Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information:

Ni-Doped Mo_2C Nanowires Supported on Ni Foam as a Binder-Free Electrode for Enhancing the Hydrogen Evolution Performance

Experimental Section

Materials Synthesis

All chemical reagents used in this experiment were of analytical grade. Prior to the synthesis, the Ni Foam (NF, 50.0 mm×10.0 mm×1.0 mm) was cleaned ultrasonically in a 3.0 mol L^{-1} HCl solution for 15 min to remove the surface oxide layer, and then placed against the wall of a Teflon-lined stainless steel autoclave at a certain angle. Afterwards, 30 mL of 0.05 mol L^{-1} $Ni(NO_3)_2$•$6H_2O$ and 0.014 mol L^{-1} $(NH_4)_6Mo_7O_{24}$•$4H_2O$ aqueous solutions was transferred into the above Teflon autoclave. The autoclave was sealed and heated at 150 ℃ for 6 h. After the hydrothermal reaction was over, the samples were completely washed with distilled water and dried in an oven. Finally, the samples were carburized to obtain Ni-doped Mo_2C nanowires on the NF ($NiMo_2C$/NF) at 700 ℃ for 2 h under the mixture gas flow of CH_4/H_2/Ar (10/20//30, volume) in a tube furnace. For purposes of comparison, Mo_2C/NF was prepared as described above without adding $Ni(NO_3)_2$•$6H_2O$. Commercial Pt/C (40 wt% Pt loading, Johnson Matthey; 5.0 mg) was ultrasonically mixed with 200 μL ethanol and 5 μL Nafion solution (5 wt.%) to obtain a well-dispersed ink, which was loaded onto the NF with an area of 1 cm^2.

Characterization and electrochemical measurements

The surface morphology and the microstructure of the catalysts were analyzed by X-ray diffraction (XRD-6000, Shimadzu), X-ray photoelectron spectroscopy (XPS, PHI 550 ESCA/SAM), field-emission scanning electron microscopy (FE-SEM, JSM-7800, Japan), transmission electron microscopy (TEM, Tecnai F20 X-Twin microscope, FEI, USA), and energy dispersive X-ray spectra (EDX, OXFORD Link-ISIS-300), respectively. Electrochemical measurements were conducted in a three-electrode cell system with an Electrochemical Workstation (CHI660D, Shanghai Chenhua Device Company, China). The electrode area of the working electrode is 1 cm^2. A Pt foil in parallel orientation to the working electrode was used as the counter electrode and a Hg/HgO as the reference electrode. Double layer capacitance of the electrodes was obtained by cyclic voltammetry at scan rate from 5 to 120 mV s^{-1}. And the catalytic performance of the prepared electrodes toward HER was systematically investigated in a 6 mol L^{-1} NaOH electrolyte. All potentials mentioned in this work were converted to the values with reference to a reversible hydrogen electrode (RHE).

Computational Methods and Models

In this work, density functional theory (DFT) calculations were carried out using the Perdew-Burke-Ernzerhof functional and Projected Augmented Wave (PAW) pseudopotentials, as embedded in the Vienna ab initio simulation package (VASP). The cutoff energy was 520 eV for the plane-wave basis set.

XRD of Mo_2C and Ni-substituted Mo_2C crystals were simulated by the Reflex software package from material studio (MS) using 2×2×2 supercells with periodic boundary conditions (Figure S1). The lattice parameters and all the atomic positions are allowed to relax until the forces on the atoms were $<0.0001 eV Å^{-1}$.

