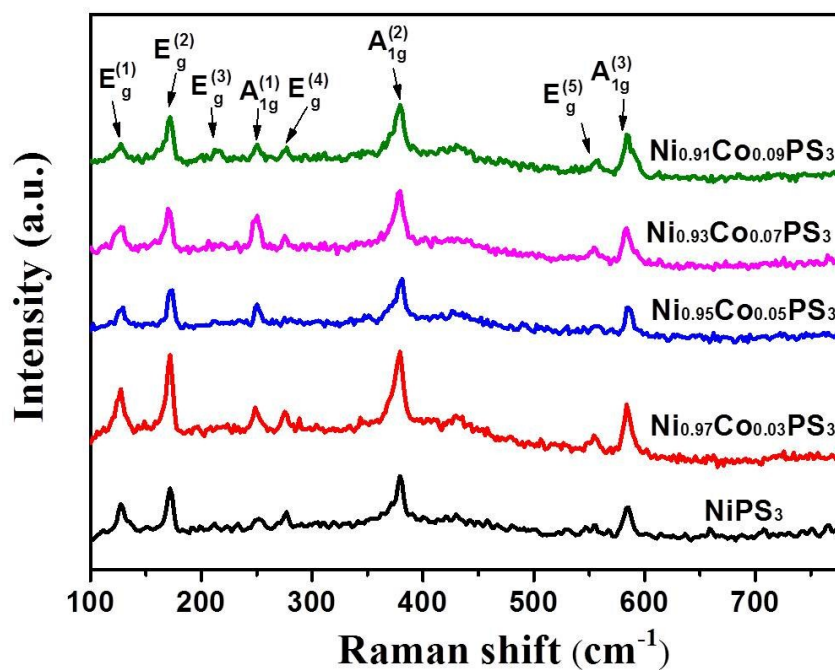


Fig. S2. Raman spectra of prepared NiPS_3 and $\text{Ni}_{1-x}\text{Co}_x\text{PS}_3$ samples.

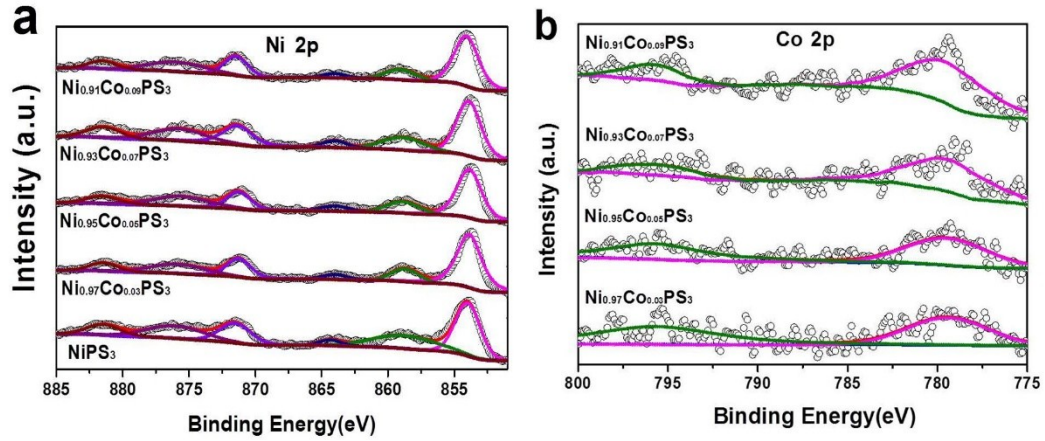


Fig. S3. XPS spectra of Ni_{1-x}Co_xPS₃ samples: (a) Ni 2p and (b) Co 2p.

