Electronic Supplementary Information

In-situ synthesis of hierarchical NiCo-MOF@$Ni_{1-x}Co_x(OH)_2$ heterostructures for enhanced pseudocapacitors and oxygen evolution reaction

Chong Jiang[a], Shuang Li[a]*, Bo Li[a], Shan Liu[a], Wen-Wen Dong[a], Ya-Pan Wu[a], Zheng-Fang Tian[b], Qichun Zhang[c]*, Dong-Sheng Li[a]*

[a]*College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang, 443002, P. R. China*

[b]*Hubei Key Laboratory of Processing and Application of Catalytic materials,Huanggang Normal University, Huanghang, 438000, P.R. China*

[c]*Department Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong SAR, 999077, P.R. China*

E-mail address: lishmail@126.com; qiczhang@cityu.edu.hk ; lidongsheng1@126.com.

S1. Additional characterization information

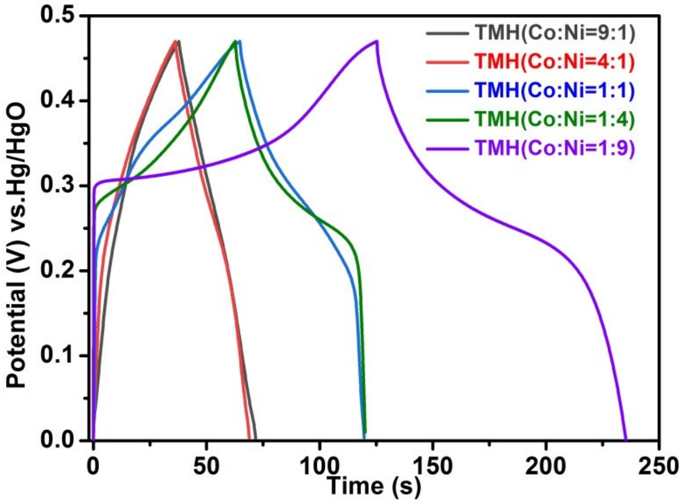

Figure S1. GCD curves at a current density of 2 A g^{-1} for TMH with different metal molar ratio. By comparison, the performance-optimal TMH with Ni/Co molar ratio = 9:1 was chose as precursor for the preparation of MOF.

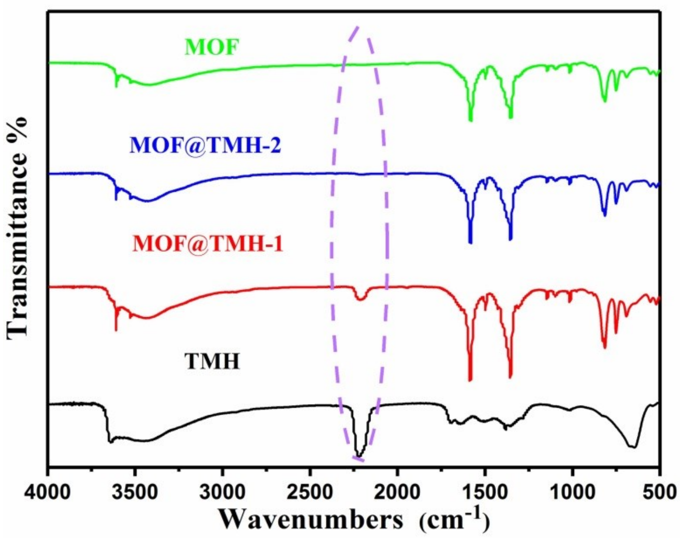

Figure S2. FT-IR spectra of the obtained TMH, MOF@TMH-1, MOF@TMH-2 and MOF.