The stable Mo_2C (001) surface was simulated by six layers of alternating Mo and C atoms to investigate the catalytic properties. The slab calculations were performed using a 4 × 4 unit cell with a 9 × 9 × 1 k-point grid. The vacuum region between the slabs is 15 Å, which is sufficiently large to ensure that the interactions between repeated slabs in a direct normal to the surface are negligible. The atoms in the top four layers were allowed to be fully relaxed whereas those in the bottom two layers were fixed at their bulk-truncated structure. Figure S2 shows the top and side views of the Mo_2C (001) surface and Ni-doped Mo_2C (001) surface. To illustrate the influence of the doping Ni on the phase stability of the Mo_2C, we have calculated the cohesive energy. The generalized cohesive energy (E_{coh}) is defined as $E_{coh} = E_{solid}(AB) - E_{atom}(A) - E_{atom}(B)$. For the adsorption strength of H adsorption on the catalyst surface, it can be calculated and expressed as $E_{ads} = E_{total} - E_{slab} - E_{adsorbate}$, in which E_{total} is the total energy of the slab with adsorbate, E_{slab} is the energy of the slab, and $E_{adsorbate}$ is half the energy of H_2 gas in the case of a hydrogen adsrobate. Thus, a negative value for E_{ads} indicates an exothermic adsorption process, with more negative values corresponding to stronger and more stable adsorptions.

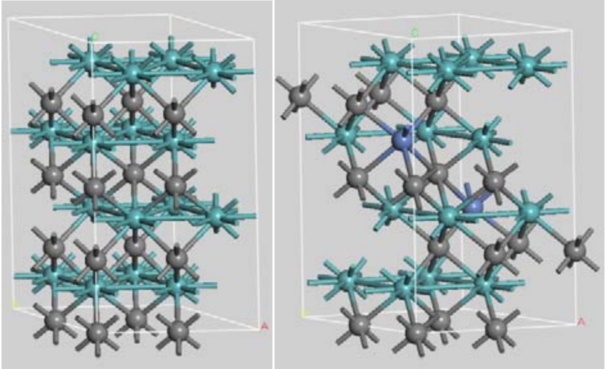

Figure S1. The supercell models of Mo_2C and $NiMo_2C$ (2×2×2), green balls for Mo atoms (Green balls: Mo; Gray balls: C atoms; Blue balls: Ni).

