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Enhancing electrocatalytic activity for hydrogen evolution by strongly coupled molybdenum nitride@nitrogen-doped carbon porous nano octahedrons

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ABSTRACT: Developing highly efficient and affordable noble metal-free catalysts towards hydrogen evolution reaction (HER) is an important step toward economical production of hydrogen. As a non-precious metal catalyst for HER, molybdenum nitride (MoN) has excellent corrosion resistance and high electrical conductivity, but its catalytic activity is still inadequate. Here we report our findings in dramatically enhancing the HER activity of MoN by creating porous MoN@nitrogen-doped carbon (MoN-NC) nano-octahedrons derived from metal-organic frameworks (MOFs). The composite catalyst displays remarkably high catalytic activity, demonstrating a low overpotential of 62 mV at the current density of 10 mA cm$^{-2}$ ($\eta_{10}$), a small Tafel slope of 54 mV dec$^{-1}$, and a large exchange current density of 0.778 mA cm$^{-2}$ while maintaining good stability. The enhancement in catalytic property is attributed to the unique nanostructure of the MoN, the high porosity of the electrode, and the synergistic effect between the MoN and the nitrogen doped carbon substrate. The performances are among the best ever reported for non-precious metal-based electrocatalysts (comparable to those of a 20% Pt/C commercial catalyst), making the porous MoN-NC nano-octahedrons one of the most active and acid-stable electrocatalysts for HER.

KEYWORDS: electrocatalysis, hydrogen evolution reaction, metal-organic frameworks, nano-octahedrons, water splitting
INTRODUCTION

Hydrogen is considered the most promising energy carrier for the future because of its highest mass-specific energy density and zero-emission. Unfortunately, hydrogen does not exist naturally on earth; it must be produced, mostly from splitting of water or reforming of hydrocarbon fuels. Accordingly, economic production of hydrogen is critical to the realization of hydrogen economy. Among various hydrogen production processes, electrolysis of water using renewable energy (such as solar, wind, or geothermal energy) is believed the most promising and sustainable option.\textsuperscript{1-6} Efficient water splitting requires active electrocatalysts for hydrogen evolution reaction (HER). Platinum-group metal (PGM) and PGM-based materials are the state-of-the-art HER catalysts because they have high HER activity and favorable stability; however, the high cost and scarcity of PGM limit their large-scale use. It is thus highly desirable to develop alternative HER catalysts with sufficient HER activity and adequate stability from low-cost, earth-abundant elements (or non-PGM materials).\textsuperscript{7,8}

To date, enormous efforts have been devoted to the development of non-PGM catalysts for HER.\textsuperscript{9,10} Typically, transition-metal-based catalysts have displayed far superior activity to metal-free catalysts for hydrogen generation from water splitting. Among the various kinds of transition-metal-based HER electrocatalysts, molybdenum (Mo)-based electrocatalysts are considered as the most promising alternatives due to the rich molybdenum resource and favorable activity.\textsuperscript{11-13} Molybdenum disulfide (MoS\textsubscript{2}), a representative of the Mo-based electrocatalysts for HER, has received the most attention during the past decades.\textsuperscript{14-17} Both experimental
and theoretical investigations have revealed that the HER activity of the MoS$_2$
originates from the sulfur edges while the basal plane has been found to be chemically
inert.$^{14,15}$ Though significant progress has been achieved in enhancing HER catalysis
of MoS$_2$, the relatively high overpotential required to drive the HER process and the
difficulty in exposing more edge sites becomes a key bottleneck for practical
application.

Aiming to achieve higher HER activity, many other Mo-based catalysts,
including molybdenum nitrides, carbides, borides, and phosphides, have been
intensively explored during the past few years. For example, Zou et al. proposed a
Mo$_2$C-NC hybrid, which exhibited an unprecedented electrocatalytic activity over a
wide pH range.$^{11}$ The synergy between ultrafine Mo$_2$C nanoparticles and N-doped
carbon was found to yield powerful nonmetallic catalytic sites on the carbon
nanolayers. Fang et al. prepared a Co-promoted MoP catalyst where the addition of
Co not only reduced the particle size and promoted the charge transfer, but also
enhanced the intrinsic activity of active sites, thus contributing to the superior HER
activity.$^{17}$ Xie et al developed atomically-thin MoN nanosheets and confirmed that the
apical Mo atoms on the surface of the nanosheets were catalytically active for HER.$^{18}$

These examples suggest that well-designed nanostructure, abundant porosity,
conductive supports, and appropriate modification of lattice structure through doping
are important attributes to achieving optimized HER activities.

