Mo_2C-Ni-Modified Nitrogen-doped Carbon Nanofiber toward Efficient Hydrogen Evolution Reaction

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Experimental section

Materials: Sodium tellurite (Na_2TeO_3) and polyvinyl pyrrolidone (PVP, K=30) were purchased from Shanghai Chemical Reagent Co. Ltd., aqueous ammonia solution (25-28% w/w %), hydrazine hydrate (85% w/w %), ethanol, isopropanol, acetone and nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) were purchased from Tianjin Guangfu Chemical Co. Ltd., ammonium molybdate (VI) tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) and D (+)-glucosamine hydrochloride were purchased from Sinopharm Chemical Reagent Co. Ltd., Nafion (5 wt. %) was purchased from Sigma-Aldrich. All the chemicals were analytical grade and used as received. Deionized water (DIW) was utilized in all experiments.

Characterizations

In order to confirm the morphologies of catalysts, transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were performed on a Tecnai G2Tf20 transmission electron microscopy operating at 300 KV. The catalysts were supported on copper micro grid by adding the ethanol suspension of catalysts. Meanwhile, Scanning

electron microscopy (SEM) images were also presented on a field-emission scanning electron microscope (JSM-6701F. JEOL) operated at an accelerating voltage of 5 kV. For the composition and chemical state of Mo_2C-Ni@N-CNFs, X-ray photoelectron spectroscopy (XPS) was conducted. XPS results were obtained on a PHI-5702 instruments. Moreover, X-ray diffraction (XRD) data were collected on a Rigaku D/max-2400 diffractormeter, utilizing Cu_{Ka} radiation as X-ray source in the range of 10-80°. Raman spectra were tested by an inVia Renishaw confocal spectrometer with 633 nm laser excitation. Electrochemical workstation (Shanghai Chenhua Equipment, China), a model CH Instrument 660E, was applied for electrochemistry.

Electrochemical Measurements

All the electrochemical data were received in the CH Instrument 660E electrochemical workstation utilizing 0.5 M H_2SO_4 (or 1.0 M KOH) solution as electrolyte, respectively. In a representative three-electrode, Pt wire as the counter electrode, glassy carbon electrode (GCE) with catalyst was served as the working electrode, and Ag/AgCl as the reference electrode, individually. Linear sweep voltammetry (LSV) was examined at scan rate of 5 mV s^{-1} when the nanocomposites remained steady at electrolyte. Electrochemical impedance spectroscopy (EIS) was conducted in the above configuration at overpotential η = -65 mV from 100 KHz to 0.01 Hz. In the experiments, the electrolyte was purged with

high-purity nitrogen gas. All the potentials displayed in this work were calibrated to a reversible hydrogen electrode (RHE) by the relation $E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + 0.209\ V$.

Before conducting electrochemical measurements, the working electrode with Mo_2C-Ni@N-CNFs nanocomposites was prepared. A simple procedure was described: (1) 4 mg of catalyst powders and 30 μL Nafion were dispersed in 1 mL of a 3:1 (v:v) water/isopropanol mixed solvents, and the above mixture was sonicated for 30 min. (2) 5 μL of the dispersion was drop-cast onto a GCE with 3 mm diameter at a catalyst loading of 0.285 mg cm^{-2}.