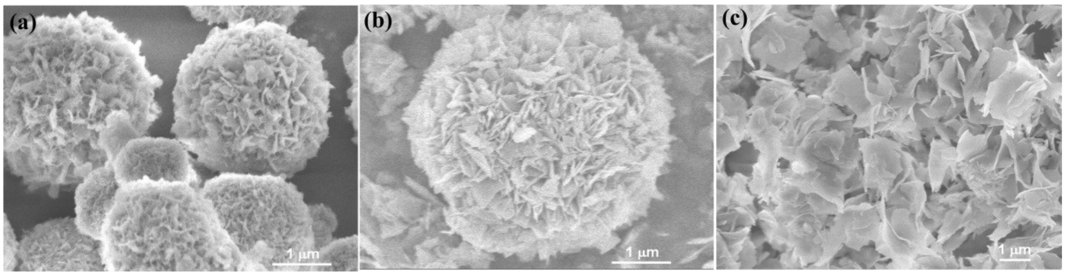

Figure S3. SEM images of the (a) TMH, (b) MOF@TMH-1 and (c) MOF.

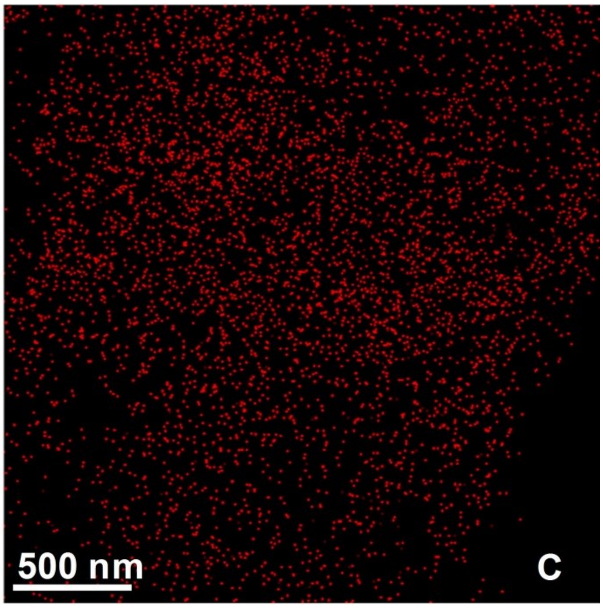

Figure S4. Elemental mapping image of carbon.

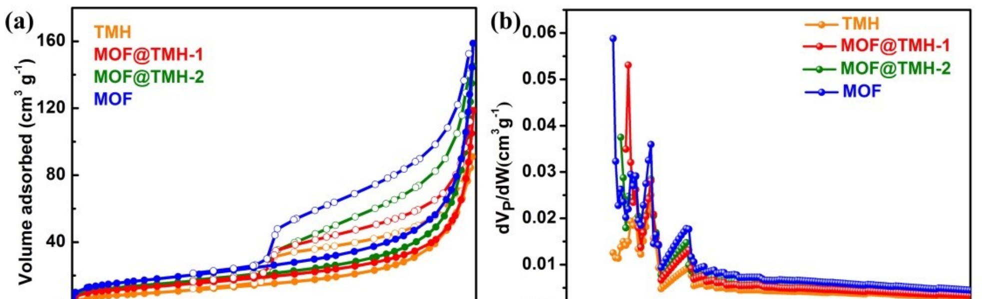

Figure S5. N_2 adsorption-desorption isotherm and pore-size distribution curve of the samples.

All samples show type-IV isotherms with a very distinct hysteresis loop of typical H3. The BET surface area of the MOF is 64.3 $m^2\ g^{-1}$, which is larger than that of MOF@TMH-2 (53.0 $m^2\ g^{-1}$), MOF@TMH-1 (48.1 $m^2\ g^{-1}$) and TMH (36.1 $m^2\ g^{-1}$).

The corresponding pore size distributions in Figure S4b shows the obvious micropore structure for the samples, from which the BDC form porous MOF with metal ions. Of note, although the specific surface area of MOF@TMH-2 is slightly lower than that of MOF, the hetero-junction formed by the presence of a small amount of TMH facilities the charge transfer, thus resulting in its electrochemical performances are better than that of MOF.