By taking advantage of the unique thermal behavior and chemical reactivity,
metal-organic frameworks (MOFs), constructed by alternatively connecting metal
ions with organic ligands in a three dimensional space, can provide a platform for the synthesis of a wide variety of functional materials for many applications. In particular, they are very appealing precursors or templates for the fabrication of porous carbon and/or metal-based nanocomposites.\textsuperscript{19-22} For example, Lou et al. have recently synthesized porous molybdenum carbide nano-octahedrons as an electrocatalyst for HER by confined carburization of molybdenum in MOFs at 800 °C under nitrogen atmosphere.\textsuperscript{23} To date, however, little attention has been paid to the fabrication of Mo-based nitrides or phosphides derived from MOFs.

As compared to molybdenum carbides (Mo\textsubscript{x}C), molybdenum nitrides (Mo\textsubscript{x}N) were reported to have poorer activity for HER.\textsuperscript{24,25} Here we report our findings in the development of porous molybdenum nitride@nitrogen-doped carbon (MoN-NC) nano-octahedrons as an outstanding electrocatalyst for HER due largely to a strong coupling effect between the two phases. The Cu-based NENU-5 MOFs were used as both the reactant and the confined reactor for modified calcination process. Instead of forming a Mo\textsubscript{x}C-C composite from calcination at elevated temperature, the precursor is converted to MoN through a two-step calcination process at a relatively low temperature (650 °C) in different atmospheres (N\textsubscript{2} and NH\textsubscript{3}). Inheriting the morphology of the nano-octahedrons, the as-prepared MoN-NC composite shows remarkable electrocatalytic activity for HER in an acidic electrolyte, far more active than the Mo\textsubscript{x}C-C catalyst derived from similar precursors\textsuperscript{23} and outperforming most non-precious metal catalysts. Specifically, it has demonstrated a small overpotential of 62 mV at 10 mA cm\textsuperscript{-2} ($\eta_{10}$), a small Tafel slope of 54 mV dec\textsuperscript{-1}, and a large
exchange current density of 0.778 mA cm\(^{-2}\). More attractively, such high performance was achieved with a rather low catalyst loading (0.145 mg cm\(^{-2}\)). The outstanding performance is attributed to the nanostructures of the MoN phase, the high porosity of the electrode, and the synergistic effect between the MoN and the nitrogen doped carbon substrate.

EXPERIMENTAL SECTION

**Preparation of NENU-5 nano-octahedrons.** NENU-5 nano-octahedrons were applied as the precursor for the synthesis of hierarchical porous MoN-CN nano-octahedrons. The synthesis of NENU-5 was followed a procedure according to a previous report.\(^{[23]}\) Typically, 0.3992 g of copper acetate monohydrate, 0.1471 g of L-glutamic acid and 0.6 g of phosphomolybdic acid hydrate were added in sequence into 80 mL of deionized water and stirred at ambient condition for 20 min. After that, 0.2814 g of 1,3,5-benzenetricarboxylic acid completely dissolved in 80 mL of ethanol was introduced into the above solution under continuous stirring. The solution turned turbid immediately due to the rapid formation of NENU-5. After stirring for 14 h, the green precipitate was collected by suction filtration, rinsed with DI water and finally dried at 70 °C for 12 h.

**Preparation of porous MoO\(_2\)-C nano-octahedrons.** The NENU-5 nano-octahedrons were transferred to a quartz boat and annealed at 650 °C for 3 h under an argon atmosphere with the temperature ramp of 2 °C min\(^{-1}\). During the calcinations, the Mo in the pores of NENU-5 was converted to MoO\(_2\), while the
organic ligands in NENU-5 were converted to solid carbon. The as-obtained sample was denoted as MoO$_2$-C-Cu. Then the copper particles were removed by dispersing the sample in 0.1 M FeCl$_3$ aqueous solution at ambient condition for 2 h. The resulting MoO$_2$-C nano-octahedrons were obtained by suction filtration, washed with DI water, followed by vacuum drying at 70 °C for 12 h.

