Ultrathin N-Doped Mo₂C Nanosheets with Exposed Active Sites as Efficient Electrocatalyst for Hydrogen Evolution Reactions

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Supporting Information

ABSTRACT: Probing competent electrocatalysts for hydrogen evolution reaction (HER) of water splitting is one of the most hopeful approaches to confront the energy and environmental crisis. Herein, we highlight ultrathin N-doped Mo₂C nanosheets (N-Mo₂C NSs) in the role of greatly efficient platinum-free-based electrocatalysts for the HER. The transformation of crystal phase and structure between MoO₂ nanosheets with a thickness of ~1.1 nm and N-Mo₂C NSs with a thickness of ~1.0 nm is studied in detail. Structural analyses make clear that the surfaces of the N-Mo₂C NSs are absolutely encompassed by apical Mo atoms, hence affording an ideal catalyst prototype to expose the role of Mo atoms for the duration of HER catalysis. Theoretical calculations demonstrate that the nanosheet structure, N doping, and particular crystalline phase of Mo₂C produce more exposed Mo active sites, including Mo atoms on the C plane and doped N atoms. Through detailed electrochemical investigations, N-Mo₂C NSs possess HER activity with an onset potential of −48.3 mV vs RHE, Tafel slope of 44.5 mV dec⁻¹, and overpotential of 99 mV vs RHE at the cathodic current density of 10 mA cm⁻² with excellent long-term stability. Lastly, the calcination temperature and dicyandiamide amount can obviously affect the phase transformation and surface structure of molybdenum carbide, resulting in an adjustable HER activity. This synthesis mechanism will facilitate the understanding and optimization of Mo-based electrocatalysts in the energy conversion field.

KEYWORDS: molybdenum carbide, nanosheet, nitrogen doping, density functional theory, hydrogen evolution reaction

Clean and sustainable hydrogen is deemed to be the most promising energy carrier in the future because of its highest mass-specific energy density and zero emission. Among various hydrogen production processes, electrochemical water splitting is considered an ideal eco-friendly way to produce clean hydrogen energy. However, efficient water splitting requires active electrocatalysts for the hydrogen evolution reaction (HER). A platinum (Pt)-based composition, as is well-known, has been utilized as ideal electrocatalysts for the HER process, because of a hydrogen absorption Gibbs free energy (ΔG_H₂) of zero. However, the high material cost and relative scarcity greatly limit its worldwide applications in the HER process. Therefore, the search for the ideal electrocatalysts for the HER process to
replace Pt-based electrocatalysts is thus highly desirable.\textsuperscript{7−10} As an alternative, Mo-based catalysts, such as MoS\textsubscript{2}, MoN, Mo\textsubscript{2}C, and MoP, have recently received great attention as potential catalysts for HER, due to their cost efficiency, rich molybdenum resources, and favorable activity.\textsuperscript{11−19} Among them, molybdenum carbide (Mo\textsubscript{2}C), an outstanding early transition-metal carbide, has intensely awakened ever-increasing attention as a high-efficiency HER electrocatalyst with high electrical conductivity and optimal hydrogen-adsorption properties, because the electronic structure of Mo\textsubscript{2}C is virtually analogous to that of Pt-group elements.\textsuperscript{20−22} It is well-known that the catalytic activities of molybdenum carbide largely hinge on its composition and surface structure and are closely associated with synthesis techniques such as chemical vapor deposition (CVD) and pyrolysis of metal complexes.\textsuperscript{23−26} Nevertheless, high-temperature processing usually brings about the coarsening of molybdenum carbide and the excess growth of carbon on the surface of molybdenum carbide, inevitably giving rise to a low density of catalytically active sites. Many efforts have been dedicated to expose more active sites by designing and synthesizing various morphologies of molybdenum carbide, such as nanoparticles,\textsuperscript{27} nanowires,\textsuperscript{28,29} hierarchical $\beta$-Mo\textsubscript{2}C nanotubes,\textsuperscript{30} vertically aligned nanosheets,\textsuperscript{30} cross-linked porous rods,\textsuperscript{31} and 2D MXene.\textsuperscript{32,33} For instance, nanoporous $\beta$-Mo\textsubscript{2}C nanowires\textsuperscript{35} and MoC\textsubscript{n} nano-octahedrons\textsuperscript{34} had been recently designed and fabricated by pyrolysis of a MoO\textsubscript{2}/amine hybrid precursor and metal–organic frameworks (MOFs) comprising molybdenum-based polyoxometalates (NENU-S), respectively. Despite these developments, owing to the lack of appropriate precursors incorporating uniformly hybridized molybdenum and carbon sources in well-organized nanostructures, the controllable preparation of two-dimensional (2D) molybdenum carbide nanocatalysts is still highly challenging.

