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MoO₃ nanosheet for efficient electrocatalytic N₂ fixation to NH₃

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The synthesis of NH₃ heavily depends on energy-intensive Haber-Bosch process with large amount of greenhouse gas emission. Electrochemical reduction offers a carbon-neutral process to convert N₂ to NH₃ at ambient conditions, but demands efficient and stable catalysts for the N₂ reduction reaction. Mo-dependent nitrogenases and synthetic molecular complexes have attracted increasing attention for N₂ fixation, however, less attention has focused on Mo-based nanocatalysts for electrochemical N₂ conversion to NH₃. Herein, we report that MoO₃ nanosheet acts as an efficient non-noble-metal catalyst for electrochemical N₂ fixation to NH₃ with excellent selectivity at room temperature and atmosphere. In 0.1 M HCl, this catalyst exhibits remarkable NRR activity with a NH3 yield of 4.80×10 $^{-10}$ mol s $^{-1}$ cm $^{-2}$ (29.43 μg h^{-1} $mg_{cat.}^{-1}$) and a Faradaic efficiency of 1.9%. Moreover, this catalyst also shows high electrochemical stability and durability. Density functional theory calculations reveal that outmost Mo atoms serve as the active sites for effective N₂ adsorption.

Fixation of atmospheric N₂ to NH₃ is a fundamental conversion to achieve hydrogen storage and earth nitrogen cycle.^{1,2} Industrially, reaction of N_2 with H_2 to form NH_3 is accomplished via the Haber-Bosch process but with inevitable high temperatures (300-400 °C) and pressures (150-250 atm).³⁻⁶ The intensive energy input (1% of the worldwide energy use) and large CO₂ emissions (1.6% of the total global CO₂ production) push researchers to explore new NH₃ synthesis technology.^{7,8} Electrochemical reduction of N_2 (N_2 + $6H^{+} + 6e^{-} \rightarrow 2NH_{3}$) is attractive for artifical N₂ fixation because it can proceed at ambient conditions using renewable hydro, wind, solar or nuclear energy-driven electricity.⁹⁻¹¹ However, this process involves difficulty in breaking the strong $N\equiv N$ triple bond of inert N₂ and challenged by N₂ activation, underlining the need of high-performance electrocatalysts for the N₂ reduction reaction (NRR).

Noble metals-based materials are efficient NRR electrocatalysts, but the high price and limited availability severely hinder their large-scale uses.^{12–15} Mo is an important element in nitrogenases that catalyze the N_2 fixation at ambient conditions in the biological system.^{16,17} Great attention has also focused on developing Mo-based molecular catalysts for N₂ reduction.^{18,19} However, these catalysts suffer from limited stability under strongly reducing conditions²⁰ and it is challenging to effectively graft them onto electrodes.²¹ More recently, Yang et al. reported on the use of Mo nanofilm as a heterogenous NRR catalyst with a NH₃ yield of 3.09×10^{-11} mol s^{-1} cm⁻² and a Faradic efficiency (FE) of 0.72%.²² Our recent work indicates that MoS₂ nanosheet array is an active NRR electrocatalysis with a higher FE of 1.17%.²³

In this communication, we report our recent finding that MoO₃ nanosheet is efficient for electrochemical N₂ fixation to NH_3 with excellent selectivity at ambient conditions. In 0.1 M HCl, such catalyst attains a NH₃ yield 4.80×10^{-10} mol s⁻¹ cm⁻² (29.43 μ g h⁻¹ mg⁻¹_{cat}) and a FE of 1.9 %. It also shows high electrochemical stability and durability. Density functional theory (DFT) calculations indicate that the outmost Mo atoms serve as the active sites for efficiently adsorbing N_2 .

