Supplementary Information (SI) for Sustainable Energy & Fuels.

Ligand-specific bimetallic electrocatalyst for efficient oxygen evolution reaction at higher current density

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Materials:

Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) purchased from Nice Chemicals (P) Ltd, cobalt (II) nitrate hexahydrate 98% purchased from AVRA and trimesic acid 95% from Sigma-Aldrich used as organic ligand for MOF synthesis, Nafion 5%, ethanol and DMF were purchased from local vendors and used without any further purification .

Material characterization

The X-ray diffraction (XRD) instrument with Cu Kα radiation (λ = 1.54 Å) was used to analyze the crystalline nature of the electrocatalyst. Scanning electron microscopy (SEM, Model EVOLS15,) was used to examine the morphology of the electrocatalyst. X-ray photoelectron spectroscopy (XPS) (K-alpha, Thermo Scientific, USA) with Al Kα radiation (1486.6 eV) was used for quantitative assessment of the elemental composition. Nitrogen physisorption experiments was carried out using BELSORP-mini II (Japan) instrument with N_2 gas to determine the BET surface

Pre-treatment of Carbon cloth:

The commercial carbon cloth was cut into a rectangular piece with a size of 1 cm × 1 cm and treated with ethanol, acetone, and distilled water separately by ultrasonication for 15 mins and then dried at 60 °C in a hot air oven. The cleaned carbon cloth was used for modification.

Electrode Preparation:

The catalyst ink was prepared by dispersing 20 mg of NiCo t-MOF electrocatalyst in a mixed solution of 300 µL of iso-propanol and 20 µL of Nafion. The mixture was sonicated for about 30 min to form homogeneous slurry. Then, the catalyst ink (100 µL) was coated on a pre-treated carbon cloth (area $1cm^2$) and dried at 60 °C for 2 h. The constructed working electrodes were used to evaluate the electrochemical activity using CV, LSV and EIS. The electrochemical measurements were carried out with CHI760E electrochemical workstation (CH Instruments) with a three-electrode cell at ambient conditions. The specimen (1cm*1cm), graphite rod and Hg/HgO were used as working, counter and reference electrodes respectively. The electrocatalytic activity was measured in 1M KOH electrolyte. The potential measured versus the Hg/HgO electrode was converted to reversible hydrogen electrode (RHE) according to the following equation.

$$\mathbf{E_{(RHE)}=E_{Hg/HgO}+E^0_{Hg/HgO}+0.0592*pH}$$

Faradaic Efficiency (FE) Calculation

Applied current density (j): 100 mAcm^{-2}

Electrode area (A): 1 cm^2

Time (t): 3600 seconds (1 hour).

Oxygen evolved (Δm): 0.45 g of oxygen is evolved during the reaction

Number of electrons per mole of O_2(n): 4 (4-electron transfer OER reaction).

Faraday constant (F): 96485 Cmol^{-1}

Molar mass of oxygen (M_{O2}): 32 gmol^{-1}

Step-by-Step FE Calculation

1. **Calculate the Total Current (I):**

The total current (I) is the current density (j) multiplied by the electrode area (A):

$$I = j \times A = \left(100 \times 10^{-3} \frac{A}{cm^2}\right) \times 1cm^2 = 0.1\ A$$

2. **Calculate the Moles of O_2 Evolved:**

The amount of oxygen evolved ((Δm = 0.45 g) can be converted to moles of O2:

$$Moles\ of\ O_2 = \frac{\Delta m}{M_{O2}} = \frac{0.45\ g}{32\ g\ mol^{-1}} = 1.40625 \times 10^{-2} mol$$

3. Calculate the total charge passed:

The total charge is given by:

$$Charge = I \times t = 0.1\ A \times 3600\ s = 360\ C$$

4. Calculate the Faradaic Efficiency:

Now, calculate the faradaic efficiency for O_2 using the following formula:

$$FE_{O2} = \frac{4 \times I \times T}{n \times F \times \Delta m} \times 100$$

Substituting the values;

$$FE_{O2} = \frac{4 \times 0.1\ A \times 3600\ s}{4 \times 96485\ Cmol^{-1} \times 1.4065 \times 10^{-2}\ mol} \times 100$$

