High-Performance N₂-to-NH₃ Conversion Electro catalyzed by Mo₂C Nanorod

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ABSTRACT: The synthesis of NH₃ is mainly dominated by the traditional energy-consuming Haber–Bosch process with a mass of CO₂ emission. Electrochemical conversion of N₂ to NH₃ emerges as a carbon-free process for the sustainable artificial N₂ reduction reaction (NRR), but requires an efficient and stable electrocatalyst. Here, we report that the Mo₂C nanorod serves as an excellent NRR electrocatalyst for artificial N₂ fixation to NH₃ with strong durability and acceptable selectivity under ambient conditions. Such a catalyst shows a high Faradaic efficiency of 8.13% and NH₃ yield of 95.1 μg h⁻¹ mg⁻¹cat at −0.3 V in 0.1 M HCl, surpassing the majority of reported electrochemical conversion NRR catalysts. Density functional theory calculation was carried out to gain further insight into the catalytic mechanism involved.

As a necessary industrial chemical, NH₃ has been employed in medication, fertilizer, fuel, and explosives, etc. Today, ever-increasing NH₃ consumption stimulates intensive research on artificial N₂ fixation technology. However, industrial-scale NH₃ production mainly depends on the Haber–Bosch process, which is performed under rigorous conditions (350–550 °C and 150–350 atm) with rather high energy consumption and CO₂ emission. Therefore, it is urgently needed to develop an energy-saving and environmentally benign technological process for NH₃ production. Electrochemical reduction has emerged as a promising method for artificial N₂ fixation under ambient conditions. However, the N₂ reduction reaction (NRR) process needs to break a rather inert molecular structure of N₂ with extremely high bond energy of about 941 kJ mol⁻¹. Thus, electrocatalysts with high activity for the NRR are a prerequisite. In nature, N₂ fixation can be catalyzed under ambient conditions by Mo-dependent nitrogenases, via multiple proton and electron transfer steps. Mo has also emerged as an interesting metal for homogeneous N₂ functionalization reactions, and some Mo-based molecular complexes have been designed and synthesized for artificial N₂ fixation. However, other than stability of these catalysts, it is also challenging to effectively graft such catalysts onto electrodes for electrochemical tests and applications. Therefore, it is highly pressing to develop Mo-based heterogeneous electrocatalysts to solve these problems. Recently, (110)-oriented Mo nanofilm was reported for N₂ reduction electrocatalysis with only a Faradaic efficiency (FE) of 0.72%. Our recent studies suggest that MoS₂, MoO₃, MoN, and Mo₂N are effective for the NRR process with Faradaic efficiencies of 1.17%, 1.9%, 1.15%, and 4.5%, respectively. As such, to develop new Mo-based electrocatalysts for the NRR with improved activity is highly desired.

Here, we present our recent study in developing the Mo₂C nanorod as a superb NRR catalyst for artificial N₂ fixation to NH₃ with strong electrochemical durability and acceptable selectivity under ambient conditions. Such Mo₂C achieves an FE as high as 8.13% with NH₃ yield of 95.1 μg h⁻¹ mg⁻¹cat at −0.3 V in 0.1 M HCl, surpassing the majority of reported electrochemical conversion NRR catalysts. Density functional theory calculation was carried out to gain further insight into the catalytic mechanism involved.