MoO₃ was made by one-step hydrothermal reaction of molybdenum metal powder, H₂O₂ aqueous solution and ethanol (see Supporting Information for preparation details). As shown in Fig. 1a, the X-ray diffraction (XRD) pattern for the product presents diffraction peaks at 12.76°, 23.34°, 25.68°, 27.34°, 33.72°, 38.92°, 45.82°, 49.26°, 55.24°, and 64.54° indexed to the (020), (110), (040), (021), (111), (060), (200), (002), (112), and (062) crystal planes of MoO₃ (JCPDS No. 05-0508), respectively.²⁴ Fig. 1b shows the X-ray photoelectron spectroscopy (XPS) survey spectrum for MoO₃, confirming the exsitence of Mo and O. Fig. 1c and 1d present the XPS spectra of MoO_3 in the Mo 3d and O 1s regions. In the Mo 3d region

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sprayed Pt on sample surface to enchance the conductivity for SEM characterizations). The EDX elemental mapping images (Fig. 2e and 2f) further confirm that Mo and O elements are uniformly distributed in the product.



(Fig. 1c), the peaks at 235.6 and 232.46 eV are assigned to

 $3d_{3/2}$ and $3d_{5/2}$ of the Mo cations in high oxidation states

(Mo⁶⁺).²⁵ The binding energy at 531.1 eV in the O 1s region (Fig.

1d) is assigned to lattice oxygen (O^{2-}) , ²⁶ and the peak at 532.4



Fig. 2a and 2b show the scanning electron microscopy (SEM) images of MoO₃, suggesting the formation of flake-like nanostructures. The transmission electron microscopy (TEM) image evidences the nanosheet nature of MoO₃ (Fig. 2c). The high-resolution TEM (HRTEM) image reveals well-resolved lattice fringes with interplanar distances of 0.40 and 0.36 nm for the (100) and (001) lattice planes of MoO₃, respectively (Fig. 2d). The energy-dispersive X-ray (EDX) spectrum (Fig. S1) concludes the existence of Mo and O elements with an atomic ratio of 24.63:75.37 (the signal for Pt element arising from





We evaluated the electrocatalytic NRR activity of MoO₃ deposited on glassy carbon electrode (MoO₃/GCE) in 0.1 M HCl, utilizing a two-compartment cell separated by Nafion membrane under ambient temperature (25 °C) and atmospheric pressure (Fig. S2). All overpotentials were reported on a reversible hydrogen electrode scale. Concentrations of produced NH₃ were spectrophotometrically determined by the indophenol blue method $^{\rm 28}$ and N_2H_4 as the possible by-product was detected by the method of Watt and Chrisp.²⁹ Corresponding calibration curve is shown in Fig. S3. Fig. S4 shows the UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after electrolysis at a series of potentials for 2 h. Obviously, NRR can be driven at applied potentials ranging from -0.20 to -0.60 V. The highest absorbance intensity of resulting electrolyte was obtained at -0.50 V. Average NH₃ yields and corresponding FEs under different potentials are calculated and shown in Fig. 3a. The highest FE (1.9%) is achieved at a potential of -0.30 V. As the potential increases from -0.30 to -0.60 V, FE decreases to 0.53%. Also note that a maximum NH₃ yield (29.43 μ g h⁻¹ mg⁻¹ $^{1}_{cat.}$; 4.80×10⁻¹⁰ mol s⁻¹ cm⁻²) can be obtained at –0.50 V, which much larger than reported aqueous-based NRR is electrocatalysts, including Mo nanofilm (3.09×10⁻¹¹ mol s⁻¹ cm⁻ 2), 22 MoS₂/CC (8.08×10⁻¹¹ mol s⁻¹ cm⁻²), 23 Fe₂O₃/CNT (3.6×10⁻¹² mol s^{-1} cm⁻²),³⁰ and Ru/C (3.43×10⁻¹² mol s^{-1} cm⁻²),³¹ etc. More detailed comparison is listed in Table S1. The corresponding performance at a lower potential of -0.40 V is also impressive with maximum NH₃ yield of 28.50 μ g h⁻¹ mg⁻¹_{cat.}. To verify that detected reduction products is generated via the NRR process of MoO₃/GCE, we performed electrolysis in N₂-saturated solution at open circuit potential and Ar-saturated solution at -0.40 V. The corresponding UV-Vis absorption spectra are presented in Fig. S5, enabling a more accurate assessment that eliminates background contributions. We also performed electrolysis in Ar-saturated solution at -0.40 V and almost no