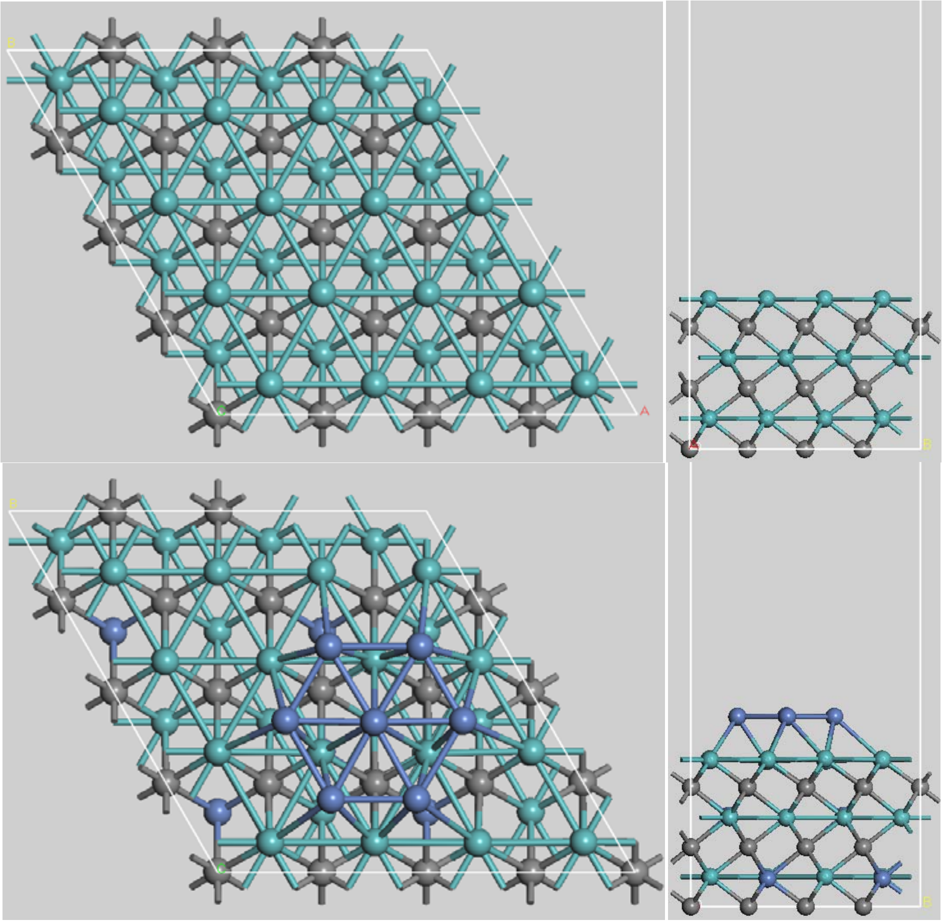

Figure S2. The top and side views of the optimized geometric structures for (a) Mo_2C (001) and (b) Ni-doped Mo_2C (001) surface (Green balls: Mo; Gray balls: C atoms; Blue balls: Ni).

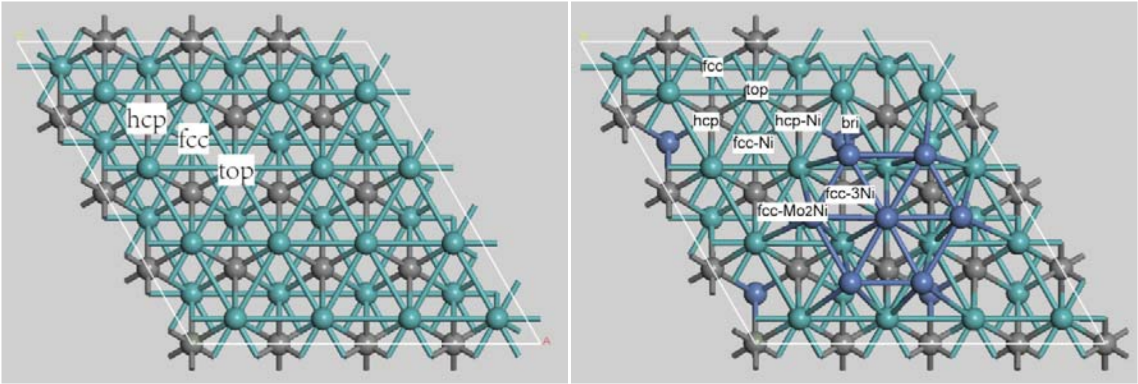

Figure S3. The adsorption sites on (a) Mo_2C (001) and (b) Ni-doped Mo_2C (001) surface (Green balls: Mo; Gray balls: C atoms; Blue balls: Ni).