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−0.3 V versus reversible hydrogen electrode (RHE) in 0.1 M HCl. The possible NRR catalytic mechanism is also studied by density functional theory (DFT) calculations. The Mo2C nanorod was derived from a Mo-based nanorod precursor (Figure S1) under Ar atmosphere (see the Supporting Information for preparation details). X-ray diffraction (XRD) analysis suggests a hexagonal phase structure of the resulting Mo2C product (JCPDS 79-0744) in Figure 1a. The scanning electron microscopy (SEM) image confirms formation of the Mo2C nanorod (Figure 1b), and the transmission electron microscopy (TEM) image indicates the nanoporous nature (Figure 1c and Figure S2). The high-resolution TEM (HRTEM) image of a nanorod (inset of Figure 1c) suggests an interplanar distance of 2.3 Å, in accordance with Mo2C (121). Energy-dispersive X-ray (EDX) analysis displays a homogeneous distribution of Mo and C in Mo2C (Figure 1d). The X-ray photoelectron spectroscopy (XPS) survey spectrum (Figure S3) suggests the presence of C and Mo elements. In the Mo 3d region (Figure 1e), the binding energies (BEs) at 228.5 and 231.5 eV are matched well with Mo3+ in Mo2C.30,31 The BEs at 229.5, 232.6, and 235.4 eV are assigned to Mo3d5/2, Mo3d3/2, and Mo6+ regions, respectively, indicating that the surface of the catalyst is oxidized, and the BE at 230.3 eV is ascribed to Mo4+.31 In Figure 1f, the BEs of the C 1s region at 284.8 and 283.5 eV are respectively, indicating that the surface of the catalyst is oxidized, and the BE at 230.3 eV is ascribed to Mo4+.31

Mo2C catalyst was dropped on a glassy carbon electrode, the resulting Mo2C/GCE was tested as an NRR working electrode under ambient conditions in an electrolytic cell separated by a Naﬁon membrane (Figure 2a). During N2 electrolysis, N2 was supplied to the cathode, and the H+ in the electrolytic cell can transfer through the HCl electrolyte solution to react with N2 for NH3 production. The potential was reported on an RHE scale. Linear sweep voltammetry (LSV) curves of Mo2C/GCE are provided in Figure S4 under N2- and Ar-saturated electrolytes (0.1 M HCl). The black line of the LSV curve is gained by N2 bubbling, which exhibits a slightly higher catalytic current, indicating that N2 is reduced to NH3. The NH3 is detected by indophenol indicator and the byproduct of N2H4 is also determined by means of Watt and Chrisp.36 The calibration curves are given in Figures S5 and S6. Figure 2b shows UV−vis absorption spectra, which are colored with indophenol indicator of the 3 h NRR process at some constant potentials. Mo2C/GCE exhibits excellent selectivity without N2H4 production (Figure S7). The NRR process of Mo2C/GCE is operated from −0.2 to −0.6 V. In Figure 2c, the FE and NH3 yields are provided. The most effective NRR rate is located at −0.3 V versus RHE, and the FE and NH3 yield are calculated as 8.13% and 95.1 μmol g−1cat, respectively. Our Mo2C/GCE compares favorably to the NRR behaviors of many aqueous-based NRR electrocatalysts under ambient conditions like Au/TiO2 (21.4 μmol h−1g−1cat),37 Au nanorods (6.042 μmol h−1g−1cat),38 and γ-Fe2O3 (0.212 μmol h−1g−1cat).39 etc. Table S1 gives a detailed comparison of NRR electrocatalysts at ambient conditions. Of note, Mo2C/GCE is even superior to some reported catalysts under severe reaction conditions (Table S2). When applied potential surpasses −0.3 V, the NRR properties (NH3 yield and FE) reduce obviously, because of competitive adsorption of nitrogen and H+ on Mo2C/GCE.9 Moreover, in Figure S8, corresponding H2 yield and the relevant FEs of the hydrogen evolution reaction (HER, a competitive process) are provided. Upon combination of the data of the HER and NRR, the remaining nearly 50% Faraday loss at low potential (−0.2 V versus RHE) could be attributed to the following three aspects: (1) capacitance consumption of catalyst, (2)
dynamic hydrogen adsorption and absorption on the catalyst, and (3) uncontrollable experimental error. Figure 2d compares the amount of NH$_3$ generated using Mo$_2$C/GCE and blank GCE as the working electrodes at −0.3 V after 3 h of electrolysis. Clearly, the bare GCE exhibits poor electrocatalytic NRR activity. It is also noted that there is almost no NH$_3$ detected in the electrolytes after similar cathodic tests in comparative experiments (Figure S9). All of these results strongly support that NH$_3$ originates from electrochemical N$_2$ reduction effectively catalyzed by the Mo$_2$C nanorod.

