Electronic Supplementary Information

Two-Dimensional Conductive Metal-Organic Frameworks with Dual Metal Sites toward Electrochemical Oxygen Evolution Reaction

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Contents:

1. Experimental Section

TOF calculation: The TOF values were estimated according to the following formula:[123]

$$\text{TOF} = \frac{number\ of\ total\ oxygen\ turnovers\ /\ cm^2}{number\ of\ active\ sites\ /\ cm^2}$$

The number of total oxygen turnovers was calculated from the current density by the following equation:

$$\text{Number of } O_2 = \left(\text{J}\frac{mA}{cm^2}\right)\left(\frac{1\ C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ O_2}{4\ mol\ e^-}\right)\left(\frac{6.022 * 10^{23}\ O_2\ molecules}{1\ mol\ O_2}\right) = 1.56 * 10^{15}\ \frac{O_2/s}{cm^2}\ per\ \frac{mA}{cm^2}$$

The number of active sites was regarded as the number of surface sites (Ni atoms are regarded as possible active sites), and calculated by the following formula:

$$\text{Nuber of active sites} = \left(\frac{number\ of\ Ni\ atoms\ /\ unit\ cell}{Volume\ /\ unit\ cell}\right)^{\frac{2}{3}}$$

Finally, the plot of current density can be converted into a TOF plot according to the following formula:

$$\text{TOF} = \frac{\left(1.56 * 10^{15}\ \frac{\frac{O_2}{s}}{cm^2}\ per\ \frac{mA}{cm^2}\right) * |J|}{Number\ of\ active\ sites * A_{ECSA}}$$

The A_{ECSA} is the electrochemical active surface area, which can be calculated from the following formula, where specific capacitance is C_{dl}, and 40 μF is a constant to convert capacitance to A_{ECSA}:

$$A_{ECSA} = \frac{specific\ capacitance}{40\ \mu F\ cm^{-2}\ per\ cm^2_{ECSA}}$$

D-band center Analysis: The d-band center (ε_d) was calculated according to following equation:[4]

$$\varepsilon_d = \frac{\int N(\varepsilon)\varepsilon\ d\varepsilon}{N(\varepsilon)\ d\varepsilon}$$

Where $N(\varepsilon)$ is the d-band DOS, ε is the energy. The integration was set in the whole range of d-band DOS.

2. ^{1}H NMR and MALDI-TOF MS

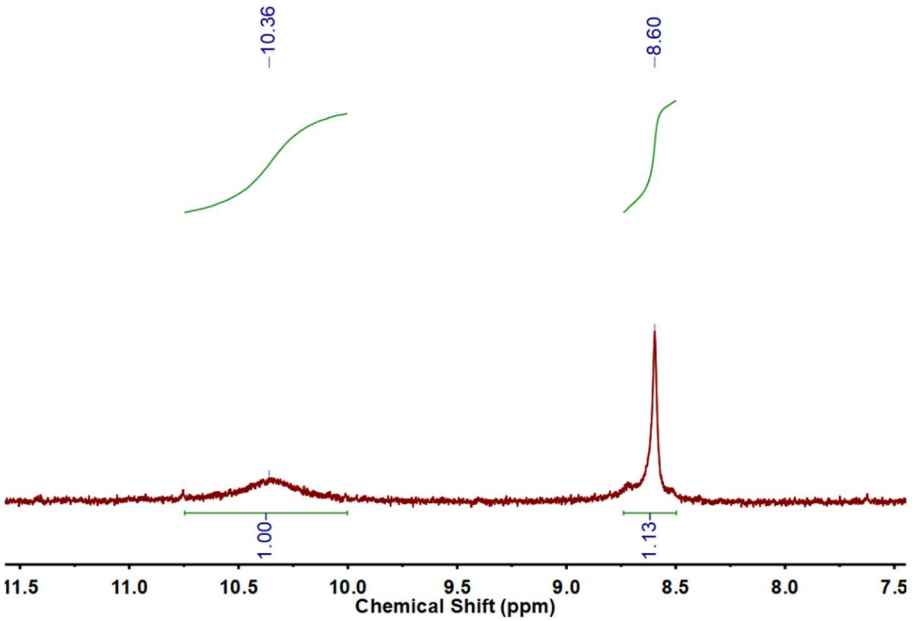

Figure S1. ^{1}H NMR spectra of NiPc.

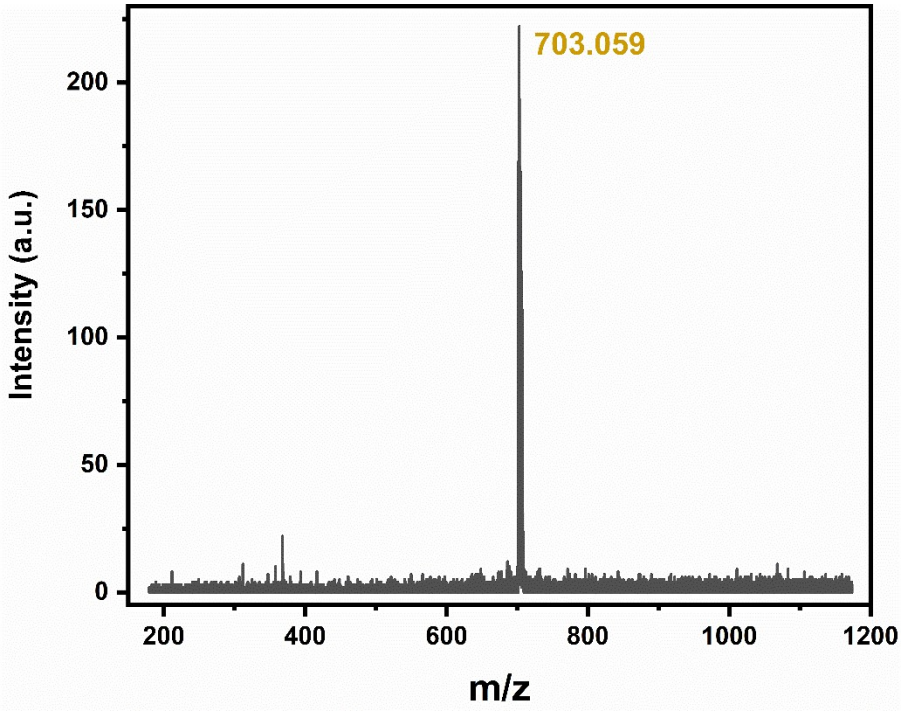

Figure S2. MALDI-TOF MS spectra of ZnPc.

