Plasma Catalytic Bubbles for Nitrogen Fixation: A Route to Green Chemistry

Renwu Zhou[1], Jing Sun[1,2], Dingxin Liu[1]

[1] 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
[2] School of Chemical Engineering, University of New South Wales (UNSW), Sydney, Australia
[3] School of Chemical and Biomolecular Engineering, University of Sydney, Darlington, NSW 2008, Australia

Abstract: Current industrial nitrogen fixation technology requires a large amount of fossil fuels, which is unsustainable and causes negative environmental impacts. Fixing nitrogen into NO_2^- and NO_3^- by electricity-driven non-thermal plasma catalysis is a promising solution, yet the underlying mechanisms remain unclear. In this study, we produce NO_2^- and NO_3^- from an air DBD plasma discharge in a water-electrode bubble reactor at ambient conditions, which their production can be further promoted by an optimized catalyst (TiO_2@GO, 5%GO), reaching 93% NO_3^- selectivity. Further analysis confirms the importance of a saturated catalyst surface with NO_x(ad) for the predominant N_2O_5 production that enables efficient NO_3^- (aq) production as a final product in water. This study provides new insights for plasma-based power-to-chemical nitrogen fixation in clean energy.

Keywords: Plasma Chemistry, Green Chemistry, Nitrogen Fixation.

1. Introduction

Nitrogen is essential for life and can be found in all living organisms. Though abundant nitrogen molecules exist in the atmosphere, it is inaccessible for most organisms due to the highly stable nitrogen triple bond. Nitrogen fixation, a major nitrogen cycle process, makes it possible for inert N_2 gas to combine with other elements to produce more functional and valuable compounds such as ammonia, nitrates, or nitrites [1]. There are three main nitrogen fixation types, namely natural, biological, and artificial [2-4]. In nature, nitrogen and oxygen gases in the air can react to form NO_x products (NO and NO_2) during lightning [5]. Biologically, microorganisms in plants or soil convert atmospheric nitrogen to ammonia by nitrogenases, the primary source of accessible nitrogen and the only known enzymes to catalyze the reaction, respectively [6]. However, to support the drastically increasing global population, natural and biological nitrogen fixations are relatively slow; thus, artificial/industrial-level nitrogen fixation is vital for modern agriculture [7]. Therefore, Haber–Bosch (H-B) process was developed to synthesize ammonia from pure N_2 and H_2. The process requires harsh operating conditions of high temperatures (>400 °C) and pressures (>200 atm) to drive the reaction and thus is highly energy-intensive [7]. Furthermore, about 1-2% total energy consumption worldwide and 2% of the total natural gas are consumed by this process, which is responsible for 300 million metric tons of CO_2 emissions annually [8, 9]. As a mature technology, the H-B process has been optimized for over a century and has nearly reached its theoretical limits of energy efficiency [10]. Due to its high level of CO_2 emissions, a green alternative process for nitrogen fixation is needed. Ideally, the new processes would operate at a small-to-medium scale, thus making decentralized production possible in an on-demand manner, powered by renewable energy sources such as solar and wind.

Recently, non-thermal plasma (NTP) technologies, which are compatible with renewable electricity, have been developed for emerging energy applications [11-13]. For nitrogen fixation applications, plasma discharges can be typically used to convert nitrogen and hydrogen to ammonia [14-16], nitrogen and water to ammonia and NO_x [9, 17] and air to NO_x [18, 19]. NTP nitrogen fixation has the potential to achieve better energy efficiencies than the H-B process, while being less dependent on fossil fuels, and is a highly promising emerging technology. The advantages of NO_x conversion to ammonia over plasma-assisted ammonia (NH_3) production are the elimination of hydrogen feedstock and better amenability for decentralization. The NTP-assisted NO_x has been used for electrocatalytic ammonia synthesis [20-22] with a much higher production rate compared to direct electrochemical nitrogen reduction reactions and much lower energy consumption in comparison to direct plasma-driven ammonia production. Early reports suggested an attractive potential strategy to produce liquid fertilizers directly (i.e., NO_3^-) instead of consuming NTP-produced NO_x for ammonia synthesis as the primary precursor [20]. To achieve this, it is important to produce high-valence NO_x, such as N_2O_5 in the gas phase because high-valence NO_x is easily dissolved in water by the absorption process to yield nitrate [23].