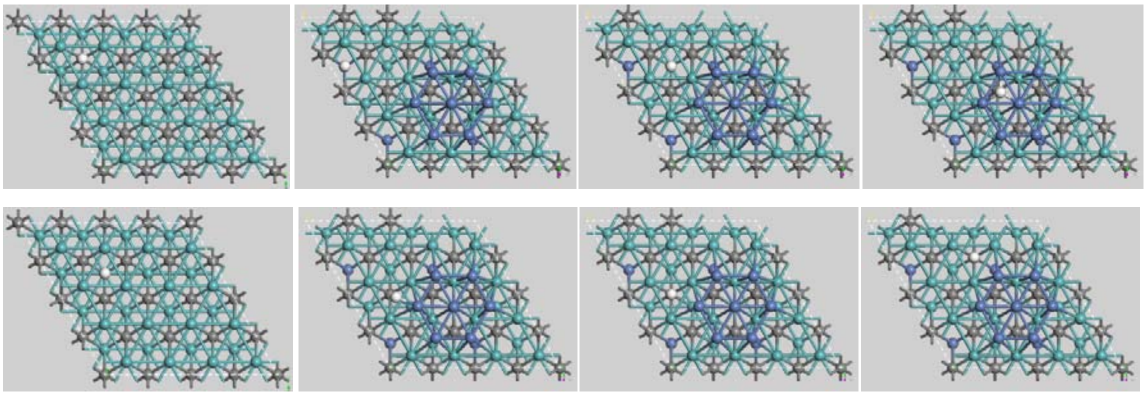

Figure S4. The stable geometric structures of the different H adsorption sites on (a_1, a_2) Mo_2C (001) and (b_1-b_6) Ni-doped Mo_2C (001) surface, respectively (Green balls: Mo; Gray balls: C atoms; Blue balls: Ni; White balls: H).

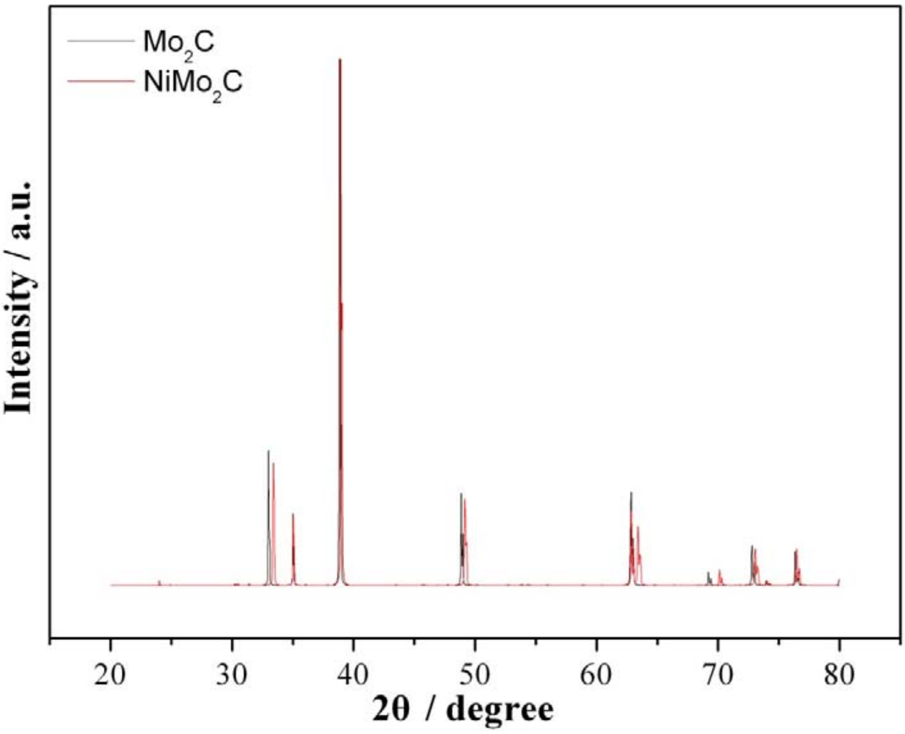

Figure S5. The simulated XRD patterns of Mo_2C and Ni-doped Mo_2C by DFT calculations.

