Green Combustion Synthesis of Co3O4-CoO Heterostructures for Efficient Alkaline Oxygen Evolution Reaction

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S1-I. Experimental section

1.1. Chemicals

Cobalt nitrate hexahydrate [Co $(NO_3)_2.6\ H_2O$] were purchased from HIMEDIA and Pomegranate (Punica granatum) peels were collected from a local fruit market. All chemicals were directly used as received without further purification. Ethanol, DI water was used throughout this work.

1.2. Electrocatalytic characterization

The catalytic performances of the electrodes for water oxidation were studied using three electrode configurations connected to Biologic Electrochemical Workstation SP-200 potentiostat at room temperature. The CoOPE-600 on glassy carbon electrode and on nickel foam (NF) were used as the working electrodes. The Ag/AgCl (sat. KCl) electrode and Pt wire were used as the reference and counter electrodes. The working NF electrode was washed with 1.0 M HCl to remove oxide layer on the nickel surface, then washed with water and acetone and dried. To prepare catalyst ink, 4.0 mg of the as-prepared CoOPE-600, CoOPE-500, CoOPE-400 and Co_3O_4-600 electrocatalyst, and 30 μL Nafion (5 wt%) was evenly dispersed in 0.5 mL of propanol, and then the as-obtained solution was treated with ultrasound for 20 min. Commercially available catalyst (IrO_2) and bare NF was used. About 1.0 mg/ml of commercial IrO_2 suspension was prepared by following the similar methodology for comparison and bare NF was used directly. The slurry was drop casting on a precleaned NF electrode and the electrode was allowed to dry at 70°C before measurement (catalyst loading 0.5 mg cm^{-2}). The freshly synthesized catalyst and commercial IrO_2 catalyst have been used directly as working electrode without further treatment. All measurements were carried out in 1.0 M KOH (aq). The OER activities of CoOPE-600 have been analyzed by OER polarization curves (LSV), electrochemical impedance spectroscopy (EIS) and Chronopotentiometry. The OER activity of the catalyst have been made by linear sweep voltammetry (LSV) on NF electrode (scan rate: 10 mV s^{-1}). The impedance of electrocatalyst was measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 100 kHz to 100 mHz with sinusoidal perturbation amplitude of 0.5 V. Here, the turnover frequency (TOF) rate of evolved molecular O_2 per surface active site per second can be calculated. The overpotential used for the calculation of TOF was set at potential of 1.6 V vs RHE. The TOF can be calculated using the equation TOF = [J * A / 4 * f * m] where, J- Current density, A- Area, F- Faraday Constant, m-the number of moles in catalyst.

1.3. Physical characterization

X-ray diffraction (XRD) of CoOPE-600 were recorded with Thermo XRD equinox 1000. The morphology of CoOPE-600 was determined by using JEOLJSM- IT 200 Field emission scanning electron microscope (FE-SEM) operated at 20 kV. JEM-2100 Plus was used to record High resolution transmission electron microscopy (HR-TEM) image of the CoOPE-600 and selected area electron diffraction (SAED) pattern also taken from JOEL, JEM-2100 Plus. The elemental composition of CoOPE-600 was analysed by XPS (X-ray photoelectron spectroscopy) with KALPHA SURFACE ANALYSIS spectrometer.

SI-II. Calculations

SI.C1. Calculation of oxygen vacancy (Ov %)

Determination of oxygen vacancy percentage from XPS analysis of O1s spectra

$O_v / (O_v + O_L + O_{H2O})$ Where, $O_V = 96406.81$, $O_L = 33186.25$ and $O_{H2O} = 112230.42$

SI. C2. Calculation of Overpotential (η)

The overpotential (η) was determined according to the formula: $\eta\ (V) = E\ (RHE) - 1.23\ V$

SI. C3. Tafel equation

$\eta = a + b \log J$, where η -overpotential (V vs. RHE), b -Tafel slope, and j- corresponding current density (mA /cm^2) as well as Tafel constant

SI. C4. Calculation of ECSA

The calculations of ECSA and roughness factor (RF) are based on the following equation: ECSA= C_{dl} / C_s; RF=ECSA/GSA, where C_{dl} - double layer capacitance of catalyst in 1.0 M KOH (mF) and C_s - specific capacitance of the catalyst ($C_s = 0.04$ mF cm^{-2} in 1.0 M KOH). In eq, RF - roughness factor and GSA - geometric surface area of the material.

