

Ultrafine Molybdenum Carbide Nanoparticles Compositd with Carbon as a Highly Active Hydrogen-Evolution Electrocatalyst

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Abstract: The replacement of platinum with non-precious-metal electrocatalysts with high efficiency and superior stability for the hydrogen-evolution reaction (HER) remains a great challenge. Herein, we report the one-step synthesis of uniform, ultrafine molybdenum carbide (Mo_2C) nanoparticles (NPs) within a carbon matrix from inexpensive starting materials (dicyanamide and ammonium molybdate). The optimized catalyst consisting of Mo_2C NPs with sizes lower than 3 nm encapsulated by ultrathin graphene shells (ca. 1–3 layers) showed superior HER activity in acidic media, with a very low onset potential of -6 mV, a small Tafel slope of 41 mV dec^{-1} , and a large exchange current density of 0.179 mA cm^{-2} , as well as good stability during operation for 12 h. These excellent properties are similar to those of state-of-the-art 20 % Pt/C and make the catalyst one of the most active acid-stable electrocatalysts ever reported for HER.

Water splitting by electrolysis to produce hydrogen has attracted much attention, because hydrogen, as a clean, sustainable energy source, is one of the most promising alternatives to fossil fuels.^[1] Platinum is the most active and catalytically stable catalyst for the hydrogen-evolution reaction (HER, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$),^[2] but its scarcity and high cost make it impractical for global-scale applications. Much effort has been made to develop cost-effective, transition-metal-based, non-platinum electrocatalysts,^[3] such as tungsten-,^[4] molybdenum-,^[5] cobalt-,^[6] iron-,^[7] and nickel-based materials;^[8] however, most of these materials have had a large overpotential (η) of 100–200 mV.

Molybdenum carbide (Mo_2C) materials are considered to be promising HER electrocatalysts owing to their low cost, high chemical stability, and high similarity to platinum-based catalysts.^[3b,5d,9] The activity of Mo_2C can be improved by introducing other elements, such as nitrogen, which may tune

the electronic state of Mo active sites in a desirable way.^[10] The construction of various nanostructures (e.g. nanooctahedrons, nanowires (NWs), nanoparticles (NPs)) also can improve the HER activity of MoC_2 owing to the enhanced exposure of surface active sites.^[5d,6c,9b,c,10] However, it is still a large challenge to controllably synthesize Mo_2C NPs with ultrasmall sizes because of the inevitable aggregation and/or excessive growth of Mo_2C NPs at high reaction temperatures, and the ready oxidation of the surface of Mo_2C NPs to MoO_x species when exposed to air. The former effect leads to a low density of active sites, whereas the latter results in poor electrical transport, both of which can limit the HER performance of Mo_2C NPs.^[9a,10]

Herein, we describe a one-step protocol for the synthesis of ultrafine Mo_2C NPs uniformly embedded within a carbon matrix (MCNs@carbon). The resulting material acted as a highly active and stable non-platinum HER electrocatalyst with an extremely low onset potential (U_{onset}) of -6 mV, a small overpotential of 78 mV to reach 10 mA cm^{-2} (η_{10}), a small Tafel slope of 41 mV dec^{-1} , and a large exchange current density (j_0) of 0.179 mA cm^{-2} , as well as good stability over 12 h during operation in $0.5 \text{ M H}_2\text{SO}_4$. To the best of our knowledge, the present material MCNs@carbon is one of most active transition-metal-based electrocatalysts for HER.^[3a,11]

To synthesize MCNs@carbon, we simply heated a mixture of dicyanamide (DCA) and ammonium molybdate at 400°C to give graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) containing MoO_x species ($\text{MoO}_x@g\text{-C}_3\text{N}_4$), and annealed the resulting material at 800°C (Figure 1 a; see the Supporting Information for details). The evolution of the color of the sample from white to black indicated the formation of carbon and/or Mo_2C at 800°C (Figure 1 b–d), as further confirmed by XRD patterns (see Figure S1 in the Supporting Information). The very broad peaks indicate that the Mo_2C nanoparticles have

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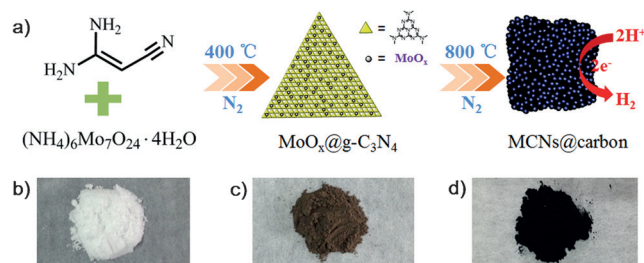


Figure 1. a) Procedure for the synthesis of MCNs@carbon as a non-platinum HER electrocatalyst. b–d) Digital photographs of a mixture of DCA and ammonium molybdate (b), $\text{MoO}_x@g\text{-C}_3\text{N}_4$ (c), and MCNs@carbon (d).

