Drastically Increase in Atomic Nitrogen Production Depending on the Dielectric Constant of Beads Filled in the Discharge Space

Yuto Tsuchida, Naoya Murakami, Tatsuya Sakakura, Yoshiyuki Takatsuji, and Tetsuya Haruyama*

Read Online

ACCESS | 📊 Metrics & More | 📰 Article Recommendations | 🆂🇮 Supporting Information

ABSTRACT: Nitrogen activation, especially dissociation (production of atomic nitrogen), is a key step for efficient nitrogen fixation, such as nitrogen reduction to produce ammonia. Nitrogen reduction reactions using water as a direct hydrogen source have been studied by many researchers as a green ammonia process. We studied the reaction mechanism and found that the nitrogen reduction could be significantly improved via efficient production of atomic nitrogen through electric discharge. In the present study, we focused on packed-bed dielectric barrier discharge (PbDBD) using dielectric beads as the packing material. The experimental results showed that more atomic nitrogen was produced in the nitrogen activation by the discharge in which the discharge space was filled with the dielectric beads than in the nitrogen activation by the discharge without using the dielectric beads. Then, it was clarified that the amount of atomic nitrogen increased as the dielectric constant of the beads to be filled increased, and the amount of atomic nitrogen produced increased up to 13.48 times. Based on the results, we attempted ammonia synthesis using water as a direct hydrogen source with the efficiently generated atomic nitrogen. When the atomic nitrogen gas generated by the PbDBD was sprayed onto the surface of the water phase and subsequently reacted as a plasma/liquid interfacial reaction, the nitrogen fixation rate increased by 7.26-fold compared to that when using the discharge without dielectric beads, and the ammonia production selectivity increased to 83.7%.
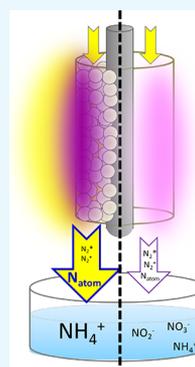
INTRODUCTION

In recent years, there have been many studies on different methods for fixing nitrogen, such as catalyst development,[1−4] electrolytic synthesis,[5−7] biochemical reactions, and biomimetic reactions.[8−10] These studies aimed at low energy consumption and on-site production, but many of the methods required large-scale facilities, which hindered on-site production. When reacting pure hydrogen gas with nitrogen, hydrogen production is indispensable. In both cases, large incidental facilities are required for the heat sources, waste heat utilization, and pure hydrogen gas production.

Among the abovementioned nitrogen fixation methods, the use of plasma is relatively popular. Various studies of plasma-driven green ammonia synthesis have been reviewed recently.[11] The research achievements can be classified in various ways, but an important aspect is the hydrogen source required for the synthesis of ammonia. Two different research approaches can be defined depending on the hydrogen source for the hydrogenation of nitrogen: hydrogen gas or water. Regarding the reaction systems without catalysts and using water as the direct hydrogen source, reports were first published by Haruyama et al. (2015, using water vapor, and 2016, at the gas/water phase interface),[12,13] Ruan et al. (2018, using water shower),[14] Hawtof et al. (2019, using water vapor),[15] Ostrikov et al. (2018, in water),[16] and Bogaerts et al. (2020, using water vapor),[17] among others. Research in this field is at the initial stage of development. These studies clearly showed that the reaction proceeds between the activated gas and water. All of these are ammonia production reactions while under different

conditions, all these initial investigations are under a similar reaction process to activated nitrogen species and subsequently reduce nitrogen. There are different species of activated nitrogen in the discharged nitrogen plasma, including atomic nitrogen ($N(^4S)$; hereafter N_{atom}), excited nitrogen molecules ($N_2(A^3\sum_u^+)$; hereafter N_2^*), and nitrogen molecular ions (N_2^+). Each activated nitrogen species has a different lifetime and reactivity.
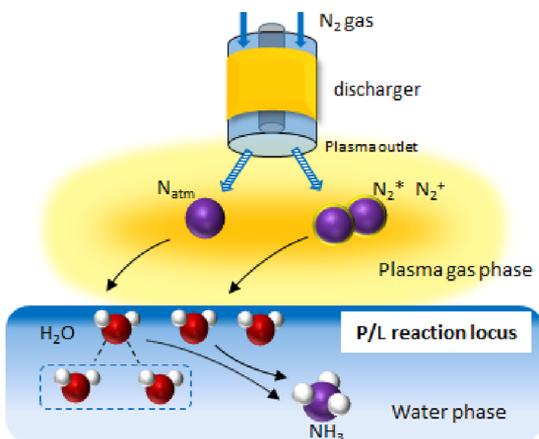
In the plasma/liquid (P/L) reaction that we discovered, nitrogen fixation (ammonia production) proceeded when the activated nitrogen gas abstracted the hydrogen from water. In the P/L reaction, once the gas phase (nitrogen) was activated, the activated nitrogen species abstracted hydrogen from water molecules and the gas−liquid interface reaction to generate ammonia went downhill in energy, as illustrated in Figure 1.[13,18−21] We have elucidated the functions of each active nitrogen species in the P/L reaction[13,18−21] and showed that by modulating the activated nitrogen species in the gas phase, the reaction pathways of reduction and oxidation could be controlled. This is because the three types of active nitrogen species have different lifetimes so that the concentration of