**Preparation of porous MoN-NC nano-octahedrons.** The MoO$_2$-C nano-octahedrons were spread out in a quartz boat and annealed at 650 °C for 6 h under ammonia flow and the heating rate was set at 2 °C min$^{-1}$. Finally, the porous MoN-NC nano-octahedrons were obtained. As control experiment, bulk MoO$_2$ was annealed under the same procedure to prepare the bulk MoN material. Caution: ammonia is a corrosive, toxic gas which must be used in a properly ventilated area.

**Characterizations.** The crystallographic information of the samples were evaluated through RT powder X-ray diffraction (XRD) measurement on a Bruker D8 Advance diffractometer with Cu Kα source over a 2θ range from 20° to 80°. The microstructure images were observed with field-emission scanning electron microscope (FE-SEM) (HITACHI S-4800), transmission electron microscope (TEM) and high-resolution transmission electron microscope (HR-TEM) (JEOL JEM-200CX). X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI550 system and the as-obtained spectra were fitted through XPSPEAK41 software. Raman spectra were collected by an HR800 UV micro-Raman spectrometer. Thermogravimetric analysis (TGA) was performed employing a WCT-1 TG Analyzer under air flow to determine the carbon content of the product. Nitrogen
adsorption-desorption isotherms were measured using an adsorption-desorption instrument (BELSORP-MINI, Japan) with nitrogen at 77 K. The samples were pretreated at 200 °C for 2 h under vacuum to remove surface-adsorbed species before analysis. Specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) equation. Pore-size distributions (PSD) were calculated with the adsorption branch of the isotherm using the QSDFT method.

**Electrochemical measurements.** Electrochemical measurements were conducted at room temperature in a standard three-electrode electrochemical cell (Pine Research Instrumentation) in an RDE configuration with a CHI 760E bipotentiostat. All tests were performed in a 0.5 M H₂SO₄ aqueous solution. An Ag/AgCl electrode (4 M KCl) and platinum wire were used as the reference and counter electrode, respectively. 2 mg of the measured material (MoN-NC nano-octahedrons, bulk MoN, commercial Pt/C) and 50 µL 5 wt% Nafion solution were dispersed in 0.5 mL water/ethanol mixture (v_water/v_ethanol=4:1) by mild sonication. Then, a 5-µL aliquot of the homogeneous catalyst ink was pipetted onto the surface of the GC substrate (0.1256 cm²), yielding an approximate catalyst loading of 0.145 mg cm⁻². The as-prepared catalyst film was dried at room temperature.

To confirm hydrogen evolution on the catalysts, we performed rotating ring disk electrode (RRDE) measurement. The potential of the Pt-ring electrode in the RRDE system was kept at -0.4626 V (vs. Ag/AgCl) to ensure the hydrogen generated from the catalysts on the disk electrode is oxidized at the ring electrode.
All currents presented in this work were normalized with respect to the geometrical surface area of GC. All the potentials shown were recorded with respect to the reversible hydrogen electrode (RHE) after IR correction using the following equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.2374 \ V$. Thousands of potential cycles were conducted with continuous argon gas in the potential region from 0 to -0.8 \ V (vs Ag/AgCl) at a sweep rate of $100 \ \text{mV s}^{-1}$ under 2400 rpm till the cyclic voltammetry curves (CVs) stay unchanged. Polarization curves were recorded using linear sweep voltammetry (LSV) from 0 to -0.6 \ V (vs Ag/AgCl) at a sweep rate of $5 \ \text{mV s}^{-1}$ under 2400 rpm. The polarization curves were replotted as overpotential ($\eta$) versus the logarithm of current density ($\log |j|$) to obtain Tafel plots. The linear portions of the Tafel plots were then fitted to the Tafel equation ($\eta = b \log |j| + a$) to obtain the Tafel slope ($b$). The cyclic voltammograms (CVs) obtained with different rates from 20 to 200 \ mV s$^{-1}$ in the potential range of 0.2-0.4 \ V (vs. RHE) were recorded to calculate the electrochemical double-layer capacitances (EDLCs), $C_{dl}$. Accelerated stability tests of the catalysts was studied at room temperature by potential cycling between 0 and -0.6 \ V (vs Ag/AgCl) at a sweep rate of $100 \ \text{mV s}^{-1}$ for a given number of cycles. The long-term stability was also tested at a constant cathodic current density of 25 mA cm$^{-2}$ for 15 hours. The electrochemical impedance spectroscopy (EIS) measurements were carried out at overpotential of 50 mV under the influence of an AC voltage of 5 mV from 100000 Hz to 0.1 Hz.

