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Ultrafast Synthesis of Molybdenum Carbide Nanoparticles for Efficient

Hydrogen Generation

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Electronic Supplementary Information

Section 1. Growth process of MoC/C

The growth of MoC/C was investigated by spraying the precursor solution through a quartz tube held at different temperatures, including 250, 550, 750, 850, and 950 °C. The corresponding samples were denoted as USP-xxx, where xxx was the temperature of the quartz tube. The composition and structure of these samples were analogous to intermediates generated at the different temperature zones of the quartz tube during the growth of the MoC/C.

When MoCl₅ was added to ethanol, the ethanolysis of MoCl₅ resulted in MoO_{2.5-(2x+1)/2}(OC₂H₅)_xCl_{x+1} (x=1, 2).^{1, 2} The USP at 250 °C produced yellow particles containing molybdenum, oxygen, carbon, and chlorine, as indicated by the survey XPS spectrum (Figure S1a). Peaks corresponding to Mo²⁺ (binding energy BE ~285.5 eV) and Mo³⁺ (BE ~285.8 eV) are found in the spectra of products synthesized at temperatures greater than 550 °C (Figure S1b), indicating the formation of molybdenum carbide. Peaks corresponding to Mo⁴⁺ (BE ~ 229.8 eV) and Mo⁵⁺ (BE ~ 229.8 eV) decrease with synthesis temperature. The formation of molybdenum carbide at temperatures higher than 550 °C is also suggested by the C1s window of the XPS spectra (Figure S1c), in which a peak with BE of 283.7 eV emerges at 550 °C. The atomic ratio of Mo to C was estimated from the survey spectra. Figure S1d shows that the ratio of Mo to C increases with increasing synthesis temperature, and then decreases at 950 °C.

The XRD pattern shows that USP-550 is composed of carbon, MoC, and MoO₂ (Figure S2). The proportion of MoO_2 decreased dramatically on temperature increase to afford USP-750. Further increase in reaction temperature to afford USP-850 resulted in the disappearance of peaks corresponding to MoO_2 and appearance of peaks corresponding to MoC/C, while temperature increase to 950 °C gave Mo_2C .

The carbon source for the carbothermal reduction of molybdenum in MoC/C is primarily the precursor (i.e., $MoO_{2.5-(2x+1)/2}(OC_2H_5)_xCl_{x+1}$), and to a lesser extent ethanol. In a control experiment the USP of an ethanol solution of phosphomolybdic acid (PMA) at 850 °C was carried out, the sample being denoted as PMA-850. Though the XRD pattern (Figure S3a) shows no peaks from MoC, XPS spectra (panel b to d in Figure S3) suggest that trace amounts of MoC are presented, as indicated by the Mo peak at 228.9 eV and the C peak at 284.3 eV. It is therefore suggested that only a limited amount of MoO₂ is carbonized into MoC by ethanol. The formation of molybdenum carbide under our conditions was

accompanied by the release of carbon from the precursor particles, as indicated by an increase in the Mo/C atomic ratio with growth temperature over the range from 250 to 850 °C (Figure S1d).

When the synthesis temperature was increased to 950 °C, the thickness of the carbon coating on the surface of the nanoparticles increased (panels c and d in Figure S4), suggesting that the pyrolysis of ethanol results in the deposition of a graphitic carbon layer on the surface of molybdenum carbide. The pyrolysis of ethanol into graphitic carbon was confirmed by a control experiment, in which an ultrathin graphitic carbon layer was found on the surface of the spheres in PMA-850 (panels e and f in Figure S3).

Based on the foregoing, the growth process of MoC/C can be summarized as follows. The volatilization of ethanol resulted in precursor particles containing molybdenum, carbon, oxygen, and chlorine. At the higher temperature heating zone, the precursor decomposed, and spheres composed of carbon, molybdenum oxide, and molybdenum carbide were formed. The carbon in the particles and a small amount of ethanol induced the carbothermal reduction of molybdenum oxide to give molybdenum carbide; carbon was also released from the particles during the carbothermal reduction. The pyrolysis of ethanol contributed to the deposition of graphitic carbon on the surface of the MoC nanoparticles, resulting in a MoC/C composite with an ultrathin carbon coating.

