## Sustainable Ammonia Synthesis from Nitrogen and Water by One-Step Plasma Catalysis

Tianqi Zhang<sup>1</sup>, Renwu Zhou<sup>1,2</sup>, Jungmi Hong<sup>1</sup>, Rusen Zhou<sup>1</sup>, and Patrick Cullen<sup>1</sup>

 <sup>1</sup> School of Chemical and Biomolecular Engineering, University of Sydney, Darlington, NSW 2008, Australia
<sup>2</sup> State Key Laboratory of Electrical Insulation and Power Equipment, Centre for Plasma Biomedicine, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an, Shanxi 710049, People's Republic of China

**Abstract:** Here, using nitrogen and water as raw materials, plasma-induced vibrational excitation is found to decrease the  $N_2$  and  $H_2O$  dissociation barriers, with the presence of matched catalysts in the nonthermal plasma discharge reactor contributing significantly to molecular dissociation on the catalyst surface. This work highlights the potential of nonthermal plasma catalysis for the activation of renewable sources to serve as a new platform for sustainable ammonia production.

Keywords: Ammonia, Green Chemistry, Plasma Chemistry

## 1. Introduction

Ammonia is one of our most important synthetic chemicals. It sustains global food production and is a potential carbon-free vector for storing and transporting hydrogen.<sup>[1, 2]</sup> The Haber-Bosch (H-B) process (N<sub>2</sub> + 3H<sub>2</sub>  $\rightarrow$  2NH<sub>3</sub>), which dominates ammonia synthesis, requires high temperatures and pressures, an ultra-pure H<sub>2</sub> feed, and large centralized production plants to achieve economic viability (Figure S3.1A). The hydrogen is currently almost exclusively derived from the reforming of fossil hydrocarbons, which results in annual CO<sub>2</sub> emissions of 300 Mt,<sup>[3]</sup> ~1.5% of all greenhouse gas emissions.<sup>[4]</sup> A green alternative, for example, a process that enables carbon-neutral and decentralized ammonia production using water as the hydrogen feedstock and powered by renewable energy sources, is urgently required.<sup>[5, 6]</sup>

Photochemical and electrochemical routes have been devised for ammonia synthesis from N<sub>2</sub> and H<sub>2</sub>O under mild conditions.<sup>[7-10]</sup> The focus of these studies lies on the suppression of the competing hydrogen evolution reaction to improve selectivity toward N<sub>2</sub> reduction and/or the design and selection of desirable catalysts to achieve the goal. However, the electrons transferred to N<sub>2</sub> molecules in photocatalysis and electrocatalysis cannot provide sufficient energy to break the strong N=N bonds (bond energy of 945 kJ mol<sup>-1</sup>). As a result, the production rate of ammonia is prohibitively low (Figure 3.1B).

Gas discharge plasmas with highly energetic electrons, generated by applying electrical energy to a feeding gas, are capable of activating inert N<sub>2</sub> molecules into more reactive, vibrationally or electronically excited states to promote dissociation of nitrogen molecules and thus facilitate the breaking of ultra-stable N=N bonds.<sup>[9, 11-13]</sup> Typically, for non-thermal plasma (NTP), the energy introduced mainly heats the electrons, creating a thermal nonequilibrium, energy-efficient and highly reactive environment suitable to couple with catalysts (termed plasma-catalysis), allowing thermodynamically unfavorable reactions to proceed under ambient conditions.<sup>[14, 15]</sup> Also, similarly to electrocatalysis, NTP can be powered by renewable electricity.<sup>[16]</sup> NTP has demonstrated encouraging yields of ammonia; however, the hydrogen species in these reports comes from highpurity H<sub>2</sub>, which is obtained from cost-demanding electrocatalytic hydrogen evolution reactions (HERs) or carbon-intensive reforming processes.<sup>[17, 18]</sup> Substitution of H<sub>2</sub>O for H<sub>2</sub> is key to making NTP-enabled ammonia synthesis sustainable. Understanding the molecular-level mechanisms of the synergetic effects of plasma-catalyst interactions for ammonia from N<sub>2</sub> and H<sub>2</sub>O is crucial for next-step studies.