Like graphene, 2D crystals are indispensable for exploring the original physical and chemical properties in the dimension limit and for numerous practical and even attractive applications.\textsuperscript{35−37} Kang and Ren et al.\textsuperscript{26} reported the preparation method of large-area and high-quality 2D ultrathin Mo\textsubscript{2}C crystals by CVD with CH\textsubscript{4} as the C source, a Mo foil as Mo source, and a Cu foil as the substrate at a high temperature of 1085 °C. However, the above synthesis process of Mo\textsubscript{2}C sheets was complicated and had a low yield rate, which was difficult to use in catalysts. In addition, Hu and his colleagues\textsuperscript{38} deduced that Mo atoms might behave like precious metals in Mo\textsubscript{2}C for HER and might well behave as the catalytic active sites. However, the catalytic sites of Mo\textsubscript{2}C were difficult to regulate and confirm due to the lack of regular structure.

Herein, we reported a very facile and appealing strategy for synthesizing uniform and ultrathin N-doped Mo\textsubscript{2}C nanosheets (N-Mo\textsubscript{2}C NSs) using MoO\textsubscript{2} nanosheets (MoO\textsubscript{2} NSs) as a template with special morphology and crystal structure by a rapid, handy, and scalable synthesis, which were utilized as a highly active electrocatalyst for HER. The transformation of the crystal phase and surface atomic structure between MoO\textsubscript{2} NSs and N-Mo\textsubscript{2}C NSs is easy to implement due to the ultrathin nanosheet structure. Theoretical calculations validated that the nanosheet structure and N doping of Mo\textsubscript{2}C could produce more exposed active sites, including N atoms and Mo atoms on the C plane of Mo\textsubscript{2}C. The as-prepared N-Mo\textsubscript{2}C NSs displayed noteworthy electrocatalytic activity for HER in both acidic (onset potential of $-48.3$ mV, Tafel slope of 44.5 mV dec\textsuperscript{−1}) and basic solutions (onset potential of $-69$ mV, Tafel slope of 65 mV dec\textsuperscript{−1}) with good catalytic and structural stability. Moreover, such a strategy will be able to develop large-scale and high-performance 2D Mo\textsubscript{2}C for diverse interesting properties and unusual applications.

**RESULTS AND DISCUSSION**

Based on prior structural data, $\beta$-Mo\textsubscript{2}C can be described as a hexagonal-close-packed structure of Mo atoms, with C atoms randomly filling half of the octahedral interstitial sites.\textsuperscript{39} A supercell of (4 × 4 × 1) molybdenum carbide and (001) surface was constructed. The different crystal planes exposed...
the different atoms, such as Mo atoms on the top plane and C atoms on the bottom plane, as shown in Scheme 1a. The top-view of the C plane and Mo plane of Mo2C and the detailed distribution of selected points for density functional theory (DFT) are shown in Scheme 1c and Figure S1. DFT calculations were used to calculate the Gibbs free energy of H* adsorption (ΔG_{H^*}) on various sites of Mo2C, such as Mo-1-T, Mo-2-T, and C-T on the top plane and Mo-B on the bottom plane, as shown in Scheme 1d. The ΔG_{H^*} values of Mo-I-T and Mo-2-T on the top plane (0.03 and 0.06 eV) were much lower than those of C-T on the top plane (0.45 eV) and Mo-B on the bottom plane (0.66 eV), implying that Mo atoms on the top plane were mainly catalytically active sites of β-Mo2C for HER. This was possibly because that Mo-1-T and Mo-2-T atoms on the top plane of Mo2C were not completely covered by C atoms, which possessed the appropriate hydrogen-binding energy. By contrast, Mo-B atoms on the bottom plane are unsaturated and possessed excessively strong hydrogen-binding energy.

Furthermore, one N atom was introduced into β-Mo2C to replace one C atom, and the effect of N doping on the ΔG_{H^*} values of Mo and C atoms was studied in Scheme 1b, c, and e. The N doping did not obviously affect the ΔG_{H^*} value of C-T on the top plane (0.4 eV), and even Mo–B on the bottom plane (0.93 eV) became more inert. The catalytically active sites of Mo-I-T (0.03 eV) and Mo-2-T (0.09 eV) atoms on the top plane of Mo2C remained after N doping. It is important that new catalytically active sites of the N atom and Mo-3-T atom on the top plane were introduced after N doping, which possessed low ΔG_{H^*} values of 0.07 and 0.3 eV, respectively, implying that N doping produced more catalytically active sites of Mo2C. So, theoretical calculations demonstrated that the Mo atoms on the C plane (top plane) of Mo2C were more active for HER and the N doping further produced more catalytically active sites, including N atoms and Mo atoms on the C plane (top plane) of Mo2C.

