Supporting information

Amorphous Iron and Cobalt Based Phosphate Nanosheets Supported on Ni Foam as Superior Catalysts for Hydrogen Evolution Reaction

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1. Experimental Procedures

1.1 Synthesis of $Fe_{1-2x/3}Co_xPO_4$ nanosheets supported on Ni foam

One piece of Ni foam was washed with ethanol, diluted HCl and deionized (DI) water several times before use. A colloidal chemical method was used for the catalyst synthesis. Typically, 1 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 1 mmol of $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 10 mL OM under ultrasonication for 1 h. In the meantime, 3 mmol Na_2HPO_4 was dissolved in 10 mL DI water under ultrasonication for 1 h. Then they were mixed and transferred into a 100 mL Teflon-lined autoclave with a piece of Ni foam partially immersed in it. The autoclave was sealed and heated in an oven at 150 ^oC for 24 h. The sample was then carefully washed with cyclohexane, ethanol and DI water several times. Finally, the sample was put into a furnace under the protection of Ar gas and heated at 200 ^oC to remove the remnant organic reagent.

1.2 Materials characterization

SEM measurements were performed on a JEOL-6700F scanning electron microscope with an accelerating voltage of 10 kV. XRD patterns were obtained on a PW1830 (Philips) Powder X-ray diffractometer fitted with Cu Kα radiation. XPS measurements were carried out on a Physical Electronics 5600 multi-technique system with an exciting source of Al with the working power of 150 W. TEM measurements were performed on a JEM 2010F (JEOL) Transmission Electron Microscope with an acceleration voltage of 200 kV. The FT-IR experiment was carried out on a Vertex 70 Hyperion 1000 FTIR spectrometer in a KBr pellet, scanning from 4000 to 400 cm^{-1}. The N_2 adsorption-desorption measurements were conducted using an autosorb-1 surface area analyzer. And the specific surface area of samples were calculated using Brunauer-Emmett-Teller (BET) method.

1.3 Electrochemical measurements

A CHI 660D electrochemical analyzer (CH Instruments, Inc. USA) was utilized for all the electrochemical measurements. A typical three-electrode system including $Fe_{1-2x/3}Co_xPO_4$/Ni foam directly as the working electrode, a carbon rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode was constructed for measurements. All potentials applied were calibrated to RHE following the equation: E(RHE) = E(SCE) + 1.068 V. All linear-sweep voltammetry (LSV) curves were obtained in a scan rate of 5 mV s^{-1} with 95% iR compensation. The durability test was conducted at a constant potential of -100 mV (vs. RHE) for over 20 h. EIS measurements were performed at a potential of -60 mV (vs. RHE) with the frequency range from 10^5 to 10^{-1} Hz. The electrochemical active surface area (ECSA) measurements were completed by a cyclic voltammetry (CV) technique with the potential scanning range within open circuit potential (OCP) ± 0.05 V at different scan rates.

