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Electronic Supplementary Information

Synthesis of nanostructured clean surface molybdenum carbides on graphene sheets as efficient and stable hydrogen evolution reaction catalysts

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Experimental section

Chemicals and Reagents

Concentrated sulfuric acid (H_2SO_4, 98 wt%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide solution (30 wt%), ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), graphite powders (325 mesh, XFNANO Material Technologic Co. Ltd., Nanjing, China), platinum on an XC-72 support (Pt/C, 47.6 wt%) was purchased from TKK, and they were all used as received without further treatment.

Synthesis of Graphite Oxide (GO)

GO powders were synthesized using a modified Hummers method. In a typical process, 2.0 g natural graphite powders were gradually added to concentrated H_2SO_4 (46 mL, 98 wt%) under stirring in an ice bath and the resulting mixture was further stirred for 15 min. Under vigorous agitation, 10.0 g $KMnO_4$ and 5.0 g $NaNO_3$ were added slowly to keep temperature of the suspension lower than 20 ^{o}C. The

temperature is then raised to 40 ^{o}C and retain for 35 minutes. Afterwards, 50 ml of deionized water was added to the mixture slowly to keep the temperature of the suspension at 95 ^{o}C. After 30 min, 200 mL deionized water and 10 ml of 30% H_2O_2 were added into the suspension. At the end of the reaction, the color of the solution changed from dark brown to yellow. The mixture was filtered and washed with 1 mol L^{-1} HCl aqueous solution (250 mL) and deionized water.

Growth of Molybdenum Carbides on Graphene Sheets

The molybdenum carbides/graphene were prepared using an in situ synthesis method. Typical procedure for preparing molybdenum carbides on graphene sheets (MoC-G and Mo_2C-G) is as follows: 0.8 g GO was first dissolved in 200 mL deionized water in a sonicated beaker for 2 h under agitation; 0.36g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 50 mL deionized water, then poured into the GO suspension for 30 min under sonication. The mixture was dried at 90 ^{o}C until turning into hydrogel-like, followed by freeze drying. (The graphite oxide (GO) exchanges with $Mo_7O_{24}^{6-}$ ions though carboxyl and hydroxyl groups at ionic level. The local exchange with those active groups on GO makes the final Molybdenum Carbides nanoparticles small and uniform.) The dried hydrogel-like mixture was further annealed in a tube furnace under Argon for 2 h to form molybdenum carbides. The ramping rate in tube furnace was controlled at 5 °C min^{-1} and final products were cooled down to 30 °C in the tube furnace at a rate of 10 °C min^{-1}. For MoC-G and Mo_2C-G syntheses, the annealing temperatures were kept at 750 °C and 900 °C, respectively.

Characterizations

X-ray diffraction (XRD) data was collected on a D/Max-III (Rigaku Co., Japan) using Cu Kα radiation operating at 30 kV and 30 mA. The 2θ angular regions between 10° and 80° were measured at a scan rate of 6° min^{-1}. Raman spectroscopy was performed on a Raman spectrometer (Renishaw Corp., UK) using a 514.5 nm wavelength He/Ne

laser. Transmission electron microscopy was performed on a field emission transmission electron microscopy (FETEM, FEI Tecnai G2 F30) operating at 300 kV.

Electrochemical Measurements.

All of the electrochemical measurements were conducted in a typical three-electrode cell with an electrolyte solution of 0.5 mol L^{-1} H_2SO_4 solution in a standard three-electrode electrochemical cell at 25 ^oC, a piece of graphite (10×1 cm^{-2}) as the counter electrode, a reversible hydrogen electrode (RHE) as the reference electrode, and a electrode with a glassy carbon disk (A=0.2826 cm^2) as the working electrode. The electrocatalytic HER activity of molybdenum carbides was investigated by depositing samples with a mass loading of 0.8 mg cm^{-2}. 5.0 mg catalysts was dispersed in 0.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt %, DuPont, USA), followed by ultrasonication for an hour to form a well-dispersed ink and then transferred onto the surface of the glass carbon electrode. After drying under infrared lamp for 5 minutes, a catalyst thin film was obtained.

