

Supporting Information

Etching dopant elements to construct active-sites rich Mo₂C for the
hydrogen evolution reaction

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Experimental Section

Synthesis and characterization

Materials: the raw materials for synthesizing Mo₂C、Al-Mo₂C and W-Mo₂C、M-Mo₂C are Mo powder (99.99%, AR), C powder (99.5%, AR), Al powder (99.0%, AR) and HCl, LiF (Aladdin, 99.95%, AR). 20 wt% Pt/C (TANAKA).

Synthesis process of Al-Mo₂C and Mo₂C: the mixture of Mo powder, Al powder and C powder with a mole ratio of 3.0:1.4 :1.9 was fully ground in a mortar for 2 hours. And then the ground powder was loaded into a tablet machine mold and pressed under the pressure of 18 MP for 10 minutes. Finally, the pressed sample was put into an alumina crucible, covered, and sent into a vacuum sintering furnace. Al-Mo₂C was obtained after sintering in vacuum at 1400 °C for 4 hours. For the Mo₂C, the molar ratio of Mo powder and C powder is 3:1.9, the other specific process is the same as the synthesis of Al-Mo₂C.

Synthesis of M-Mo₂C and W-Mo₂C: 0.5 g of LiF and 15 ml of HCl were added into the 50 ml polytetrafluoroethylene beaker and stirred in a temperature-controlled magnetic agitator, then 0.5 g of Al-Mo₂C (or Mo₂C) samples were dispersed into the above mixed solution. After etching at 51 °C for 48 hours, the samples were washed many times with deionized water and anhydrous ethanol, and finally dried in vacuum at 60 °C for 12 h, obtaining the M-Mo₂C (or W-Mo₂C).

Characterizations

XRD patterns were collected by using a /max-23000 configured with a Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) source. X-ray photoelectron spectrum (XPS) data are collected from a K-Alpha+ X-ray photoelectron spectrometer, and the binding energy of the C 1s peak at 284.8 eV is used as an internal reference. The scanning electron microscopy (SEM) images and element mapping were obtained from a Nova nano SEM 450 at 5 kV. High resolution transmission electron microscopy (HRTEM) images were taken on a JEM 2100 with field emission gun transmission electron microscope at the voltage of 200 kV. The Raman test was carried out on the InviaQontor Confocal Micro Raman Spectrometer (Labram HR evolution). The

electron paramagnetic resonance (EPR) spectrum was recorded on a E500 Bruker EPR spectrometer (room temperature, 0.998 mW, X-band).

Hydrogen evolution reaction test

The binder solution was prepared by mixing 5 wt% Nafion solution (60 μL) with ethanol (940 μL). The uniform catalyst ink was prepared by dispersing 2 mg of catalyst into a binder solution (1 ml) and ultrasonic treated for 1 h. After that, 10 μL of the ink was dropped and casted onto a glassy carbon electrode with a diameter of 3 mm to dry naturally (the loading per unit area of catalyst was about $0.286 \text{ mg}\cdot\text{cm}^{-2}$). Electrochemical measurements were performed in 0.5 M H_2SO_4 solution using a CHI760 electrochemical workstation with a standard three-electrode setup. A saturated calomel electrode (SCE) was used as the reference electrode, the catalyst loaded glassy carbon electrode was used as the working electrode, and a graphite rod was used as the counter electrode (5 mm in diameter). Before the measurement, Ar gas was introduced into the electrolytic cell to purge the electrolyte until Ar saturation is achieved. Linear sweep voltammetry (LSV) was performed at the scanning rate of $5 \text{ mV}\cdot\text{S}^{-1}$. Electrochemical impedance spectroscopy (EIS) tests were carried out in the frequency range of 100000 to 0.1 Hz. The Cyclic Voltammetry (CV) test was performed under the open circuit voltage plus or minus 50 mV, and the scan rate was 20 mV, 40 mV, 60 mV, 80 mV, 100 mV and 120 mV, respectively. The electrochemical stability of the samples was assessed using the current-time (i-t) curve by long-term chronoamperometry. All tested potentials were converted to reversible hydrogen electrode (RHE) potentials, which can be calculated from the equation $E (\text{RHE}) = E (\text{SCE}) + 0.242 \text{ V} + 0.0591 \text{ pH}$. And all electrochemical measurements were not compensated for iR .

Supplementary Figures

Table S1 The percentage of Al and Mo content for Al-Mo₂C with lamellar structure by ICP analysis

Sample	Concentration of Al (%)	Concentration of Mo (%)	Al: Mo	Concentration of Al (wt%)
Al-Mo ₂ C	75.868	593.95	12.77	5.66