Results and Discussion

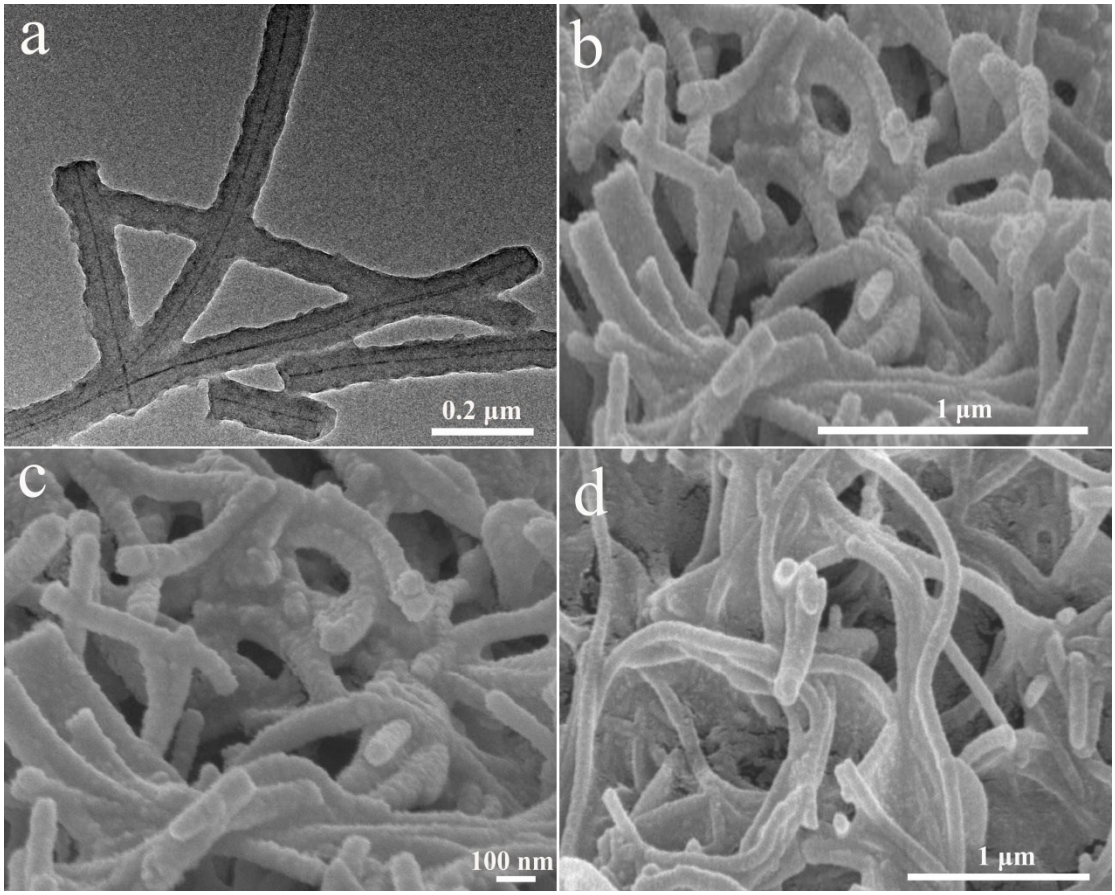

Figure S1. (a) TEM image of the precursor; (b,c) SEM images of $MoNi_{0.046}$@900; (d) SEM image of $MoNi_{0.046}$@1000.

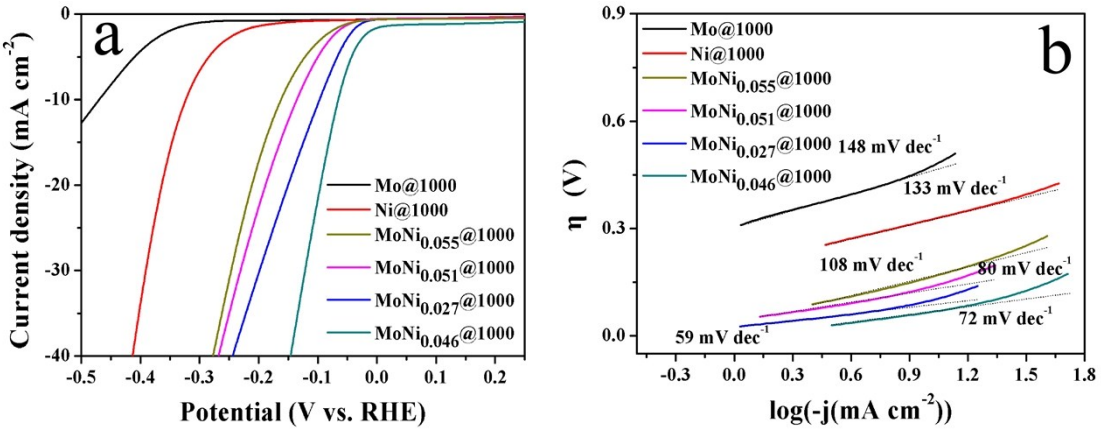

Figure S2. (a) Polarization curves and (b) Tafel slopes for these samples with different molar ratio of Mo and Ni in 0.5 M H_2SO_4.

Table S1. Onset potentials, exchange current density (j_0), overpotentials at a current density of 10 mA cm^{-2}, Tafel slopes and TOF for various catalysts in 0.5 M H_2SO_4.