RESULTS AND DISCUSSION
Schematically illustrated in Scheme 1 is the procedure used for the fabrication of the MoN-NC nano-octahedrons. In step I, the as-prepared NENU-5 nano-octahedrons were converted to porous MoO$_2$-Cu-C nano-octahedrons by annealing in argon atmosphere at 650 °C for 3 h. At such a low temperature, the reaction between MoO$_2$ and solid carbon was effectively suppressed.$^{26}$ In step II, the metallic Cu nanoparticles in the nano-octahedrons were etched by aqueous solution of FeCl$_3$. In step III, a subsequent thermal transformation process took place in ammonia to form MoN nanoparticles and, simultaneously, nitrogen doped into the carbon framework to form porous octahedron-shaped MoN-NC nanocomposite.

![Scheme 1](image.png)

**Scheme 1.** Procedure for the synthesis of MoN-NC nano-octahedrons derived from Mo-based MOFs.

The SEM image shown in Figure S1 confirmed that NENU-5 nano-octahedrons were successfully formed from the facile and scalable co-precipitation synthesis. Representative field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the as-obtained MoN-NC nanocomposites are shown in Figure 1. The low-magnification SEM image in Figure 1a reveals that the octahedral shape of the NENU-5 particles, with the average particle size of ~800 nm, was well maintained in the final product after the multi-step
treatments. As seen from the SEM image in Figure 1b, the rough surface of the octahedron-shaped nanoparticles is rich in nanopores, suggesting their porous nature. The TEM image shown in Figure 1c reveals more detailed morphological features; the sample appears as rhombic under TEM observation. Through a closer observation on the edge of these nano-octahedrons (Figure 1d), numerous clusters (dark spots as marked by white circles inside the figure) embedded in an amorphous carbon matrix were detected. Clear lattice spacing of 0.245 nm was measured for such dot spots from the HR-TEM pattern (inset of Figure 1d), which is coincident with the spacing of the (200) crystal planes for the MoN phase (JCPDS No. 89-2904), suggesting the MoN origin of such nanoclusters. From Figure 1d, it is clearly demonstrated both the MoN phase and the carbon phase were strongly coupled. Such intimate contact allows the efficient charge transfer between the two phases to create a synergistic effect. Moreover, the scanning transmission electron microscopy (STEM) image and the corresponding energy disperse spectrum (EDS) elemental mapping analysis of the selected region reveal the distribution of the elements in the composite. As shown in Figure 1e, all elements (Mo, N, and C) are homogeneously distributed, demonstrating the uniform distribution of the MoN nanoparticles and carbon (nitrogen-doped) inside these octahedrons.
Figure 1. (a) Low and (b) High magnification SEM, (c) TEM, (d) HRTEM images of the porous MoN-NC nano-octahedrons. (e) S-TEM image and the corresponding elemental mapping of molybdenum, nitrogen, and carbon.

The porous nature of the as-synthesized MoN-NC nano-octahedrons was confirmed by the nitrogen adsorption-desorption measurement. The sample possesses a type IV isotherm (Figure S2a). The large hysteresis loop at medium and high pressure region suggests the presence of mesopores. The pore size of the material was further analyzed based on the isotherm (Figure S2b), which shows a hierarchical size distribution centered at 14 nm. The pore volume was calculated to be as high as 0.33 mL g$^{-1}$. Such rich mesopores and high porosity allow the easy penetration of liquid electrolyte and help increase the exposed active sites for HER.$^{28-34}$ A good electrocatalytic activity for HER is then expected. Based on the nitrogen
adsorption-desorption isotherm, the Brunauer-Emmett-Teller (BET) specific surface area was calculated to be 243.5 m$^2$ g$^{-1}$. For comparison, the specific surface area of bulk-phase MoN was also measured. As shown in Figure S2c&d, much smaller hysteresis loop was observed in the nitrogen adosprtion-desorption profile, suggesting the lack of mesopores, and the BET area was calculated to be 26.8 m$^2$ g$^{-1}$, which is only 1/9 that of the MoN-NC nano-octahedrons. Clearly, the characteristic porous structure of MOFs precursor and the presence of amorphous carbon contributed to the rich porous structure of MoN-NC sample.$^{19-21}$

