Electronic Supplementary Information (ESI)

Electrochemical fixation of CO_2 over Mo plate to prepare Mo_2C film for electrocatalytic hydrogen evolution

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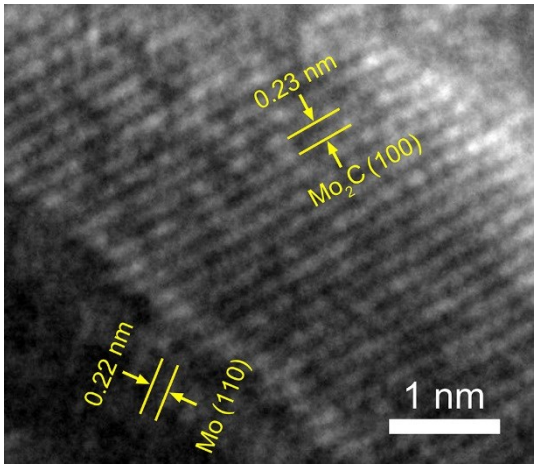

Fig. S1 High-resolution TEM image of the Mo_2C/Mo-60.

The film is extremely stable and can hardly peel off from the substrate even upon violent ultrasonication. For TEM test, powder is scratched from the substrate by a blade. The TEM image in Fig. S1 is based on the scratched powder.

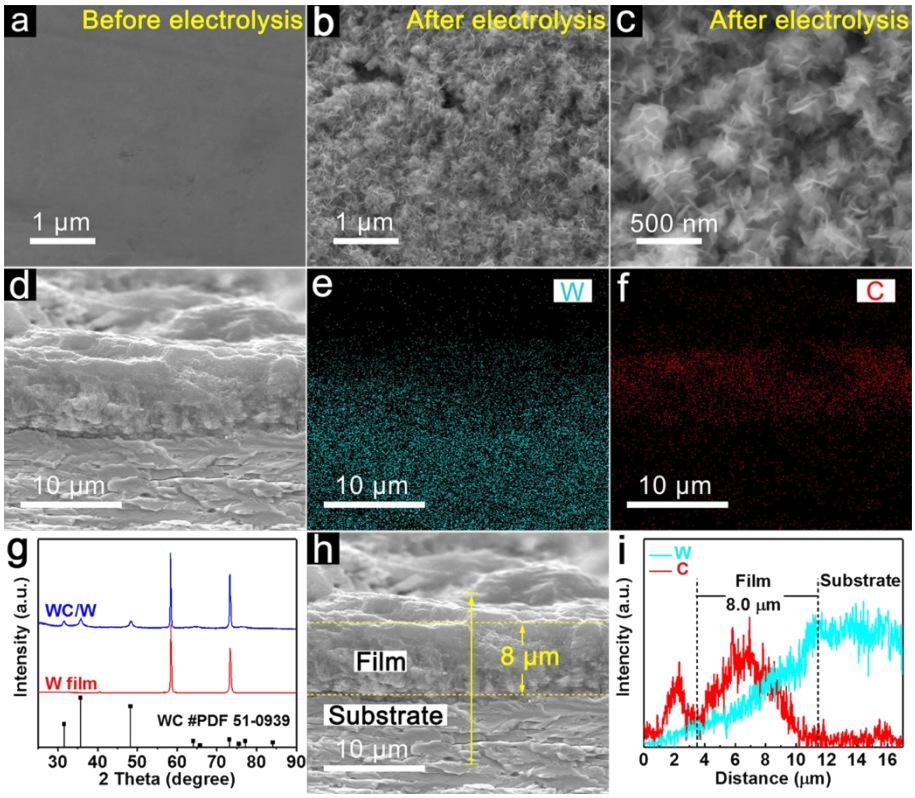

Fig. S2 Typical SEM images of W plate (a) before electrolysis and (b-c) after electrolysis. Elemental distribution mappings (d-f) after electrolysis. (g) XRD patterns of WC/W and Mo film. Cross-sectional SEM images of W plates after electrolysis (h) and corresponding EDS results of linear sweep analysis (i). Electrolysis time: 120 min.; Cell voltage: 3.1 V.

