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Atomically dispersed Mo catalysts for high-efficiency ambient N₂ fixation

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Abstract: NH₃ synthesis by electrocatalytic N₂ reduction reaction (NRR) under ambient conditions is an appealing alternative to the industrial method that requires high temperature and pressure. Herein, we report single Mo atoms anchored to N-doped porous carbon, which works as a costeffective catalyst for NRR. Benefiting from the optimally high density of active sites and hierarchically porous carbon frameworks, this catalyst achieves a high NH₃ yield rate (34.0 ± 3.6 μg_{NH3} h⁻¹ mg_{cat.}⁻¹) and a high Faradaic efficiency (14.6 ± 1.6 %) in 0.1 M KOH at room temperature. These are considerably higher values compared with those for previously reported non-precious-metal electrocatalysts. Moreover, this catalyst displays no obvious current drop during a 50,000second NRR. Similarly, high activity and durability are also achieved in 0.1 M HCl by the catalyst. This work may provide a promising lead for designing efficient and robust single-atom non-precious-metal catalysts toward electrolytic NRR.

Fixation of naturally abundant nitrogen (N₂) into ammonia (NH₃) is one of the most important and challenging chemical transformations required for eliminating hunger and generating potential carbon-free condensed fuels.^[1-4] From an energy-saving perspective, green fixation methods for NH₃ from N₂ are strongly desired because the Haber-Bosch process, the main industrial process for producing NH₃, requires extremely harsh reaction conditions (400–600 °C, 20–40 MPa) and causes pollution and greenhouse gas emissions.^[5-7] The electrocatalytic

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Supporting information for this article is given via a link at the end of the document. N_2 reduction reaction (NRR) offers a promising carbon-free strategy toward cleaner and more sustainable NH_3 production.^[8-27] However, the efficiency of NRR suffers from a parallel hydrogen evolution reaction (HER) in aqueous solutions on traditional NRR electrocatalysts.^[7]

Consequently, a variety of noble metal-based, non-noble metal-based and metal-free materials have been developed for NRR electrocatalysts at ambient conditions with aqueous electrolytes.^[8,14-26] Of them, electrocatalysts based on noble metals, such as Au,^[8,14] Ru,^[15,16] and Rh,^[17] show favorable activities with hollow Au nanocages exhibiting the reported highest Faradaic efficiency (FE) of 30.2 % and the corresponding NH₃ yield rate of 3.9 µg h⁻¹ cm^{-2,[14]} and their further advances would overcome the barrier of their high costs for their widespread use. Non-noble metal-based catalysts have also been extensively investigated to develop cost-effective and high-performance NRR electrocatalysts, including Fe₂O₃-CNT,^[18] Mo₂C/C,^[19] Bi₄V₂O₁₁/CeO₂,^[20] MoS₂,^[21] Ti₃C₂T_x,^[22] etc. A notable example involves the $Bi_4V_2O_{11}/CeO_2$ hybrid for producing NH₃, where the highest FE and NH₃ yield rate were achieved to be 10.16 % and 23.21 µg h⁻¹ mg_{cat.}⁻¹, respectively.^[20] Metal-free catalysts, such as boron carbide,^[23] porous carbon,^[24] and their derivatives^[25,26] are another type of alternative materials, of which boron carbide (B₄C) nanosheets presented the highest FE of 15.95 % and the corresponding NH₃ yield rate of 26.57 μ g h⁻¹ mg-1_{cat}.^[23] These significant breakthroughs guide the scientific community to pay attention to developing cost-effective and high-performance NRR electrocatalysts for achieving both of high FE and high NH₃ yield rate in aqueous solution at ambient conditions.

