Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ultrathin Trimetallic Metal-Organic Frameworks Nanosheets for Highly Efficient Oxygen Evolution Reaction

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Experimental Section

Synthesis of Ni-ZIF:

Ni foam (2×3 cm) soaked in 3 M HCl for 30 minutes with ultrasonic cleaning, then washed with absolute ethanol and deionized water for 10 min, respectively. The synthesis of Ni-ZIF was based on a previous procedure. Typically, $C_4H_6N_2$ (4 mmol, 330 mg) and $Ni(NO_3)_2{\cdot}6H_2O$ (1 mmol, 290 mg) were added to 17.5 mL methanol, repectively. An aqueous solution containing $C_4H_6N_2$ was quickly added into the aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$, and the mixture was transferred into a 50 mL Teflon-lined autoclave with Ni foam. Then, the autoclave was sealed and maintained at 180 °C for 6 h in an oven. The sample was then taken out, cleaned with deionized water, and dried overnight.

Synthesis of NiFe-ZIF:

The preparation process of pure NiFe-ZIF was same as that of Ni-ZIF, except that using different molar ratios of Ni(NO3)2·6H2O ((0.91 mmol, 0.83 mmol and 0.77 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.09 mmol, 0.17 mmol and 0.23 mmol) at the beginning.

Synthesis of NiFeCo-ZIF:

NiFeCo-ZIF have the same preparation process with Ni-ZIF except using different molar ratios of $Co(NO_3)_2$ (0.017 mmol, 0.034 mmol, 0.051 mmol and 0.068 mmol).

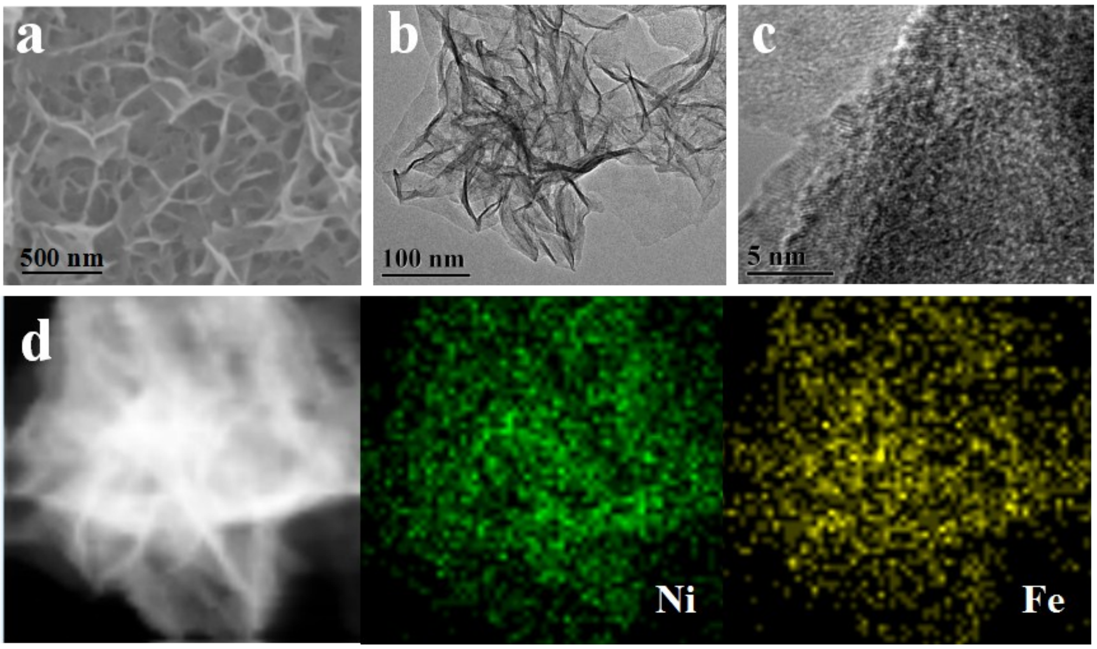

Figure S1 a) SEM, b) TEM, c) HRTEM and d) mapping images of $NiFe_{0.2}$-ZIF.