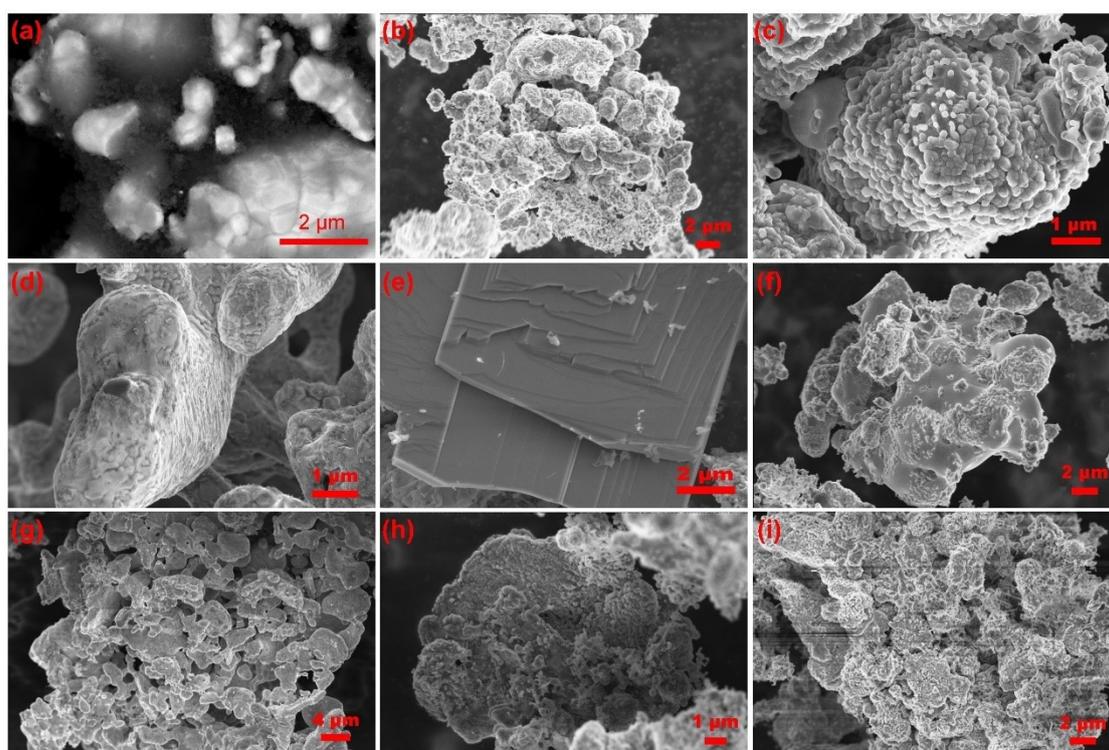


Figure S1 SEM images of Al- Mo₂C. (a) the molar ratio of Mo: C equals to 3: 1.9; (b) the molar ratio of Mo: Al: C equals to 3: 1.1: 1.9; (c) the molar ratio of Mo: Al: C equals to 3: 1.2: 1.9; (d) the molar ratio of Mo: Al: C equals to 3: 1.3: 1.9; (e) the molar ratio of Mo: Al: C equals to 3: 1.4: 1.9; (f) the molar ratio of Mo: Al: C equals to 3: 1.5: 1.9; (g) the molar ratio of Mo: Al: C equals to 3: 1.6: 1.9; (h) the molar ratio of Mo: Al: C equals to 3: 1.7: 1.9; (h) the molar ratio of Mo: Al: C equals to 3: 1.8: 1.9. It can be seen from the above figure that the molar ratio of Mo, Al, and C is 3: 1.4: 1.9, which can synthesize lamellar Al-Mo₂C.

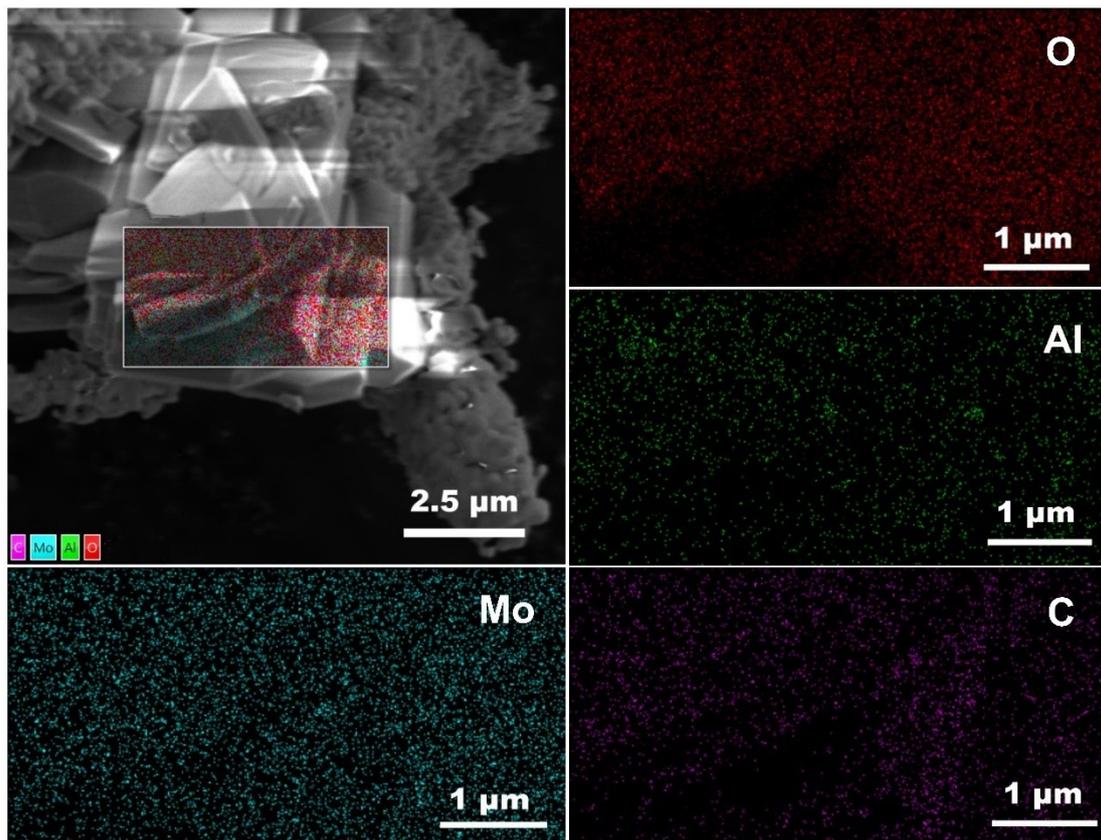


Figure S2 The SEM images and the regional element mapping of Al- Mo₂C.

