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CRITICAL REVIEW
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Heterogeneous catalytic oxidation for lignin valorization into valuable
chemicals: what results? What limitations? What trends?

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Excitation of H$_2$O at plasma/water interface by UV irradiation for elevation of ammonia production

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Abbreviations
P/L reaction, plasma/liquid interface reaction (P/L reaction); VUV, vacuum ultraviolet; UV, ultraviolet.

Abstract

Ammonia is well known to be a very important chemical substance for human life. Simultaneously, the conventional ammonia production process needs pure nitrogen and pure hydrogen. Hydrogen has been produced from either liquid natural gas (LNG) or coal. In this study, water is used as direct hydrogen source for ammonia production, thereby obviating the need for catalysts or water electrolysis. We have studied and developed a plasma/liquid interface reaction (P/L reaction) that can be used to produce ammonia from air (nitrogen) and water at ambient temperature and pressure, without any catalysts. In this study, the P/L reaction entails enhanced ultraviolet (UV) irradiation of the surface of the water phase. Nitrogen plasma/water interface reaction locus can produce ammonia. In contrast, the vacuum ultraviolet (VUV) irradiated interface reaction locus produces increase of ammonia. In a spin trap electron spin resonance (st-ESR) experiment, large amounts of atomic H (H·) were produced by UV irradiation, especially by VUV irradiation. The derived H· effectively enhanced the P/L reaction rate.

Introduction

Ammonia (NH_3) has been widely used as agricultural fertilizer[1,2], reductant in NO_x removal catalysts[3], cuprammonium rayon (cupro)[4], and other applications. More recently, it has additionally been used as hydrogen carrier[5]. The amount of ammonia being produced is 160 million tons / year and about 80% of this is used for fertilizer. It is said that the increase in the population can be attributed to the increasing use of ammonia as fertilizer. Ammonia is typically mass-produced by the Haber-Bosch (H-B) process from H_2 and N_2 on a large scale. Thus, the H-B process is suitable for producing high-purity ammonia in a large-scale chemical plant, which includes process for hydrogen production and various other products. This means the H-B process is required to be a combination of various processes. If the demand for ammonia increases, technology that enables onsite production is necessary, apart from mass synthesis technology. Clearly, there is a need for a new process to produce ammonia employing one-step production from air and water, with the aim of possible transport and onsite production.

An ammonia production process starting from N_2 is tasked with breaking the N≡N bond, which is known to be a very strong bond and requires the use of high temperature and pressure to break [6]. The H-B process overcomes the N≡N bond to

expend any amount of energy at high temperature (> 673 K) and high pressure (> 200

bar)[7–10]. However, for on-site production, normal temperature and pressure would be

desirable. Therefore, on-site production would need to break the N≡N bond at ambient

temperature and pressure.

Methods other than the H-B method have been developed for processing near room

temperature, such as catalytic processes to produce ammonia starting from N_2 and H_2

or a nitrogen source and hydrogen source. Ammonia synthesis using Ru has been

widely researched in the field of supported catalysts [11,12]. Ru-based catalysts are known

for their high activity and high rate of reaction for ammonia synthesis. Although these

catalytic reactions low energy compared with the H-B process, they have not yet

achieved ammonia synthesis under normal temperature and pressure. Nitric acid

(NO_3^-) is alternative source of N_2 and contained in agricultural waste produced by the

bacterial decomposition of fertilizers[13]. The synthesis of ammonia from nitric acid

achieved at atmospheric pressure, but is not adequate for large-scale conversion to

ammonia by way of selective reaction on catalysts.

A method using plasma for disconnection of the N≡N bond in N_2 has been

developed[14–16]. In ammonia synthesis using plasma it is possible to bleak the N≡N bond

required for catalysts because of nitrogen activation by the plasma. In this case, N_2

forms activated nitrogen, which is atomic nitrogen (N or N·) and excited nitrogen molecules (N_2^*) in the plasma phase. However, the activated nitrogen needs a possible high-efficiency reaction and hydrogen supply. In contrast to the above methods, our method is distinctive in that it presents a reaction system at normal temperature and atmospheric pressure where water is directly used as a hydrogen source. At the same time, it seems to overcome the problems associated with on-site production. In our recent study, a one-step ammonia synthesis from air (or N_2) and water through a plasma/liquid interface reaction (P/L reaction) was successfully performed[17]. Hydrogen production is unnecessary because the P/L reaction can be performed by direct hydrogen abstraction from water with a simple process at ambient temperature and pressure without any catalyst. In the P/L reaction, the hydrogen of the outer-most surface water molecules in the liquid phase form special reaction field that contribute to the gas phase side[18]. In our previous reports, we also described that the irradiation of the surface of the water phase with ultraviolet (UV) light in the P/L reaction locus to enhance ammonia production.