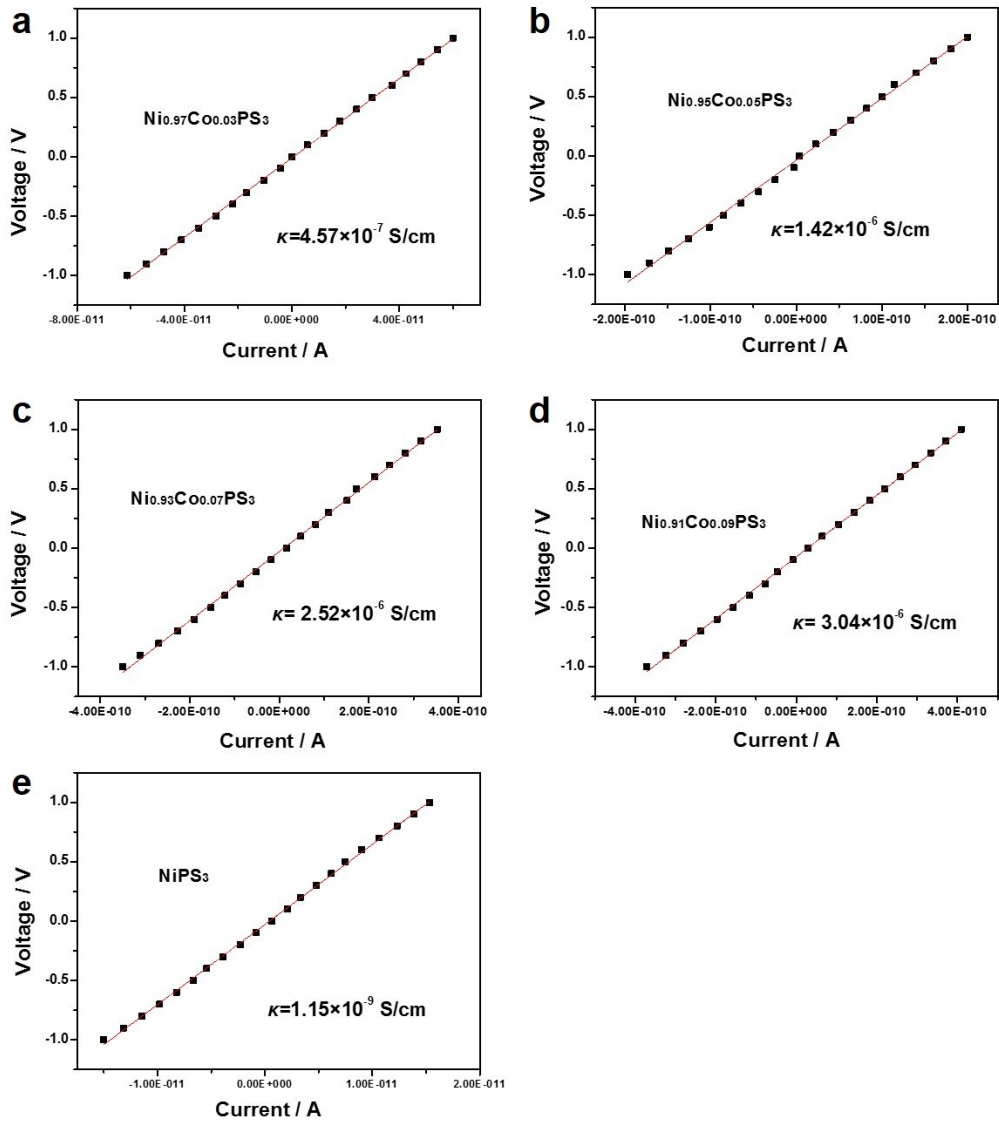


Fig. S4. Electrical conductivity of Ni_{1-x}Co_xPS₃ samples (a-d) and NiPS₃ (e).