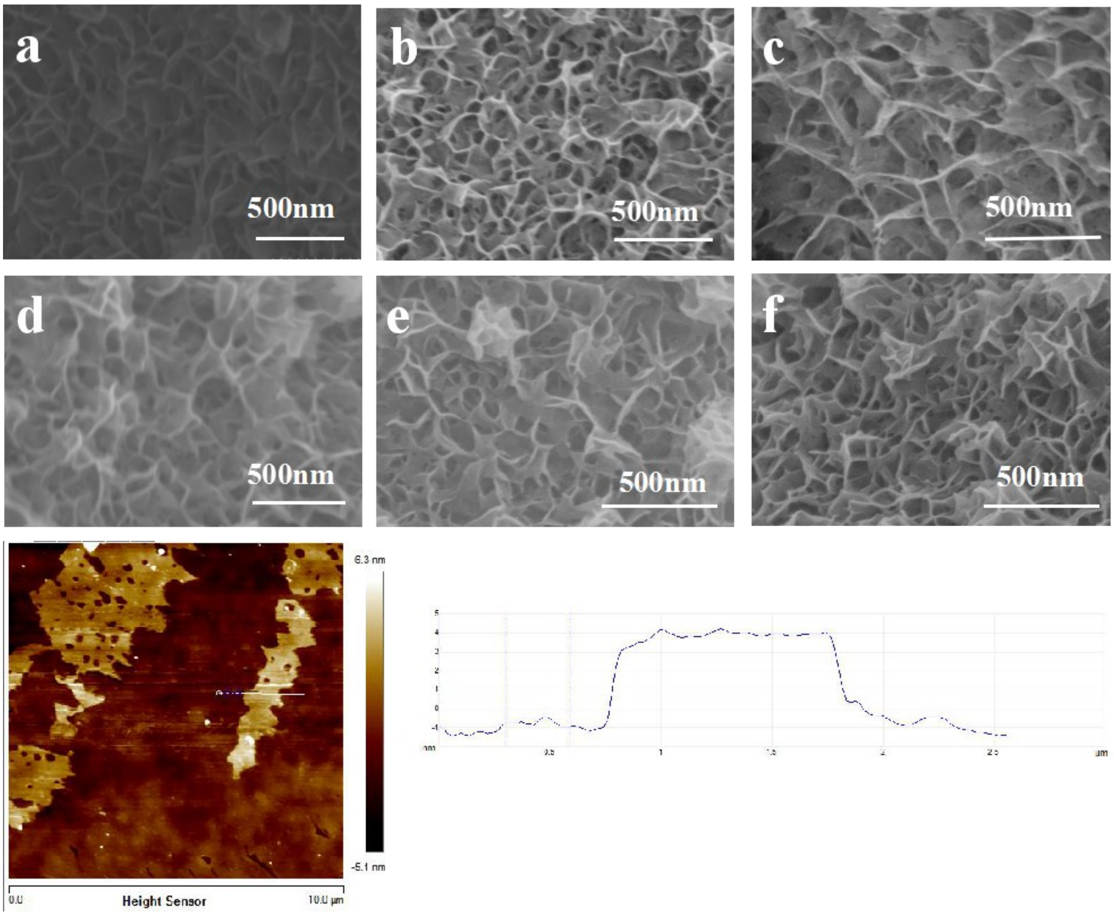

Figure S2 SEM of a) Ni-ZIF, b) $NiFe_{0.1}$-ZIF, c) $NiFe_{0.3}$-ZIF, d) $NiFe_{0.2}Co_{0.1}$-ZIF, e) $NiFe_{0.2}Co_{0.2}$-ZIF, f) $NiFe_{0.2}Co_{0.4}$-ZIF and e) AFM image of $NiFe_{0.2}Co_{0.3}$-ZIF.