The HER experiments were conducted on an Autolab PGSTAT 302 (ECO Chemie, Netherlands) electrochemical workstation at 25 ^oC in thermostatic water bath. Linear sweep voltammetry (LSV) tests were performed at a scan rate of 5 mV s^{-1}. Before the HER activity testing, the electrodes were pre-treated by cycling the potential between -0.4 and +0.4 V at a sweep rate of 50 mV s^{-1} for 30 cycles to activate the catalysts, remove surface contamination and stabilize the current. The longer-term (20 h) stability was also tested under controlled potentials.

For comparison, 46.7 wt% platinum on VC-72 catalyst (Pt/C from TKK, Japan) was measured under similar conditions and the loading is 12.5 μg_{pt} cm^{-2}.

Additional experimental data

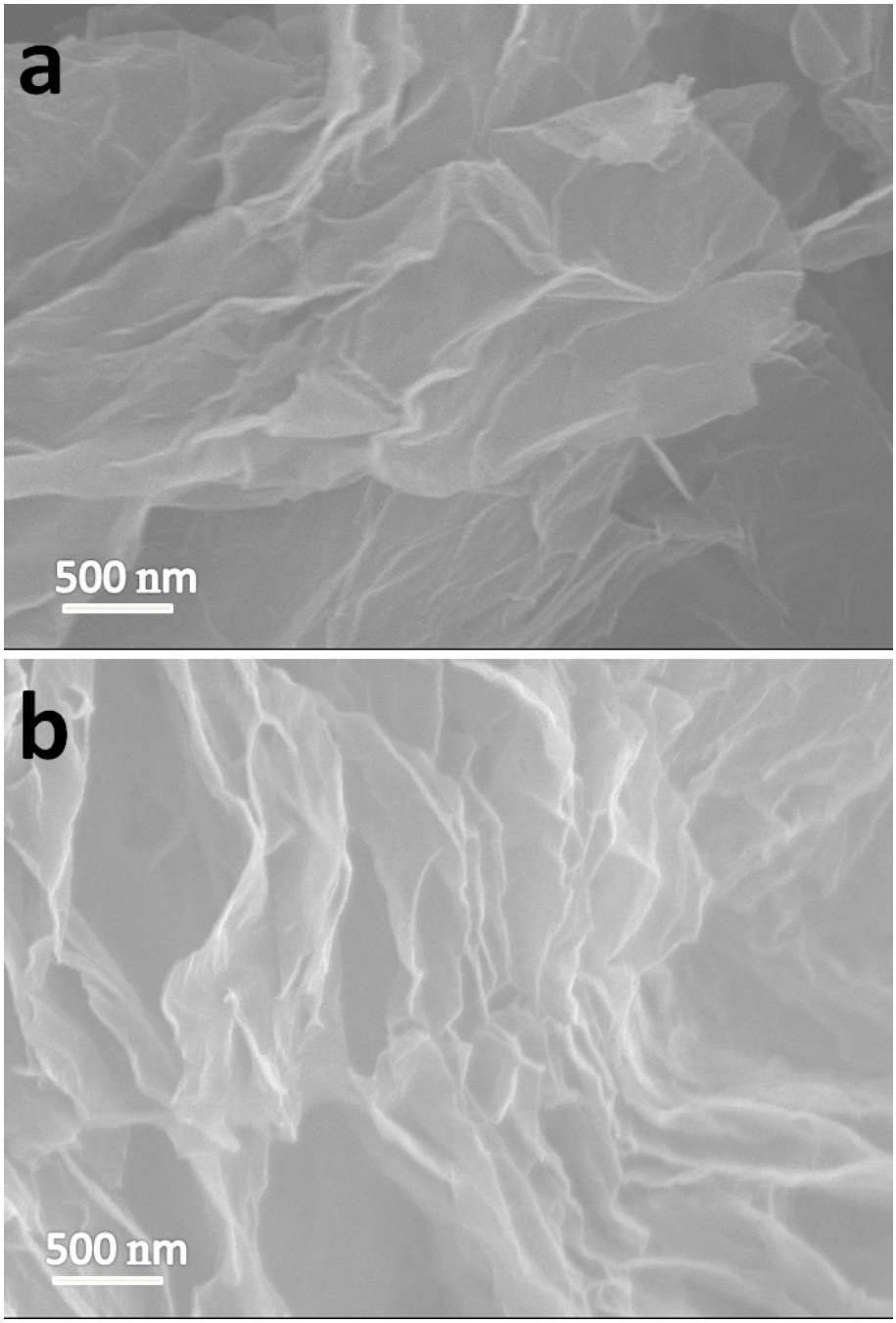


Fig. S1 SEM images of (a) MoC-G and (b) Mo_2C-G.

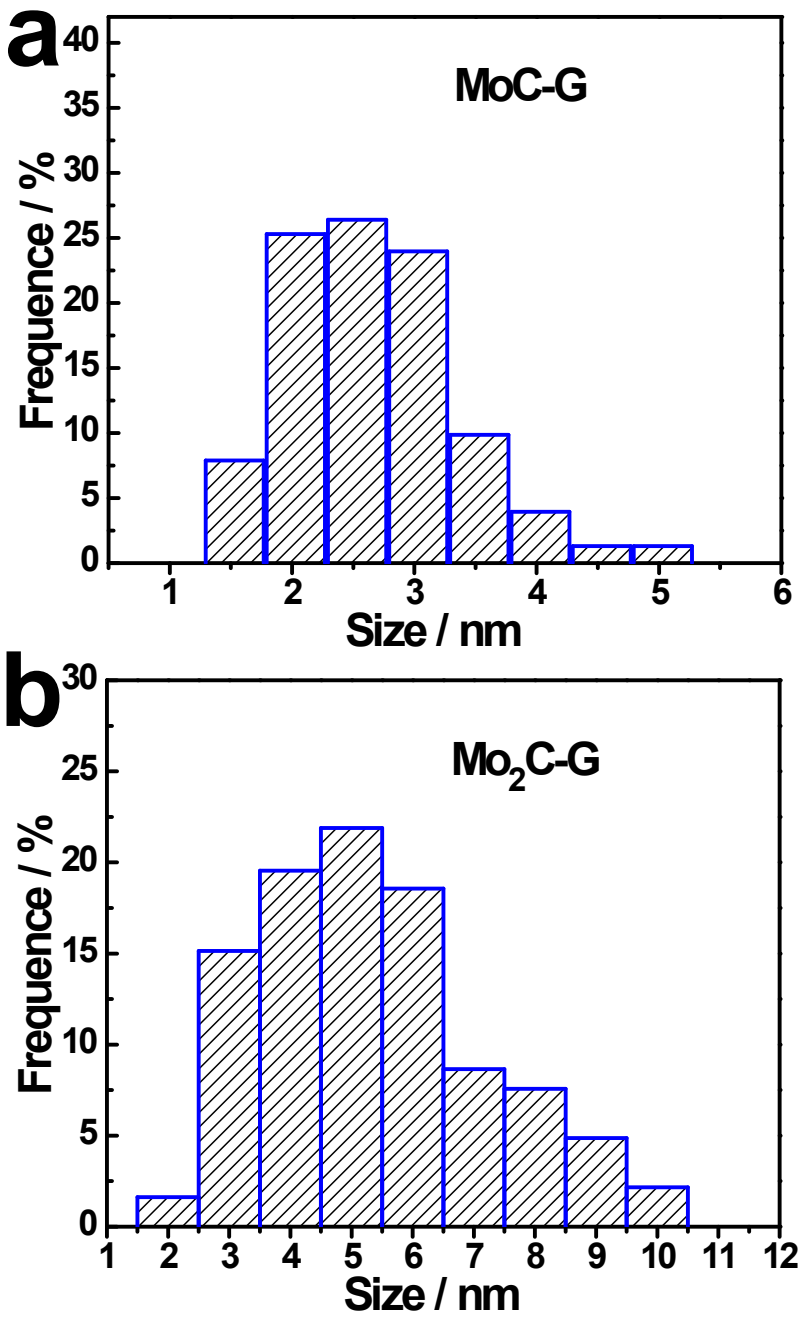


Fig. S2 The size-distribution histograms of the (a) MoC-G and (b) Mo_2C-G.

