Electronic Supplementary Information

Superaerophobic P-doped Ni(OH)₂/NiMoO₄ hierarchical nanosheet

arrays grown on Ni foam for electrocatalytic overall water splitting

Wenguang Xi,^{a†}Gang Yan,^{a,b†} Huaqiao Tan,^{a*} Liguang Xiao,^b Sihang Cheng,^a Shifa Ullah Khan, ^a Yonghui Wang,^{a*} and Yangguang Li^{a*}

a: Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, P.R. China. E-mail: liyg658@nenu.edu.cn, tanhq870@nenu.edu.cn

b: College of Material Science and Engineering, Jilin Jianzhu University

Experimental Section

Preparation of catalyst

Ni(OH)₂

The chemicals used here are analytically pure and directly used no purification. Ni(OH)₂ nanosheet arrays were grown on Ni foam by simple hydrothermal method. The Ni foam with size about 2 * 0.5 cm was cleaned by ultrasonication in diluted hydrochloric acid, ethanol and distilled water for 10 min in turn. Briefly, 1.45 g Ni(NO₃)₂ and 1.4 g hexamine were dissolved in 90 mL distilled water. After stirring for 30 min, this solution was transferred to PTFE stainless steel autoclave and heated at 100 °C for 10 h. After cooled down to room temperature, the as-prepared sample was cleaned with distilled water and further dried at 80 °C.

P-Ni(OH)₂/NiMoO₄

In a similar process, the Ni(OH)₂ precursor was immersed in 30 mL solution containing 0.436 g Ni(NO₃)₂ and 0.363 g Na₂MoO₄. This mixture solution was transferred to PTFE stainless steel autoclave and heated at 150 °C for 6 h. After cooled down naturally, the Ni(OH)₂/NiMoO₄ hierarchical nanoarrays was obtained. Hypophosphite is used as phosphorus source for phosphorization. NaH₂PO₂·2H₂O (0.1 g) and one piece Ni(OH)₂/NiMoO₄ were placed at upstream and downstream side of the furnace. After annealed at 300 °C for 2 hours under nitrogen atmosphere, the P-Ni(OH)₂/NiMoO₄ sample was obtained. P-Ni(OH)₂ and P-NiMoO₄ were prepared by a method similar to that of P-Ni(OH)₂/NiMoO₄.

Catalyst characterization

Powder X-Ray diffraction (PXRD) data were acquired with a Rigaku D/max-II B X-ray diffractometer using Cu-Ka radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectroscopy (XPS)

was carried out using an ESCALABMKII spectrometer and the X-ray source was achromatic Al-Ka (1486.6 eV). The transmission electron microscope JEOL-2100F was used to acquire the electron transmission microscopy (TEM) and HRTEM images. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with a JEOL JSM 4800F scanning electron microscope.

Electrochemical measurement

CHI 760E electrochemical workstation (Shanghai Chenhua, China) was used to test the electrochemical performance of catalysts in a typical three-electrode system. The electrolyte was 1 M KOH (pH = 14). P-Ni(OH)₂/NiMoO₄ works directly as a working electrode. Carbon rod and saturated calomel electrode (SCE) as the counter electrode and the reference electrode, respectively. 5mg contrast samples of Pt/C (20 %) and IrO₂ was dispersed into 100 μ L of 0.5 % Nafion solution and a homogeneous ink was obtained, respectively. The tested potentials vs. SCE are converted to the reversible hydrogen electrode (RHE) based on $E_{vs. RHE} = E_{vs. SCE} + E^{o}_{SCE} + 0.059$ pH ($E^{o}_{SCE} = 0.2412$ V). The linear sweep voltammetry (LSV) curves were obtained at the scan rate of 1 mV s⁻¹. The ECSA (electrochemical surface area) was evaluated with cyclic voltammograms (CV). The i-t curves were tested to study the stability of catalysts. The electrochemical impedance spectroscopy (EIS) was conducted from at certain potential with frequency from 0.1 kHz to 100 kHz. The faradaic efficiency of electrocatalyst toward HER and OER was carried out. The H₂ or O₂ was collected with water drainage method. The polarization curves data of HER and OER have been made with iR compensation.

Adhesion force and contact angle underwater measurment

The adhesion force between the gas bubbles and electrode was measured by a high-sensitivity micro-electromechanical balance system (Dataphysics DCAT11, Germany). The electrode was placed in a quartz cell (5 cm \times 5 cm \times 5 cm) filled with distilled water. Gas bubble was suspended on a metal ring in the water, and the force of this balance system was initially set to zero. Subsequently, the electrode surfaces were moved upward at a moving rate of 0.02 mm s⁻¹ until the electrode surface contacted the bubble. The adhesion force was gradually increased and the shape of bubble changed from spherical to elliptical. At last, the electrode moved down and the contact was reduced to near zero.

The bubble CA was measured by the captive bubble method (Dataphysics OCA20) according to the reference ^[1]. The volume of the gas bubble was about 3 μ L for each testing. All experiments have been repeated >3 times.

