Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

NiCoFe Alloy Multishell hollow Spheres with lattice distortion to Trigger Efficient Hydrogen Evolution in Acidic Medium

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Experimental Section

Chemicals and materials

All the chemicals used in this study are commercially available reagents: hexahydrate cobalt nitrate ($Co(NO_3)_2.6H_2O$) (MACKLIN), nanohydrate iron nitrate ($Fe(NO_3)_3.9H_2O$) (aladdin), and nickel acetate ($Ni(CH_3CO_2)_2$) (ajkeshiji), urea (MACKLIN), PVP (MACKLIN), and ethylene glycol (EG) (MACKLIN), citric acid (aladdin) and *N*,*N*-dimethylformamide (DMF) (aladdin).

Preparation of graphitic carbon supported multishell hollow NiCoFe nanospheres

Multishell hollow NiCoFe alloy nanospheres graphitic carbon supported were synthesized by hydrothermal method. 0.1912 g of ($Ni(CH_3CO_2)_2$), 0.2259 g of ($Co(NO_3)_2.6H_2O$), 0.2154 g of ($Fe(NO_3)_3.9H_2O$), 0.4414 g of urea, 0.700 g PVP, 80 mg of citric acid and 2 ml ethylene glycoal were added in 15 ml DMF solution with continuous stirring. Then the above homogenous mixture was added to an autoclave, which was then sealed and kept in an oven at 180 °C for 24 hours. The autoclave was cooled down to room temperature and the black products were then washed with ethanol for three times and dispersed in ethanol solvent for further characterization.

Preparation of graphitic carbon supported solid NiCoFe nanospheres

For the synthesis of graphitic carbon supported solid NiCoFe alloy nanospheres all the above parameter kept same except 0.4414 g of urea were not added.

Preparation of graphitic carbon supported hollow NiCoFe nanospheres

For the synthesis of graphitic carbon supported hollow NiCoFe alloy nanospheres all the above parameter kept same except citric acid were not added and we obtained hollow spheres instead of multishell spheres.

Electrochemical test

The electrochemical test was carried out by using a CHI650D electrochemical analyzer (CHI instrument, USA). A conventional three-electrode cell was used including a graphite rod as a counter electrode, a saturated calomel as the reference electrode, and the nickel foam with a working area of 1X1 cm as the working electrode with a catalyst loading of $1mg/cm^2$. The catalyst was dispersed in H_2O, ethanol and Nafion solution by sonication for one hour to make a homogenous catalyst ink. The catalyst ink was transferred to the surface of the nickel foam electrode and dried at room temperature. The electrochemical measurements were performed in 0.5 M H_2SO_4 at a scan rate of 2 mVs^{-1}. Tafel plot was obtained by taking advantage of Tafel plot function. The time-dependent curve was used to check the electrocatalytic stability of the material at overpotential of 16 mV. The electrochemical

impedance (EIS) measurement was carried out from 100 kHz to 0.01 Hz in the same configuration. The electrochemical surface area (ESCA) measurement performed by using cyclic voltammetry at different scan rates.

Characterization technique

Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) were recorded on a HITACHI H-7700 TEM with an accelerating voltage of 100 kV and FEI Tecnai G2 F20 S-Twin high-resolution equipped with energy dispersive spectrometer (EDS) analyses at 200 kV. The sample for HRTEM was prepared by dropping ethanol dispersion on carbon-coated Cu grid. X-ray diffraction (XRD) pattern was obtained with a Bruker D8-advance X-ray powder diffractometer operated at 40 kV and instrument run at a scan rate of 0.02 deg/s in the angle range of 30° to 90° and the wavelength of incident radiation was $\lambda = 1.5418$ Å. XPS measurements were conducted on a scanning X-ray microprobe (Thermo Fisher Model ESCALAB 250Xi) operated at 250 kV, 55 eV with monochromated Al Kα radiation. Ni, Co and Fe L-edge soft X-ray absorption spectroscopy (sXAS) measurements were carried out in Taiwan Synchrotron Radiation Facility.