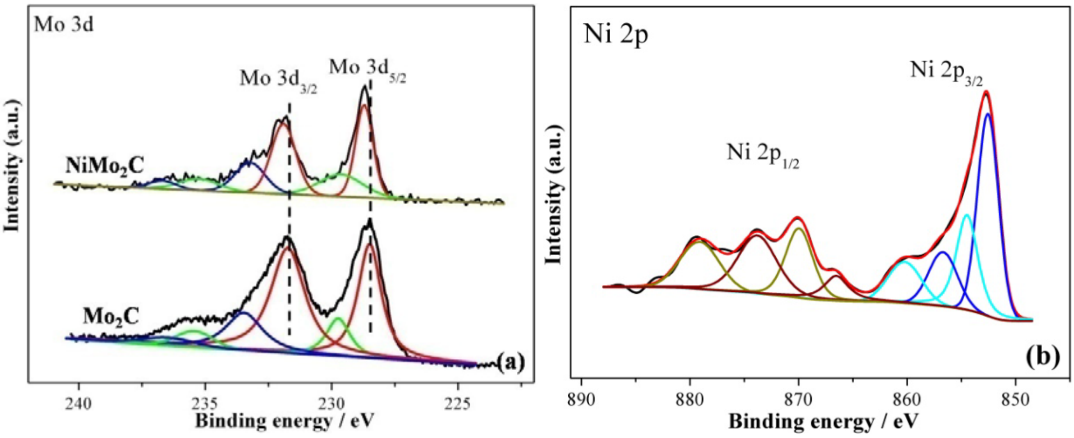

Figure S6. (a) Mo 3d XPS spectra of Mo_2C and $NiMo_2C$; and (b) Ni 2p XPS spectra of $NiMo_2C$

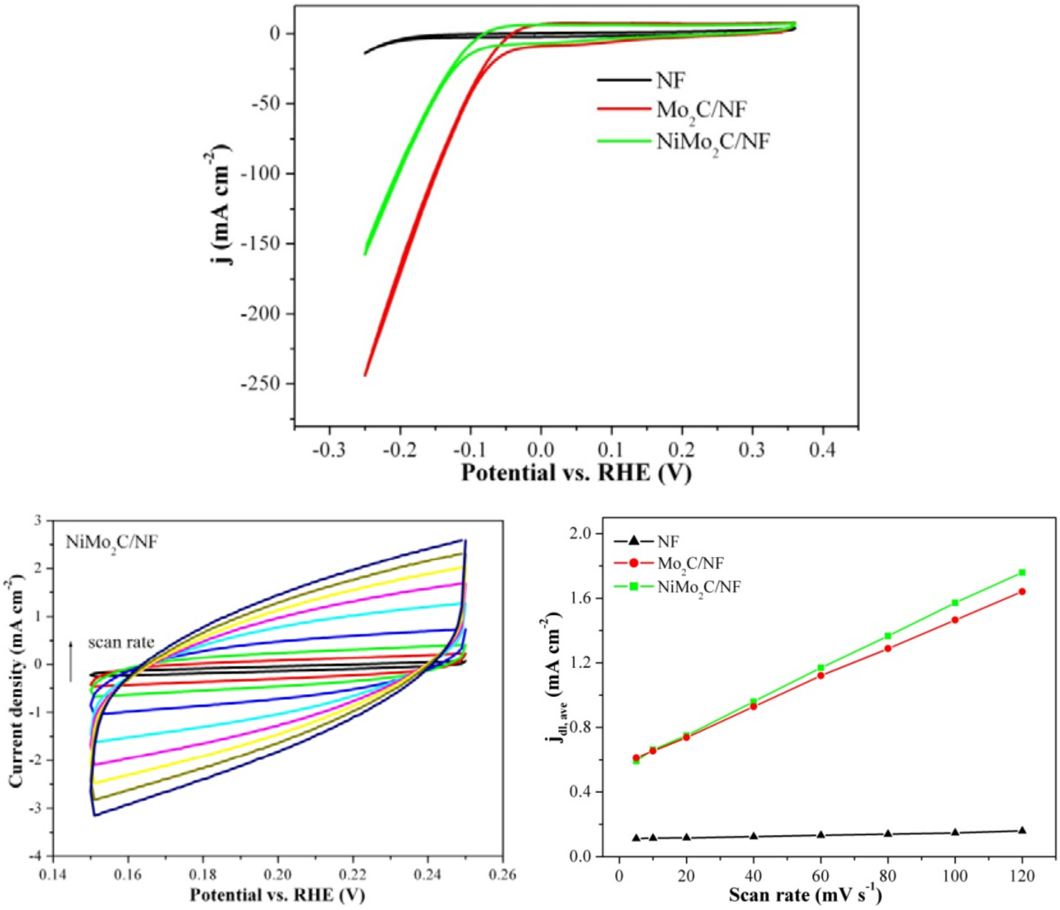

Figure S7. (a) CVs of the NF, Mo_2C/NF, and $NiMo_2C$/NF in 6 M NaOH electrolyte with a scan rate of 50 mV s^{-1}; (b) CVs in the double layer region for the typical $NiMo_2C$/NF at different scan rate, (c) scan-rate dependence of the mean capacitive currents at 0.20V vs. RHE for NF, Mo_2C/NF and $NiMo_2C$/NF.