Section 2. Growth of MoC@C

With SiO₂ nanoparticles added to the growth solution, the content of C in the product (MoC@C) is larger than that in MoC/C. In a control experiment, the USP of an ethanol solution of SiO₂ nanoparticles and PMA at 850 °C resulted in MoO₂ nanoparticles encapsulated by a thick carbon layer (panels h to i in Figure S3), whereas the USP of an ethanol solution of PMA produced an ultrathin carbon layer on the surface of the MoO₂ spheres (panels e and f in Figure S3). We therefore suggest that the pyrolysis of ethanol into carbon can be enhanced by SiO₂ nanoparticles, and the deposition of the thick carbon coating on the surface of the MoC nanoparticles is associated with the pyrolysis of ethanol catalyzed by the SiO₂ nanoparticles.

Section 3. Estimation of the MoC weigh content in the composite

At 750 °C, all MoC nanoparticles were oxidized to MoO₃, and all carbon was removed. The weight percent of MoC in the samples was computed according to the following equation:

$$\frac{1 * wt_{MoC}}{M_{MoC}} = \frac{w_{remain}}{M_{MoO3}}$$

where wt_{MoC} is the weight percent of MoC, M_{MoC} is the formula weight of MoC, W_{remain} is the weight of MoO₃ suggested by the TGA curve (Figure S5), and M_{MoO3} is the formula weight of MoO₃.

Section 4. Estimation of the electrochemically active surface area

To measure the electrochemical capacitance, the potential was swept in the range 0.10 to 0.20 V vs. RHE at different scan rates, including 5, 10, 15, 20, 25, 30, and 35 mV s^{-1,3,4} The CV curves of the MoC/C are plotted in Figure S9a, while those of the MoC@C are presented in Figure S9b. The capacitance current density ($\Delta J = J_a - J_c$ at 0.15 V vs. RHE) was plotted against the scan rate (Figure 5b) and the specific capacitance was obtained by a data fitting of the plot, being 16.5 mF cm⁻² for the MoC/C and 26.2 mF cm⁻² for the MoC@C. An electrochemically-active surface area (EASA) was estimated from the specific capacitance using the specific capacitance value for a flat standard with 1 cm² of real surface area. In general, the specific capacitance for a flat surface area of 40 µF cm⁻² was adopted.

Calculated electrochemically-active surface areas.

AMoC/C EASA = $(16.5 \text{ mF cm}^{-2})/(40 \text{ }\mu\text{F cm}^{-2} \text{ per cm} 2 \text{ ECSA}) = 413 \text{ cm} 2 \text{ ECSA}$ AMoC@C EASA = $(26.2 \text{ mF cm}^{-2})/(40 \text{ }\mu\text{F cm}^{-2} \text{ per cm} 2 \text{ ECSA}) = 655 \text{ cm} 2 \text{ ECSA}$

Section 5. DFT Calculations

The DFT calculations were carried out using CASTEP (Cambridge Serial Total Energy Package)⁵ with a plane-wave basis set and ultrasoft pseudo-potentials.⁶ The exchange correlation contribution to the total electronic energy was treated in a generalized gradient corrected (GGA) approximation (Perdew-Burke-Ernzerhoff functional).⁷ A plane-wave energy cutoff of 270 eV was used for the rapid comparison

of different adsorption configurations while 360 eV was used for the adsorption energy calculations. The Monkhorst-Pack ($3 \times 3 \times 1$) k-point mesh was utilized for the first Brillouin zone integrations. The structural parameters were determined using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique. The thresholds for the converged structures were as follows: energy change less than 1×10^{-5} eV atom⁻¹, the maximum residual force less than 0.02 eV Å⁻¹, the maximum displacement of atoms less than 0.001 Å, and the maximum stress less than 0.05 GPa. Van der waals (vdW) interaction is included using a dispersion correction term with DFT-D3 method.⁸

