Supporting Information

Direct Converting Metal Organic Frameworks into Ultrafine Phosphide Nanocomposites in Multicomponent Plasma for Wide pH Hydrogen Evolution

Yanru Guo^a, Chunmei Zhang^b, Yong Wu^a, Hongen Yu^a, Shaojun Zhang^a, Aijun Du^b, Kostya (Ken) Ostrikov^b, Jie Zheng^{*a}, and Xingguo Li^{*a}

Experimental Procedures

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.. Red phosphorus were purchased from Beijing Chemical Industry Group 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 obtained from Alfa-Asear Co. Ltd.. All reagents were used without further purification.

Synthesis procedure of the phosphides

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.The mixture was stirred for 30 min to obtain homogeneous solution. Then the solution was put into the reactor made by Teflon and the Ni foam (3.5 cm \times 6.5 cm) was soaked below the liquid level. The Ni foam was pretreated by 0.5 M H₂SO₄, H₂O and EtOH with the assistance of sonication to remove the pollutant over the surface. After reaction for 12 h at 100 °C, Ni-MOF-74@Ni foam was collected by washed several times by EtOH and H₂O, and then dried under the vacuum at 150 °C overnight.

Synthesis of Ni₂P@C and Ni₁₂P₅@NC nanostructure

Various nickel phosphides (Ni₂P and Ni₁₂P₅) nanocrystals were prepared with the plasma-assisted sintering system. Ni MOF-74 grown on Ni foam was used as precursor and treated at 300 °C for 1 h in a mixture of NH₃/Ar or H₂/Ar flow (NH₃ plasma: NH₃ 20 sccm and Ar 10 sccm; H₂ plasma: H₂ 20 sccm and Ar 10 sccm). The red phosphorous was put in the upstream over the same temperature region. Plasma was generated by inductively coupled coil driven by a 13.56 MHz radio-frequency power with

input power of 120 W. Pure Ar plasma and NH₃ gas without plasma were also used as working gases under same conditions for comparison. Before heating, the system was pumped into vacuum to obtain a low pressure.

Structural characterizations

The crystalline phases of the prepared sample were characterized by powder X-ray diffraction (XRD, PANalytical X'Pert3, Cu K α). The morphology and microstructure were characterized by scanning electron microscopy (SEM, Merlin Compact, ZEISS, 10 kV) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F, 200 kV). The valence state of element was investigated using X-ray photoelectron spectroscopy (XPS, AXIS-Supra spectrometer, Kratos Analytical, monochromatic Al K α radiation). Thermogravimetric analysis (TGA) curves were operated by thermogravimetric analysis (TGA, Q600 SDT thermoanalyzer, in high purity N₂). Elemental analysis was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Prodigy 7, Leeman). Optical emission spectra (OES) of the discharge emissions were acquired with a computer controlled Ocean Optics 153 spectrometer (HR2000+), to which the light from the plasma is coupled via an optical fiber.

Electrochemical measurements

All electrochemical measurements were conducted on the electrochemical workstation (CHI 760D) in a three-electrode system at room temperature. A clean graphite rod was used as the counter electrode and a saturated calomel electrode (SCE) was applied as the reference electrode. The catalysts grown on Ni foam worked as the working electrode directly. Electrochemical measurements were carried in 1 M KOH solution and 0.5 M H₂SO₄ solution. The measured potentials vs SCE were converted to the RHE scale according to the Nernst equation ($E_{RHE} = E_{SCE} + 0.0591pH + 0.2415$ V). The current density in this paper was the apparent current density based on the geometric area of the electrode. The linear scan voltammetry (LSV) was collected at a scan rate of 1 mV s⁻¹. Before the LSV measurements, the catalysts was measured after 50 cycles of cyclic voltammetry (CV) to reaching a stable state. All

polarization curves were corrected by the 85% iR drop compensation. The electrochemical impedance spectroscopy (EIS) was collected at the potential corresponded to the current at 10 mA cm⁻² with an AC amplitude of 5 mV in a frequency range from 100 kHz to 0.01 Hz. The long term stability was performed by chronopotentiometry method at a continuous current density of 20 mA cm⁻² for 16h.

