Supporting Information

Rational design of atomically dispersed nickle active sites in β -Mo₂C for hydrogen evolution

reaction at all pH values

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Materials and Preparation of the Catalysts

Chemicals used in reactions are commercially available and were used without purification. All solutions used in synthesis and electrochemical experiments were prepared using Millipore water.

Preparation of NiMo/MoM [Ni(bpe)₂**MoO**₄]. 0.16 mmol (39 mg) Ni(NO₃)₂·6H₂O and 0.16 mmol (38.8 mg) Na₂MoO₄·2H₂O were first dissolved in 5 mL H₂O in a long thin test tube. Then 5 mL of CH₃CN/H₂O mixture (v/v = 1:2) was layered over the above solution. The ligand of bpe (36.4 mg, 0.2 mmol) in 5 mL of CH₃CN/H₂O (v/v = 2:1) was layered over the buffer layer. All operations were carried out at 25 °C, the green product of NiMo/MOM was isolated after 72 hours. The product was washed with ethanol and dried at 60 °C. Yield: 54 mg (57% yield based on bpe). *Anal.* Calcd for Ni(bpe)₂MoO₄.2H₂O (C₁₂H₁₄MoN₂NiO₆): C, 35.95; H, 3.23; N, 6.41. Found: C, 35.78; H, 3.17; N, 6.23.

Preparation of Ni/\beta-Mo₂C. The as-synthesized NiMo/MOM was firstly heated from room temperature to 800 °C under N₂ atmosphere with a heating rate of 5 °C/min, and then maintained at this temperature for 5 h and naturally cooled down to room temperature under N₂ flow. The resulting product was then washed by excess concentrated HCl for several times to ensure complete removal of unstable species. Finally, the obtained product was dried at 60 °C overnight and used as an electrocatalyst for the HER reaction.

Preparation of mixed-Ni/Mo₂C. The mixed-Ni/Mo₂C was synthesized by directly mixing NiCl₂·6H₂O, NaMoO₄·2H₂O and bpe ligand with a ratio of 1:1:1.25, followed by the same procedure as used for the preparation of Ni/ β -Mo₂C.

Characterizations

Elemental analyses were performed using an Elementar Vario EL elemental analyzer. The thermogravimetric analysis (TGA) was performed under a N₂ atmosphere with a ramp rate of 10 °C/min utilizing a Netzsch TG-209 Thermogravimetry Analyzer from room temperature to 800 °C.

The powder X-ray (PXRD) diffraction patterns were recorded on a PANalytical PW3040/60 diffractometer equipped with monochromatic Cu K α radiation (λ = 0.15418 nm). The Raman spectra were recorded using a JY Labram HR. The BET surface area was determined using N₂ adsorption/desorption isotherm measurements at -196 °C on an automatic volumetric adsorption equipment (BELSORP-max). The scanning electron microscopy (SEM) was performed on a JSM-7001F at an acceleration voltage of 10 kV. The transmission electron microscopy (TEM) was performed on a JEM2010-HR transmission electron microscope. X-ray photon spectroscopy (XPS) was recorded by a scanning X-ray microprobe (ESCALab250). Binding energy (BE) values were referenced to the C 1s binding energy of adventitious carbon contamination which was taken to be 284.6 eV.