In this study, we are investigating the effect of UV irradiation by the P/L reaction to enhance ammonia production. This is a conspicuous effect because the water molecules in the outermost layer of the liquid phase surface can be excited efficiently

by UV irradiation from the plasma gas phase side (as conceptually illustrated in Figure 1). We report the advantage of ammonia synthesis with increasing hydrogen abstraction by atomic nitrogen from an excited vacuum ultraviolet (VUV)/UV irradiated water phase surface of the P/L reaction locus.

Results and discussion

Ammonia synthesis with modulation of vacuum ultraviolet irradiation

The water molecules dissociate into hydrogen atoms and hydroxyl radicals under vacuum ultraviolet irradiation (VUV, 185 nm)[19,20]:

$$H_2O \rightarrow OH\cdot + H\cdot \qquad\qquad (1)$$

In addition, even under UV irradiation (254 nm), water molecules containing hydrogen peroxide dissociate into hydroxyl radicals, hydrogen ions, hydroxyl ions, and the perhydroxyl radical.

$$2H_2O_2 \rightarrow OH^- + OH\cdot + HO_2^- + H^+ \qquad\qquad (2)$$

Increasing the source of hydrogen by VUV/UV irradiation was confirmed to increase the amount of ammonia. Actually, the activated air (Plasma phase)/water (Liquid phase) interfacial reaction (P/L reaction) is considered to consist of many reactions to form ammonia[21]. Activated N_2, mainly atomic nitrogen, has a very short lifetime, and readily recombines to form N_2. However, atomic nitrogen could react with hydrogen generated

by VUV/UV irradiation or extract hydrogen from H_2O. Thus, there are numerous forms

of hydrogen in water (Liquid phase) that could bind with atomic nitrogen.

Figure 4 (a) shows the production of ammonia as a function of wavelength. We

confirmed the synthesis of ammonia from water and N_2 or N-plasma. In cases of

reaction with UV irradiation at certain wavelengths (172, 185+254, 248, 280, 310, and

340nm), small amounts of ammonia are produced even if the gas phase is N_2 (not

plasma gas). These results suggest that the ammonia is derived from UV-excited water

(which may produce H·) and N_2. The production of ammonia by water and N-plasma is

higher than from water and N_2. Especially, the result shows the largest amount of

ammonia produced is from N- plasma under UV irradiation (185 nm and 254 nm). We

confirmed that the ammonium concentration generated only by N-plasma and by

N-plasma with irradiation other wavelengths (248 nm, 280 nm, 310 nm, and 340 nm) is

not much different. We considered wavelengths of 200 nm or less to most effectively

contribute to the synthesis of ammonia. This is because we found the largest amount

of ammonia to be generated at wavelengths of 185 nm and 254 nm whereas not much

is generated at 248 nm. Figure 4 (b) shows the relationship between the spin

concentration and the wavelength change. The largest spin concentration is generated

at 200 nm or less. Equation (1) shows the water dissociation wavelength at 185 nm.

Equation (1) is apparent from the relationship between the spin concentration and wavelength. Since both the spin concentrations and ammonium ion concentrations are high at the dissociation wavelength of water of 185 nm, it suggested that H· and N-plasma reacted. The spin concentration is the highest at 172 nm, but we obtained the fact that a low ammonium ion concentration at 172 nm. This suggests that ammonia is decomposed at the wavelength of 172 nm[22].

Spin concentration in water phase

Figure 5 shows the relationship between spin concentration and time changes. We confirmed that H· and OH· are generated because of exposing the outermost surface of water to UV radiation. The spin concentration increases with time. However, although the spins concentration increased as a result of UV irradiation, the production rate of spins slowed with the lapse of time. We considered the reason for the decrease in the production rate of spins, to be that the UV irradiation depth was such that the radiation only reaches the water on the surface and radicals are not generated in the bulk liquid. The radicals on the water surface are trapped by 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and become DMPO - H and DMPO - OH. Therefore, less free DMPO occurs on the water surface.