SI.C5. Determination of Mass activity

Mass activity (A g^{-1}) is another quantitative parameter which defines the catalytic activity of a catalyst in terms of the current produced at a specific overpotential in ampere per 1 g of the catalyst (Current normalized by the loaded mass of the catalyst).

Mass activity = Current/ unit loading mass of electrocatalyst (A $g^{-1}_{catalyst}$ at a given potential)

SI. C6. Calculation of exchange current density

The exchange current (j_0) is another metric that is often used to estimate the intrinsic electrocatalytic performance. It corresponds to the current exchanged across the interface of the electrode at η = 0 V. As no overpotential is applied, the value of i_0 strongly depends on the reaction activation energy at the surface of the electrocatalyst. The exchange current is, however, only meaningful when normalized to the active surface area of the catalyst on the electrode, making the estimation of the absolute value of exchange current density complicated. The normalized exchange current density $j_0 = i_0/A_{Geom}$ x ECSA).

SI. C7. Determination of Energy of activation

With the CVs results, we can obtain the apparent activation energy (E_a) calculated using the Arrhenius equation: ln j = -Ea/RT +b, where j- current density, R-gas constant, T-Temperature and b-slope.

SI.C8. Faradaic efficiency determination from RRDE

In order to evaluate the faradaic efficiency and reaction mechanism of CoOPE-600 catalyst for OER, rotating ring-disk electrode (RRDE) voltammograms were carried out based on a glassy carbon disk electrode and Pt ring electrode. The CoOPE-600 catalyst, as prepared, was coated onto RRDE by following the procedure described above. The Faradaic Efficiency for CoOPE-600 in OER process was calculated by using Rotating Ring-Disk (RRD) technique as follows:

Ring current (I_{ring}) = 0.0378 mA

Disc current (I_{disc}) = 0.1594 mA

Collection Efficiency (N) = 0.245 (The Collection Efficiency (N) value calculated experimentally by using ferri/ferrocyanide system in 0.1 M KCl with 0.1 M $K_3[Fe(CN)_6]$, the data are given Table)

S. No	Rotation speed (RPM)	Disc current (mA)	Ring current (mA)	Collection Efficiency (N)
1	300	0.2836	0.052741	0.185996
2	600	0.3240	0.089011	0.274725
3	900	0.4015	0.096751	0.240973
4	1200	0.4670	0.067973	0.145552
5	1500	0.6574	0.249465	0.379472
			Average	**0.245343**

Faradaic Efficiency in of OER process: $Iring/N * Idisc * 100$

: 0.966*100 = 96.6 %

SI. C9. Calculation of hydrogen generation

Based on the displaced amount of water due to the hydrogen bubbles the amount of hydrogen generated was calculated using the below relationships.

Amount of hydrogen generated in 1 h = amount of water displaced in liters

$$\text{Amount of hydrogen generated in moles for 1 h} = \frac{\text{Amount of water displaced (liters)}}{\text{22.4 liters}}$$

The H_2 generation rate was calculated from the electrical charge passed through the electrode using the equation given below.

