Benchmarking Photocatalysts for Dinitrogen Photoreduction Reaction

Po-Wei Huang, Danae A. Chipoco Haro, Hakhyeon Song, Andrew J. Medford*, Marta C. Hatzell*

*Corresponding Author

marta.hatzell@me.gatech.edu & ajm@gatech.edu

M. C. Hatzell

George W. Woodruff School of Mechanical Engineering and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

Email: marta.hatzell@me.gatech.edu

P.-W. Huang and **A. J. Medford**

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, United States

D. A. Chipoco Haro

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

H. Song

George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

The BIGGER PICTURE

Ammonia is important for producing synthetic fertilizers, and it sustains the growing global population. The current process for ammonia production (Haber-Bosch process) produces 500 million tons of CO_2 each year. Photocatalytic nitrogen reduction reaction (pNRR) for ammonia production does not involve a carbon source and relies on available feedstocks: energy from sunlight, water as a proton source, and air as a nitrogen source. The pNRR is widely reported, but one of the main challenges in pNRR research is to detect ammonia reliably due to adventitious ammonia contamination and nitrogen-containing impurities. We developed a setup to suppress adventitious ammonia contamination and benchmark three photocatalysts. Our results suggest standardization of ammonia measurements in the pNRR field are critical to ensuring reliable results.

SUMMARY

The photocatalytic nitrogen reduction reaction (pNRR) for NH_3 production is often discussed as an attractive sustainable alternative to the thermocatalytic Haber-Bosch process. One of the main challenges in pNRR research is the lack of reliable detection of photochemically produced NH_3, since NH_3 concentrations are often low and nitrogen-containing impurities are ubiquitous in the environment, feedstocks and catalysts. Herein, we identify three key sources of contamination to perform a systematic study to quantify and reduce contamination in the: (i) feed gases $^{15}N_2$, $^{14}N_2$, and Ar, (ii) material precursors, and (iii) hole scavengers (i.e., methanol) used in photocatalysis. We developed a custom photoreactor setup to minimize contamination and used control experiments without a light source, with Ar feed gas, and $^{15}N_2$ isotopic labeling to benchmark three catalysts (Fe-BiOBr, g-C_3N_4/Fe_2O_3, and OV-TiO_2). All three chosen catalysts have previously been reported to be active for pNRR. The results indicate that the pNRR rates of all three catalysts under bench-marking conditions are much lower than previously reported, and in some cases have negligible activity. We suggest essential control experiments to contribute to the standardization of NH_3 measurements in the pNRR field and to help the field elucidate the photoactivity of catalysts toward pNRR.

INTRODUCTION

Nitrogen-based fertilizers (e.g., potassium nitrate, ammonia (NH_3), or urea) have had a profound impact on modern society by ensuring food production. Throughout history, these fertilizers have heavily relied on natural sources such as bird guano or coke deposits.[1,2] In the 20th century, concerns about the ability of naturally sourced fertilizers to sustain the continuously growing population prompted research on development of synthetic fertilizers.[3] One early idea, pioneered by N.R. Dhar in 1941, was the suggestion of light-assisted NH_3 production in soils,[4] which was later advanced in 1977 when Shrauzer and Guth reported conversion of N_2 into NH_3 through a photocatalytic reduction over TiO_2.[5] This breakthrough sparked great research interest in the photocatalytic nitrogen reduction reaction (pNRR).[6–8] However, subsequent studies led to divergent findings. In 1992, Edwards et al. first raised the concern about the effect of adventitious

NH_3 contamination on the interpretation of experimental results.[9] This cast doubt on the feasibility of pNRR and sparked a contentious debate in Angewandte Chemie.[10–12] The lack of consensus and the successful industrialization of thermocatalytic NH_3 synthesis via the Haber-Bosch process led to a decline in studies of pNRR during the following decades.

Current NH_3 production occurs through the Haber-Bosch process, a thermocatalytic process that converts N_2 and H_2 into NH_3. This process is associated with 500 million tons of annual CO_2 emissions, mainly due to its reliance on fossil hydrocarbons (coal or methane) to produce hydrogen feedstock. To meet the Paris Agreement goal of net-zero CO_2 emissions by 2050, current research is actively exploring carbon-neutral or negative alternatives for next-generation NH_3 production. One approach that has already been deployed is to couple carbon capture/storage/utilization techniques with the Haber-Bosch plants to lower CO_2 emissions. Another approach is to replace the H_2 production in the Haber-Bosch process with renewable processes (e.g., water electrolysis or even photolysis). This pathway has gained great attention since it retains the high thermochemical efficiency of the Haber-Bosch process (≥70% in industrial processes) while significantly reducing CO_2 emissions (theoretically can reach carbon-free NH_3 manufacturing). The feasibility of the process depends on the cost of electricity, development of electrocatalytic water splitting, and the implementation of carbon tax, but we can expect this technology on the market in the near future. pNRR as another carbon-free pathway for the synthesis of NH_3 has regained attention (**Fig. 1a**). Unlike the aforementioned sequential processes (where hydrogen production and N_2 reduction reaction are separate processes), pNRR utilizes solar energy to directly convert water (the proton source) and air (the nitrogen source) into NH_3 and produces only environmentally friendly by-products (oxygen). Research has found the development of pNRR very attractive in the pursuit of process intensification and decentralized clean production. Additionally, the development of pNRR technology has also raised interest from the perspective of fundamental science development, since nitrogen photofixation is the process found in nature to regulate the global nitrogen cycle.