Recently, the plasma-electrochemical integrated systems have been proposed as an alternative way for nitrogen reduction using N<sub>2</sub> and H<sub>2</sub>O. In these systems, the plasma is utilized for nitrogen activation to subsequently lower the energy barrier to initiate electrochemical processes for nitrogen fixation. One study of significant advance to our study developed a continuous and scalable plasmaelectrochemical hybrid technology for sustainable and facile production of ammonia via a NOx intermediary approach, with a world-leading production rate of green ammonia yielding 23.2 mg h<sup>-1</sup> (3.95 g kWh<sup>-1</sup>).<sup>[7]</sup> Sharma et al. established a plasma-assisted electrochemical approach, in which the hydrogen production (from water oxidation) and nitrogen activation (by the low-pressure plasma at 500  $^{\circ}$ C) were separated, with an energy efficiency of 0.101 g kWh<sup>-1</sup><sup>[19]</sup>. More recently, Muzammil et al. developed a hybrid plasma-thermal catalytic system, combing a plasma-enabled NOx production and a thermal catalysis process, with a relatively high gas flow rate of N<sub>2</sub> (20 L min<sup>-1</sup>) but a high energy efficiency (2.94 g kWh<sup>-1</sup>).<sup>[20]</sup> Nevertheless, the relative complexity of the systems and some challenging process conditions (e.g., low pressure, high temperature or high gas flow rate) may primarily hinder the upscaling of this technology and bring some inevitable environmental challenges.

In our study, we demonstrate a more straightforward one-step process, where both the water dissociation and nitrogen activation are driven by the atmospheric nonthermal plasma under ambient pressure and temperature. Experiments were performed for different reactor configurations, catalysts, discharge powers and gas flow rates with different  $H_2O$  vapor saturations. An optimized configuration of an advanced plasma reactor, packed with a ruthenium (Ru) catalyst, was found to achieve an ammonia production rate of 2.67 mmol  $g_{cat.}^{-1}$  h<sup>-1</sup>. Using spectroscopic and theoretical studies, we elucidate that the high ammonia production is a result of the efficient dissociative adsorption of H<sub>2</sub>O and vibrationally excited N<sub>2</sub>(v) by the plasma-catalyst interactions, predominantly through Eley-Rideal (E-R) reactions.



Fig. 1. Plasma reactor designs and performance.



Fig. 2. Catalyst evaluation for ammonia synthesis.

We begin by studying the effect of the plasma reactor features on the ammonia production rates. Four different reactor configurations (Figure S3.1) are developed: a water-grounded double dielectric barrier discharge (W-DDBD), water-grounded single dielectric barrier discharge (W-DBD), double dielectric barrier discharge – watercooled (DDBD-W) and single dielectric barrier discharge – water-cooled (DBD-W). The configuration markedly affects the NH<sub>3</sub> synthesis performance (Figure 3.1C). While the W-DDBD, W-DBD, DDBD-W reactors show similar ammonia synthesis rates (7.0-9.0  $\mu$ mol h<sup>-1</sup>), the DBD-W using a copper foil sheet as the ground electrode instead of water leads to a significant increase of the NH<sub>3</sub> synthesis rate by a factor of ~10 (65.5  $\mu$ mol h<sup>-1</sup>). The electrical characteristic measurement results (Figure S3.2) show that DBD-W configuration provides a highly enhanced current response, which leads to desirable plasma conditions with a significantly increased electron density and minimized NH<sub>3</sub> dissociation in the gas phase by high energy electrons,<sup>[21]</sup> in comparison to the other three DBD reactors (Figure S3.3). Therefore, the remaining studies are performed based on the DBD-W reactor. We investigate the effect of the feeding gas flow rates and the water vapor content on the NH<sub>3</sub> production in the DBD-W system. Increasing the gas flow rate results in an improved NH<sub>3</sub> synthesis rate (Figure 3.1D): the rate increasing from 1.53 to 65.4 µmol h<sup>-1</sup> for gas flow rates rising from 0.2 to 1.0 standard litre per minute (SLM), at 100% H<sub>2</sub>O saturation. Higher H<sub>2</sub>O vapor contents also lead to higher production rates of NH<sub>3</sub>.