Catalyst	Onset potential (mV)	Tafel slope (mV dec^{-1})	Overpotential (at 10 mA cm^{-2}) (mV)	j_0 (mA cm^{-2})	TOF (s^{-1})
Pt/C	-4	34	40	0.688	1.43
Ni@1000	-143	133	323	0.036	0.07
Mo@1000	-278	148	470	0.008	0.02
$MoNi_{0.027}$@1000	-21	59	97	0.401	0.83
$MoNi_{0.046}$@1000	-17	72	65	1.268	2.64
$MoNi_{0.051}$@1000	-58	80	136	0.300	0.62
$MoNi_{0.055}$@1000	-83	108	162	0.382	0.79

Table S2. Summary of representative catalysts for HER activity in acidic

electrolytes.

Catalyst	Current density	Overpotential	Electrolyte solution	Reference
Mo_2C-Ni @N-CNFs	10 mA cm^{-2}	65 mV	0.5 M H_2SO_4	*This work*
Co-Mo_2C nanowires	10 mA cm^{-2}	140 mV	0.5 M H_2SO_4	*Adv. Funct. Mater. 2016, 26, 5594*
Mo_2CT_x	10 mA cm^{-2}	283mV	0.5 M H_2SO_4	*ACS Energ. Lett. 2016, 1, 589*
NS-Mo_2C nanosheets	10 mA cm^{-2}	86mV	0.5 M H_2SO_4	*Small. 2015, 11, 6281*
Mo_xC-Ni @NCV	10 mA cm^{-2}	68mV	0.5 M H_2SO_4	*J. Am. Chem. Soc. 2015, 137, 15753*
MoS_2QDs @Graphene	10 mA cm^{-2}	140mV	0.5 M H_2SO_4	*Appl. Surf. Sci. 2017, 401, 194*
Ni-hollow Mo_2C	10 mA cm^{-2}	192mV	0.5 M H_2SO_4	*Chem. Mater. 2016, 28, 6318*
MoP	10 mA cm^{-2}	105mV	0.5 M H_2SO_4	*J. Mater. Chem. A. 2016, 4, 63*
HD-p$MoSe_2$ /NG	10 mA cm^{-2}	106 mV	0.5 M H_2SO_4	*Nanoscale. 2017,10.1039/C7NR00354D*
NiMo-Mo_2C/C	1 mA cm^{-2}	90 mV	0.5 M H_2SO_4	*Electrochim. Acta, 2016, 222, 747-754*

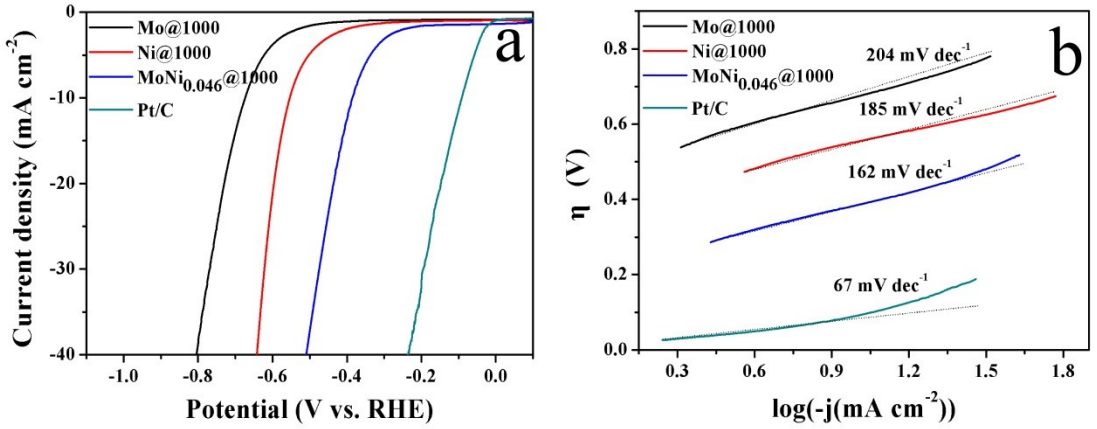

Figure S3. (a) Polarization curves and (b) Tafel plots of $MoNi_{0.046}$@1000 and Pt/C in 1 M KOH (PH = 14).

