Supporting Information

Novel Two-Dimensional Nickel Phthalocyanine-Based Metal-Organic Framework for Highly Efficient Water Oxidation Catalysis

Hongxing Jia,[a] Yuchuan Yao,[a] Jiangtao Zhao,[b] Yuyue Gao,[a] Zhenlin Luo,[b] Pingwu Du[a]*

[a] Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, *i*ChEM (Collaborative Innovation Center of Chemistry for Energy Materials), University of Science and Technology of China (USTC), 96 Jinzhai Road, Hefei, Anhui Province, 230026, P. R. China.

[b] National Synchrotron Radiation Laboratory, University of Science and Technology of China (USTC), 96 Jinzhai Road, Hefei, Anhui Province, 230026, P.R.China.

*E-mail: dupingwu@ustc.edu.cn

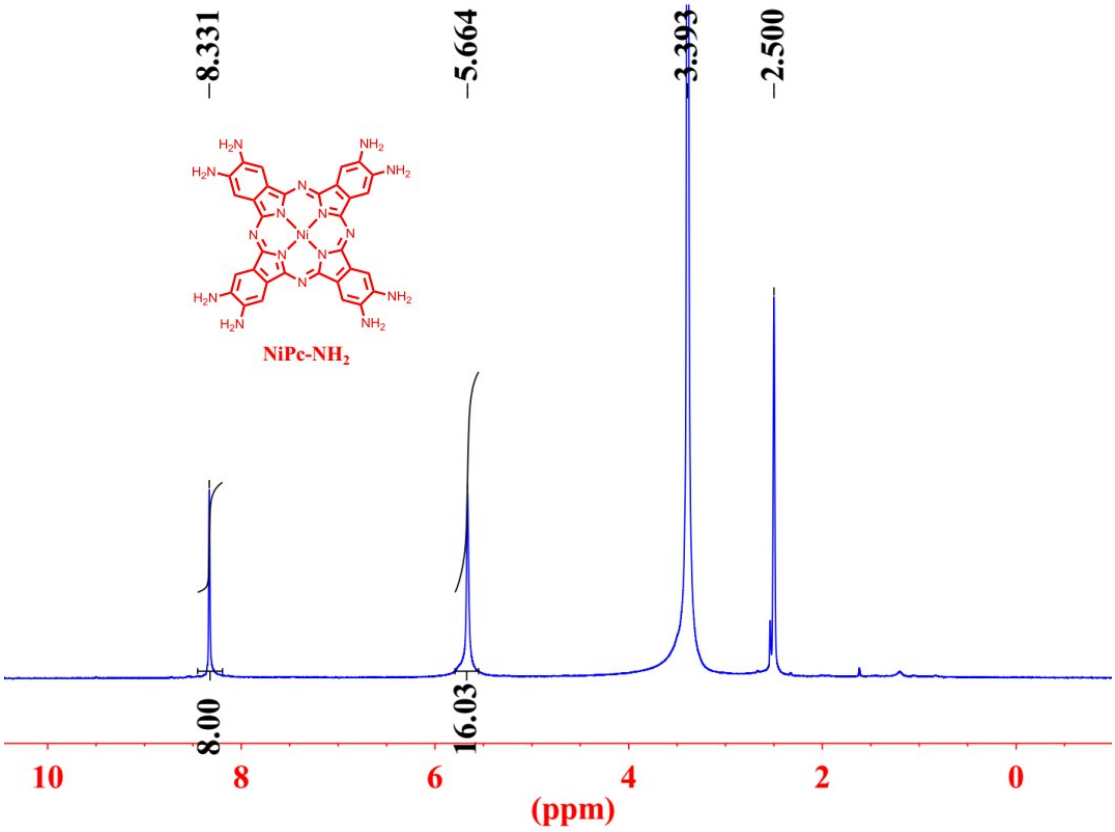

Figure S1. ^{1}H NMR spectrum of NiPc-NH_2 in DMSO-d_6.