3. FT-IR Spectra

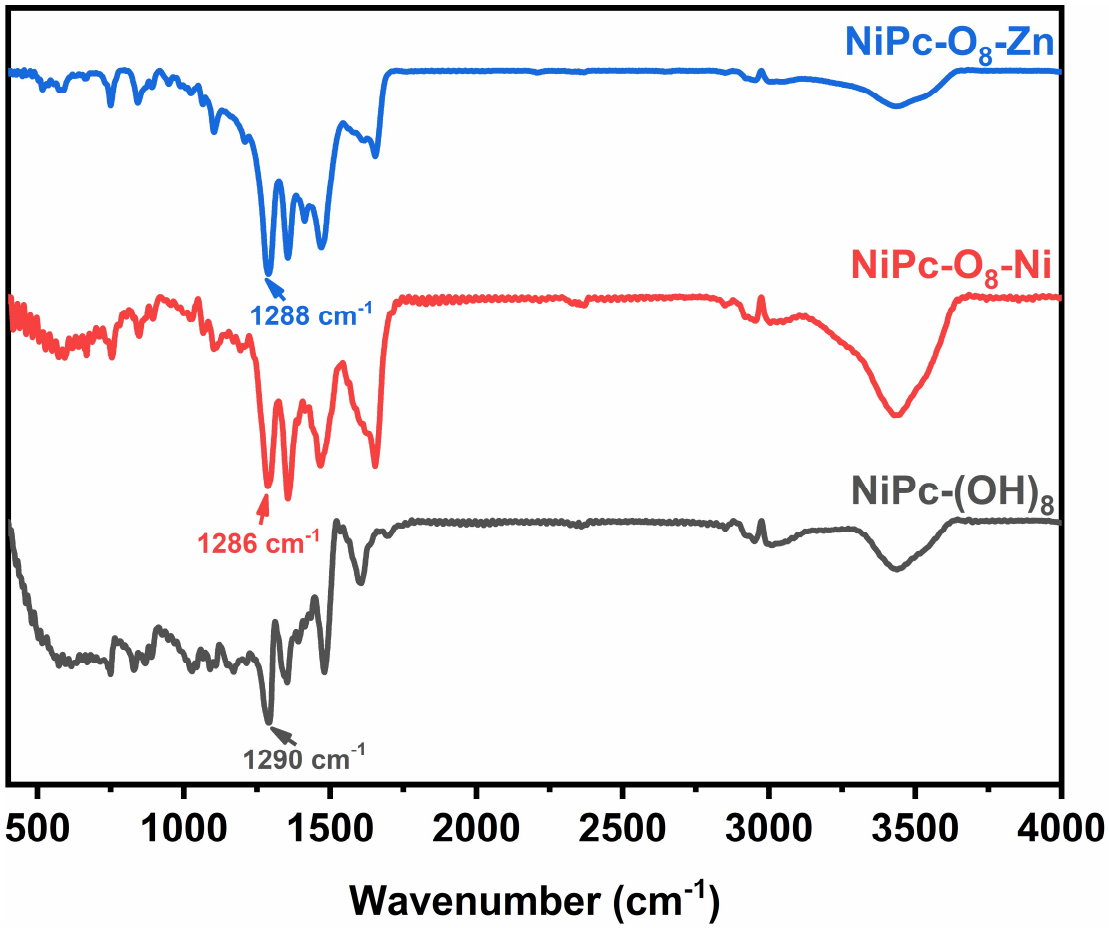

Figure S3. FT-IR spectra of NiPc, NiPc-Ni and NiPc-Zn.

4. PXRD Measurements

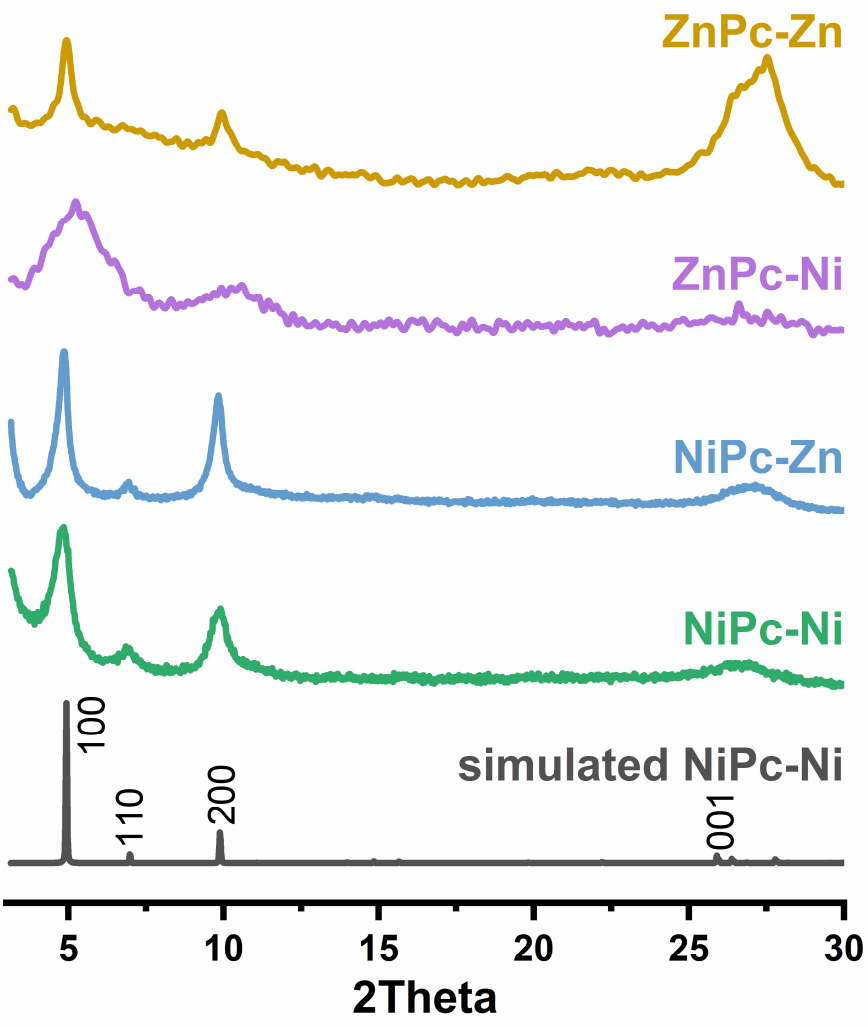

Figure S4. PXRD patterns of NiPc-Ni, NiPc-Zn, ZnPc-Ni and ZnPc-Zn.