Similar with the Mo_2C-coated Mo plates, the electrochemical treatment of tungsten substrate was conducted at 3.1 V for 2 h in 900 °C molten Li_2CO_3. Then the W plate cathode was lifted out from the molten salt and cooled to room temperature. Finally, the tungsten carbide-coated tungsten plate (denoted as WC/W) was obtained after rinsing and drying at 60 °C.

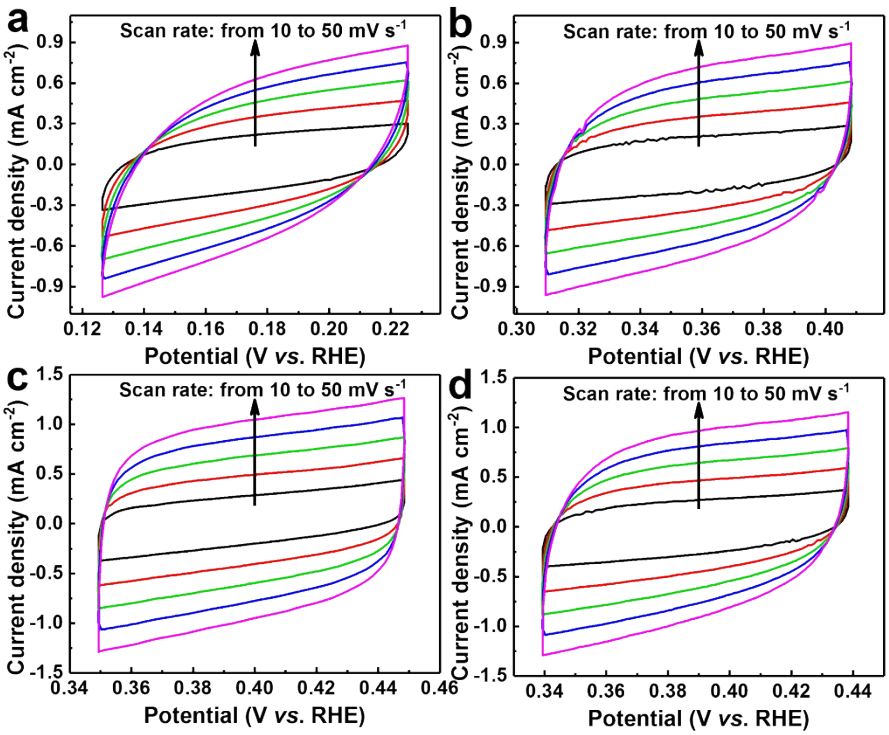

Fig. S3 CV curves measured at different scan rates from 10 to 50 mV s^{-1} in 0.5 M H_2SO_4 for Mo_2C/Mo samples: (a) Mo_2C/Mo-10, (b) Mo_2C/Mo-30, (c) Mo_2C/Mo-60, and (d) Mo_2C/Mo-120.

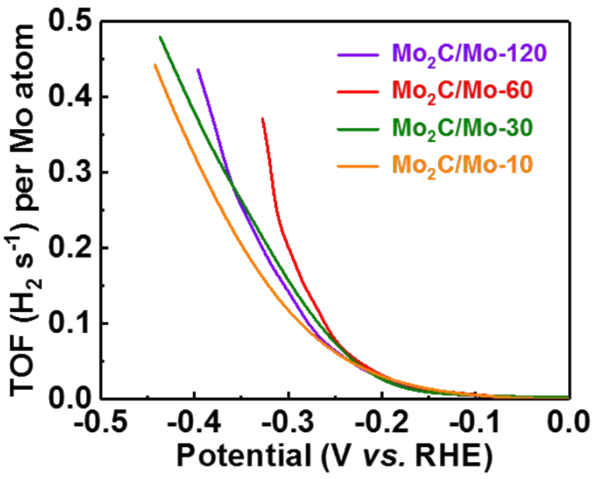

Fig. S4 TOFs of Mo_2C/Mo-10, Mo_2C/Mo-30, Mo_2C/Mo-60 and Mo_2C/Mo-120.