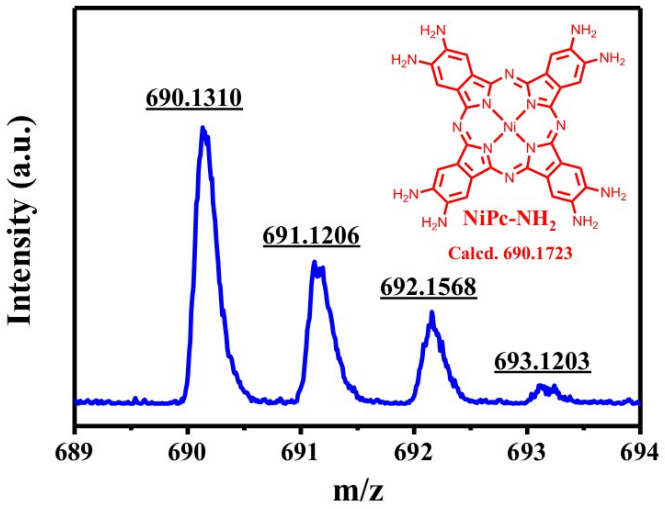

Figure S2. Mass spectrometry for NiPc-NH_2.

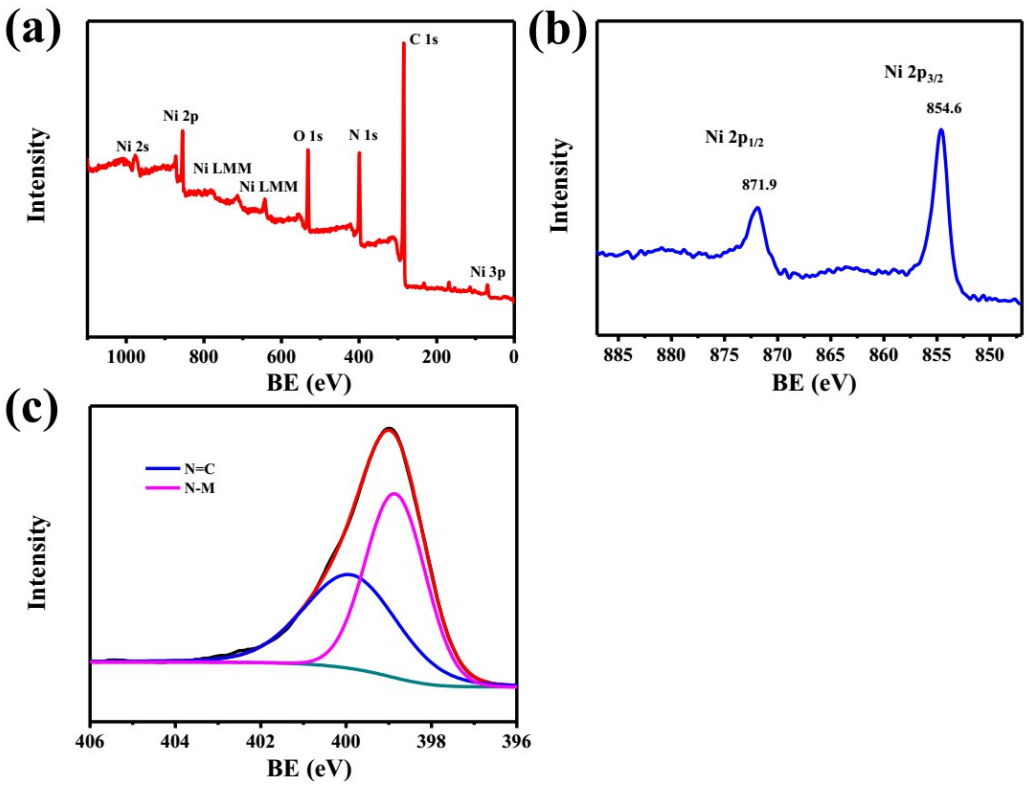

Figure S3. XPS data for NiPc-MOF: (a) survey scan; (b) Ni 2p spectrum; and (c) N 1s spectrum.