Figure 1. Schematic illustration of the plasma/liquid (P/L) reaction.

Table 1. Three Types of Dielectric Beads Used in the Packed-Bed Dielectric Barrier Discharge (PbDBD) System[a]

beads for PbDBD	details
glass	dielectric constant: 3.1
	shape: spherical
	diameter: 3 mm
	manufacturer: Toshin Riko Co.
alumina	dielectric constant: 9.5
	shape: spherical
	diameter: 3 mm
	manufacturer: Nikkato Co.
titania	dielectric constant: 133
	shape: Spherical
	diameter: 3 mm
	manufacturer: Sakai Chemical Co.

[a]The dielectric constant of each bead is based on the value measured by each bead maker.

each active species at the fabricated reaction locus is different. It was shown in the previously reported results that obtaining the most reactive N_{atom} improves the amount of ammonia produced and the selectivity for production.[19,20] Our rationale of ammonia production is similar to other reported nitrogen reduction reactions using water as a direct hydrogen source. We have studied the nitrogen discharge environment while quantifying the atomic nitrogen in the discharge. Here, we focused on the packed-bed barrier discharge (PbDBD), in which the discharge space is filled with dielectric beads.

In this study, we found that the discharge amount of atomic nitrogen can be increased in proportion to the dielectric constant of the beads filled in the PbDBD. In addition to an increase in the amount of activated nitrogen species in general, the amount of highly reactive N_{atom} is also increased. This is supported by vacuum ultraviolet (VUV) spectroscopic analysis that is used to quantify the atomic nitrogen generated by the discharge. We also performed a P/L reaction using PbDBD and found that both the nitrogen fixation rate and the ratio of ammonia production have been improved under the new experimental condition.
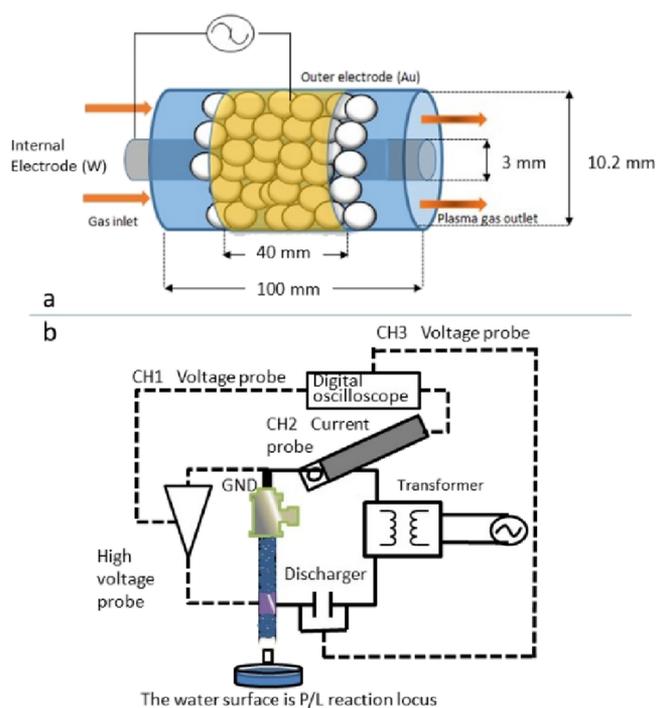
■ EXPERIMENTAL SECTION

Packed-Bed Dielectric Barrier Discharge (PbDBD) and Plasma/Liquid Interfacial Reaction (P/L Reaction). The plasma gas phase was produced by electric discharge. In the present study, we designed and manufactured the PbDBD system, and we confirmed, by the experiment, that PbDBD would efficiently activate nitrogen, especially to generate the most reactive N_{atom}. The discharge space in the discharger was filled with dielectric beads to minimize any gaps. Three types of dielectric beads having different dielectric constants were used (Table 1). Discharge experiments were conducted under four different conditions: filled with glass, alumina, or titania beads and without the use of beads. As shown in Figure 2, the gap between the internal electrode and the outer shell tube (made of quartz glass) was designed to be 3 mm, which is the same as the diameter of the dielectric beads. Therefore, when filled, the dielectric beads fit snugly in one layer.

