Supporting Information

Plasma modification of a Ni based metal organic framework for efficient hydrogen evolution

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Keywords: metal organic framework, plasma, Ni based catalyst, hydrogen evolution reaction, water splitting

Experimental Section

I.Materials:

Nickel nitrate (Ni(NO₃)₂·6H₂O, 98 wt%), ethanol (\geq 99.7 wt%), and potassium hydroxide (KOH, \geq 85.0 wt%) were purchased from Xilong Chemical Co. Ltd.. 2,5- dihydroxyterephthalic acid (DHTA, 98 wt%) was obtained from Chemsoon Co. Ltd.. Nickel foam (NF) and carbon rod were purchased from Shandong Haike Chemical Group Co.. Commercial platinum on carbon (Pt/C, 10 wt %) and nafion solution (5 wt% in a mixture of lower aliphatic alcohols and water) were purchased from Alfa-Asear Co. Ltd.. All reagents were used without further purification.

II. Additional Methods:

Preparation of Ni/C composites

Synthesis of Ni MOF-74.

1.2 g Ni(NO₃)₂·6H₂O and 300 mg 2,5-dihydroxyterephthalic acid was dissolved in 75 mL DMF, EtOH and H₂O mixture with volume ratio of 1:1:1. Then put this mixture into the reactor made by Teflon, soaking the ultrasounded Ni foam (3.5 cm \times 6.5 cm) below the liquid level. After reaction for 12 h at 100 °C, the fine yellow crystalline product grown on Ni foam (Ni-MOF-74/NF) was collected by centrifugation and washed several times with EtOH and H₂O. Finally, the product was totally dried under the vacuum at 150 °C overnight.

Synthesis of Ni@NC nanostructure

To obtain Ni@NC nanostructure, the plasma-assisted sintering system was established. Ni MOF-74 grown on Ni foam was used as precursor for plasma-assisted annealing at temperatures from 250 °C -

350 °C for 1 h. The tube furnace was first evacuated into 0.1 Pa with a rotary pump to obtain a low pressure and then flushed with high purity Ar (99.999%) three times to remove oxygen and moisture. The precursor was heated to appointed temperature at 15 °C/min under a NH₃: Ar (2:1) (NH₃ 20 sccm, Ar 10 sccm) as working gases. Plasma was generated in the coil region by a 13.56 MHz radio-frequency power with input power of 120 W. Pure Ar plasma and NH₃ gas without plasma are also used as working gases under same conditions for comparison.

Structural characterizations

The crystal structures of the composites were characterized by X-ray diffraction (XRD, PANalytical X'Pert3, Cu K α). Scanning electron microscopy (SEM, Hitachi S4800, 10 kV) with energy dispersive X-ray spectroscopy (EDS) analysis and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, 200 kV) were used to characterize morphology and microstructure. The valence state of element was investigated using X-ray photoelectron spectroscopy (XPS, AXIS-Ultra spectrometer, Kratos Analytical, using monochromatic Al K α radiation). Raman Spectroscopy were collected on a LabRAM (HORIBA Ltd) with a 532 nm laser line (HORIBA) and the thermogravimetric analysis (TGA) curves were operated by thermogravimetric analysis (TGA, Q600 SDT thermoanalyzer, in high purity N₂). Online mass spectroscopy (MS) is obtained on Ominstar Pfeiffer Prisma Plus Mass Spectrometer-Residual Gas Analyser (MS-RGA).

Electrochemical measurements

All electrochemical measurements were conducted on the electrochemical workstation (CHI 760D) in a three-electrode system, with a clean platinum foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the catalysts directly grown on Ni foam as the working electrode. Electrochemical measurements were carried in 1 M KOH solution. The measured potentials vs SCE were converted to the RHE scale according to the Nernst equation ($E_{RHE} = E_{SCE} + 0.0591 \text{pH}$ + 0.2415 V). The linear scan voltammetry (LSV) was performed at a scan rate of 1 mV s⁻¹, which was measured after 50 cycles of cyclic voltammetry (CV) to reaching a stable state. The electrochemical impedance spectroscopy (EIS) was tested at the potential which is corresponding to the current at 10 mA cm⁻² in a frequency range from 100 kHz to 0.01 Hz with an AC amplitude of 5 mV. Water electrolysis is performed on a home-designed eletrolyzer driven by a commercial polycrystalline silicon solar cell. A piece of Nafion membrane is used to separate two electrodes. The electrochemical measurements were iR-compensated by the following equation: E (With iR compensation) = E (Without iR compensation) - IR. The ohmic resistance used to iR-compensate in home-designed eletrolyzer was 1.2 Ω measured by electrochemical impedance spectroscopy (EIS).

