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Electronic Supplementary information

Synergism between polydopamine and polyurethane in the synthesis of Ni-Fe alloy monoliths

List of figures:

Materials and Methods:

Iron (III) chloride hexahydrate (Sigma Aldrich), nickel chloride (Nice Chemicals) and dopamine hydrochloride (Alfa Aesar), ammonium persulfate (Merck), hexamethylene-1, 6-triisocyante homopolymer (N3300, Bayer), N,N'-dimethylformamide and acetone (Sisco research laboratories) were used as received.

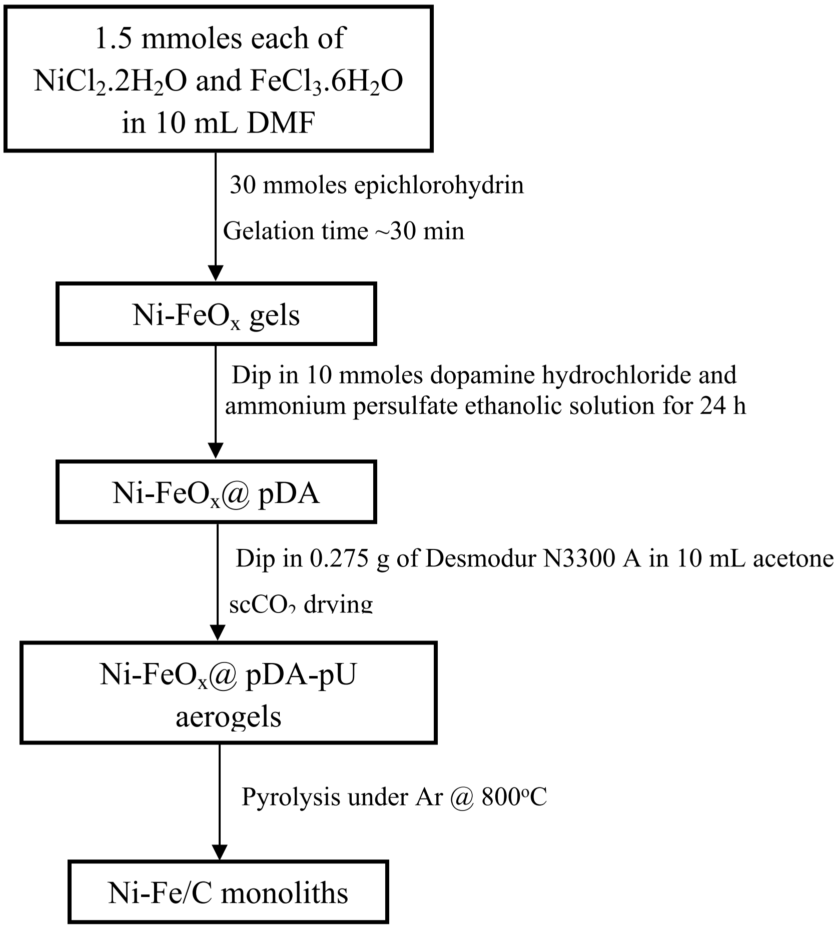
Infrared spectroscopy for the samples was done on a Bruker Tensor 27 FT-IR spectrometer. X-ray diffraction patterns were recorded using a Bruker D8 Advance X-ray diffractometer with a Cu K_α radiation ($\lambda = 1.5418$ Å). Surface morphology was studied using Field Emission Scanning Electron Microscope (Zeiss supra 55VP). Cyclic voltammetric experiments were performed on a BASi100 workstation. BET isotherms were obtained using nitrogen adsorption/desorption porosimetry (Quantachrome Autosorb-1 surface area analyser).

Synthesis of Ni-Fe monoliths

In a typical synthetic procedure, Ni-FeO_x gels were prepared by mixing 1.5 mmoles each of $NiCl_2.6H_2O$ and $FeCl_3.6H_2O$ in 10 mL of N,N'-dimethylformamide (DMF) followed by the addition of 30 mmoles (2.75 mL) of epichlorohydrin. The sol was poured into polypropylene moulds and the gelation time of Ni-FeO_x gels was found to be 20 minutes. The gels were washed with DMF (3 × 8 h) followed by ethanol washes (3 × 8 h) to remove the unreacted precursors.

