

Electronic Supplementary Information for
Bimetal-organic framework MIL-53(Co-Fe): efficiency
and robust electrocatalyst for the oxygen evolution
reaction

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Experimental Section

Materials: All chemical reagents were analytically pure. Nickel foam (NF; area: 2 cm × 3 cm) was bought from Shenzhen Green and Creative Environmental Science and Technology Co., Ltd. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; Aladdin), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; Aladdin), terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, TPA; Aladdin), hydrochloric acid (HCl; Aladdin), N,N-dimethylformamide (DMF; Beijing Chemical), ethanol and deionized water were used.

Preparation of MIL-53(Co)/NF and MIL-53(Fe)/NF: 0.1369 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.498 g of TPA were first added to 35 mL of DMF, and after stirring uniformly, 2.5 mL of ethanol and 2.5 mL of water were added. This was stirred vigorously for half an hour and rapidly transferred into a 50 ml autoclave. Then, fresh NF (2 × 3 cm) was infused in the homogeneous solution. The autoclave was kept at the temperature of 125°C for 12 h in one electric oven and then naturally cooled to ambient temperature. The material was removed, rinsed several times with deionized water, and dried in a vacuum oven at 60°C. MIL-53(Fe)/NF prepared in a similar method by replace 0.1369 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with 0.1352 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Preparation of MIL-53(Co-Fe)/NF: 0.1369g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1352 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.498 g of TPA were added to 35 mL DMF, stirred for 45 min at the room temperature. This was stirred vigorously for half an hour and rapidly transferred into a 50 ml autoclave. Then, fresh NF (2 × 3 cm) was infused in the homogeneous solution. Solution was put in one Teflon-lined stainless autoclave and reacted at the temperature of 125°C for 12 h with a piece of pretreated NF. After cooling, this was rinsed for a few times with deionized water and dried at the temperature of 60°C.

Characterizations: A LabX XRD-6100 X-ray diffractometer with Cu $K\alpha$ radiation (40 kV, 30 mA) of 0.154 nm wavelength (Shimadzu, Japan) was used to acquire XRD data. An XL30 ESEM FEG scanning electron microscope (SEM) was used to obtain measurements at a 20 kV accelerating voltage. An ESCALABMK II X-ray photoelectron spectrometer using Mg was used to acquire XPS spectra. The potassium

bromide pellet method was used with an FTIR spectrometer (Nicolet-6700) to obtain spectra at an ambient temperature.

Electrochemical measurements: Electrochemical performance was measured using a CHI 660E electrochemical analyzer. The working electrode is MIL-53(Co-Fe)/NF, the counter electrode is graphite plate, and Hg/HgO electrode is used as the reference. Each potential was reported as one form of reversible hydrogen electrode (RHE), calculated as follows: $E(\text{RHE}) = E(\text{Hg/HgO}) + (0.098 + 0.059 \text{ pH}) \text{ V}$.

Electrochemical active surface area (ECSA): The electrochemical active surface area (ECSA) of the catalyst was estimated from the double-layer capacitance (C_{dl}). Therefore, the electrochemical capacitance was evaluated via cyclic voltammetry in the potential range of 1.32-1.42 V vs. RHE. Each CV segment was swept four times at each scan rate (10, 20, 30, 40, 50, 60 mV s⁻¹).¹

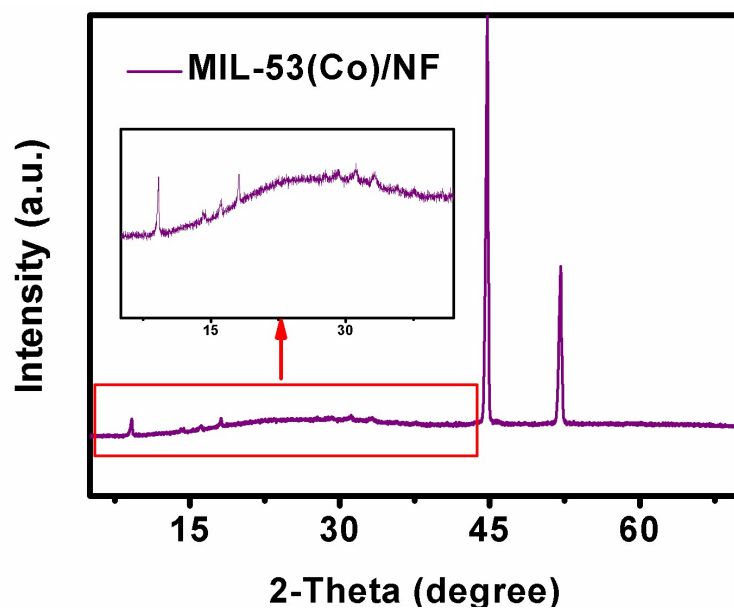


Figure S1. XRD pattern for MIL-53 (Co)/NF.