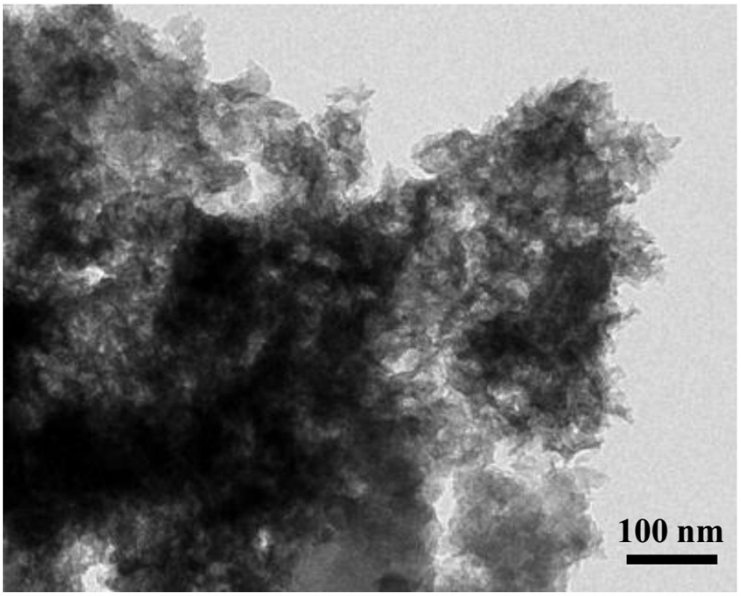

Figure S4. TEM image of NiPc-MOF material.

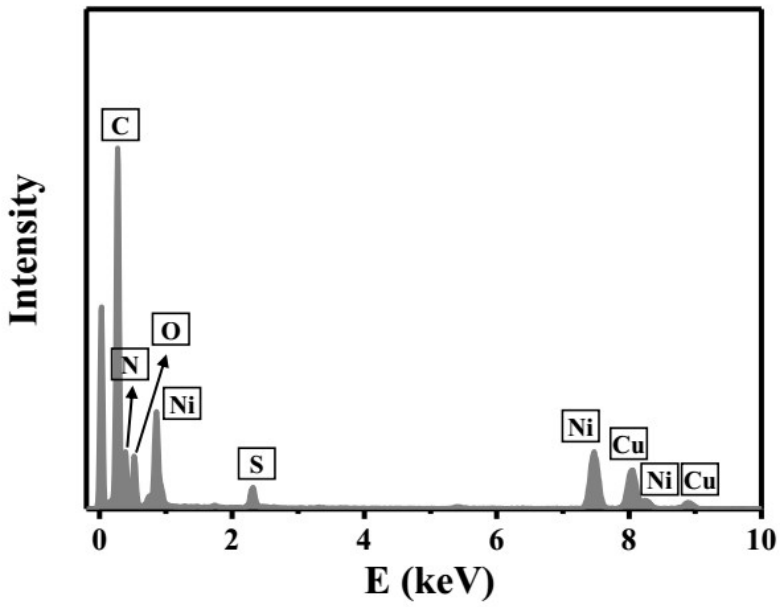

Figure S5. EDX data of NiPc-MOF. The Cu signal represented the copper plate substrate, while the presence of S was attributed to the adsorbed DMSO during the reaction.

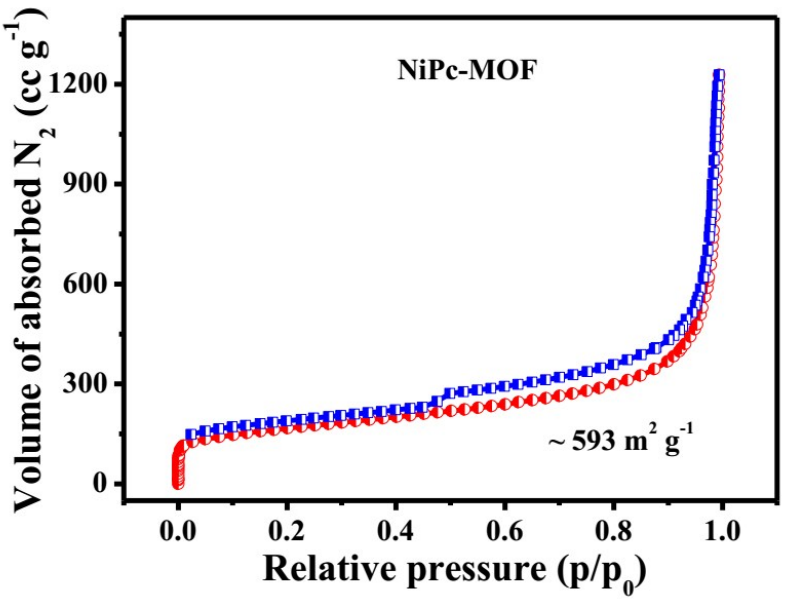

Figure S6. Nitrogen adsorption isotherm plot of bulk NiPc-MOF powder.

