Electronic Supplementary Information (ESI) for

Ni (II)-Doped Anionic Metal-organic Framework Nanowire Arrays for Enhancing Oxygen Evolution Reaction

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Part I: Experimental Section

1. Structural determination

All powder X-ray diffraction (PXRD) analyses were tested by a Rigaku Dmax2500 diffractometer with Cu Kα radiation using a step size of 0.05°. Fourier transform infrared (FT-IR) spectra were taken on a Nicolet Magna 750 FT−IR spectrometer in the 4000−500 cm^{-1} region by using KBr pellets.

2. Electrochemical characterization

OER measurements were performed in a three-electrode glass cell. All the electrochemical data were conducted at room temperature on CHI760 D in 1.0 M KOH. Electrochemical impedance spectroscopy (EIS) measurements were tested by applying an AC voltage with 5 mV amplitude in a frequency range from 1000000 to 1 Hz. The collected results were adjusted with iR correction to decrease the influence of ohmic resistance. The synthesized samples grown on a substrate (e.g., Cu foam 0.8cm x0.8 cm) were used as the working electrode for electrochemical characterizations. The current density in this work was normalized to the geometrical surface area and the measured potentials *vs.* Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{RHE} = E_{Ag/Ag/Cl}$+ 0.059 × pH + 0.213). To ensure the O_2/H2O equilibrium at 1.23 V vs. RHE, the flow of N_2 was maintained over the electrolyte (1.0 MKOH) during electrochemical measurements in order. The polarization curves were recorded with the scan rate of 5 mV s^{-1}. The working electrodes were scanned for several times beforethe stable polarization curves were collected.

The Tafel slope was calculated according to Tafel equation as follows:

$\eta = b \cdot log(j/j_0)$

η: the overpotential,

b: the Tafel slope,

j: the current density,

j_0: the exchange current density.

The onset potentials were determined based on the beginning of the linear region in the Tafel plots.

The overpotential: $\eta = E\ (vs.\ RHE) - 1.23$

3. Synthesis of JXUN-4

A mixture of $Zn(NO_3)_3 \cdot 6H_2O$ (31 mg), adenine (7mg), and 4,4′ -biphenyldicarboxylic acid (13mg) in a N, N-dimethylformamide (DMF; 5mL) / water (H_2O; 1mL) solution were placed in a 20 mL vial.The vessel heated at 120 °C for 3 days, and then cooled to room temperature. Crystalline samples were filtered, washed with DMF, distilled water and ethanol, and then dried at ambient temperature.

4. JXUN-4 grown on Cu foam (JXUN-4 -NA/CF)

Firstly, a Cu foam was cleaned with absolute ethanol and Milli-Q water through ultrasonication method and was placed in a 20 mL vial. Secondly, A mixture of $Zn(NO_3)_3 \cdot 6H_2O$ (31 mg), adenine (7mg), and 4, 4′ - biphenyldicarboxylic acid (13mg) in a DMF(6mL) / water (7mL) solution were placed in a 20 mL vial, which was heated at 120 °C for 72 hours, and then cooled down to room temperature at a rate of 5°C h^{-1},the Cu foam with attached nanowire array (JXUN-4 -NA/CF**)** was obtained.

5. Synthesis of Ni@JXUN-4-NA on Cu foam (Ni@JXUN-4-NA-CF)

The fresh JXUN-4 -NA/CF was successively washed with DMF, H_2O and methanol before immersing it in $Ni(NO_3)_2$ (50 mM) solution for 18, 10, and 2h, respectively. The Ni (II) ions were captured and doped in the anionic structure of JXUN-4-NA/CF. Further, Energy-dispersive X-ray spectroscopy (EDS) measurement demonstrated Ni contents were, respectively, 4.6, 2.8 and 0.5 %.

6. Ni@JXUN-4 coated on Cu Foam (Ni@JXUN-4/CF)

The as-synthesized JXUN-4 crystals were washed with distilled water and methanol before immersion in $Ni(NO_3)_2$ (50 mM) for 18h. The Ni^{2+} ions were captured in the framework of anionic MOFs (Ni@JXUN-4/CF). Further, ICP measurement demonstrated Ni contents was 5.0 %. The as-synthesized Fe@JXUN-4/CF was ultrasonically dispersed in the mixture of 1 mL of Milli-Q water and ethanol, and then transferred onto Cu foam with a loading amount of ~ 0.26 mg cm^{-2}. The obtained electrode was subjected to overnight solvent evaporation at room temperature, subsequent coating with mixed Nafion solution (0.05 wt.%).