The resurgence of pNRR research has also benefited from advances in modern photochemistry and catalyst design. Defects, such as oxygen vacancies (OVs) are closely linked to the photocatalytic yield of NH_3, leading to the common hypothesis that OV is the active site for pNRR.[24,25] Additionally, materials with smaller bandgaps (e.g., bismuth oxyhalides, graphitic carbon nitride, etc.) that respond to visible light have been reported to exhibit photoactivity towards pNRR.[26,27] Despite the progress on the development of active photocatalysts for pNRR, the current NH_3 yield from photocatalytic routes remains low. The low yield makes the results susceptible to the influence of adventitious NH_3 contamination in the environment (**Fig. 1b**). Concerns about false positives from adventitious NH_3 are not unfounded. Recent studies in eNRR have revealed that several catalysts, initially reported to be highly active, were later discovered to be inactive in reducing N_2.[28–30] Triggered by these irreproducible results, a series of discussions ensued, encompassing the identification and elimination of contamination sources, the development of reliable techniques for measuring low concentrations of ammonia, and the establishment of standardized testing protocols for the field.[30–33] Considering that current photocatalytic NH_3 yields are at least an order of magnitude lower than those achieved through electrocatalytic approaches, and given the additional concern regarding the photostability of nitrogen-containing photocatalysts,[34] the issue of contamination becomes even more critical in the field of pNRR.

Recently, discussions on contamination have gradually gained attention in the field of pNRR, with proposed methodologies and good experimental practices to suppress adventitious NH_3.[31,33,35,36] Here, we take a step further to benchmark and reexamine some of the reported photocatalysts, leveraging current knowledge of contamination issues and ammonia quantification. We developed a setup aimed at suppressing contamination from feed gases, equipment/reactors, and catalysts. We synthesized three photocatalysts previously reported to have high activity for photocatalytic NH_3 synthesis (Fe-BiOBr, g-C_3N_4/Fe_2O_3, and OV-TiO_2) and tested their photoactivity using the custom setup with strict controls. The results indicate that NH_3 synthesized from N_2 is negligible in all cases. We suggest essential control experiments that should be used to ensure rigor and reproducibility within the field.

RESULTS AND DISCUSSION

Currently, there are no standardized testing protocols for pNRR.[36] We have chosen experimental parameters that are commonly used in the field or fall within the range described in the literature (e.g. 300W Xenon lamp, solid-liquid suspension reactor, and 50 SCCM flow rate) for the evaluation of the photocatalyst (**Table S1**). Given previously discussed concerns about contamination leading to misleading results, a crucial first step is to carefully inspect and remove any potential contaminants before evaluating the activity of the photocatalysts. Here, we discuss several key aspects of decontamination, such as feed gas treatment, reactor design, and cleaning procedures. Our objective is to minimize contamination interference and establish a rigorous photochemical system for pNRR benchmarking.

In pNRR studies, the feed gas (i.e., N_2) is the most common source of contamination. According to a previous report,[32] even with ultrahigh purity N_2 gas (99. 999\%), in the worst case scenario where all impurities are assumed to be nitrogenous contaminants (NH_3 and NO_x) that can dissolve in the solvent, hundreds to thousands of ppm nitrogenous contaminants (varying by flow rate, duration of bubbling, and the amount of solvent in the reactor) can be introduced into the experiment. This scenario of nitrogenous contamination results in levels of NH_3 much higher than the synthesized NH_3 concentration reported in most pNRR studies (**Fig. 1b**). This makes feed gas pretreatment an essential decontamination step. Although most current studies acknowledge the importance of gas pretreatment, there is still a lack of consensus on the specific methods used to treat gases. This has resulted in the adoption of various approaches in different studies. The absence of systematic discussions evaluating the effectiveness of different gas treatment methods has prevented standardization. Here, we select the three most common pretreatments used in aqueous-based pNRR studies (water trap, acid trap, and alkaline trap) and evaluate their cleaning effects by comparing the levels of NH_3, NO_2^-, and NO_3^- in the reactor after bubbling.