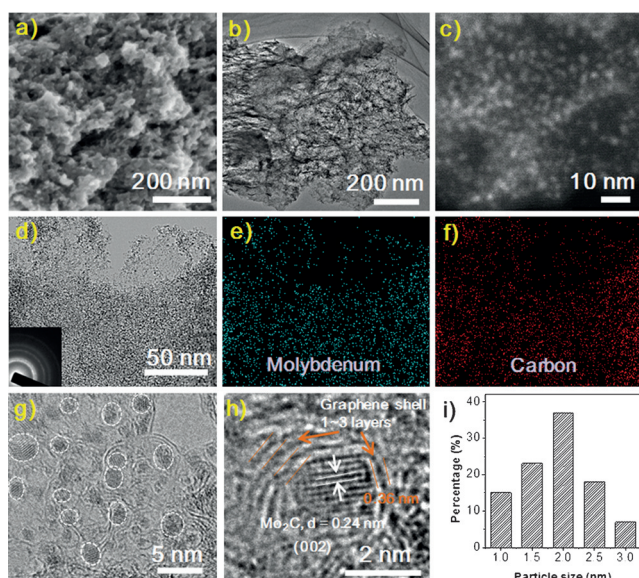


Figure 2. Analysis of Mo₂C NPs in MoDCA-5. a) SEM, b) TEM, c) HAADF STEM images. d–f) Simultaneously acquired TEM image (d; inset: SAED) and XEDS elemental mapping of molybdenum (e) and carbon (f). g, h) HRTEM images. i) Particle-size distribution.

extremely small nanometer diameters and that the carbon exists as ultrathin graphene layers with short-range order.^[5d,12] Notably, no carbon was produced when pure g-C₃N₄ was used instead of MoO_x@g-C₃N₄ (see Figure S2),^[13] thus confirming the key role of Mo in the catalytic growth of carbon from the decomposed intermediates at high temperature.^[14]

For clarification, the as-prepared sample was named MoDCA-*x*, which indicates the mass ratio (*x*) of DCA and the Mo compound in the precursor. The resulting material MoDCA-5 had a loose, porous texture, as shown by SEM and TEM (Figure 2a,b). High-angle annular dark-field (HAADF) scanning transition electron microscopy (STEM) as well as TEM indicated the presence of numerous small nanocrystallites (Figure 2c,d). Selected-area electron diffraction (SAED) confirmed the polycrystalline nature of the material (inset of Figure 2d), and X-ray energy-dispersive spectroscopy (XEDS) elemental mapping indicated the uniform distribution of C and Mo elements, except for small amounts

of N and O (Figure 2e,f; see also Figures S3 and S4 and Table S1 in the Supporting Information). The N doping is beneficial for improving the interaction of active sites with H⁺.^[6a] High-resolution TEM (HRTEM) images indicated that most Mo₂C NPs were encapsulated by graphene shells with short-range order (ca. 1–3 layers; Figure 2g,h). The NPs had a uniform size of generally less than 3 nm (Figure 2i) with a *d* spacing of 0.24 nm, which is ascribed to the (002) plane of Mo₂C. The high dispersion and ultrasmall size of the Mo₂C NPs are ascribed to the confining effect of the g-C₃N₄ matrix, which prohibits Mo₂C NPs from aggregation and/or excessive growth. The presence of free carbon in MoDCA-5 was also verified by Raman spectroscopy (see Figure S5), and the content of free carbon was 54.8%, as determined by thermogravimetric analysis (see Figure S6).