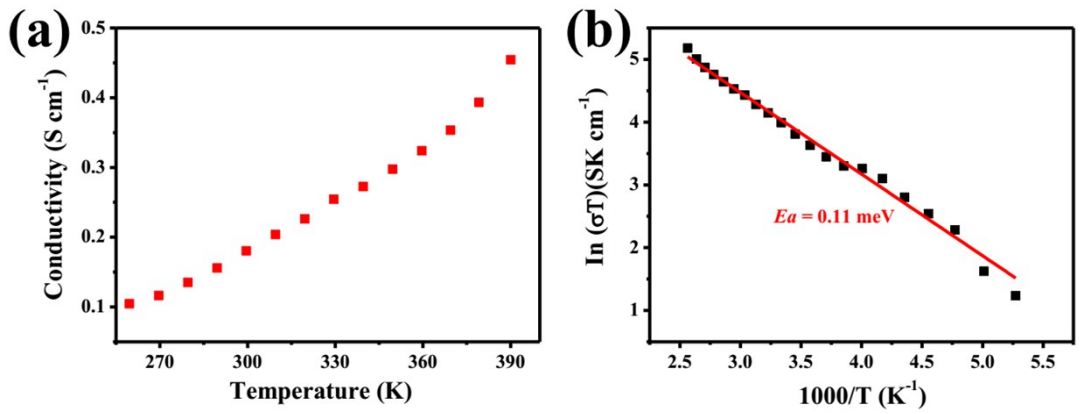

Figure S7. (a) Electrical conductivities of NiPc-MOF (~150 nm thick film on quartz). (b) Arrhenius plot of the conductivity for NiPc-MOF. The activation energy of NiPc-MOF was calculated to be 0.11 meV.

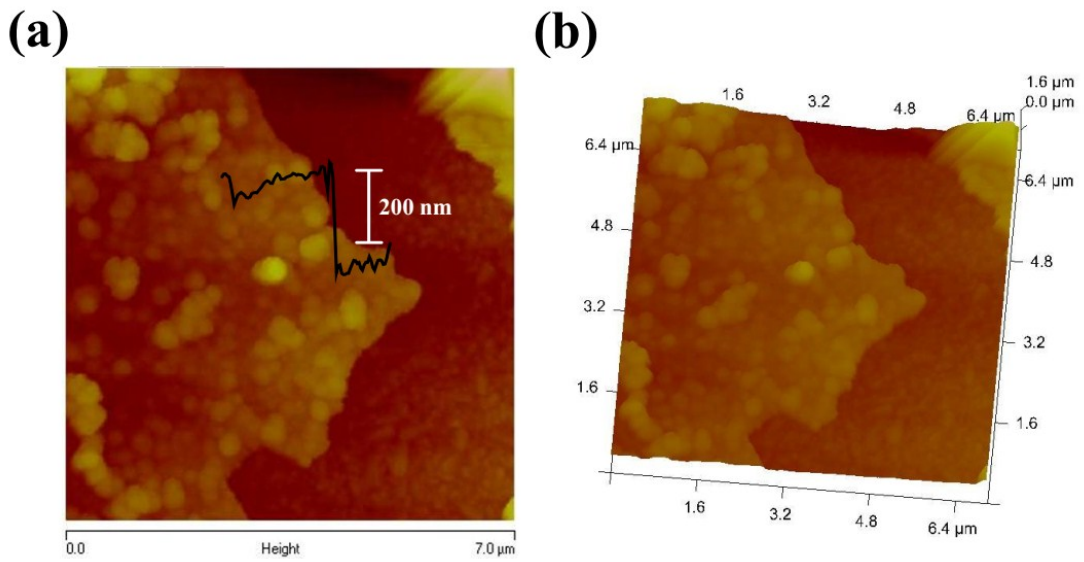

Figure S8. (a) SPM height profile (black line) and corresponding morphology image of a typical NiPc-MOF film on FTO. (b) 3D SPM image of the corresponding NiPc-MOF film.