Deionized water (DI water), 0.05M H_2SO_4 (acid trap) or 0.1M KOH with 0.1M $KMnO_4$ (alkaline trap) were added to the gas washing bottles as gas traps that were

connected to a reactor with 30mL of DI water. The gases (N_2 or Ar) were flowed continuously for 4 hours through the gas trap and then the reactor at a rate of 50 SCCM. The flow rate, the amount of solution in the reactor, and the total duration of the bubbling are set to be identical to those used in subsequent photocatalysis experiments. The results show that the concentrations of NH_3 and NO_2^- are quite low (**Fig. 2a**), averaging around 3 ppb even without any treatment. This makes NH_3 and NO_2^- unlikely to be the main contributor to contamination. However, the content of NO_3^- is relatively high, being two orders of magnitude greater than that of NH_3 and NO_2^-, around 0.1 ppm without any treatment. In both eNRR and pNRR, NO_3^- has already been identified as a nitrogenous contaminant that cannot be overlooked, as it is thermodynamically easier to form NH_3 from NO_3^- compared to N_2.[21,32,37] Therefore, for pNRR studies with NH_3 concentrations that fall within this range, extra care is required. Our findings indicate that the alkaline trap exhibits better decontamination efficacy to remove NO_3^-. This is consistent with previous studies suggesting that the alkaline trap can stabilize gaseous NO_x intermediates, thus retaining them in the gas trap.[32] It is worth noting that these contamination levels may vary depending on experimental conditions. Therefore, we recommend using the alkaline trap for aqueous systems and reporting the concentrations of nitrogenous contaminants after purification as a reference for future pNRR research.

In addition, we custom-built a stainless steel photoreactor (**Fig. 2b**), with all nitrogen-free components (**Fig. S1-2**; **Table S2**). The photoreactor is designed not only to prevent potential contamination from nitrogen-containing materials but also to minimize exposure to the environment during sampling, thus reducing the risk of contamination. In addition, the photoreactor is equipped with a water jacket connected to a water circulation system to regulate the temperature during the reaction. Under our experimental conditions, the temperature of 30 mL of DI water can increase by ~10°C after irradiation with a 300W Xenon lamp (full spectrum) for 4 hours (**Fig. S3**). Considering the potential impact of temperature on catalytic performance, we maintained the temperature at 23°C throughout photocatalytic testing. Furthermore, we strictly adhere to a customized cleaning procedure (**Fig. S4**) between experiments. This cleaning procedure includes sonication and rinsing with an ethanol solution (10 vol%), an alkaline solution (0.1 mM KOH), and fresh DI water, and shows better decontamination effect compared to rinsing

with DI water only (**Fig. S5**). This process aims to eradicate any organic or inorganic nitrogenous contaminants that may remain from previous experimental runs. Our system consists of a gas flow meter, an alkaline trap, a water trap, and a custom-built reactor (**Fig. S6**). Adding all these efforts of decontamination (gas treatment and rigorous cleaning), the background concentration of NH_3 in our system during blank tests (without the presence of a photocatalyst) is ~1 ppb. The low concentration NH_3 allows us to exclude the impact of adventitious nitrogen contamination when examining catalyst activity.

Bismuth oxyhalides (BiOX, where X = Cl, Br, I), graphitic carbon nitrides (g-C_3N_4), and defective-TiO_2 are the most commonly reported classes of materials in current pNRR research (**Table S1** and **Fig. 1b**). Here, we selected three representative photocatalysts from these materials to synthesize and test: Fe-BiOBr, g-C_3N_4/Fe_2O_3, and OV-TiO_2 (**Fig. 3a**). X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS) were performed to verify the formation of the target materials (**Fig. S7-9**). Before transfer to the photoreactor, 30 mg of the as-prepared photocatalyst was mixed with 30 mL of DI water, followed by 30 minutes of sonication to ensure proper dispersion of the photocatalyst in the solution. The solution was bubbled with N_2 or Ar for 30 min in the photoreactor, which was then continuously flushed with N_2 or Ar under full-spectrum irradiation, denoted as N_2 light and Ar light, respectively. A control experiment was conducted under the same conditions as N_2 light, with the only difference being the absence of the light source, denoted as N_2 dark. The results show that under the same N_2 environment, the samples exposed to light (N_2 light) show an increase in the concentration of NH_3 compared to the samples kept in the dark (N_2 dark) (**Fig. 3b**). In addition, the observed color change in the solution provides additional evidence that photochemical reactions occur under irradiation of the samples (**Fig. S10-12**). However, a similar increase in NH_3 concentration was observed in both N_2 light and Ar light experiments. One possible explanation is that the photogenerated NH_3 we measured originates from the photoconversion of nitrogen-containing impurities (N impurities) rather than pNRR. Furthermore, the concentration of NH_3 in the solution increased after sonication, especially in the cases of Fe-BiOBr and g-C_3N_4/Fe_2O_3. This also suggests that these photocatalysts introduced nitrogenous contamination (**Fig. S13**). Nitrogenous contamination could be attributed to the use of urea and nitrates in the synthesis process of these two catalysts, which convert to NH_3 and other N impurities (including but not limited to NO_2^- and NO_3^-) during high-temperature reactions. The NH_3 and N impurities remaining in the photocatalyst are released into the DI water during the sonication step, leading to an increase in NH_3 concentration prior to irradiation. Upon exposure to light, the N impurities transform into NH_3, resulting in similar NH_3