Table S1. Lattice parameters of MPc-M' MOFs

Lattice parameters	NiPc-Ni	NiPc-Zn	ZnPc-Ni	ZnPc-Zn
a (Å)	17.8963	17.9504	17.9396	17.9936
b (Å)	17.8963	17.9504	17.9396	17.9936
c (Å)	3.4372	3.4317	3.4337	3.4283
α (º)	90	90	90	90
β (º)	90	90	90	90
γ (º)	90	90	90	90

5. SEM Images

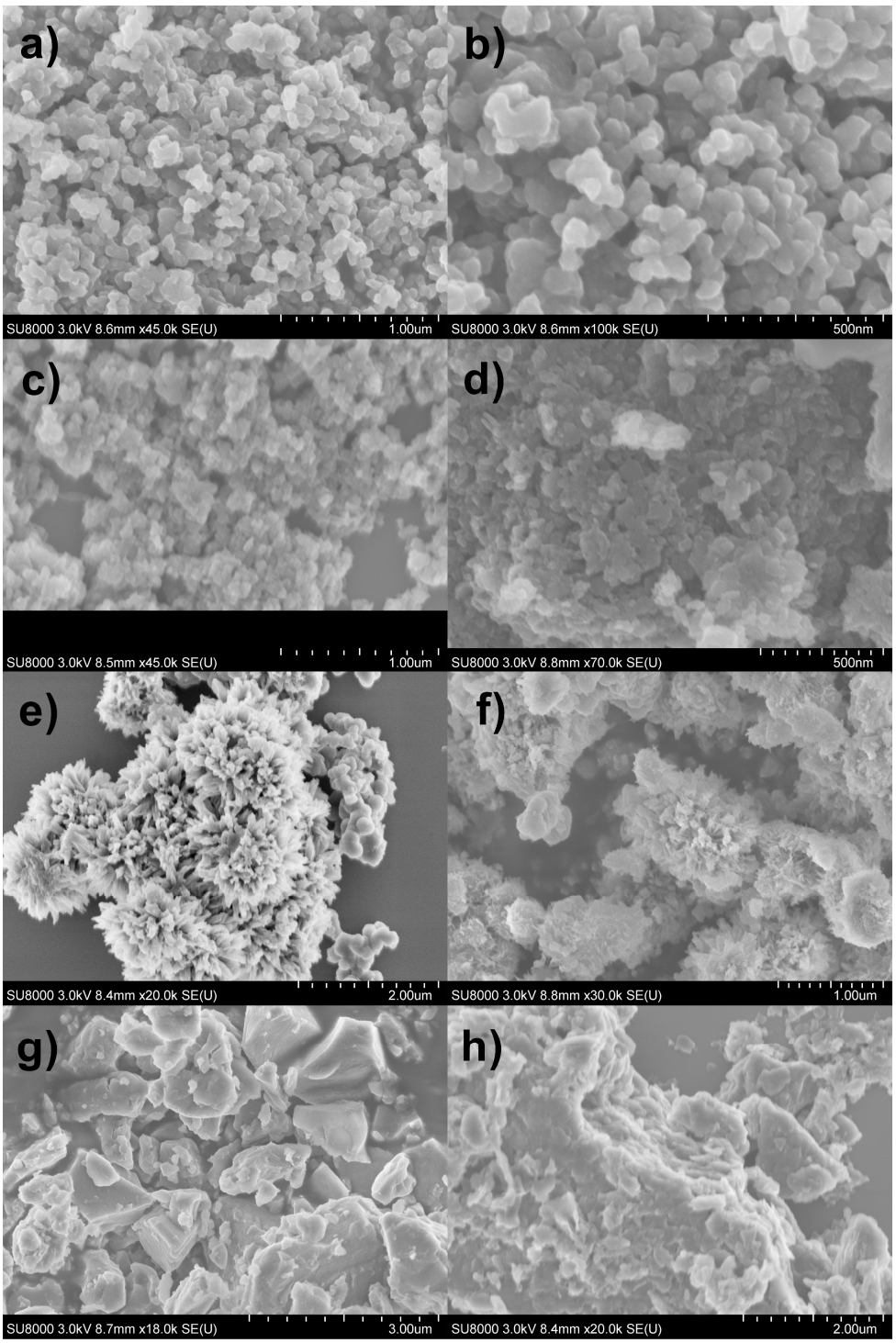

Figure S5. SEM images of NiPc-Ni (a, b), NiPc-Zn (c, d), ZnPc-Ni (e, f), ZnPc-Zn (g, h).