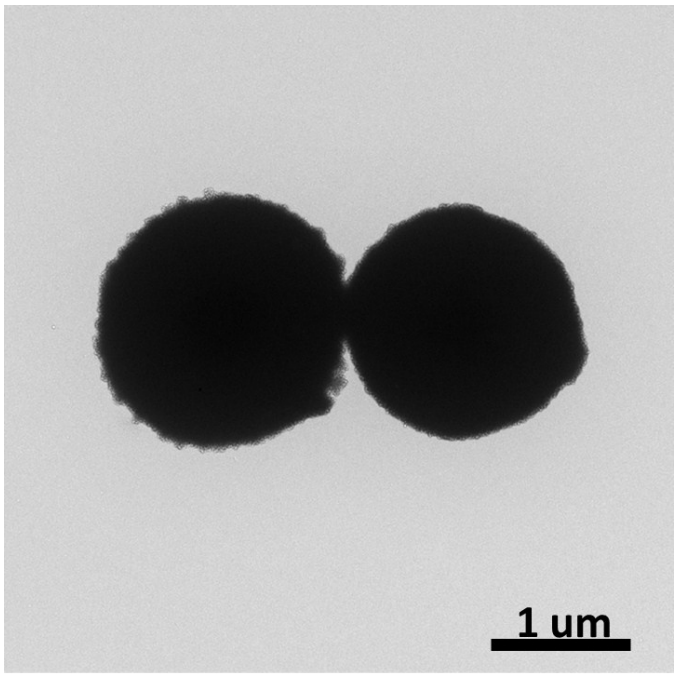

Figure SI 1. TEM image of NiCoFe alloy spheres without using urea.

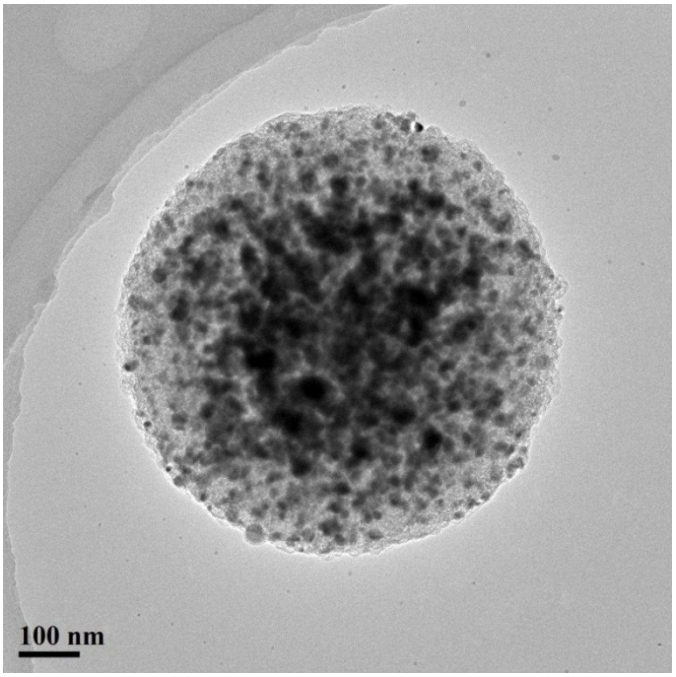

Figure SI 2. Enlareged TEM image of NiCoFe alloy spheres wtihout using urea.

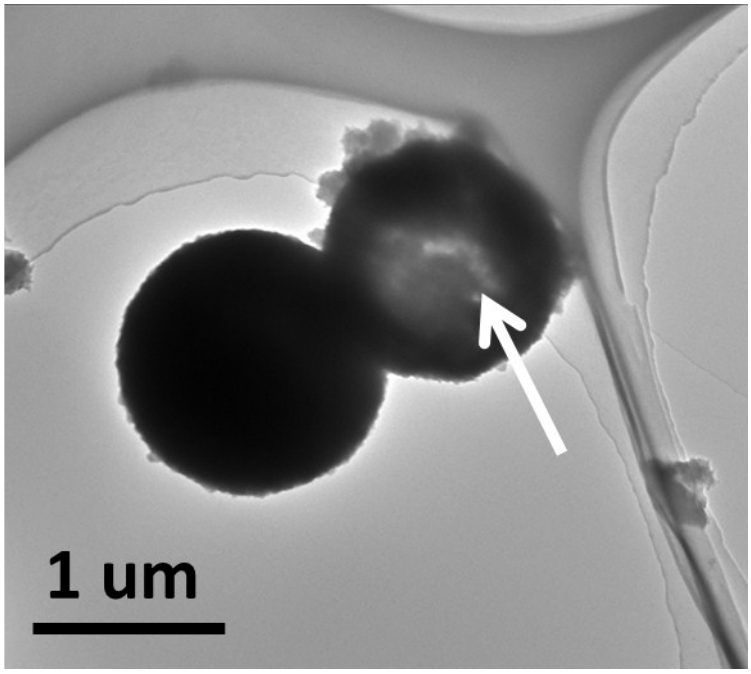

Figure SI 3. TEM image of NiCoFe alloy spheres without using citric acid.