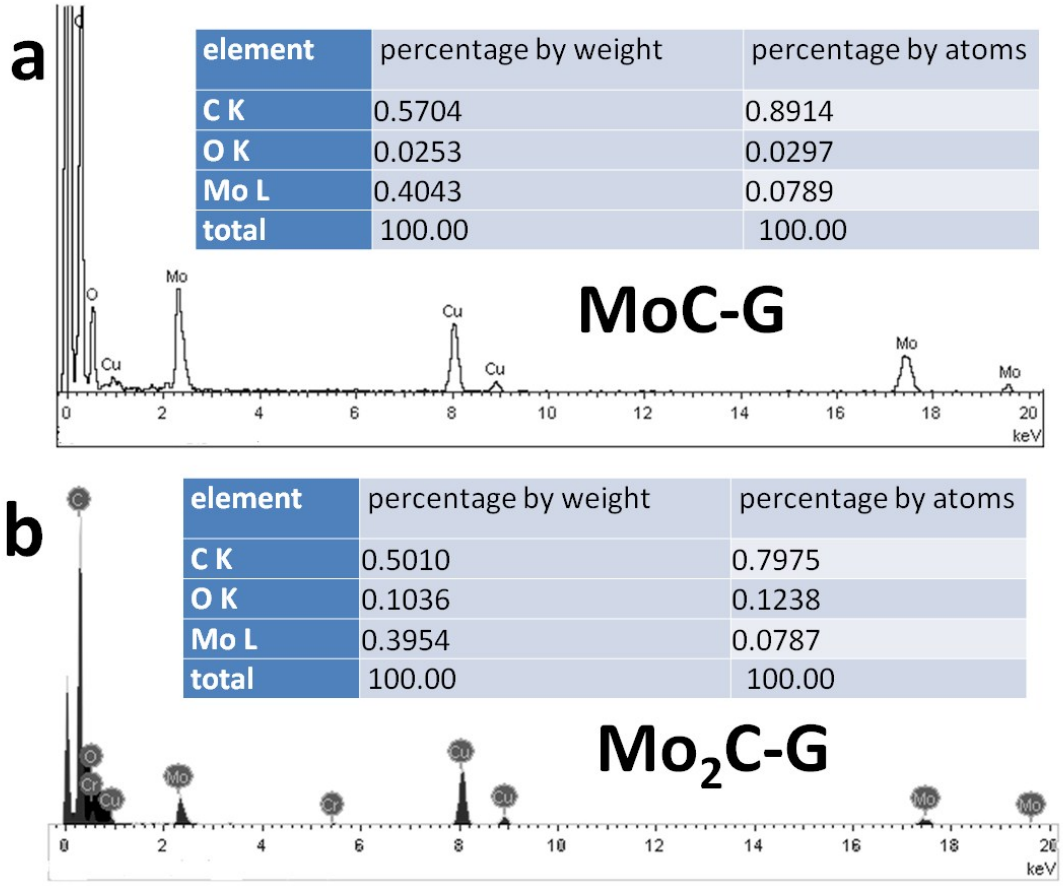


Fig. S3 Energy dispersive spectrometry (EDS) of the (a) MoC-G and (b) Mo_2C-G.