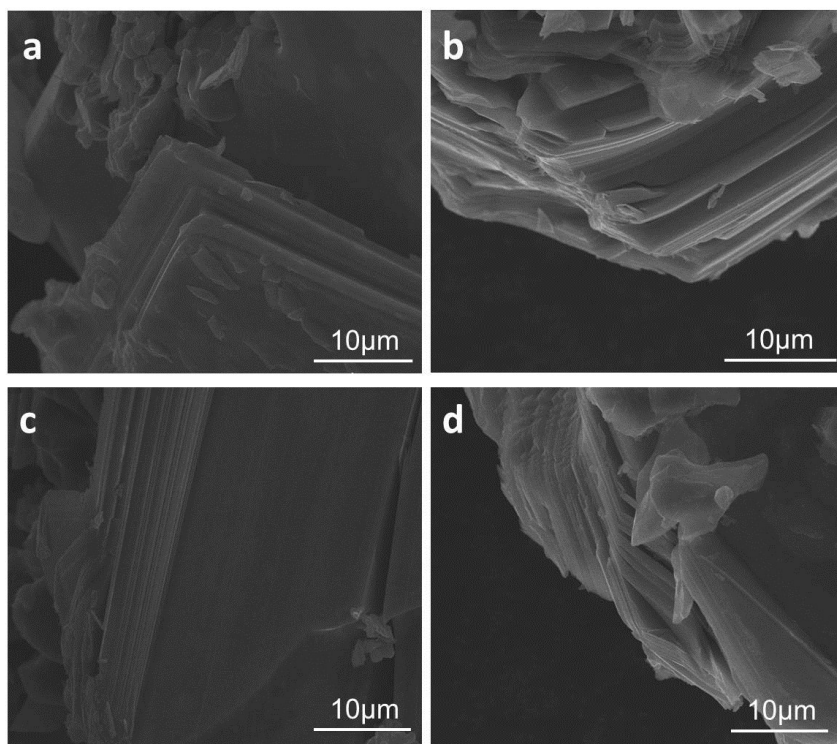


Fig. S5. SEM images of bulk NiPS₃ (a), Ni_{0.97}Co_{0.03}PS₃ (b), Ni_{0.93}Co_{0.07}PS₃ (c) and Ni_{0.91}Co_{0.09}PS₃ (d) samples.

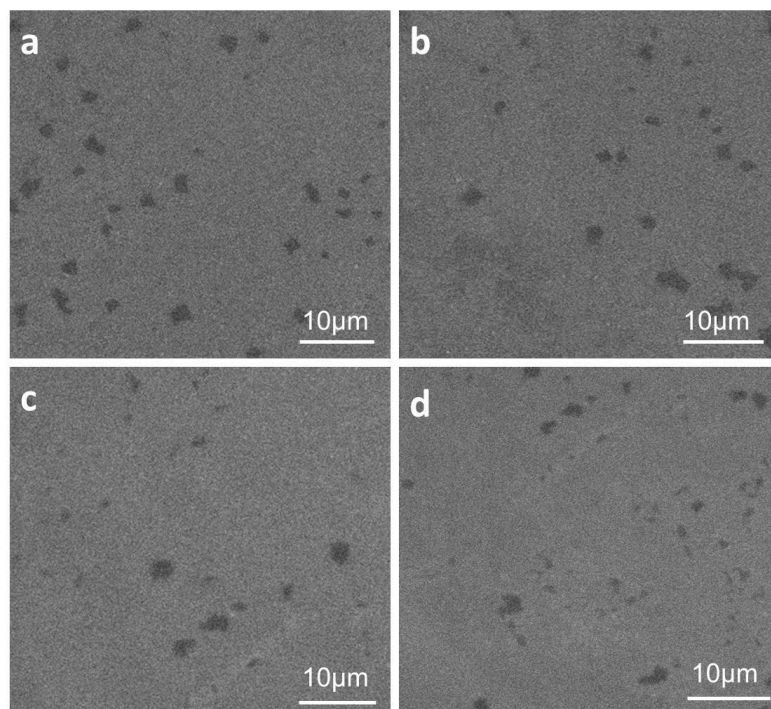


Fig. S6. SEM images of exfoliated bulk NiPS₃ (a), Ni_{0.97}Co_{0.03}PS₃ (b), Ni_{0.93}Co_{0.07}PS₃ (c) and Ni_{0.91}Co_{0.09}PS₃ (d) nanosheets.