8.JXUN-4 coated on Cu Foam (JXUN-4/CF)

The procedure for preparation of JXUN-4/CF was the same as that for Ni@JXUN-4/CF except for using JXUN-4 instead of Ni@JXUN-4.

9. Preparation of RuO_2 electrode on Cu foam (RuO_2/CF)

The procedure for preparation of RuO_2/CF was the same as that for JXUN-4/CF except for using RuO_2 instead of JXUN-4.

Part II: Supplementary Results

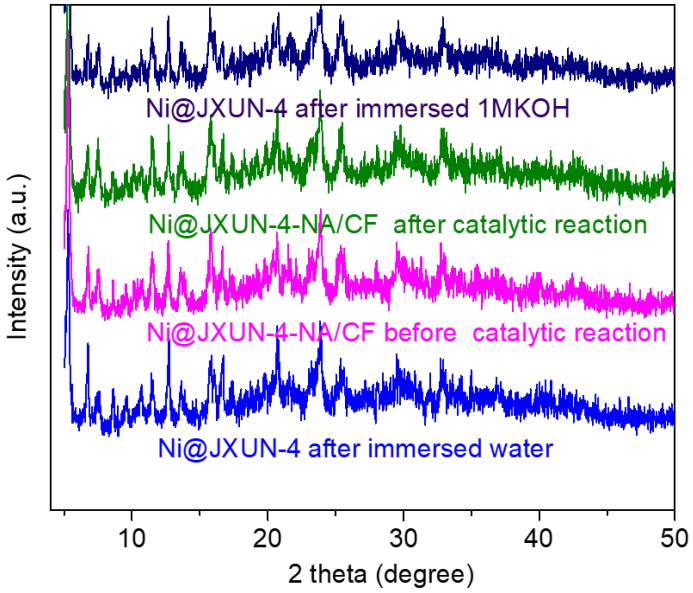

Figure S1. The PXRD patterns of Ni@JXUN-4 based samples under different conditions.

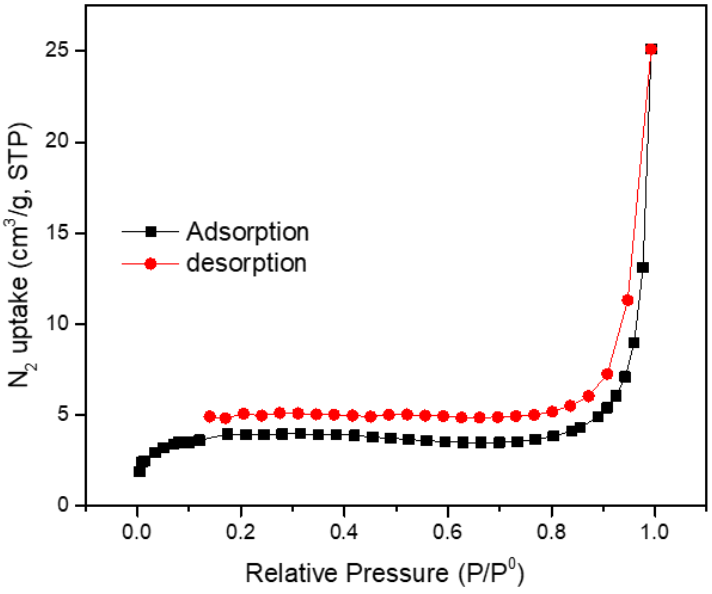

Figure S2. The N_2 sorption isotherms of Ni@JXUN-4.

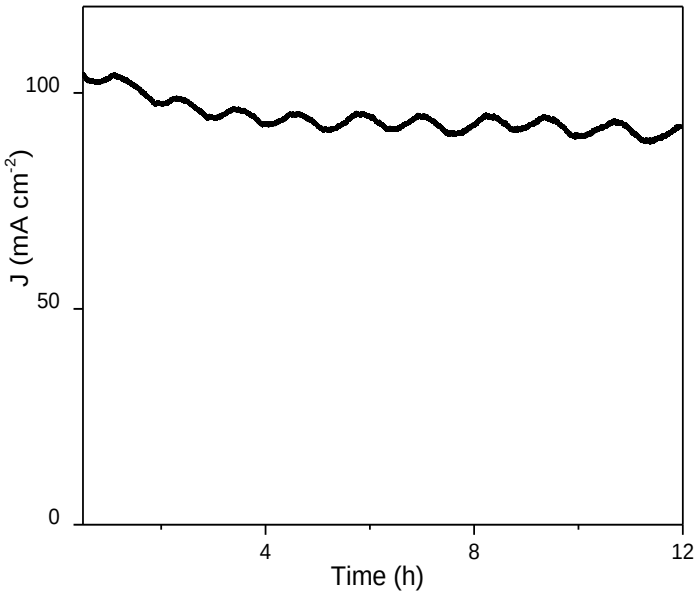

Figure S3. Chronoamperometric curves for Ni@JXUN-4-NA/CF electrocatalyst at a fixed overpotential of 0.52 V(Ag/AgCl)