6. TEM Images

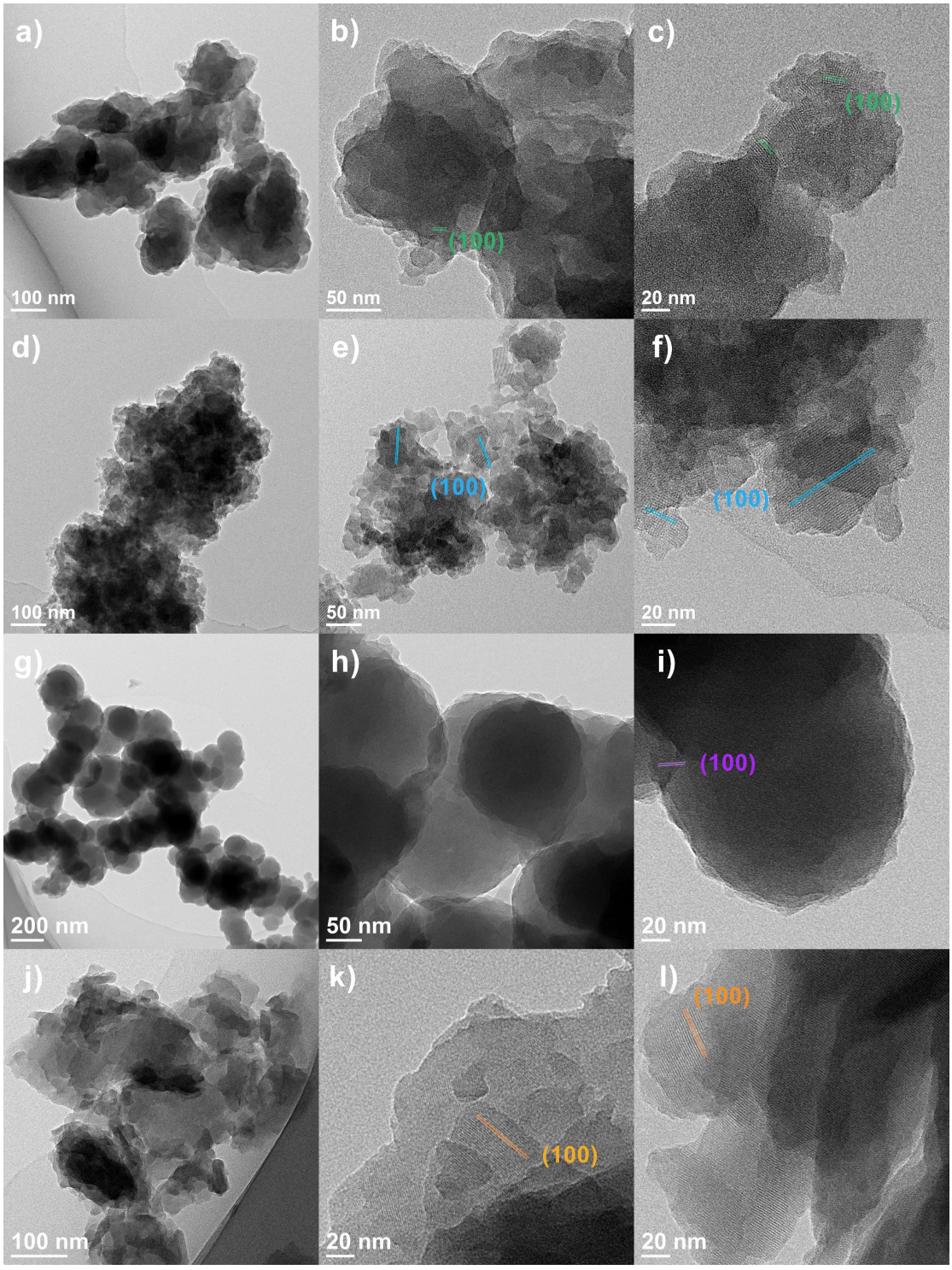

Figure S6. TEM images of NiPc-Ni (a-c), NiPc-Zn (d-f), ZnPc-Ni (g-i), ZnPc-Zn (j-l).

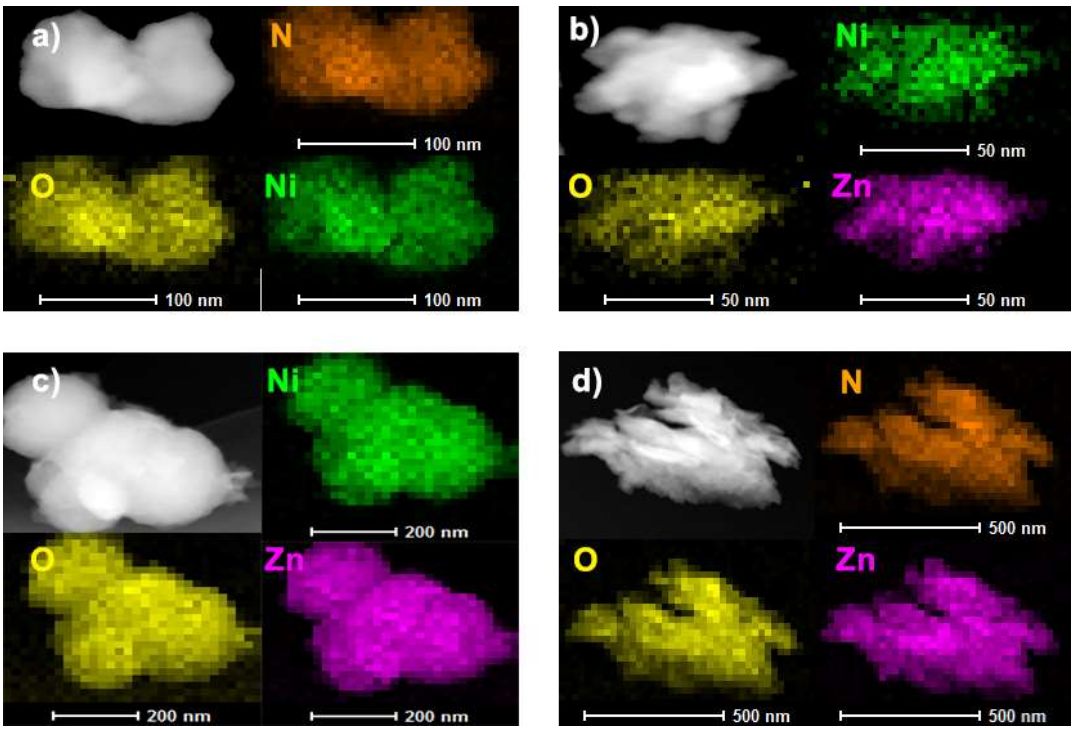

Figure S7. EDX mapping images of NiPc-Ni (a), NiPc-Zn (b), ZnPc-Ni (c), ZnPc-Zn (d).