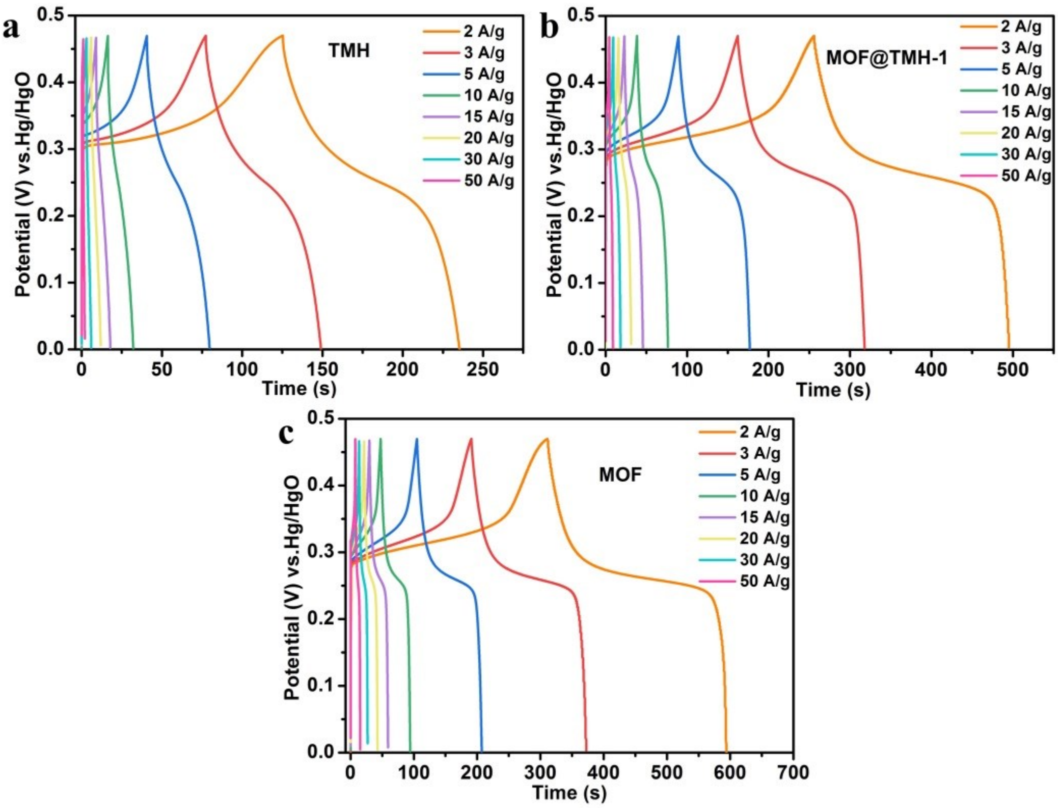

Figure S6. GCD curves at various current densities of TMH, MOF@TMH-1 and MOF.