The nitrogen gas introduced into the discharger was the nitrogen of high-purity G1 grade supplied by Taiyo Nippon Sanso Co., Ltd. The G1-grade nitrogen gas contains >99.99995% of N_2, with nearly negligible impurities, such as <0.1 ppm of O_2 and CO_2, < 0.05 ppm of total hydrocarbon (THC), < 0.01 ppm of NOx, and < 0.01 ppm of SO_2.

Figure 2. (a) Packed-bed dielectric barrier discharge (PbDBD) system. (b) Circuit system for discharge and setup for P/L reaction.

The nitrogen discharger was powered by AC at 5 kV (20 kHz), and the pure G1 grade nitrogen gas flowed through the discharger at an optimal rate of 3 L/min for the quantitative analysis of $N(^4S)$ and N_2 $(A^3\Sigma u^+)$ as well as for the P/L reaction.

The gas outlet of the discharger was vertically set at 20 mm above the water surface (the surface of water phase is the P/L reaction locus), and the distance between the discharge field and the water surface was constant at 60 mm. The water phase was 10 mL of ultra-pure water (specific electrical resistivity of deionized water was 18.2 MΩcm^{-1}) in a glass Petri dish with a water phase surface (P/L reaction locus) area of 8.29 cm^2, as shown in Figure 2b. The reaction time was 5 min.

Measurement of the Emission Spectrum of Nitrogen Plasma. The spectrum of the discharge plasma was measured to identify the active nitrogen species produced by the discharge. The outer shell of the discharger was made of quartz

glass. The light emitted at the outer shell of the discharge locus through a UV optical fiber was analyzed with an optical fiber spectrophotometer (Shimadzu).

Plasma/Liquid (P/L) Reaction. The experimental setup of the P/L reaction is shown in Figure 2. All experiments were performed under an anaerobic atmosphere in a glove box, which was filled with the nitrogen gas (with residual oxygen of 50 ppm or less) continuously supplied from a nitrogen generator.

The plasma/liquid (P/L) reaction developed by us synthesizes ammonia from nitrogen and water only. In other words, instead of using hydrogen gas, water is used as the direct hydrogen source to reduce the nitrogen (addition of hydrogen to nitrogen). This process does not need an additional catalyst or prior production of hydrogen. It is expected that the P/L reaction can be used for on-site nitrogen fixation since water can be procured locally, without prior production of hydrogen. In the P/L reaction, once the gas phase (nitrogen) is activated, the activated nitrogen species abstracts the hydrogen from water molecules and the ammonia is generated.[19,20]

Determination of P/L Reaction Products. The production of nitrogen-containing compounds from the P/L reaction was analyzed by ion chromatography (HIC-NS; Shimadzu). A Shim-pack IC-C4 column (Shimadzu) was used for determination of ammonia (NH_3), and a Shim-pack IC-SA3 column (Shimadzu) was used for determination of both nitrate ion (NO_3^-) and nitrite ion (NO_2^-). Standard samples and the accuracy of calibration curve for quantitative analysis are described in Figure S1.

N_{atom} Measurement: Vacuum Ultraviolet (VUV) Spectroscopy. Many active nitrogen species are present in plasma. Among them, N_{atom} has a short lifetime and a high reactivity, and with that, it is an important active species for the P/L reactions. The dissociation energy of the nitrogen molecule is 9.76 eV.

$$N_2 + e^- \rightarrow N(^4S) + N(^4S) + e^-$$
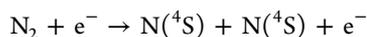
The electronic states of Natom include $N(^2D)$, $N(^2P)$, $N(^4P)$, and $N(^4S)$. There are many combinations of dissociated nitrogen atom (N) and N at different excited states with the $N(^4S)$ state. The maximum absorption wavelength of $N(^4S)$ is 120 nm as the transition from $N(^4S)$ to $N(^4P)$.[9] Therefore, the transmitted light intensity was measured by irradiating the plasma using extreme ultraviolet rays at a wavelength of 120 nm. The VUV spectroscopic system is described in detail in our previous reports.[19,20]