Figure 3a shows the polarization curves obtained for MoDCA-*x* and a blank glassy-carbon (GC) electrode, as well as the state-of-the-art catalyst 20% Pt/C (catalyst loading: 0.25 mg cm⁻² on the surface of GC). The optimized annealing temperature was 800 °C owing to the smaller size of the Mo₂C NPs (see Figure S7). As expected, both bare GC and MoO_x@g-C₃N₄ showed very limited HER activity (Figure 3a; see also Figure S8). In sharp comparison, MoDCA-5 prepared at 800 °C had a very small *U*_{onset} value of approximately –6 mV (Figure 3a), which is very close to the thermodynamic potential of HER (i.e., 0 mV) as well as the *U*_{onset} value of

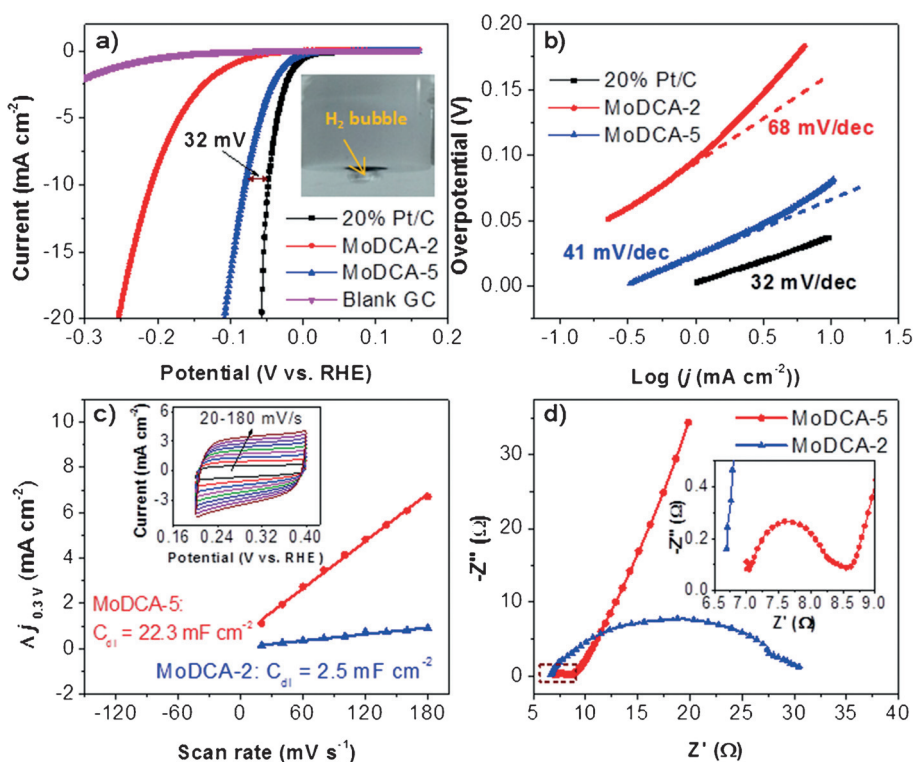


Figure 3. a) Polarization curves after *iR* compensation for a blank GC electrode, MoDCA-*x*, and 20% Pt/C in 0.5 M H₂SO₄ at a scan rate of 2 mV s⁻¹ (inset: photograph showing the production of H₂ bubbles on the surface of MoDCA-5). b) Tafel plots of MoDCA-*x* and 20% Pt/C. c) Capacitive current at 0.3 V as a function of scan rate for MoDCA-*x* ($\Delta j_{0.3} = j_a - j_c$; inset: cyclic voltammograms (CVs) for MoDCA-5 with different rates from 20 to 180 mV s⁻¹ in the potential range of 0.2–0.4 V). d) Electrochemical impedance spectroscopy (EIS) Nyquist plots collected at a bias voltage of –150 mV for MoDCA-5 and –550 mV for MoDCA-2. RHE = reversible hydrogen electrode.

state-of-the-art 20% Pt/C, which is a benchmark HER electrocatalyst. A very small η_{10} value of 78 mV, only 32 mV larger than that for Pt/C, was required for MoDCA-5, thus indicating its exceptional HER electrocatalytic activity. In terms of η_{10} , MoDCA-5 is comparable to MoP|S (64 mV)^[5b] and CoP NPs (75 mV)^[6c] and significantly outperforms many other transition-metal-based HER electrocatalysts, including Mo₂C-based materials (140–192 mV), MoB (220 mV), MoP (90–150 mV), MoS₂ (180–200 mV), WS₂ (142–230 mV), WCN (220 mV), Co₂P (134 mV), Co@NCNTs (270 mV), Ni₂P (100 mV), and FeCo@NCNTs (280 mV), although it is somewhat inferior to metallic WO₂-C NWs (58 mV)^[4a] and Ni₃P₄ NPs (23 mV)^[8a] (see Table S2 for a detailed comparison). However, the mass loading for Ni₃P₄ as a compressed pellet is as high as 157 mg cm⁻².^[8a] Moreover, a decrease in the DCA/ammonium molybdate mass ratio to 2 resulted in a larger U_{onset} value of -62 mV and η_{10} value of 205 mV for the resulting material MoDCA-2 than for MoDCA-5, thus indicating that MoDCA-5 is much superior in HER activity to MoDCA-2.