[1] Z. Y. Lu, M. Sun, T. H. Xu, Y. J. Li, W. W. Xu, Z. Chang, Y. Ding, X. M. Sun, and L. Jiang. Adv. Mater. 2015, 27, 2361–2366



Fig. S1. From left to right are the photographic images of Ni foam, $Ni(OH)_2$, $NiMoO_4$ and $P-Ni(OH)_2/NiMoO_4$.



Fig. S2. Scanning Electron Microscope of $Ni(OH)_2$ nanosheets array on Ni foam at different magnification.



Fig. S3. Scanning Electron Microscope of NiMoO₄ nanosheets array on Ni foam at different magnification.



Fig. S4. Scanning Electron Microscope of Ni(OH)₂/NiMoO₄ nanosheets array on Ni foam at different magnification.



Fig. S5. Scanning Electron Microscope of P-Ni(OH)₂/NiMoO₄ nanosheets array on Ni foam at different magnification.



Fig. S6. Cross-sectional view of P-Ni(OH)₂/NiMoO₄ nanosheets array on Ni foam at different magnification.



Atom	Weight%	Atom%
Ni	51.9	27.0
Мо	5.4	1.7
0	31.6	60.4
Р	11.7	10.9

Fig. S7. The energy dispersive X-ray (EDX) spectra of P-Ni(OH)₂/NiMoO₄.



Fig. S8. The survey X-ray photoelectron spectroscopy of P-Ni(OH)₂/NiMoO₄.



Fig. S9. The LSV curves of P-Ni(OH)₂/NiMoO₄ before and after iR correction.



Fig. S10. Cyclic voltammograms (CVs) of P-Ni(OH)₂/NiMoO₄ with sweep rates in the range of 80–240 mV dec⁻¹ and a potential range from 0.46 to 0.37 V.



Fig. S11. Electrochemical impedance spectra (EIS) of P-Ni(OH)₂/NiMoO₄ measured with overpotentials from 50 to 250 mV.



Fig. S12. The XRD pattern of catalyst after 3000 circles CV sweep at the potential from 0 to -0.25 V (vs. RHE).



Fig. S13. The SEM images of catalyst (a) before and (b) after 3000 circles CV sweep at the potential from 0 to -0.25 V (vs. RHE), (c) before and (d) after 3000 circles CV sweep at the potential from 1.3 to 1.65 V (vs. RHE).



Fig. S14. OER Faradaic efficiency of P-Ni(OH)₂/NiMoO₄ at $\eta = 500$ mV.



Fig. S15. Demonstration of water-splitting powered by an AA battery with a voltage of 1.5 V.

Table. S1 Comparison of the HER performance of P-Ni(OH)₂/NiMoO₄ with some representative catalysts reported recently.

Catalyst	Overpotential (mV) at the Corresponding j		Potential (V) of water splitting at	Reference
	HER	OER	10 mA cm ⁻²	
P-Ni(OH) ₂ /NiMoO ₄	$\eta_{10} = 60$	$\eta_{10} = 270$	$\eta_{10} = 1.55$	This work
SrNb _{0.1} Co _{0.7} Fe _{0.2} O ₃ – perovskite nanorods	η ₁₀ =232	$\eta_{10} = 370$	$\eta_{10} = 1.68$	Adv. Energy Mater. 2017, 1602122
Hierarchical NiCo ₂ O ₄ hollow microcuboid	$\eta_{10} = 110$	$\eta_{10} = 290$	$\eta_{10} = 1.65$	Angew.Chem.Int. Ed. 2016, 55,6290 – 6294
Porous MoO ₂ sheets	$\eta_{10} = 25$	$\eta_{10} = 260$	$\eta_{13} = 1.53$	Adv. Mater. 2016, 28, 3785–3790
Copmact MoO ₂ /Ni foam	$\eta_{10} = 124$	$\eta_{10} = 330$	$\eta_{10} = 1.73$	Adv. Mater. 2016, 28, 3785–3790
lithium-induced ultra- small NiFeOx nanoparticles	$\eta_{10} = 88$	$\eta_{10} = 230$	$\eta_{10} = 1.55$	Nat. Comm. 2015, 6, 7261.
NiFe/NiCo ₂ O ₄	$\eta_{10} = 105$	η ₁ =240	$\eta_{10} = 1.67$	Adv. Funct. Mater., 2016, 26, 3515
Co ₃ O ₄ nanocrystal/carbon fiber	η ₁₀ =155	$\eta_{10} = 380$	$\eta_{10} = 1.91$	Chem. Commun., 2015, 51, 8066
CoO _x @CN	η ₁₀ =235	$\eta_{10} = 260$	$\eta_{10} = 1.55$	J. Am. Chem. Soc. 2015, 137, 2688–2694
NiFe LDHNS@ DG10	η ₂₀ =115	$\eta_{10} = 210$	$\eta_{20} = 1.5$	Adv. Mater. 2017, 29, 1700017