Electronic Supplementary Information:

Molybdenum Carbide Stabilized on Graphene with High Electrocatalytic Activity for Hydrogen Evolution Reaction

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Experimental Section

Chemicals. Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), sulfuric acid (H_2SO_4), potassium nitrate (KNO₃), potassium permanganate (KMnO₄) and ethanol were purchased from Shanghai Chemical Reagent Co. Ltd. Graphite and Pt/C (5 wt% Pt on Vulcan carbon black) were purchased from Alfa Aesar. Nafion (5 wt%) and glucose were obtained from Sigma-Aldrich.

Synthesis of Mo₂C/RGO hybrid. GO was made by a modified Hummer's method.¹ Glucose (0.25 g) and (NH₄)₆Mo₇O₂₄·4H₂O (1 g) were dissolved in 25 ml DI water. Then GO solution (5 ml) containing GO (20 mg) was added to the mixed solution. The mixture was sonicated at room temperature for approximately 20 min until a homogeneous solution was achieved. Then the solution was transferred to a 50 ml Teflon-lined stainless steel autoclave. It was heated in an oven at 200 °C for 12 h with no intentional control of ramping or cooling rate. Product was collected by centrifugation at 8000 rpm for 5 min, washed with DI water and ethanol and dried at 80 °C for 20 h. After expelling air for 1 h at room temperature using argon, the products obtained above were calcined at 750 °C for 4 h in an argon flow. The resulting powder can be collected after the tube furnace cooling down to room temperature. The bare Mo₂C was prepared by a similar process without adding GO sheets.

Electrochemical measurements. 4 mg of catalyst and 80 μ l Nafion solution (5 wt%) were dispersed in 1 ml of 4:1 v/v water/ethanol by at least 30 min sonication to form a homogeneous ink. Then 5 μ l of the catalyst ink (containing 20 μ g of catalyst) was loaded onto a glassy carbon electrode of 3 mm in diameter (loading 0.285 mg cm⁻²). For comparison, the electrodes were also modified with commercial Pt/C (5 wt%). All electrochemical studies were performed using a CHI 660 pontentiostat (CH Instruments, China) in a three-electrode setup with modified glass carbon working electrodes, Ag/AgCl/KCl (3.5 M) electrodes as reference, Pt mesh as a counter electrode, and are de-aerated with argon before use. The electrocatalytic activity of

the catalysts towards HER was examined by polarization curves using linear sweep voltammetry (LSV) with a scan rate of 5 mV s⁻¹ in 0.5 M H_2SO_4 at room temperature. All of the potentials in our manuscript were calibrated to a reversible hydrogen electrode (RHE).

Characterizations

The crystal structure was determined using X-ray diffraction (Bruker D8 Advanced Diffractometer with Cu K α radiation). The structure of the catalysts was examined by SEM (Hitachi S4800) and TEM (Tecnai 30, 300 kV). Further, the chemical states of the elements in catalysts were studied by XPS (Kratos Axis Ultra DLD), and the binding energy of the C 1s peak at 284.8 eV was taken as an internal reference. Raman spectrum of powder samples were recorded on Raman microscope (Renishaw, inVia+Reflex) with a laser excitation wavelength of 514.5 nm.



Figure S1: SEM image of the hydrothermal product of Mo₂C/RGO hybrid.



Figure S2: TEM image of the graphene oxide.



Intensity / a.u.

2θ/°

Figure S3: XRD pattern of graphene oxide.



nsity / a.u.

Figure S4: XPS C 1s spectrum (without background, black) and the fitting peaks (cyan) of Mo₂C/RGO. C–O: light magenta, C=O: orange, carbidic carbon: red, adventitious carbon: green.

Reference:

1. W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339-1339.