Simplifying;

$$FE_{O2} = \frac{1440}{4 \times 96485 \times 1.40625 \times 10^{-2}} \times 100$$

$$FE_{O2} = \frac{1440}{542.625} \times 100$$

$$FE_{O2} = 92.7\%$$

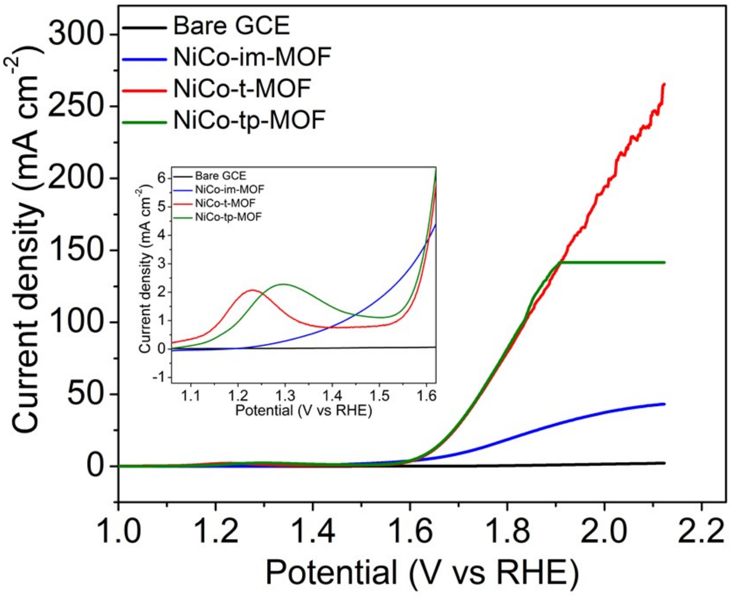

Fig. S1. OER studies of Bare GCE, NiCo-im-MOF/GCE, NiCo-t-MOF/GCE and NiCo-tp-MOF/GCE at a scan rate of 5 mV/s in 1 M KOH solution. Inset: the zoomed portion shows the oxidation peaks of Ni^{2+} to Ni^{3+} and Co^{2+} to Co^{3+} in the potential of 1.2 to 1.4 V vs RHE

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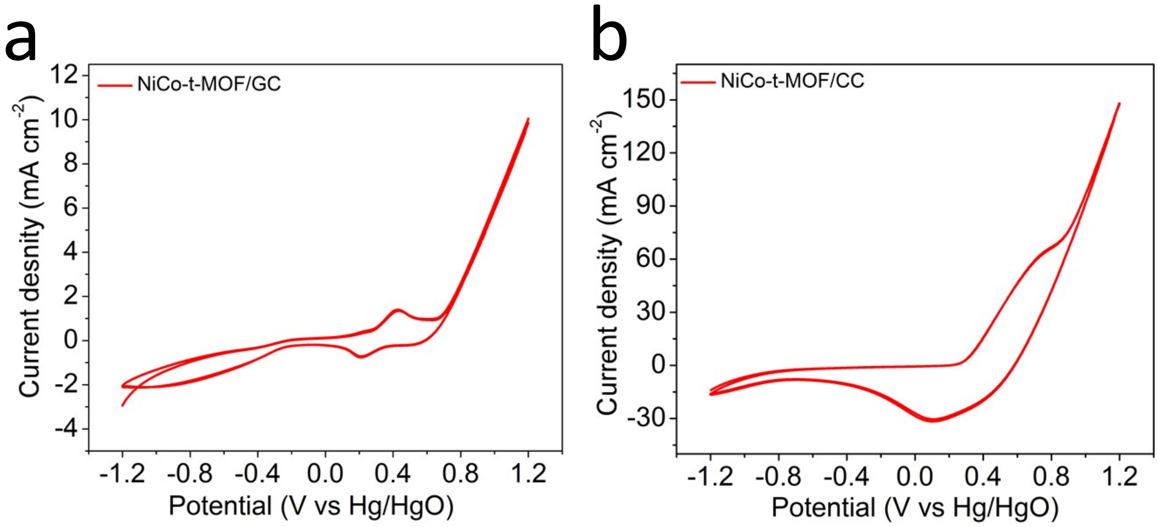

Fig. S2. Cyclic voltammogram of NiCo t-MOF on GCE and Carbon cloth (CC) in 1M KOH solution at the scan rate 50 mV/s.