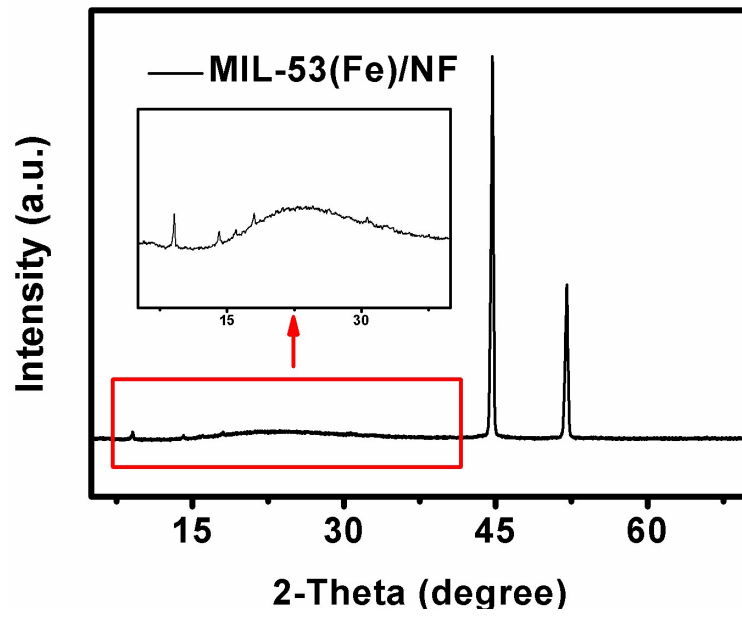


Figure S2. XRD pattern for MIL-53 (Fe)/NF.

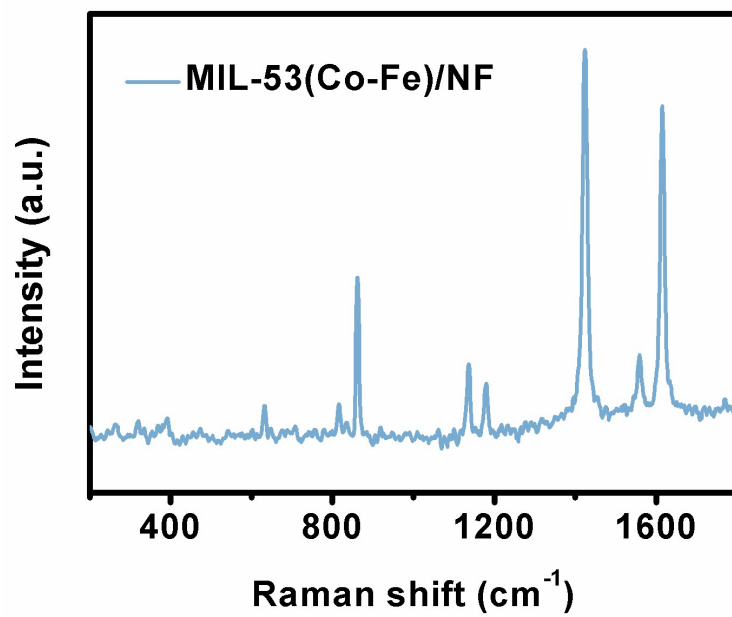


Figure S3. Raman spectrum for MIL-53 (Co-Fe)/NF.