A nanosheet is a 2D structure with a specific atom alignment that well simplifies the catalysis model as an ideal material model to survey the catalytic sites during HER catalysis. Herein, a two-step process was developed to synthesize the N-Mo2C NSs, as shown in Figure S2. First, in step a, the regular MoO2 NSs were obtained by annealing MoO3 powders in an Ar random MoO3 nanoparticles (2 μm) at the end of the quartz tube (Figure S5), and no MoO2 NSs were synthesized on the quartz tube wall. The Ar gas instead of Ar showed the hexagonal nanosheet-shaped morphology of several micrometers, which possessed a smooth surface and margins (Figure 1a,b). The large-scale SEM image showed the hexagonal nanosheet was evenly distributed (Figure 1a), suggesting the practicability of the synthetic process. After calcination with dicyandiamide at 700 °C, the N-Mo2C NSs were obtained. As shown in Figure 1c and d, the nanosheets remained, but the surfaces became coarse. The blue and homogeneous aqueous dispersions of MoO2 NSs and the gray and homogeneous aqueous dispersions of N-Mo2C NSs confirmed the ultrathin 2D structure, which was stable for five months (inset of Figure 1a,c). The specific surface areas of MoO2 NSs and N-Mo2C NSs were quantitatively measured using N2 adsorption–desorption isotherms. As shown in Figure 1e, MoO2 NSs showed type II, implying the planar structure, confirmed by Langmuir monolayer adsorption. In comparison, N-Mo2C NSs showed the type IV isotherms with an obvious pore size distribution of 2−40 nm (inset of Figure 1e). The Brunauer–Emmet–Teller (BET) specific surface area of porous N-Mo2C NSs (30.6 m2 g−1) was almost tripled from...
10.6 m² g⁻¹ of MoO₂ NSs, which was consistent with above SEM results.

X-ray diffraction (XRD) patterns confirmed that the crystal phase transformation from MoO₂ to Mo₂C, which provided proof of a solid-state reaction between the molybdenum and dicyandiamide. As shown in Figure 1f, MoO₂ with monoclinic symmetry crystal structure was obtained (a = 5.611 Å, b = 4.856 Å, c = 5.628 Å, space group P21/c (14), PDF# 73-1249). After reaction with dicyandiamide, the characteristic peaks corresponding to the (100), (002), (101), (102), (110), and (103) crystal facets of the hexagonal β-Mo₂C phase were observed (a = 3.012 Å, b = 3.012 Å, c = 4.735 Å, space group P63/mmm, PDF# 35-0787). Compared to pure Mo₂C NSs synthesized by glucose, the XRD peaks of N-Mo₂C NSs slightly shifted to a higher diffraction angle (Figure S7). By N doping into the lattice of β-Mo₂C, N-doped β-Mo₂C (100) shifted to a higher angle, indicating that the lattice parameters a/b in β-Mo₂C decreased after N doping into the lattice, which was similar to the doped Mo₂C.40,41

The binding states and quantitative chemical compositions of MoO₂ NSs and N-Mo₂C NSs were investigated by X-ray photoelectron spectroscopy (XPS) (Figure 1g, h). The Mo 3d₃/₂ and Mo 3d₅/₂ of Mo⁴⁺ were observed at 232.9 and 229.1 eV, and a trace of Mo⁶⁺ species in an oxidic surrounding was also detected at 235.8 eV (Mo 3d₃/₂) and 232.5 eV (Mo 3d₅/₂), as a result of the oxidation for a small amount of Mo⁴⁺ exposed to air (Figure 1g).42,43 After reaction with dicyandiamide, additional XPS peaks corresponding to N 1s were detected at 398.5 eV (Figure 1h), signifying a successful N doping (17.2 at %) into Mo₂C. The N doping was beneficial to withdraw electrons and active hydrogens caused by the lone electron pair.44 The main Mo²⁺ with peaks at 228.6 and 231.6 eV (Mo 3d₃/₂ and Mo 3d₅/₂) was observed in N-Mo₂C NSs (Figure 1g). Compared with that in pure Mo₂C NSs, these shifted peaks for Mo²⁺ in N-Mo₂C NSs with larger binding energy indicated the enriched electrons around Mo (Figure S8), suggesting the successful N doping into Mo₂C NSs.