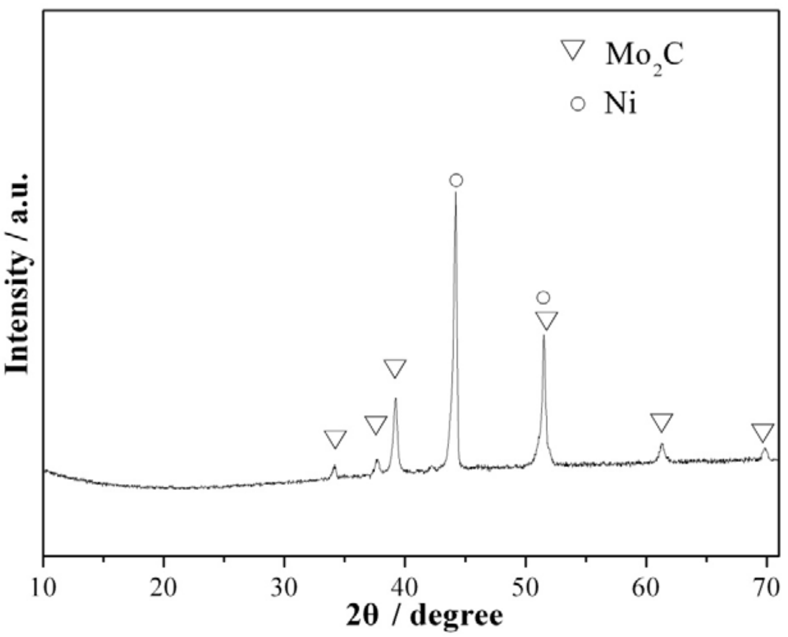

Figure S8. XRD pattern of $NiMo_2C$/NF after 10000 CV scans in 6 M NaOH.

Table S1. Comparison of the HER parameters of different non-Pt catalysts

Catalysts	**Substrate**	**Current density (i, mA cm^{-2})**	**η at the corresponding i (mV)**	**Exchange current density (i_0, mA cm^{-2})**	**Ref.**
Bulk Mo_2C	Glass carbon electrode	10	190	1.3×10^{-3}	[12]
Mo_2C/CNT	Carbon paper	10	152	1.4×10^{-2}	[13]
Mo_2C nanowires	Glass carbon electrode	60	200	-	[14]
Mo_2C/CNT-GR	Glass carbon electrode	10	130	6.2×10^{-2}	[15]
Mo_2C nanorod	Glass carbon electrode	10	150	3.3×10^{-2}	[17]
Mo_2C/GCSs	Glass carbon electrode	10	200	1.25×10^{-2}	[18]
$NiMoN_x$/C	Glass carbon electrode	5	220	0.24	[7]
Ni_2P/Ti	Ti plate	10 100	116 180	0.49	[8]
CoP/CNT	Glass carbon electrode	10	122	0.13	[9]
$CoSe_2$ NP/CP	Carbon paper	10 100	139 184	$(4.9 \pm 1.4) \times 10^{-3}$	[31]
FeP/Ti	Ti foil	10	85	-	[30]
MoO_3-MoS_2/FTO	FTO	10	310	8.2×10^{-5}	[11]
MoS_2/grapheme/NF	Grapheme/Ni Foam	10	141	-	[32]
$NiMo_2C$/NF	Ni Foam	10 100	47 150	0.51	This work