7. XPS Spectra

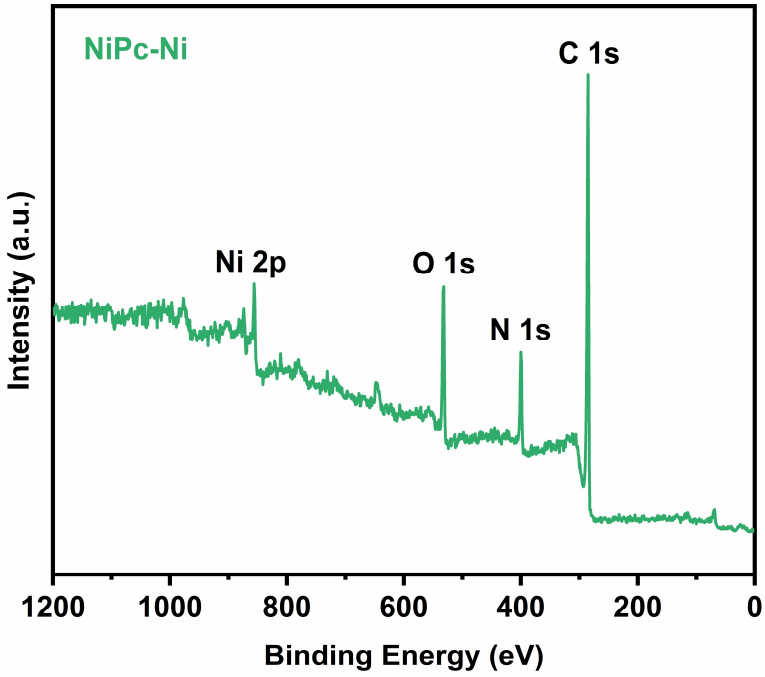

Figure S8. XPS survey spectra of **NiPc-Ni**

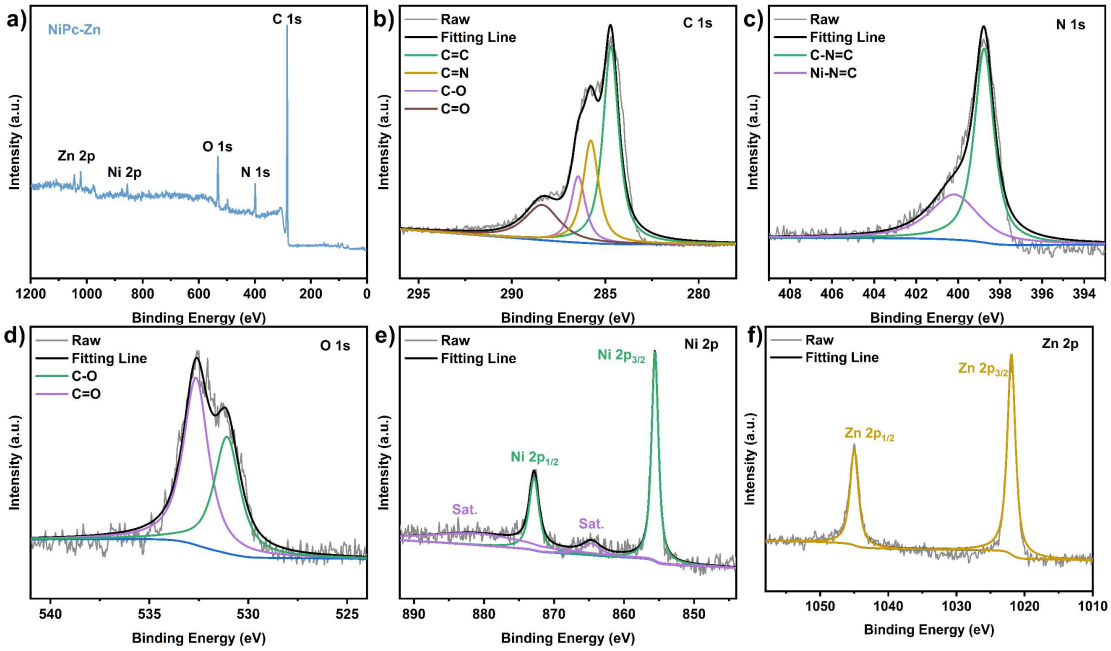

Figure S9. XPS spectra of **NiPc-Zn**: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Ni 2p, f) Zn 2p. There is a integral ratio of 58:42 for C=O : C-O.

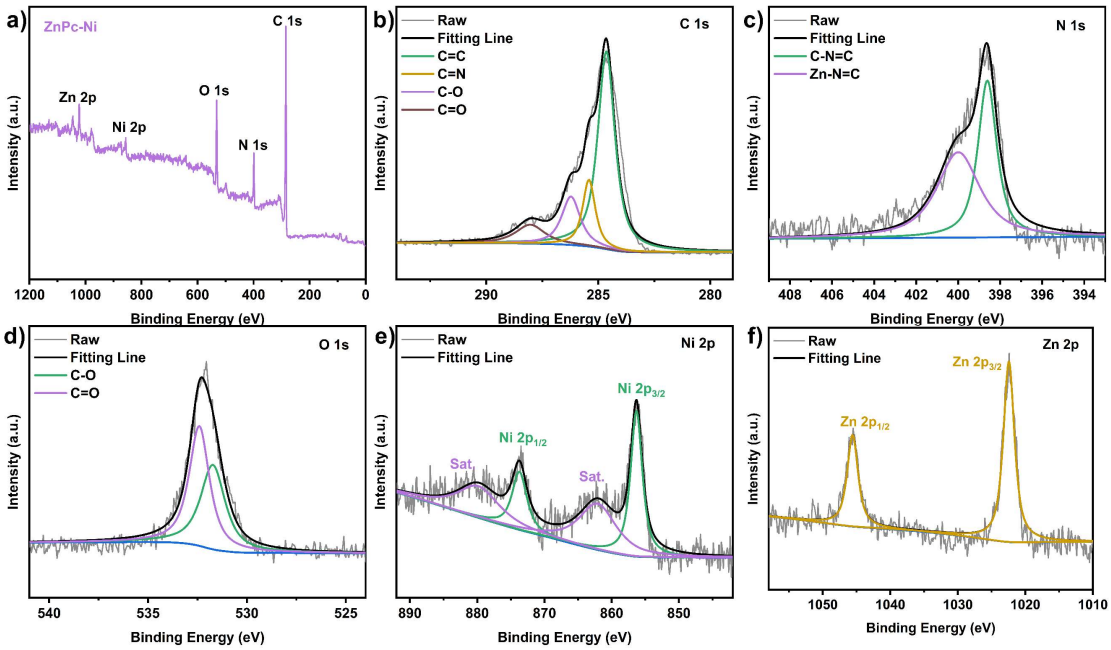

Figure S10. XPS spectra of **ZnPc-Ni**: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Ni 2p, f) Zn 2p. There is a integral ratio of 54:46 for C=O : C-O.