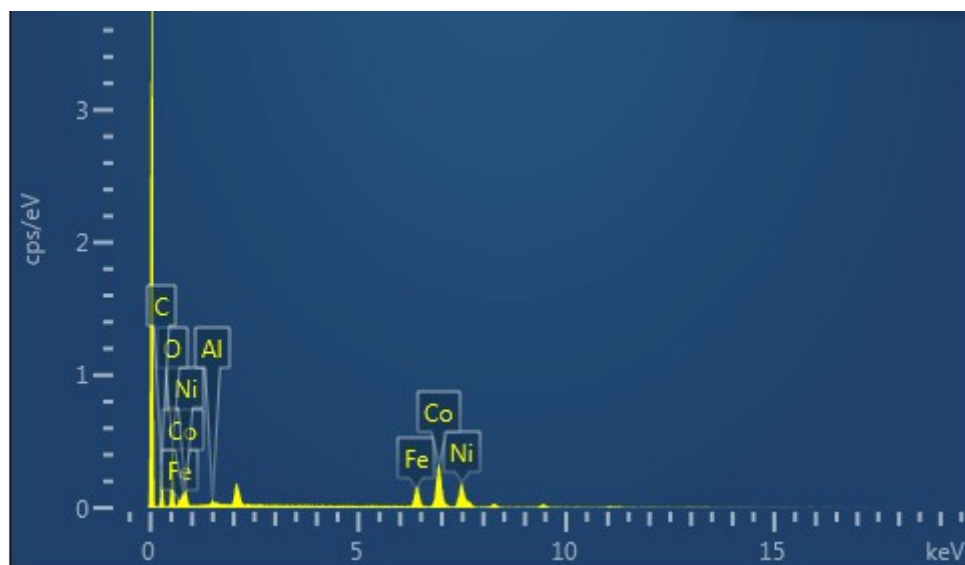


Figure S4. EDX spectrum of MIL-53 (Co-Fe)/NF.

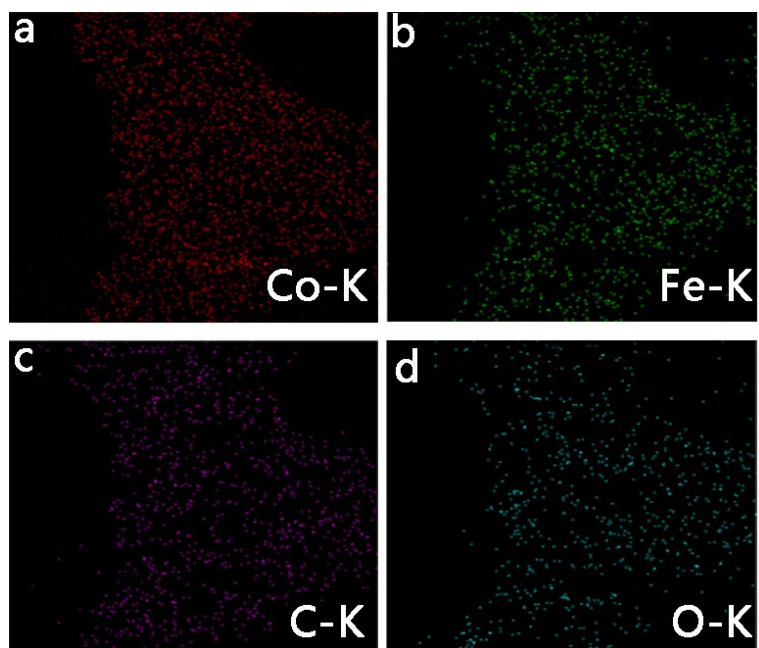


Figure S5. Elemental mappings for MIL-53 (Co-Fe)/NF.

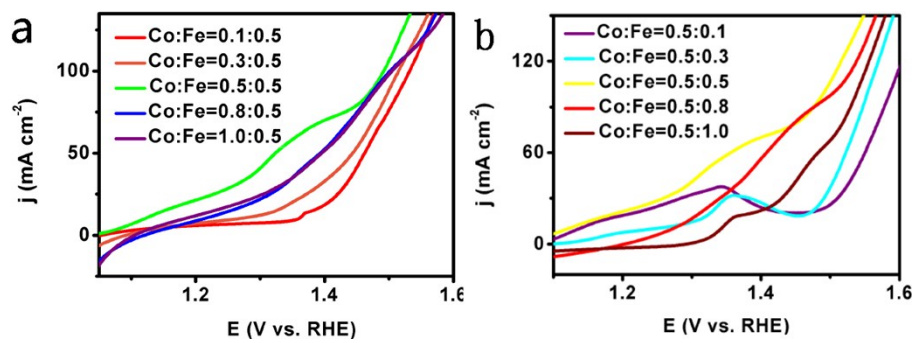


Figure S6. LSV curves of MIL-53(Co-Fe)/NF with different mole ratios of Co/Fe.