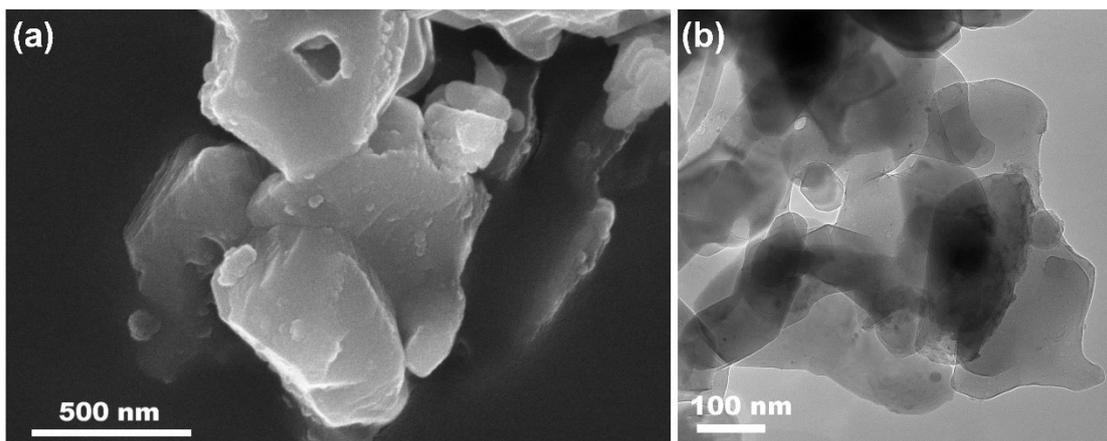


Figure S3 (a) SEM and (b) TEM images of M-Mo₂C.

Discussion:

According to SEM (Figure S3a), after etching Al, M-Mo₂C presents the phenomenon of lamellar accumulation, but the lamellar size is significantly smaller than Al-Mo₂C (Figure S1e). After ultrasonic dispersion, TEM of M-Mo₂C (Figure 2e or Figure S3b) shows that M-Mo₂C was a small layered morphology at low magnification. This means the Al-Mo₂C is etched and stripped into scattered pieces, which gives the M-Mo₂C more edges and surface area.