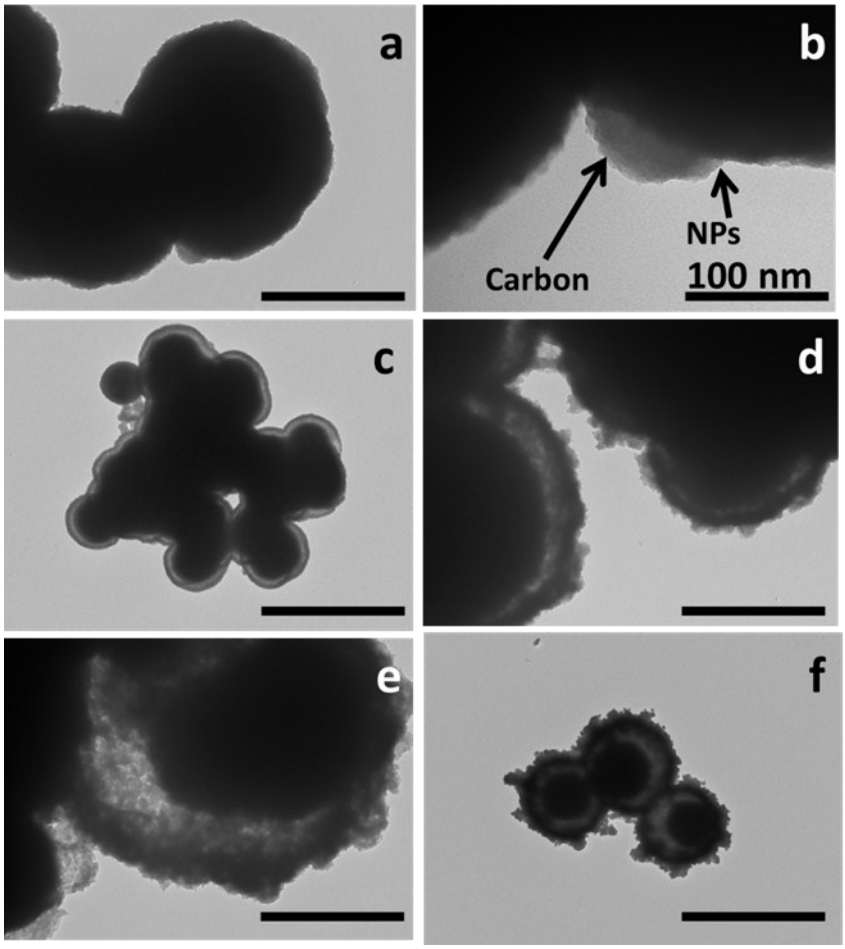

Figure SI 4. TEM image of NiCoFe alloy spheres at diffrent time of reaction (scale bar is 500 nm).