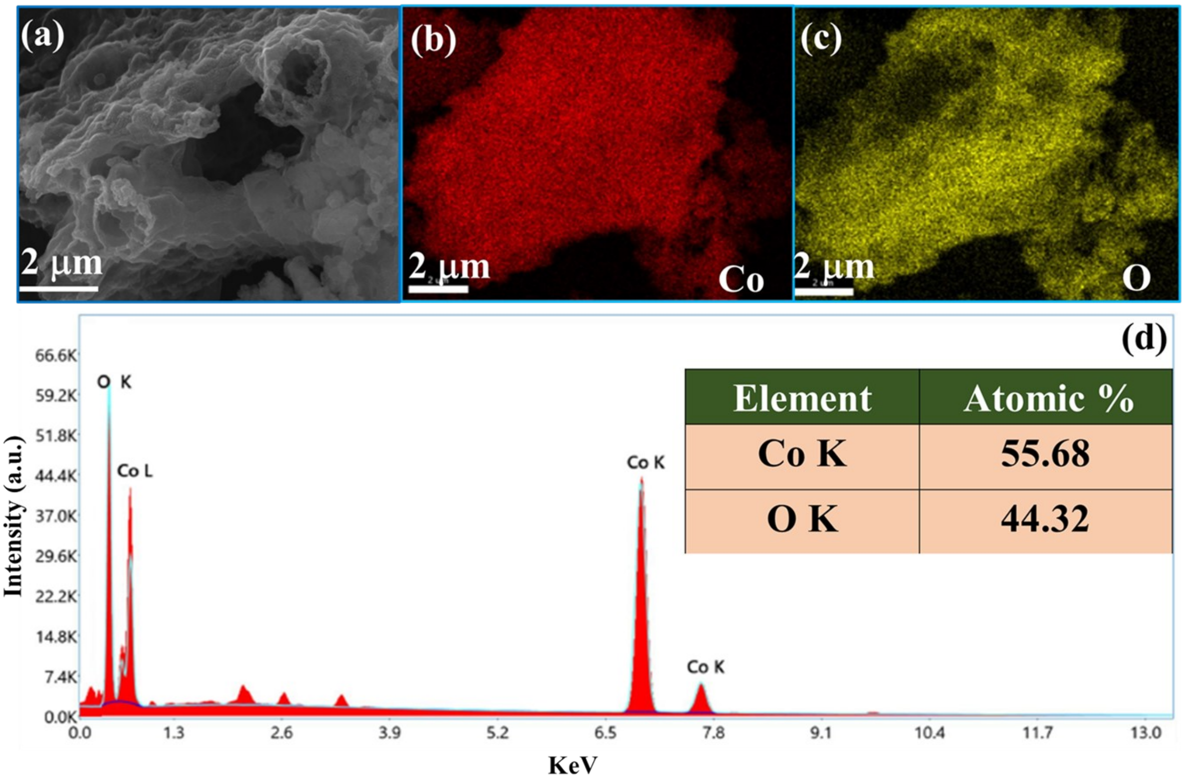
Current obtained during electrolysis x Time duration for each potential = Coulomb

$$\frac{\text{Coulomb x F}}{\text{96485C}} = \text{No. of moles of e- for } H_2 \text{ generation}$$

$$\frac{\text{No. of moles of electron for } H_2 \text{ generation x 1 mole of } H_2 \text{ gas}}{\text{2 moles of electron}} = \text{Moles of } H_2 \text{ generated}$$

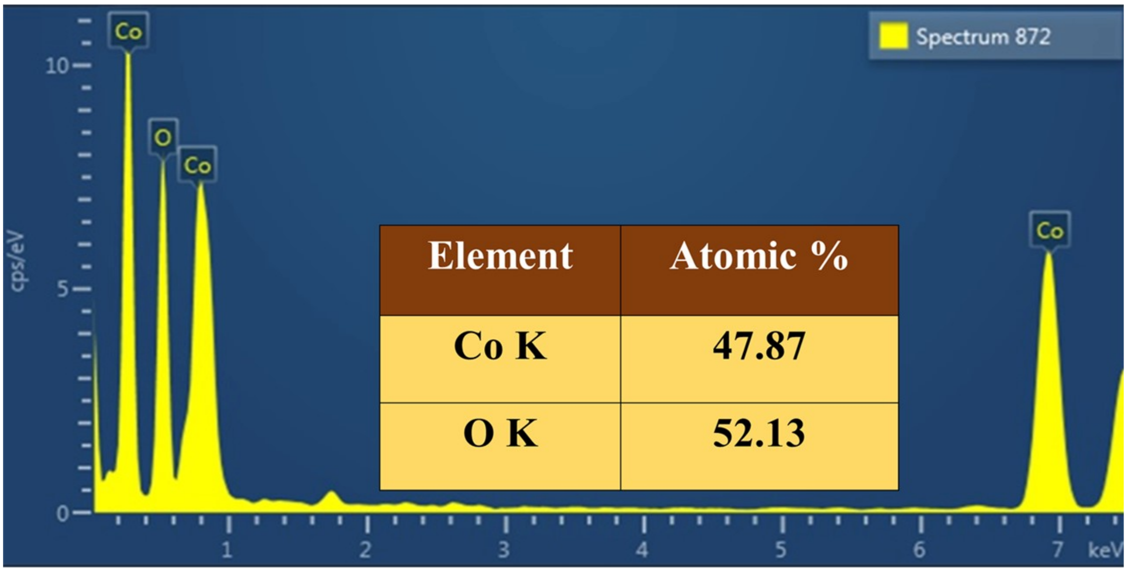
SI–III. Figures

Figure S1. FESEM images of CoOPE-600; (a- c) Elemental mapping of Co and O and (d) FESEM- EDX spectrum of CoOPE-600 (inset: Elemental composition)