This result suggested that the amount of spins trapped by the spin-trapping method, in which DMPO captures the radicals formed by UV irradiation because of the water molecules changing to H· and OH·, depends on the surface area of the water phase and the depth of the UV.

Relationship between spin concentration and ammonia concentration

We investigated the relationship between the spin concentration and ammonia (NH_4^+) (Figure 6). The ammonia concentration due to plasma only (triangles) and UV (185 nm + 254 nm) + plasma (squares) increases with time. The result obtained by combining UV + plasma is more than twice the increase compared with plasma alone. We confirmed that N-plasma (activated nitrogen) directly reacts with water molecules, as ammonia is generated by only N-plasma.

$$N + nH_2O \rightarrow NH_3 + \text{by-Products} \qquad (3)$$

where the byproducts include NOH, NO_3^-, NO_2^-, H_2O, H_2O_2, H_2, and OH, and so on.

The amount of produced ammonia was more than doubled by UV irradiation. This result was expected in that activated nitrogen and H· were expected to easily bond. However, it is clear from Figure 6 that in the short time (within 30 s) there is not much difference between ammonia formation by plasma and UV + plasma. This result is

attributed to the increasing spin concentration (circles) as a function of time. Since the

spin concentration is initially low, the amount of H · and OH · is also considered to be

low in the beginning. We predicted that the H· and activated nitrogen under UV

irradiation can be more easily coupled than the direct reaction of water and activated

nitrogen. Therefore, it is conceivable that slight H· formed by the excitation of water

due to UV did not react with activated N-plasma in the initial short period of time. The

amount of ammonia produced is the same irrespective of whether plasma or UV +

plasma are used. The main reaction in a short time is considered to be the production

of ammonia by N-plasma directly extracting H from water molecules. Since the

difference between plasma and UV + plasma in terms of producing ammonia occurs for

over 1 minute, the reaction is mainly with H· generated by UV irradiation. At the same

time, ammonia production by N-plasma directly extracting H from water molecules is

proceeding. It is noteworthy that the ammonia concentration produced by UV +

plasma is close to the value obtained by adding the ammonia concentration produced

by plasma and the spin concentration. It is clear that the H· amount produced by UV

irradiation is used for ammonia production. In addition, it is indicated that activated

nitrogen easily binds with H·. We considered activated nitrogen to require easily

reacting molecules, because activated nitrogen has a very short life. If H· is present in

the reaction field, activated nitrogen reacts with H· to become NH. NH is expected to dissolve in water. Since ammonia has the composition of NH_3 (with three times as much H as N), it is necessary to have a H· concentration of at least three times in the reaction between N and H·. (3)
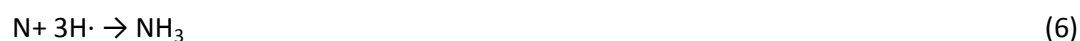
The result of our observation clearly that the spin concentration (OH·, H·) is related to the composition of ammonia. We confirmed the amount of spins generated by UV irradiation mainly by detecting the signal of OH · and the small H · signal. H· radicals produced by UV irradiation has a very short lifetime and recombines to form hydrogen.[23]

$$2H· \rightarrow H_2 \tag{4}$$
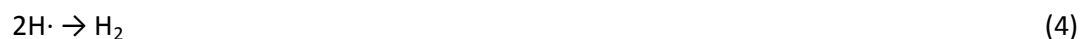
It is known that the hydroxyl radical (OH·) is reduced by H_2.[24]

$$H_2 + OH· \rightarrow H_2O + H· \tag{5}$$

The relationship in Equation (4) and (5) suggests that sufficient H· is present to reacts with activated nitrogen. We obtained the result in Figure 6 that shows the amount of ammonia produced by using UV + plasma is more than twice as much as that obtained with plasma alone. Under UV irradiation, it is considered that besides the direct reaction of activated nitrogen with H_2O, NH reacts with H_2O or H· to produce NH_3.

$$N+ 3H· \rightarrow NH_3 \tag{6}$$

$$NH + nH_2O \rightarrow NH_3 + \text{By-Products} \qquad (7)$$

$$NH + 2H\cdot \rightarrow NH_3 \qquad (8)$$

Since H· generated by UV irradiation reacts with activated nitrogen, it is important to form a reaction field in which short lifetime activated nitrogen can immediately react. Therefore, a reaction field in which larger amounts of H· is present in the water phase could possibly produce larger amounts of ammonia.