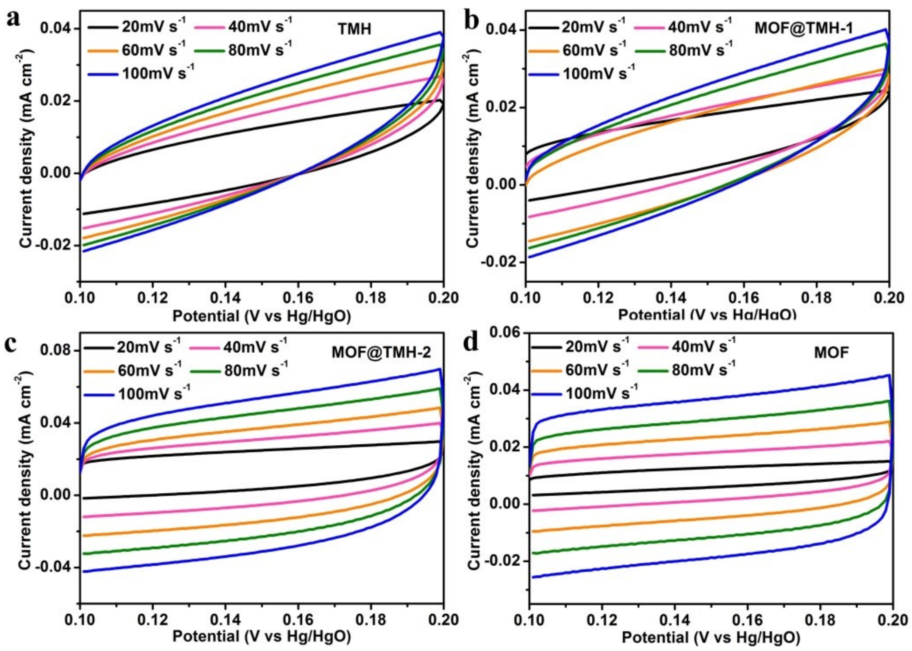

Figure S7. (a-d) Cyclic voltammetry curves of TMH, MOF@TMH-1, MOF@TMH-2 and MOF in the region of 0.1-0.2 V (vs Hg/HgO).

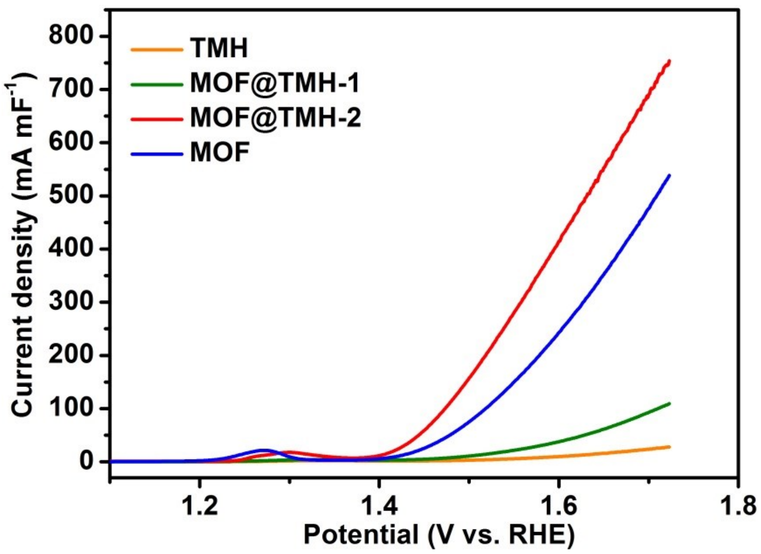

Figure S8. Polarization curves normalized by the C_{dl} of TMH, MOF@TMH-1, MOF@TMH-2 and MOF.

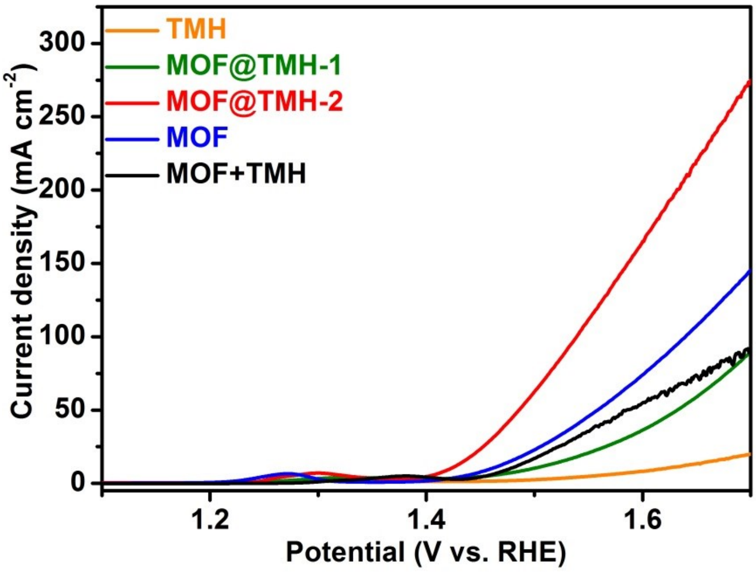

Figure S9. Polarization curves of TMH, MOF@TMH-1, MOF@TMH-2, MOF and MOF+TMH that prepared by mechanically mixed of TMH and NiCo-BDC.