A monochromatic light of 120 nm was extracted from a deuterium lamp using a monochromator. An optical chamber was mounted at the output of the monochromator through the magnesium fluoride window. The output gas of the discharger was introduced into the optical chamber and was irradiated by monochromatic light in the direction perpendicular to the gas flow. The transmitted light was recorded by a photomultiplier as a photodetector. The discharge was repeatedly turned on and off at 1 min interval so that the plasma gas was generated and led to the optical chamber in every 60 s. According to Yang et al.,[9] the N_{atom} density was calculated using the transmittance, which was obtained from the ratio of the photodetector signals with and without the plasma gas.

In the present study, a discharger was used (Figure 2). Four discharge conditions similar to the production of ammonia

have been applied to measure N_{atom} by a VUV spectroscopic study.

Determination of Electric Power in PbDBD. The discharge power was obtained based on the Lissajous curve analysis.[10] At the first step, a high-voltage probe (P6015A, 100 MΩ; Tektronix) and a current probe (CT6701; Hioki) were connected to the discharge circuit (Figure 2b), and the output was displayed as a Lissajous curve on the oscilloscope (TDS2024C; Tektronix). The area of the Lissajous curve in Figure 3 and in Figure S3b in the Supporting Information
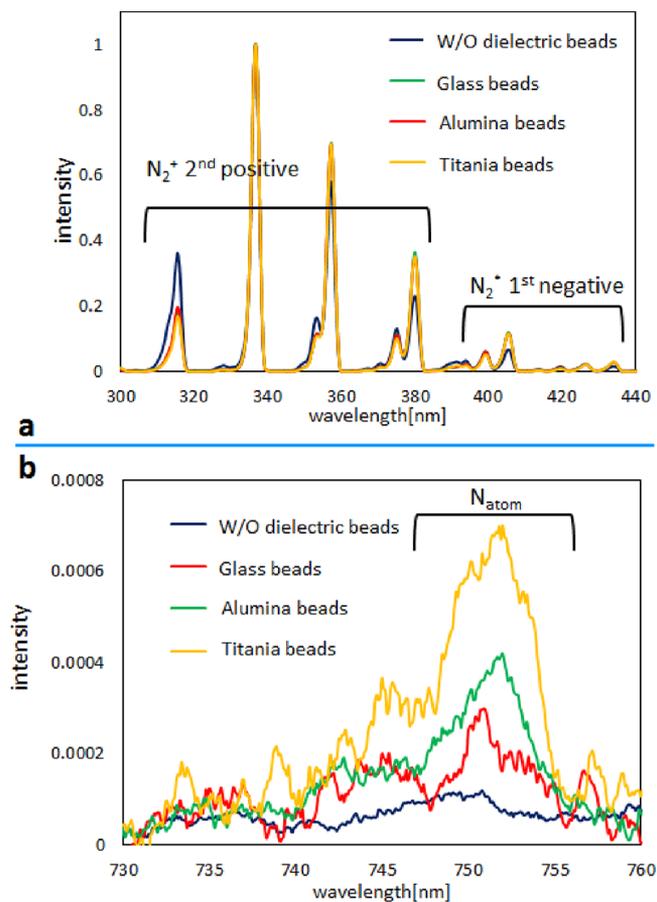
Figure 3. (a) Discharge emission spectrum derived from N_2^+ and N_2^* due to the difference in the dielectric beads filling the discharge space. (b) Discharge emission spectrum derived from N_{atom} due to the difference in the dielectric beads filling the discharge space. Discharge voltage dependence of the plasma emission spectra is shown in Figure S2.

indicates the input energy of the discharge. The discharge power was obtained based on the area value of this Lissajous curve. The electric charge was calculated based on the capacitance of the capacitor (10,000 pF), and the power value was calculated from the relationship between the electric charge, the voltage measured by the oscillogram, and the applied frequency.