The unit cell (a = b = 12.3 Å, c = 38.6 Å) was composed of four (111) MoC layers with Motermination, graphene (0, 1, 2, or 3 layers), and a vacuum region. A 4 x 4 (111) MoC supercell was employed to fit a 5 x 5 graphene supercell, the model being denoted by MoC/XC where X is the number of graphene layers covering the (111) MoC surface. The thickness of the vacuum slab was 21 Å in the MoC/3C. In the model that involved (111) MoC, the bottom two layers of MoC (four atomic layers) were fixed, and the other atoms were allowed to relax.

The differential adsorption energy of H adsorption was chosen to describe the stability of hydrogen, the equation being given below:

 $\Delta E_{H} = E(nH^{*}) - E((n-1)H^{*}) - 1/2E(H_{2})_{\text{where }} E(nH^{*}) \text{ is the total energy of the model with n}$ hydrogen atoms adsorbed on the surface, $E((n-1)H^{*})$ is the total energy of the model with (n-1) hydrogen atoms adsorbed on the surface, and $E(H_{2})$ is the total energy of a hydrogen molecule in the gas phase. n is 1 in our calculations.

The Gibbs free energy for hydrogen adsorption was calculated as below:

 $\Delta G_{H}^{o} = \Delta E_{H} + \Delta E_{ZPE} - T\Delta S_{H}$ where ΔE_{ZPE} is the difference in zero-point energy between the adsorbed state and the gas phase and ΔS_{H} is the entropy difference between the adsorbed state and the gas phase. The overall corrections are taken as:⁹

$$\Delta G_H^o = \Delta E_H + 0.378 \ eV$$



Figure S1. (a) Survey, (b) Mo 3d window, and (c) C1s window XPS spectra of products synthesized at different temperatures. (d) Atomic ratio of Mo to C in the products synthesized at different temperatures.



Figure S2. XRD patterns of products synthesized at different temperatures. ●: MoO₂, JCPDS No. 78-1072; ▲: MoC, JCPDS No. 65-280; ■: Mo₂C, JCPDS: 1-1188; +: C.



Figure S3. (a) XRD pattern of PMA-850, and (b) Mo window, (c) O window, and (d) C window XPS spectra of PMA-850. (e) TEM image and (f) HRTEM image of PMA-850. (g) XRD, (h) TEM, and (i) HRTEM images of PMA-SiO₂-850. PMA-850 was synthesized by the USP of an ethanol solution of PMA at 850 °C. PMA-SiO₂-850 was synthesized under similar conditions to those of PMA-850, except that SiO₂ nanoparticles were added to the ethanol solution and removed after the USP. Particles in (f) and (i) can be indexed to MoO₂, and the arrows in (f) and (i) indicate the carbon layer coatings on the surface of the particles.



Figure S4. (a,c) TEM images and (b,d) HRTEM images of (a,b) USP-750 and (c,d) USP-950. The lattice pattern in (b) can be indexed to the [3 -1 4] zone axis of cubic phase MoC (JCPDS 65-280). The Mo₂C (JCPDS 1-1188) particle in (d) is aligned along the [2 1 -2] zone axis. One carbon layer was found on the surface of the MoC particle in (b), whereas three carbon layers were found on the surface of the Mo₂C particle.



Figure S5. TGA curves of MoC/C and MoC@C measured in an oxygen atmosphere.



Figure S6. Polarization curves of samples synthesized at different temperatures: (a) USP without the SiO_2 nanoparticles template and (b) USP with the SiO_2 nanoparticles as template. The samples are denoted as USP-xxx, where xxx is the temperature of the quartz tube and SiO_2 indicates that SiO_2 nanoparticles were added as template. All potentials were corrected for the iR drop.