Transmission electron microscopy (TEM) was applied to further analyze the crystal structure of MoO₂ NSs and N-Mo₂C NSs. Like graphene nanosheets, an obvious wrinkle was observed on the hexagonal MoO₂ NSs, as shown in Figure 2a. Due to ultimately thin shapes, the two pieces of MoO₂ NSs overlaid together, which were transparent to an electron beam. The well-defined lattice fringes with a spacing of 0.34 nm matching with the (011) plane of MoO₂ were observed. The monocystal nature of the MoO₂ NSs was further proved by the selected area electron diffraction pattern (inset of Figure 2b). After the carbonization and N doping, TEM images further indicated that the morphologies of N-Mo₂C NSs were porous and ultrathin nanosheets (Figures 2c,f and S9). It is worth mentioning that the N-Mo₂C NSs maintained hexagonal nanosheets. This was possibly the reason for the small transformation stress of the ultrathin nanosheet structure during the carbonation process. The single set of diffraction spots with 6-fold symmetry clearly indicated the single-crystalline nature and the presence of hexagonal crystalline structures of the nanosheet (Figures 2d,e and S10).45 The bright lattice fringes shown in Figure 2f indicated that the nanosheets were highly crystallized and porous. A representative HRTEM image clearly showed the long-range order lattice fringes with interplanar spacings of 0.15 and 0.26 nm matching with the (110) and (100) planes of Mo₂C (Figure 2f), respectively. It was confirmed that the crystal orientation [001] was perpendicular to the nanosheet, and the crystal structure of β-Mo₂C situated in the [001] zone axis is shown in Figure S10. As exemplified in Figure 2g, the elemental mapping characterization demonstrated that the nanosheet was evenly comprised of Mo, C, and N elements, confirming the successful synthesis of N-Mo₂C NSs. In addition, the thicknesses of MoO₂ NSs and N-Mo₂C NSs were measured by atomic force microscopy.
(AFM), as shown in Figure 2h,i. Interestingly, compared with MoO2 NSs (~1.1 nm, Figures 2h-2 and S11a), the N-Mo2C NSs obtained via carbonization and N doping became slightly thinner (~1.0 nm, Figures 2i-2 and S11b). As confirmed by HRTEM images in Figure 2b and f, the (200) and (002) planes were perpendicular to the MoO2 NSs and N-Mo2C NSs, with the interplanar spacings of 0.241 nm (Figure 2h-3) and 0.237 nm (Figure 2i-3), respectively, which caused a thinner nanosheet after the crystalline phase transformation. It is worth noting that MoO2 NSs and N-Mo2C NSs were too thin and easily destroyed by ultrasonic dispersion. So, only shapeless sheets with sizes of 0.1–0.2 μm and thicknesses of ~1 nm were observed by AFM.

In order to examine the effect of nanosheet structure and N doping on the HER activity, the blank samples of Mo2C NSs (Figure S12) and N-Mo2C nanoparticles with sizes of 0.2–0.4 μm (Figure S13) were synthesized. The electrocatalytic HER performances of the N-Mo2C NSs and blank samples including MoO2 NSs, N-Mo2C nanoparticles, Mo2C NSs, and 20 wt % Pt/C were evaluated by applying the linear scan voltammogram (LSV) in 0.5 M H2SO4 (Figure 3a). The MoO2 NS-modified electrode showed a large onset potential of >−500 mV vs RHE (defined as the potential at 1 mA cm−2 of the cathodic current density) for the HER. The N-Mo2C NSs had the smallest onset potential of −48.3 mV vs RHE, much smaller than the value of MoO2 NSs (~290 mV) and N-Mo2C nanoparticles (~193 mV), but still worse than that of 20 wt % Pt/C (~0 mV). For a running current density of 10 mA cm−2, N-Mo2C NSs required an overpotential of only 99 mV, much lower than that observed on the MoO2 NSs (~463 mV) and N-Mo2C nanoparticles (319.5 mV), indicating that the robust sheet structure and N doping reduced the energy input for activating HER.