Computational methods

The calculations were performed using DFT within generalized gradient approximation of the Perdew–Burke–Ernzerhof (PBE) functional, as implemented in the Vienna ab initio simulation package (VASP).^[1-3] A long-range van der Waals interaction (DFT-D3 method) was incorporated to correct total energy.^[4] The electron wave functions were expanded using the plane waves with a cut off energy of 500 eV. The geometries were optimized until the energy and the force were converged

to 0.001 eV/Å and 10⁻⁶ eV, respectively. Since Ni atoms is magnetic atoms, spin polarization was considered throughout the calculations. For the k-point sampling, we used a single Γ point mesh 1 × 1 × 1 in reciprocal space during geometry optimization. The standard hydrogen electrode (USHE) was theoretically defined in solution [pH = 0, p (H₂) = 1 bar].

We can describe the overall HER pathway as following equation under standard conditions:

$$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2} H_{2}(g), \Delta G^{0} = 0 \ eV$$
 (1)

Eq. (1) include an initial state $H^+(aq) + e^-$, an intermediate adsorbed H_* , and the final product, $\frac{1}{2}H_2(g)$. The total energy of $H^+(aq) + e^-$, is equal to $\frac{1}{2}H_2(g)$. The free energy of the adsorption atomic hydrogen $\binom{\Delta G_{H^*}^0}{H^*}$ is calculated as:

$$\Delta G_{H^*}^{\ 0} = \Delta E_H + \Delta E_{ZPE} - TS_H \tag{2}$$

 ΔE_H represents the differential hydrogen adsorption energy and can be described by:

$$\Delta E_{H} = \Delta E_{H*} - E_{*} - \frac{1}{2}E_{H_{2}}$$
(3)

where * denotes the catalyst. $E_{H*} E_*$ and E_{H_2} represents total energies of catalyst plus one H adsorbed hydrogen atoms, the total energies of catalyst without adsorbed hydrogen atoms and H₂ gas, respectively. ΔE_{ZPE} is the difference corresponding to the zero point energy between the adsorbed state and the gas phase. The contributions from the catalysts to both ΔE_{ZPE} and ΔS_H are small and can be neglected. Therefore, ΔE_{ZPE} is obtained by [5]:

$$\Delta E_{ZPE} = \Delta E_{ZPE}^{\ H} - \frac{1}{2} \Delta E_{ZPE}^{\ H_2} \tag{4}$$

where E_{ZPE}^{H} is the zero-point energy of one adsorbed atomic hydrogens on the catalyst without the contribution of the catalyst. $\Delta E_{ZPE}^{H_2}$ is the zero-point energy of H₂ in the gas phase. $S_{H_2}^{0}$ is the entropy of H₂ gas at the standard condition.^[6] The ΔS_H can be obtained by:

$$\Delta S_H \cong -\frac{1}{2} S_{H_2}^0 \tag{5}$$

The calculated vibrational frequency for H_2 gas is 4390 cm⁻¹, the vibrational frequency of H adsorbed on M@C60 is 2810 cm⁻¹, which is not sensitive to metal atom.^[7] Therefore the overall corrections are taken as:

$$\Delta E_{H*}^{\ 0} = \Delta E_H + \ 0.24 \ eV \tag{6}$$

In the volcano-shaped diagram, the theoretical exchange current i_0 are calculated using the average Gibbs free-energy of hydrogen adsorption (${}^{\Delta G}_{H^*}{}^0$) on catalysts. The exchange current is based on the Norskov's assumption^[8] (see the reference for details). If the ${}^{\Delta G}_{H^*}{}^0 \leq 0$ 0, the following expressing for the exchange current at pH = 0 is obtained by:

$$i_0 = -ek_0 \frac{1}{1 + exp^{[m]}(-\Delta G_{H_*}^0 / k_b T)}$$
(7)

If the $\Delta G_{H_*}^0 > 0$, the exchange current is obtained by: $i_0 = -ek_0 \frac{1}{1 + exp^{[i0]}(\Delta G_{H_*}^0 / k_b T)}$ (8)

where k_0 is the rate constant.