2. Supplementary Results

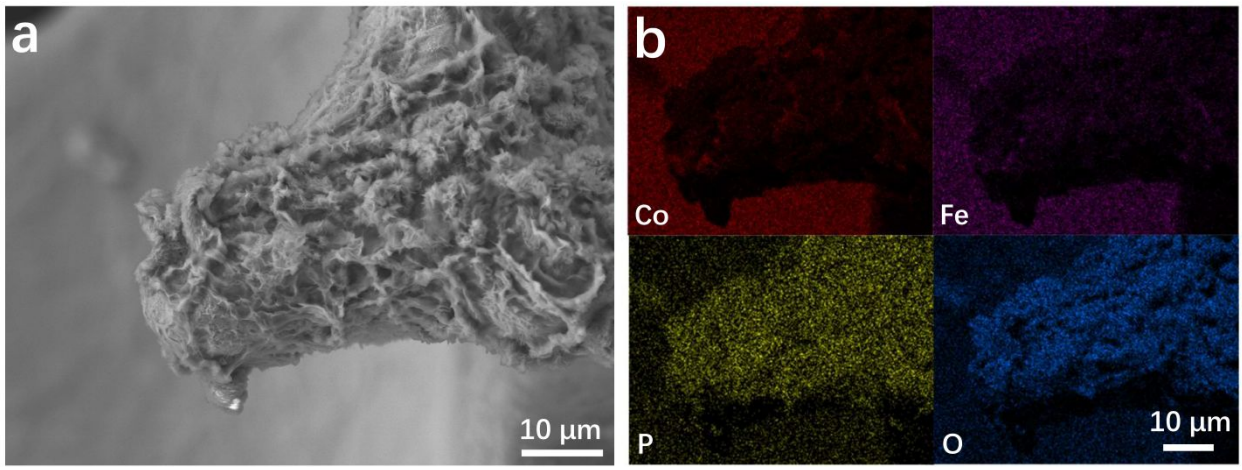

Figure S1. (a) SEM images of $Fe_{1-2x/3}Co_xPO_4$ on Ni foam. (b) The elemental mapping of the Co, Fe, P and O elements of the catalyst.