Electrochemical Measurements

The electrochemical properties of the as-synthesized samples (Ni/ β -Mo₂C and mixed-Ni/Mo₂C) were investigated employing a CHI 760D electrochemical workstation (Shanghai Chenhua Co., China) in a standard three-electrode system at room temperature. A glassy carbon electrode (GCE, 3 mm in diameter, $S = 0.071 \text{ cm}^2$) with catalysts loaded on it was used as the working electrode, an Ag/AgCl with saturated KCl and a graphite rod were used as the reference electrode and the counter electrode, respectively. For working electrode fabrication, 4 mg of the assynthesized sample was dispersed in 3 mL of 1:1 v/v H_2O/C_2H_5OH and 64 μ L Nafion, followed by sonication for 30 min to form a homogeneous ink. Then 10 µL of the ink was drop-casted onto the GCE and then dried in an ambient environment for measurements. The final mass loading of the electrocatalyst is 0.14 mg cm⁻². Commercial 20% Pt/C catalyst was used as a reference sample. The working electrode of commercial Pt/C electrocatalyst was prepared under the same conditions as those used for Ni/ β -Mo₂C. Linear sweep voltammetry (LSV) was tested at a scan rate of 2 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) spectra were recorded on a PARSTAT 2273 electrochemical system with the frequency ranged from 10⁻¹ to 10⁵ Hz at an amplitude of 5 mV. The electrochemical stability of the catalysts was tested by sweeping the cyclic voltammetry (CV) between -0.3 and 0.05 V vs reversible hydrogen electrode (RHE) at a scan rate of 100 mV s⁻¹. To estimate the electrochemical active surface area of the catalysts, CV was tested within the potential window of 0.225-0.345 V vs RHE at various scan rates (10, 25, 50, 75,

100, and 150mV s⁻¹). All the potentials were tested against Ag/AgCl electrode and converted to RHE using the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.197 \text{ V}.$



Fig. S1 Experimental (red curve) and simulated (black curve) XRD patterns of the NiMo/MOM.



Fig. S2 TGA curve of NiMo/MOM. The NiMo/MOM shows a small weight loss of 1.04% before 160 $^{\circ}$ C, which corresponds to the loss of solvent H₂O molecules. With the increase of temperature, the framework was collapsed and decomposed.



Fig. S3 a) SEM and b) TEM images of the as-synthesized Ni/ β -Mo₂C.



Element	Line	Intensity (c/s)	Atomic ratio%
С	Κα	17.76	27.3
Ν	Κα	10.03	3.59
0	Κα	2.87	1.819
Ni	Κα	71.17	11.80
Мо	Lα	465.52	55.491
Total			100.000

Fig. S4 EDS spectrum and the determined elemental ratio of Ni/ β -Mo₂C. The Cu signal comes from the Cu grid.



Fig. S5 Raman spectrum of Ni/ β -Mo₂C.

The finger bands around 345, 487, and 740 cm⁻¹ are associated with MoO_2 , and bands around 983, 820, and 283 cm⁻¹ can be ascribed to MoO_3 , which can be attributed to the partial surface oxidation of the as-obtained molybdenum carbide nanoparticles in air.



Fig. S6 a) N₂ adsorption-desorption isotherms and b) the corresponding BJH pore distribution of Ni/ β -Mo₂C.



Fig. S7 The XPS survey spectrum of Ni/ β -Mo₂C.



Fig. S8 XPS profiles of a) C 1s; b) Ni 2p; c) Mo 3d and d) N 1s in Ni/ β -Mo₂C.

In C 1s XPS spectrum, it can be observed that three C species with binding energies at 284.6, 286.1, and 288.1 eV that are related to the graphite C, C=O, and O=C-O groups, respectively. In Ni 2p XPS spectrum, the binding energies at 852.8 eV for Ni $2p_{3/2}$ and 870.5 eV for Ni $2p_{1/2}$ are spin-orbit characteristics of Ni⁰, and two shake-up satellites,. The high-resolution Mo 3d spectrum can be fitted to two doublets. The doublet centered at higher binding energy (235.7/232.3 eV) is attributed to the Mo(VI) oxidation state, and the pair of peaks located at (228.1/231.6 eV) confirms the presence of the Mo-C bonds in the Ni/ β -Mo₂C. Besides, the N 1s spectrum is divided into three different peaks at 396.9, 399.0 and 401.1 eV, which are assigned to Mo-N bond, pyridinic N and graphitic N, respectively. The pyridinic N and graphitic N can effectively increase the electron density in the carbon layers, due to their lone-pair electrons.



Fig. S9 XRD pattern of the mixed-Ni/Mo₂C. The hexagonal β -Mo₂C (JCPDS No. 35-0787) and Ni (JCPDS, No. 65-2412) can be identified in the mixed-Ni/Mo₂C. The peak at 26.05° originates from graphitic carbon.



Fig. S10 The XPS survey spectrum of mixed-Ni/Mo₂C.