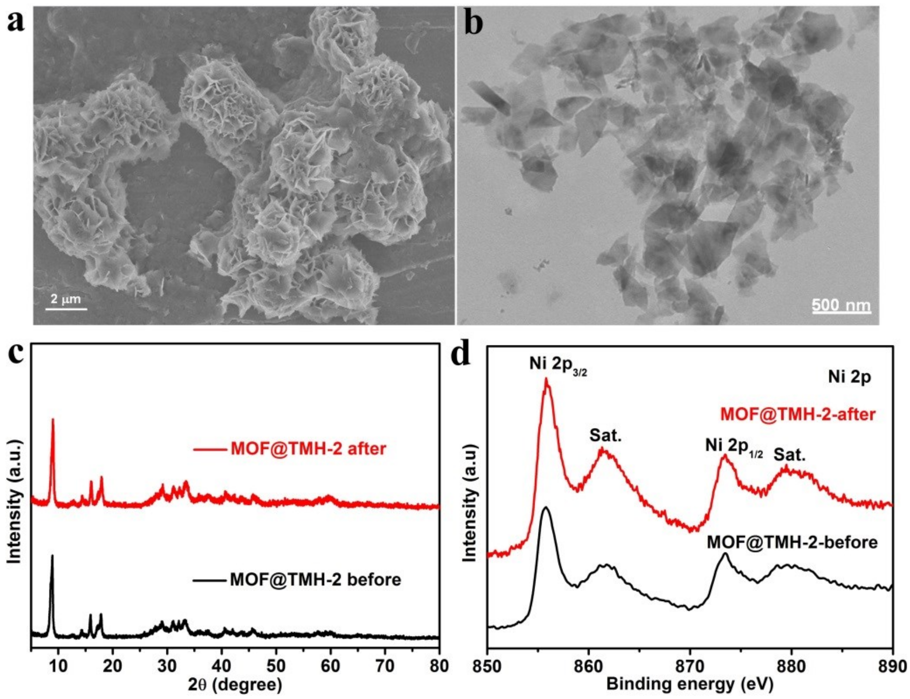

Figure S10. The SEM, TEM, XRD and XPS of MOF@TMH-2 after stability test.

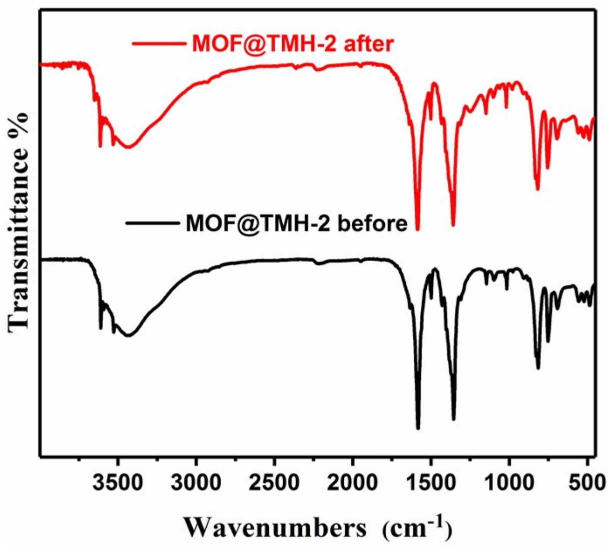

Figure S11. The FT-IR of MOF@TMH-2 after stability test.