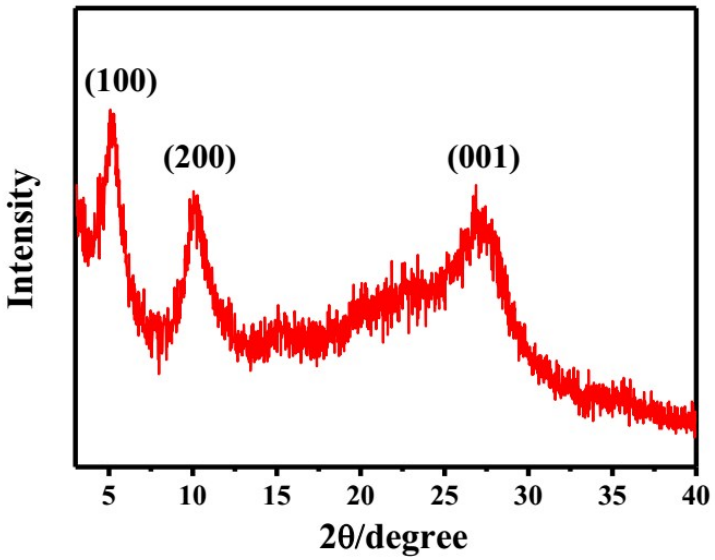

Figure S9. Powder XRD pattern of NiPc-MOF film scratched from FTO.

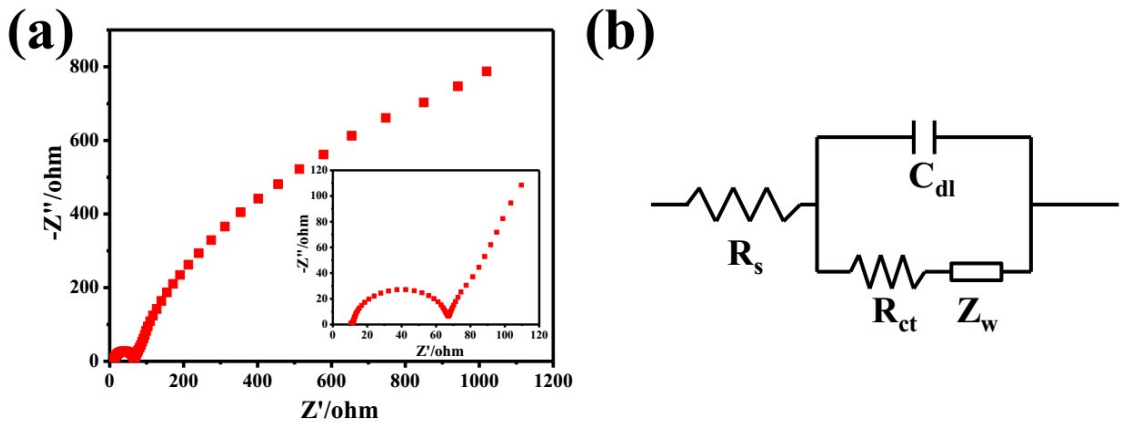

Figure S10. (a) Nyquist plots of the NiPc-MOF modified FTO in 1.0 M KOH in the frequency range of 10^{-2} to 10^{4} Hz. Inset: impedance data in the high-frequency range showing the lower electrochemical series resistance values for NiPc-MOF. (b) Equivalent circuit for fitting impedance spectra. R_s is the electrolyte resistance, C_{dl} is the double-layer capacitance, R_{ct} is the charge-transfer resistance, and Z_w is the Warburg impedance. The fitted R_s is 11.3 Ω and the R_{ct} of the NiPc-MOF modified FTO was estimated to be 52.3 Ω.