Figure S7. (a) Polarization curves and (b) Tafel plots of MoC/C, MoC@C, and Pt/C. Potentials in (a) and (b) were corrected for the iR drop. (c) Amperometric (i–t) curve of MoC/C. Inset of (c) shows polarization curves measured before and after i-t measurement. (d) A comparison of theoretical and detected volume of hydrogen generated in a potentiostatic electrolysis. All measurements were carried out in 1 M KOH.

Table S1. Performance comparison.

Reference	Catalyst	Mass density (mg cm ⁻²)	$\begin{array}{l} \eta_{20}{}^{[a]} \\ (mV) \end{array}$	Tafel slope (mV/dec)	$J_0^{[b]}$ (mA cm ⁻²)	J 100 mass activity ^[e] (mA cm ⁻² g ⁻¹)	Counter electrode	Electrolyte
Nature Commun. 7 (2016) 11204-11211	Mo ₂ C@NPC /NPRGO	0.14	55	33.6	1.09	428.57	Pt wire	0.5 M H ₂ SO ₄
J. Am. Chem. Soc. 137 (2015) 15753– 15759	Mo _x C-Ni@NCV	1.1	110	45	0.95×10 ⁻³	15.91	Platinum sheet	0.5 M H ₂ SO ₄
Angew. Chem. Int. Ed. 54 (2015) 14723- 14727	Mo ₂ C NPs@N-doped graphene	0.25	105	41	0.178	68	Pt plate	0.5 M H ₂ SO ₄
J. Mater. Chem. A 3	Mo ₂ C/CNT	8.2	$250 (\eta_{10}^{[c]})$	251	1.43	0.24	Pt	0.1 M HClO ₄
(2015) 15505–15512 Energy Environ. Sci. 7 (2014) 387-392	Mo ₂ C/CXG Nanoporous Mo ₂ C NWs	0.21	170 (η ₁₀) 150	53	1.69	0.48	Platinum	0.5 M H ₂ SO ₄
Chem. Commun. 50, (2014) 13135–13137	Mo ₂ C–RGO	0.285	150	57.3		14.04	Pt mesh	0.5 M H ₂ SO ₄
ACS Nano 8 (2014) 5164–5173	Mo ₂ C NPs on CNT- graphene	0.65	145	58	6.2×10 ⁻²	6.15	Pt wire	0.5 M H ₂ SO ₄
Angew. Chem. Int. Ed. 53 (2014) 5131- 5136	α-WC/CB β-Mo _{0.06} W _{0.94} C/CB	0.724	260 (η ₁₀) 220 (η ₁₀)			0.276 0.276	Pt wire	0.5 M H ₂ SO ₄
J. Am. Chem. Soc. 134 (2012) 3025–3033	W ₂ C film WC film		>300	69 91	6.7 5.6		Pt gauze	0.5 M H ₂ SO ₄
Angew. Chem. Int. Ed. 51 (2012) 12703- 12706	Commercial Mo ₂ C	1.4	225	56	1.3×10 ⁻³	0.14	Platinum wire	0.5 M H ₂ SO ₄
Nature Commun. 7 (2016) 13216-13222	W ₂ C/MWNT	0.556	145	45		7.19	Graphite rod	0.5 M H ₂ SO ₄
Chem. Sci. 7 (2016) 3399–3405	MoC- Mo ₂ C	0.14	152	43	1.1×10-2	28.57	Graphite	0.5 M H ₂ SO ₄
J. Mater. Chem. A 4 (2016) 6006-6013	nanoMoC@GS	0.76	150	43	15.1×10-3	2.63	Graphite rod	0.5 M H ₂ SO ₄
Small 12 (2016) 2859- 2865	3D hierarchical porous Mo ₂ C framework	0.28	125	60	2.8×10 ⁻¹	42.86	Graphite rod	0.5 M H ₂ SO ₄
Angew. Chem. Int. Ed. (2015) 54, 10752- 10757	Mo ₂ C@NC	0.28	124 (ŋ ₁₀)	60	9.6×10 ⁻²	17.86	Carbon rod	0.5 M H ₂ SO ₄
Nature Commun. 6 (2015) 6512	Mesoporous Mo ₂ C nano-octahedrons	0.8	160	53	2.3×10 ⁻²	2.5	Graphite rod	0.5 M H ₂ SO ₄
Adv. Funct. Mater. 25 (2015) 1520-1526	Mo ₂ C-WC composite nanowires	1.28	150	52	2.9×10 ⁻²	0.78	Carbon rod	0.5 M H ₂ SO ₄
J. Mater. Chem. A 3 (2015) 8361-8368	α−Mo ₂ C	0.102	220	56		0.98	Graphite rod	0.5 M H ₂ SO ₄
Chem. Commun. 51 (2015) 8323_8325	MoC/G MocC/G	0.8	245 170	88 57	2.55×10 ⁻² 2.58×10 ⁻²	2.5 3.375	Graphite	0.5 M H ₂ SO ₄
Energy Environ. Sci. 6 (2013) 943-951	Mo ₂ C/CNT	2	140 $(\eta_8^{[d]})$	55.2	1.4×10 ⁻²	1.5		0.1 M HClO4
Energy Environ. Sci. 6 (2013) 1818-1826	Mo ₁ Soy	0.47	177 (η ₁₀)	66.4	1.3×10 ⁻²	1.49		0.1 M HClO ₄
ACS Nano 10 (2016) 11337-11343	Mo ₂ C on C flower	0.28	144(η ₁₀)	55		7.14		0.5 M H ₂ SO ₄
This work	MoC/C MoC@C	0.57	144 157	63.6 193.3	0.104 0.390	7.02 7.89	Graphite rod	0.5 M H ₂ SO ₄