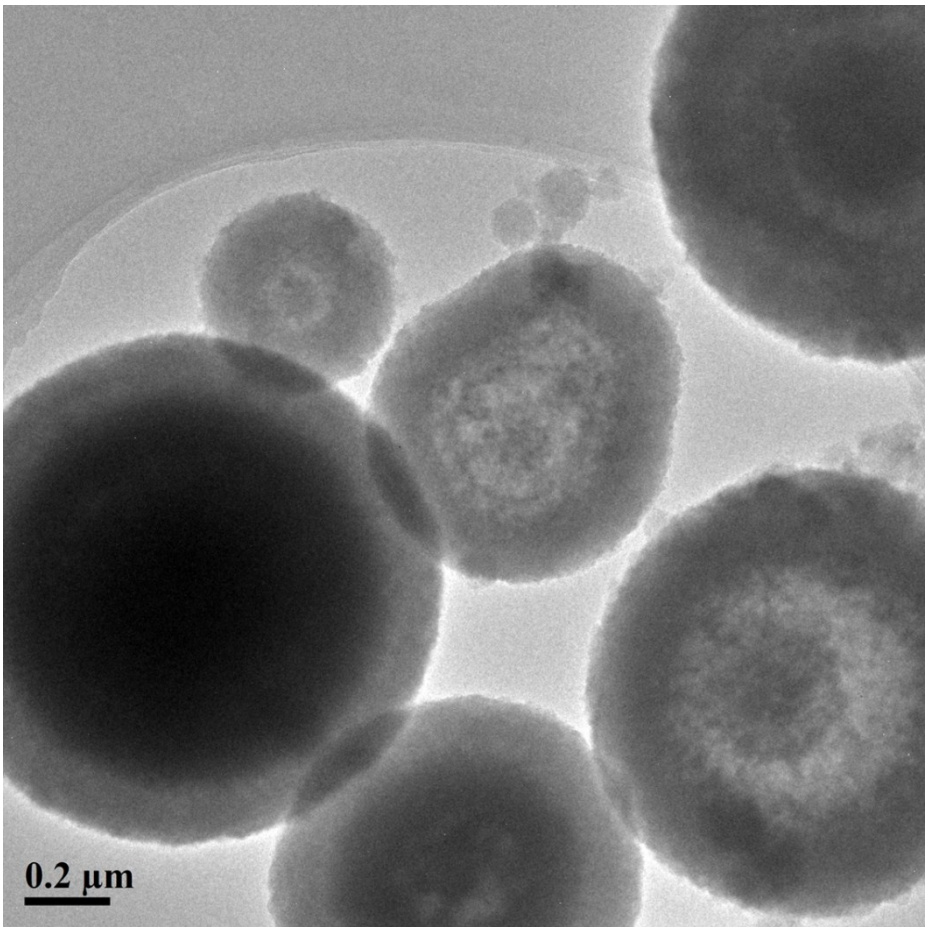

Figure SI 5. TEM image of NiCoFe alloy spheres at the reaction time of 24 hours.

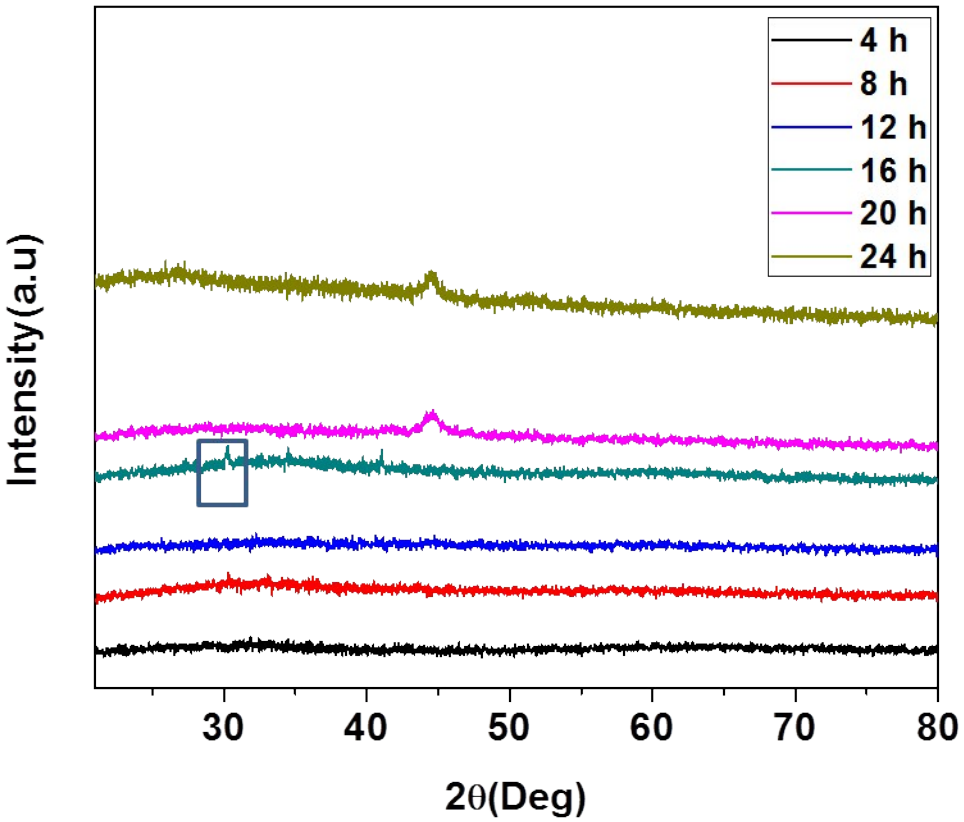

Figure SI 6. XRD ptteren of NiCoFe alloy mutishell hollow spheres at diffrent reaction time.