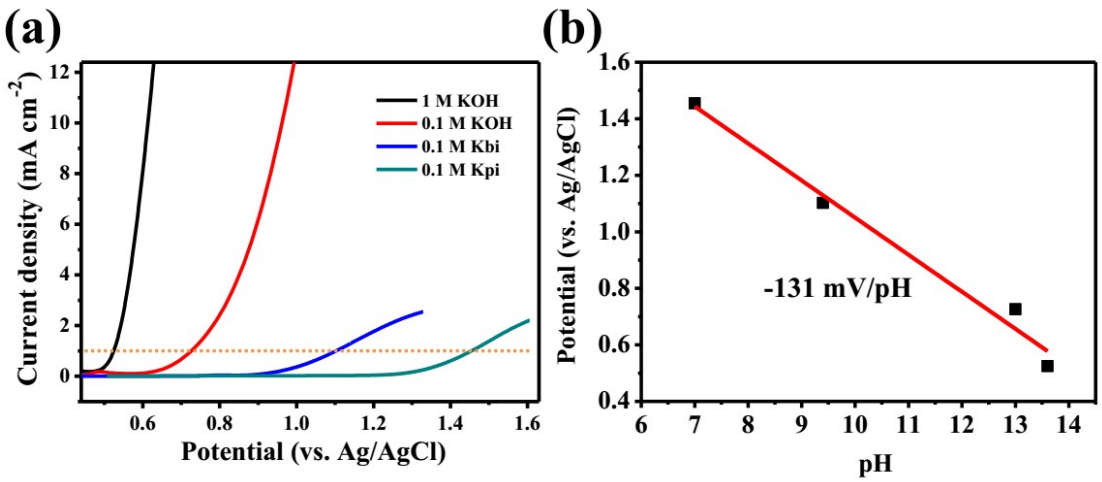

Figure S11. (a) pH dependence of LSV using NiPc-MOF modified FTO working electrode versus Ag/AgCl at pH 7, 9.4, 13, and 13.6. The scan rate was 10 mV/s. (b) Potentials (measured at 1.0 mA cm^{-2}) versus pH values with a slope of -131 mV/pH unit.

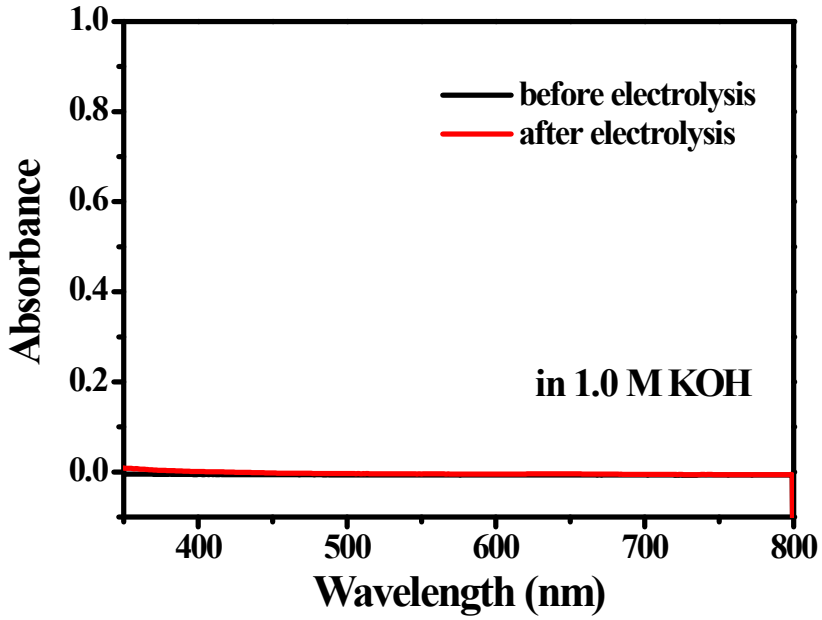

Figure S12. UV-vis absorption spectra of the electrolyte solution before (black) and after (red) long-term chronopotentiometry testing for NiPc-MOF modified FTO.

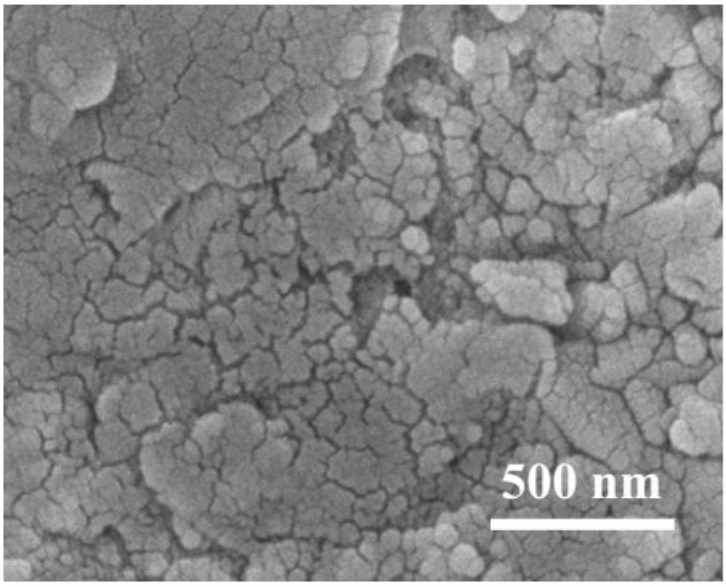

Figure S13. The SEM image of NiPc-MOF film on FTO substrate after long-term OER chronopotentiometry test.