concentrations in both N_2 light and Ar light. In particular, all materials were subjected to three rounds of cleaning with ethanol and DI water after synthesis, which is the widely adopted procedure for cleaning photocatalysts according in the literature.[38–41] Our results suggest that materials synthesized from nitrogen-containing precursors require extra caution during cleaning. If the NH_3 difference between the N_2 light and Ar light experiments is not significant (at least an order of magnitude difference), the concentrations of NH_3, NO_2^-, and NO_3^- prior to irradiation should be measured and reported.

The standard benchmark tests presented in **Fig. 3b** utilized a pure aqueous solvent (i.e., DI water). However, hole scavengers are commonly used to suppress recombination and increase photoactivity.[42–44] Methanol is commonly used in pNRR studies as a hole scavenger (**Table S1**). Experiments carried out in 10 vol% methanol solution show a higher concentration of NH_3 than those carried out in DI water (**Fig. 4**). Specifically, in both Fe-BiOBr and g-C_3N_4/Fe_2O_3, the NH_3 concentration increase by 22% and 32% respectively. However, if we conduct the same photocatalytic experiment but replace N_2 with Ar, a similar increase in NH_3 can be observed. The adventitious NH_3 content in the 10 vol% methanol solution was measured to be less than 1 ppb (**Fig. S14**), suggesting that the increase in the concentration of NH_3 is probably due to other N impurities present in the methanol solution, which can be converted into NH_3 through photoconversion, rather than through the photoreduction of N_2 into NH_3. Similar false positive results are observed even using high-purity methanol from different suppliers (**Fig. S14**). One hypothesis is that the increase in NH_3 originates from the photoconversion of NO_3^-, since we have detected the existence of NO_3^- in the methanol solution from the ion chromatography measurement (**Fig. S15**). However, whether NO_3^- is the impurity that leads to false positive results requires further verification and is beyond the scope of this work. Our results here show that methanol (or organic hole scavengers in general) may contain N impurities. Therefore, we recommend that for future studies involving hole scavengers, conducting an Ar control in a solution containing the same hole scavenger (referred to as the hole scavenger Ar control) is essential to validate the hole scavenger effect.

Our photocatalytic test results indicate that these three materials (Fe-BiOBr, g-C_3N_4/Fe_2O_3, and OV-TiO_2) are not active for the pNRR under these conditions. This work

does not aim to refute the theoretical feasibility of pNRR, as it is thermodynamically viable,[21] but suggests that the results in the literature might not be repeatable under the carefully controlled conditions reported here. Furthermore, these results do not conflict with spectroscopic evidence that dinitrogen is activated or reduced in the presence of carbon on TiO_2,[45,46] but indicate that these carbon-mediated reactions with N_2 likely do not result in the catalytic formation of NH_3. We also acknowledge that the catalytic performance of materials is closely related to the synthesis process. Varying material properties, such as surface/bulk defects, may result in different pNRR performances[47,48]. Therefore, we do not intend to discredit these previous reports since we cannot confirm that our materials are identical. However, we seek to reiterate the importance of rigorous testing procedures and encourage independent reproducibility testing between groups where possible, and encourage researchers to submit erratums if their results cannot be reproduced under carefully controlled conditions in their own labs.

As awareness of contamination issues continues to grow, an increasing number of studies in this field are reporting isotope labeling nuclear magnetic resonance (NMR) results to support the production of photofixed NH_3. However, the $^{15}N_2$ gas itself carries isotopic contamination.[30,49] The NMR spectrum (**Fig. 5**) shows that solutions bubbled with 98% $^{15}N_2$, the most used isotopic N_2 gas in the field, exhibit clear doubled peaks (corresponding to 1.16 ppm of $^{15}NH_3$) without irradiation. Pretreatment of $^{15}N_2$ with an alkaline trap (0.1M KOH with 0.1M $KMnO_4$) can effectively prevent the interference of adventitious $^{15}NH_3$. Based on our results, strict gas treatment for $^{15}N_2$ gas is necessary. If $^{15}N_2$ gas is not pretreated, simply reporting the characteristic double peaks from ^{1}H NMR measurements is insufficient to verify the origin of NH_3 because it could potentially be introduced from impurities in the $^{15}N_2$ gas. Currently, the most rigorous standard is still the quantitative isotopic analysis \cite{andersen2019rigorous} where the NH_3 concentration measured using isotope labeling NMR should align with the results of other measurements (e.g., ion chromatography or the colorimetric method).[50] We also recommend including isotopic NMR results obtained without irradiation (referred to as isotopic dark control) to ensure the absence of contamination from $^{15}N_2$.