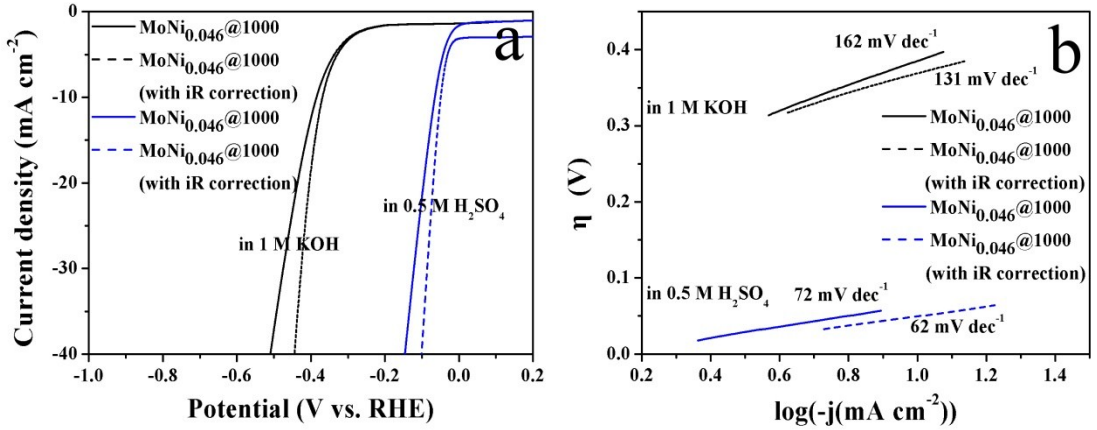

Figure S4. (a) Polarization curves for $MoNi_{0.046}$@1000 both in acidic and alkaline electrolytes (Dashed lines correspond to the iR corrected curves). (b) Tafel slope for the sample $MoNi_{0.046}$@1000 before and after iR correction.

Table S3. Onset potentials, j_0, overpotentials at a current density of 10 mA cm^{-2}, Tafel slopes and TOF for $MoNi_{0.046}$@1000 and Pt/C in 1 M KOH.

Catalyst	Onset potential (mV)	Tafel slope (mV dec^{-1})	Overpotential (at 10 mA cm^{-2}) (mV)	j_0 (mA cm^{-2})	TOF(s^{-1})

Pt/C	-21	67	90	0.726	1.51
$MoNi_{0.046}$@1000	-200	162	383	0.042	0.09

Table S4. Summary of representative catalysts for HER activity in alkaline electrolytes.

Catalyst	Current density	Overpotential	Electrolyte solution	Reference
Mo_2C-Ni @N-CNFs	10 mA cm^{-2}	383 mV	1.0 M KOH	*This work*
Co-NR CNTs	10 mA cm^{-2}	370 mV	1.0 M KOH	*Angew. Chem. Int. Ed. 2014, 53, 4372*
Ni	10 mA cm^{-2}	400mV	1.0 M KOH	*Angew. Chem. Int. Ed. 2012, 51, 12703*
Electrodeposi -ted Co-sulfide	1 mA cm^{-2}	480mV	1.0 M KOH	*J. Am. Chem. Soc. 2013, 135, 17699*