To get information about the phase evolution during the synthesis of the MoN-NC composite, XRD patterns of the samples obtained at different stages of synthesis were characterized and shown in Figure S3 and Figure 2. In addition to the diffraction peaks for the MoO$_2$ phase, three additional sharp and strong diffraction peaks were observed at 2-theta of 43.1°, 50.2° and 73.9° from the XRD patterns of the sample after the first thermal treatment (step I), which can be assigned, respectively, to the (111), (200), and (220) diffraction planes of metallic Cu phase (Figure S3). At 650 °C, the reaction of MoO$_2$ with carbon was suppressed due to kinetic limitation; thus, no MoC$_x$ phase was detected at this stage. As depicted in Figure 2a, all diffraction peaks assignable to metallic Cu phase disappeared completely after the Fe$^{3+}$ etching (step II) and the new diffraction patterns overlap satisfactorily with that of a monoclinic MoO$_2$ phase (JCPDS No. 78-1070), suggesting that the metallic Cu was successfully removed after the second step treatment. After a further nitridation reaction (step III), five characterized peaks for the crystallized MoN phase (JCPDS
No. 89-2904) appeared while all diffraction peaks for the monoclinic MoO$_2$ were no
longer observable, suggesting that all MoO$_2$ nanocrystals were successfully converted
to MoN phase. The resulting products after the step II and the step III were further
analyzed using Raman spectroscopy to characterize the state of the carbon phase in
the composites (Figure 2b). Obviously, both spectra display D-band at 1349 cm$^{-1}$ and
G-band at 1600 cm$^{-1}$, respectively. The D band is defect induced Raman features,
while the G band is related to the in-plane vibrations of the sp$^2$ carbon atoms.$^{33,34}$ The
intensity ratio of D band to G band ($I_D/I_G$) increased from 1.26 for MoO$_2$-C (after
the step II) to 1.35 for MoN-NC nano-octahedrons (after the step III), suggesting that
more structural defects for the carbon phase in the MoN-NC composite than in the
MoO$_2$-C phase after the step II, presumably originated from the nitrogen doping in the
carbon framework.$^{29,35}$ The successful doping of nitrogen into carbon structure will be
discussed later. The content of carbon in the nanocomposite turned out to be around
32.0 wt% based on thermogravimetric analysis (Figure S4 with detailed illustration).

To probe the surface property of the as-synthesized MoN-NC composite, we
performed XPS analyses. Distinct peaks in the overview survey spectrum (Figure S5a,
supporting information) clearly show the concomitance of Mo, O, N and C elements.
The high-resolution Mo 3d spectrum can be fitted to three doublets (Figure 2c). The
doublet centered at higher binding energy (235.9/232.7 eV) is attributed to the Mo
(VI) oxidation state, the other pair of peaks (232.9/229.7 eV) confirms the presence of
Mo (IV) oxidation state,$^{26,28,33}$ and the last two weak peaks located at 232.5 eV and
229.2 eV reveal the Mo-N bonds in the molybdenum nitride.$^{36}$ The dominant
oxidation states for Mo (Mo$^{5+}$ and Mo$^{4+}$), as explained by previous studies, are likely originated from the slight oxidation of surface during the sample preparation for XPS measurements.\textsuperscript{26,28} In the corresponding N 1s spectrum (Figure 2d), two individual peaks (N1) at 395.02/397.82 eV are referred to MoN nanoparticles, while the peaks of pyridinic N (N2, 399.03 eV) and graphitic N (N3, 401.57 eV)\textsuperscript{36} clearly indicate the successful incorporation of nitrogen atoms into the carbon substrate. The N doping was also confirmed in the C 1s spectrum (Figure S5b), which has a peak at 286.0 eV, the characteristic peak of carbon in C-N.\textsuperscript{35,36} It is generally believed that N doping can introduce more charge carriers and improve the interaction of active sites with proton, which is expected to enhance the catalytic activity.\textsuperscript{28,29,35}
Figure 2. (a) XRD patterns and (b) Raman spectra of the intermediate MoO$_2$-C and the as-obtained MoN-NC nano-octahedrons. (c, d) high-resolution XPS spectra of Mo 3d and N 1s of the MoN-NC nano-octahedrons.