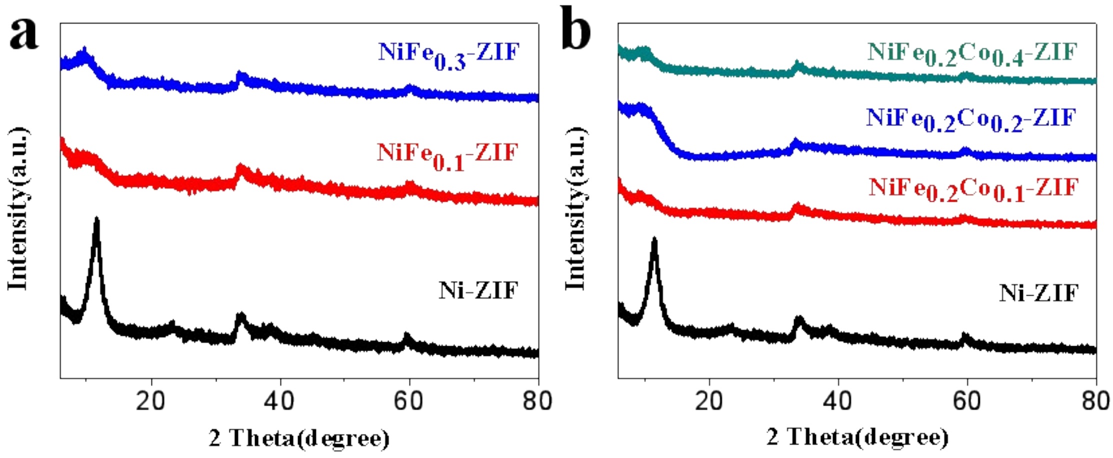

Figure S3 XRD patterns of a) Ni-ZIF, $NiFe_{0.1}$-ZIF and $NiFe_{0.3}$-ZIF, b) Ni-ZIF, $NiFe_{0.2}Co_{0.1}$-ZIF, $NiFe_{0.2}Co_{0.2}$-ZIF and $NiFe_{0.2}Co_{0.4}$-ZIF.

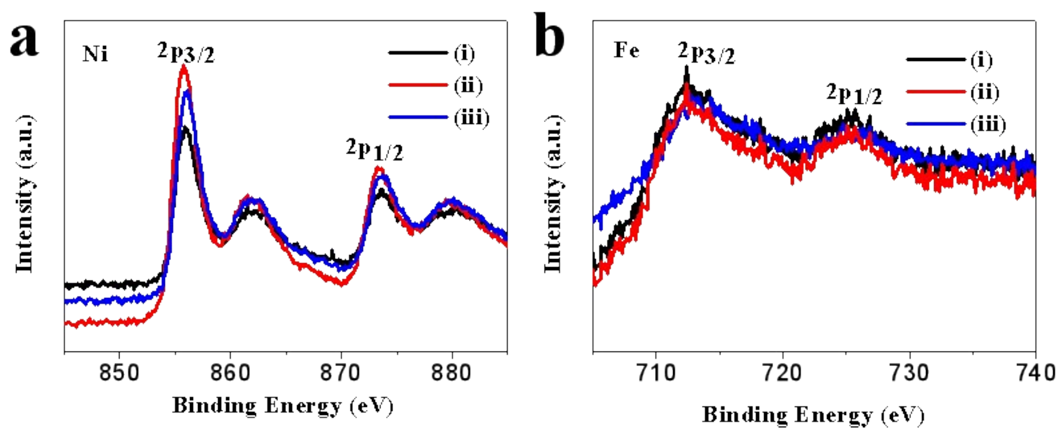

Figure S4 XPS spectra of a) Ni and b) Fe of Ni-ZIF (i), $NiFe_{0.1}$-ZIF (ii) and $NiFe_{0.3}$-ZIF (iii).