CONCLUSION

Adventitious NH_3 and N-impurities obscure the study of the photoactivity of catalysts in pNRR. Here, we examine possible sources of contamination: (i) feed gases (N_2 and Ar) flowing into the system, (ii) precursors used in the synthesis of catalysts, and (iii) hole scavenger used during reaction. The three catalysts (Fe-BiOBr, g-C_3N_4/Fe_2O_3, and OV-TiO_2) compared with our custom-built photoreactor, cleaning protocol, and control experiments did not show photoactivity towards pNRR. We aim to raise awareness of the importance of control experiments in elucidating the photoactivity of catalysts for pNRR. The reactor ii) introduces gas treatment (e.g., alkaline trap) in the system to pretreat the feed gas (even isotopically labeled N_2) prior to the reactor, (ii) rigorously cleans the catalyst before using it and reports nitrogenous contamination after catalyst sonication, (iii) performs hole scavenger Ar control experiment to confirm the hole scavenger effect, and (iv) employs quantitative isotopically labeled NMR experiments with cleaned gases to confirm any observed photocatalytic activity. Although these steps require considerable time and resources, they are critical to ensuring the reliability and reproducibility of reported pNRR rates.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

All of the experimental data are available from the lead contact upon reasonable request.

Materials availability

This study did not generate new materials.

Data and code availability

This study did not generate any datasets.

Photocatalytic experiments

The photocatalytic performance of the selected photocatalysts (as-prepared OV-TiO_2, Fe-BiOBr, g-C_3N_4/Fe_2O_3 or commercial p25 TiO_2) was evaluated under full-spectrum irradiation, using a 300 W Xenon lamp (Newport Corporation) as the light source. In a typical experiment, 30 mg of photocatalysts was added to 30 mL of solution (i.e., deionized water or 10 vol% methanol solution), followed by 30 minutes of sonication to obtain a well-dispersed mixture. The mixture was then transferred to our custom-built photoreactor (Fig. S1 & 2). The photoreactor was equipped with a water recirculation attachment to maintain a constant temperature of 23°C. The mixture was continuously stirred in the dark (200 rpm) while ultra-high-purity N_2 or Ar was bubbled through the solution at a flow rate of 50 mL/min for 30 minutes to obtain a saturated aqueous solution. To avoid contamination from the feed gases (N_2 and Ar), the gases were pretreated through an alkaline trap (0.1 M $KMnO_4$ in 0.1 M KOH) to remove adventitious ammonia and NO_x. The photoreactor was then continuously aerated with N_2 or Ar at a 50 mL/min flow rate under full-spectrum irradiation with continuous stirring. For dark control experiments, the experimental setup was identical to that of the N_2 light experiment, except without the exposure to light. The setup for the $^{15}N_2$ contamination experiment, shown in Fig. 5, was very similar to the dark control experiment, except that the nitrogen gas ($^{14}N_2$) was switched to isotope-labeled $^{15}N_2$ gas. After 30 minutes of bubbling, we turned off the gas flow and closed both the gas inlet and outlet of the photoreactor to make it a closed system. The cleaning of the photoreactor strictly follows the cleaning procedure (Fig. S4) we established before every experiment. Additionally, all other equipment, including vials, tubes, filters, cuvettes, and caps, were cleaned with DI water to suppress ammonia contamination before every experiment (and measurement).

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at Chem Catalysis.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and the Gordon and Betty Moore Foundation. D.A.C.H. was partially supported by the RBI Graduate Research Fellowship from the Renewable Bioproducts Institute at Georgia Institute of Technology. We would like to acknowledge Prof. Faisal M. Alamgir from the School of Materials Science and Engineering at the Georgia Institute of Technology for his assistance in the analysis and the discussion of material characterizations.

AUTHOR CONTRIBUTIONS

P.-W.H. designed and performed research, analyzed data, and wrote the paper; D.A.C.H. designed and performed research, analyzed data, and wrote the paper; H.S. performed research, analyzed data, and wrote paper; A.J.M. designed research, analyzed data, and wrote the paper; and M.C.H. designed research, analyzed data, wrote the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCE

1. Sachs, J.D., and Warner, A.M. (1999). The big push, natural resource booms and growth. J. Dev. Econ. *59*, 43–76. https://doi.org/10.1016/S0304-3878(99)00005-X.

2. Rouwenhorst, K.H.R., Travis, A.S., and Lefferts, L. (2022). 1921–2021: A Century of Renewable Ammonia Synthesis. Sustain. Chem. *3*, 149–171. https://doi.org/10.3390/suschem3020011.

3. Russel, D.A., and Williams, G.G. (1977). History of Chemical Fertilizer Development. Soil Sci. Soc. Am. J. *41*, 260–265. https://doi.org/10.2136/sssaj1977.03615995004100020020x.

4. Dhar, N., Seshacharyulu, E., and Biswas, N. (1941). New aspects of nitrogen fixation and loss in soils. Proc. Natl. Inst. Sci. India.