Polydopamine was coated on Ni-FeO_x gels by dipping the wet gels in an ethanolic solution containing 10 mmoles of dopamine hydrochloride and 2 mmoles of ammonium persulfate for 24 h at room temperature [*Q. Wei, F. Zhang, J. Li, B. Li and C. Zha, Polym. Chem., 2010, 1, 1430–1433*]. The polydopamine coated gels were washed with ethanol and acetone (3 × 8 h) followed by dipping in 0.275g of hexamethylene-1,6-triisocyanate homopolymer (Desmodur N3300 A) dissolved in 10 mL of acetone for 24 hours. The wet gels were dried in an autoclave using $scCO_2$. The obtained Ni-FeO_x aerogels were converted to Ni-Fe alloy monoliths by pyrolysis under flowing Ar at 800^{o}C.

Synthetic Scheme for Ni-Fe alloy monoliths



Electrochemical experiments:

A three-electrode cell with Hg/HgO as reference electrode and a Pt foil as the counter electrode was used. The glassy carbon disk portion of the RRDE was modified with the Ni-Fe-monolithic catalyst and employed for studying the oxygen evolution reaction. 0.1M KOH was used as the supporting electrolyte. Prior to modification, the glassy carbon electrode was well-polished with 1, 0.3 and 0.05 micron sized alumina powder and sonicated for about 5 minutes. A thin film of the Ni-Fe catalyst was prepared in order to perform thin-film hydrodynamic voltammetry, following the method of Behm et al [S1]. For this, 5μL Ni-Fe catalyst ink was prepared by sonicating a mixture of 5 mg Ni-Fe catalyst in 1ml of 1% Nafion equivalent to the 80 μg cm^{-2} of the catalyst coated on the glassy carbon surface [Note: This Nafion film was soaked in 0.1M NaOH solution to exchange protons with Na$^+$ ions]. Voltammetric responses of Ni, Ni-Fe and Fe were recorded in a potential range between 0 to 0.6 V *vs.* Hg/HgO at a scan rate of 50 mVs^{-1}. For studies on OER electrocatalysis, a potential range of 0 to 0.8 V *vs*. Hg/HgO and a scan rate of 5 mVs^{-1} were chosen [S2]. All the potential values are referred against Hg/HgO electrode and water oxidation curves are cited in RHE scale.

Faradaic efficiency calculation:

The OER Faradaic efficiency for the Ni-Fe monoliths was determined using RRDE voltammetry based on the reported procedures [S3]. In order to calculate Faradaic efficiency, one needs to first find the collection efficiency of the ring electrode. RRDE experiments were carried out using a VMP3 multi-channel potentiostat (Biologic Inc), a rotator (MSR), Au Disk-Pt Ring (AFE6R2AUPT), of Pine instruments USA.

RRDE-Collection Efficiency Calculation: In a typical RRDE collection experiment, the complete product generated at the disk electrode will not reach the ring electrode. The flow pattern at a rotating electrode generally sweeps anywhere from 20% to 30% of the disk products past the ring electrode. The percentage of material which is collected at the ring electrode is often called the "collection efficiency" of the RRDE. One may empirically measure the collection efficiency of a specific RRDE before using it for any quantitative work. This is normally done using a well-defined electrochemical system such as the ferricyanide-ferrocyanide redox couple. This system can be used to measure stable collection efficiency at rates between 200 and 2500 rpm. The ring collection efficiency was calculated to be 30% (or expressed as 0.3), as measured using a $[Fe(CN)_6]^{3-/4-}$ redox couple. The ring potential was set at 0.23V *vs.* Ag/AgCl.