Further insight into the catalytic activity of MoDCA-*x* was obtained by extracting the slopes from the Tafel plots in Figure 3b ($\eta = b \log j + a$, in which b is Tafel slope, j is the current density, and a is the intercept relative to j_0).^[15] The Tafel slope for commercial Pt/C is 32 mV dec⁻¹, which is smaller than the values of 41 and 68 mV dec⁻¹ for MoDCA-5 and MoDCA-2, respectively. The smaller Tafel slope value of MoDCA-5 indicates its superior HER activity. These values also demonstrate that HER on MoDCA-*x* proceeds by a Volmer–Heyrovsky mechanism, in which the fast discharge of a proton is followed by rate-limiting electrochemical recombination with an additional proton.^[8b] The j_0 value of MoDCA-5 was determined to be 0.178 mA cm⁻², and is thus over 10 times that of MoDCA-2 (0.017 mA cm⁻²). The Tafel slope and j_0 values are both significantly superior to those of various Mo/W/Co/Ni-based HER electrocatalysts, such as MoB, Mo₂C, WS₂, Ni₃P, and Co₂P (see Table S2).

Both MoDCA-5 and MoDCA-2 are composed of ultra-fine Mo₂C nanoparticles encapsulated by graphene layers (see Figure S9), but the HER activity of MoDCA-5 is higher than that of MoDCA-2. The difference in activity can be attributed to the following five points: a) Whereas MoDCA-2 exhibits a macroporous network of dense walls (see Figure S4), the loose texture of MoDCA-5 with hierarchical nanopores (13–20 nm, 102 nm) enables the ready, fast diffusion of the electrolyte into the small nanopores and thus the more efficient utilization of active sites in MoDCA-5 (see Table S3). b) The Brunauer–Emmett–Teller (BET) specific surface area (70 m² g⁻¹) of MoDCA-5 is 5 times that of MoDCA-2 (14 m² g⁻¹). Consequently, more catalytic sites should be accessible, thus resulting in the increased activity of MoDCA-5 (see Figure S10 and Table S3). c) The double-layer capacitance (C_{dl})—representing the electrochemically active surface area (ECSA)—of MoDCA-5 is 22.3 mF cm⁻²; nearly 8 times as high as the value of 2.5 mF cm⁻² for MoDCA-2 (Figure 3c; see also Figure S11). Thus, the large j_0 value of MoDCA-5 may be associated with its large ECSA as well as its large BET surface area.^[16] d) The higher content of free carbon of MoDCA-5 (54.8%) as compared to

MoDCA-2 (38.1%) could effectively lower the electrical resistance of MoDCA-5 (see Figure S6), thus promoting fast electron transport to active sites. Indeed, the electrical conductivity of MoDCA-5 (26.1 S cm⁻¹) is larger than that of MoDCA-2 (0.29 S cm⁻¹). e) MoDCA-5 has a significantly lower charge-transfer impedance (1.5 Ω) than MoDCA-2 (24 Ω), which leads to more facile electrode kinetics for MoDCA-5 toward HER (Figure 3d; see also Figure S12).

The HER performance of transition-metal-based materials is highly correlated with the chemical environment of the metal. The Mo 3d core level XPS spectra are split into 3d_{5/2} and 3d_{3/2} peaks because of spin–orbital coupling (Figure 4).

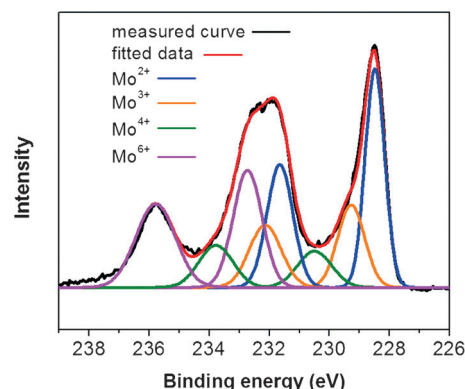


Figure 4. Mo 3d core level XPS spectrum of MoDCA-5.