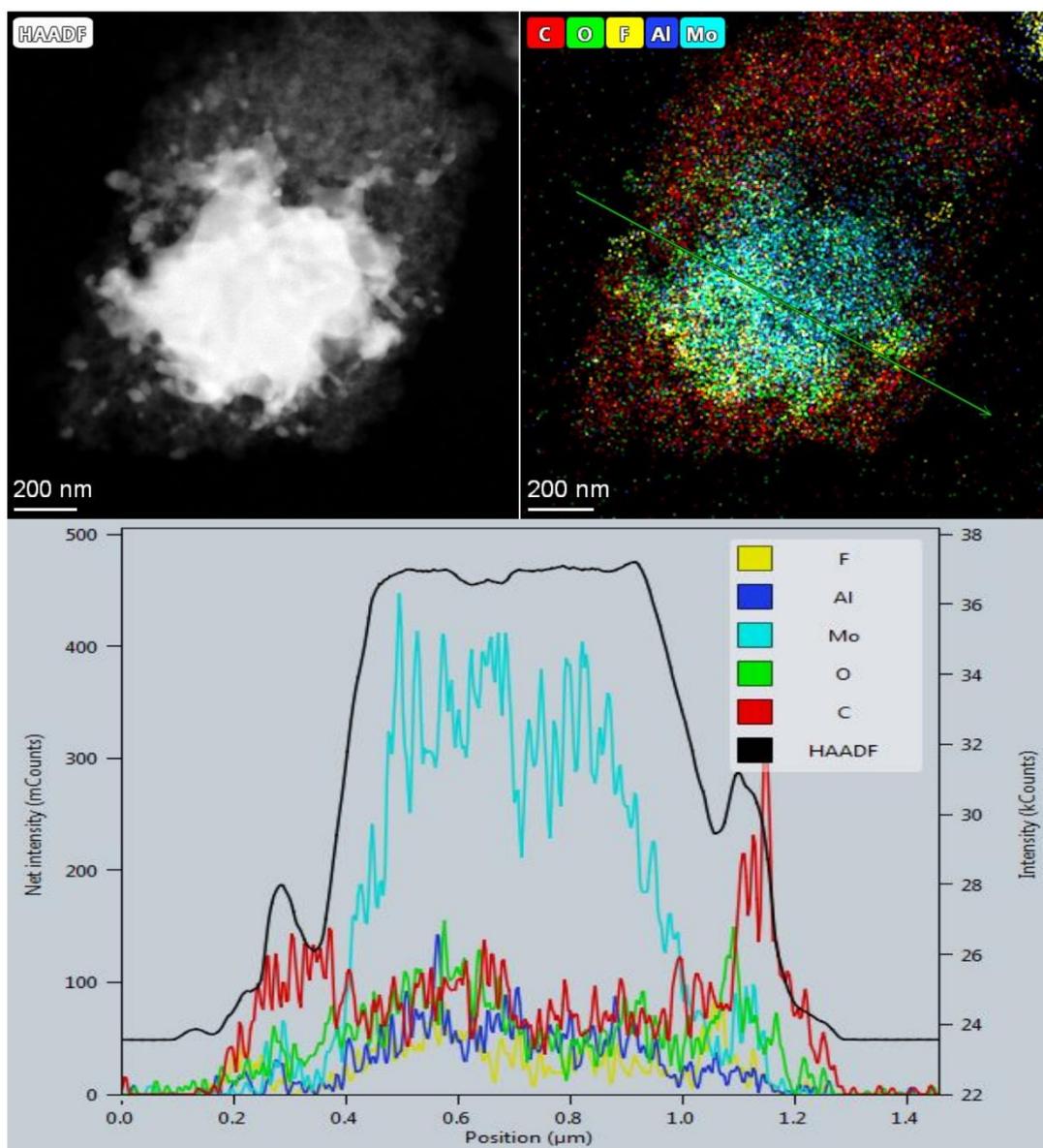


Figure S4 The TEM images and the regional element mapping of M-Mo₂C.