The collection efficiency, N_{CL}, calculated from the current response of $K_3Fe(CN)_6$ (5 mM) in 0.1M KCl was found to be 30 ± 1%. Ar gas was purged into the electrochemical cell for 30 min before the experiment and remained throughout the experiment. 5 µL of the Nafion ink solution containing 5 mg/mL Ni-Fe monolithic catalyst was drop-cast on the Au disk electrode. The Au disk electrode was held at open circuit potential of OER to determine the ring background current, while the Pt ring electrode was held at -0.5 V *vs*. Hg/HgO. The ring background current was found to be 20 µA. The disk electrode was then subjected to sequential 1 minute current steps at 0.1, 0.2, 05 and 1 $mAcm^{-2}$ at 1600 rpm, while the ring was held constant at -0.5 V *vs*. Hg/HgO. Faradaic efficiency was calculated based on the ratio of disk and ring currents using the following equation:

$$\varepsilon = \frac{2i_r}{i_d N_{CL}}$$

i_r = Ring current (A); i_d = Disk current (A); N_{CL} = Collection efficiency (%)
ε = Faradaic efficiency (%)

Turn-over frequency calculation:

The turn-over frequency (TOF) was calculated based on the number of Ni sites in the Ni-Fe monolithic catalyst, according to the procedure followed by A.T.Bell [S2].

$$\mathrm{TOF}_{\max} = \frac{I * N_A}{4FN_{atoms}}$$

where, I, N_A, $N_{atoms,}$ F represent the current obtained at 700 mV, Avogadro number ($6.023 \times 10^{23}\ \mathrm{mol}^{-1}$), number of atoms on the surface and Faraday constant (96500 C/mol) respectively. $\mathrm{TOF}_{\max}$ was estimated from the surface area of film and the number of Ni atoms on the surface using a value of 6.4×10^{14} Ni atoms per cm^2 area [S2].

The electrochemically active surface area (ECSA) is significant since it's directly linked to the actual surface involved in the catalytically activity. In the case of Ni surface, determination of active surface area employs the charge (Q) under the CV peak corresponding to Ni (II/III). The ECSA is then calculated from the charge density associated with the formation of 1 monolayer, i.e., equal to $514\ \mu\mathrm{C\ cm}^{-2}$ [S3]

$$\mathrm{ECSA} = \frac{Q}{514\mu C\ cm^{-2}}$$

Q= Charge (Coulombs)