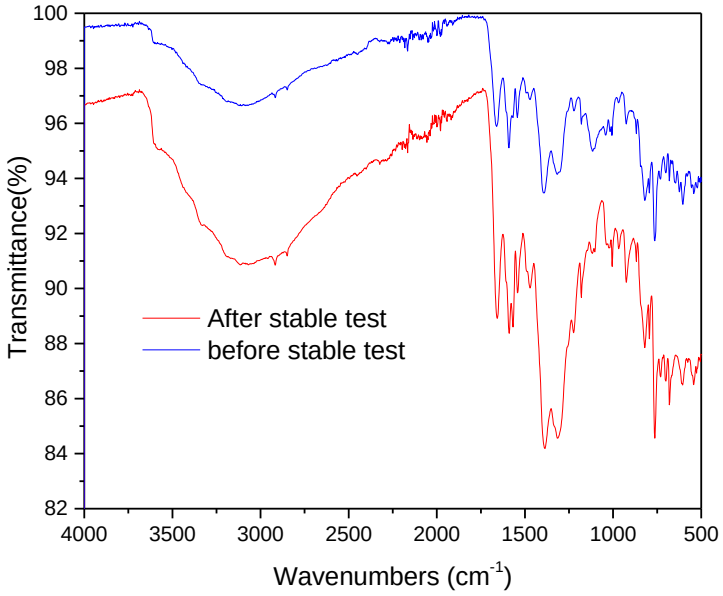

Figure S4. FT-IR patterns of Ni@JXUN-4-NA/CF electrocatalyst before and after OER stability test.

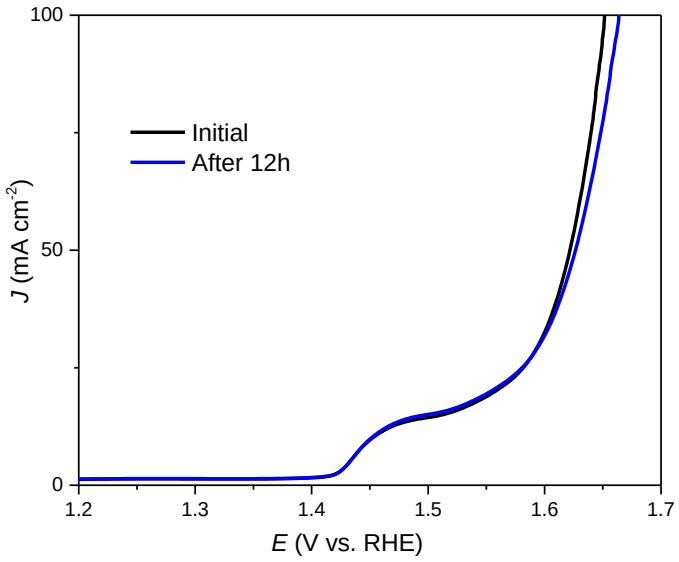

Figure S5. LSV plots of Ni@JXUN-4-NA/CF electrocatalyst before and after a 12 h stability test.

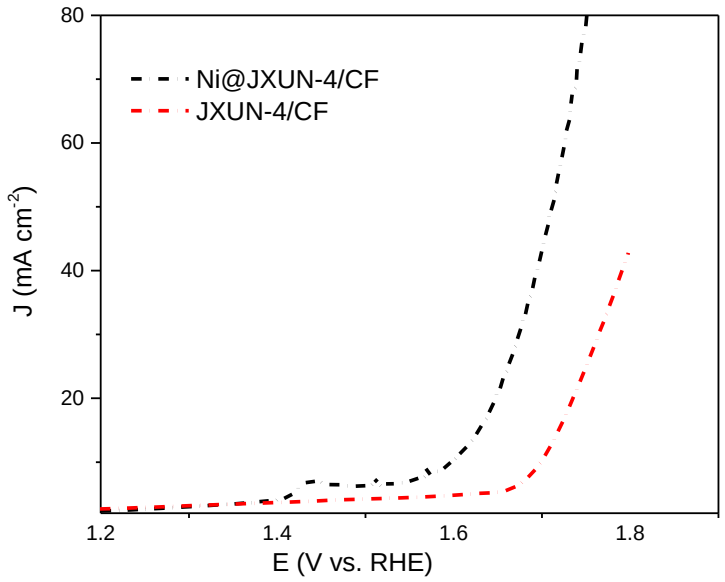

Figure S6. LSV plots of Ni@JXUN-4/CF and JXUN-4/CF electrocatalyst.