However, the reactions in NTPs are challenging to control, with the selectivity rarely optimized toward the desired products. To this end, research on plasma-catalytic reactions involving NTPs combined with heterogeneous catalysts (commonly referred to as "plasma catalysis") has recently attracted strong interest [24]. The synergistic combination of plasmas and catalysts leads to significant improvements in process performance and product selectivity for many plasma-activated reactions, including ammonia synthesis, NO_x synthesis, CH_4 activation, CO_2 hydrogenation and the water-gas shift reaction. Substantial evidence suggests that plasma-catalyst interactions can influence plasma discharges by enhancing the electric field, changing the discharge type, and/or facilitating micro-discharge formation in catalyst pores. In general, most of the plasma-assisted catalysis for N_2 fixation has been limited on gas phase reactions (NO_x gas), which is less sustainable and valuable compared to liquid phase reactions. In many studies on NO_x production, the solvation process of NO_x to liquid and the importance of the valence state of NO_x (e.g., N_2O_5) for water absorption process has not been taken into account. Moreover, the underlying mechanisms of the plasma catalyst interactions remain unclear, which results in a lack of theoretical guidance for further breakthroughs in both NO_x production rates and reduced energy consumption. To this end, increasing our understanding of the underlying plasma catalytic mechanisms for plasma-driven NO_x synthesis from the air and its fixation as NO_2^- and NO_3^- is critical for the sustainable artificial nitrogen fixation.

With the rapidly emerging field of plasma catalysis, especially with progress in nitrogen fixation, a better understanding of the underlying plasma chemical processes in the gas phase and on the catalyst surface is vital. In this work, a dielectric barrier discharge (DBD) enabled process was developed in a water-electrode bubble reactor (Fig. 1). A TiO_2-based catalyst was introduced to enhance the selectivity and production rate in the plasma-assisted nitrogen fixation. To reveal the underlying reaction mechanisms for plasma-catalytic NO_x synthesis under ambient conditions, systematic evaluations of plasma discharges and catalysts, electrical and optical plasma diagnostics and catalyst characterizations were carried out. Moreover, plasma chemical modelling was developed to study the critical intermediate species and chemical pathways for nitrogen fixation by including surface reactions related to surface adsorbed $NO_{x(ad)}$ species in the given plasma system. Finally, a reaction pathway for the plasma-catalytic NO_x synthesis process is proposed based on the experimental and modelling results.

2. Results and Discussion

Fig. 2 shows the N_2 fixation (fixed as NO_3^- and NO_2^-) performances under different process conditions and catalyst integration. Here, the air was introduced into the reactor (quartz tube) from the top, flowing through the gap between the high-voltage electrode and the quartz tube wall (plasma discharge region), and eventually discharged with the activated gas diffusing via the micro-holes into the water (Fig. 1). First, the effect of air-flow rates (0.01, 0.05, 0.1 and 0.2 L/min) was investigated (Fig. 2)) without introducing the catalyst. A low air-flow rate provides sufficient residence time for the reactant reactions in the discharge area. Results showed the highest NO_x^- production rate was obtained at 0.1 L/min air-flow, while the selectivity towards NO_3^- (~40%) did not change noticeably. Therefore, the gas flow rate of 0.1 L/min was selected for the further study. Additionally, the plasma discharge scheme shifts from a glow to a spark when the gas velocity increases (e.g., 1 L/min).