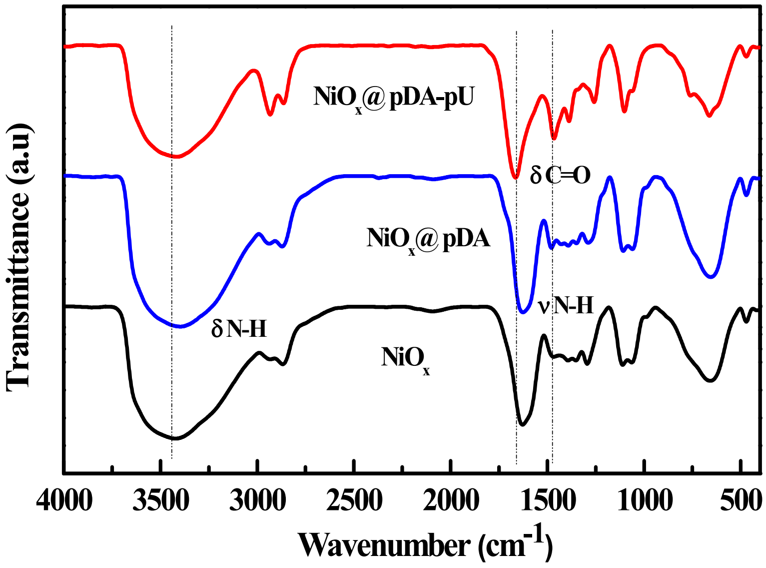


Figure S1: FTIR spectra of NiO$_x$, NiO$_x$@pDA and NiO$_x$@pDA-pU

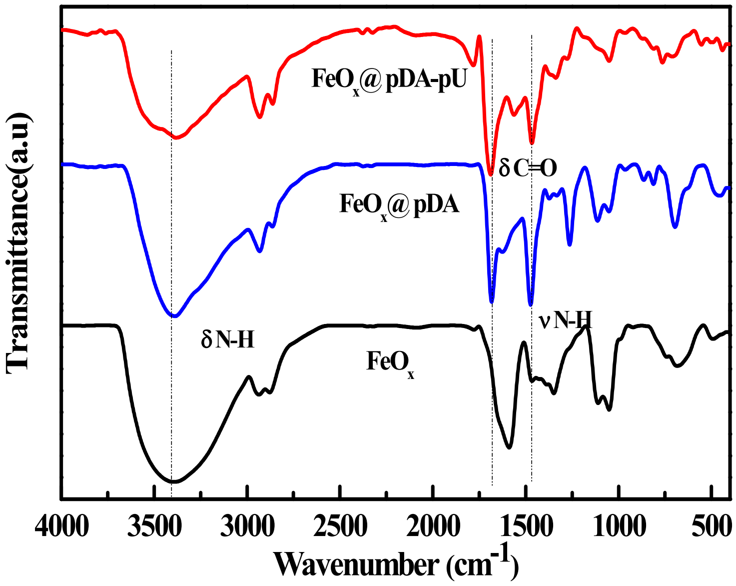


Figure S2: FTIR spectrum of FeO$_x$, FeO$_x$@pDA and FeO$_x$@pDA-pU

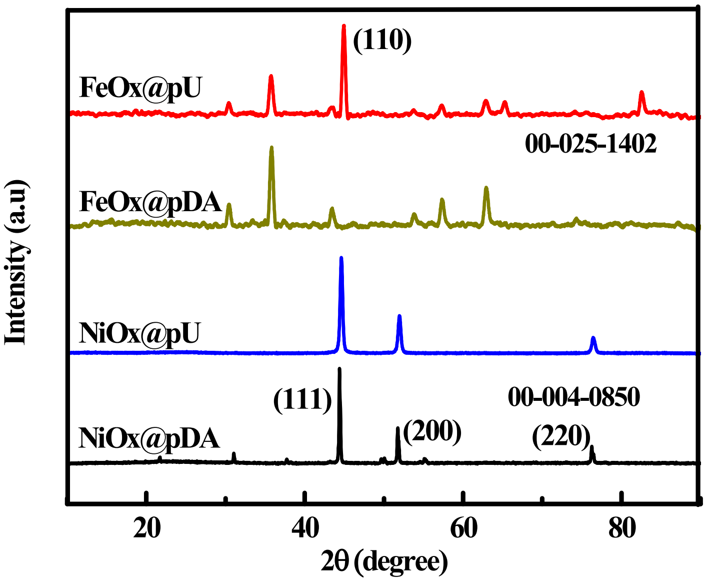


Figure S3: XRD of NiO$_x$@pDA, FeO$_x$@pDA and NiO$_x$@pDA, FeO$_x$@pU pyrolyzed at 800 ^{o}C