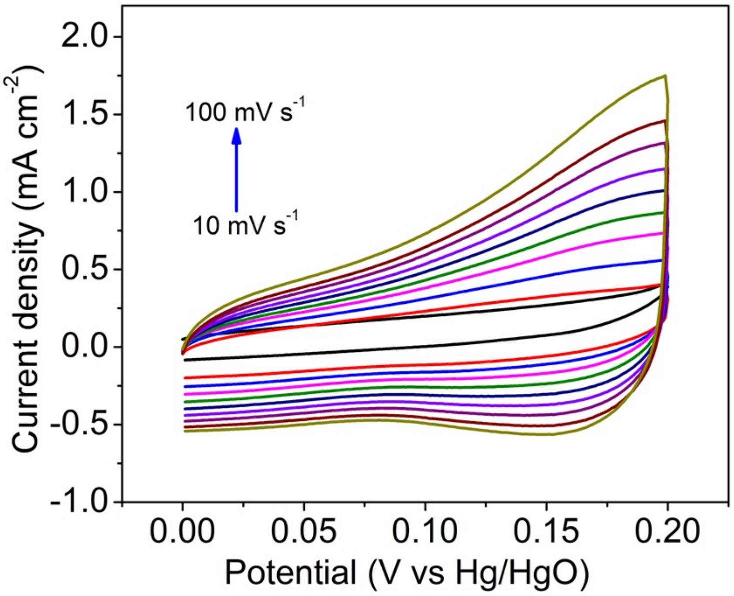

Fig. S3 CVs at different scan rates for NiCo-t-MOF in 1 M KOH solution

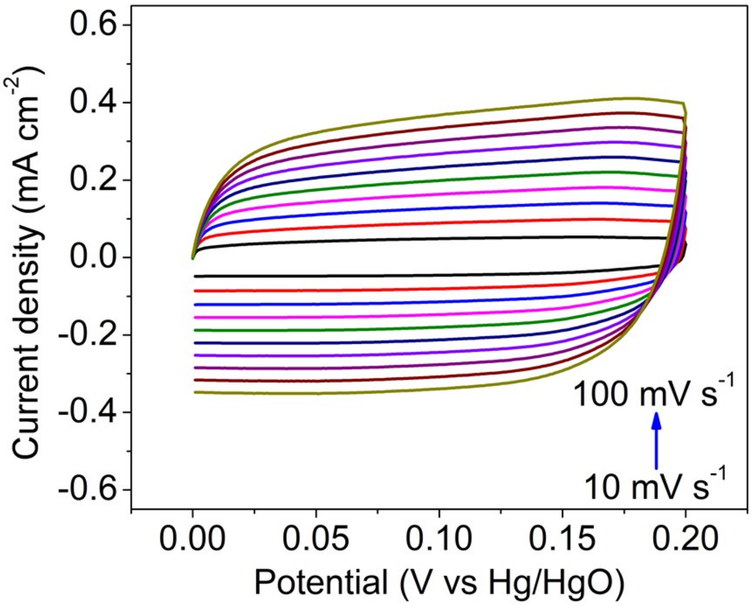

Fig. S4 CVs at different scan rates for RuO_2 in 1 M KOH solution.