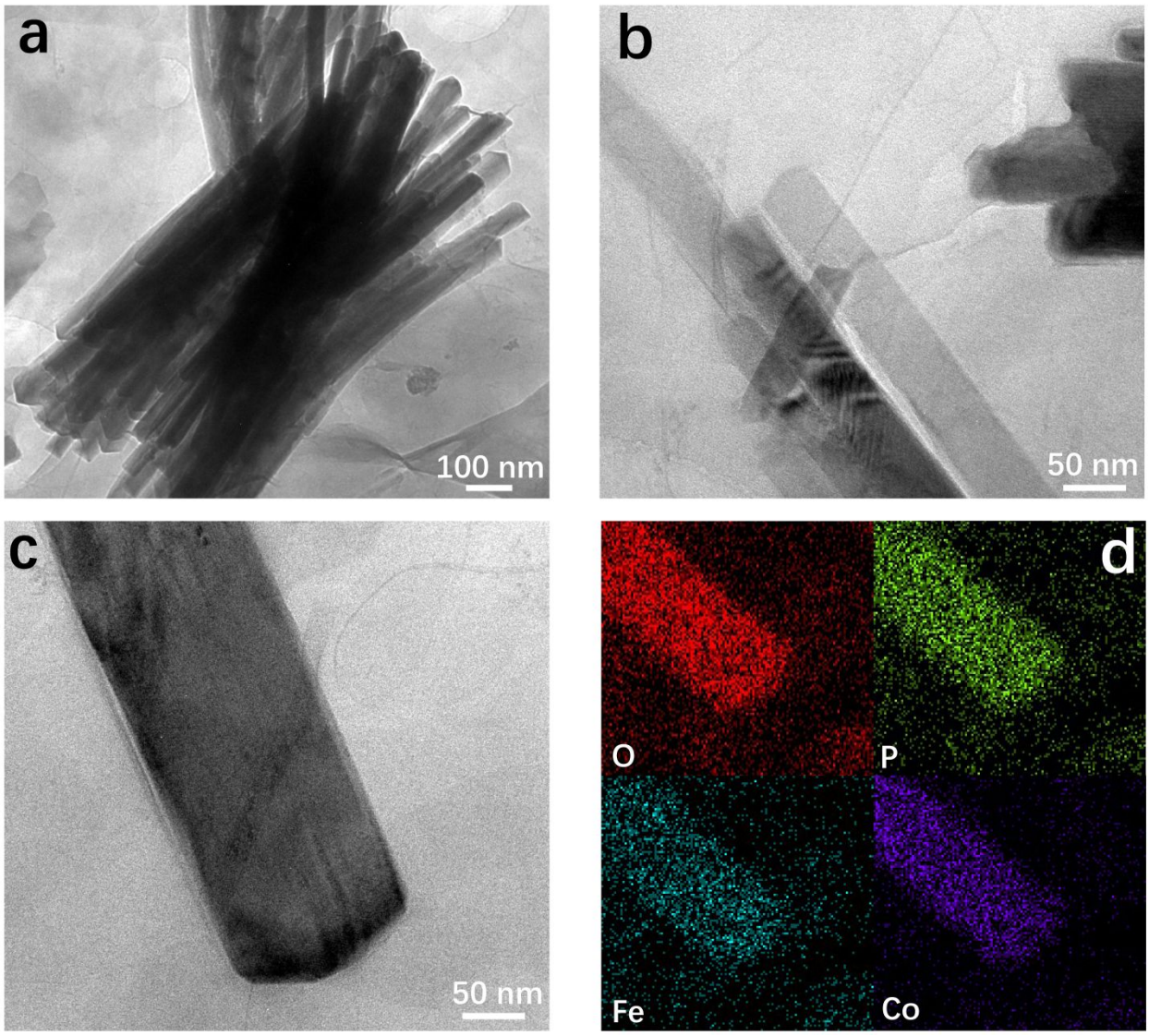

Figure S2. Transmission electron microscopy (TEM) images of (a) a bundle of $Fe_{1-2x/3}Co_xPO_4$ nanorods and (b) single $Fe_{1-2x/3}Co_xPO_4$ nanorod collected from the reaction solution. (c-d) TEM elemental mapping of a single nanoraod.

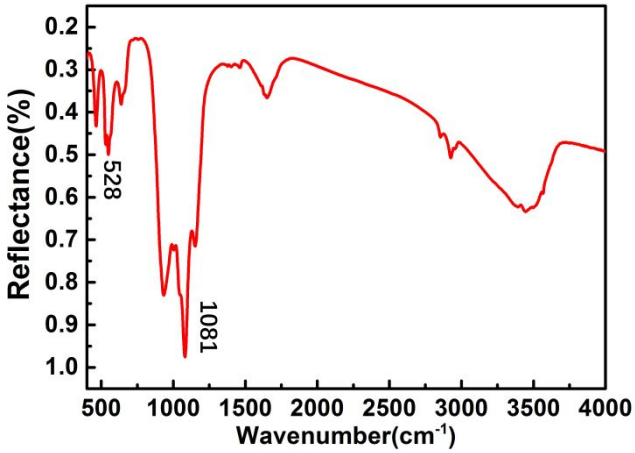

Figure S3. FTIR spectra of as-grown catalyst, confirming the existence of PO_4^{3-}.

Table S1. Comparison of HER efficiency of $Fe_{1-2x/3}Co_xPO_4$ nanosheets on Ni foam with some representative catalysts reported recently.

Catalysts	Substrate	Electrolyte	η_{10} (mV)	Tafel slope (mV/dec)	Reference
$Fe_{0.72}Co_{0.42}PO_4$ nanosheets	Ni foam	1.0 M KOH	77	80.7	This work
Co_2P nanorods	Ti foil	1.0 M KOH	152	N/A	[1]
Porous Co-based film	Au film	1.0 M KOH	~375	N/A	[2]
WC	Ni foam	0.1 M KOH	220	N/A	[3]
$Co(S_xSe_{1-x})_2$ nanoparticles	Carbon fiber	1.0 M KOH	122	85.7	[4]
MoS_2−Ni_3S_2 Heteronanorods	Ni foam	1.0 M KOH	98	61	[5]
CdS-MoO_3/Ni_3S_2	Ni foam	1.0 M KOH	121	110	[6]
NiSe/Ni_3Se_2	Ni foam	1.0 M KOH	92	101.2	[7]
N-doped C dots / Ni_3S_2	Ni foam	1.0 M KOH	187 @ 20 mA cm^{-2}	127	[8]
$NiCo_2S_4$ nanoflakes	Ni foam	1.0 M KOH	169	97.1	[9]
NiSe	Ni foam	1.0 M NaOH	177	58.2	[10]