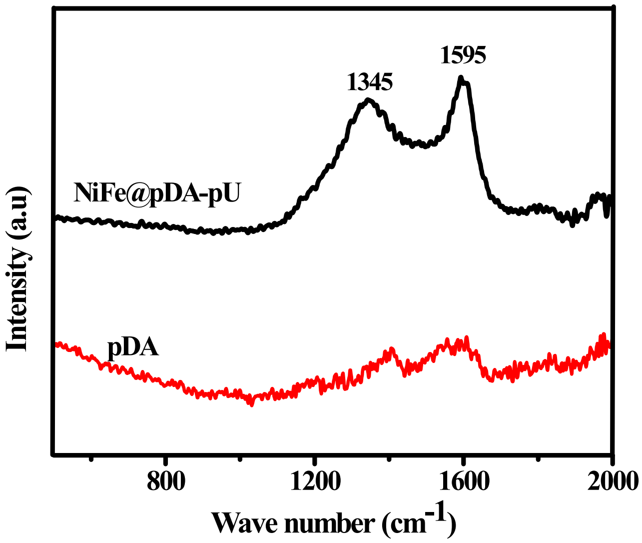


Figure S4: Raman spectra of pDA and Ni-Fe@pDA-pU

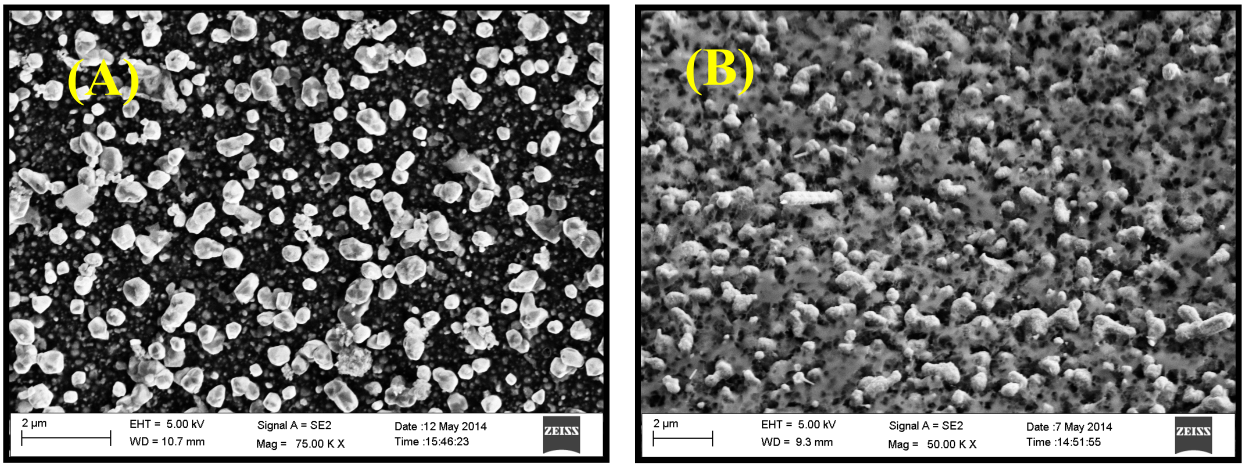


Figure S5: FE-SEM images of (A) Ni and (B) Fe monoliths

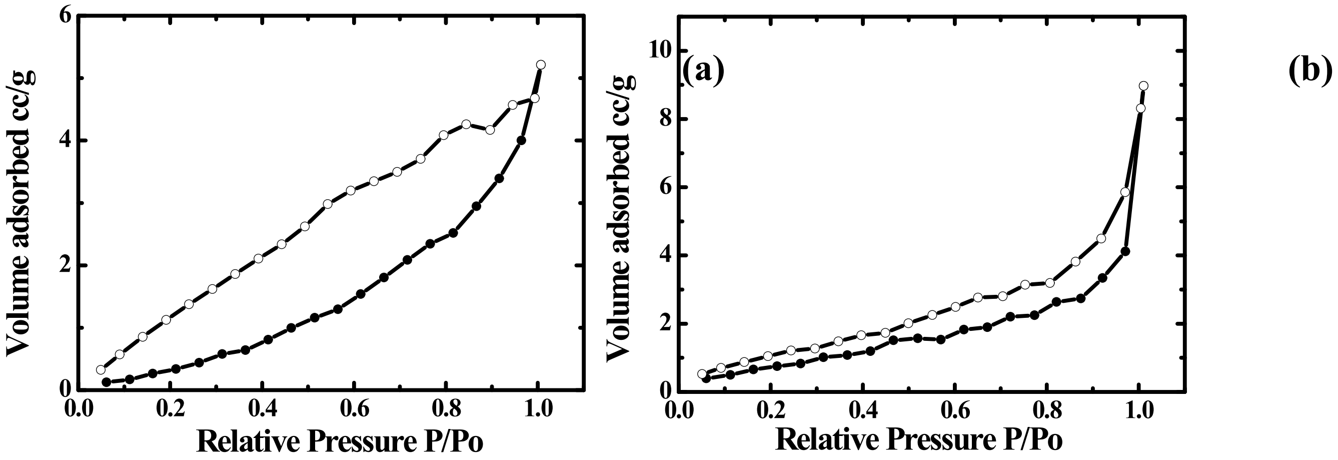


Figure S6: BET isotherms of (a) Ni- and (b) Fe-monoliths

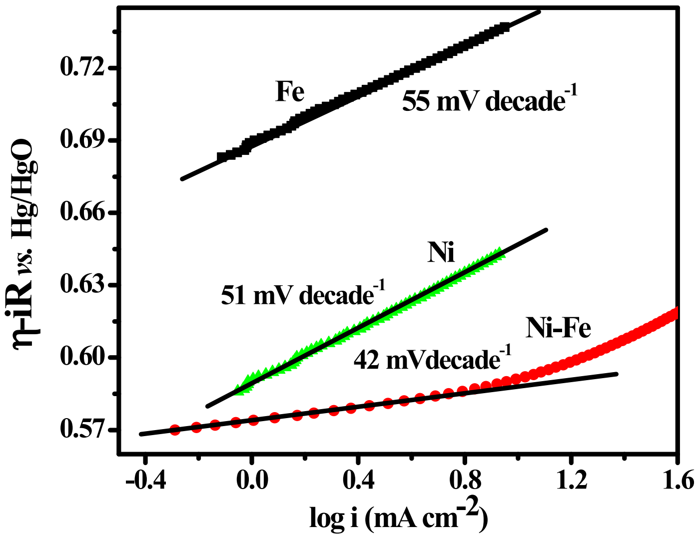