■ RESULTS AND DISCUSSION

The activation of nitrogen was performed by discharge and facilitated by means of PbDBD. The activated nitrogen was investigated based on the emission spectra of the plasma, as shown in Figure 3. The N_{atom}-derived plasma emission intensity from the discharge system not filled with dielectric

beads was used as a negative control, which was compared with the corresponding emission intensity facilitated with three types of beads of different dielectric constants. The results indicate that the higher the dielectric constant of the beads, the greater amount of the generated N_{atom} is in the order of glass, alumina, and titania beads with dielectric constants of 3.1, 9.5, and 133, respectively. N_{atom} is generated by the dissociation of nitrogen molecules (N_2) and has three unpaired electrons, making it extremely reactive.

It is plausible that the increase in the amount of Natom produced may greatly increase the extent of nitrogen reduction reactions with water. On the other hand, the amount of N_2^+ and N_2^* produced did not change significantly in comparison with the emission intensity (Figure 3a). Therefore, the emission spectroscopy is advantageous when obtaining qualitative information from these spectra. However, it is difficult to measure the absolute intensity of the light emission, making it unsuitable for quantitative use.

On the other hand, the absorption characteristics of atomic nitrogen in the deep ultraviolet (vacuum ultraviolet) wavelength region can be analyzed precisely, and its molecular extinction coefficient has also been clarified. That is, vacuum ultraviolet spectroscopy is the optimal method for quantifying the atomic nitrogen (Figure S5 shows an analytical system for quantifying atomic nitrogen by VUV spectroscopy). Comparing to the case without dielectric beads filling the discharge space, the quantified amount of atomic nitrogen has been increased by 2.39 times, 3.52 times, and 13.48 times with glass, aluminum, and titania beads packed in the discharge space, respectively, as shown by the orange line in Figure 4. While it is
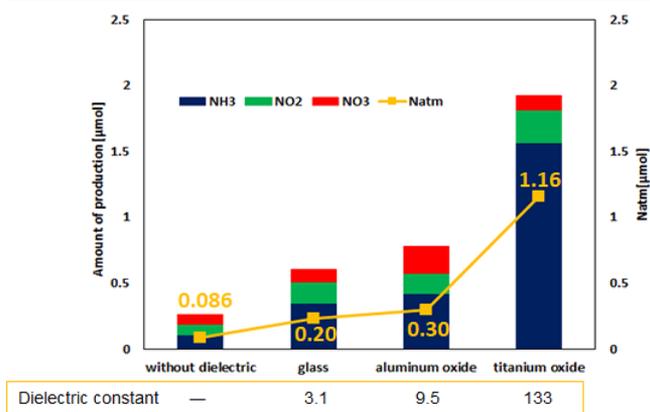
Figure 4. Relationship between the differences in the dielectric beads filling the discharge space of the packed-bed dielectric barrier discharge system, the N_{atom} generated at that time, and the amount of nitrogen fixed by the P/L reaction.

clear that in PbDBD, the higher the dielectric constant of the beads filled in the nitrogen discharge space, the larger the production of atomic nitrogen, the associated mechanism has not yet been clarified. On one hand, there is not a remarkable difference of the corresponding performance based on the Lissajous plots of the system without dielectric beads and the system filled with titania beads at the time of discharge (Figure 5b). On the other hand, the difference in the respective oscillogram ($i-t$) is clear, suggesting that the presence of a strong dielectric in the discharge space improves the efficiency of electron donation, resulting in an increase in the amount of atomic nitrogen produced. Also, interestingly, when comparing the Lissajous plots of the system W/O dielectric beads and the
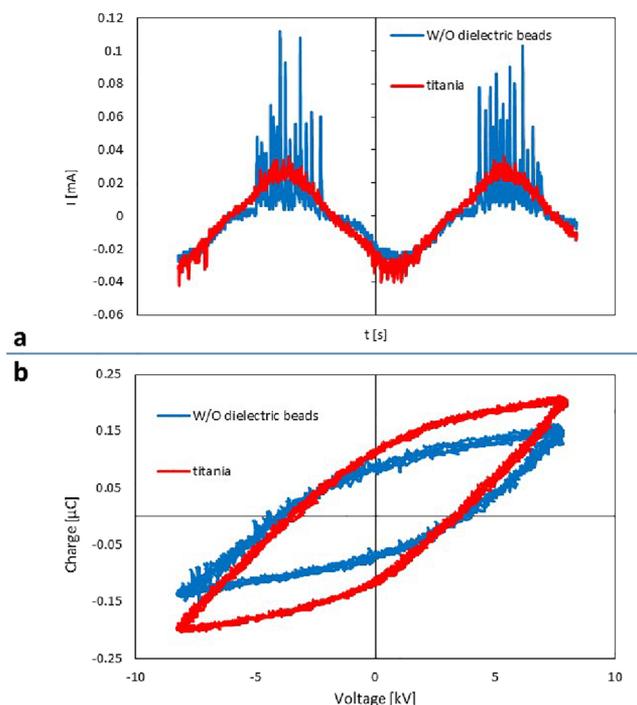
Figure 5. Analysis of electric power efficiency using oscillograms. (a) Time vs current graph. (b) Voltage vs charge graph. Figure S3 shows the oscillogram and Lissajous plots for the PbDBD filled with other dielectric beads.