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apparent NH₃ was detected (Fig. S6 and S7). ¹⁵N isotopic labeling experiment was performed as an alternative method to verify the NH₃ originated from N₂ in 0.1 M HCl electrolyte (Fig. S8). The ¹H NMR spectra identified the obtained a doublet coupling for ¹⁵NH₄^{+,5} Only ¹⁵NH₄⁺ was observed after electrolysis in the ¹⁵N₂-saturated electrolyte. These results confirm that the NH₃ in the electrolyte was indeed generated via electrocatalytic N₂ reduction by MoO₃/GCE. We also investigated the catalytic ability of bare GCE. Obviously, bare GCE has low activity for the NRR (Fig. S9). Furthermore, No N₂H₄ was detected, indicating MoO₃/GCE possesses excellent selectivity (Fig. S10).

Stability is another critical parameter to evaluate the performance of catalysts. Under sustained N₂ gas flowing, 24-h electrolysis at -0.40 V only leads to a slight decrease in current density (Fig. S11), confirming its strong stability. After NRR for 24 h, the NH₃ yield rate only shows a slight decrease compared with those after 2 h electrolysis (Fig. S12), suggesting MoO₃/GCE still exhibit effective catalysis after long-term NRR. Consecutive recycling tests (Fig. 3b) were conducted at -0.40 V, showing almost no variation in NH₃ yields and FEs, which indicate high stability of MoO₃/GCE. Fig. 3c shows the long-term electrolysis at different potentials in N₂-saturated 0.1 M HCl solution, indicating high durability of MoO₃/GCE. By varying the N₂ flow rate, NH₃ yield and FE at -0.40 V are also steady without any apparent change (Fig. 3d), suggesting that the N₂ diffusion is a non-rate-determining step.



The NRR process on catalyst was proposed as hydrogenation of the adsorbed N₂ molecule by adding H atom one by one. Fig. 4 shows the free energy profile of the NRR on MoO₃. At the beginning, an intact N₂ molecule is physically adsorbed on the top of the outmost Mo atom (structure a) with an adsorption energy of -0.08 eV and the length of 2.97 Å for the N-Mo bond. The addition of the first hydrogen atom is to form *N₂H (structure b), which is uphill in free energy with the energy change of 2.12 eV. As addition of other two hydrogen atoms to form *NNH₃, the steps become downhill in free energy. Because of the hydrogen bond with the adjacent O atoms, the *NNH₃ group prefers to locate the hollow position (structure c). Nevertheless, release of the first ammonia molecule meets the potential determining step with the largest free energy change of 2.25 eV for the process of from *NNH₃ to *N, where the adsorbed N atom moves back to the top site of the Mo atom with the bond length of 2.89 Å (structure d). Subsequently, the following reduction processes are exergonic steps.

In summary, MoO₃ nanosheet is proved as an efficient nonnoble-metal electrocatalyst for artifical N₂ fixation to NH₃ with excellent selectivity at ambient conditions. It achieves a NH₃ yield of 4.80×10^{-10} mol s⁻¹ cm⁻² (29.43 µg h⁻¹ mg⁻¹_{cat}) and a FE of 1.9%, with high electrochemical stability and durability. DFT calculations reveal that the outmost Mo atoms act as the active sites for effective N₂ adsorption. This study not only offers us an attractive earth-abundant catalyst material for electrochemical NH₃ synthesis, but would open exciting new avenues to the rational design of Mo oxides-based nanocatalysts with enhanced performances for applications.

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