The activity of metal-based nanocatalysts is highly influenced by their size.^[27] It has been established that metal atoms with unsaturated coordination are likely to the active catalytic centers.^[27] Therefore, when optimization catalysts, it is highly desired to simultaneously decrease the size of a catalyst and increase the fraction of metal atoms that has unsaturated coordination. On the basis of this aspect, atomically dispersed catalysts with mononuclear non-precious-metal complexes or single non-precious-metal atoms anchored on supports would be a promising candidate for NRR catalysts, because of their maximum atom efficiency, unique catalytic performances, and unsaturated metal coordination environment.^[28-32] Considering that nearly all natural N2 fixations are achieved with the enzyme nitrogenase produced in bacteria and the active center of the nitrogenase is an Mo-based structure,^[33] single Mo atoms could be a promising catalyst. Moreover, a density functional theory (DFT) simulation in 2017 has predicted that single Mo atoms immobilized on defective boron nitride (BN) monolayers can be a potential NRR electrocatalyst to yield NH₃,^[34] in which atomically dispersed Mo atoms bonded to N atoms will contribute good performances in activating N₂ molecules and stabilizing N₂H while destabilizing NH₂ species during the NRR.

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This theoretical work shows that single-atom anchor sites can be a possible alternative to the ambient condition enzymic reaction; however, the poor electrical conductivity of BN should be carefully considered if one wants to realize and use this material for the NRR.

Herein, we fabricated and optimized single Mo atoms anchored on N-doped porous carbon (SA-Mo/NPC) and employed them as a catalyst (Figure 1a) for electrochemically catalyzing the NRR. Due to the optimized abundance of single active sites and the 3D hierarchically porous feature, the catalyst exhibited a remarkable FE of NH₃ formation up to 14.6 \pm 1.6 % (corresponding to an NH₃ yield rate of 34.0 \pm 3.6 μ g_{NH3} h⁻¹ mg_{cat.}⁻¹) at -0.3 V relative to the reversible hydrogen electrode (vs RHE) in 0.1 M KOH at room temperature. This is among the best reported NRR electrocatalyst performances (Table S1). Moreover, SA-Mo/NPC showed negligible activity decay in an NRR electrolysis as long as 50,000 s. Meantime, similarly high NRR activity and robust durability were also exhibited by SA-Mo/NPC in 0.1 M HCl. This work provides a promising route for the development of efficient and robust single-atom catalysts for the N₂ fixation.



Figure 1. Structure of SA-Mo/NPC. (a) Schematic illustration of SA-Mo/NPC and its corresponding atomic structure model. (b) TEM image. (c) Mo EDS mapping revealing the homogeneous distribution of Mo on the carbon support, in which the inset is the corresponding HAADF-STEM image. (d) Atomic-resolution HAADF-STEM image. (e) EELS spectra from areas A and B in the atomic-resolution HAADF-STEM image of the inset, in which areas A and B does and does not contain single Mo atoms, respectively. The two orange arrows point to the signals of Mo $M_{4,5}$ and $M_{2,3}$ edges, respectively.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) characterizations show that SA-Mo/NPC has 3D interconnected carbon frameworks with randomly opened porous structure (Figures 1b and S1). Brunauer-Emmett-Teller (BET) analysis gives its specific surface area to be 302.3 m² g⁻¹ and indicates the hierarchical existence of meso- and macro-porous features (Figure S2). Such a 3D porous structure was etched by NH₃, which was produced from decomposition of the hydroxylamine hydrochloride precursor. It is of advantage to the accessibility of active sites and the mass transport during electrochemical catalytic processes.^[31] Further, elemental mapping performed by energy-dispersive X-ray spectroscopy (EDS) manifests the existence of Mo, C and N and their homogenous distributions over the entire architectures (Figures 1c and S3). High-resolution TEM (HRTEM) imaging and selected area electron diffraction (SAED) demonstrate the amorphousness of SA-Mo/NPC (Figure S4). This finding coincides well with X-ray diffraction (XRD) measurements (Figure S5), in which no reflection peaks exist for Mo-related crystals and only humps from amorphous carbon are found. Using aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) technique with sub-Å resolution, many isolated bright dots on carbon surfaces are observed (Figures 1d and S6). They are identified by electron energy-loss spectroscopy (EELS) to be Mo atoms (Figure 1e). In addition, the Mo loading was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis, and its value corresponding to Figure 1d is 9.54 wt%.