[a] η_{20} : Overpotential required to drive a current density of 20 mA cm⁻². [b] J_0 : Exchange current density. [c] η_{10} : Overpotential required to drive a current density of 10 mA cm⁻². [d] η_8 : Overpotential required to drive a current density of 8 mA cm⁻². [e] J 100 mass activity: Current density according to the loading mass of catalysts at overpotential of 100 mV. J 100 mass activity=j/m, where j is the current density and m is the loading mass of catalysts on the electrode.



Figure S8. The CV curves of the initial and 1000th scans in CV sweeps measured in (a) acidic and (b) basic solutions.



Figure S9. (a) TEM and (b) HRTEM images of the MoC/C scrapped from GCE after potentiostatic electrolysis experiment.



Figure S10. Equivalent circuit used to fit the EIS data. R_0 is series resistance, CPE_1 and R_1 are the constant phase element and the resistance describing electron transport at the substrate/catalyst interface, respectively, CPE_{d1} is the constant phase element of the catalyst/electrolyte interface, and R_{ct} is the charge-transfer resistance at the catalyst/electrolyte interface.

Sample	R _s	Q ₁	n_1	R_1	Q _{dl}	n _{dl}	R _{ct}
	(Ω)	(F cm ⁻² S ⁿ⁻¹)		(Ω)	$(F \text{ cm}^{-2} \text{ S}^{n-1})$		(Ω)
MoC/C	4.428	4.058e-5	0.7369	14.44	1.357e-3	0.5267	62.48
MoC@C	8.237	7.615e-5	0.6855	8.614	4.817e-3	0.625	101.9

Table S2. Fitting results from the EIS spectra of MoC/C and MoC@C in acidic solution



Figure S11. CV curves in the region 0.1 - 0.2 V vs. RHE for (a) MoC/C and (b) MoC@C.



Figure S12. The theoretical models of the studied systems. The gray, cyan, and yellow balls represent C, Mo, and H atoms, respectively. (a) Gr, (b) MoC, (c) MoC/1C, (d) MoC/2C, and (e) MoC/3C. Models of the (111) MoC surface coated with a graphene layer(s) are denoted as MoC/XC, where X is the number of graphene layers.



Figure S13. (a) XRD patterns and (b) EDS spectra of Fe-Mo₂C@C. (c) TEM and (d) HRTEM images of Fe-Mo₂C@C.



Figure S14. Polarization curves of Fe-Mo₂C@C.

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