Fig. S11 XPS profiles of a) C 1s; b) Ni 2p; c) Mo 3d and d) N 1s in mixed-Ni/Mo₂C.

The survey photoelectron spectrum (Fig. S10) shows the presence of Ni, Mo, O, N, and CN in mixed-Ni/Mo₂C. In Fig. S11a, the peaks at 284.6 and 285.7 eV are assigned to C=C and C=O groups, respectively. In Fig. S11b, Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks of mixed-Ni/Mo₂C occur at binding energies of 853.0 and 870.7 eV, respectively. In Fig. S11c, the fitted curves of Mo 3d spectra can be divided into the valence states of Mo²⁺ and Mo⁶⁺. The pair of peaks (235.2/232.9 eV) is attributed the Mo⁶⁺ state, and the other pair of peaks located at (229.2/231.6 eV) confirms the presence of Mo²⁺ state. In Fig. S11d, The high resolution N 1s spectrum can be identified as that of pyridinicN (399.1 eV) and graphitic N (400.6 eV).

Cu		
Mo		
Qu	Cu	
	Cu	
MP	Ni Cu	
Mo Mo	Ni Ni Cu	
S.M. Mo	Ni Qu	

Element	Line	Intensity (c/s)	Atomic %
С	Κ α	8.53	33.2
Ν	Κα	6.68	9.65
0	Κα	4.45	1.45
Ni	Κα	103.18	23.98
Мо	Lα	206.57	30.29
Total		8.53	100.000

Fig. S12 EDX spectrum and the determined elemental ratio of mixed-Ni/Mo₂C. The Cu signal comes from the Cu grid.



Fig. S13. SEM images of the mixed-Ni/Mo₂C.



Fig. S14 CVs of a) Ni/ β -Mo₂C and b) mixed-Ni/Mo₂C at scan rates ranging from 10 to 150 mV s⁻¹ in 0.5 M H₂SO₄.



Fig. S15 Specific HER activity of Ni/ β -Mo₂C and b) mixed-Ni/Mo₂C in 0.5 M H₂SO₄. The specific HER activity is calculated by normalizing the current based on the corresponding ECSA. The ECSA is determined via dividing C_{dl} by 0.04 mF cm⁻² (The specific capacitance is usually found to be in the range of 0.02-0.06 mF cm⁻² for 1 cm² surface, and it is assumed as 0.04 mF cm⁻² in the calculations of ECSA).



Fig. S16 a) Initial LSV curve and the curve after 1000 CV cycles of Ni/ β -Mo₂C. d) Chronoamperometry of Ni/ β -Mo₂C at the overpotential (η) of 171 mV in 0.5 M H₂SO₄.



Fig. S17 CVs of a) Ni/ β -Mo₂C and b) mixed-Ni/Mo₂C in 1.0 M PBS; c) Ni/ β -Mo₂C and d) mixed-Ni/Mo₂C in 1.0 M KOH at scan rates ranging from 10 to 150 mV s⁻¹.



Fig. S18 Estimation of the double–layer capacitance (C_{dl}) of a) Ni/ β -Mo₂C and b) mixed-Ni/Mo₂C. The difference in current density ($\Delta j = j_a - j_c$) at 0.285 V vs RHE plotted as a function of scan rate fitted to a linear regression, where the slope is twice C_{dl} .



Fig.S19 Specific HER activity of Ni/ β -Mo₂C and mixed-Ni/Mo₂C in a) 1.0 M PBS and b) 1.0 M KOH The specific HER activity is calculated by normalizing the current based on the corresponding ECSA. The ECSA is determined via dividing C_a by 0.04 mF cm⁻².



Fig.S20 Nyquist plots of Ni/ β -Mo₂C and mixed-Ni/Mo₂C obtained in a) 1.0 M PBS and b) 1 M KOH, respectively.

2. Supplementary Tables

Table S1. Comparison of the HER activities of the Ni/ β -Mo₂C and other reported Pt-free catalysts in 0.5 M H₂SO₄.