Figure 2. Synchrotron radiation XANES measurements and XPS spectra. (a) XANES and (b) FT-EXAFS curves of SA-Mo/NPC at Mo K-edge. (c) Mo 3d, (d) N 1s and (e) C 1s XPS spectra of SA-Mo/NPC.

To explore the local structure of Mo speciation, synchrotronradiation-based hard X-ray absorption spectroscopy (XAS) measurements were performed. The Mo K-edge X-ray absorption near-edge structure (XANES) of SA-Mo/NPC, with a Mo foil and Mo₂C as references, is displayed in Figure 2a. A shift in the Mo K-edge to a higher energy compared with the references indicates that the valence of Mo species in SA-Mo/NPC is > +2.[31] We compare the XANES spectrum of SA-Mo/NPC with MoO_3 and MoO_2 references and find that the single site is predominantly +6 (Figure S7). To figure out the component ratio of Mo⁶⁺ to Mo⁴⁺, which will be further verified by X-ray photoelectron spectroscopy (XPS) results, we fit the SA-Mo/NPC XANES spectrum using the spectra of MoO₃ and MoO₂ references. The best fit gives about 82.5% of Mo6+ and 17.5% of Mo⁴⁺. The Fourier transform (FT) k²-weighted extended X-ray absorption fine structure (EXAFS) spectra of SA-Mo/NPC and the references are shown in Figure 2b. The strongest peak of SA-Mo/NPC is located at ~1.2 Å, which is associated with the

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Mo-C or Mo-N contribution,^[31] and thus its existence indicates that the Mo atoms in SA-Mo/NPC are mainly bonded with C or N. Meanwhile, the peak corresponding to the Mo-Mo signal at ~2.6 Å is very weak and much lower than the Mo-C/N peak, manifesting that most of the Mo atoms are isolated from each other. The above results are in a good agreement with Figures 1d and S6, which show that only a slight fraction of the Mo atoms are close to each other and their positions are all disordered. Therefore, it is rationally concluded that the Mo atoms in SA-Mo/NPC with the Mo loading of 9.54 wt %, most are in the form of single Mo atoms bonded with C or N atoms, and a slight fraction have weak interactions with neighboring Mo atoms and thus are in the form of clusters. XPS measurement was further performed to investigate the surface composition and valence states of SA-Mo/NPC. Figure 2c confirms the coexistence of Mo4+ and Mo6+ [ref. 35] with 74% Mo6+ and 26% of Mo4+, not far from the XANES result. Comparing the XPS spetra of SA-Mo/NPC with the Mo loading of 9.54 wt % (Figures 1d and S6) and the control sample containing clusters with the Mo loading of 13.40 wt% (Figure S8), we find that the valence state of Mo in SA-Mo/NPC is the coexistence of Mo⁴⁺ and Mo⁶⁺. while Mo³⁺ appears in the control sample (Figure S9).^[36] Thus. the absence of the characteristic peaks dervied from Mo clusters in SA-Mo/NPC reinforces that the quantity of Mo clusters in this sample is ignorable. In the XPS spectrum of N 1s, the peaks at 401.1. 400.1 and 398.5 eV indicate the presence of pyrrolic N. graphitic N and pyridinic N,[37] while the peak at 396.1 eV corresponds to the N-Mo bonds (Figure 2d).^[38] Additionally, Figure 2e shows the formation of C-Mo bonds,^[39] suggesting the strong electronic coupling at the interfaces between Mo atoms and the carbon support. Based on the above results, 3D Ndoped porous carbon frameworks bearing abundant atomically dispersed Mo atoms are well confirmed.