Computational methods

The geometries were studied by DFT within generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) functional, as implemented in the Vienna ab initio simulation package (VASP)^[1]. The supercell of 8.64 × 8.64 × 25 Å³ and 11.75 × 11.75 × 25 Å³ were used to simulate with and without H adsorbed Ni₁₂P₅ and Ni₂P compounds. The supercells were large enough to reduce the interaction between H in adjacent cells and the vacuum space is at least 15 Å. A long-range van der Waals interaction (DFT-D3 method) was incorporated to correct total energy^[2]. For the k-point sampling, we used 5 × 5 × 1 and 3 × 3 × 1 mesh in reciprocal space for Ni₁₂P₅ and Ni₂P film during geometry optimization. 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. The standard hydrogen electrode (USHE) was theoretically defined in solution (pH = 0, p (H₂) = 1 bar). The assessment of HER catalytic activity is based on the reaction free energy of hydrogen adsorption ($\Delta G_{H^{-1}}^{0}$)^[3], defined as

$$\Delta G_{H^*}^0 = \Delta E_H + \Delta E_{ZPE} - TS_H \tag{1}$$

 ΔE_{H} is the hydrogen adsorption energy and can be described by:

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

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. ΔE_{ZPE} is used as 0.04 eV as reported by Nørskov's work^[4].

Meanwhile, ΔS_H can be obtained by:

$$\Delta S_H \cong -\frac{1}{2} S_{H_2}^0 \tag{3}$$

where $S_{H_2}^0$ is the entropy of H₂ in the gas phase at standard conditions.

The value of $S_{H_2}^0$ under standard conditions is used and changes little within the working conditions of electrocatalytic water splitting. Therefore, $\Delta E_{ZPE} - TS_H$ is a constant for all the systems, and the calculated $\Delta G_{H^*}^0$ is thereby determined by the adsorption energy of H atom (ΔE_H). Therefore, the overall corrections are taken as^[4]:

$$\Delta G_{H*}^0 = \Delta E_H + 0.24 \ eV \tag{4}$$

The optimal value for HER is $\Delta G_{H^*}^0 = 0$, which means that the smaller the $|\Delta G_{H^*}^0|$ value is, the better HER performance the material has.

To describe the water dissociate step of HER in alkaline solution, the free energies (at reduction potential $U_0 = 0$ V vs. RHE) for are defined as:

$$G_0 = G_{cat} + G_{H^2O} \tag{5}$$

$$G_{l} = G_{cat - (H-OH)^{*}}$$
(6)

The free energy is calculated by the following equation²

$$G = E + ZPE - TS \tag{7}$$

Where E, ZPE, and TS are the total electronic energy, the zero point energy correction, and the entropy correction, respectively. In this work, ΔG_{H_2O} ($\Delta G_{H_2O} = G_1 - G_0$) was used as the activity descriptor for the Volmer step.

Supporting Figures and Tables



Fig. S1 Photo of the light glow of NH_3 plasma in the quartz tube.



Fig. S2 SEM images of NH₃-thermal sample.



Fig. S3 TEM images of NH₃-plasma sample.



Fig. S4 Raman spectra of NH_3 -plasma and H_2 -plasma.



Fig. S5 SEM images of NH₃-plasma sample after 16 h galvanostatic electrolysis at 10 mA cm⁻² in 1.0 M KOH.



Fig. S6 SEM images of H₂-plasma sample after 16 h galvanostatic electrolysis at 10 mA cm⁻² in 1.0 M KOH.



Fig. S7 Ni $2p_{3/2}$ and P 2p spectra of NH₃-plasma sample after 16 h galvanostatic electrolysis at 20 mA cm⁻².



Fig. S8 SEM images of NH_3 -plasma sample after 16 h galvanostatic electrolysis at 10 mA cm⁻² in 0.5 M H_2SO_4 .



Fig. S9 SEM images of H_2 -plasma sample after 16 h galvanostatic electrolysis at 10 mA cm⁻² in 0.5 M H_2 SO₄.



Fig. S10 XRD patterns of Ni MOF-74 derived samples in different conditions.



Fig. S11 LSV and Tafel slopes of various electrocatalysts in 1.0 M KOH.