5. Schrauzer, G., and Guth, T. (1977). Photolysis of water and photoreduction of nitrogen on titanium dioxide. J. Am. Chem. Soc. *99*, 7189–7193.

6. Soria, J., Conesa, J., Augugliaro, V., Palmisano, L., Schiavello, M., and Sclafani, A. (1991). Dinitrogen photoreduction to ammonia over titanium dioxide powders doped with ferric ions. J. Phys. Chem. *95*, 274–282.

7. Augugliaro, V., Lauricella, A., Rizzuti, L., Schiavello, M., and Sclafani, A. (1982). Conversion of solar energy to chemical energy by photoassisted processes—I. Preliminary results on ammonia production over doped titanium dioxide catalysts in a fluidized bed reactor. Int. J. Hydrog. Energy *7*, 845–849.

8. Augugliaro, V., D'Alba, F., Rizzuti, L., Schiavello, M., and Sclafani, A. (1982). Conversion of solar energy to chemical energy by photoassisted processes—II. Influence of the iron content on the activity of doped titanium dioxide catalysts for ammonia photoproduction. Int. J. Hydrog. Energy *7*, 851–855. https://doi.org/10.1016/0360-3199(82)90002-7.

9. Edwards, J.G., Davies, J.A., Boucher, D.L., and Mennad, A. (1992). An Opinion on the Heterogeneous Photoreactions of N2 with H2O. Angew. Chem. Int. Ed. Engl. *31*, 480–482. https://doi.org/10.1002/anie.199204801.

10. Augugliaro, V., and Soria, J. (1993). Concerning "an opinion on the heterogeneous photoreduction of N2 with H2O": first letter. Angew. Chem. Int. Ed. Engl. *32*, 550–550.

11. Palmisano, L., Schiavello, M., and Sclafani, A. (1993). Concerning "An Opinion on the Heterogeneous Photoreduction of N2 with H2O": Second Letter. Angew. Chem. Int. Ed. Engl. *32*, 551–551. https://doi.org/10.1002/anie.199305511.

12. Davies, J.A., and Edwards, J.G. (1993). Reply: Standards of Demonstration for the Heterogeneous Photoreactions of N2 with H2O. Angew. Chem. Int. Ed. Engl. *32*, 552–553. https://doi.org/10.1002/anie.199305521.

13. Schlögl, R. (2003). Catalytic synthesis of ammonia—a "never-ending story"? Angew. Chem. Int. Ed. *42*, 2004–2008.

14. David, W. and others (2020). Ammonia: Zero-carbon fertiliser, fuel and energy store. Policy Brief.

15. Van der Hoeven, M., Kobayashi, Y., and Diercks, R. (2013). Technology roadmap: Energy and GHG reductions in the chemical industry via catalytic processes. Int. Energy Agency Paris *56*.

16. Schiffer, Z.J., and Manthiram, K. (2017). Electrification and Decarbonization of the Chemical Industry. Joule *1*, 10–14. https://doi.org/10.1016/j.joule.2017.07.008.

17. Mallapragada, D.S., Dvorkin, Y., Modestino, M.A., Esposito, D.V., Smith, W.A., Hodge, B.-M., Harold, M.P., Donnelly, V.M., Nuz, A., Bloomquist, C., et al. (2023). Decarbonization of the chemical industry through electrification: Barriers and opportunities. Joule *7*, 23–41. https://doi.org/10.1016/j.joule.2022.12.008.

18. Comer, B.M., Fuentes, P., Dimkpa, C.O., Liu, Y.-H., Fernandez, C.A., Arora, P., Realff, M., Singh, U., Hatzell, M.C., and Medford, A.J. (2019). Prospects and Challenges for Solar Fertilizers. Joule *3*, 1578–1605. https://doi.org/10.1016/j.joule.2019.05.001.

19. Fernandez, C.A., Hortance, N.M., Liu, Y.-H., Lim, J., Hatzell, K.B., and Hatzell, M.C. (2020). Opportunities for intermediate temperature renewable ammonia electrosynthesis. J. Mater. Chem. A *8*, 15591–15606.

20. David, W.I., Agnew, G.D., Bañares-Alcántara, R., Barth, J., Hansen, J.B., Bréquigny, P., De Joannon, M., Stott, S.F., Stott, C.F., Guati-Rojo, A., et al. (2024). 2023 roadmap on ammonia as a carbon-free fuel. J. Phys. Energy *6*, 021501.

21. Medford, A.J., and Hatzell, M.C. (2017). Photon-Driven Nitrogen Fixation: Current Progress, Thermodynamic Considerations, and Future Outlook. ACS Catal. *7*, 2624–2643. https://doi.org/10.1021/acscatal.7b00439.

22. Liu, Y.-H., Fernández, C.A., Varanasi, S.A., Bui, N.N., Song, L., and Hatzell, M.C. (2021). Prospects for aerobic photocatalytic nitrogen fixation. ACS Energy Lett. *7*, 24–29.