Figure 3b displayed the Tafel plots (log j−η) of the HER. Twenty wt % Pt/C with a Tafel slope of 31.2 mV dec−1 followed the known Tafel mechanism. The N-Mo2C NSs had a smaller Tafel slope of 44.5 mV dec−1 than those of Mo2C NSs (144.4 mV dec−1) and N-Mo2C nanoparticles (101.7 mV dec−1), signifying that the HER on this catalyst was dominated by the recombination-limited Volmer–Tafel mechanism. The exchange current density (j0) of the N-Mo2C NSs was calculated to be 0.1 mA cm−2 (Figure S14). This value was much smaller than that of MoO2 NSs (5.25 × 10−3 mA cm−2) and N-Mo2C nanoparticles (2.57 × 10−2 mA cm−2). The established HER free-energy diagram provided a quantitative relationship between the measured electrochemical activity and theoretical ΔGHER. For further evaluation of the electrocatalytic properties of the N-Mo2C NSs in comparison with some typical molybdenum-based electrocatalysts, the normalized experimental value of log(j0) along with theoretically calculated ΔGHER was marked on a volcano-shaped plot shown in Figure 3c. It can be seen that the experimental exchange current densities of N-Mo2C NSs are close to the expected exchange current values in the volcano plot, indicating a good correlation between the theoretical calculation and experimental results. Table S1 summarizes a detailed comparison with other representative molybdenum-based electrocatalysts. Noteworthily, the obtained N-Mo2C NSs possessed a marvelous HER activity with an onset potential of −48.3 mV vs RHE, a Tafel slope of 44.5 mV dec−1, and an overpotential of 99 mV vs RHE at 10 mA cm−2, which were obviously better than or comparable to those of the Mo-based HER electrocatalysts in 0.5 M H2SO4 such as β-Mo2C nanotubes (~82 mV, 58 mV dec−1, 136 mV),40 Mo2C nanowires (~70 mV, 53 mV dec−1, 200 mV),53 N, P-Mo2C@C (~−100 mV, 56 mV dec−1, 141 mV),41 Mo2C@N-doped carbon (~60 mV, 60 mV dec−1, 124 mV),42 Mo2C/3D N-doped carbon nanofiber (~105 mV, 70 mV dec−1, 192 mV),46 Mo2C/hierarchical carbon microflowers (~85 mV, 55 mV dec−1, 144 mV),27 Mo2C-carbon sphere (~100 mV, 85 mV dec−1, 164 mV),54 Mo2C/CNT (~63 mV, 65 mV dec−1, 152 mV),58 Mo2C/graphitic...
carbon sheets (−120 mV, 62.6 mV dec$^{-1}$, 200 mV)\textsuperscript{59} Mo$_2$C/graphene (−87 mV, 73 mV dec$^{-1}$, 236 mV),\textsuperscript{60} etc. Furthermore, the N-Mo$_2$C NSs also had high HER catalytic activities in 1.0 M KOH (onset potential of −69 mV, overpotential of 140 mV, and Tafel slope of 65 mV dec$^{-1}$) and 1.0 M phosphate-buffered saline (onset potential of −92.5 mV, overpotential of 200 mV, and Tafel slope of 88 mV dec$^{-1}$) (Figure S15).

To explicate the charge transfer mechanism, electrochemical impedance spectroscopy (EIS) analyses were done on these catalysts as shown in Figure 3d. Clearly, the fitting results confirmed that the lowest resistance ($R_e$) and charge transfer resistance ($R_q$) of N-Mo$_2$C NSs were only 7.5 and 20 Ω at the overpotential of 220 mV, respectively, representing the fastest electrocatalytic reaction rate. The $R_q$ of the N-Mo$_2$C NSs at overpotentials of 120 and 220 mV showed decreased values from 96 Ω to 20 Ω (Figure S16). At lower overpotentials, e.g., 120 mV, a semicircle could be formed in the Nyquist plots, indicating low charge transfer resistance between the N-Mo$_2$C NSs and electrolyte.

The strong correlation between the HER catalysis and electrochemical area of N-Mo$_2$C NSs was accessed by electrochemical double-layer capacitance (Figure 3e). The capacitance of N-Mo$_2$C NSs (6.54 mF cm$^{-2}$) was nearly 5 times, 4.4 times, and 1.5 times larger than those of Mo$_2$C nanoparticles (1.35 mF cm$^{-2}$), Mo$_2$C NSs (1.47 mF cm$^{-2}$), and MoO$_2$ NSs (4.35 mF cm$^{-2}$). However, after being corrected by electrochemical area, the HER performance of N-Mo$_2$C NSs still possessed the lowest onset potential (Figure S17), implying that the larger electrochemical area only increased the number of active sites, but did not enhance the nature of the HER activity. It is worth noting that the cyclic voltammetry (CV) curves of the N-Mo$_2$C NSs had a nearly rectangular shape (Figure S18), indicating the high electrical conductivity.