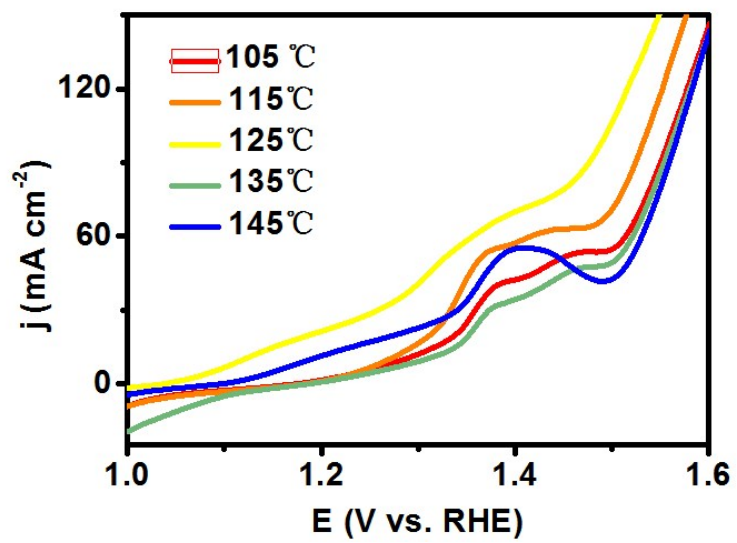


Figure S7. LSV curves of MIL-53(Co-Fe)/NF with different solvothermal temperature.

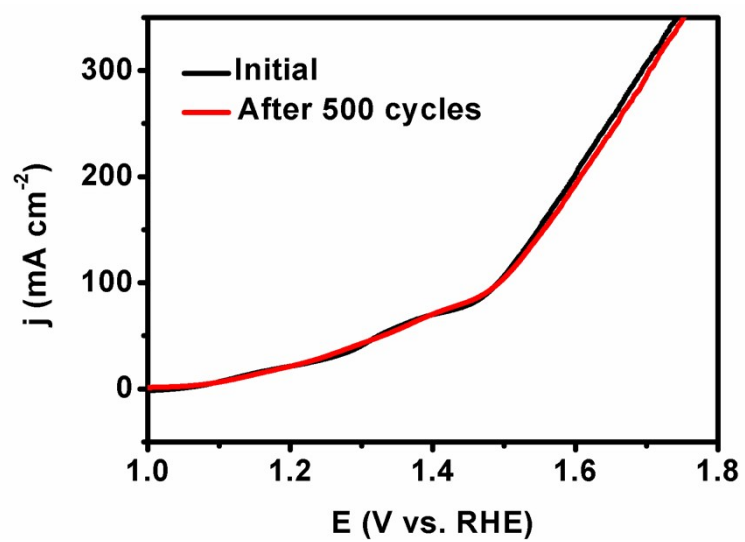


Figure S8. LSV curves recorded for MIL-53(Co-Fe)/NF before and after 500 cyclic voltammetry in 1.0 M KOH for OER.

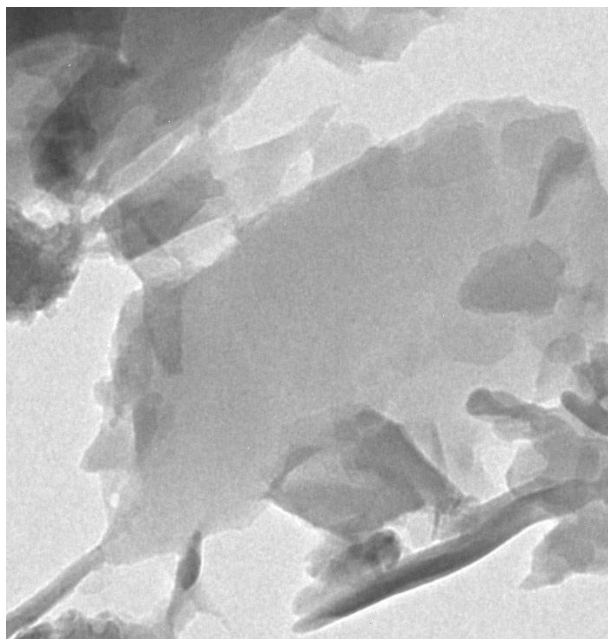


Figure S9. HRTEM after stability test of MIL-53 (Co-Fe)/NF.