The electrocatalytic performance of the as-prepared MoN-NC nano-octahedrons for HER was then evaluated in a 0.5 M H$_2$SO$_4$ electrolyte using a three-electrode system. The intermediate MoO$_2$-C, bulk-phase MoN and commercial Pt/C (20 wt%) were also tested for direct comparison. During the test, the same catalyst loading of approximately 0.145 mg cm$^{-2}$ was applied for all four electrodes to ensure reasonable comparison. The typical polarization curves of the four electrodes are illustrated in Figure 3a. The intermediate MoO$_2$-C and the bulk-phase MoN show rather poor performance for HER, indicated by a large initial overpotential of 121 mV and a large overpotential of 291 and 258 mV at the representative current density of 10 mA cm$^{-2}$ ($\eta_{10}$), respectively. In stark contrast, the activated MoN-NC nano-octahedrons electrode displays a very small $U_{\text{onset}}$ value (near zero, close to that of benchmark Pt/C); the corresponding $\eta_{10}$ value is 62 mV, only 42 mV more than that of the commercial 20 wt% Pt/C (20 mV), but significantly outperforms many leading non-precious metal-based catalysts for HER in an acidic electrolyte (Table S1). The RRDE measurement confirmed that H$_2$ was produced selectively by all catalysts (Figure S6). After normalization by specific surface area (Figure S7), the MoN-NC catalyst still exhibited better HER activity than the bulk MoN. More attractively, such outstanding performance of the MoN-NC catalyst was achieved with very low loading (0.145 mg cm$^{-2}$); in contrast, the mass loading of catalyst for many tests reported in the literature is ~0.3 mg cm$^{-2}$ or even higher than 1.0 mg cm$^{-2}$ in some cases (Table
S1). The results imply that the as-prepared MoN-NC nano-octahedrons have very high electrocatalytic activity for HER.

It is worth noting that, similar to many Mo-based catalysts,\textsuperscript{28,35} the electrochemical activation by cyclic voltammetry (CV) scans played a pivotal role in revealing the actual electrochemical performance of the MoN-NC catalysts (Figure S8), since a progressive increase in electrocatalytic activity for HER was observed with the number of CV cycling in the early stage of the test until a steady performance was reached. To understand the mechanism of the activation process, we performed XPS analysis of the activated MoN-NC nano-octahedrons. Compared with the freshly prepared sample, the intensity of the Mo\textsuperscript{6+} and Mo\textsuperscript{4+} peaks became less prominent after the activation, indicating some dissolution of the surface metal oxides during the repeated CV scans (Figure S9a&d).\textsuperscript{28} From Figure S9b&e, the intensity of the N1 doublet (for MoN) increased in the track of N 1s electron. Interestingly, new oxidized forms of carbon were observed in the region of high binding energy and labeled as epoxy carbon and carboxyl group, respectively (Figure S9c&f). It can be intuitively speculated that, after the activation process, the increased exposure of MoN as well as the growth of negatively charged carboxyl/epoxy group on the surface of carbon enhanced the bonding to proton, leading to significant improvement in HER activity.\textsuperscript{37}

It also should be mentioned that the performance of the current MoN-NC nano-octahedrons is significantly better than the reported MoC\textsubscript{x}-C nano-octahedrons
derived from similar MOF precursor.\textsuperscript{23} Here, the MoC\textsubscript{x}-C catalyst was synthesized by strictly following the synthetic process from Prof. Lou’s report, and two catalyst loadings of 0.145 and 0.8 mg cm\textsuperscript{2} were applied during the test. Shown in Figure S10a is a comparison of the performance for the MoN-NC (0.145 mg cm\textsuperscript{2}), the MoC\textsubscript{x}-C (0.145 and 0.8 mg cm\textsuperscript{2}) as prepared in lab, and the MoC\textsubscript{x}-C (0.8 mg cm\textsuperscript{2}) reported by Lou \textit{et al.}\textsuperscript{23} At a catalyst loading of 0.8 mg cm\textsuperscript{2}, our result for the as-prepared MoC\textsubscript{x}-C matched pretty well with that of Lou’s work, confirming the reproducibility of the work. At a catalyst loading of 0.145 mg cm\textsuperscript{2}, the MoC\textsubscript{x}-C showed a large overpotential of 191 mV at the current density of 10 mA cm\textsuperscript{2}, as a comparison of only 62 mV for the MoN-NC nano-octahedrons electrode. Also, the nitrogen-doped blank carbon was prepared following the same procedure as that of MoN-NC without the addition of Mo source, and the carbon after nitrogen doping shows significant improvement in catalytic activity for HER (Figure S10b). Apparently, the N dopants in the carbon substrate of the MoN-NC composite contributed to the enhanced catalytic activity since MoN was reported to have poorer activity for HER than Mo\textsubscript{2}C\textsubscript{2}.\textsuperscript{24,25} As demonstrated in the literature, nitrogen atoms with lone-pair electrons in carbon lattice can interact with protons or water better than carbon atoms, thus enhancing the reactivity between electrocatalyst and reactants. More significantly, due to the relatively high electronegativity of N compared with that of C, the dopants render higher positive charge density on their adjacent carbon atoms, by virtue of which these carbon atoms become catalytic active sites.\textsuperscript{33,39,40} The synergy likely created between MoN and NC due to the strong coupling effect could also contribute
to the activity of MoN-NC for HER. Nevertheless, more in-depth investigations are needed to gain deeper insight into the mechanism of the improvement.