system filled with titania beads at the time of discharge, there is no remarkable difference in their respective performance (Figure 5b). On the other hand, in Figure 5a, the difference is clear in the oscillogram ($i-t$), suggesting that the presence of a strong dielectric in the discharge space improves the electron donation efficiency, resulting in an increase in the amount of atomic nitrogen produced. Although there are few studies that even mention quantitative comparisons of individual activation (excitation and dissociation) products due to discharge, there are many reports that mention power efficiency and discharge characteristics. It has been reported that the strength of electric field in the discharge space is averaged and dispersed by filling with dielectric particles.[22] We hope that the results of research by simulation researchers will deepen our understanding in the future. The oscillograms of the case where the discharge space is filled with dielectric beads and the case where the same discharger is not filled with beads are shown in Figure 5 and Figure S3.

The spikes that appear on the oscillograms indicate electron emission in the discharge. It is believed that the more uniform and abundant the spikes are along the time axis, the higher the activation efficiency of the nitrogen gas is due to the discharge. Looking at the oscillograms of the time (x-axis) and current (y-axis), in the case of discharge without dielectric beads, the current spike is large but only at the peak of the current sine wave. On the other hand, in the case of PbDBD in which titania beads are filled in the dielectric space, many fine current spikes are evenly distributed along the time axis (Figure 5a and Figure S3a). The area of the Lissajous curve in Figure 5b and Figure S3b indicates the input energy in the discharge. The discharge power was obtained based on the area value of this Lissajous curve and the applied frequency. As a result, the discharge power of PbDBD (filled with titania beads) was 28.98 W. In contrast, in the non-dielectric discharge (not filled

with dielectric beads; non-PbDBD), the power was 23.62 W, a difference of 1.2-fold. This indicates that there is no remarkable difference in the power requirement. However, even with a nearly same power input, the efficiency of the P/L reaction in the presence of dielectric material has been greatly improved. For example, the amount of nitrogen fixation in the P/L reaction under non-PbDBD discharge was 0.052 μmol/min, whereas the amount of nitrogen fixation in the presence of titania beads was 0.37 μmol/min. This constitutes a 4.5-fold improvement regarding the efficiency of nitrogen fixation.

As the amount of atomic nitrogen produced can be increased in the presence of PbDBD, the P/L reaction was also performed in the presence of PbDBD, and the products were quantified as shown by the histograms in Figure 4. Clearly, in the absence of PbDBD, the total amount of nitrogen fixation (products of the P/L reaction) was the lowest. The breakdown of the product was ~41% ammonia, ~30% NO_2^-, and ~28% NO_3^-. In contrast, the addition of dielectric materials to the discharge area clearly improves the efficiency of the P/L reaction and the selectivity of the product, where the selectivity of ammonia has been increased by 83.7% (for the case of titania). Also, the selectivity of the P/L reaction to produce ammonia is clearly related to the dielectric constant of the dielectric beads in the PbDBD system. As shown in Figure 4, the amount of ammonia production by the P/L reaction increased by about 5-fold when the beads filled in the discharger were changed from glass to titania respectively.

Comparing to our previous results, the present study greatly improves the selectivity of the product (i.e., NH_3) and the power efficiency in the P/L reactions. While we have reported that the hydrogen abstraction of water by atomic nitrogen is the most efficient approach,[19,20] there is not a technology to the best of our knowledge that could efficiently generate the atomic nitrogen. The findings obtained in this research might be the beginning to selectively and efficiently produce atomic nitrogen.

Nevertheless, by further elucidating the mechanism behind this improvement in selectivity of ammonia, we believe that both the efficiency of the P/L reaction and the selectivity of the ideal product (NH_3) can be further improved.