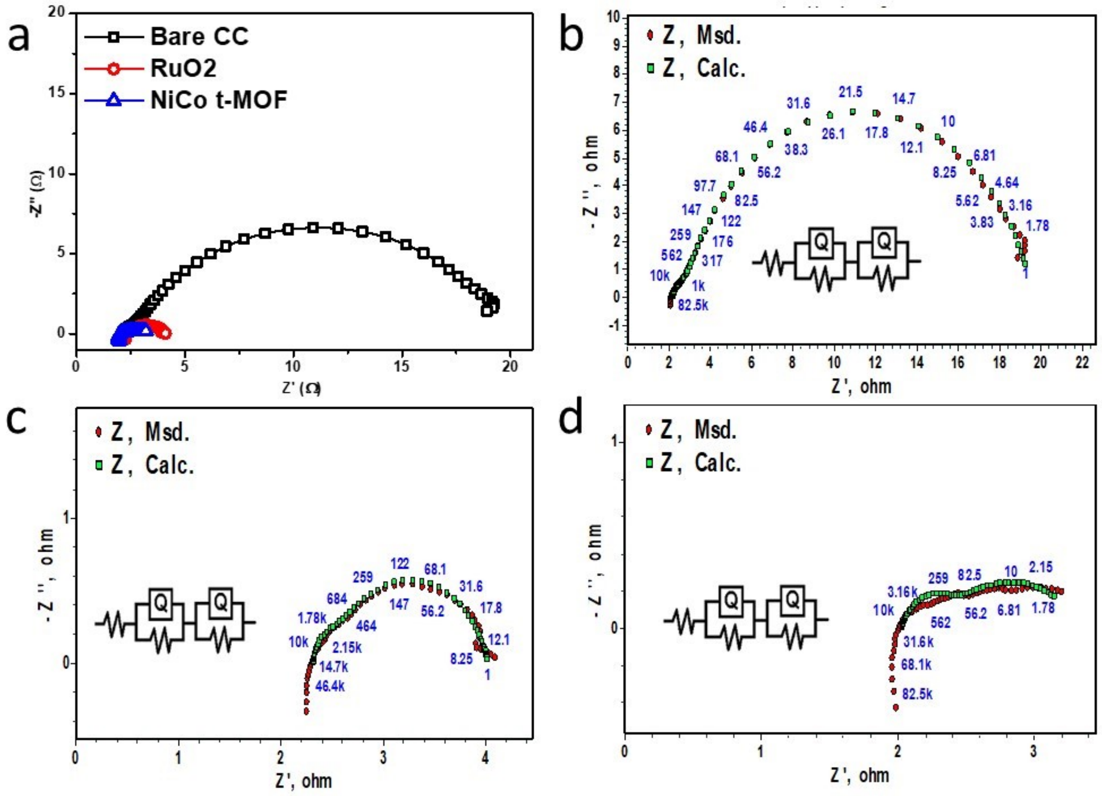

Fig. S5(a) Cole-Cole (Nyquist) plot along with fitted curves and an equivalent circuit for (b) Bare CC, (c) RuO_2 and (d) NiCo-t-MOF

Table S1: Equivalent circuit parameters

Compound	**Equivalent circuit**	R_s	Q_g	R_g	Q_{gb}	R_{gb}	$R_g + R_{gb}$
Bare CC	R(QR)(QR)	2.133	0.952E-3	16.8	0.387E-3	0.6574	17.45
RuO_2	R(QR)(QR)	2.313	3.317E-3	1.481	0.396E-3	0.2291	1.71
NiCo-t-MOF	R(QR)(QR)	2.024	11.67	0.9849	2.704E-3	0.3417	1.32

