Supporting Information

3D Self-assembly of Ultrafine Molybdenum Carbide Confined in N-doped Carbon Nanosheets for Efficient Hydrogen Production

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Experimental Section

Preparation of ultrafine molybdenum carbide confined in nitrogen-doped carbon nanosheet hierarchical architectures (denoted as MoC-HAs). The representative MoC-HAs are prepared as follows. A certain amount (20 mg) of ammonium molybdate (AM) tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) was added to the mixed solution of 5 ml deionized water and 4 ml ethanol in 20 ml glass bottle. After the mixture becomes transparent with 1-2 min stirring, 150 mg of dopamine hydrochloride was added to the above solution. Then, a dark red suspension was observed due to the formation of Mo-dopamine complex. After being stirring for 15 min, 0.5 ml of ammonia was added dropwise to the above suspension in order to trigger the polymerization of dopamine (DA) hydrochloride. The suspension was reacted for 120 min. The dark-red precipitate was recovered using centrifugation at 10000 rpm for 3 min, followed by washing with ethanol for two times and drying at 60 °C in air. In order to obtain MoC-HAs, the as-prepared production was annealed under N₂/Ar flow at 900 °C for 4 h with a heating rate of 3 °C min⁻¹. Moreover, in order to investigate the effects of molybdenum carbide and volume ratios of deionized water and ethanol, we conducted control experiments in which only one factor was changed at a time. The added amounts of ammonium molybdate (AM) are varied in the range of 10, 20 and 40 mg and the samples named as AM-10/20/40. The samples denoted as WE-18/54/81 were prepared with different volume ratios of deionized water (W) and ethanol (E) of 1:8, 5:4 and 8:1. The names of AM-20 and WE-54 represent the same sample.

Material Characterization. Scanning electron microscopy (SEM) graphs were acquired with a Hitachi SU8010 Field Emission Gun Scanning Electron Microscope at 5 kV. Transmission electron microscopy (TEM) graphs were observed by using a Hitachi H-7700 TEM operating at 100 kV. High-resolution transmission electron microscopy (HRTEM), dark-field scanning transmission electron microscopy (STEM), as well as energy dispersive X-ray (EDX) element mapping tests were performed on a FEI Tecnai G2 F20 STwin microscope at 200 kV. X-ray diffraction (XRD) patterns of the samples were measured on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ =1.5418 Å). The Raman spectra were recorded by a Horiba JY H-800 Raman spectrometer. N₂ adsorption-desorption isotherms were measured on a Micromeritics ASAP 2010 automatic adsorption instrument at 77 K. Before the measurements, calcined samples were degassed in vacuum at 200 °C for 2 h. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation and pore size distributions were obtained by the BarrettJoyner-Halenda (BJH) method using desorption branch data. Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C min⁻¹ from room temperature to 1000 °C under an oxygen atmosphere (Mettler Toledo, TGA/SDTA 851e). X-ray photoelectron spectroscopy (XPS) signals were collected by a Thermo Fisher ESCALAB 250Xi spectrometer applying monochromatic Al Ka X-ray sources (1486.6 eV) at 2.0 kV and 20 mA.

Electrochemical Measurements. All HER performance was conducted on CHI electrochemical workstation (Shanghai Chenhua Co., China) using a three-electrode configuration in 1 M KOH. A glassy carbon electrode (5 mm in diameter), a saturated

calomel electrode (SCE), and a graphite rod were used as the working, reference, and counter electrodes, respectively. The catalyst (5 mg) was dispersed in 1 mL of the mixture solution containing 0.5 mL deionized water, 0.45 mL of ethanol and 50 μ L of 0.5 wt % Nafion solution by ultrasonication for 30 min. Then, 8 μ L of catalyst suspension was pipetted on the surface of glassy carbon electrode. All potentials were converted to a reversible hydrogen electrode (RHE): E(RHE) =E(SCE) + (0.242 + 0.059 pH) V. Linear sweep voltammetry (LSV) was recorded from -430 to 0 mV (vs RHE, in 1 M KOH) at a scan rate of 5 mV s⁻¹. EIS measurements were performed with frequency from 0.1 to 100 000 Hz at an overpotential of 180 mV. The long-term stability tests were carried out using a chronoamperometry technique at an overpotential of 230 mV.