In conclusion, we have greatly improved our nitrogen fixation system by filling the discharge space with materials of high dielectric constants that not only increases the production of the most reactive nitrogen species (N_{atom}) but also increases the selectivity of ammonia among the final product pool. This is a significant finding in the studies of nitrogen reduction reactions using water as a direct hydrogen source.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04201.

Calibration curve accuracy for analyzing P/L reaction products, discharge voltage dependence of plasma emission spectra, oscillograms of discharge conducted under four different conditions, Lissajous plots of discharge under four different conditions, evaluation of the effect of the specific surface area of titania beads filled in the discharge space, and experimental setup of the VUV spectroscopic system for quantification of atomic nitrogen (PDF)

AUTHOR INFORMATION

Corresponding Author

Tetsuya Haruyama − Division of Functional Interface Engineering, Department of Biological Functions and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka 808-0196, Japan; ⓞ orcid.org/0000-0001-6396-1472; Email: haruyama@life.kyutech.ac.jp

Authors

Yuto Tsuchida − Division of Functional Interface Engineering, Department of Biological Functions and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka 808-0196, Japan

Naoya Murakami − Division of Photo-functional Nanomaterials, Department of Biological Functions and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka 808-0196, Japan; ⓞ orcid.org/0000-0003-2444-8603

Tatsuya Sakakura − Division of Functional Interface Engineering, Department of Biological Functions and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka 808-0196, Japan

Yoshiyuki Takatsuji − Division of Functional Interface Engineering, Department of Biological Functions and Engineering, Kyushu Institute of Technology, Kitakyushu, Fukuoka 808-0196, Japan

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c04201

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

ABBREVIATIONS

P/L reaction plasma/liquid interfacial reaction; N_{atom} atomic nitrogen; N_2^* excited nitrogen molecule; N_2^+ nitrogen ion; $N_2(A^3\Sigma_u^+)$ metastable excited species of the lowest level excited state among N_2^*; $N(^4S)$ ground state of atomic nitrogen; PbDBD packed-bed dielectric barrier discharge; VUV vacuum ultraviolet

REFERENCES

(1) Aika, K.-i.; Hori, H.; Ozaki, A. Activation of Nitrogen by Alkali Metal Promoted Transition Metal I. Ammonia synthesis over ruthenium promoted by alkali metal. J. Catal. 1972, 27, 424−431.

(2) Liang, C.; Wei, Z.; Xin, Q.; Li, C. Ammonia synthesis over Ru/C catalysts with different carbon supports promoted by barium and potassium compounds. Appl. Catal., A. 2001, 208, 193−201.

(3) Inoue, Y.; Kitano, M.; Kim, S. W.; Yokoyama, T.; Hara, M.; Hosono, H. Highly dispersed Ru on electrode $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)^4$ as a catalyst for ammonia synthesis. ACS Catal. 2014, 4, 674−680.

(4) Kitano, M.; Kanbara, S.; Inoue, Y.; Kuganathan, N.; Sushko, P. V.; Yokoyama, T.; Hara, M.; Hosono, H. Electride support boosts nitrogen dissociation over ruthenium catalyst and shifts the bottleneck in ammonia synthesis. Nat. Commun. 2015, 6, 6731.

(5) Cheng, S.; Gao, Y. J.; Yan, Y. L.; Gao, X.; Zhang, S. H.; Zhuang, G. L.; Deng, S. W.; Wei, Z. Z.; Zhong, X.; Wang, J. G. Oxygen vacancy enhancing mechanism of nitrogen reduction reaction property in Ru/TiO2. J. Energy Chem. 2019, 39, 144−151.

(6) Cui, B.; Zhang, J.; Liu, S.; Liu, X.; Xiang, W.; Liu, L.; Xin, H.; Lefler, M. J.; Licht, S. Electrochemical synthesis of ammonia directly from N_2 and water over iron-based catalysts supported on activated carbon. *Green Chem.* **2017**, *19*, 298−304.

(7) Abghoui, Y.; Garden, A. L.; Howalt, J. G.; Vegge, T.; Skúlason, E. Electroreduction of N_2 to ammonia at ambient conditions on mononitrides of Zr, Nb, Cr, and V: A DFT guide for experiments. *ACS Catal.* **2016**, *6*, 635−646.

(8) MacKay, B. A.; Fryzuk, M. D. Dinitrogen coordination chemistry: on the biomimetic borderlands. *Chem. Rev.* **2004**, *104*, 385−402.