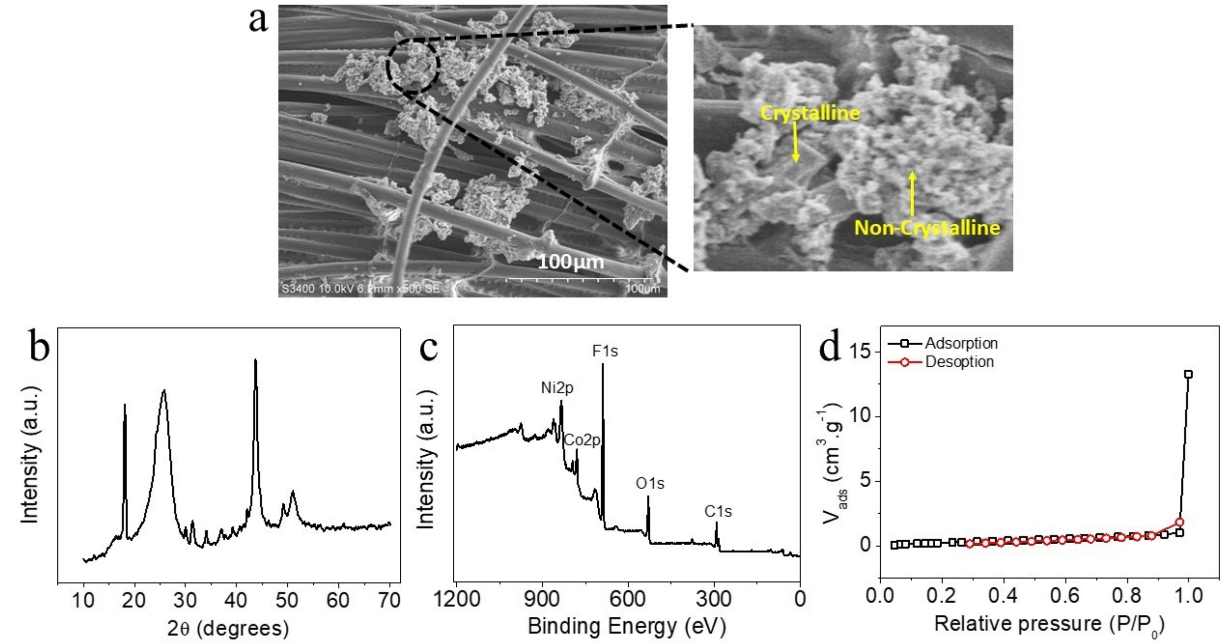

Fig S6.(a) SEM images, (b) XRD and (c) N_2 adsorption–desorption isotherms for NiCo-t-MOF after stability tests

Proposed possible OER mechanism with reference to NiCo-t-MOF

1. **Adsorption of hydroxide (OH^-)**

   NiCo t-MOF-OH^- (adsorbed)

2. **Oxidation of hydroxide (OH^-) to oxygen species (M-O)**

   NiCo-t-MOF-OH^- (adsorbed) →NiCo-t-MOF-O(adsorbed) + e^-

3. **Coupling of oxygen species (M-O) to form O_2**

   2 NiCo-t-MOF-O(adsorbed) → O_2 + 2 NiCo-t-MOF

4. **Desorption of O_2 and regeneration of catalyst (desorbed from NiCo-t-MOF)**

   Overall OER reaction in alkaline medium

   $4\ OH^- \rightarrow O_{2(g)} + 2H_2O_{(l)} + 4\ e^-$

Table S2. Comparison of the NiCo-t-MOF/CC with the reported catalyst materials

Electrocatalyst	**Overpotential** **(η, mV@mA cm^{-2})**	**Tafel slope** **(mV dec^{-1})**	**Stability**	**Ref**
$Mn_xFe_{3-x}O_4$	510 mV@100	-	10 h	[1]
$Zn_{0.3}Co_{2.7}(PO_4)_2$	390 mV@50	-	25 h	[2]
Co_2B	380 mV@10	45	-	[3]
$NiO/NiCo_2O_4$	336 mV@50	93.2	40 h	[4]
NiCo alloy	390 mV @ 100	69.4	15 h	[5]
$CoNiTe_2$/NF	181 mV@10	44	24 h	[6]
Te/Fe-NiOOH	220 mV@10	93	20 h	[7]
CoTe@NR/NF	350 mV@100	75	24 h	[8]
$Cu(OH)_2$@Co	355 mV@100	70.2	20h	[9]
Ni_3Te_2–CoTe	392@100	68	24h	[10]
$NiSe_2$	235 mV@10	63.1	80 h	[11]
NixPy-325	320 mV@10	72.2	60 h	[12]
NiCo-t-MOF/CC	440 mV@100	81	62 h	This work

Table S3. OER electrocatalysts in the full-cell configuration water electrolyser where commercial Pt-based catalysts are used as cathodic HER electrocatalyst and designed catalysts used as the anodic OER electrocatalyst in the two-electrode configuration.

Cell configuration	**Electrolyte**	**Cell voltage**	**Stability**	**Ref**
Pt/C||Ru@NiCo-MOF-4	1 M KOH	1.57 V @ 10 mA cm^{-2}	-	[13]
Pt/C||RuO_2	1 M KOH	1.62 V @ 10 mA cm^{-2}	-	[14]
Pt net||NiO/$NiCo_2O_4$/NF	1 M KOH	1.67 V @ 20 mA cm^{-2}	30 h	[15]
Pt||NiS/CoNC	1 M KOH	1.33 V@ 10 mA cm^{-2}	-	[16]
Pt/C||0.7Sr	4 M KOH	1.62 V @ 10 mA cm^{-2}	200 h	[17]
Pt/C||NiCo-t-MOF	1 M KOH	1.49 V @ 10 mA cm^{-2}	30 h	This work

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