To further improve the NH3 production rate, a model Ru catalyst - the most active metal catalyst in the H-B process - is packed into the discharge area. Different oxides (*i.e.*, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO) were tested as supports. Catalyst characterization results, including TEM, XPS, XRD and NH<sub>3</sub>-TPD, are shown in Figure S3.4-S3.6 Compared to other metal oxide supports (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>), MgO with strong basicity enhances the N<sub>2</sub> dissociation rate by donating sufficient number of electrons to lower the dissociation barrier and thereby improve the ammonia synthesis rate, which is consistent with our results in Figure 3.2. In contrast, the  $Al_2O_3$  packed case only produces a relatively small amount of ammonia, possibly due to the significantly lower electron density, which leads to a lower concentration of active radicals, atoms and ions than the other oxide cases (Figure S3.7 and S3.8). The competition with N(s) hydrogenation by the strong interrupting effect of surface-adsorbed oxygen species, and a slower desorption of ammonia from the alumina surface because of relatively strong binding are other possible reasons.<sup>[22]</sup> NH<sub>3</sub>-TPD measurement results (Figure S6B) show the high density of strong acid sites on the Al2O3 surface in comparison to the other supports, leading to a slight reduction of NH<sub>3</sub> yield.<sup>[21, 23]</sup> The presence of Ru supported on these oxides, especially on MgO, markedly enhances the synthesis rate to 2,661 µmol g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup> (Figure 3.2A). Electrical measurements of the DBD reactor coupled with various catalysts show that the packing catalysts can provide higher electron density and electron energy than the plasma-only (N<sub>2</sub>/H<sub>2</sub>O) case. All QV Lissajous Figures

(Figure S3.7) for various catalysts at the same input conditions (Discharge voltage  $V_{p-p}$ : 9.08 kV for MgO, 8.27 kV for SiO<sub>2</sub>, 7.86 kV for Al<sub>2</sub>O<sub>3</sub>, 8.23 kV for Ru/MgO, 9.15 kV for Ru/SiO<sub>2</sub>, and 10.57 kV for Ru/Al<sub>2</sub>O<sub>3</sub>) show a similar typical parallelogram shape, indicating that the plasma properties do not change significantly using the same electrode configuration, which is consistent with other studies.<sup>[24]</sup>

The NH<sub>3</sub> synthesis rate increases with the specific energy input (SEI) (Figure 3.2B). SEI is adjusted by varying the discharge power at a constant gas flow rate of 1.0 SLM. Specifically, the NH<sub>3</sub> synthesis rate increases from 2,050 to 2,661 µmol g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup> when the SEI increases from 1.33 to 4.20 kJ L<sup>-1</sup> in the presence of the Ru/MgO catalyst. However, the energy efficiency of ammonia synthesis decreases with increasing SEI (Figure S3.9). This may be attributed to the fact that increasing the SEI shifts the electron energy distribution function to higher energies, leading to an increased probability of ionization and dissociation reactions, which consume much energy. The lowest energy pathway is vibrational excitation of molecules followed by dissociative adsorption on the catalyst surface. The catalysts show a stable NH<sub>3</sub> production rate over a 5-h period (Figure 3.2C), and the main physicochemical properties of the catalysts remain unchanged (Figure S3.4). The NH<sub>3</sub> synthesis rate and the energy efficiency of Ru/MgO remain constant over five reuse cycles (Figure 3.2D), suggesting the long-term stability of the catalysts under the N2 and H2O reactions. A further comparison of the physicochemical properties of the fresh and spent catalysts, as determined by N2-BET and XPS measurements (Figure S3.4 and S3.5), also suggests that the reactions in plasma do not have a significant impact on the catalyst structures and surfaces.

## 3.Summary

In summary, this work presents a plasma-catalysis avenue that enables ambient ammonia synthesis directly using renewable sources: N<sub>2</sub>, H<sub>2</sub>O and electricity. Through process designs and computational studies on catalytic activity, our innovation is leaping the "unfavorable" reaction toward favorable ammonia production. A high rate of ammonia production (2.67 mmol  $g_{cat}$ <sup>-1</sup> h<sup>-1</sup>) has been demonstrated with a low activation energy of dissociative adsorption of N<sub>2</sub> on the catalyst surface, paving a new way for supplementing the Haber-Bosch process. This progress in sustainable ammonia synthesis only requiring nitrogen and water is expected to set a new benchmark for sustainable ammonia synthesis and to be a precursor to lead further innovation in broad plasma catalysis research.

## 4. References

[1] D. R. MacFarlane, P. V. Cherepanov, J. Choi, B. H. Suryanto, R. Y. Hodgetts, J. M. Bakker, F. M. F. Vallana, A. N. Simonov, Joule 2020.