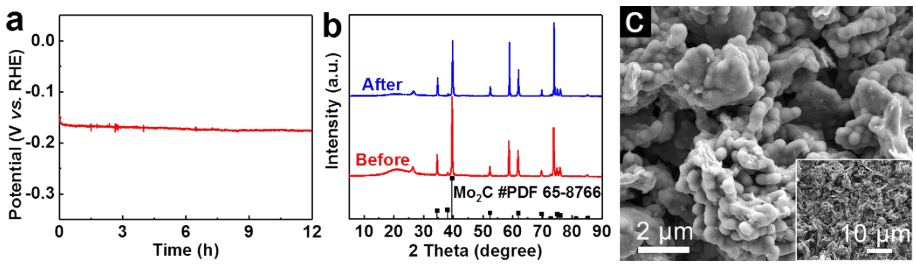

Fig. S5 (a) Long-term HER stability test of Mo_2C/Mo-60 at 10 mA cm^{-2}. (b) XRD patterns of Mo_2C/Mo-60 before and after stability test. (c) SEM image after stability test.

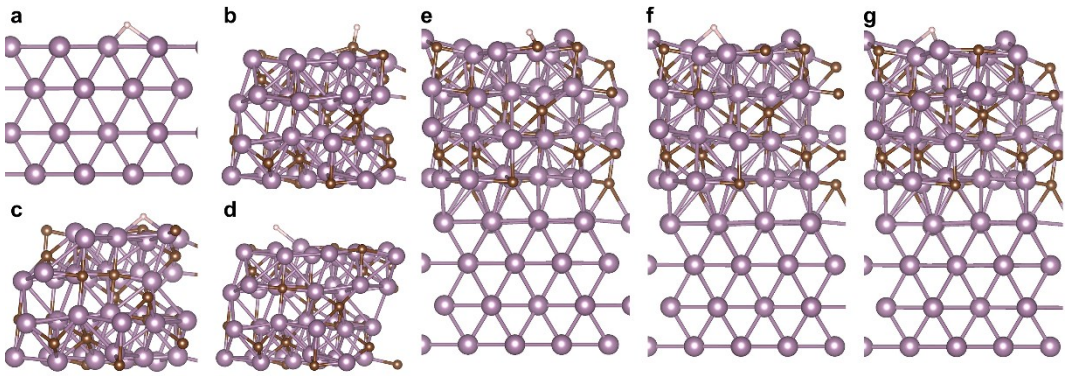

Fig. S6 Optimized geometry structures of hydrogen adsorption on (a) the surface Mo site of Mo (110), the surface (b) C, (c) Mo1 and (d) Mo2 sites of Mo_2C (121) and (e) C, (f) Mo1 and (g) Mo2 sites of Mo (110)-Mo_2C (121).

Table S1 The electrochemical properties of all the tested samples

Samples	Overpotential (mV) @10 mA cm^{-2}	Tafel slope (mV dec^{-1})	R_s (Ω)	R_{ct} (Ω)
Pt/C	25	45.3	2.20	9.9
Mo film	375	321.6	1.78	177.7
Mo_2C/Mo	149	77.9	2.15	23.8

Table S2 Comparison of Mo_2C-based catalysts for HER performance in 0.5 M H_2SO_4

Catalyst	Overpotential (mV) @10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Preparation method	Reference
Mo_2C/Mo	149	77.9	molten salt	This work
Ni-Mo_2C_{CB}/CFP	121.4	116.9	molten salt	1
Mo_2C/RGO	130	57.3	hydrothermal	2
Mo_2C/CC	140	124	hydrothermal	3
Mo_2C/NC	140	116	hydrothermal	4
L-Mo_2C	170	77	molten salt	5
Mo_2C-G	150	55	hydrothermal	6
H-Mo_2C/C	160	66	electrospinning	7
MoS_2/CS_2	208	43	Colloidal synthesis	8
MoS_2@$FePS_3$	168	127	hydrothermal	9

Supplementary references

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