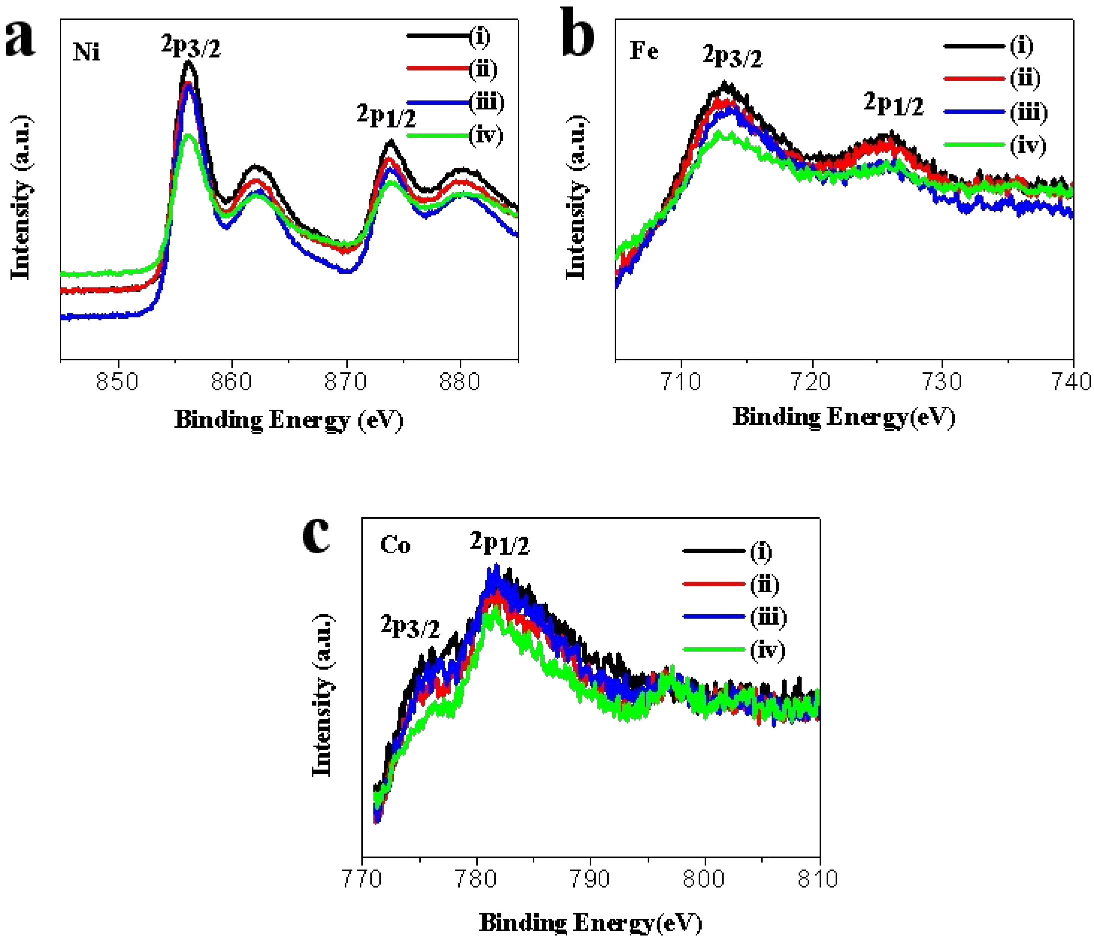

Figure S5 XPS spectra of a) Ni, b) Fe and c) Co of $NiFe_{0.2}Co_{0.1}$-ZIF (i), $NiFe_{0.2}Co_{0.2}$-ZIF (ii), $NiFe_{0.2}Co_{0.3}$-ZIF (iii) and $NiFe_{0.2}Co_{0.4}$-ZIF (iv).

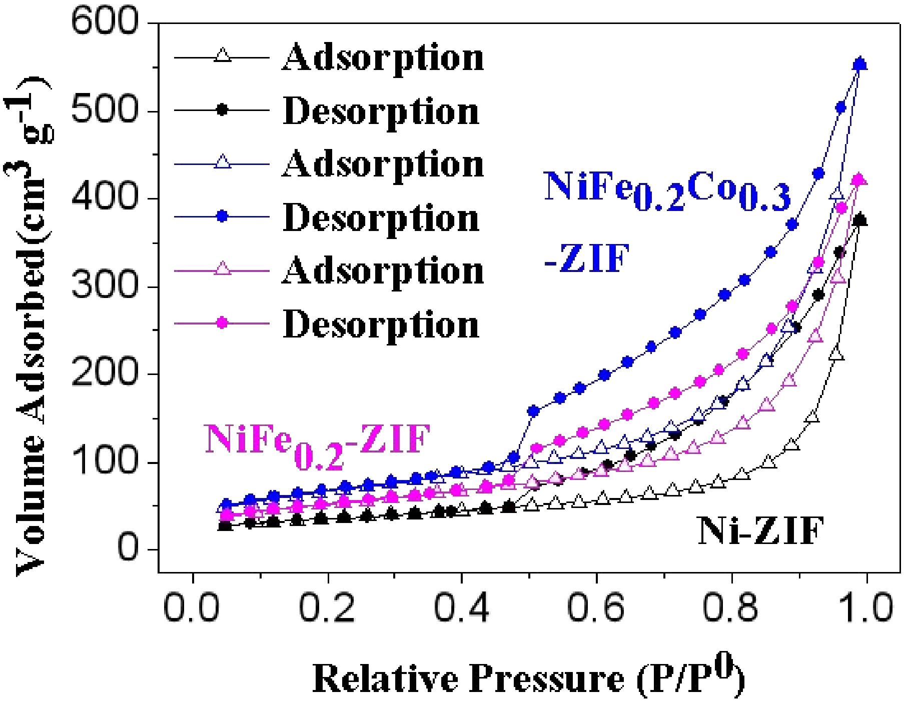

Figure S6 N_2 adsorption-desorption isotherms of the as-prepared of Ni-ZIF, $NiFe_{0.2}$-ZIF, $NiFe_{0.2}Co_{0.3}$-ZIF.