Element	Atomic %
Co K	55.68
O K	44.32

Figure S2. HR-TEM - EDX spectrum of CoOPE-600 (inset: Elemental composition)



Element	Atomic %
Co K	47.87
O K	52.13

Figure S3. (a) Overpotential comparison of as prepared electrocatalysts and (b) Comparison LSV curves of CoOPE-600 /GC under before and after OER stability in GC electrode

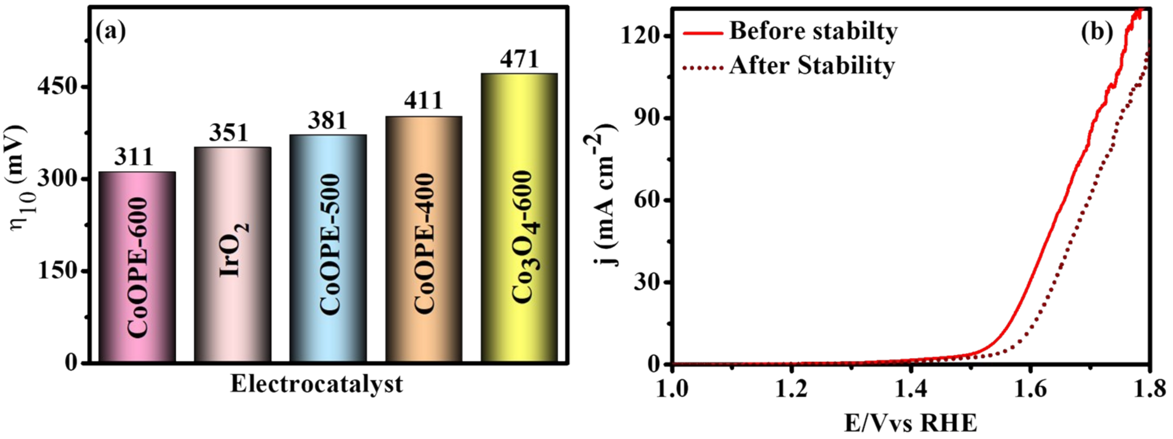


Figure S4. (a) Overpotential comparison of as prepared electrocatalysts and (b) Comparison LSV curves of CoOPE-600 /NF under before and after OER stability in NF electrode

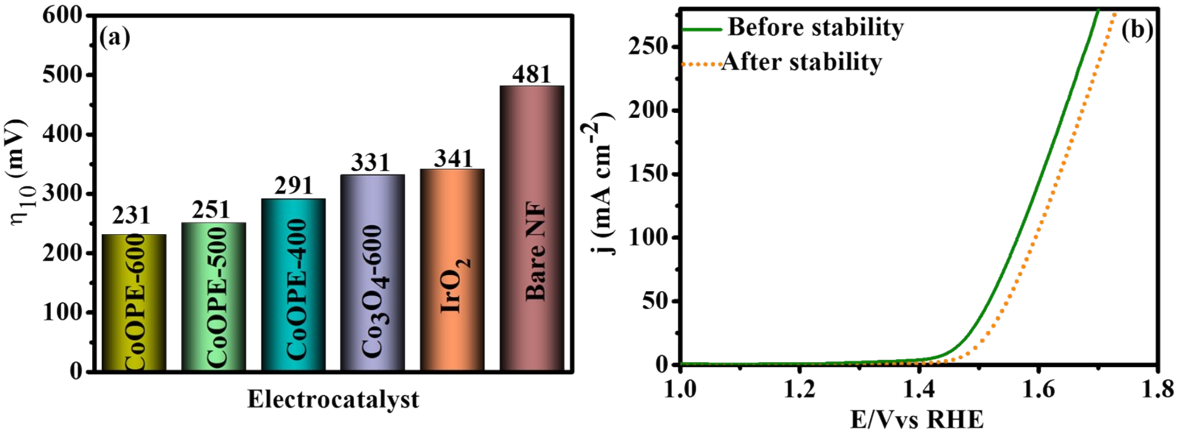


Figure S5. (a) Exchange current density (j_0) of as prepared catalysts towards OER and (b) Radar chart illustration of Turn over frequency (s^{-1})