The N-Mo$_2$C NSs exhibited not only great catalytic activity but also good catalytic durability, which was evaluated by time-dependent current (Figure 3f) and LSV after $i$−$t$ testing (Figure 3g). The current density of 10 mV cm$^{-2}$ after a 12 h $i$−$t$ testing (Figure 3g), TEM, and XPS spectra (Figures S19) showed that the nanosheet structure was well-preserved and did not show any change of valence states after $i$−$t$ testing at 110 mV for 12 h, confirming the structure stability of N-Mo$_2$C NSs. The residual naphthol was also observed on the surface of nanosheets due to the exfoliation from the glassy carbon electrode. Last, the gathered bubbles on the N-Mo$_2$C NSs-modified electrode were established to be hydrogen through gas chromatography analysis, and the hydrogen production rate was 6.23 mmol mg$^{-1}$ h$^{-1}$, which was almost the same as the theoretical calculation (Figure 3h).

The obtained Faradaic efficiency (FE) was nearly 100%, implying that N-Mo$_2$C NSs was an excellent HER electrocatalyst with superior stability in acid media.

The dicyandiamide amount and calcination temperature obviously affected the morphology, phase transformation, and composition of obtained molybdenum carbide and produced different HER activities. Our DFT calculation verified that MoC possessed weaker HER activity than that of Mo$_2$C due to the oversaturated carbon atoms, as shown in Figure 4a. The $\Delta G_{\text{HE}}$ value of the Mo atom of MoC (0.24 eV) was much larger than those of Mo atoms on the C plane of Mo$_2$C (0.03 and −0.06 eV). In addition, the C atom in MoC (−1.26 eV) was also more inert than that of Mo$_2$C (−0.45 eV), implying that Mo$_2$C exhibited a higher HER activity than that of MoC. The dicyandiamide amount affected the crystalline phase and surface structure of molybdenum carbide during the calcining process. The incomplete transformation from MoO$_2$ NSs to N-Mo$_2$C NSs was detected with insufficient dicyandiamide (0.5 g, Figure 4b,c). With excess dicyandiamide (4 g), the crystal phase of molybdenum carbide was transformed into $\eta$-MoC (PDF# 06-0546), and amorphous carbon at $2\theta \approx 25^\circ$ was detected in Figure 4b. The phase transformation and changed surface structure were also confirmed by the Raman spectra ($I_D/I_G$ ratio of integrated intensities of D and G bands, Figure 4c) and SEM images (rough surface, Figure S20). With an increasing amount of dicyandiamide, the $I_D/I_G$ value (ratio of integrated...
intensities of D and G bands) increased from 1.4 of 1 g to 2.0 of 2 g and 2.2 of 4 g, showing the increased disordered carbon on the surface of the nanosheets. The polarization curves for HER showed that the N-Mo2C NSs synthesized with the appropriate amount of dicyandiamide possessed the best HER performance (1 g, Figure 4d,e), which needed not only successfully transformed MoO2 NSs to N-Mo2C NSs, but also prevented the phase transformation from Mo2C to MoC. In addition, the excess carbon on the surface of Mo2C NSs produced by the more dicyandiamide (Figure 4c) covered the active sites of Mo2C, which was confirmed by the decreased electrochemical area (Figure 4f).

In addition, the different temperatures (600, 700, 800, and 900 °C) were studied for the influence of N-Mo2C NSs. At 600 °C, only diffraction peaks of MoO2 were detected (Figure S21). Because that the dicyandiamide powder was decomposed to ionized molecules of carbon and nitrogen above 700 °C, the low carbonization temperature could not transform MoO2 NSs into N-Mo2C NSs. Similar to N-Mo2C NSs obtained at 700 °C, the samples obtained at 800 °C also possessed the crystal structure of β-Mo2C and the nanosheet morphology (Figures S21, S22). However, the sheet structure of N-Mo2C-900 °C began to collapse and formed a lot of nanoparticles due to the high calcination temperature (Figure S21c). Besides, the molybdenum carbide synthesized at 900 °C possessed different crystal phases of η-Mo2C (space group Pm2, PDF# 06-0546), γ-MoC (space group P63/mmc, PDF# 45-1015), and a few β-Mo2C (space group P63/mmm, PDF# 35-0787), as shown in Figure S21. The N doping amounts of samples obtained at different temperatures were characterized by XPS in Figure S23a and summarized in Figure S23b. Compared to the N doping amount of 17.2 at. % in N-Mo2C-700, the increased value (30 at. %) of N-Mo2C-600 was due to the incomplete decomposition of dicyandiamide at low calcination temperatures. Also, the decreased N doping amounts of 8.97 at. % (N-Mo2C-800) and 6.32 at. % (N-Mo2C-900) were attributed to the decomposition of the unstable N-doped structure at high calcination temperatures. The different phase transformation and composition of N-Mo2C NSs caused the different HER activity. As shown in Figure S24, the sample obtained at 600 °C possessed the worst HER activity with the onset potential of ~200 mV and Tafel slope of 86 mV dec⁻¹ due to the unsuccessful transformation from MoO2 NSs to N-Mo2C NSs. The β-Mo2C samples obtained at 700 and 800 °C possessed similar HER activity with onset potential of ~48.3 mV (Tafel slope of 44.5 mV dec⁻¹) and ~50 mV (Tafel slope of 53 mV dec⁻¹), respectively. The η-Mo2C/γ-MoC obtained at 900 °C (~103 mV, 62 mV dec⁻¹) possessed the worst HER activity due to the MoO2 phase (Figures 4a and S21), the collapse of the nanosheet structure (Figure S22), decreased N doping amount (Figure S23), and enlarged charge transfer resistance (Figure S25).