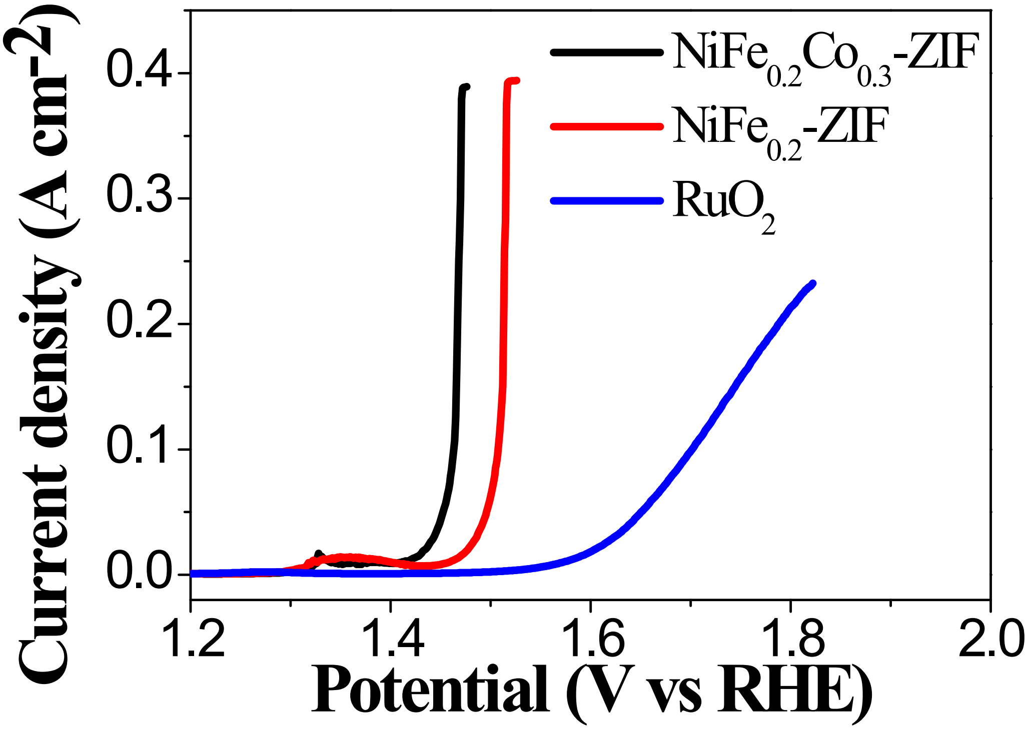

Figure S7 LSV of $NiFe_{0.2}$-ZIF, $NiFe_{0.2}Co_{o.3}$-ZIF and RuO_2

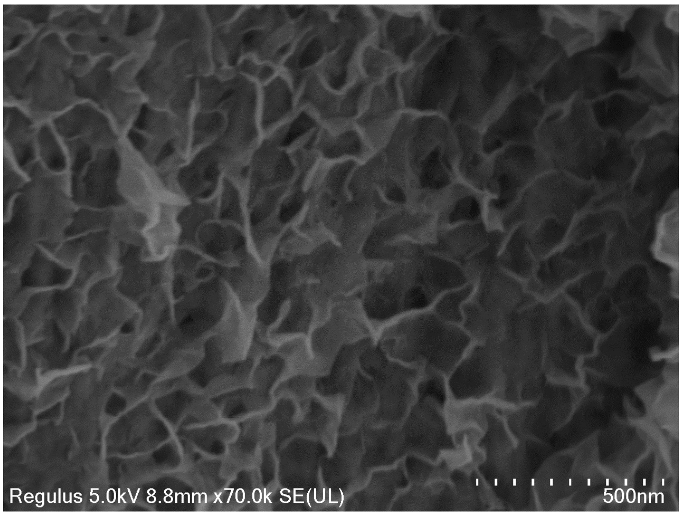

Figure S8 SEM of $NiFe_{0.2}Co_{o.3}$-ZIF after OER test.