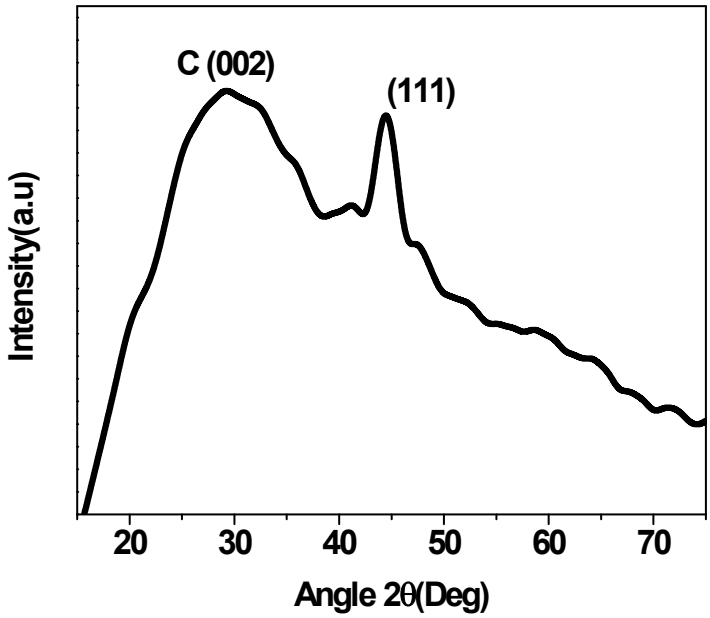

Figure SI 7. XRD ptteren of NiCoFe alloy mutishell hollow spheres after 24 hours reaction time.

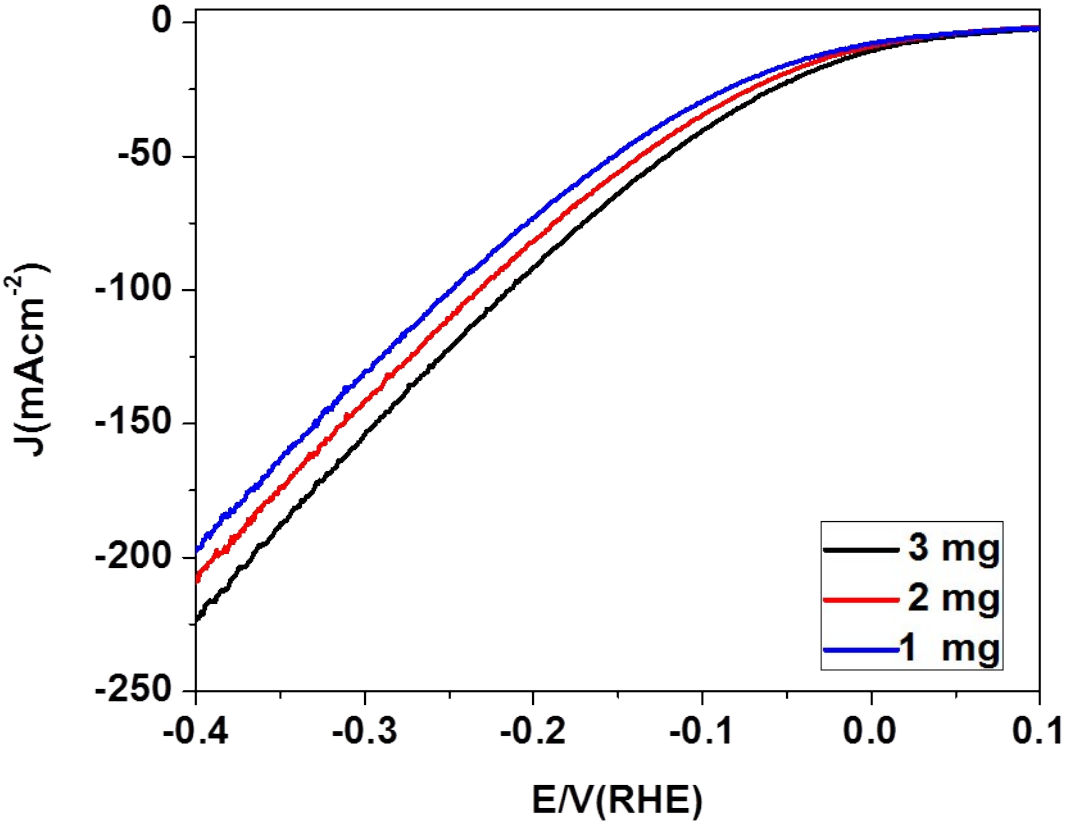

Figure SI 8. Polarization curve of NiCoFe alloy hollow spheres at the diffrent loading of catalyst.