Influence of increasing ammonia production by UV irradiation

Figure 7 shows that the reaction was initiated after sufficient generation of H· by UV irradiation. We prepared UV-irradiated water 20 minutes before the synthesis reaction of ammonia (pre-UV irradiation). In this way, the concentration of ammonia that was produced increased due to the creation of a reaction field in which the activated nitrogen was enabled to fully react with H·. In the initial stage of the reaction (10 s of Figure 7), there was no difference in the ammonia concentration produced between the plasma-only reaction and UV + plasma reaction, but a marked increase was observed when pre-UV irradiation was employed. From Figure 5, the spin concentration was approximately 50 µM (at 1200 seconds), suggesting that it was sufficiently consumed for increasing the ammonia production. The actual increase in concentration was approximately 25 µM, which means that half of the spin

concentration was consumed. The activated nitrogen is expected to react with the entire spin concentration, and that the amount of ammonia produced is increased by increasing the spin concentration by extending the UV irradiation time. The reason why activated nitrogen did not react sufficiently within a short time despite the increased spin concentration, is that the amount of activated nitrogen produced by the plasma may affect the concentration of ammonia. In the 300 s shown in Figure 7, an increase in the ammonia concentration included the spin concentration. Within the reaction time of 300 s, the concentration of ammonia is only about 30 μM when plasma only is used. The spin concentration generated by irradiation with UV for 20 minutes was approximately 50 μM, and the increment of this ammonia concentration was 80 μM (Figure 7 striped bar) including spins concentration 50 μM and ammonia concentration 30 μM generated by plasma alone. Here, we suggested that the spin concentration generated by UV irradiation is largely related to the production of ammonia. In the P/L reaction, activated nitrogen reacts with most of the generated H· to become NH, which in turn dissolves in the water to form ammonia. At the same time, since the reaction is proceeding only with plasma, a reaction of activated nitrogen obtaining H directly from H_2O is also carried out. In summary, the formation of ammonia is rate limiting in the process in which activated nitrogen reacts with H· to become NH in water, and it is

important to form a reaction field in which activated nitrogen would be enabled to react quickly. In order to increase the ammonia concentration, it is most important that a reaction field in which a large amount of activated nitrogen is generated and additional H· is present. The ammonia concentration would be expected to increase by forming a reaction field between the gas phase of N-plasma and the water phase forming H on the outermost surface (P/L reaction).

Experimental

Interfacial reaction (P/L reaction) between UV irradiated water surface (liquid phase) and activated nitrogen (plasma phase)

The interfacial reaction mechanism is shown in Figure 1. The interfacial reaction occurs between the UV irradiated liquid phase and the plasma gas phase (P/L reaction). UV light sources of 185 nm and 254 nm (6 W) were used (Sankyo Denki Co., Ltd Japan). Other wavelengths (172 nm, 248 nm, 280 nm, 310 nm, and 340 nm) were used for comparison (248 nm, 280 nm, 310 nm, 340 nm were generated by a MAX-303 instrument, Asahi Spectra Co., Ltd Japan, and 172 nm by USHIO INC Japan). The plasma gas produced by dielectric barrier discharge (Figure 2) using pure nitrogen (99.99%), which was introduced into the reactor at 4 Lmin^{-1}. For the preparation of the plasma

gas, the applied primary voltage was 6 V_{p-p} and the frequency was 18 kHz. Discharge

voltage was determined with a high-voltage probe (attenuation factor: 1:1000) and a

current probe (output rate: 1 V/A) that were connected to an oscilloscope (TDS2024C,

Tektronix Inc. USA). The discharge voltage was 5.09 kV. Pure deionized water was used

for the pure water phase (specific electric resistance of deionized water ≥18.2 MΩcm^{-1}),

which was contained in a round flat glass dish (8.39 cm^2) placed inside the reactor. The

reaction locus (water phase) is located 114 mm from the end of the discharge

electrode. In the liquid phase, water molecules are excited by UV irradiation. Then, the

nitrogen in the plasma phase and water molecules dissociated by UV irradiation were

reacted. Figure 3 illustrates three types of reaction locus and reaction procedures.