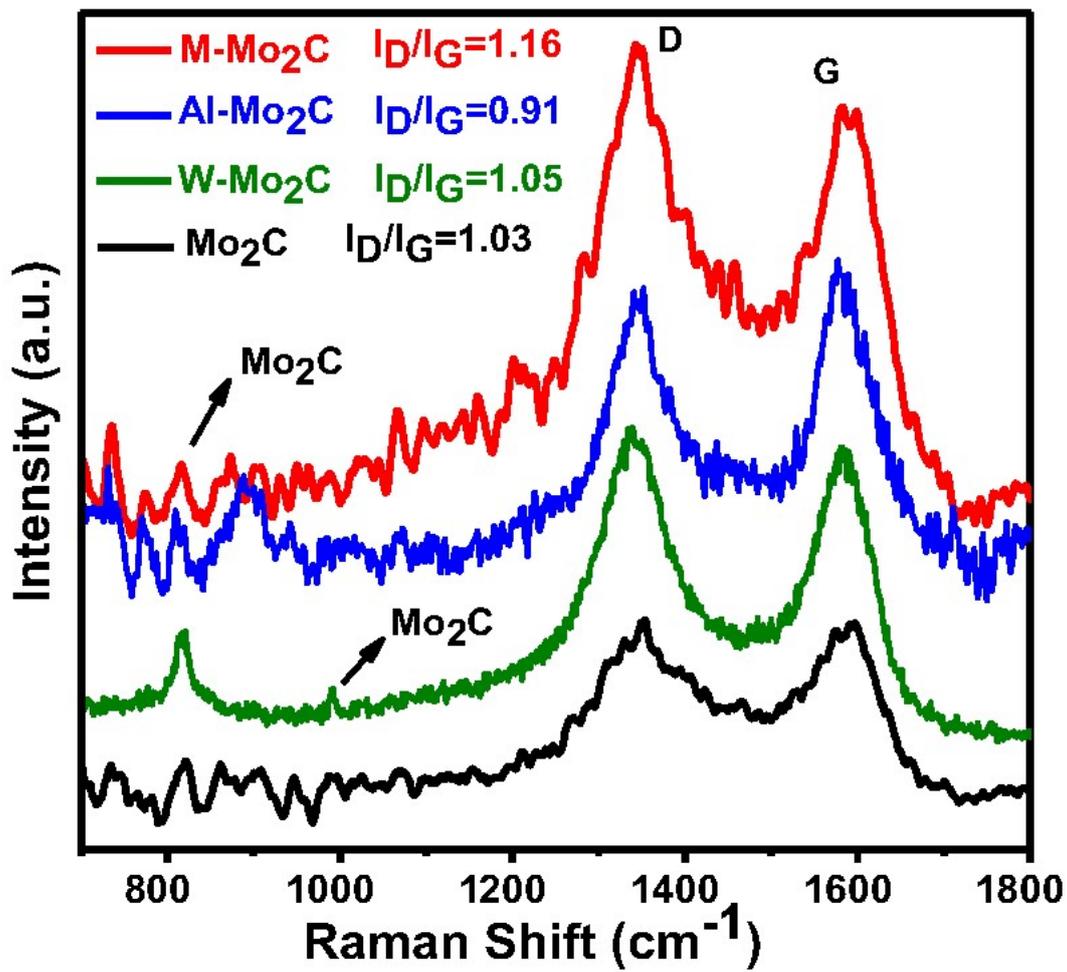


Figure S5 Raman spectra of Mo₂C, W-Mo₂C, M-Mo₂C and Al-Mo₂C

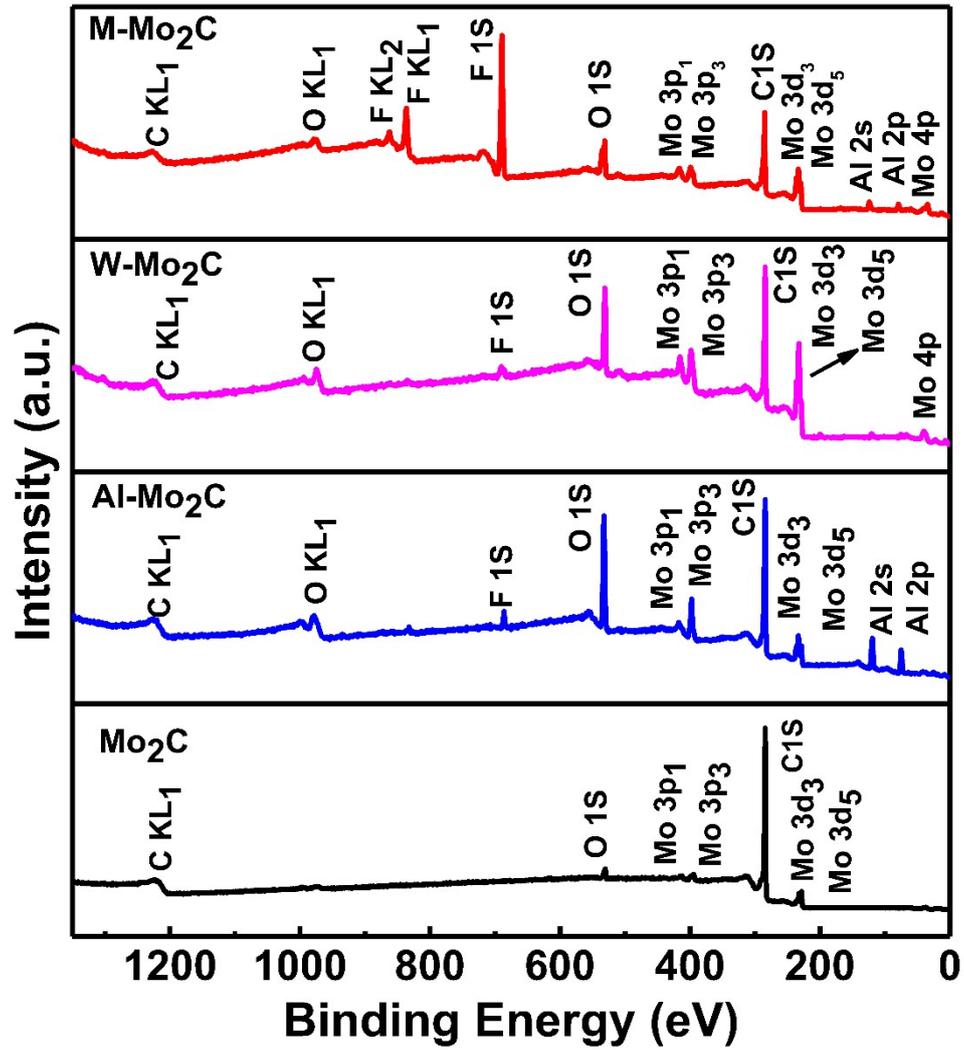


Figure S6 The XPS spectra of Mo₂C, W-Mo₂C, Al-Mo₂C and M-Mo₂C.

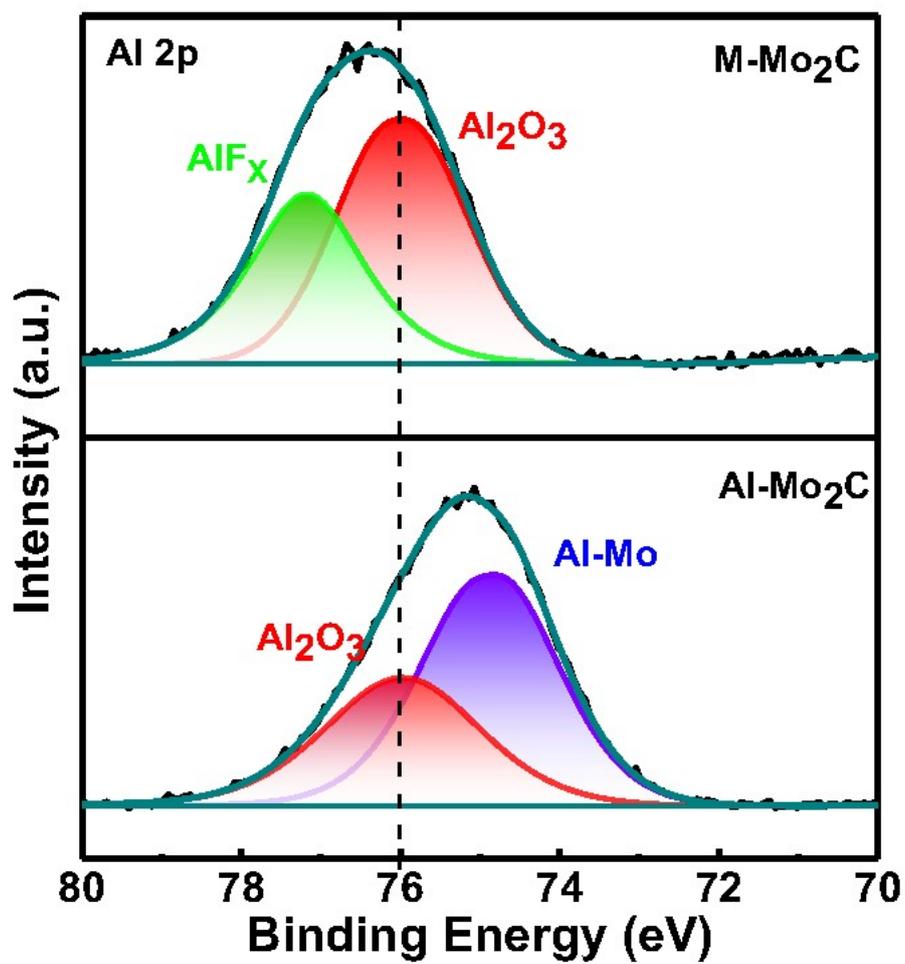


Figure S7 XPS spectra of Al 2p for M-Mo₂C and Al-Mo₂C.