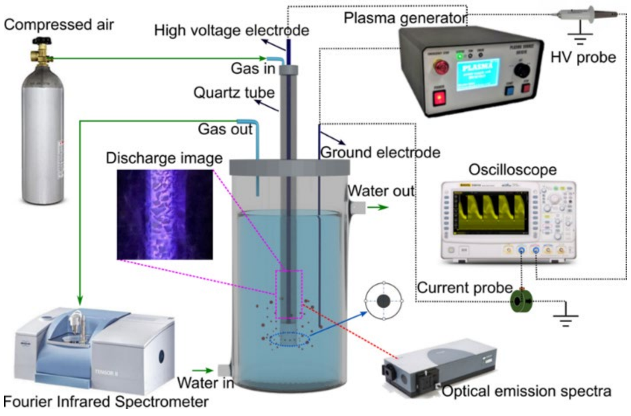

Fig. 1. Schematic diagram of the experimental setup

As fixing atmospheric nitrogen (N_2) to NO_3^- and NO_2^- is an oxidation process, we studied the effect of O_2 addition on the conversion performance. A varied amount of O_2 gas was mixed with air fed to the reactor at a constant flow rate of 0.1 L/min. The results (Fig. 2b) show that the addition of oxygen enhanced the NO_x^- production rate from ~ 25 nmol/s to 42 nmol/s until it levelled out at oxygen to a total flow rate ratio of 20% (a total of 36% of O_2 in the mixture). Here, adding O_2 content did not further improve the nitrate production rate and product selectivity. Overall, considering the cost of ambient air and the limited effect of O_2 addition, only air was used as the feed gas.

With a fixed air-flow rate of 0.1 L/min, the N_2 fixation performance was studied when the TiO_2@GO catalyst (three different ratios of TiO_2 and GO) was added to the plasma reactor. Conventionally, catalysts are used in their powder form for directly packed in the reactor. However, when the reactor was packed with powdered catalyst, the non-uniform diffusion of the gas in the voids increased the gas velocity in some areas while the pressure dropped at the bottom of the reactor. In our experiment, powder catalysts mainly resulted in high pressures inside the reactor. Also, fine catalyst powder that is deposited in the bottom of the reactor leaked into the liquid, leading to blockage of the micro-holes, which disrupts the gas bubbles discharge. To ensure controlled space for the plasma discharge and minimize the column pressure drop, structured catalysts are developed here using Graphene oxide (GO) as a binder and self-layering template. GO is a more processable form of graphene that is widely used as an additive in composites and additive manufacturing.

In the control group (no catalyst added), nitrogen was fixed at ~28 nmol/s with 30% selectivity towards NO_3^-. After packing by TiO_2@GO with the ratio of 2.5 wt% and 5 wt% GO, the NO_x^- production rate increased from 28 nmol/s to 59 nmol/s with an increase of 93% selectivity towards NO_3^-. Further increases in the GO content (i.e., TiO_2@50 wt %GO) did not show a positive synergetic effect on the NO_x^- synthesis in our air-NTP system. However, using a high concentration of GO (50%) as the TiO_2 catalyst binder (TiO_2@50%GO) has nearly the same performance for NO_x^- synthesis as using NTP without any catalysts. This is because that when the amount of GO is very high, the GO layer will be too thick to be removed by the air plasma (See Fig. 4f and Fig. 14d), and therefore, the active sites of TiO_2 will not be exposed to the plasma discharge. The result indicates that GO alone has negligible catalytic property for NO_x^- synthesis and under our designed experimental conditions, the effect of material packing was controlled in