Figure 3(a) shows the reaction locus between the plasma gas phase and water phase

without UV irradiation. Figure 3(b) shows the reaction locus between the plasma gas

and water phase with UV irradiation. Figure 3(c) shows a two-step reaction procedure

with pre-excitation of the water phase with UV irradiation. During the pre-excitation,

the H· that was generated appeared at the water phase surface, after which the water

surface forms the reaction locus with the plasma gas phase.

Quantitative analysis of produced ammonia and spins

The ammonia that was produced was detected by ion chromatography (Prominence

HIC-NS, SHIMADZU Co, Japan) with Shim-pack IC-C4 column (SHIMADZU).

Electron Spin Resonance (ESR) can be used to quantify the concentration of spins (JES-X310, JEOL RESONANCE Inc Japan). It is known that 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) is a spin-trapping agent for the OH radical and H radical. Thus, the spin concentration was determined by the spin-trapping method using DMPO. The magnetic field for ESR measurements was 335±10 [mT], the time constant was 0.1 [s], and the modulation width was 0.2 [mT].

Conclusions

Ammonia was successfully produced by using a P/L reaction. A reaction field containing activated nitrogen required for molecules that are able to readily bind because of their short lifetime. We formed a suitable reaction field by irradiating the water phase with UV radiation. This ensures the presence of a sufficient supply of H · in the water phase for reaction with activated nitrogen. As a result, the amount of ammonia that was produced could be increased. It became clear that the spin concentration greatly contributes to the production of ammonia. In addition, prior irradiation of the water phase with UV radiation for reaction with the activated nitrogen, dramatically

increased the amount of ammonia that was produced. In conclusion, increasing the amount of activated nitrogen in the gas phase and increasing the H· in the liquid phase by a large amount enhances the production of ammonia in the liquid phase.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare

Figure Captions

Figure 1. Schematic illustration of ammonia production through Plasma/Liquid interfacial reaction (P/L reaction). Pure N_2 was introduced into the discharger to produce N-plasma (activated nitrogen), which was introduced into the reactor. The P/L interface (reaction locus) was formed with the water phase with 2.5 mL pure water in a flat glass dish. The reaction locus was irradiated by UV light of arbitrary wavelength.

Figure 2. Illustration of dielectric barrier discharge device (discharger) for plasma gas production.

Figure 3. Illustration of each reaction field by Plasma/Liquid interfacial reaction (P/L reaction). Interfacial reaction at N-plasma/water phase (a) without and (b) with UV irradiation. (c) Water irradiated with UV light after which interfacial reaction between N-plasma and water phase was carried out for specified reaction times.

Figure 4. Ammonia and spins production on water phase surface under UV irradiation of arbitrary wavelength. (a) Ammonia production under UV irradiation of various wavelengths (172, 185+254, 248, 280, 310, and 340 nm). Water (2.5 mL) irradiated at various UV wavelengths (open bars). N-plasma reacted only with water (border bar). N-plasma reacted with water under UV irradiation (filled bars). (b) Spin production under UV irradiation of various wavelengths (172, 185+254, 248, 280, 310, and 340 nm). Water (2.5 mL) irradiated at various UV wavelengths (dotted line open bars). N-plasma reacted only with water (dotted line border bar). N-plasma reacted with water under UV irradiation (dotted line filled bars).
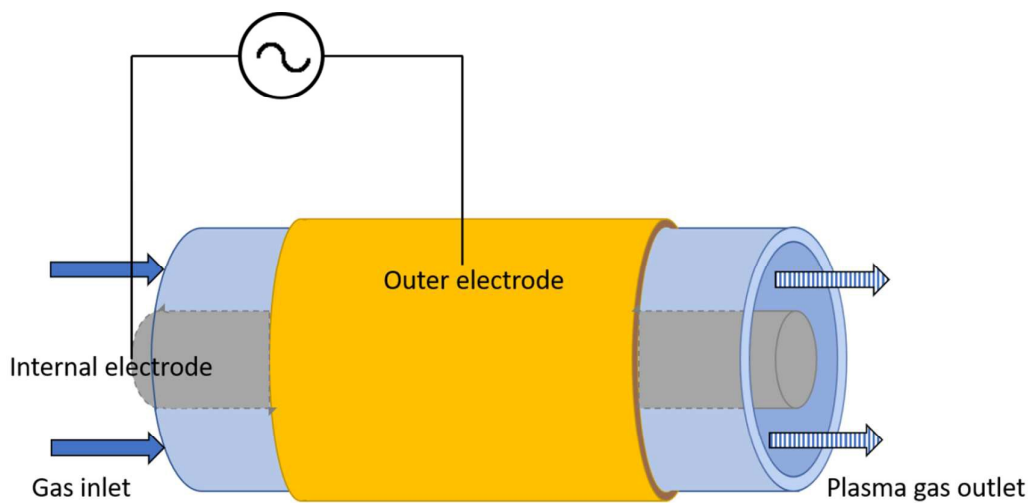
Figure 5. Spin production as a function of duration of UV irradiation. Water phase surface was irradiated by UV light (185nm+254nm). Production of spins were trapped by 0.1M 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) in water phase.