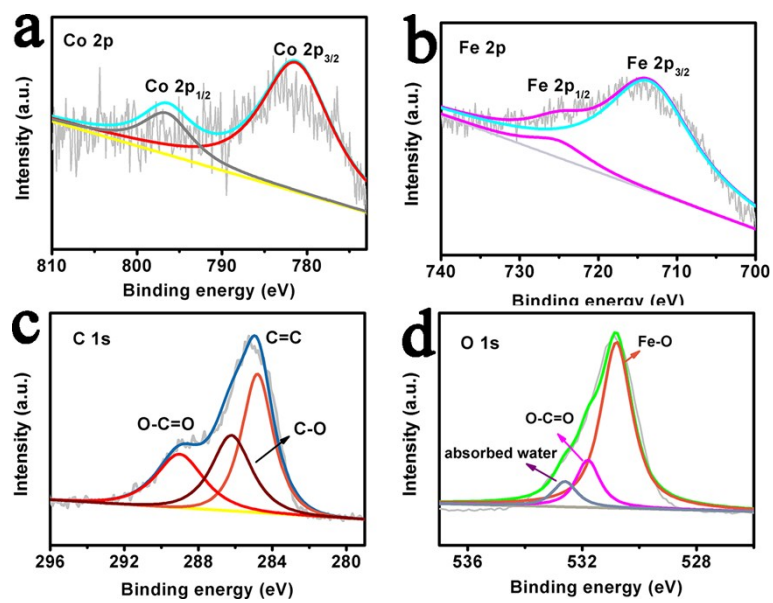


Figure S10. XPS analysis after stability testing after stability test of MIL-53 (Co-Fe)/NF.

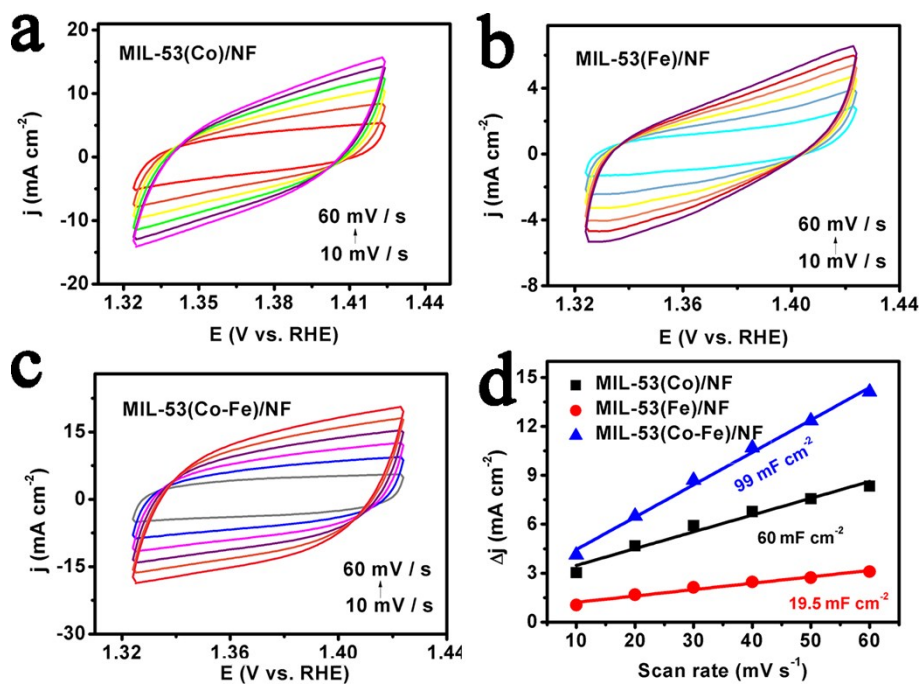


Figure S11. Cyclic voltammograms collected at various scan rates (10, 20, 30, 40 and 50 mV s⁻¹) for (a) MIL-53(Co)/NF, (b) MIL-53(Fe)/NF and (c) MIL-53(Co-Fe)/NF in 1.0 M KOH. (d) The difference (Δj) between capacitive currents as a function of scan rates for MIL-53(Co)/NF, MIL-53(Fe)/NF and MIL-53(Co-Fe)/NF.