Figure S7: Tafel plots for monoliths of Fe, Ni, and Ni-Fe modified glassy carbon electrodes in 0.1 M KOH; Scan rate: 2 mV/s

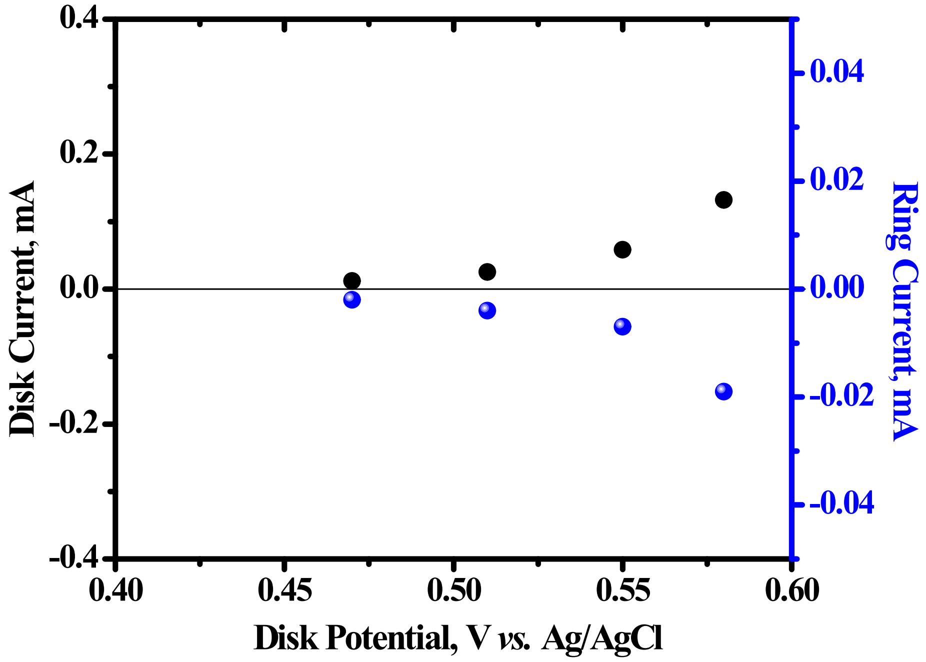


Figure S8: Determination of Faradaic efficiency of oxygen evolution reaction on Ni-Fe Monoliths [Disk current vs Disk potential (black); Ring Current vs Disk potential (blue)]