Durability is a critical parameter to assess the properties of NRR catalysts. In Figure 3a, Mo$_2$C/GCE exhibits excellent durability at each given potential. The catalytic experiments were performed six times using the same catalyst. Because of the strong durability of the catalyst (Figure 3b), the FE and NH$_3$ yield are rather stable at ambient conditions for the NRR (at potential of −0.3 V versus RHE in Figure 3c). The values of NH$_3$ produced are listed as an average of six catalytic runs. Meanwhile, 25 h long-term electrolysis at −0.3 V demonstrates nearly unchanged current density (Figure 3d). After electrolysis, such Mo$_2$C/GCE exhibits an excellent NRR performance (Figure S10) before its real longevity of 58 h (Figure S11). After the durability test, the pH of the electrolyte is changed from 1 to 1.2. The negligible change is due to the usage of a Nafion membrane (Figure 2a) in the two-compartment cell, where H$^+$ is supplied from the anode to cathode continuously during H$^+$ consumption when the NRR occurs. Meanwhile, we also carried out an NRR electrocatalytic experiment in 0.05 M H$_2$SO$_4$ electrolyte. The results indicate that there are no variations in both conditions (Figure S12).

Figure S18 shows the NRR performance of the catalyst electrode by alternating 3 h cycles of N$_2$-/Ar-saturated electrolyte solutions, respectively. The NH$_3$ can only be detected in the electrocatalysis process of the N$_2$-saturated HCl solution, while Ar-saturated electrolytes exhibit blank results, further ensuring the electrocatalytic NRR process on Mo$_2$C/GCE. Moreover, the time-dependent experiment further confirms the results (Figure 3e). For verification that the ammonia is derived from the N$_2$ gas supplied, a $^{15}$N isotopic labeling experiment is carried out. In Figure 3f of the $^1$H nuclear magnetic resonance ($^1$H NMR) spectra, the standard sample displays a doublet coupling for $^{15}$NH$_4^+$. $^{15}$N$_2$ is used as the feeding gas with $^{15}$NH$_4^+$ formation, and Ar is used as the feeding gas.
feeding gas without any NH$_4^+$ formation. These results provide vital evidence to ensure that the produced NH$_3$ is electrocatalytically reduced by Mo$_2$C.

For an understanding of the mechanism of the NRR process occurring on the catalyst Mo$_2$C (121) surface, extensive first-principles calculations were performed to investigate the adsorption of NH$_x$ species, the free energy profile, as well as the electronic structures of the critical steps. The results are presented in Figure 4. It is known that the N$_2$ molecule adsorption and the first hydrogenation reaction ($^*$N$_2$ $\rightarrow$ *NNH) to open the N≡N bond are the critical steps to determine the NRR performance. Upon full relaxation, our results show that the N$_2$ molecule is tilted on the exposed Mo atom of the Mo$_2$C (121) surface with the elongated N—N bond length of 1.13 Å, yielding a large adsorption energy of 1.39 eV and short N—Mo distance (2.08 Å). The strong chemical adsorption of N$_2$ implies that Mo$_2$C would be quite active to catalyze the dissociation of the N$_2$ molecule. The atom-projected density of state (DOS) (Figure 4b) shows different features of the two N atoms in the *N$_2$ configuration. The N$_2$ packet below the Fermi level is entirely covered by the Mo atom within −1.0 and 0 eV, verifying the Mo—N$_2$ chemical bonding. However, the curve of the N1 atom below the Fermi level is negligible. The charge density difference of the *N$_2$ state visualized in Figure 4d shows that the electron depletion occurs at the N1—N$_2$ region and accumulates at the Mo—N$_2$ bond, inducing the dissociation of the N$_2$ molecule. The chemical bonding of the N$_1$ atom to the outmost Mo atom leads to a significant decrease of the free energy of *N$_2$ down by 0.91 eV under the zero electrical potential. Realizing the first hydrogenation step is of great importance for the NRR process. As shown in Figure 4a, the moderate free energy change of 0.74 eV suggests that it is feasible for this step on the Mo$_2$C (121) surface to take place.