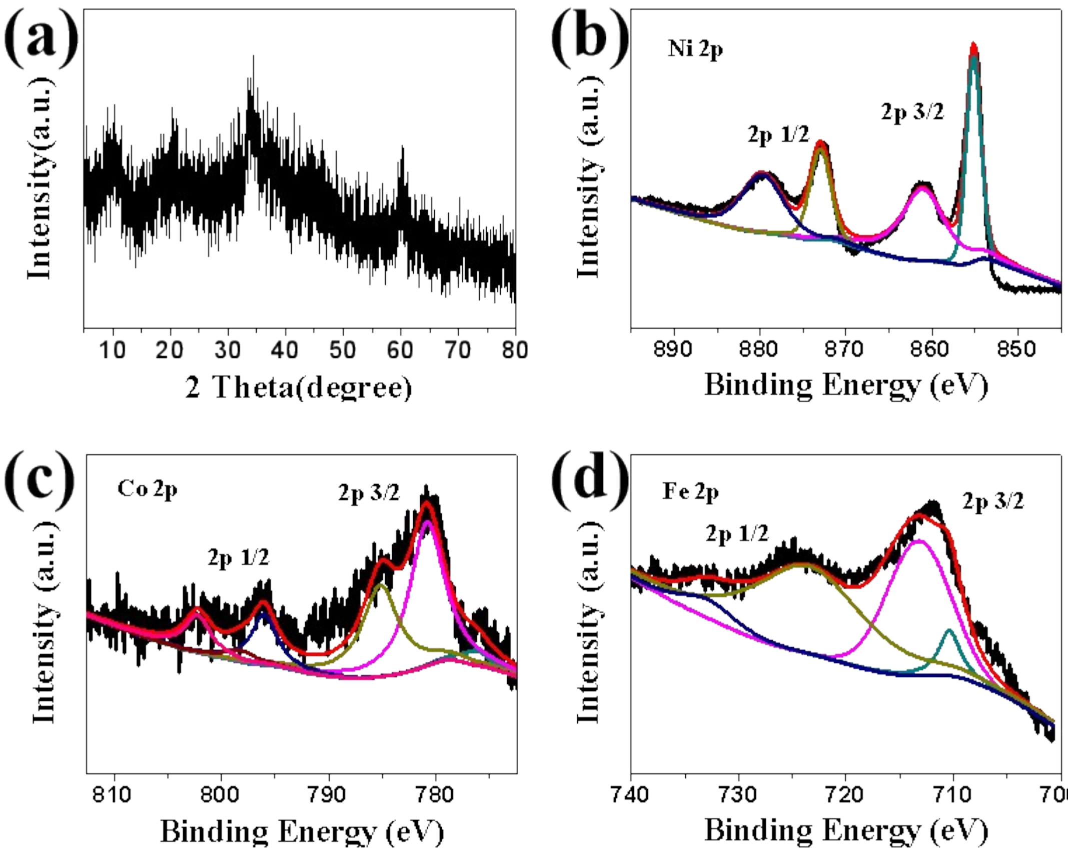

Figure S9 a) SEM, b) Ni 2p, c) Co 2p, d) Fe 2p of $NiFe_{0.2}Co_{0.3}$-ZIF after OER test.

	Single metal	Bimetallic			Trimetallic			
	Ni-ZIF	$NiFe_{0.1}$-ZIF	$NiFe_{0.2}$-ZIF	$NiFe_{0.3}$-ZIF	$NiFe_{0.2}Co_{0.1}$-ZIF	$NiFe_{0.2}Co_{0.2}$-ZIF	$NiFe_{0.2}Co_{0.3}$-ZIF	$NiFe_{0.2}Co_{0.4}$-ZIF
Overpotential (mV)	469	285	259	273	252	234	216	240
Tafel slope ($mV\cdot dec^{-1}$)	187	51.02	47	43.75	39.47	36.45	23.25	38.26

Table S1 OER performance of trimetallic, bimetallic and single metal ZIF materials

