Electrochemical Dinitrogen Reduction to Ammonia by Mo$_2$N: Catalysis or Decomposition?
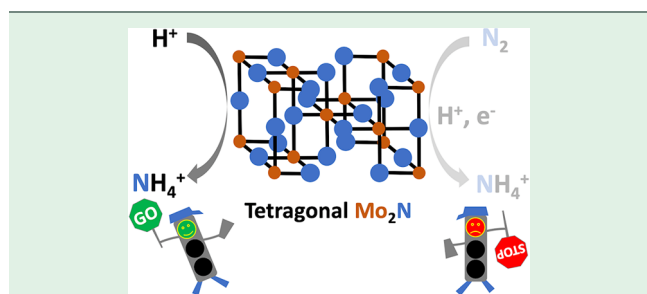
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S *Supporting Information*

ABSTRACT: Instead of catalyzing electrochemical reduction of N$_2$, we found that tetragonal Mo$_2$N undergoes decomposition and results in the generation of ammonia. The present results call urgent attention to the need to carefully evaluate the catalytic nature of the dinitrogen reduction reaction by nitrogen-containing materials.

The century-old Haber−Bosch process remains the only industrial process achieving the large-scale N$_2$ reduction to ammonia production of more than 150 million tons per year.[1−3] Despite its wide application, the Haber−Bosch process is massively energy-consuming for the production of H$_2$ feedstock (ca. 2% of the world's energy supply), is heavily dependent on fossil fuels (3%−5% of the world's natural gas production), and is a significant greenhouse gas emitter.[1−3] Therefore, milder, more energy efficient, and CO$_2$-neutral alternative methods are of great interest for both scientific research and industrial applications.[1−3] Electrochemical synthesis of ammonia from dinitrogen (N$_2$) in the presence of catalysts represents a highly attractive approach.[1−3] Electrochemical devices for the dinitrogen reduction reaction (NRR) could be easily integrated into renewable energy systems, thus reducing the consumption of fossil fuels and the emission of CO$_2$. Because of these potential benefits, electrocatalytic N$_2$ fixation has been under intensive exploration over the past few years and has become a hot topic in catalysis. A number of heterogeneous electrocatalysts have been reported with various claimed performance for the NRR, including noble metals,[4,5] metal oxides,[6] metal sulfides,[7] metal nitrides,[8,9] and metal-free catalysts.[10] Homogeneous electrocatalytic NNR was also recently demonstrated.[11] Metal nitrides have been studied both theoretically and experimentally, indicating their potential capability of electrocatalytic N$_2$ reduction.[8,9,12] However, the presence of nitrogen in the catalyst and the chemical stability problem of the nitride materials could result in ambiguous results.[13] Herein, we carefully examined the catalytic ability of tetragonal Mo$_2$N for the NRR. It is revealed that Mo$_2$N undergoes fast chemical decomposition in aqueous electrolytes and showed no catalytic activity for the NRR.

Tetragonal Mo$_2$N was synthesized via the well-known "urea glass" route according to the literature.[14] In Figure S1, XRD analysis revealed a pure tetragonal phase Mo$_2$N with a good crystallinity that is in line with the standard PDF card. The morphology of the material was studied by SEM, displaying partially aggregated nanoparticles (30−50 nm) with a homogeneous distribution of Mo and N elements (Figure S2).

The synthesized Mo$_2$N was evaluated for the NRR at ambient conditions. Although carbon paper is the most common substrate for catalyst loading in NRR studies, titanium (Ti) was selected as the substrate in this study because of its inertness against hydrogen evolution reaction (HER). To be in accordance with other reported metal nitride catalyzed NRR experiments, our electrochemical studies were conducted in 0.1 M HCl solution (pH 1). Linear sweep voltammetry (LSV) curves were collected on a Mo$_2$N@Ti electrode in both argon- and dinitrogen-saturated electrolytes. As shown in Figure 1A, a slight current increase in the dinitrogen-saturated electrolyte indicated the possibility of catalytic N$_2$ reduction taking place at more negative potential less than −0.22 V. When the catalyst was subjected to controlled potential electrolysis, the current density experienced dramatic change from less than 10 μA cm^{-2} at 0.05 V to 3.3 mA cm^{-2} at −0.25 V vs RHE, which was attributed to the more favorable HER. After bulk electrolysis for 1 h at potential from −0.25 to 0.05 V vs RHE (Figure 1B), the amount of ammonia was detected by UV−vis spectroscopy using the Indophenol-blue assay (Figures 1C and S4). Assuming N$_2$ was eletrocatalytically reduced to ammonia, the highest faradaic efficiency (FE) was obtained at −0.05 V vs RHE up to 42.3% with a yield of 1.99 μg mg^{-1} h^{-1} (Figure 1D). At 0.05 V, the reaction showed the highest yield of 2.73 μg mg^{-1} h^{-1} with a good FE of 28.4%. When the potential was applied to −0.15 V,
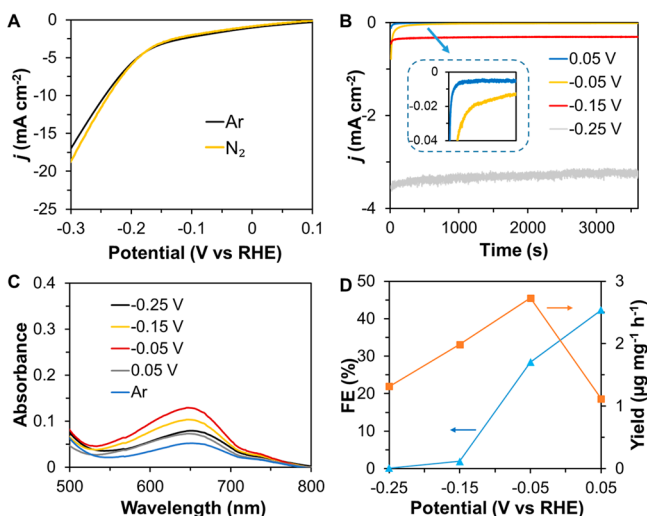
Figure 1. (A) LSV curves for Mo$_2$N@Ti electrode. Scan rate: 50 mV s^{-1}. (B) Chronoamperometric curves for electrolysis at various controlled potentials with N$_2$ as the feed gas. (C) Indophenol-blue assay quantifying ammonium after electrolysis at various controlled potentials. (D) Faradaic efficiency and reaction rate at different potentials.