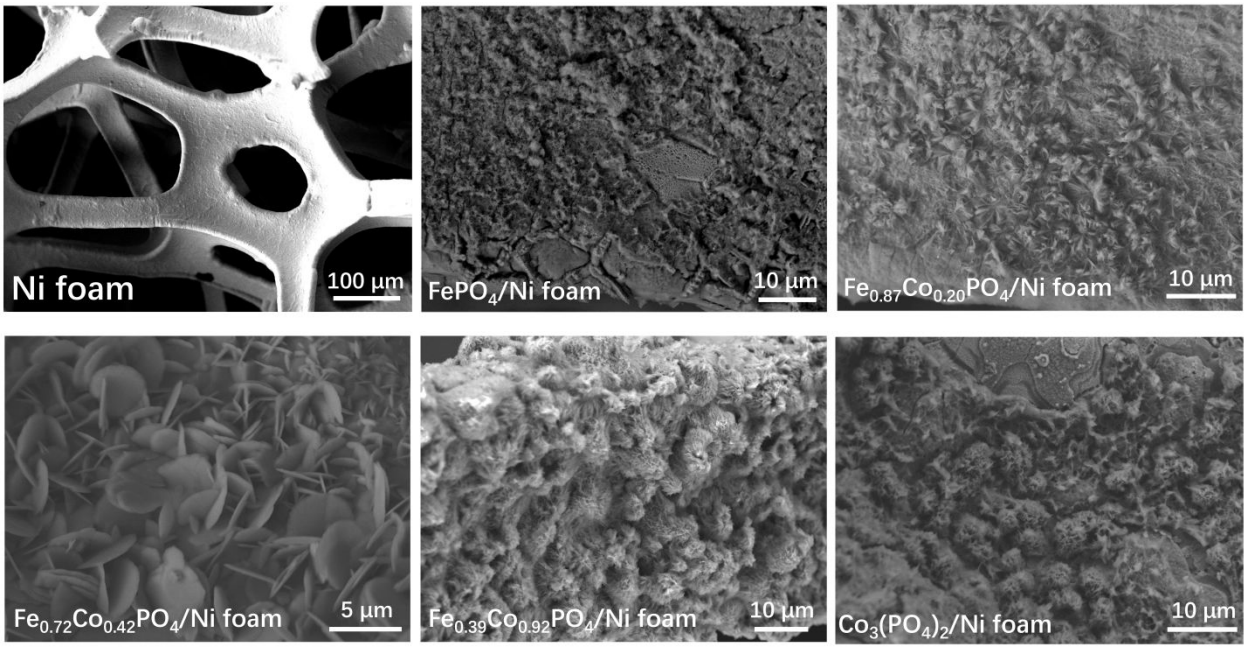

Figure S4. SEM images of Ni foam and various catalysts on Ni foam.

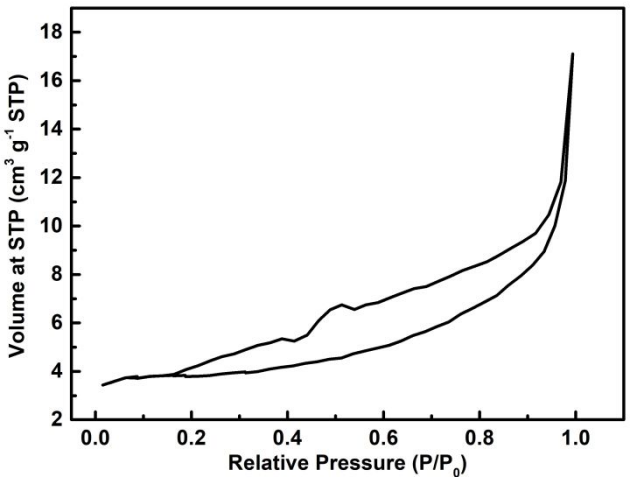

Figure S5. Typical N_2 adsorption desorption curve of $Fe_{0.72}Co_{0.42}PO_4$ nanosheets/Ni foam.

Table S2. A summary of BET surface areas of different catalysts on Ni foam.

Catalysts	BET surface area ($m^2 g^{-1}$)
$FePO_4$	1.989
$Fe_{0.87}Co_{0.20}PO_4$	1.961
$Fe_{0.72}Co_{0.42}PO_4$	11.551
$Fe_{0.39}Co_{0.92}PO_4$	1.237
$Co_3(PO_4)_2$	0.436

Table S3. A summary of total resistance of the cell (R_s) extracted from the Electrical Equivalent circuit model.