Figure 6. Triadic relationship among number of spins, ammonia concentration, and duration of UV irradiation. Reaction time is within 300 s. N-plasma was introduced to reactor in which petri dish (8.39 cm^2) containing water (2.5 mL) is set. N-plasma reacted with water (triangles). N-plasma reacted with water under185 nm+254 nm UV irradiation (squares). Change in spin concentration as a function of time within 5 min (circles).

Figure 7. Comparison of triadic conditions of P/L reaction. Ammonia concentration at reaction time of 10 s and 300 s. (a) Interfacial reaction at N-plasma/water phase (2.5 mL) without (open bars) and (b) with 185 nm+254 nm UV irradiation (filled bars). (c) Water UV irradiated for 1200 s, after which interfacial reaction between N-plasma and water phase was performed for specified reaction times (striped bar).
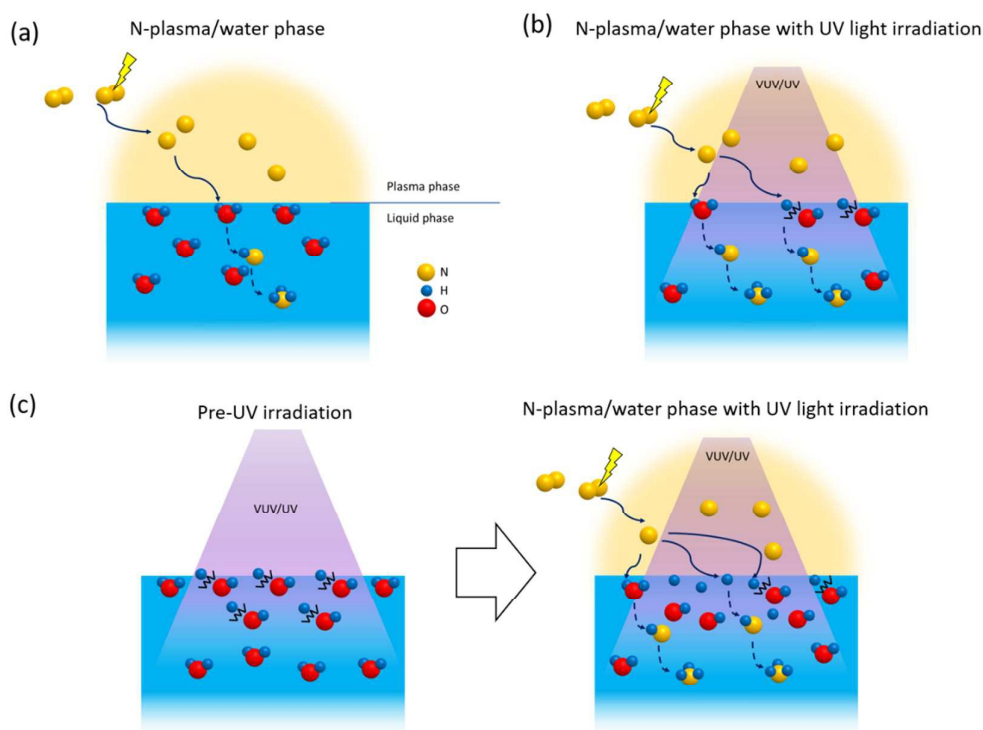
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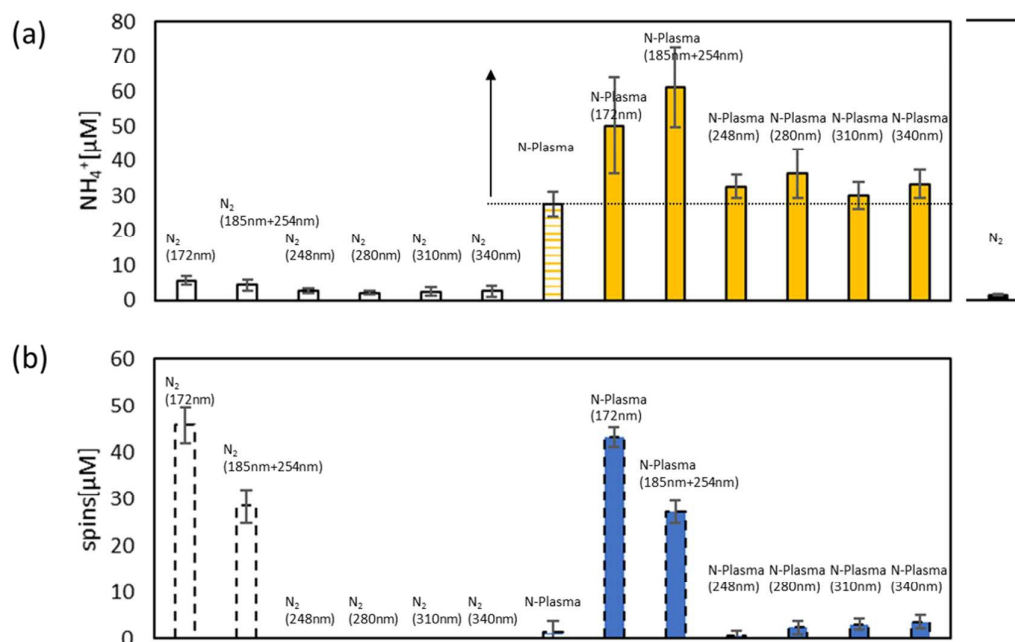