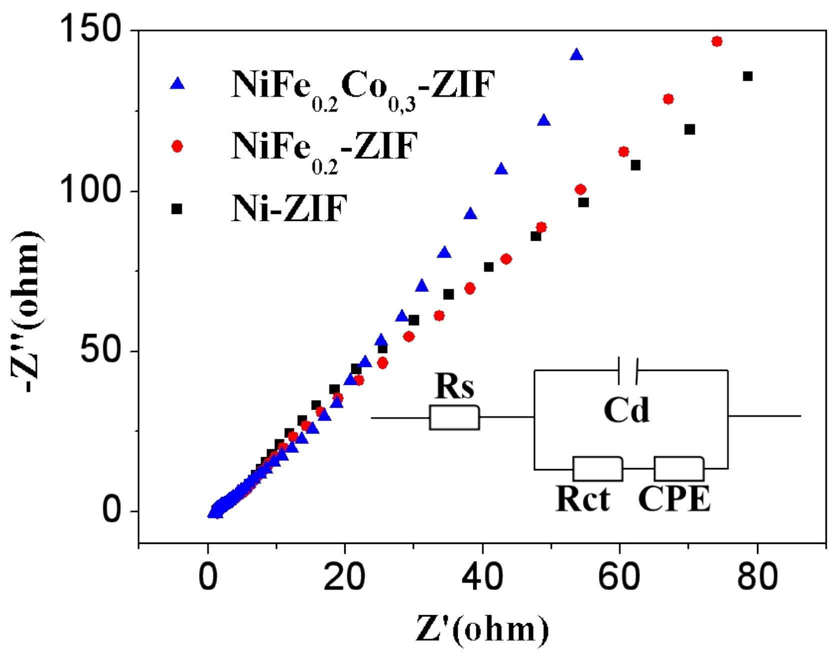

Figure S10 Nyquist plots of Ni-ZIF, $NiFe_{0.2}$-ZIF, $NiFe_{0.2}Co_{0.3}$-ZIF catalyst, insert shows the equivalent circuit model of the studied system

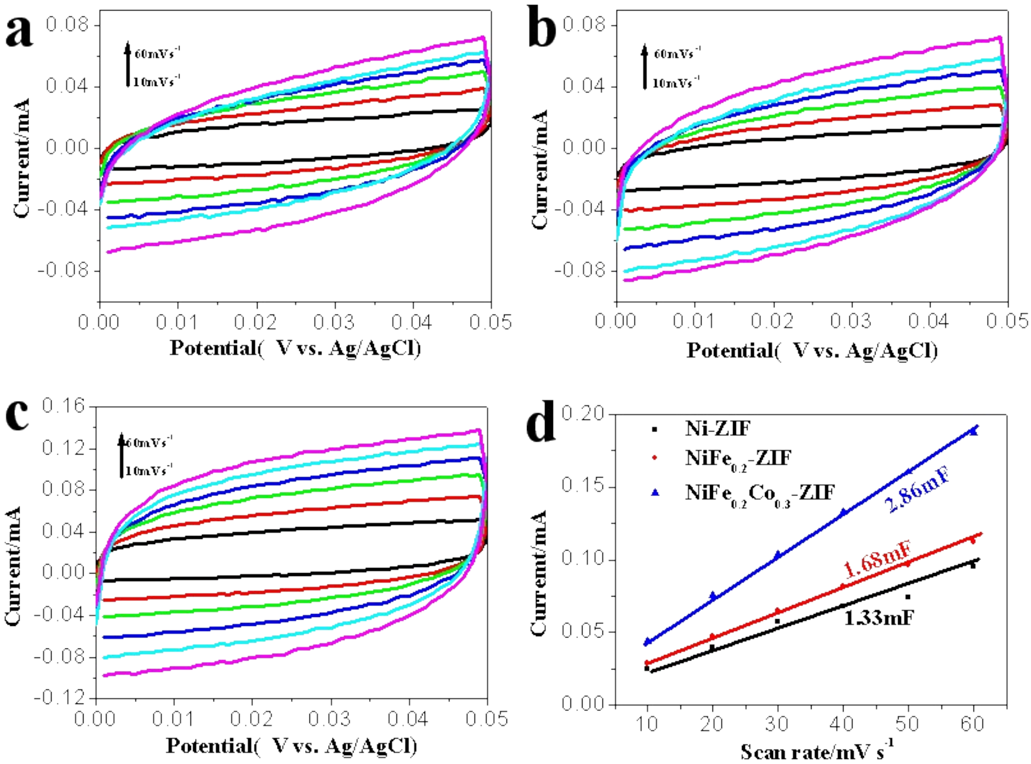

Figure S11 a), b) and c) CV curves at scan rates from 10 to 60 mV s^{-1} of the Ni-ZIF, $NiFe_{0.2}$-ZIF, $NiFe_{0.2}Co_{o.3}$-ZIF catalyst; d) Capacitive J versus scan rate for the as-prepared electrocatalysts. The linear slope, equivalent to the double-layer capacitance Cdl, was used to represent the ECSA.