Fig. S12 (a) The capacitive currents were plotted against the scan rate for estimation of C_{dl} by linear fitting the corresponding plots. Cyclic voltammetry of (b) NH₃-plasma and (c) H₂-plasma at different scan rates (10, 20, 40, 60, 80mV s⁻¹) in 1 M KOH.

Fig. S13 (a) The capacitive currents were plotted against the scan rate for estimation of C_{dl} by linear fitting the corresponding plots. Cyclic voltammetry of (b) NH₃-plasma and (c) H₂-plasma at different scan rates (10, 20, 40, 60, 80mV s⁻¹) in 0.5 M H₂SO₄.

Fig. S14 EIS of various electrocatalysts in 1.0 M KOH.

Fig. S15 Top and side views of the most favorable H adsorption sites for Pt (111).

Fig. S16 Top and side views of the water dissociation step for (a) $Ni_{12}P_5@NC$ and (b) $Ni_2P@C$. Grey, purple, brown, blue, red and pink balls represent Ni, P, C, N, O and H atoms, respectively; (c) Gibbs free energy ($\triangle G$) profile of the HER in alkaline condition.

sample	C (wt%)	N (wt%)		
Pristine Ni MOF-74	28.44	-		
NH3 plasma	9.25	1.85		
H ₂ plasma	18.64	-		

Table S1. The elemental analysis of the various samples

Catalyst	P source	Temperature (°C)	Substrate	Electrolyte	Current density (mA cm ⁻²)	Overpot ential	Reference
Ni ₁₂ P ₅ @NC	Red P	300	Nickel foam	1 M KOH	20	50	This work
Ni ₂ P@C	Red P	300	Nickel foam	1 M KOH	20	76	This work
CP@Ni-P	Red P	500	Carbon fiber paper	1 M KOH	10	98	[5]
Ni ₂ P@NC	NH ₄ H ₂ PO ₄	700	GCE	1 M KOH	10	~320	[6]
Ni ₂ P-Me	NiO ₃ PCH ₃	700	GCE	1 M KOH	10	87	[7]
MoP@NCH Ss	H ₃ PMo ₁₂ O ₄₀	900	GCE	1 M KOH	10	92	[8]
CoP/NiCoP	TOP(trioctylpho sphine)	330	Ti foil	1 M KOH	10	133	[9]
СоР	NaH ₂ PO ₂	300	Carbon cloth	1 M KOH	10	67	[10]
CoP/Ni ₅ P ₄ / CoP	Red P	500	Nickel foam	1 M KOH	10	71	[11]
					100	140	
Ni ₁₂ P ₅ @NC	Red P	300	Nickel foam	1 M KOH	20	82	This work
Ni ₂ P@C	Red P	300	Nickel foam	1 M KOH	20	110	This work
Co-Ni-P	Red P	500	Nickel foam	0.5 M H ₂ SO ₄	10	68	[12]
MoP@PC	(NH ₄) ₂ HPO ₄	850	GCE	0.5 M H ₂ SO ₄	10	153	[13]
Ni ₂ P@NC	NH ₄ H ₂ PO ₄	700	GCE	$0.5 \text{ M H}_2\text{SO}_4$	10	138	[8]
Cu ₃ P@NPP C	NaH ₂ PO ₂	250	GCE	$0.5 \text{ M H}_2\text{SO}_4$	10	89	[14]
Co ₂ P	triphenylphosph ine	120	Ti foil	$0.5 \ M \ H_2 SO_4$	10	134	[15]
MoP	(NH ₄) ₂ HPO ₄	800	GCE	$0.5 \text{ M H}_2\text{SO}_4$	10	140	[16]
MoPC _x	phenylphosphon ic acid	800	GCE	0.5 M H ₂ SO ₄	10	108	[17]
Co _x Ni _x P	NaH ₂ PO ₂	350	GCE	0.5 M H ₂ SO ₄	10	148	[18]
CoP/Ni ₅ P ₄ / CoP	Red P	500	Nickel foam	0.5 M H ₂ SO ₄	10	33	[11]
					100	85	

Table S2. Comparison of HER activity for $Ni_{12}P_5$ @NC and Ni_2P @C and recently reported transition metal phosphides catalysts.

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