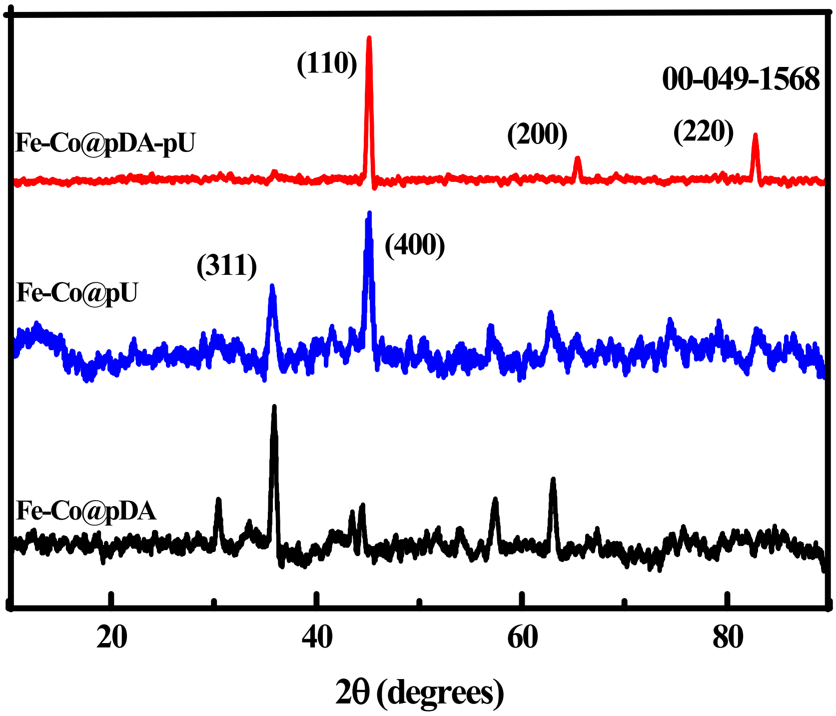


Figure S9: XRD of Fe-CoO$_x$@pDA, Fe-CoO$_x$@pU and Fe-Co@pDA-pU pyrolyzed at 800 °C

Table S1

Overpotential, Tafel slope and TOF comparison of Ni-Fe monolith-coated electrode§

Synthesis/materials	η, mV@ 10 mA cm^{-2}	Tafel slope (mV)	TOF, s^{-1}	Ref
Electrodeposited Ni-FeO$_x$	~300	~40	87$^{(a)}$	[S2]
Amorphous Ni-FeO$_x$ nanoparticles	280	32	0.21$^{(b)}$	[S4]
Ni-Fe LDH/CNT	300	35	0.56$^{(b)}$	[S5]
Ni-FeO$_x$ *(solution-cast)*	336	30	0.06$^{(b)}$	[S6]
Ni-Fe monoliths	375	42	125$^{(a)}$	this work

(a) TOF$_{max}$, by taking the measured surface area of a film and calculating the number of Ni atoms at the surface using a value of 6.4×10^{14} Ni atoms per cm^2 area

(b) Based on the calculation of the number of nickel atoms in the film to be active for OER (TOF$_{min}$ lower bound), using elemental analysis

§ **Note**: A value of η = 350 mV@10 mAcm^{-2} for the electrodeposited NiFeO$_x$ for OER in 1.0M KOH solution has been benchmarked by Jaramillo's group [*C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, J. Am. Chem. Soc., 2013, 135, 16977*]. To the knowledge of the authors, no work has been reported for OER using NiFe alloy thus precluding the possibility of its comparison.

Table S2

Determination of TOF for Ni-Fe monolith catalyst for OER

Methods	Procedure	Formula	TOF (s^{-1})
Cyclic voltammetry	Calculating the surface area of the film to get the number of Ni atoms of the surface using 6.4×10^{14} Ni atoms per cm^2 area	$\frac{i \times N_A}{4FN_{atoms}}$	125 (TOF_{max})
RRDE	Calculating the number of moles of active metals drop casted on the electrode	$\frac{i_{ring}}{4 \times F \times N_{CL} \times m}$	1.47

where, I, N_A N_{atoms}, F represent the current obtained at 700mV, Avogadro number, number of atoms at the surface and Faraday constant respectively. TOF_{max} can be estimated by taking the measured surface area of a film and computing the number of Ni atoms on the surface using a value of6.4×10^{14} Ni atoms per cm^2. i_{ring} = ring current, N_{CL} = collection efficiency of ring electrode and m = number of moles of active metals (drop-cast on the electrode surface).

References

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