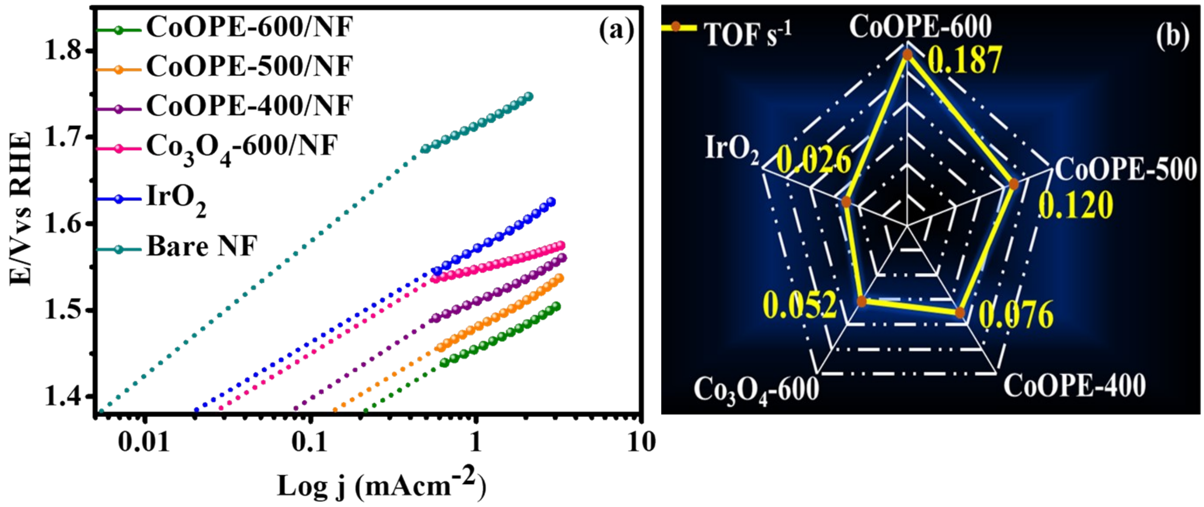
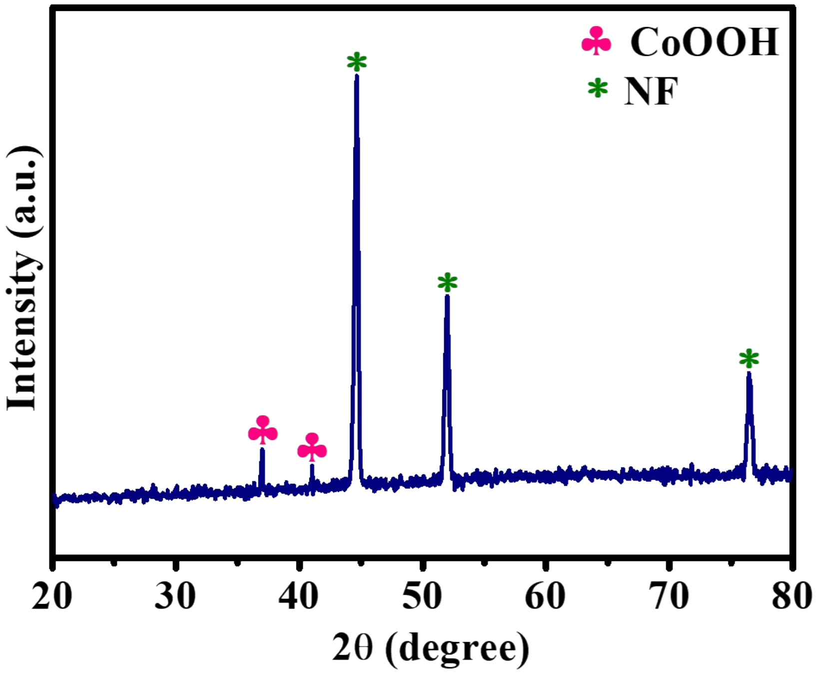


Figure S6. Post-XRD Spectra of CoOPE-600



SI-IV. Tables

Table S1. Comparison of OER performances of CoOPE-600 with recently reported metal- based electrocatalysts