Catalyst	<i>j_{0 (}</i> mA cm ⁻²)	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Reference
Ni/β-Mo₂C	0.25	155	69	This work
mixed-Ni/Mo ₂ C	-	450	147	This work
β-Mo ₂ C	0.017	172	62	Angew.Chem. Int.Ed. 2015 , 54,15395
NiMo ₂ C@C	0.22	169	100	J. Mater. Chem. A, 2017 , 5, 5000
Mo ₂ C QDs/NGCLs	0.2	136	68.4	Chem. Commun., 2016 , 52, 12753
Mo ₂ C	0.009	270	67	J. Am. Chem. Soc. 2015 , 137, 7035
FeP NPs@NPC	0.126	130	67	Nanoscale, 2017 , <i>9</i> , 3555
WS₂@P-N- Ographene film	0.0071	125	52.7	Adv. Mater., 2015 , 27, 4234
CoSe2 NP/CP		139	42.1	J. Am. Chem. Soc., 2014 , 136, 4897
Mo ₂ C@NC	0.096	124	60	Angew. Chem. Int. Ed., 2015 , 54, 10752
Mo ₂ C/NCNT	0.1146	147	71	J. Mater. Chem. A, 2015 , <i>3</i> , 5783
P-Mo ₂ C@C nanowires	-	89	42	Energy Environ. Sci., 2017 , 10, 1262

Table S2. Comparison of the HER activities of the Ni/ β -Mo ₂ C and other reported Pt-free catalys
in 1 M PBS.

Catalyst	<i>j_{0 (}</i> mA cm ⁻²)	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Reference
Ni/β-Mo₂C	0.061	149	66	This work
mixed-Ni/Mo ₂ C	-	354	147	This work
FeP NPs@NPC	-	214	136	Nanoscale, 2017 , <i>9</i> , 3555
Mo ₂ C QDs/NGCLs	-	136	81.9	Chem. Commun., 2016 , 52, 12753
Co ₂ N/TM	-	290	126	Catal. Sci. Technol., 2017 , 7, 2689
Ni ₃ S ₂ /Ni	-	220	118	J. Hydrogen Energy, 2015 , 40, 4727
Mo ₂ C@NC	-	156	-	Angew. Chem. Int. Ed., 2015 , 54, 10752
Mo ₂ C/NCNT	-	645	-	J. Mater. Chem. A, 2015 , 3, 5783

Table S3. Comparison of the HER activities of the Ni/ β -Mo₂C and other reported Pt-free catalysts in 1 M KOH.

Catalvst	<i>j₀</i> ,mA cm ⁻²)	<i>n</i> ₁₀ (mV)	Tafel slope	Deference
		710 ()	(mV dec ⁻¹)	Kelefence
Ni/β-Mo₂C	0.22	157	61	This work
mixed-Ni/Mo ₂ C	-	474	148	This work
NiFe LDH/NF	-	210	-	Science, 2014 ,345, 1593
β-Mo ₂ C	0.087	112	55	Angew. Chem. Int. Ed. 2015 , 54,15395
NiMo ₂ C@C	0.08	181	84	J. Mater. Chem. A, 2017 , 5, 5000
Mo ₂ C QDs/NGCLs	-	111	57.8	Chem. Commun., 2016 , 52, 12753
Ni/Mo ₂ C-PC	0.098	179	145	Chem. Sci., 2017 , <i>8</i> , 968
NiMo ₃ S ₄	0.039	-	98	Angew. Chem. Int. Ed. 2016 , 55, 15240
Mo ₂ C	0.0044	270	78	J. Am. Chem. Soc. 2015 , 137, 7035
FeP NPs@NPC	-	214	82	Nanoscale, 2017 , 9, 3555
Ni ₃ S ₂ /Ni	-	123	110	J. Hydrogen Energy, 2015 , 40, 4727
CoP NARs	-	209	129	J. Am. Chem. Soc. 2014 , 136, 7587
NiCoP nanocubes	-	150	60.6	Chem. Commun., 2016 , 52, 1633
a-CoSe/Ti	-	84	121	Chem. Commun., 2015 , 51, 16683
NiCoP NWAs/NF	-	104	54	J. Mater. Chem. A 2017 , 5, 14838