Figure 3. NRR electrochemical performances of SA-Mo/NPC in 0.1 M KOH. (a) Linear sweep voltammetric curves in an N₂-saturated (red line) KOH solution and an Ar-saturated (black line). *j* is current density. (b) NH₃ yield rate (red) and FE (blue) at each given potential. (c) NH₃ yield rates of SA-Mo/NPC samples with different Mo loadings. (d) Chronoamperometric curve and FE stability. The samples corresponding to (a, b and d) have the Mo loading of 9.54 wt%. Each error bar represents a standard deviation from six measurements.

All NRR electrochemical tests were performed at room temperature and atmospheric pressure. In an Ar-saturated KOH solution (Figure 3a), the increase in the current density (*j*) after – 0.25 V vs RHE was caused by the HER, which competes with the NRR. By contrast, a clearly increased reduction current density was observed in an N₂-saturated KOH, suggesting that the catalytic reduction of N₂ to NH₃ is taking place in this system.

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The corresponding NH₃ concentrations, FEs and NH₃ yield rates were measured and obtained using the Nessler's test (see more details in the Experimental section and Figures S10 and S11, which show that the values of FEs and NH₃ yield rates are derived from NH₃ concentrations and reaction times).^[9,40] The highest yield rate and its corresponding NH₃ concentration and FE of SA-Mo/NPC were achieved at -0.3 V vs RHE (Figure 3b), which reached 34.0 \pm 3.6 μg_{NH3} h^{-1} mg_{cat.} ^{-1} (corresponding to 34.0 \pm 3.6 μg_{NH3} h^-1 cm^-2; see Figure S11 and its caption for details), 50.0 ± 5.3 µM at 1 h and 14.6 ± 1.6 %, respectively, comparable to those of the best reported NRR catalysts under similar conditions (Table S1). Further, the NH₃ concentration at -0.3 V vs RHE was also measured by another independent method, ion chromatography (see details in the Experimental section), which directly gave the concentration value to be 47.6 μ M at 1 h. Within error bars, this value equals the one (50.0 ± 5.3 µM) obtained by the Nessler's test, indicating the validity of our experiments. Meanwhile, the high selectivity of SA-Mo/NPC for NH₃ was verified, as no hydrazine was detected. It should be pointed out that if all this extra increased reduction current is used for the NRR under the N2-saturated environment (Figure 3a), the NH₃ yield rate at -0.3 V vs. RHE is calculated to be 119.6 μg_{NH3} h⁻¹ mg_{cat.}⁻¹, higher than the actual value (34.0 ± 3.6 μg_{NH3} h⁻¹ mg_{cat.}⁻¹). This difference between the theoretical and the actual ones is mainly ascribed to the coexistence of competitive hydrogen evolution. Additionally, when N2 was replaced with Ar under electrolysis, no NH₃ was detected, confirming that the bubbled N₂ is the raw source of NH₃ (see Figures S12, S13 and their captions for details). Ammonia contaminations in N2, electrolytes and the catalyst are also excluded (see Figures S14-S16 and their captions for details).[41-43] Further, ¹H nuclear magnetic resonance (NMR) detection with isotope-labelled ¹⁵N₂ (ref. 44) confirms that the ammonia detected in the NRR experiments was produced from the NRR (see Figure S17 and its caption for details).

To explore the effect of the Mo loading in the NRR, potentiostatic tests for SA-Mo/NPC samples with different Mo loadings were conducted under -0.3 V vs RHE. As shown in Figure 3c, when the Mo content was changed from 0 to 13.40 wt%, the NH₃ yield rate gradually increased at first, reached the top point at 9.54 wt% and then decreased. This optimization process suggests the following mechanism: The previous DFT calculation in 2017 has proven that Mo-N sites are active for the NRR,^[34] because they can activate N₂ molecules and stabilize N_2H while destabilizing NH_2 species, which is an NRRimprovement effect. Hence, it is rational to conclude that if the Mo content in an SA-Mo/NPC sample is too low, the improvement effect should be very slight. Thus, increasing the Mo content, namely the density of the atomically dispersed active sites, can make this effect more obvious. But, when the Mo content is too large, we have found that Mo nanoclusters appear, which decrease the amount of the Mo-N sites and thus worsen the effect (see Figures S8 and S18 for details). This worsening also indicates the core role of atomically dispersed Mo atoms bonded to N atoms in the NRR electrocatalysis.