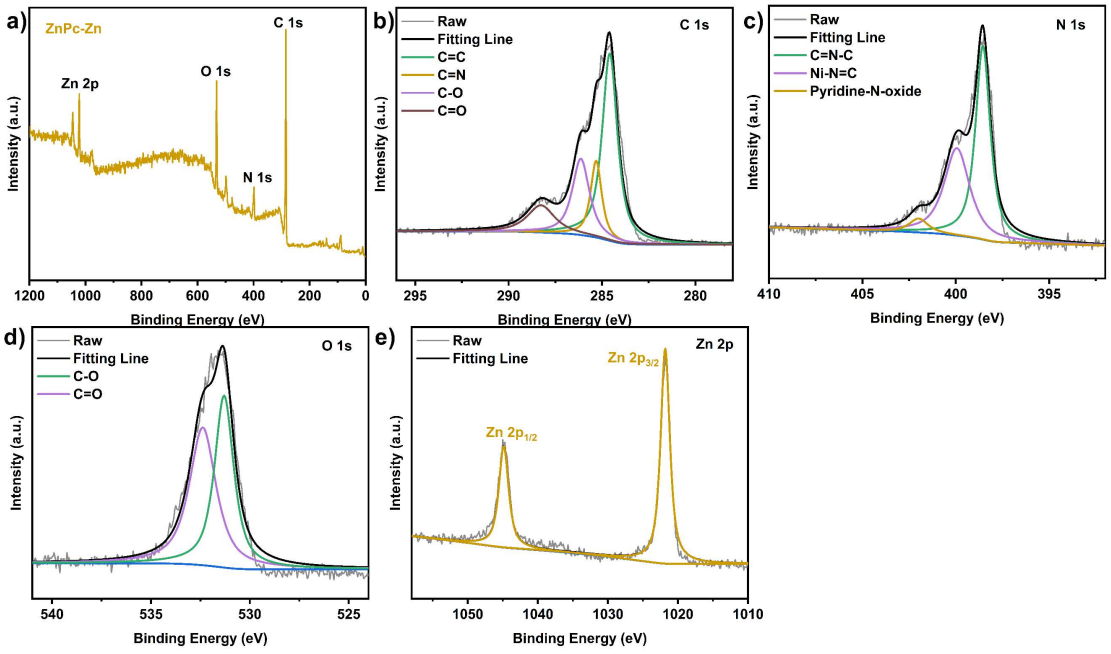

Figure S11. XPS spectra of **ZnPc-Zn**: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Zn 2p. There is a integral ratio of 53:47 for C=O : C-O.

8. ECSA Measurements

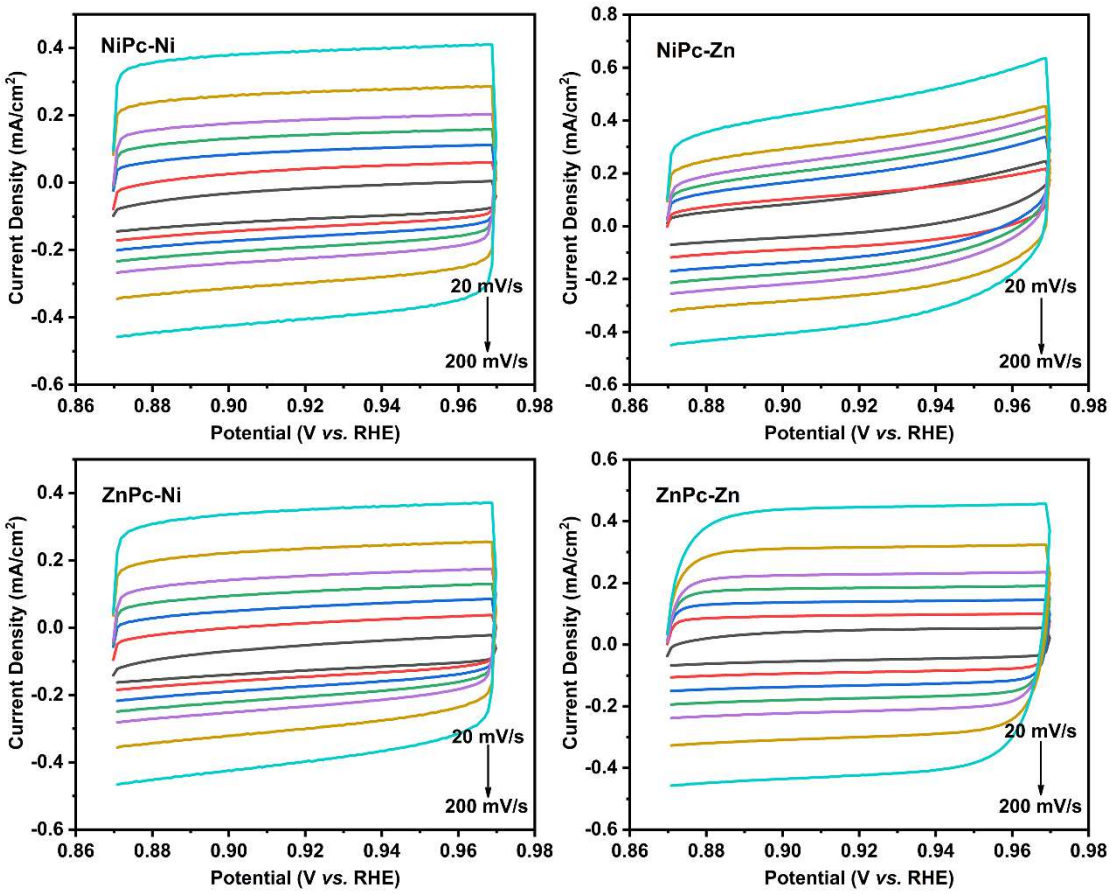

Figure S12. CVs in non-faradaic region of four MOFs.