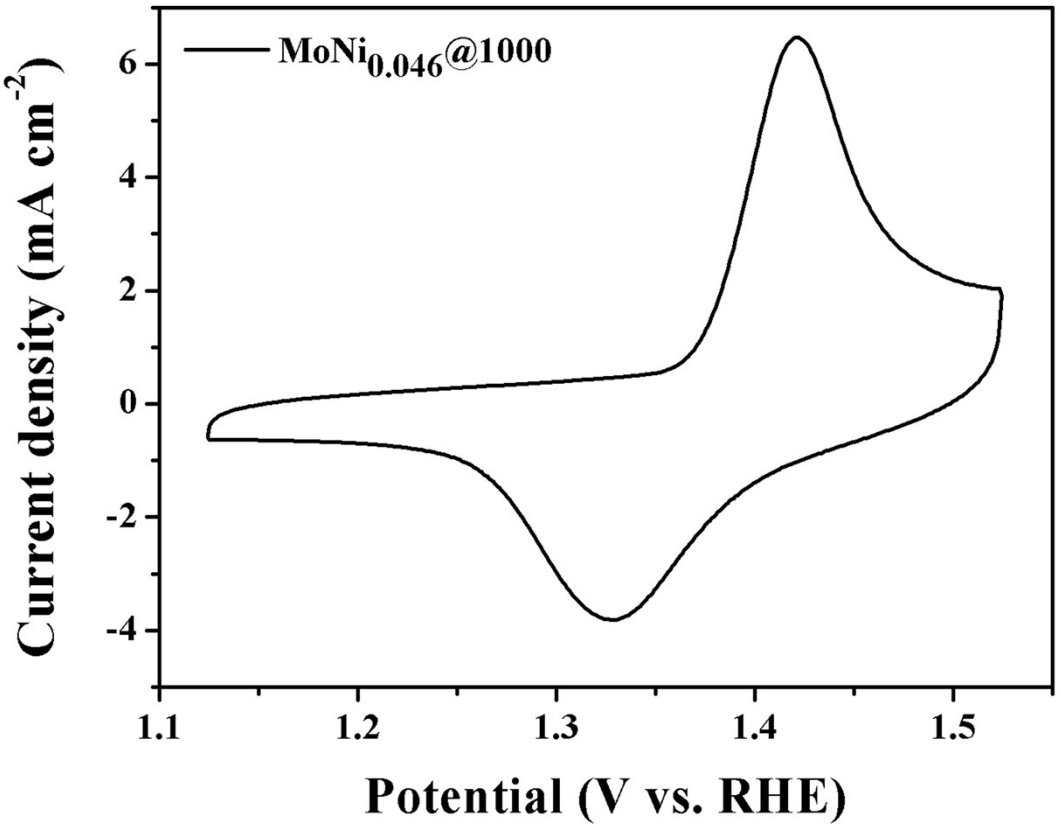

Figure S5. Cyclic voltammetry of $MoNi_{0.046}$@1000 in 1.0 M KOH with the scan rate of 10 mV s^{-1}.

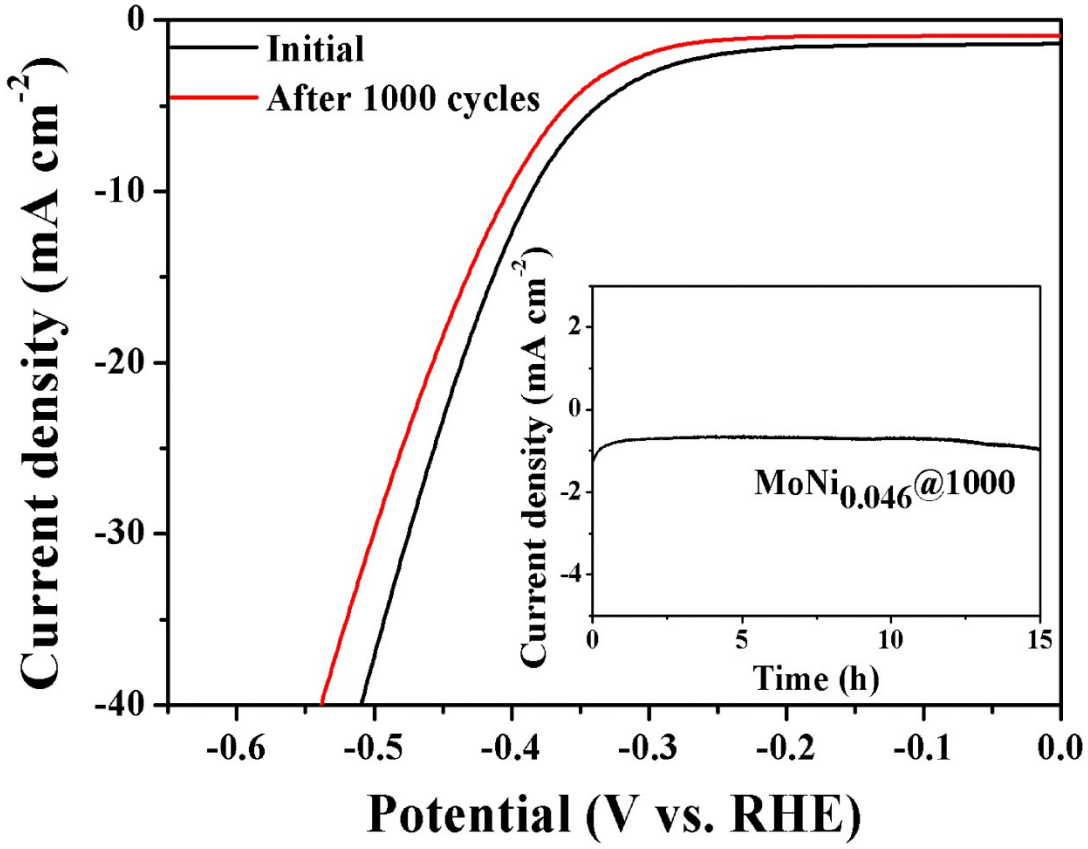

Figure S6. Durability test: the polarization curves of $MoNi_{0.046}$@1000 measured before and after 1000 cycles, and the time dependence current density curves under static overpotential of -340mV for 15 h in 1 M KOH.