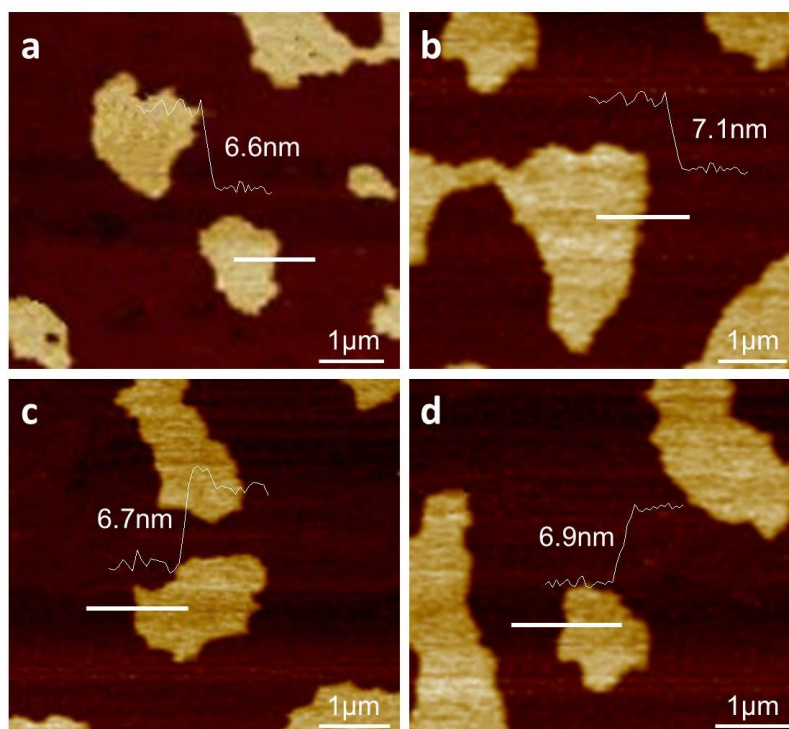


Fig. S7. AFM images of exfoliated bulk NiPS_3 (a), $\text{Ni}_{0.97}\text{Co}_{0.03}\text{PS}_3$ (b), $\text{Ni}_{0.93}\text{Co}_{0.07}\text{PS}_3$ (c) and $\text{Ni}_{0.91}\text{Co}_{0.09}\text{PS}_3$ (d) nanosheets.

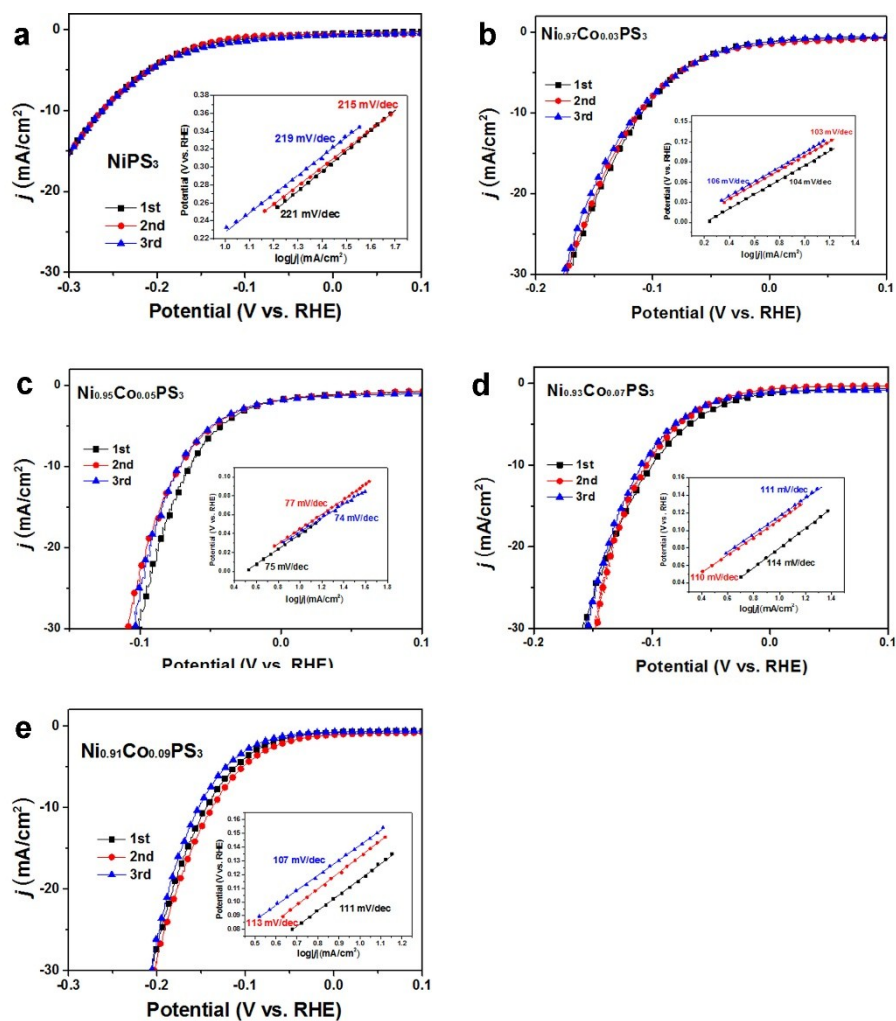


Fig. S8. LSV curves and Tafel plots (inset) of as-prepared NiPS₃(a), Ni_{0.97}Co_{0.03}PS₃ (b), Ni_{0.95}Co_{0.05}PS₃ (c), Ni_{0.93}Co_{0.07}PS₃ (d) and Ni_{0.91}Co_{0.09}PS₃ (e) nanosheet samples from three independent batches.