Table S1. Comparison of the specific capacitances of present work and the other electrode materials in a three-electrode system

Materials	Test Condition	Specific capacitance (F g^{-1})	Electrolyte solution	Current collector	Ref.
MOF@TMH-2	2 A g^{-1}	1855.3	1 M KOH	Glassy carbon disk (GC)	This work
PPy@NiCo$(OH)_2$	2 A g^{-1}	1350.11	6 M KOH	Ni foam (NF)	1
CoNi-MOF	2 A g^{-1}	1044	1 M KOH	CFP	2
Ni-Co sulfides	2 A g^{-1}	1304	6 M KOH	NF	3
2D Co-MOF Ns	2 A g^{-1}	1106	3 M KOH	NF	4
Co-MOF	2 A g^{-1}	958.1	3 M KOH	NF	5
CNT@Ni$(OH)_2$	2 A g^{-1}	1136	1 M KOH	NF	6
Ni/Co-LDH-7:3	2 A g^{-1}	1626.4	6 M KOH	NF	7
Co-Mn-HTS	2 A g^{-1}	1093	2 M KOH	NF	8
PPNF@Ni−Co MOF-3	2 A g^{-1}	956.6	3 M KOH	NF	9
NiCo-BDC nanosheets	2 A g^{-1}	1296.33	1 M KOH	NF	10
CNMO NWs	2 A g^{-1}	554	1 M KOH	NF	11
Porous Co_3O_4 microspindles	2 A g^{-1}	136	1 M KOH	NF	12
$NiCo_2O_4$@MnO_2	2 A g^{-1}	688.4	1 M KOH	NF	13
H-NiOOH/GS	2 A g^{-1}	1160	2 M KOH	NF	14
Ni/Co-MOF	2 A g^{-1}	839	3 M KOH	Stainless steel grid	15
CoO/Co-Cu-S-2 HTHSs	2 A g^{-1}	2300	6 M KOH	NF	16
Ni_3S_2/$CoNi_2S_4$/NF	2 A g^{-1}	2435	6 M KOH	NF	17

Table S2. Comparison of the overpotential at 10 mA cm^{-2} of present work and the other OER catalysts in a three-electrode system

Catalyst	Electrolyte (KOH)	Substrate	Overpotential (mV) (at 10 mA cm^{-2})	Ref.
MOF@TMH-2 (NiCo-BDC@NiCo$(OH)_2$)	1 M	glassy carbon (GC)	193	This work
NiCo-UMOFNs	1 M	GC	250	18
Ni-BDC/Ni$(OH)_2$	1 M	GC	320	19
MIL-88A/Ni$(OH)_2$-CC	1 M	carbon cloth (CC)	250	20
NiFe-UMNS	1 M	GC	260	21
Fe-Ni LDH/MOFs	1 M	GC	255	22
Fe$(OH)_3$@Co-MOF-74	1 M	carbon paper(CP)	292	23
NiCo-BDC BMNSs	1 M	Ni foam (NF)	230	24
CoFeCr LDH/NF	1 M	NF	200	25
Ni-MOF@Fe-MOF powder	1 M	GC	265	26
NH_2-MIL88B(Fe_2Ni)	1 M	NF	240	27
Ni_3S_2/Ni foam	1 M	NF	260	28
Co-PB/Pt	1 M	GC	300	29
Co$(TCNQ)_2$	1 M	Co foil	310	30
NF/NiFe-LDH	1 M	NF	250	31
NF/Ni_3S_2	1 M	NF	260	32
Co(OH)F/NF	1 M	NF	270	33
FeNiOOH	1 M	GC	280	34
Ni/Ni$(OH)_2$	1 M	CP	270	35
Cu$(OH)_2$/Co$(OH)_2$	1 M	Cu foil	283	36
Co@CoO_x	1 M	GC	289	37
$Zn_xCo_{3-x}O_4$	1 M	Ti foil	320	38
Pt QDs@Fe-MOF	1 M	NF	144	39
Gelled-FeCoW	1 M	Au foam	191	40

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