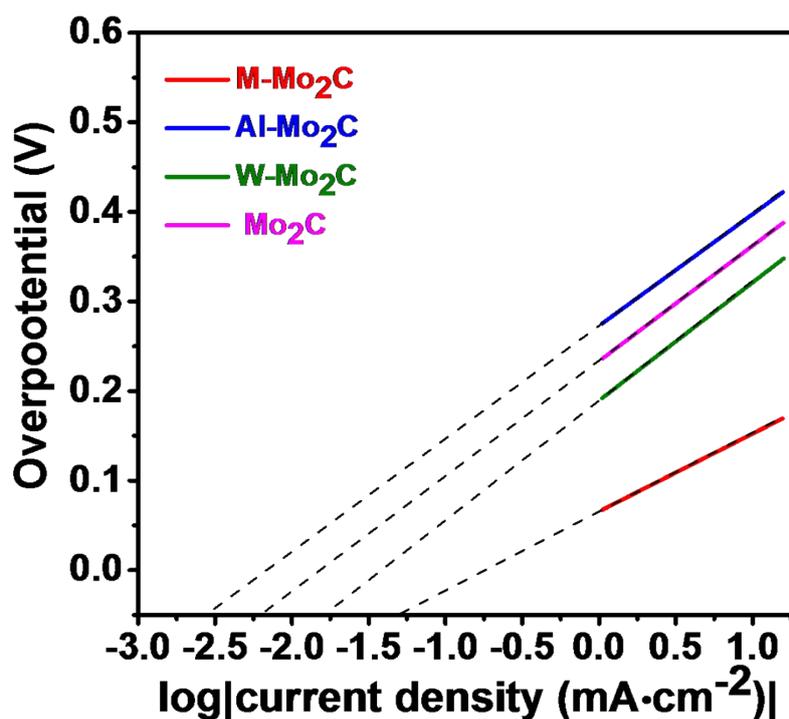


Figure S8 The exchange current densities of different electrocatalysts were determined by the intercepts of corresponding Tafel curves with horizontal axis when the overpotential (V vs. RHE) equals zero.

Table S2 Calculated exchange current densities of varying samples.

Electrocatalysts	Log(J/mA·cm ⁻²) at $\eta = 0$ V	Exchangecurrent densit (uA·cm ⁻²)
Mo ₂ C	-2.26	5.49
W-Mo ₂ C	-1.78	16.59
Al-Mo ₂ C	-2.64	2.29
M- Mo ₂ C	-1.30	50.13