Figure S1. TEM image of polydopamine without addition of [Mo₇O₂₄]⁶⁻.



Figure S2. TEM images of the as-prepared Mo-HAs WE-18, WE-54 and WE-81 with increasing volume ratios of water (W) to ethanol (E) from 1:8, 5:4 to 8:1.



Figure S3. XPS C 1s spectrum of electrocatalyst AM-20/WE-54.



Figure S4. XRD patterns of samples AM-10, AM-40, WE-18 and WE-81 obtained in control experiments.



Figure S5. Raman spectra of samples AM-10, AM-40, WE-18 and WE-81 obtained in control experiments.



Figure S6. Thermogravimetic analysis (TGA) curves of control samples.



Figure S7. TEM images of annealed samples (a) WE-18, (b) WE-81, (c) AM-10 and (d) AM-40.



Figure S8. N₂ physisorption isotherms (a and b) and pore size distributions (c and d) of WE-18 and WE-81, respectively.



Figure S9. N₂ physisorption isotherms (a and b) and pore size distributions (c and d) of AM-10 and AM-40, respectively.



Figure S10. Electrical equivalent circuit models for fitting the EIS response of: two-time constant model, including the series resistance (Rs), the charge transfer resistance (Rct) denotes, resistance related to the porosity of the electrode surface (Rp) and constant phase elements (CPE1 and CPE2).

Catalysts	Basic media	Catalyst amount (mg cm ⁻²)	η (mV) at 10 mA cm ⁻¹	Tafel slope (mV dec ⁻¹)	Ref.
MoC-HAs (AM-20)	1 M KOH	0.41	128	82	This work
MoCx octahedrons	1 M KOH	0.8	151	59	Nat. Commun., 2015, 6, 6512.
Ni/Mo ₂ C-PC	1 M KOH	0.5	179	101	Chem. Sci. 2017, 8, 968.
Mo ₂ C@NPC-4	1 M NaOH	0.27	141	47.5	J. Mater. Chem. A, 2017 , 5, 5178.
Mo ₂ C@porous carbon	1.0 M KOH	1.0	165	/	J. Mater. Chem. A, 2016 , 4, 16225.
Mo ₂ C nanotubes	0.1 M KOH	0.75	112	55	Angew. Chem. Int. Ed. 2015, 54, 15395.
Mo ₂ C@NC	0.1 M KOH	0.28	60	/	Angew. Chem. Int. Ed. 2015, 54, 10752
MoC 0.654@CNS	0.1 M KOH	-	220	/	J. Am. Chem. Soc. 2015 , 137, 5480
Ni-Mo ₂ C nanorods	1 M KOH	0.43	140	49	Appl. Catal. B 2014, 154, 232.
WC-CNTs	0.1 M KOH	-	165	72	ACS Nano 2015, 9, 5125.
MoS ₂ nanosheet arrays	1 M KOH	-	190	100	<i>Electrochim. Acta</i> 2015 , 168, 256.
Ni-NiO-Cr ₂ O ₃	1 M KOH	-	150	/	Angew. Chem. Int. Ed. 2015 , 54,11989
Ni ₃ S ₂ /nickel foam	1 M NaOH	-	223	/	J. Am. Chem. Soc. 2015, 137, 14023.
Ni/NiO-CNT	1 M KOH		80	82	Nat. Commun. 2014, 5, 4695
MoP	1 M KOH	0.86	130	48	Energy Environ. Sci. 2014, 7, 2624.
(Ni _x , Mn _y , Co _z)S ₄ /rGo	0.1 M KOH	0.2	151	52	Acs catal. 2017, 7, 819-832
CoP NW arrays	1 M KOH	0.92	209	129	J. Am. Chem. Soc. 2014, 136, 7587.
WP NW arrays	1 M KOH	2.0	150	102	<i>ACS Appl. Mater. Interfaces</i> 2014 , 6, 21874.
Co-embedded N-rich CNTs	1 M KOH	0.28	370	/	Angew. Chem. Int. Ed. 2014, 53, 4372.
CoOx/N-Doped Carbon Hybrids	1 M KOH	0.42	232	115	J. Am. Chem. Soc. 2015, 137, 2688

Table S1 Comparisons of HER performance of MoC-HAs with other reported electrocatalysts in basic media.