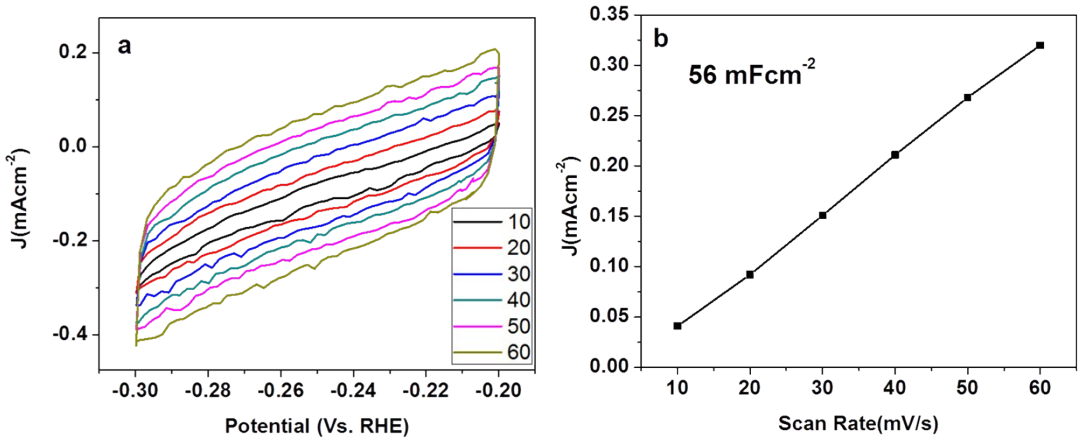

Figure SI 9. Cyclic voltammograms (CV) curves NiCoFe alloy multishell hollow spheres (a), and current density as a function of scan rate (mV/s) derived from (a) of NiCoFe alloy multishell hollow spheres (b).

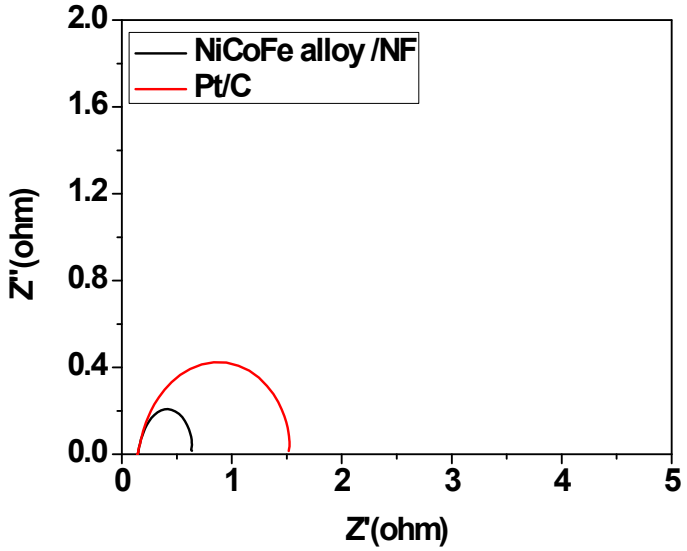

Figure SI 10. Electrochemical impedance spectra of NiCoFe alloy and Pt/C.

Table 1. Comparison of activity of different catalyst in 0.5 M H_2SO_4.

Sr. No	Catalyst	η_{10} (mV)	References
1	MoCx	142	Nat. Commun. 2015, 6, 6512
2	CoP@BCN-1	87	Adv. Energy Mater. 2017, 7, 1601671
3	$NiCo_2Px$/CF	104	Adv. Mater. 2017, 29, 1605502
4	CoMoP@C	41	Energy Environ. Sci. 2017, 10, 788
5	α-iron-nickel sulphide	105	J. Am. Chem. Soc. 2015, 137, 11900
6	Ni_5P_4-Ni_2P-NS	120	Angew. Chem. Int. Ed. 2015, 54, 8188
7	CoS_2 NW	145	J. Am. Chem. Soc. 2014, 136, 10053
8	CoS_2	107	Green Energy Environ. 2017, 2, 134
9	MoS_2/CoS_2	87	J. Mater. Chem. A 2015, 3, 22886
10	MoxC-Ni@NCV	68	J. Am. Chem. Soc. 2015, 137, 15753
11	CoP	65	J. Am. Chem. Soc. 2014, 136, 7587
12	CoS_2@NSC/CFP	95	ChemCatChem 2017, 10, 796
13	CoS_2/P	67	Chem. Commun. 2015, 51, 14160
14	CoS_2/RGO-CNT	142	Angew. Chem. 2014, 126, 12802
15	NiCoFe alloy/NF	16	This work