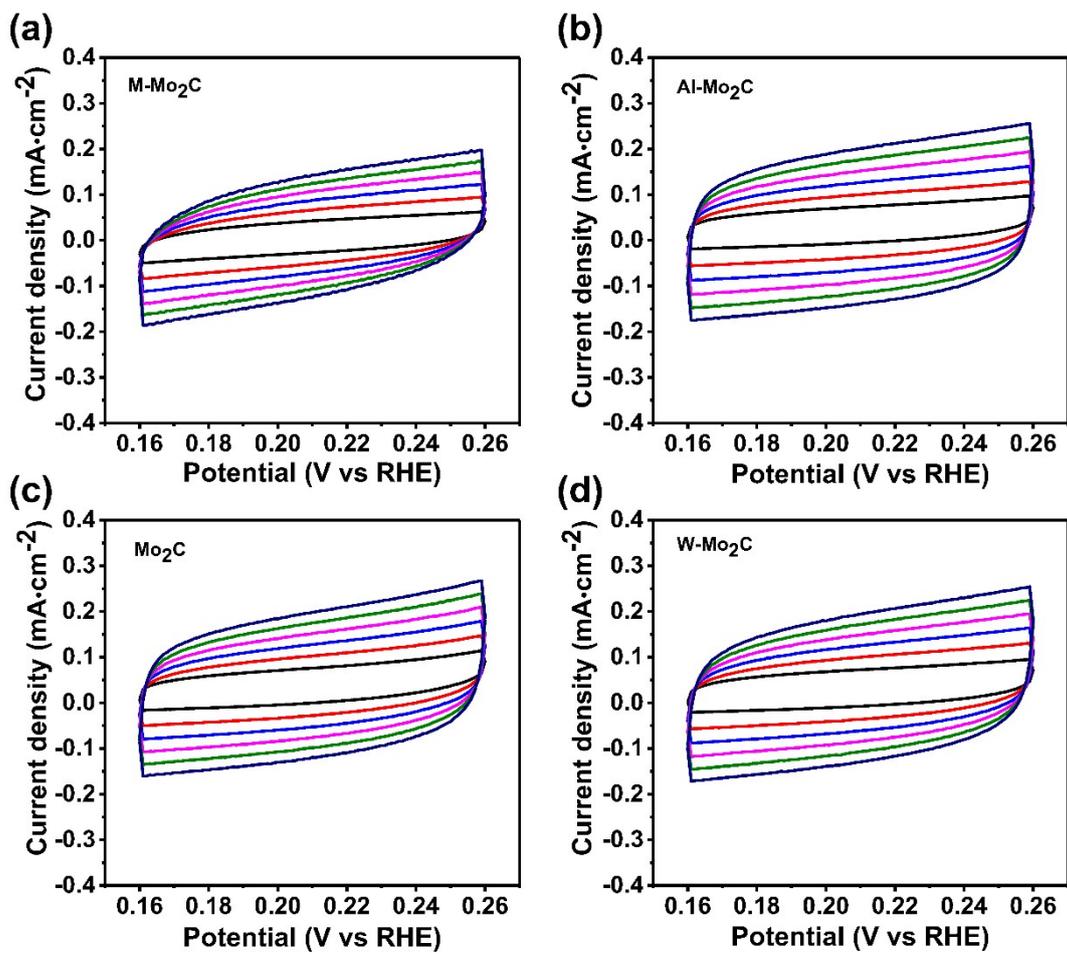


Figure S9 CV curves of (a) M-Mo₂C, (b) Al-Mo₂C, (c) Mo₂C, and (d) W-Mo₂C of 20 mV, 40 mV, 60 mV, 80 mV, 100 mV, and 120 mV.

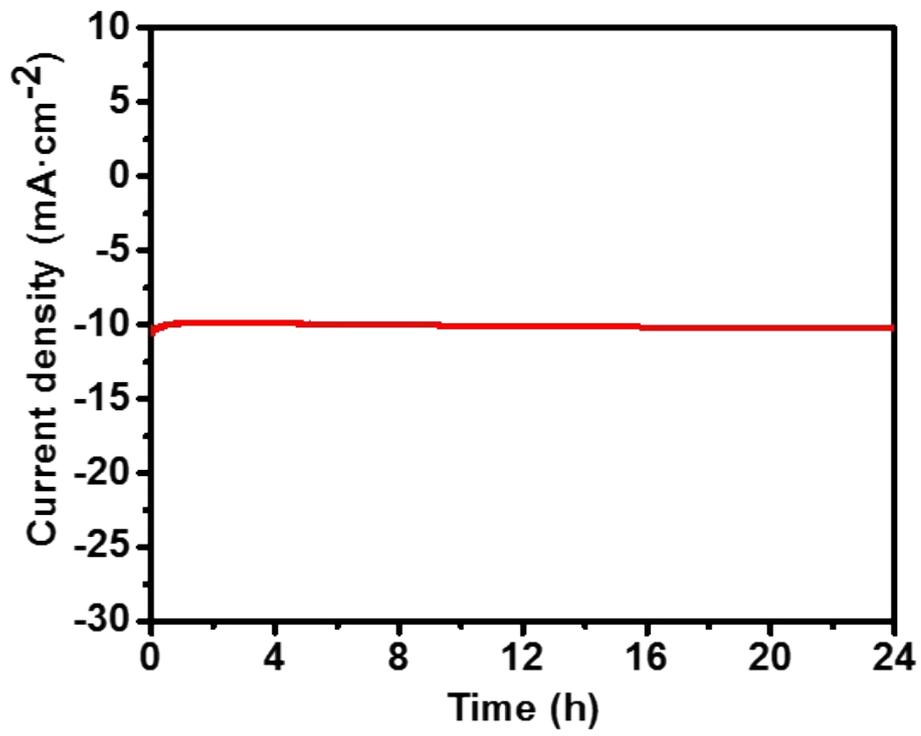


Figure S10 The i-t curve test of M-Mo₂C.