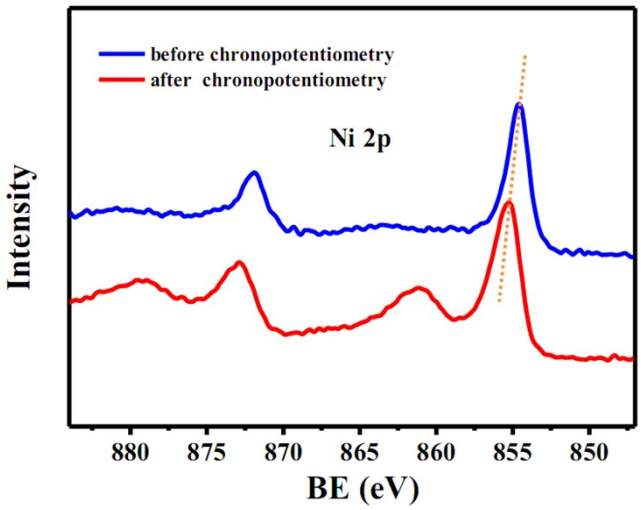

Figure S14. Ni 2p spectra of NiPc-MOF before and after long-term chronopotentiometry test.

Table S1. ICP-AES data of Ni for NiPc-MOF

	nickel content ($\mu g\ cm^{-2}$)	Catalyst loading ($\mu g\ cm^{-2}$)	nickel sites ($mol\ cm^{-2}$)
NiPc-MOF	1.68	7.6	2.86×10^{-8}

Table S2. The OER activity for selected molecular-based catalysts

catalysts	electrolyte	Onset potentials (V)	Mass activity (A g^{-1})	TOF (s^{-1})	Tafel slope (mV dec^{-1})	References
NiPc-MOF	**pH = 13.6 1 M KOH**	**1.48**	**883.3, η = 350 mV**	**2.5, η = 350 mV**	**74**	**This work**
$[NiL(H_2O)_2](ClO_4)_2$	pH = 6.5 0.3 M acetate buffer	1.73				*ChemSusChem* 2016, 9, 485
$CoH^{\beta F}CX\text{-}CO_2H$	pH = 7 0.1 M phosphate buffer	1.86		0.81, η = 780 mV	120	*J. Am. Chem. Soc.* 2011, 133, 9178
$(CoP)_n$-MWCNTs	pH = 13.6 1 M KOH	1.50[a]	141.4, η = 410 mV		60.8	*Chem. Mater.* 2015, 27, 4586
Ru(bpa)(pic)-MWCNTs	pH = 7, 0.1 M aqueous Na_2SO_4	1.53		0.3, η = 580 mV	160	*Angew. Chem. Int. Ed.* 2011, 50, 12276
Co-TpBpy	pH = 7, 0.1 M phosphate buffer	1.63		0.23, η = 400 mV	59	*Chem. Mater.* 2016, 28, 4375
polyoxometalate-ruthenium @MWCNT	pH = 7, phosphate buffer	1.72[a]		0.01, η = 350 mV	280	*Nat. Chem.* 2010, 2, 826
Pb-TCPP	1 M KOH	1.60[a]	50, η = 470 mV	0.0014, η = 470 mV	106.2	*Dalton Trans.* 2016, 45, 61
$[\{[4,4'\text{-}(HO)_2OPCH_2]_2bpy\}_2Ru^{II}(bpm)Ru^{II}(Mebimpy)\text{-}(OH_2)]^{4+}$	pH = 1, 0.1 M HOTf	1.54[a]		0.6, η = 570 mV，1 M $HClO_4$		*Angew. Chem. Int. Ed.* 2009, 48, 9473

[a]: the onset potentials were judged from the reported LSV or CV curves.