(9) Yang, X.; Chang, X.; Tei, R.; Nagatsu, M. Effect of excited nitrogen atoms on inactivation of spore-forming microorganisms in low pressure N_2/O_2 surface-wave plasma. *J. Phys. D: Appl. Phys.* **2016**, *49*, 235205−235216.

(10) Tanaka, H.; Arashiba, K.; Kuriyama, S.; Sasada, A.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Unique behaviour of dinitrogen-bridged dimolybdenum complexes bearing pincer ligand towards catalytic formation of ammonia. *Nat. Commun.* **2014**, *5*, 3737.

(11) Rouwenhorst, K. H. R.; Engelmann, Y.; Veer, K. V.; Postma, R. S.; Bogaerts, A.; Lefferts, L. Plasma-driven catalysis: green ammonia synthesis with intermittent electricity. *Green Chem.* **2020**, *22*, 6258−6287.

(12) Matsuo, K.; Takatsuji, Y.; Kohno, M.; Kamachi, T.; Nakata, H.; Haruyama, T. Dispersed-phase interfaces between mist water particles and oxygen plasma efficiently produce singlet oxygen ($^1O_2$) and hydroxyl radical (·OH). *Electrochemistry* **2015**, *83*, 721−724.

(13) Haruyama, T.; Namise, T.; Shimoshimizu, N.; Uemura, S.; Takatsuji, Y.; Hino, M.; Yamasaki, R.; Kamachi, T.; Kohno, M. Non-catalyzed One-step Synthesis of Ammonia from Atmospheric Air and Water. *Green Chem.* **2016**, *18*, 4536−4541.

(14) Peng, P.; Chen, P.; Addy, M.; Cheng, Y.; Zhang, Y.; Anderson, E.; Zhou, N.; Schiappacasse, C.; Hatzenbeller, R.; Fan, L.; Liu, S.; Chen, D.; Liu, J.; Liu, Y.; Ruan, R. In Situ plasma-assisted atmospheric nitrogen fixation using water and spray-type Jet Plasma. *Chem. Commun.* **2018**, *54*, 12658.

(15) Hawtof, R.; Ghosh, S.; Guarr, E.; Xu, C.; Sankaran, R. M.; Renner, J. N. Catalyst-free, highly selective synthesis of ammonia from nitrogen and water by a plasma electrolytic system. *Sci. Adv.* **2019**, *5*, No. eaat5778.

(16) Zhou, R.; Prasad, K.; Fang, Z.; Speight, R.; Bazaka, K.; Ostrikov, K. Cold Atmospheric Plasma Activated Water as a Prospective Disinfectant: The Crucial Role of Peroxynitrite. *Green Chem.* **2018**, *20*, 5276−5284.

(17) Gorbanev, Y.; Vervloessem, E.; Nikiforov, A.; Bogaerts, A. Nitrogen Fixation with water vapor by nonequilibrium plasma: toward sustainable ammonia production. *ACS Sustainable Chem. Eng.* **2020**, *8*, 2996−3004.

(18) Sakakura, T.; Uemura, S.; Hino, M.; Kiyomatsu, S.; Takatsuji, Y.; Yamasaki, R.; Morimoto, M.; Haruyama, T. Excitation of H_2O at the plasma/water interface by UV irradiation for the elevation of ammonia production. *Green Chem.* **2018**, *20*, 627−633.

(19) Sakakura, T.; Murakami, N.; Takatsuji, Y.; Morimoto, M.; Haruyama, T. Contribution of discharge excited atomic N, N_2^*, and N_2^+ to a plasma/liquid interfacial reaction as suggested by quantitative analysis. *ChemPhysChem* **2019**, *20*, 1467−1474.

(20) Sakakura, T.; Murakami, N.; Takatsuji, Y.; Haruyama, T. Nitrogen fixation in a plasma/liquid interfacial reaction and its switching between reduction and oxidation. *J. Phys. Chem. C* **2020**, *124*, 9401−9408.

(21) Sakakura, T.; Takatsuji, Y.; Morimoto, M.; Haruyama, T. Nitrogen fixation through the plasma/liquid interfacial reaction with controlled conditions of each phase as the reaction locus. *Electrochemistry* **2020**, *88*, 190−194.

(22) Kim, J.; Jeoung, J.; Jeon, J.; Kim, J.; Mok, Y. S.; Ha, K.-S. Effects of dielectric particles on non-oxidative coupling of methane in a dielectric barrier discharge plasma reactor. *Chem. Eng. J.* **2019**, *377*, 119896.