Catalysts	R_s (Ohm)
$FePO_4$	2.22
$Fe_{0.87}Co_{0.20}PO_4$	2.01
$Fe_{0.72}Co_{0.42}PO_4$	1.68
$Fe_{0.39}Co_{0.92}PO_4$	1.08
$Co_3(PO_4)_2$	1.90
Ni foam	1.73

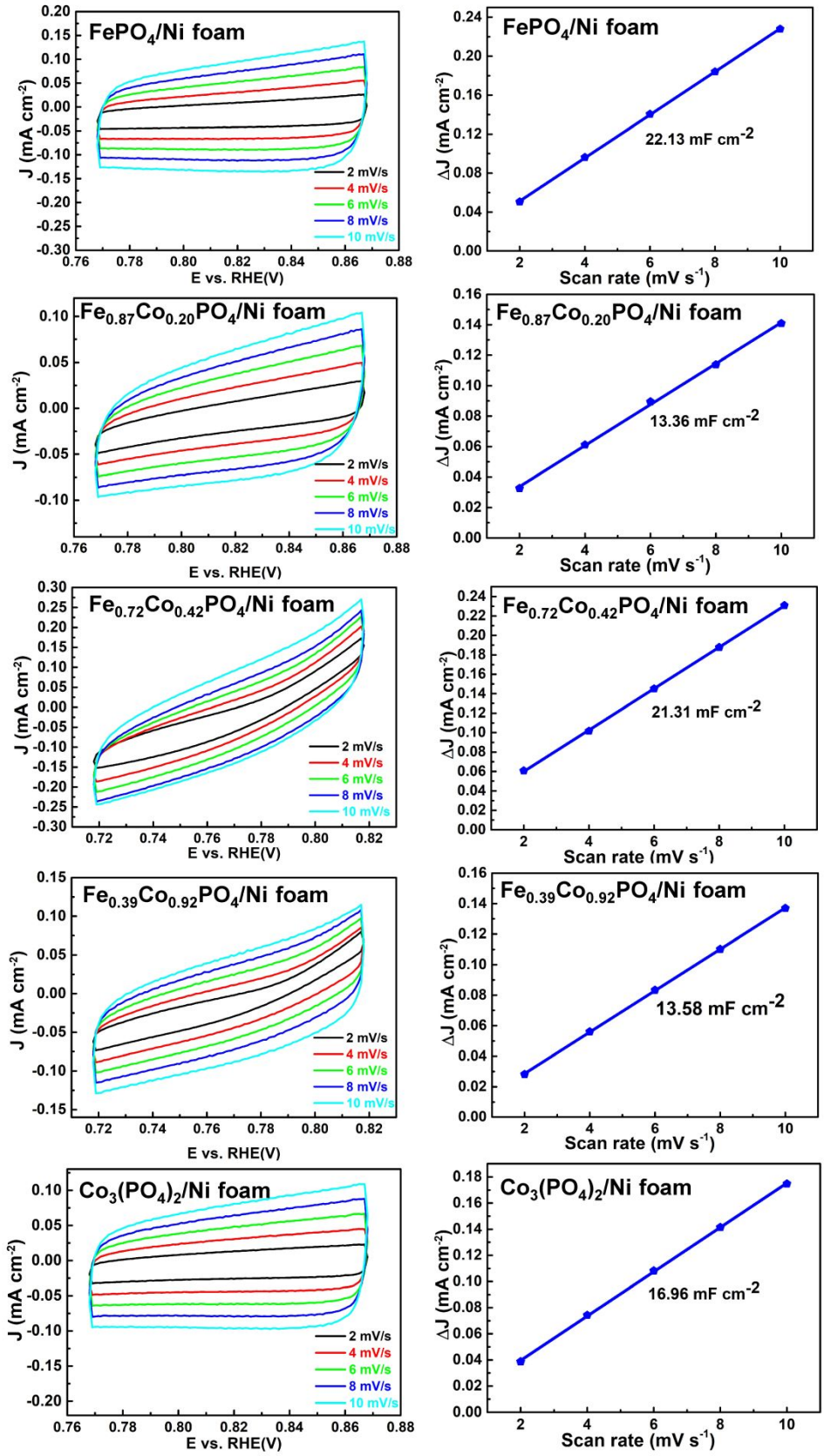

Figure S6. The summary of ECSA for different catalysts.

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