9. TOF calculation

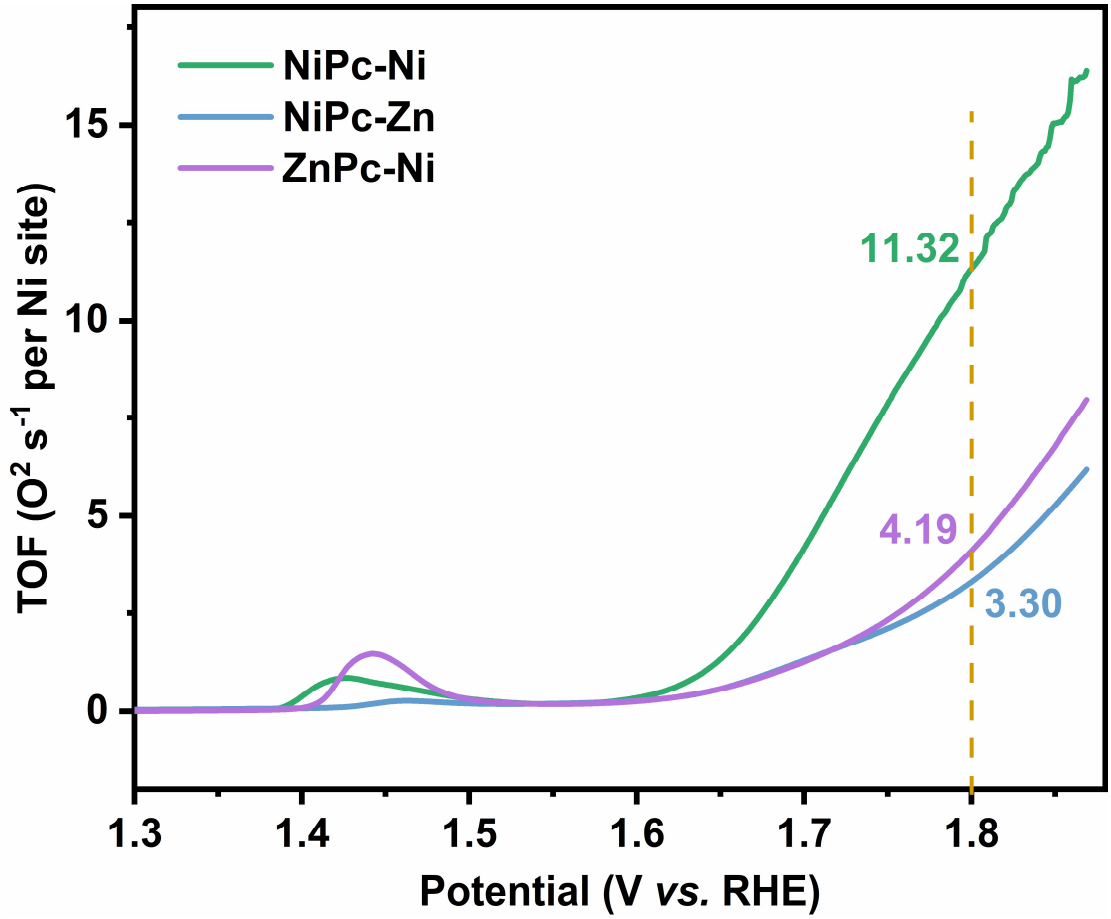

Figure S13. TOF of NiPc-Ni, NiPc-Zn and ZnPc-Ni based on LSV tests.

10. Band Structure Calculations

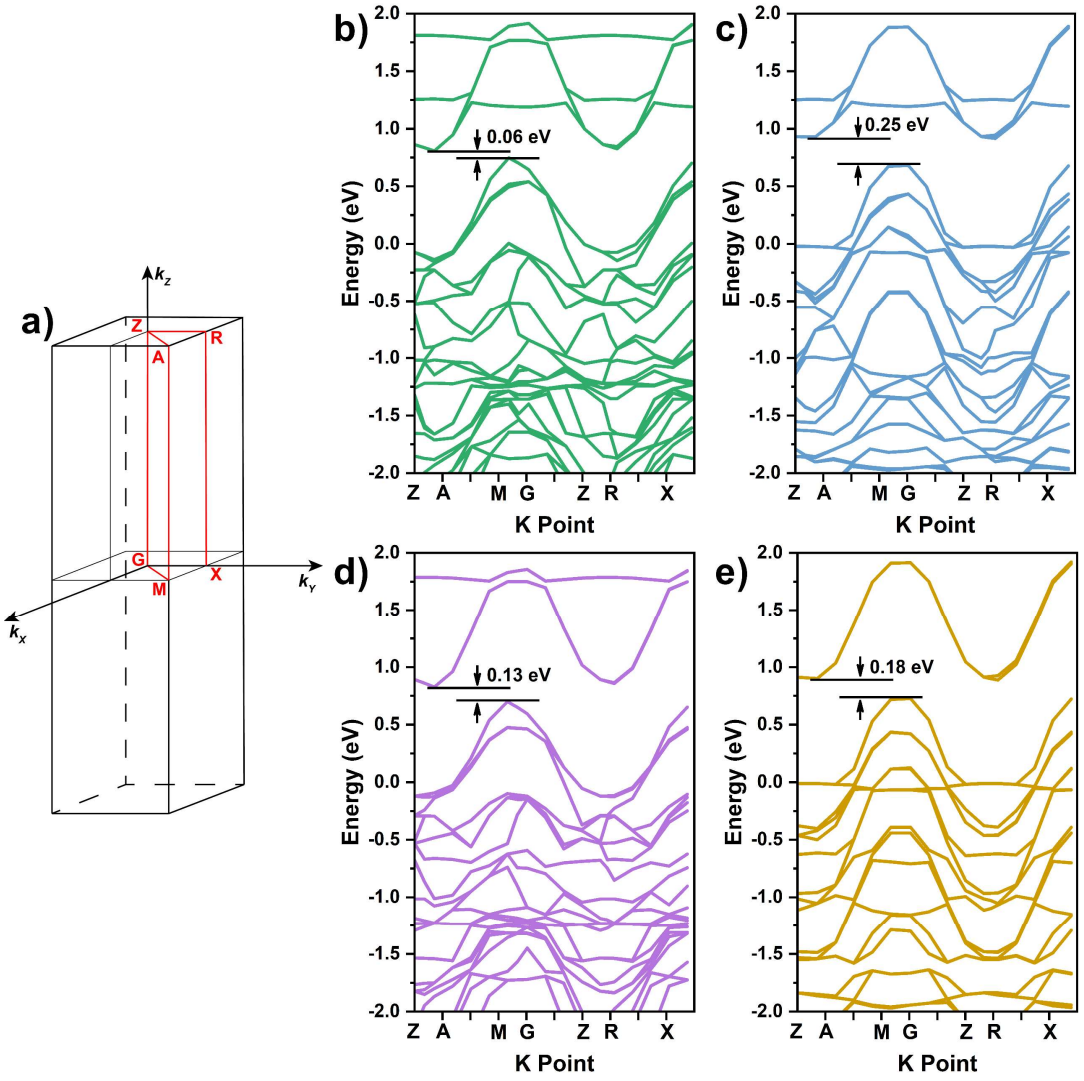

Figure S14. a) Brillouin zone and K-path selection for MOFs. b-e) Band structure and indirect band-gap of NiPc-Ni, NiPc-Zn, ZnPc-Ni, and ZnPc-Zn, respectively.