23. Song, H., Chipoco Haro, D.A., Huang, P.-W., Barrera, L., and Hatzell, M.C. (2023). Progress in Photochemical and Electrochemical C–N Bond Formation for Urea Synthesis. Acc. Chem. Res. *56*, 2944–2953.

24. Li, H., Shang, J., Ai, Z., and Zhang, L. (2015). Efficient Visible Light Nitrogen Fixation with BiOBr Nanosheets of Oxygen Vacancies on the Exposed {001} Facets. J. Am. Chem. Soc. *137*, 6393–6399. https://doi.org/10.1021/jacs.5b03105.

25. Hirakawa, H., Hashimoto, M., Shiraishi, Y., and Hirai, T. (2017). Photocatalytic Conversion of Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. J. Am. Chem. Soc. *139*, 10929–10936. https://doi.org/10.1021/jacs.7b06634.

26. Li, J., Li, H., Zhan, G., and Zhang, L. (2017). Solar Water Splitting and Nitrogen Fixation with Layered Bismuth Oxyhalides. Acc. Chem. Res. *50*, 112–121. https://doi.org/10.1021/acs.accounts.6b00523.

27. Zhang, D., He, W., Ye, J., Gao, X., Wang, D., and Song, J. (2021). Polymeric Carbon Nitride-Derived Photocatalysts for Water Splitting and Nitrogen Fixation. Small *17*, 2005149. https://doi.org/10.1002/smll.202005149.

28. Hao, Y.-C., Chen, L.-W., and Yin, A.-X. (2022). Reply to: Reassessment of the catalytic activity of bismuth for aqueous nitrogen electroreduction. Nat. Catal. *5*, 385–387. https://doi.org/10.1038/s41929-022-00786-3.

29. Choi, J., Du, H.-L., Chatti, M., Suryanto, B.H.R., Simonov, A.N., and MacFarlane, D.R. (2022). Reassessment of the catalytic activity of bismuth for aqueous nitrogen electroreduction. Nat. Catal. *5*, 382–384. https://doi.org/10.1038/s41929-022-00785-4.

30. Andersen, S.Z., Čolić, V., Yang, S., Schwalbe, J.A., Nielander, A.C., McEnaney, J.M., Enemark-Rasmussen, K., Baker, J.G., Singh, A.R., Rohr, B.A., et al. (2019). A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements. Nature *570*, 504–508. https://doi.org/10.1038/s41586-019-1260-x.

31. Iriawan, H., Andersen, S.Z., Zhang, X., Comer, B.M., Barrio, J., Chen, P., Medford, A.J., Stephens, I.E.L., Chorkendorff, I., and Shao-Horn, Y. (2021). Methods for nitrogen activation by reduction and oxidation. Nat. Rev. Methods Primer *1*, 1–26. https://doi.org/10.1038/s43586-021-00053-y.

32. Choi, J., Suryanto, B.H.R., Wang, D., Du, H.-L., Hodgetts, R.Y., Ferrero Vallana, F.M., MacFarlane, D.R., and Simonov, A.N. (2020). Identification and elimination of false positives in electrochemical nitrogen reduction studies. Nat. Commun. *11*, 5546. https://doi.org/10.1038/s41467-020-19130-z.

33. Zhao, Y., Shi, R., Bian, X., Zhou, C., Zhao, Y., Zhang, S., Wu, F., Waterhouse, G.I.N., Wu, L.-Z., Tung, C.-H., et al. (2019). Ammonia Detection Methods in Photocatalytic and Electrocatalytic Experiments: How to Improve the Reliability of NH3 Production Rates? Adv. Sci. *6*, 1802109. https://doi.org/10.1002/advs.201802109.

34. Wang, W., Zhang, H., Zhang, S., Liu, Y., Wang, G., Sun, C., and Zhao, H. (2019). Potassium-ion-assisted regeneration of active cyano groups in carbon nitride nanoribbons: visible-light-driven photocatalytic nitrogen reduction. Angew. Chem. Int. Ed. *58*, 16644–16650.

35. Gao, X., Wen, Y., Qu, D., An, L., Luan, S., Jiang, W., Zong, X., Liu, X., and Sun, Z. (2018). Interference Effect of Alcohol on Nessler's Reagent in Photocatalytic Nitrogen Fixation. ACS Sustain. Chem. Eng. *6*, 5342–5348. https://doi.org/10.1021/acssuschemeng.8b00110.

36. Huang, P.-W., and Hatzell, M.C. (2022). Prospects and good experimental practices for photocatalytic ammonia synthesis. Nat. Commun. *13*, 7908. https://doi.org/10.1038/s41467-022-35489-7.

37. Comer, B.M., and Medford, A.J. (2018). Analysis of Photocatalytic Nitrogen Fixation on Rutile TiO2(110). ACS Sustain. Chem. Eng. *6*, 4648–4660. https://doi.org/10.1021/acssuschemeng.7b03652.