To verify the possible effect of the coexistence of Mo–C moieties (Figure 2e) on the NRR activity of SA-Mo/NPC, we also investigated the catalytic ability of Mo nanoclusters anchored on carbon (NC-Mo/C) for comparison (see Figures S19 and S20 for details). The highest NH₃ yield rate and corresponding FE were measured to be 1.6 \pm 0.2 μ g_{NH3} h⁻¹ mg_{cat.}⁻¹ and 2.1 \pm 0.3 %, respectively, at –0.45 V vs RHE (Figure S21), suggesting that Mo–C can catalyze the NRR to NH₃. This finding resembles the

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observed activity on the Mo₂C nanodots embedded in carbon nanosheets.^[19] Besides the NRR activity, the stability is another critical factor to evaluate an electrocatalyst. As depicted in Figure 3d, SA-Mo/NPC with the optimal Mo loading of 9.54 wt% did not show any obvious decay in the current density during an NRR process as long as 50,000 s, and its FE for producing NH₃ was always no smaller than 14.4 %, ranging from 14.4 % to 16.8 %, indicating its superior electrocatalytic stability. This finding agrees well with the morphology observation (Figure S22) and valence state analysis (Figure S23) of SA-Mo/NPC, which shows the persistence of single Mo atoms.

Importantly, SA-Mo/NPC also displayed a good NRR performance in acidic media (0.1 M HCI). As shown in Figure S24a, an optimum FE of 6.8 ± 0.3% was achieved at -0.25 V vs RHE. The corresponding NH₃ concentration at 1h and NH₃ yield rate were 46.3 \pm 1.8 μ M and 31.5 \pm 1.2 μ g_{NH3} h⁻¹ mg_{cat}⁻¹ (corresponding to 31.5 \pm 1.2 μ g_{NH3} h⁻¹ cm⁻²), respectively (Figures S25 and S26). These values were measured by the indophenol blue method (see details in the Experimental section). We also used the ¹H NMR to measure independently the NH_3 concentration and found it to be 45.2 μM at 1 h (Figure S27). This value equals the above one (46.3 \pm 1.8 μ M) within error bars, also indicating the validity of our experiments. Again, in 0.1 M HCl, SA-Mo/NPC demonstrated a remarkable durability (Figure S24b), which shows that no obvious decays existed in the current density during a 50,000-s NRR process and that the FE was always no smaller than 6.1 % and ranged from 6.1 % to 7.2 %.

In conclusion, we have demonstrated experimentally for the first time that the electrocatalytic NRR is indeed feasible at ambient conditions by using atomically dispersed non-precious-metal-based active sites as heterogeneous electrocatalysts. Remarkably, the as-fabricated electrocatalyst with an optimally high density of single Mo atoms anchored on N-doped porous carbon enables standout NRR performances, which provides a new opportunity to develop advanced catalysts for the N₂ fixation. Together with previously reported studies, ^[44-47] our work containing experimental optimizations may give a fundamental insight into the experimentally valuable design of efficient and robust catalysts toward ambient NH₃ synthesis and thus a lead to the practical application of the ambient NRR.

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Conflict of interest

The authors declare no competing financial interests.

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Atomically dispersed Mo catalysts for high-efficiency ambient N₂ fixation

Single Mo atoms anchored on N-doped porous carbon were designed and synthesized for the electrocatalytic reduction of N_2 to NH_3 . This catalyst exhibited high electrocatalytic activity and high stability. This performance can be attributed to its structure with the conductive carbon support, high porosity and existence of single-atom Mo.