11. Stability Test

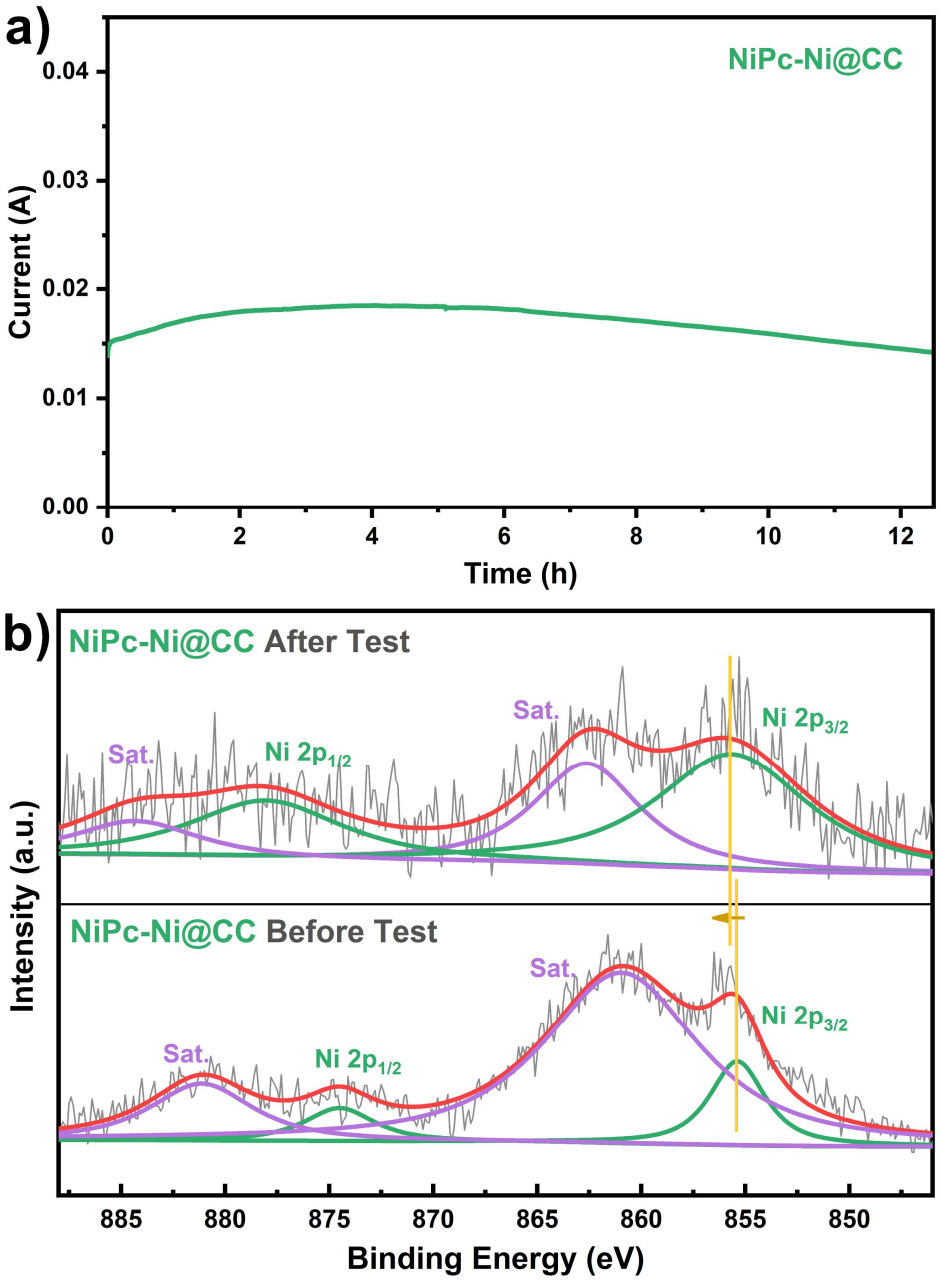

Figure S15. a) Chronoamperometry test of NiPc-Ni @Carbon Cloth. b) Ni 2p XPS spectra before and after chronoamperometry test.

12. Comparison Table

Table S2. Comparisons of the OER activity of MOF-based catalysts.

Catalyst	Electrolyte	onset overpotential (mV)	overpotential @ j=10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Substrate	Ref.
NiPc-Ni	**1.0 M KOH**	**319**	**427**	**83**	**GC**	**This work**
Pb-TCPP	1.0 M KOH	-	470	106.2	GC	Dalton Trans., 2016, 45, 61-65
ZIF-67	1.0 M KOH	350	550	316.9	GC	Nano Energy., 2017, 41, 417-425
UTSA-16	1.0 M KOH	320	408	77	GC	ACS Appl. Mater. Interfaces, 2017, 9, 7193-7201
Fe-MOF	1.0 M KOH	-	443	74	GC	J. Mater. Chem. A., 2020, 8, 3658-3666
Ni-Cu(BDC)	1.0 M KOH	-	375	179.7	GC	New J. Chem., 2020, 44, 2459-2464
$Ni_{5.7}Ru_{0.3}(HHTP)_3$	0.1 M KOH	290	390	61	GC	Chem. Commun., 2020, 56, 13615-13618.
Co-AIM NU-1000	pH 11	400	-	90	FTO	ACS Appl. Mater. Interfaces., 2015, 7, 28223-28230
$[Co_3(HHTP)_2]_n$	0.1 M KOH	340	490	83	FTO	Chem. Commun., 2018, 54, 13579-13582
NNU-23	0.1 M KOH	-	365	81.8	Carbon Cloth	Angew. Chem. Int. Ed., 2018, 57, 9660-9664

References:

[1] J. Kibsgaard and T. F. Jaramillo, *Angew. Chem. Int. Ed*., 2014, **53**, 14433-14437.

[2] Z. Liu, Z. Zhao, Y. Wang, S. Dou, D. Yan, D. Liu, Z. Xia and S. Wang, *Adv. Mater*., 2017, **29**, 1606207.

[3] Z. Chen, Y. Song, J. Cai, X. Zheng, D. Han, Y. Wu, Y. Zang, S. Niu, Y. Liu, J. Zhu, X. Liu, and G. Wang, *Angew. Chem. Int. Ed*., 2018, **57**, 5076.

[4] Z. Chen, Y. Song, J. Cai, X. Zheng, D. Han, Y. Wu, Y. Zang, S. Niu, Y. Liu, J. Zhu, X. Liu and G. Wang, *Angew. Chem. Int. Ed*., 2018, **57**, 5076.