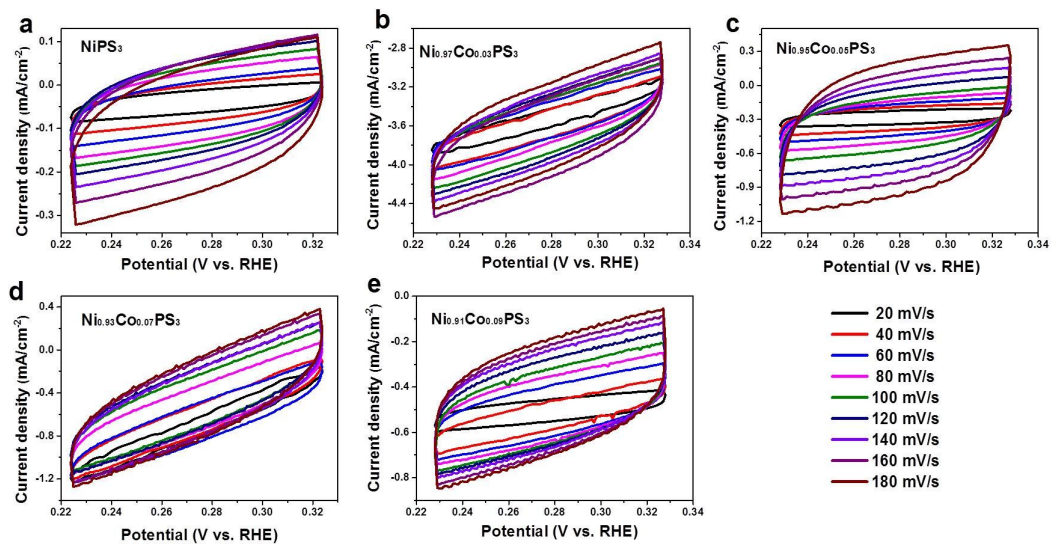


Fig. S9. Cyclic voltammograms of as-prepared NiPS₃(a), Ni_{0.97}Co_{0.03}PS₃ (b), Ni_{0.95}Co_{0.05}PS₃ (c), Ni_{0.93}Co_{0.07}PS₃ (d) and Ni_{0.91}Co_{0.09}PS₃ (e) nanosheet samples under different scan rates.

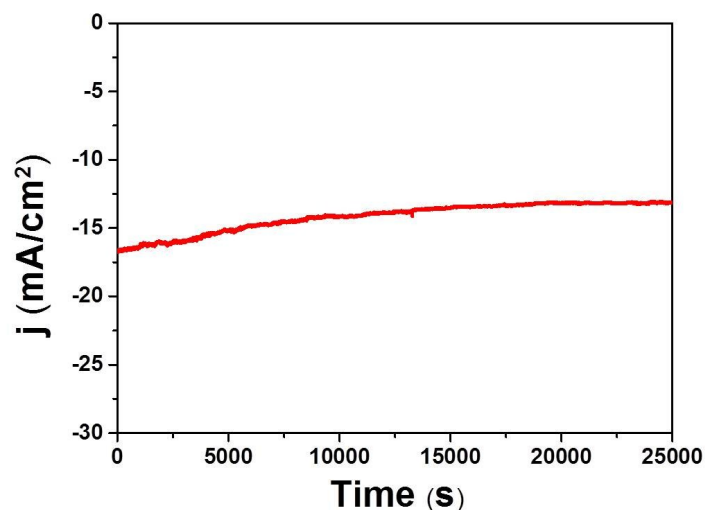


Fig. S10. Time-dependent current density under a constant overpotential at 180 mV of Ni_{0.95}Co_{0.05}PS₃ NSs as an HER catalyst.

Table S1. Ni/Co Atomic ratios of Ni_{1-x}Co_xPS₃ samples by XPS

Sample	Ni _{0.97} Co _{0.03} PS ₃	Ni _{0.95} Co _{0.05} PS ₃	Ni _{0.93} Co _{0.07} PS ₃	Ni _{0.91} Co _{0.09} PS ₃
Ni/Co(Atomic ratio)	30.4	18.5	12.6	9.4