FE dramatically dropped to 1.93%. In all the experiments, no hydrazine product was detected.

The obtained results which appeared very exciting prompted us to conduct ^{15}N$_2$ controlled experiments to confirm the catalytic nature of the NRR. It is worth noting that non-negligible amounts of ^{15}NH$_4^+$, ^{15}NO$_2^-$, and other impurities exist in the commercialized ^{15}N$_2$ gas.[15] It is also noted that the reported ^{15}N$_2$ controlled experiments seldom included pretreatment, resulting in ambiguous results. Thus, before the test, the ^{15}N$_2$ gas was treated by 50 mM sulfuric acid overnight to remove any NH$_3$ impurity by formation of NH$_4^+$. After bulk electrolysis under the purified ^{15}N$_2$ gas for 1 h, ^{1}H NMR experiments were carried out to quantify the formation of ^{15}NH$_4^+$. To our surprise, no ^{15}NH$_4^+$ was detected by H NMR (i.e., no doublet peaks), while a significant amount of ^{14}NH$_4^+$ was observed (Figure 2A).
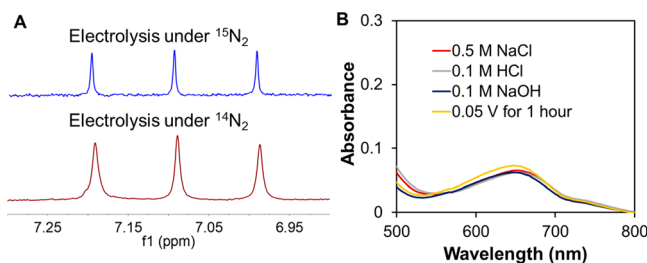

Figure 2. (A) ^{1}H NMR spectra of ammonium in the sampled electrolytes after 1 h of electrolysis in the presence of saturated ^{15}N$_2$ and ^{14}N$_2$. (B) Indophenol-blue assay quantifying ammonium after the electrodes were immersed in the different supporting electrolytes (labeled) for 1 h.

The finding suggested the ammonia formation likely originates from a chemical decomposition process of Mo$_2$N rather than a catalytic process. In order to further elucidate the chemical decomposition of Mo$_2$N, the Mo$_2$N@Ti electrodes were treated in 0.1 M HCl, 0.1 M NaOH, and 0.5 M NaCl solutions. After the electrodes were incubated for 1 h, the detected ammonia for all conditions was just slightly less than the electrolysis at 0.05 V vs

RHE (see Figure 2B). We assume that the decomposition of Mo$_2$N could be accelerated under the electrochemical reduction conditions. Moreover, it is found that Mo$_2$N displayed much poorer stability in alkaline condition than in acidic and neutral conditions. As shown in Figure S3, after 96 h of treatment, much more ammonia was detected in the NaOH solution than in the HCl and NaCl solutions. Mo$_2$N was even totally dissolved in NaOH solution after 1 week.

The failure of the ^{15}N$_2$ isotope-labeling experiment and the observed chemical decomposition lead us to draw the conclusion that Mo$_2$N has no catalytic activity for electrochemical N$_2$ reduction. The present results raise an urgent alert to the application of other metal nitrides and even nitrogen-containing materials for the NRR. In addition to the decomposition of potential catalytic materials, we highlight several other apparent pitfalls to avoid in claiming catalytic NRR. First, nitrogen contaminants in dinitrogen gas, solvents, and other reactants need pretreatment to mitigate background ammonia.[15] Second, ^{15}N labeling experiments must be conducted to confirm the formation of ammonium from dinitrogen. Third, turnover number (>1) for a catalytic process needs to be demonstrated, which requires carefully evaluation of the loading of a catalyst and the yield of ammonium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b00648.

Experimental details and additional data (PDF)

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Notes
The authors declare no competing financial interest.

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