Figure 4. (a) Free energy profile for the NRR process under different electrical potentials. An asterisk (*) denotes as the adsorption site. The competitive processes are represented as the light lines. The inserted images are the reactions with uphill free energy changes. (b, c) Atom-projected DOS of the *N$_2$ and *NNH configurations; (d, e) charge density difference of the *N$_2$ and *NNH configurations, respectively. The isosurface level is 0.0013 e Å$^{-3}$.

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without the electrical potential. The DOS of the *NNH configuration in Figure 4c makes evident the chemical bonding interactions of H—N1—N2—Mo at the energy range from −1.0 to 0 eV. The amplified DOS of the N2 atom suggests the enhanced bonding interactions with the anchored Mo atom. The results are consistent with the charge density difference analysis in Figure 4e.

Sequentially, there are different pathways for other hydrogen atoms to go to the next hydrogenation steps. In principle, the second hydrogen might go either on the distal pathway to bond with the lower Mo-anchored N atom to form *NNNH, or on the alternating path to form *NNH2 with the upper H-bonded N atom. The free energy diagram shows that *NNH2 formation is an exothermic reaction and thus more energetically preferable, while it is uphill in free energy with 0.49 eV energy change to form *NNNH. Sequential addition of the third hydrogen to form *NNH3 is also favorable since it is steeply downhill in the free energy. Because of the relatively strong binding interactions with the exposed Mo atoms, NH3 needs an external energy of 0.76 eV to escape from the surface, which is the potential-determining step. Hydrogenation of the retained *N is feasibly realized to form *NH because the uphill free energy change is only 0.08 eV. Of note, the subsequent processes for *NH2 and *NH formation are downhill. The release of the second NH3 needs a high free energy change of 1.15 eV. The competitive reaction steps represented by the light black line might also take place under the experimental conditions because it is easy to overcome the 0.49 eV uphill free energy change for the *NNH → *NNNH step, and it is downhill in free energy from *NNNH to *NNH2NH3. After the release of the first NH3 molecule, there is no difference in the rest of the steps in both pathways. As for the influence of the applied electric potential on the NRR process, the energy profiles under U = −0.1, −0.3, and −0.5 V are shown in Figure 4a. The results indicate that application of the electrical potential is beneficial for the decrease of all the uphill energy changes; e.g., the value of 0.74 eV without external electric potential for addition of the first H atom is reduced to 0.24 eV under the electric potential of U = −0.5 V. The uphill energy change of 0.49 eV on the alternating pathway (light black line) is gradually reduced to 0.39, 0.19, and 0 eV with the applied electrical potential U = −0.1, −0.3, and −0.5 V, respectively. Therefore, the external electric potential promotes the NRR process.

In summary, the Mo2C nanorod is proven experimentally as an efficient and durable catalyst for electrochemical conversion of N2 to NH3 with good selectivity under ambient conditions. Such Mo2C/GCE achieves a high FE of 8.13% and NH3 yield of 95.1 μg h−1 mg−1cat at potential of −0.3 V, with strong electrochemical durability in 0.1 M HCl electrolyte. This research not only supplies an efficient earth-abundant nanocatalyst toward NH3 electrosynthesis, but also opens up a new path to the rational design and development of Mo-based nanomaterials as effective electrocatalysts for artificial N2 fixing.48

Additional experimental details and images including SEM, TEM, HRTEM, XRD, XPS, UV–vis absorption spectra, LSV and calibration curves, NH3 yield and FE, and H2 yield and FE (PDF)

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Notes
The authors declare no competing financial interest. Safety statement: no unexpected or unusually high safety hazards were encountered.

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