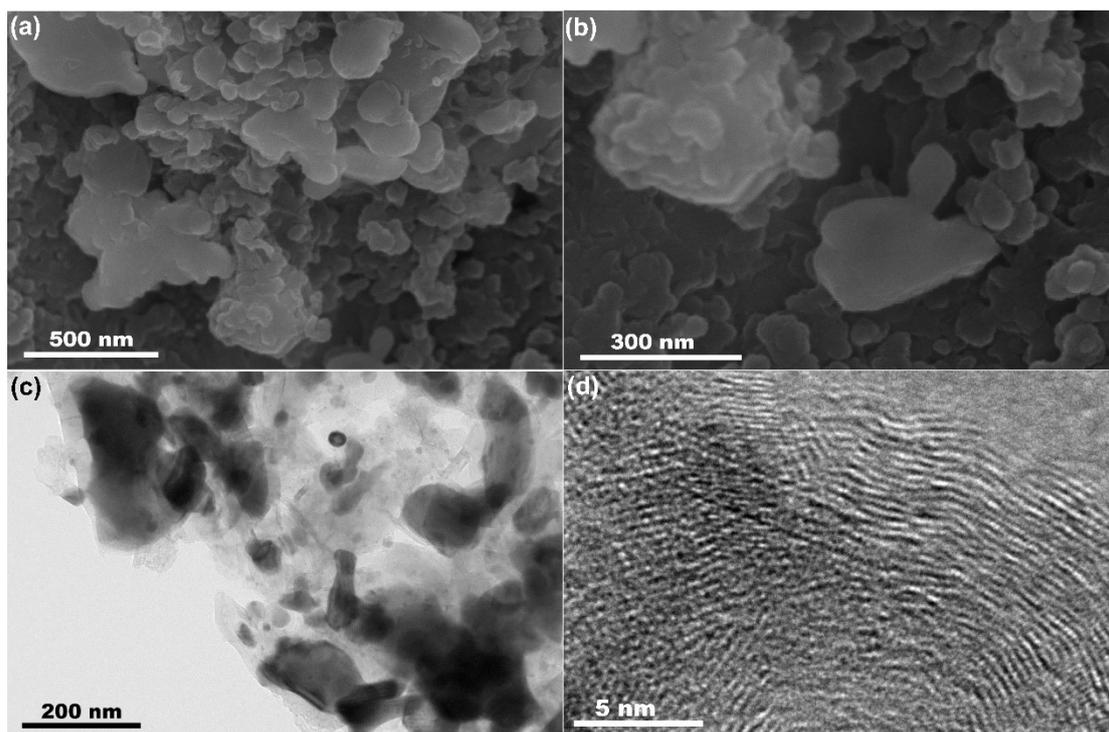


Figure S11 (a-b) SEM and (c-d) TEM images of M-Mo₂C after long-term electrochemical test.

Discussion:

According to SEM and (c-d) TEM images of M-Mo₂C after long-term electrochemical test (Figure S11), M-Mo₂C still exhibit the layered morphology and the lattice fringe still presents the disorder morphology. This indicates the morphology of M-Mo₂C did not change significantly after 24 h reaction.

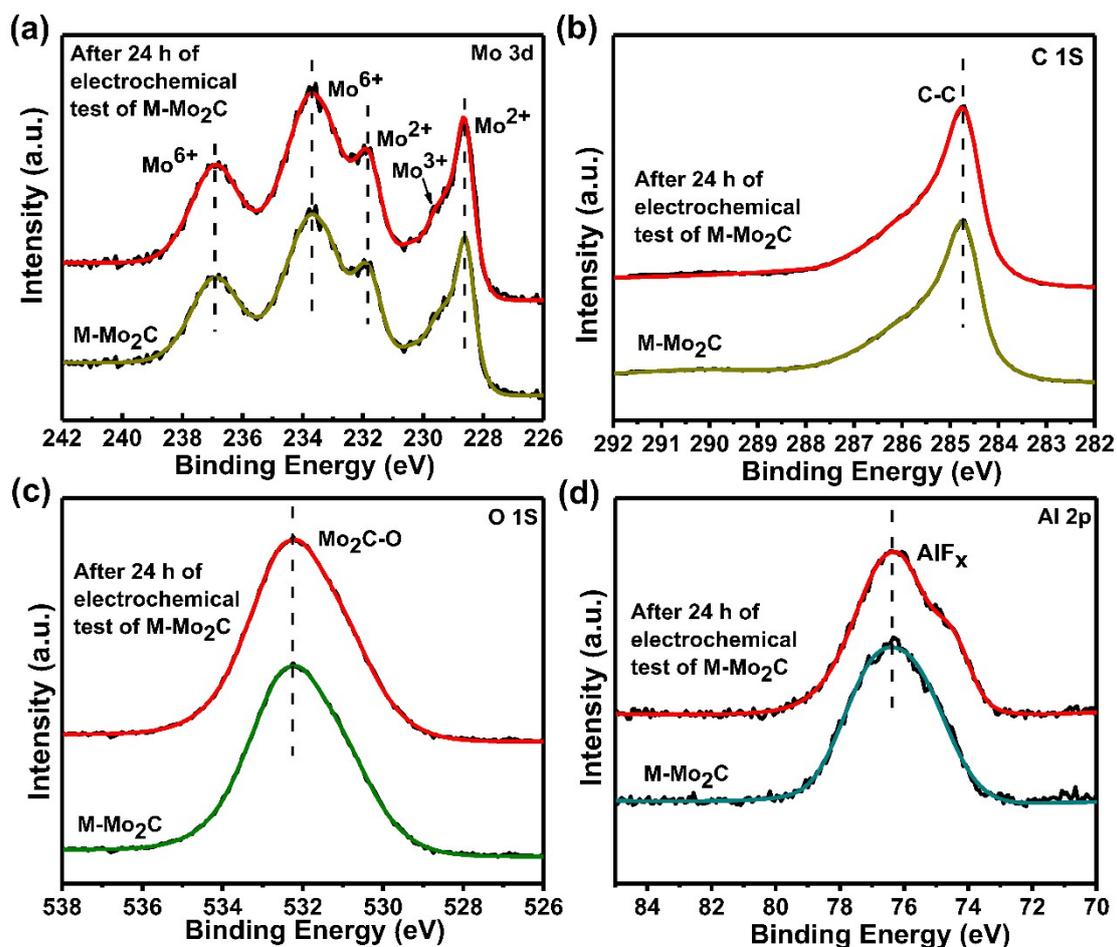


Figure S12 XPS spectra of (a) Mo 3d, (b) C 1s, (c) O 1s and (d) Al 2p for the M-Mo₂C after long-term electrochemical test.

Discussion:

According to XPS spectra for the M-Mo₂C after long-term electrochemical test (Figure S12), the banding energy of Mo 3d, C 1s, O 1s and Al 2p remains basically unchanged, which indicates that the surface structure of Mo₂C remains unchanged. This indicates the structure of M-Mo₂C has good stability after 24 h reaction.