CONCLUSIONS

In summary, the N-Mo2C NSs were fabricated by a two-step approach of using ultrathin MoO2 NSs as template and a Mo source on a large scale and in a handy way. The obtained N-Mo2C NSs possessed a single-crystal structure and ultrathin thickness of ~1.0 nm. Theoretical studies revealed that the 2D structure, N doping, and crystallinity of β-Mo2C produced more active sites for HER, including exposed Mo atoms on the C plane and N atoms. The as-synthesized N-Mo2C NSs possessed high HER activity with a low onset potential (~48.3 mV vs RHE at 1 mA cm⁻²), small overpotential (99 mV vs RHE at 10 mA cm⁻²), small Tafel slope (44.5 mV dec⁻¹), high exchange current density (0.1 mA cm⁻²), and excellent long-term stability (little decay after 12 h of testing). The excellent HER performance of N-Mo2C NSs was attributed to the following aspects. First, the 2D structure of Mo2C NSs with large electrochemical area facilitated the diffusion among the electrocatalyst, electrolyte, and gas. Second, the particular crystalline phase and high-proportioned C planes of Mo2C NSs exposed more Mo active sites (Mo-1-T and Mo-2-T). Third, the synergistic manipulation of N doping with the electron density states produced more active sites (Mo-3-T and N-T). This study provides not only an attractive electrocatalyst with excellent activity toward the HER but also a facile, easy to understand mechanism to optimize Mo-based electrocatalysts for water splitting.

EXPERIMENTAL SECTION

Preparation of N-Doped Mo2C Nanosheets. The setup is a typical CVD system, which constitutes a clean quartz tube and a tube furnace. First, MoO2 NSs were grown on the quartz tube tail by a chemical vapor reduction process using commercial MoO3 powders (99.9%, 0.5 g, Aladdin). The reaction was performed in the presence of mixed Ar–H2 (10% H2 gases) (200 scm) at 900 °C for 60 min, and the purple MoO2 NSs were collected at the tail end of the quartz tube. Second, commercial dicyandiamide powders (C2H4N4, 99.99%, 1 g, Aladdin) were mixed with 100 mg of obtained MoO2 NSs, which were placed in the tube furnace with Ar–H2 gas to remove air. The mixture was calcined at 450 °C for 2 h and then 700 °C for 2 h to form N-Mo2C NSs.

For comparison, the pure Mo2C NSs were made by the same conditions, but with glucose instead of dicyandiamide. The N-doped Mo2C nanoparticles were also synthesized with MoO2 nanoparticles and dicyandiamide by the same heating process. Additionally, the calcination temperatures (600, 800, and 900 °C) and amount of dicyandiamide were considered with respect to the effect on the structure and catalytic activities of the samples.

Characterization. Phase compositions of the samples were determined by a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.154 06 nm). Morphologies of the samples were observed by a field emission scanning electron microscope (MERLIN Compact, Carl Zeiss) and a transmission electron microscope (a JEM-2100F field emission electron microscope, JPN) at an acceleration voltage of 200 kV. The MoO2 NSs and N-Mo2C NSs were analyzed by means of AFM (Dimension Icon, Bruker, Santa Barbara, CA, USA), operated at room temperature and ambient conditions. X-ray photoelectron spectroscopic measurement was implemented with a PHI X-ray instrument (ULvac-Phi). BET surface areas were determined by using a Quantachrome Autosorb-IQ2 instrument with nitrogen adsorption at 77 K using the Barrett–Joyner–Halenda method. TGA-DSC curves were measured by a TGA/DSC1 Mettler-Toledo thermal analyzer at a heating rate of 5 °C min⁻¹ in a stream of air (50 mL min⁻¹).