The peak fitting of the Mo 3d XPS peak for MoDCA-5 suggests that there are four oxidation states (+2, +3, +4, and +6) for Mo on the surface of Mo₂C NPs. Mo⁴⁺ and Mo⁶⁺ are derived from MoO₂ and MoO₃, respectively, both of which are thought to be inactive for HER.^[9a] It has been reported that the surface of Mo₂C NPs can be readily contaminated with molybdenum oxides when exposed to air.^[17] Mo²⁺ and Mo³⁺ are assigned as carbides and nitrides, respectively,^[17b,18] thus implying N doping of the Mo₂C nanoparticles. Moreover, the resulting graphene shells are also doped with some nitrogen atoms, which mainly exist in the form of pyridinic nitrogen atoms (see Figure S13). When MoO_x@g-C₃N₄ is annealed at 800 °C, the C,N-rich precursor not only acts as a carbon source to reduce MoO_x species to form carbides, but also provides nitrogen atoms, which are doped into Mo₂C and the graphene layers. After the electrochemical oxidation of Mo²⁺ and Mo³⁺ to Mo⁶⁺ on the surface of MoDCA-5 by scanning the potential up to 2.22 V, the HER activity was almost negligible (see Figure S14), which strongly implies that Mo²⁺ and Mo³⁺ species serve as the active sites in HER.^[3a,5c,11,17b] Furthermore, this activity could be maintained with only a small loss of 20 mV at η_{10} after 2000 CV sweeps. About 93% of the catalytic current density was maintained after long-term durability testing for 12 h at a fixed overpotential of 78 mV. These results indicate the high stability of MoDCA-5 for HER (Figure 5).

The comprehensive HER performance of MoDCA-5 is among the highest observed for transition-metal-based electrocatalysts (see Table S2). Such superior HER activity has not even been observed for other Mo₂C-based electrocata-

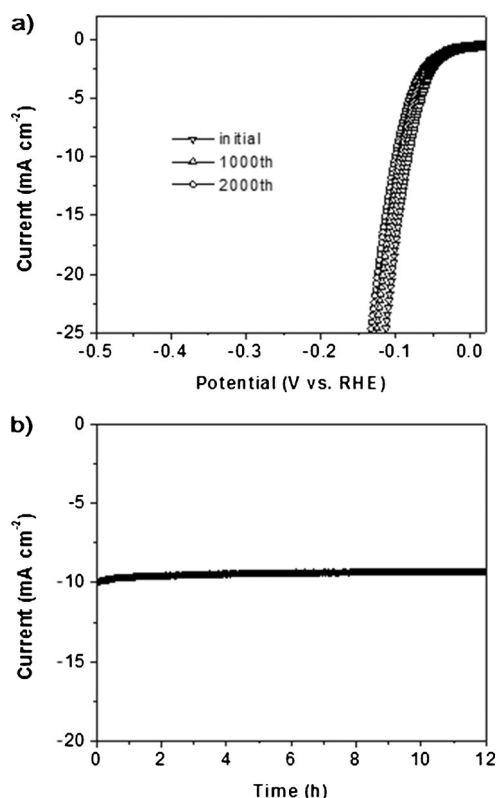


Figure 5. a) Polarization curves for MoDCA-5 initially and after 1000 and 2000 CV scans. b) Time-dependent current-density curve for MoDCA-5 at a static overpotential of 78 mV over 12 h.

lysts. The unique nanostructure of Mo₂C NPs encapsulated by ultrathin graphene shells can not only efficiently stop the aggregation and excessive growth of ultrafine Mo₂C NPs synthesized at high temperature, but can also reduce the electrical resistance between neighboring surface-oxide Mo₂C NPs. The former property is favorable for the exposure of more active sites for H⁺ adsorption, whereas the latter helps improve electron transport to active sites. Moreover, the doping N atoms can not only interact with H⁺ better than C atoms owing to the presence of long-pair electrons on the N atoms,^[6a] but also favorably modify the electronic structures of adjacent Mo and C atoms, thus enhancing the interaction with H⁺. Also, the ultrathin graphene shells can promote electron penetration from the Mo₂C core to the graphene surface^[12,19] to improve reactivity for HER.

In summary, we have developed a one-step strategy for the controllable synthesis of uniform, ultrafine Mo₂C NPs, with sizes lower than 3 nm, encapsulated by ultrathin graphene shells (ca. 1–3 layers) by simply annealing a mixture of low-cost dicyanamide and ammonium molybdate. The resulting nanocomposite acted as a hydrogen-evolving electrocatalyst with superior activity and good long-term stability in an acidic medium. The superior HER activity can be attributed to the cooperative/synergistic effects of ultrafine Mo₂C NPs, ultrathin graphene shells, and N dopant. This effective method might be extended to the design and preparation of other carbide NPs (e.g. tungsten carbide@carbon; see Figure S15) for various electrocatalytic applications.

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