Electrocatalyst	Electrolyte/ substrate	Overpotential (mV)	Reference
CoOPE-600	**1 M KOH/NF**	**311/231**	**This work**
Co-SPC600	1 M KOH/ NF	260	*Energy & Fuels,* 2025, **39**,10610−10627
N-Co_3O_4/N-CNs	1 M KOH/NF	354	*J. Alloys Compd,* 2023, **965**, 171479.
$NiCo_2O_4$@$CoMoO_4$/NF-7	1 M KOH/NF	265	*J. Mater. Chem. A,* 2018, **6**,16950-8.
$NiCo_2O_4$/NiCoP	1 M KOH/NF	295	*Catal. Sci. Technol,*2020, **10**, 5559-65.
Co-MOF	1 M KOH/NF	280	*Dalton Trans,* **2019, 48,**10557-10564
Co_3O_4/$NiCo_2O_4$	1 M KOH/NF	340	*Appl. Mater. Interfaces,* 2018, **10**, 10890-10897.
Co_3O_4@Mo-Co_3S_4-Ni_3S_2	1 M KOH/NF	320	*Chem. Eng. J*, 2021, **413**, 127482
Co_3O_4@CoO	1 M KOH/NF	550	*ChemCatChem,* 2024,**16**, 202301327
CoO/CoxN,	1 M KOH/NF	360	*Sustain.Mater.Technol,* 2021, **29**,00293
Co_3O_4-CoO	1 M KOH/NF	337	*Mater.Lett*, 2023, **34,** 134196
CoOx-Co-OH	0.1 M KOH/NF	280	*Energy & Fuels,* 2024, **38**, 6938-6949
CoO/Co	1 M KOH/NF	350	*ACS Energy Lett,* 2017, **2,** 1208-1213
Fe- Co_3O_4 NBs nanoclusters	1 M KOH/NF	265	*Energy Storage Mater*, 2024, **66,** 103236
CuO/ Co_3O_4	1 M KOH/NF	270	*ACS Appl. Eng. Mater*, 2023, **1**, 606-615
Co_3O_4–x/GO	1 M KOH/NF	280	*ACS Appl. Mater. Interf*, 2022, **14,** 43508-43516
Co_3O_4- Fe_2O_3–Ni Foam	1 M KOH/NF	350	*Adv. Mater. Interf*, 2021, **8,** 2100763
Co_3O_4 nanostructures	1 M KOH/NF	260	*Electrochim. Acta,* 2021, **398**, 13933
Co@CF-NG	melamine	400	*J. Mater. Chem. A* 2018, **6,** 489−497.

	foam		

Table S2. Comparison of overall water splitting performances of NiMoO-NC with reported metal -based electrocatalysts

Electrocatalyst	Electrolyte	Cell Voltage (V)	Reference
CoOPE-600	1 M KOH	**1.56**	**This work**
CoP/NPMG	1 M KOH	1.60	*Nanoscale,* 2018, **10**, 2603−2612.
$Co_{1-\delta}Fe_{\delta}$LDH/g-CNx	1 M KOH	1.61	*Nano Energy,* 2017**, 39**, 30-43.
Co@N-CNTF	1 M KOH	1.71	*J. Mater. Chem. A,* 2019**, 7,** 3664-3672.
Co^{II}@M$\Vert$$Co^{0}$@M	1 M KOH	1.63	*Small*, 2025, **21**, 2501949.
SFCNF/$Co_{1-x}S$@CoN	1 M KOH	1.58	*Small* 2020**, 16**, 2002432.
$CoMoO_4$/AC	1 M KOH	1.60	*J. Electroanal. Chem,* 2025, **996**,119339.
UCoOx/NF	1 M KOH	1.57	*Catal. Sci. Technol*, 2025, **15,** 6456
Ni- Co_3O_4	0.5 M H_2SO_4	1.86	*Appl Calal B- Environ,* 2024, **358**, 124367.
Ru- Co_3O_4/ CoN-L	1 M KOH	1.60	*J. Colloid Interface Sci.* 2024, **676**, 647–656.
CoMoP@ Co_3O_4	1 M KOH	1.61	*ACS Appl. Mater. Interfaces* 2021, **13,** 55263– 55271,
Co-Mo-N	1 M KOH	1.59	*Appl. Surf Sci*, 2023, **623**, 156989.
Co_3O_4@Ni_3Se_4/NF	1 M KOH	1.74	*ChemNanoMat*, 2019, **5**, 814-9