Shown in Figure 3b are some Tafel plots constructed from steady-state polarization measurements to reveal the HER activity from a kinetic viewpoint. Tafel slopes of 36, 54, 134 and 148 mV dec\(^{-1}\) were obtained for the commercial Pt/C catalyst, the MoN-NC composite, the bulk MoN and the intermediate MoO\(_2\)-C, respectively. According to the three principal steps involved in the hydrogen evolution (Volmer reaction, Tafel slope 120 mV dec\(^{-1}\); Tafel reaction, Tafel slope 30 mV dec\(^{-1}\); Heyrovsky reaction, Tafel slope 40mV dec\(^{-1}\),\(^{39,40}\) the HER mechanism of the MoN-NC nano-octahedrons catalyst follows the Volmer-Heyrovsky reaction where the electrochemical desorption is the rate-determining step. The exchange current density \(j_0\), determined from the extrapolation of the Tafel plots (Figure S11), of the MoN-NC nano-octahedrons is \(\sim0.778\) mA cm\(^{-2}\), which is over 6 times that of the bulk MoN (0.125 mA cm\(^{-2}\)).\(^{39,40}\) Both the Tafel slope and \(j_0\) are either comparable with or even superior to those of the leading transition metal-based HER electrocatalysts, such as Mo\(_x\)C nanooctahedron prepared by a similar method,\(^{23}\) Mo\(_x\)C-Ni@NCV,\(^{28}\) MoP|S,\(^{41}\) P-WN/rGO\(^{42}\), and CoP nanoparticles\(^{43}\) (see Table S1).

Moreover, the low Tafel slope of the MoN-NC nano-octahedrons catalyst is attributed mainly to the strong electronic coupling between the MoN nanoparticles and N-doped carbon substrate.\(^{39}\) The fast charge transfer is also reflected by the electrochemical impedance spectra (EIS) shown in Figure 3c (at \(\eta=50\) mV). As expected, the
MoN-NC composite catalyst exhibits much lower charge transfer resistance than the bulk MoN and the intermediate MoO$_2$-C catalysts.

To further illustrate the superior HER performance of the as-prepared MoN-NC nano-octahedrons, the electrochemically active surface area (ECSA) was estimated from the corresponding electrochemical double-layer capacitances ($C_{dl}$).\textsuperscript{39,40} Voltammetric study of the MoN-NC nano-octahedrons within the potential range of +0.2 to 0.4 V (Figure 3d), where no Faradaic reaction occurred, implies a large $C_{dl}$ value of 10.1 mF cm$^{-2}$, which is much larger than those of the bulk-phase MoN and the intermediate MoO$_2$-C (Figure S12). This suggests that the MoN-NC composite possesses a higher ECSA, which allows more effective accessibility of its active sites.\textsuperscript{28,40} Such large ECSA for the MoN-NC could be resulted from its high specific surface area (243.5 m$^2$ g$^{-1}$), the potential catalyst role of NC, and the synergy from the strong coupling effect of the two phases (MoN and NC).
Figure 3. (a) Polarization curves (iR-compensated) in 0.5 M H$_2$SO$_4$ at a scan rate of 5 mV s$^{-1}$ and (b) the corresponding Tafel plots of the MoN-NC nano-octahedrons, intermediate MoO$_2$-C, bulk MoN, and 20% Pt/C catalysts. (c) EIS Nyquist plots of MoN-NC, intermediate MoO$_2$-C, and bulk MoN catalysts collected at HER overpotential of 50 mV. (d) CV curves recorded for MoN-NC nano-octahedrons catalyst at 20 to 200 mV s$^{-1}$ in the potential range of 0.2-0.4 V (inset: Linear fitting of the capacitive currents versus CV scan rates for MoN-NC nano-octahedrons).