Electrochemistry. Electrochemical measurements were operated with an electrochemical workstation (CHI 760C, CH Instruments Inc.) in a 0.5 M H2SO4 aqueous solution. An Hg/Hg2Cl2 electrode (SCE, saturated KCl aqueous solution) and carbon rod were used as the reference and counter electrodes, respectively. A 5 mg amount of the catalyst powders was dispersed in 1 mL of 2:1 (v/v) water/ethanol mixed solvents along with 40 μL of Nafion solution (~5% in a mixture of alcohols and water, Sigma-Aldrich) and sonicated for 30 min. Then, 5 μL of the above solution was drop-cast onto the surface of the glassy carbon (GC) electrode at a catalyst loading of 0.357 mg cm⁻². The current densities were evaluated in terms of the geometrical surface area of the GC electrode. Polarization curves were acquired by sweeping the potential from 0 to −0.5 V vs RHE at a potential sweep rate of 5 mV s⁻¹ in 0.5 M H2SO4 (pH 0.25), 1.0 M phosphate buffer (pH 7), and 1.0 M KOH (pH 14), which were used as electrolytes.
individually. EIS was carried out with an amplitude of 0.005 V and a frequency range from 100 kHz to 0.01 Hz. The main arc in each EIS spectrum was fitted using a simplified Randles equivalent circuit, which consisted of a resistance ($R_p$) in series with a parallel arrangement of a charge transfer resistance ($R_{ct}$) and a constant phase element, and the fitting parameters were estimated through the application of the Levenberg–Marquardt minimization procedure. Cyclic voltammetry was used to probe the electrochemical double-layer capacitance at nonfaradaic potentials as a means to estimate the effective electrochemical active area. Current–time responses were monitored for 12 h by chronoamperometric measurements. The rate of hydrogen gas production was quantified by gas chromatographic measurements (GC-2060F, Lu Nan Analytical Instruments, LTD., China).

**DFT Calculations.** In this work, the Gibbs free energy of H atoms on the Mo-terminated and C-terminated (001) surface of Mo$_2$C was studied using DFT, and the model was established in reference to the work of Wang et al.\(^6\) The calculation was performed using VASP (Vienna ab initio simulation package) with the projected augmented-wave method.\(^{1,6,2}\) The generalized gradient approximation was used, with exchange correlation following the approach of Perdew–Burke–Ernzerhof.\(^6\)\(^3,6,4\) The cutoff energy for the plane-wave basis was set to 520 eV. The Brillouin zone integration was performed on a Γ-centered $5 \times 5 \times 1$ k mesh. All the atoms were fully relaxed until the maximum residual forces of each atom were less than 0.02 eV Å$^{-1}$; the convergence criterion for the self-consistent electronic cycle achieved a difference between the energies of the system in two consecutive steps of smaller than 10$^{-3}$ eV, and the two layers of atoms on the bottom were fixed when hydrogen was absorbed to the surface of Mo$_2$C. The calculation method for Gibbs free energy followed the widely used method of J. K. Norskov et al.\(^6,7,6\)\(^4\) In addition, the catalytic sites of MoC were also studied using DFT. A $4 \times 4 \times 2$ supercell with a vacuum layer of 15 Å was constructed, and then the (001) facet was considered in structural models of Mo$_2$C and MoC were also studied using DFT. A $4 \times 4 \times 2$ supercell with a vacuum layer of 15 Å was constructed, and then the (001) facet was considered in structural models of Mo$_2$C and MoC were also studied using DFT.

**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b06607.

**Top-view and the calculated sites, synthesis process, digital photograph, TGA-DSC, XRD, SEM, XPS, thickness histograms, exchange current density, polarization curves, Tafel slopes, Nyquist plots, cyclic voltammograms, and comparison of the HER performance (PDF)**

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by Tip-top Scientific and Technical Innovative Youth Talents of Guangdong Special Support Program (2016TQ033541), Guangdong Natural Science Funds for Distinguished Young Scholar (2017B030360001), the National Natural Science Foundation of China (51572096), and Guangdong Innovative and Entrepreneurial Research Team Program (2014ZT05N200).


Highly Active Electrocatalysts for Alkaline Hydrogen Evolution. ACS Nano 2016, 10, 8851−8860.