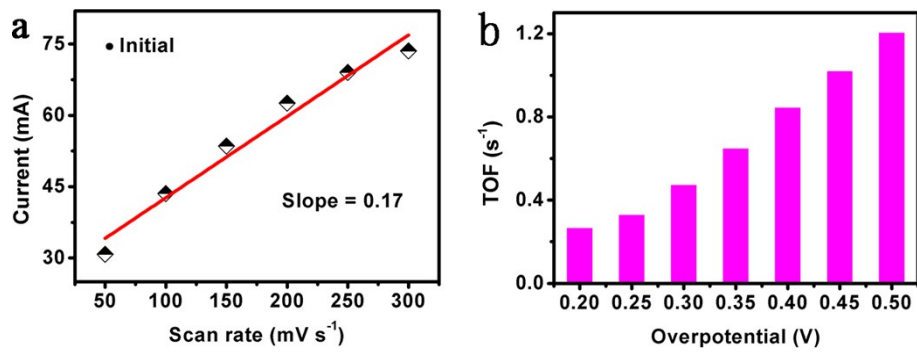


Figure S12. (a) Plot of oxidation peak current versus the scan rate from CVs. (b) TOF of MIL-53(Co-Fe)/NF at various overpotential.

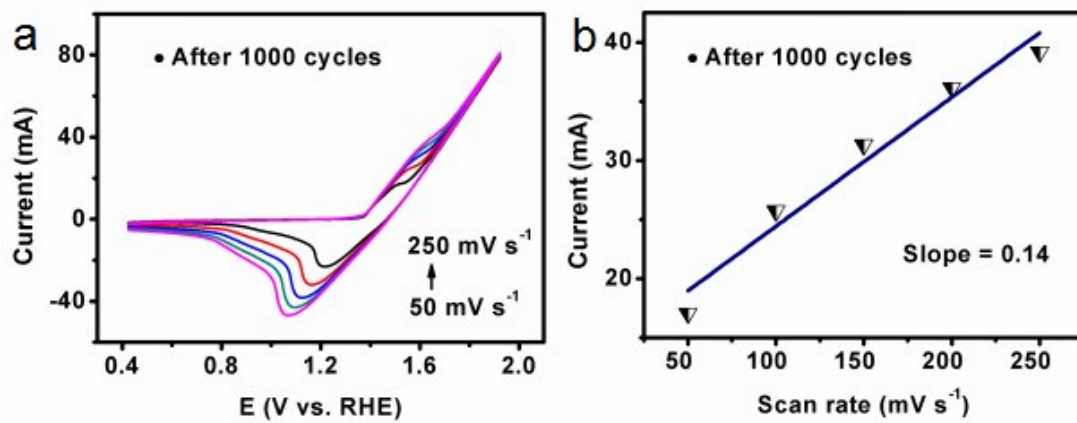


Figure S13. Plot of oxidation peak current versus the scan rate from CVs.

Table S1. Comparison of catalytic performance for MIL-53(Co-Fe)/NF with other reported OECs.

Catalyst	j (mA cm ⁻²)	η (mV)	Electrolyte	Ref.
MIL-53(Co-Fe)/NF	100	262	1.0 M KOH	This work
MIL-53(Co)/NF	50	281	1.0 M KOH	
MIL-53(Fe)/NF	50	320	1.0 M KOH	
CoFeLDHs	10	233	1.0 M KOH	2
Co-CuO	100	330	1.0 M KOH	3
CoO-vac	10	306	1.0 M KOH	4
NiFeCrLDH	25	225	1.0 M KOH	5
CoOOH	10	266	1.0 M KOH	6
Au/NiFe LDH	10	237	1.0 M KOH	7
NiFe LDH	10	263	1.0 M KOH	
CTGU-10c2	10	240	1.0 M KOH	8
CuFe ₂ O ₄	10	367	1.0 M KOH	9
CoFe ₂ O ₄	10	414	0.1 M KOH	
NiFe ₂ O ₄	10	433	0.1 M KOH	
Co _{0.15} Fe _{0.85} N _{0.5} NSs	10	266	1.0 M KOH	10
Ni ₁₄ O ₁₃ /NiFe LDH	30	205	1.0 M KOH	11
Ni-BDC/Ni(OH) ₂	82.5	370	1.0 M KOH	12

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