To evaluate the stability of the MoN-NC nano-octahedrons electrocatalyst, we collected polarization curves before and after 3000 continuous cyclic voltammetric (CV) sweeps (Figure 4a). Clearly, there is negligible degradation in term of both the HER onset overpotential and the cathodic current density, suggesting long-term stability of the material under operating conditions. TEM examination of the cycled MoN-NC nano-octahedrons (Figure 4b) indicated that the octahedron morphology and crystallinity were well maintained after the cycling test. Moreover, the
current-time plot at a static potential of 88 mV was depicted in Figure 4c. The current density has no obvious decrease over 15 h, further confirming the stability of the material.

![Figure 4](image)

**Figure 4.** (a) Polarization curves for MoN-NC nano-octahedrons. (b) TEM image of the MoN-NC nano-octahedrons after 3,000 cycling CV scans (at 5 mV/s within a potential range of -0.6-0 V vs. RHE). (c) Current density as a function of time for MoN-NC nano-octahedrons sat at a constant overpotential of 88 mV.

On the basis of above analysis, the enhanced HER catalytic activity of the MoN-NC nano-octahedrons can be attributed to the following main factors. First, the growth of MoN nanoparticles are limited within the carbonaceous matrix derived from the organic ligands of MOFs, which is beneficial to expose more active sites. Second, the carbon matrix not only hampers the aggregation of MoN nanoparticles and thus reduces the particle-to-particle interfacial resistance, but also acts as a highly efficient conductive framework and provides paths for rapid electron transfer from the
MoN nanoparticles to the electrode. Importantly, nitrogen doping can improve the conductivity of the carbon support and increase the H^+ adsorption sites which further enhance the HER activity. Third, the highly porous structure is expected to enlarge the contact surface between electrode and liquid electrolyte, and facilitate the charge and mass transfer during the electrochemical reactions. Fourth, the strong coupling between the MoN phase and the NC substrate may create a synergistic effect, which helps improve the HER activity of MoN phase. Last, the uniform and robust structure derived from the MOF precursor effectively prohibited the detachment or aggregation of MoN, contributing to excellent operation stability of the MoN-NC catalyst.\textsuperscript{35}

CONCLUSIONS

In summary, MoN-NC nano-octahedrons have been synthesized using a metal-organic-framework-assisted strategy with controlled calcinations. The unique features of this catalyst include nano-sized nanoparticles of MoN uniformly dispersed on a highly porous N-doped carbon matrix. The as-prepared MoN-NC nano-octahedrons exhibit prominent electrocatalytic activity, representing one of the best non-precious metal-based HER catalysts in an acid electrolyte ever reported. This study not only provides a novel electrocatalyst with excellent activity towards HER but also opens a new avenue to fabrication of high-performance electrocatalysts from MOFs for HER, ORR, or other applications.

ASSOCIATED CONTENT
**Supporting Information.** This material is available free of charge via the Internet at http://pubs.acs.org. FESEM image of NENU-5; N₂ sorption isotherms; XRD pattern; TGA curve; XPS spectra; RRDE measurements of H₂ evolution; Polarization curves normalized by specific surface area; Polarization curves before and after CV activation; XPS spectra before and after CV activation; Polarization curves compared with MoCₓ-C; exchange current calculation; Electrochemical CV scans; Table S1.

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**Notes**

The authors declare no competing financial interest.

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Scheme 1. Procedure for the synthesis of MoN-NC nano-octahedrons derived from Mo-based MOFs.

NENU-5 \[\xrightarrow{650 \degree C, \text{Argon}}\] MoO\(_2\)-C-Cu \[\xrightarrow{\text{Etching}}\] MoO\(_2\)-C \[\xrightarrow{650 \degree C, \text{Amonia}}\] MoN-NC

1234x415mm (96 x 96 DPI)
Figure 1 (a) Low and (b) High magnification SEM, (c) TEM, (d) HRTEM images of the porous MoN-NC nano-octahedrons. (e) S-TEM image and the corresponding elemental mapping images of molybdenum, nitrogen and carbon.

470x468mm (96 x 96 DPI)
Figure 2. (a) XRD patterns and (b) Raman spectra of the intermediate MoO2-C and the as-obtained MoN-NC nano-octahedrons. (c, d) high-resolution XPS spectra of Mo 3d and N 1s of the MoN-NC nano-octahedrons.

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