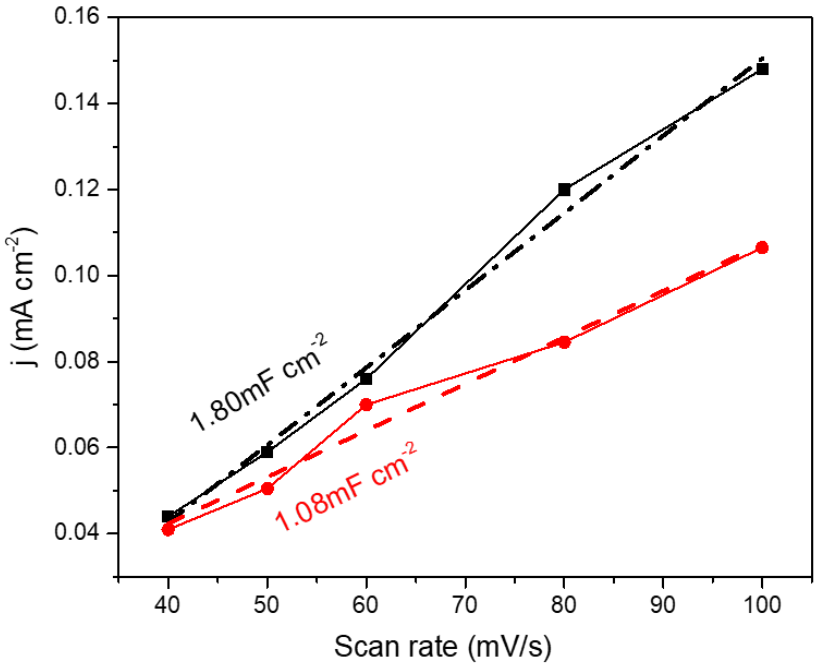

Figure S7. linear relationship of the current density at 1.1 V (vs. RHE) vs. scan rates for Ni@JXUN-4-NA/CF (black line) and JXUN-4-NA/CF (red line).

Table S1. Comparison of electrocatalytic OER activities for Ni@JXUN-4-NA/CF with reported MOFs-based electrocatalysts.

Catalyst	Over-potential	Substrate	Ref
Co/MIL-100(Fe)	734 at 5mA cm^{-2}	GCE	*Int. J. Hydrogen Energy*, **2014**, *39*,16179
Co-ZIF-9	510 at 1 mA cm^{-2}	FTO	*Nanoscale, **2014**, 6, 9930*
NU-1000	566 at 10 mA cm^{-2}	FTO	*ACS Appl. Mater. Interfaces **2015**, 7, 28223*
MAF-X27-OH	292 at 10 mA cm^{-2}	Cu Foil	*J. Am. Chem. Soc.,* **2016**, *138*, 8336
Co-WOC-1	390 at 1 mA cm^{-2}	GCE	*Angew. Chem. Int. Ed., **2016**, 55, 2425*
Ni/Fe-BTC	270 at 10 mA cm^{-2}	NF	*ACS Appl. Mater. Interfaces*, **2016**, *8*, 16736
Titanium carbide-CoBDC	410 at 10 mA cm^{-2}	GCE	*ACS Nano, **2017**, 11,5800*
CoO_x-ZIF	318 at 10 mA cm^{-2}	GCE	*Adv. Funct. Mater*. **2017**, 1702546.
Ni-MOF	320 at 100 mA cm^{-2}	NF	*Inorg. Chem. Front.*, **2018**,*5*, 1570
CoZIF-9(III)	380 at 10 mA cm^{-2}	NF	*Adv. Sci.* **2018**, *5*, 1801029
NiFe-MOF-74	223 at 10 mA cm^{-2}	NF	*Chem. Commun.*, **2018**, *54*, 7046
Ni@JXUN-4-NA	**310** at 20 mA cm^{-2}	**CF**	**This work**

CF: Cu foam, NF: Ni foam, GCE: glassy carbon electrode