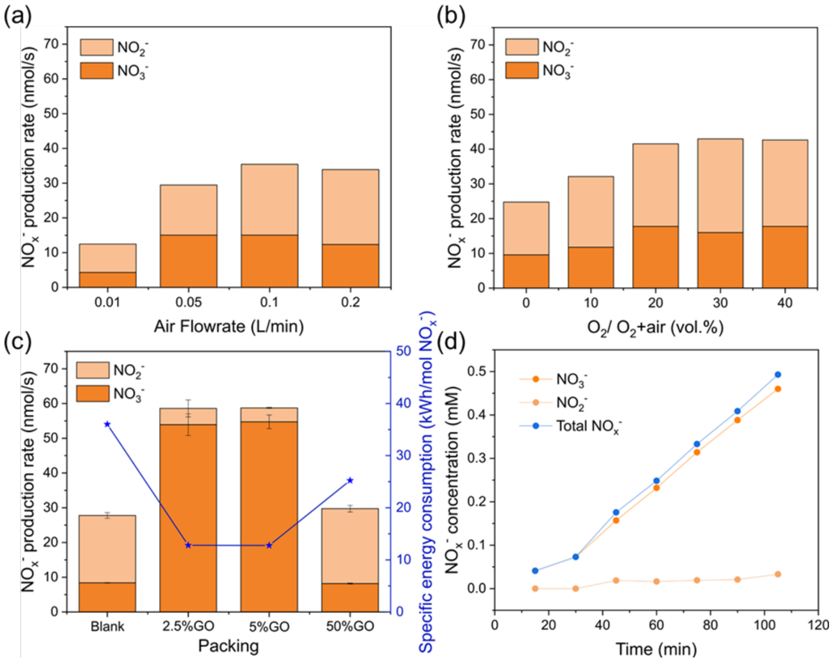

Fig. 2. NO_3^- and NO_2^- production rates based on 15min sampling time (a) with various feed air gas flow rates; (b) with addtional O_2 gas input while the total feed gas flow rate was kept at 0.1 L/min; (c) packed with as-prepared catalyst TiO_2 with different ratios of GO; (d) the time-dependent concentration of NO_3^- and NO_2^- during 105 min of the plasma discharge.

order to affect the plasma discharge significantly. It should be noted that the NO_x^- synthesis rate is still limited due to the low air-flow rate and low power input. By further adjusting the air-flow rates (e.g., 1 L/min) and other discharge conditions, it may be possible to increase the NO_x^- production rate. However, in this work, we mainly focus on investigating the role of the catalyst TiO_2@GO in the plasma catalytic reactions, where the high fixation selectivity towards nitrate is achieved.

Furthermore, we undertook a batch experiment with a successive sampling of nitrate and nitrite to evaluate the stability of the catalytic performance of TiO_2@GO as a function of time (Fig. 2d). The result shows a relatively slower NO_x^- production rate (21 nmol/s) in the first 30 minutes, followed by a higher and more stable NO_x^- production rate (57 nmol/s). The result suggests that an initial activation time is required for establishing a strong interaction between the catalyst and plasma.

To better understand the gas phase trends and the interaction between the plasma and packing materials, the catalyst TiO_2@GO was studied after the plasma exposure. SEM and XPS techniques were used to characterize the bulk and surface properties, respectively. The SEM image of the spent catalyst demonstrates that the thin GO layer on the catalyst surface was gently removed by the interaction with air plasmas, while the structure of the catalyst was maintained. When the GO concentration is too high (e.g., 50%), it is difficult to remove the thick GO layer from the TiO_2 surface. Most of the surface was still covered by the GO after 1 h of plasma discharge. The surface GO transforms to CO_2 and is expelled with the air flow, leading