38. Zhao, Y., Zhao, Y., Shi, R., Wang, B., Waterhouse, G.I.N., Wu, L.-Z., Tung, C.-H., and Zhang, T. (2019). Tuning Oxygen Vacancies in Ultrathin TiO2 Nanosheets to Boost Photocatalytic Nitrogen Fixation up to 700 nm. Adv. Mater. *31*, 1806482. https://doi.org/10.1002/adma.201806482.

39. Zhang, S., Zhao, Y., Shi, R., Zhou, C., Waterhouse, G.I.N., Wu, L.-Z., Tung, C.-H., and Zhang, T. (2020). Efficient Photocatalytic Nitrogen Fixation over Cuδ+-Modified Defective ZnAl-Layered Double Hydroxide Nanosheets. Adv. Energy Mater. *10*, 1901973. https://doi.org/10.1002/aenm.201901973.

40. Zhang, S., Zhao, Y., Shi, R., Zhou, C., Waterhouse, G.I.N., Wang, Z., Weng, Y., and Zhang, T. (2021). Sub-3 nm Ultrafine Cu2O for Visible Light Driven Nitrogen Fixation. Angew. Chem. Int. Ed. *60*, 2554–2560. https://doi.org/10.1002/anie.202013594.

41. Liu, Y., Hu, Z., and Yu, J.C. (2020). Fe Enhanced Visible-Light-Driven Nitrogen Fixation on BiOBr Nanosheets. Chem. Mater. *32*, 1488–1494. https://doi.org/10.1021/acs.chemmater.9b04448.

42. Zhang, G., Yang, X., He, C., Zhang, P., and Mi, H. (2020). Constructing a tunable defect structure in TiO 2 for photocatalytic nitrogen fixation. J. Mater. Chem. A *8*, 334–341. https://doi.org/10.1039/C9TA10471B.

43. Cao, S., Zhou, N., Gao, F., Chen, H., and Jiang, F. (2017). All-solid-state Z-scheme 3,4-dihydroxybenzaldehyde-functionalized Ga2O3/graphitic carbon nitride photocatalyst with aromatic rings as electron mediators for visible-light photocatalytic nitrogen fixation. Appl. Catal. B Environ. *218*, 600–610. https://doi.org/10.1016/j.apcatb.2017.07.013.

44. Yao, C., Wang, R., Wang, Z., Lei, H., Dong, X., and He, C. (2019). Highly dispersive and stable Fe 3+ active sites on 2D graphitic carbon nitride nanosheets for efficient visible-light photocatalytic nitrogen fixation. J. Mater. Chem. A *7*, 27547–27559. https://doi.org/10.1039/C9TA09201C.

45. Huang, P.-W., Tian, N., Rajh, T., Liu, Y.-H., Innocenti, G., Sievers, C., Medford, A.J., and Hatzell, M.C. (2023). Formation of carbon-induced nitrogen-centered radicals on titanium dioxide under illumination. JACS Au *3*, 3283–3289.

46. Comer, B.M., Liu, Y.-H., Dixit, M.B., Hatzell, K.B., Ye, Y., Crumlin, E.J., Hatzell, M.C., and Medford, A.J. (2018). The Role of Adventitious Carbon in Photo-catalytic Nitrogen Fixation by Titania. J. Am. Chem. Soc. *140*, 15157–15160. https://doi.org/10.1021/jacs.8b08464.

47. Zou, X., Liu, J., Su, J., Zuo, F., Chen, J., and Feng, P. (2013). Facile Synthesis of Thermal- and Photostable Titania with Paramagnetic Oxygen Vacancies for Visible-Light Photocatalysis. Chem. – Eur. J. *19*, 2866–2873. https://doi.org/10.1002/chem.201202833.

48. Han, Q., Wu, C., Jiao, H., Xu, R., Wang, Y., Xie, J., Guo, Q., and Tang, J. (2021). Rational design of high-concentration Ti3+ in porous carbon-doped TiO2 nanosheets for efficient photocatalytic ammonia synthesis. Adv. Mater. *33*, 2008180.

49. Dabundo, R., Lehmann, M.F., Treibergs, L., Tobias, C.R., Altabet, M.A., Moisander, P.H., and Granger, J. (2014). The contamination of commercial 15N2 gas stocks with 15N-labeled nitrate and ammonium and consequences for nitrogen fixation measurements. PloS One *9*, e110335. https://doi.org/10.1371/journal.pone.0110335.

50. Huang, P.-W., Song, H., Yoo, J., Chipoco Haro, D.A., Lee, H.M., Medford, A.J., and Hatzell, M.C. (2024). Impact of Local Microenvironments on the Selectivity of Electrocatalytic Nitrate Reduction in a BPM-MEA System. Adv. Energy Mater., 2304202.