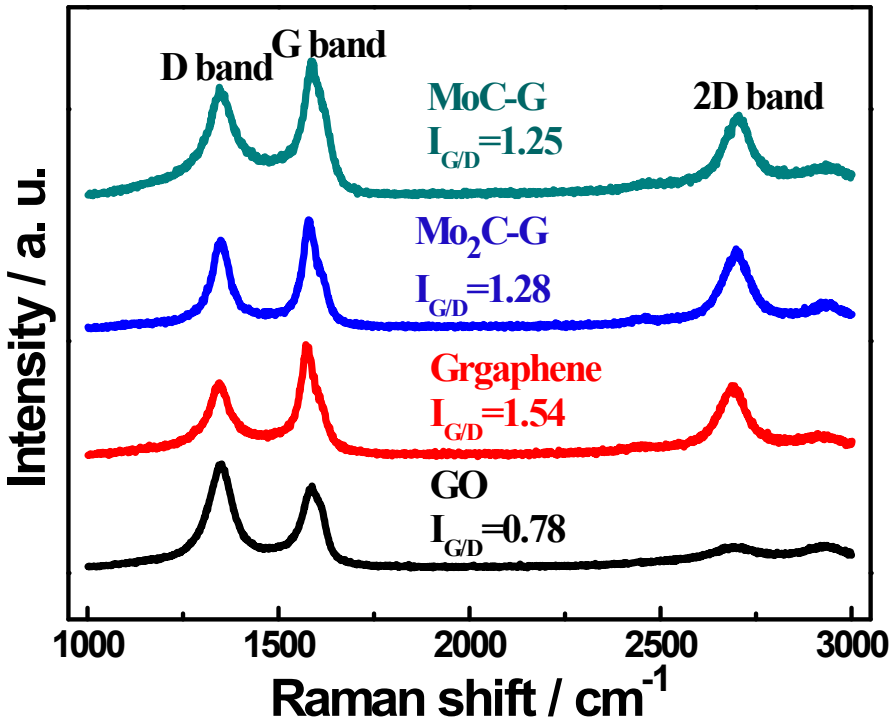
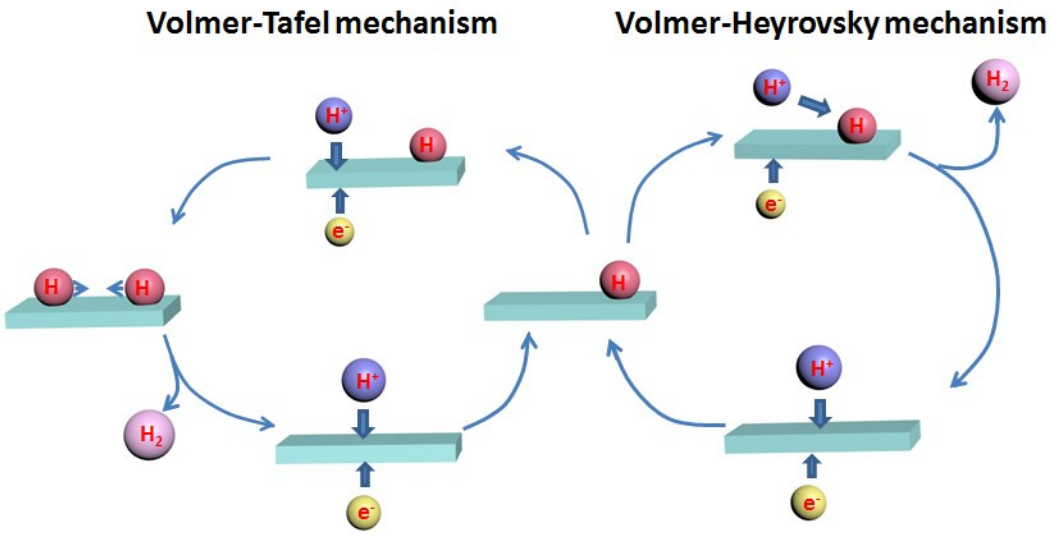


Fig. S4. Comparison of the Raman Spectra of the GO, graphene, MoC-G and Mo_2C-G.