Fig. S1 The equipment diagram of plasma-assisted system and photos of Ni MOF-74/NF and derived Ni@NC sample.



Fig. S2 TGA curve of Ni MOF-74.



Fig. S3 N_2 adsorption-desorption isotherm of pristine Ni MOF-74.



Fig. S4 SEM images of bare Ni foam and Ni MOF-74 grown on Ni foam.



Fig. S5 SEM images of NH₃-plasma-250°C and NH₃-plasma-350°C samples.



Fig. S6 Summary of the I_D/I_G , $I_{D''}/I_G$ and $I_{D+D''}/I_G$ ratios in the Raman spectra of prepared samples.



Fig. S7 Overall XPS survey of pristine Ni MOF-74 and NH₃-plasma sample.



Fig. S8 Ni 2p and C 1s spectra of the NH₃-plasma sample.



Fig. S9 Overall XPS survey of NH₃-thermal sample.



Fig. S10 FT-IR comparison of pristine Ni MOF-74 and various derived samples.



Fig. S11 HER polarization curves and the corresponding Tafel plots of various samples prepared at different temperature.



Fig. S12 EIS of various samples prepared at different temperature.



Fig. S13 EIS of various MOF-derived samples.



Fig. S14 Chronopotentiometry of the NH_3 -plasma sample at a constant current density of 10 mA cm⁻² for 18 h.



Fig. S15 Chronopotentiometry of the NH_3 -plasma sample at different current density of 10, 20 40, 60, 80 and 100 mA cm⁻².



Fig. S16 The linear scanning polarization curves of NH₃-plasma and NH₃-plasma after 18 h stability test.



Fig. S17 EIS of two-electrode electrolyzer for overall splitting.



Fig. S18 The optimized structure of the Ni_{30} cluster and carbon cage. Green, brown, pink balls are represented for Ni, C, H atoms, respectively.



Fig. S19 The optimized structure of the $Ni_{30}@C_{180}$, $Ni_{30}@C_{175}N_5$ and $Ni_{30}@C_{169}N_{11}$. Green, grey, brown, pink balls are represented for Ni, N, C, H atoms, respectively.

Table S	I The	elemental	analysis	of the	various	samples
			2			

sample	C (wt%)	N (wt%)	
Pristine Ni MOF-74	28.44	-	
NH3-plasma	7.28	2.23	
NH ₃ -thermal	9.96	1.36	
Ar plasma	20.23	-	

Catalyst	Electrolyte	Mass	Overpotential	Substrate	Reference
		loading	@10 mA		
		(mg cm ⁻²)	cm ⁻² (mV)		
Ni@NC	1 M KOH	1.1	61	Nickel foam	This work
Faca@NC	0.5 M	0.295	262	GCE	[9]
recowing	H_2SO_4	0.285			
Fe ₃ C/Mo ₂ C@NPGC	1 M KOH	0.14	98	GCE	[10]
CoO _x @CN	1 M KOH	0.42	232	Nickel foam	[11]
Co@NG	1 M KOH	1.08	200	GCE	[12]
CuCo@NC	1 M KOH	0.182	145	GCE	[13]
Co-P/NC	1 M KOH	1.0	154	GCE	[14]
Fe-Co@N-		-	87	GCE	[15]
CNTs@rGO	ТМКОН				
Nicher	0.5 M	0.29	48	Graphite	[16]
	H ₂ SO ₄	0.38		plate	
Co@NCN-800	1 M KOH	0.28	200	GCE	[17]

Table S2 Comparison of HER activity for Ni@NC and recently reported noble metal-free (mainlyTMs@carbon) catalysts.

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