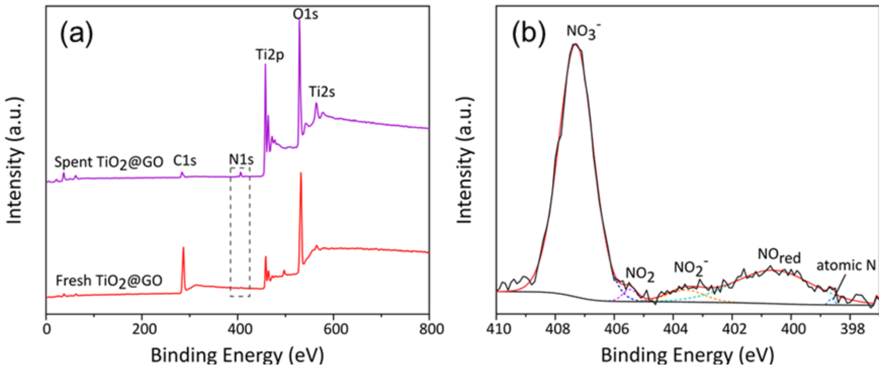

Fig. 3. (a) Full survey of XPS spectra for fresh and spent TiO_2@GO; (b) Newly formed N1s spectrum for spent TiO_2@GO

to better performance once the TiO_2 is exposed to the plasma.

A full survey of the XPS spectra and N1s spectrum (Fig. 3) of the spent TiO_2@GO show the newly formed surface-bound nitrogen-containing species, indicating the presence of the NO_x, generated by plasma and surface reactions, adsorbed on the catalyst surface. Result shows the changes in the atomic fractions of the four main elements (C, Ti, O, N) between the fresh and spent catalyst. The atomic fraction of C was reduced from 49.75% to 10.21% while that of Ti increased from 5.81% to 25.65%, indicating that most of the GO layer is removed and more TiO_2 is exposed. The newly appearing element N supports the theory that NO_x species are involved in the surface reaction.

The adsorption of NO_2, NO, and N_2O on metal oxides, including TiO_2, Al_2O_3 and Fe_2O_3, have been well investigated. The main reported adsorbed species at room temperature are NO_3^- (407.0 to 407.6 eV), physisorbed NO_2 (405.4 to 406.0 eV), $NO_{2,chem.}$ or NO_2^- (403.5 to 404.0 eV), NO (400.5 to 403 eV), and atomic N (396.8 to 400 eV). The main product of NO_2 from adsorption is the nitrate anion, formed through a disproportionation process as considered in the model:

$$2NO_{2,ads} \rightarrow NO_{3,ads}^- + NO_{ads}^+$$

Air plasma produced NO_x and its adsorption on the catalyst yields five different types of surface-bound species at 407.3, 405.5, 403.6, 400.6 and 398.6 eV (Fig. 3b), which are attributed to NO_3^- (407.3 eV), to weakly adsorbed NO_2 (405.5 eV), tentatively to $NO_{2,chem.}/NO_2^-$ (noted NO_2^- in this paper) (403.6 eV), to NO_{red} (400.6 eV) and a small fraction to atomic N (398.6 eV). The variety of nitrogenated species formed on the catalyst surface can be attributed to the initial adsorption of NO_x to the surface and the intermediates as well as the products from the surface reactions. The peak at 400.6 eV is located between the previous reported binding energies for NO and N, and the larger full width at half maximum (fwhm, 3.1 eV) in this case indicated the possible presence of several reduced nitrogenated species, such as NO^+, NO^-, and N^+, or different adsorption modes of NO.

3. Conclusion

Sustainable plasma catalysis for nitrogen fixation (fixed as NO_3^- and NO_2^-) using an optimized catalyst (TiO2@GO, 5%GO) has been achieved at ambient pressure and room temperature with a water-electrode DBD reactor. Compared to plasma synthesis of NOx^- without a catalyst, plasma catalysis significantly enhanced the NOx^- production rate from 28nmol/s to 59 nmol/s, an over 100% improvement in the production rate, and its selectivity towards NO_3^- from 35% to 93%. It is suggested that the observed performance is due to the physico-chemical synergetic effects caused by the TiO2@GO catalyst, with a plasma kinetic model providing support for enhanced NOx production by the introduced surface reactions. N2O5 was predicted to be the predominant species for the low-temperature DBD plasma conditions and was found to be closely correlated to nitrate production in the aqueous medium.

4. References

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