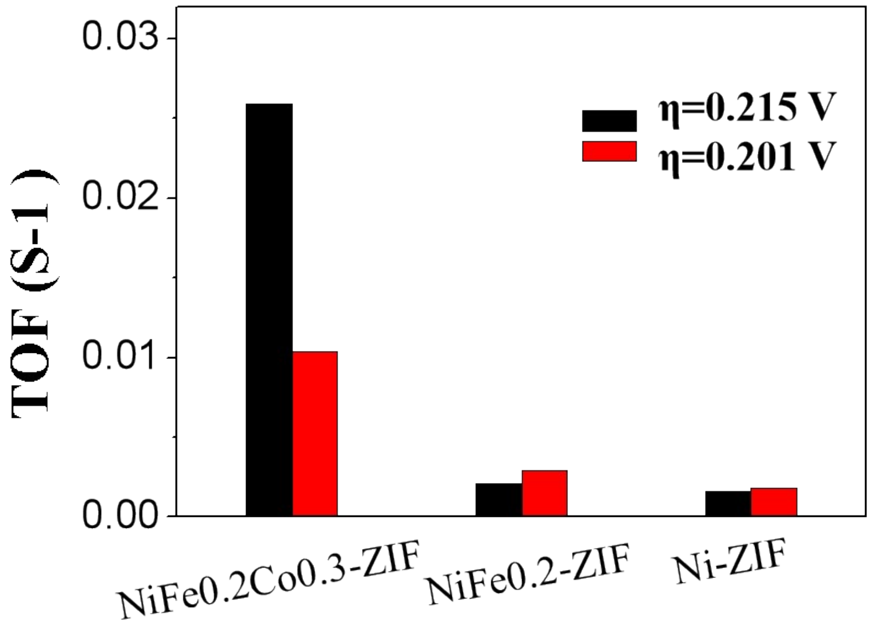

Figure S12 TOFs at η = 201 and 215 mV of Ni-ZIF, $NiFe_{0.2}$-ZIF, $NiFe_{0.2}Co_{0.3}$-ZIF catalyst.

Catalysts	Electrolyte	Overpotential (mV)	Tafel slope (mV·dec-1)	References
$NiFe_{0.2}$-ZIF/NF $NiFe_{0.2}Co_{0.3}$-ZIF/NF	1.0 M KOH	262@100 mA·cm^{-2} 216@100 mA·cm^{-2}	43.75 23.25	This work
MIL-53 (FeNi)/NF	1.0 M KOH	233@50 mA cm^{-2}	31.3	Adv Energy Mater. 2018, 1800584.
NiFe-UMNs	1.0 M KOH	260@10 mA cm^{-2}	30	Nano Energy. 2018, 44, 345-352.
NiFe-MOF-74	1.0 M KOH	223@10 mA cm^{-2}	76	Chem Commun (Camb) 2018.
Fe/Ni2.4/Co0.4-MIL-53/NF	1.0 M KOH	238@100 mA cm^{-2}	71.3	Angew. Chem. Int. Ed. 2018, 57, 1888-1892.
Ni-MOF@Fe-MOF	1.0 M KOH	265@10 mA cm^{-2}	82	Adv Funct Mater 2018, 1801554.
NNU-23	0.1 M KOH	365@10 mA cm^{-2}	77.2	Angew. Chem. Int. Ed. 2018, 57 (31), 9660-9664.
Fe−Co−P alloy	1.0 M KOH	252@10 mA cm^{-2}	30.7	Acs Nano 2018, 12 (1), 158-167.
Ni–Co–P hollow nanobricks	1.0 M KOH	270@10 mA cm^{-2}	76	Energy & Environmental Science 2018, 11 (4), 872-880.
(Ni,Fe)3Se4 ultrathin nanosheets	1.0 M KOH	225@10 mA cm^{-2}	41	Nanoscale 2018, 10 (11), 5163-5170.
NiCoFe-LDHs/NF	0.1 M KOH	200@40 mA cm^{-2}	78	J. Mater. Chem. A. 2016, 4, 7245-7250.
Co6.25Fe18.75Ni75Ox mesoporous nanosheet	1.0 M KOH	186@10 mA cm^{-2}	38.5	J Mater Chem A 2018, 6 (1), 167-178.

Table S2 Comparisons of OER performance for various metal-based and MOFs-based electrocatalysts.