[2] B. H. Suryanto, K. Matuszek, J. Choi, R. Y. Hodgetts, H.-L. Du, J. M. Bakker, C. S. Kang, P. V. Cherepanov, A. N. Simonov, D. R. MacFarlane, Science 2021, 372, 1187-1191.

[3] F. Jiao, B. Xu, Adv. Mater. 2018, 31, e1805173.

[4] L. Wang, M. Xia, H. Wang, K. Huang, C. Qian,

C. T. Maravelias, G. A. Ozin, Joule 2018, 2, 1055-1074.

[5] J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis, P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider, R. R. Schrock, Science 2018, 360, eaar6611.

[6] A. J. Martín, T. Shinagawa, J. Pérez-Ramírez, Chem 2019, 5, 263-283.

[7] J. Sun, D. Alam, R. Daiyan, H. Masood, T. Zhang, R. Zhou, P. J. Cullen, E. C. Lovell, A. R. Jalili, R. Amal, Energy Environ. Sci. 2021, 14, 865-872.

[8] J. Wang, L. Yu, L. Hu, G. Chen, H. Xin, X. Feng, Nat. Commun. 2018, 9, 1-7.

[9] R. Hawtof, S. Ghosh, E. Guarr, C. Xu, R. M. Sankaran, J. N. Renner, Sci. Adv. 2019, 5, eaat5778.

[10] J. Zheng, Y. Lyu, M. Qiao, R. Wang, Y. Zhou, H. Li, C. Chen, Y. Li, H. Zhou, S. Wang, Chem 2019, 5, 617-633.

[11] P. Mehta, P. Barboun, F. A. Herrera, J. Kim, P. Rumbach, D. B. Go, J. C. Hicks, W. F. Schneider, Nat. Catal. 2018, 1, 269-275.

[12] L. R. Winter, B. Ashford, J. Hong, A. B. Murphy, J. G. Chen, ACS Catal. 2020, 10, 14763-14774.

[13] L. Hollevoet, F. Jardali, Y. Gorbanev, J. Creel, A. Bogaerts, J. A. Martens, Angew. Chem. Int. Ed. 2020, 132, 24033-24037.

[14] E. C. Neyts, K. Ostrikov, M. K. Sunkara, A. Bogaerts, Chem. Rev. 2015, 115, 13408-13446.

[15] X. Zhang, Y. Liu, M. Zhang, T. Yu, B. Chen, Y. Xu, M. Crocker, X. Zhu, Y. Zhu, R. Wang, Chem 2020, 6, 3312-3328.

[16] A. Bogaerts, E. C. Neyts, ACS Energy Lett. 2018, 3, 1013-1027.

[17] P. Peng, C. Schiappacasse, N. Zhou, M. Addy, Y. Cheng, Y. Zhang, K. Ding, Y. Wang, P. Chen, R. Ruan, ChemSusChem 2019, 12, 3702-3712.

[18] Z. Zhou, Z. Pei, L. Wei, S. Zhao, X. Jian, Y. Chen, Energy Environ. Sci. 2020, 13, 3185-3206.

[19] R. K. Sharma, H. Patel, U. Mushtaq, V. Kyriakou, G. Zafeiropoulos, F. Peeters, S. Welzel, M. C. van de Sanden, M. N. Tsampas, ACS Energy Lett. 2020, 6, 313-319.

[20] I. Muzammil, Y.-N. Kim, H. Kang, D. K. Dinh, S. Choi, C. Jung, Y.-H. Song, E. Kim, J. M. Kim, D. H. Lee, ACS Energy Lett. 2021, 6, 3004-3010.

[21] E. Carrasco, M. Jiménez-Redondo, I. Tanarro, V.

J. Herrero, Phys. Chem. Chem. Phys. 2011, 13, 19561-19572.

[22] X. Zhu, X. Hu, X. Wu, Y. Cai, H. Zhang, X. Tu, J. Phys. D 2020, 53, 164002.

[23] Y. Wang, M. Craven, X. Yu, J. Ding, P. Bryant, J. Huang, X. Tu, ACS Catal. 2019, 9, 10780-10793.

[24] B. S. Patil, A. S. Van Kaathoven, F. J. Peeters, N.

Cherkasov, J. Lang, Q. Wang, V. Hessel, J. Phys. D 2020, 53, 144003.