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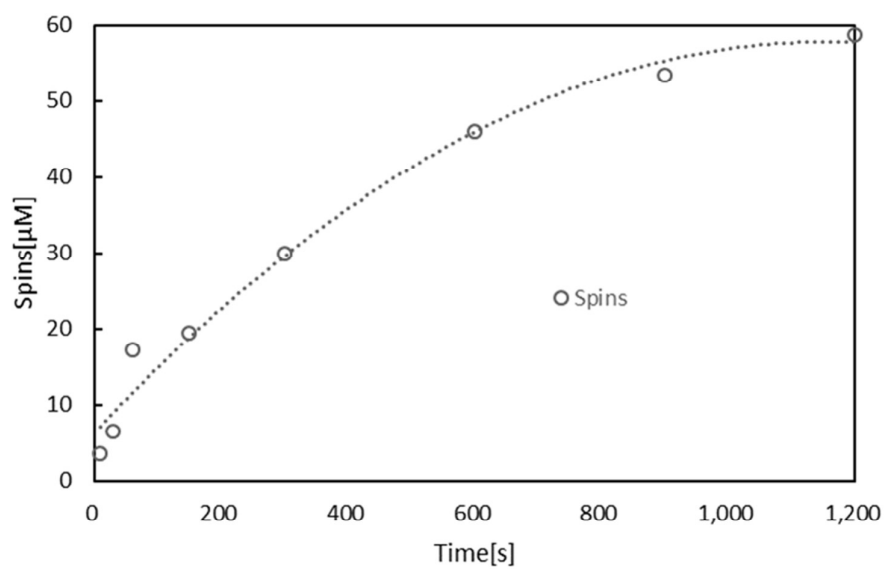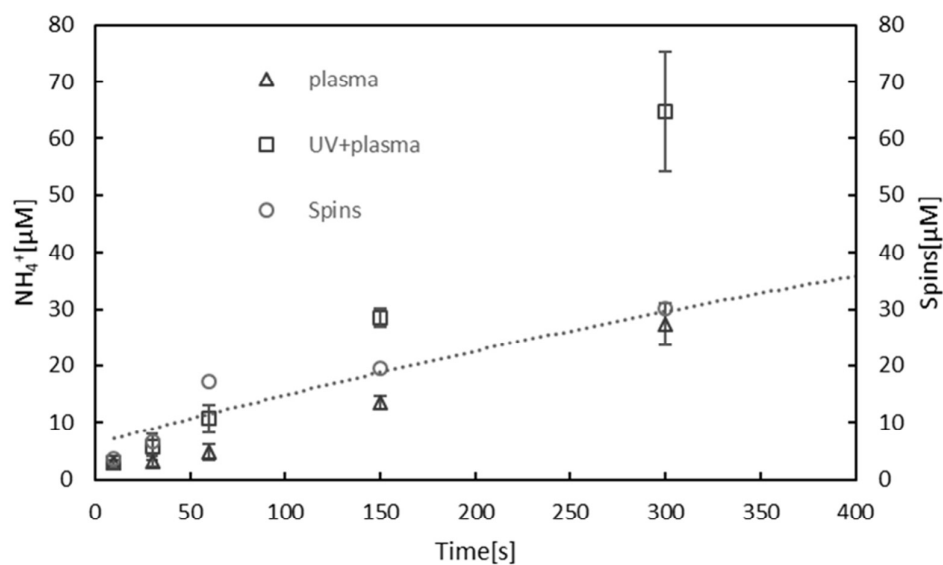
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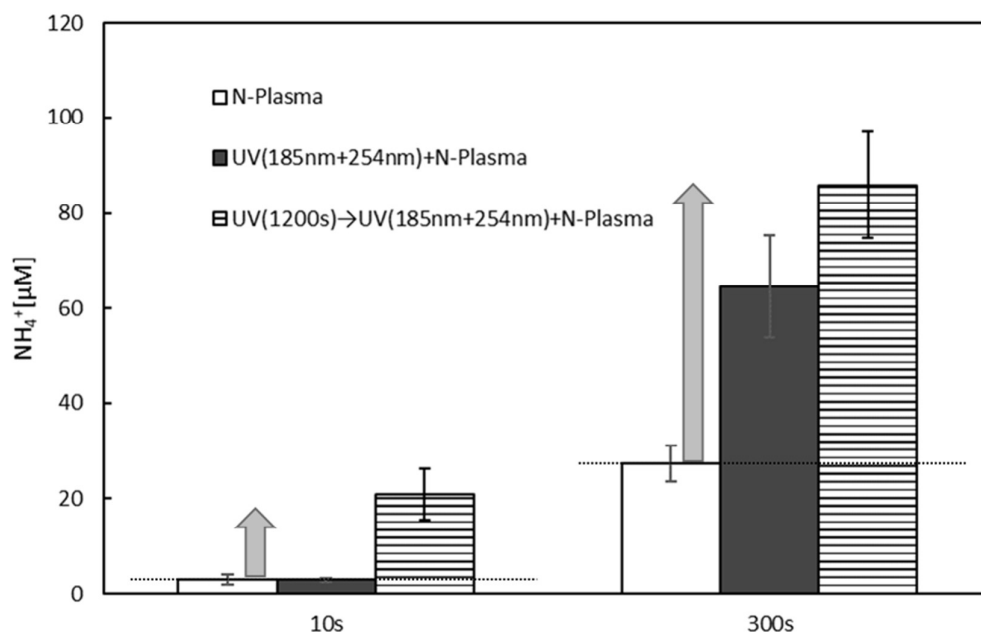
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Supplemental (Graphical Abstract)
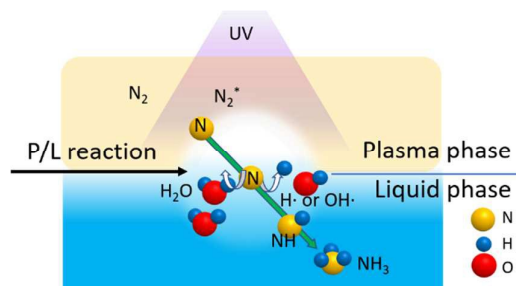
Interfacial reaction between UV irradiated water phase (H· provides) and electron-discharged nitrogen-gas phase (N atom provides) produces ammonia efficiently.