As shown in Scheme S1, in acidic solution, the evolution of the hydrogen though a multi-step process on the surface of an electrode. The first step of HER is the Volmer or discharge reaction, in this step, an electron from external circuit transfer to the surface of the catalyst, and couple with a proton to yield an absorbed hydrogen atom: $H_3O^+ + e^- \rightarrow H_{abs} + H_2O$. The following step is the formation of H_2, which may occur via two different reaction pathways. One is possible pathway is Tafel or combination reaction, in which two absorbed hydrogen atoms combine on the surface of the electrode to evolve H_2: $H_{abs} + H_{abs} \rightarrow H_2$. The other possible pathway is Heyrovsky or ion + atom reaction, in which a second electron from external circuit transfer to the surface of the catalyst and an absorbed hydrogen atom couple with a proton to yield H_2: $H_3O^+ + e^- + H_{abs} \rightarrow H_2 + H_2O$.



Scheme S1. The illustration of the mechanism of hydrogen evolution reaction on the surface of an electrode in acidic solutions.[S1]

Table S1. Comparison of the crystal planes of MoC and Mo_2C.

catalyst	*Structure*	*Stacking sequence*	*Space group*	*crystal planes*
Mo_2C/CNT-GR[S2]	Hexagonal	ABAB	P63/mmc(194)	(0002): 0.236 nm; $(10\bar{1}1)$: 0.226 nm
MoC-G	Cubic	ABCABC	Fm-3m(225)	(111): 0.247 nm; (220): 0.150 nm
Mo_2C-G	Hexagonal	ABAB	P63/mmc(194)	$(10\bar{1}0)$: 0.260 nm; $(10\bar{1}1)$: 0.227 nm

Table S2. HER performance comparison of the various catalysts in acid media.

catalyst	E_0 / *mV*	η_{10} / *mV*	*Loading / mg cm*$^{-2}$	*Tafel slope / mV dec*$^{-1}$	j_0 / *mA cm*$^{-2}$
Pt/C	~0	35		30	0.27
Bulk Mo_2C	120	304	0.8	116	3.79×10^{-3}
MoC-G	30	221	0.8	88	2.55×10^{-2}
Mo_2C-G	~0	150	0.8	57	2.58×10^{-2}

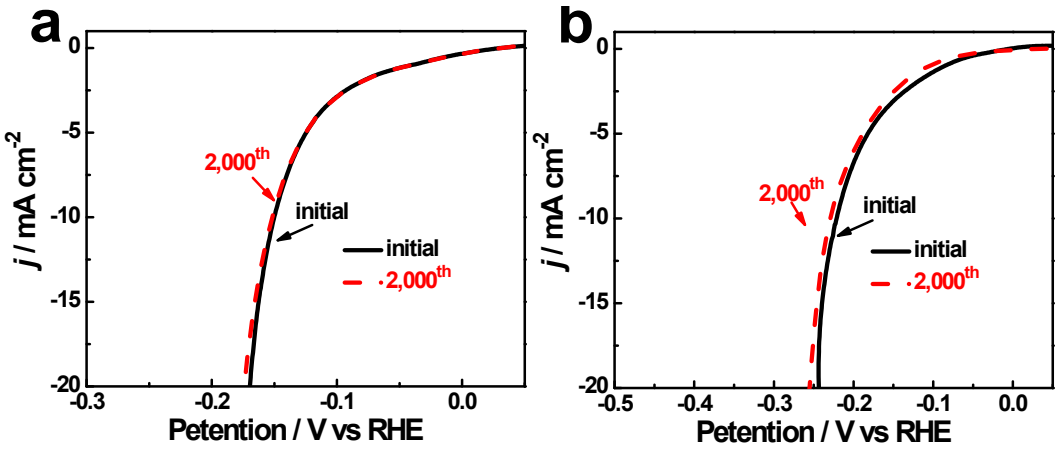


Fig. S5. HER perfoemances of (a) MoC-G and (b) Mo_2C-G before and after a continuous potential swept for 2,000 cycles.

References

S1 C. G. Morales-Guio, L.-A. Stern and X. Hu, *Chem. Soc. Rev.*, 2014, 43, 6555.

S2 D. H. Youn, S. Han, J. Y. Kim, J. Y. Kim, H. Park, S. H. Choi and J. S. Lee, *ACS Nano*, 2014, 8, 5164.