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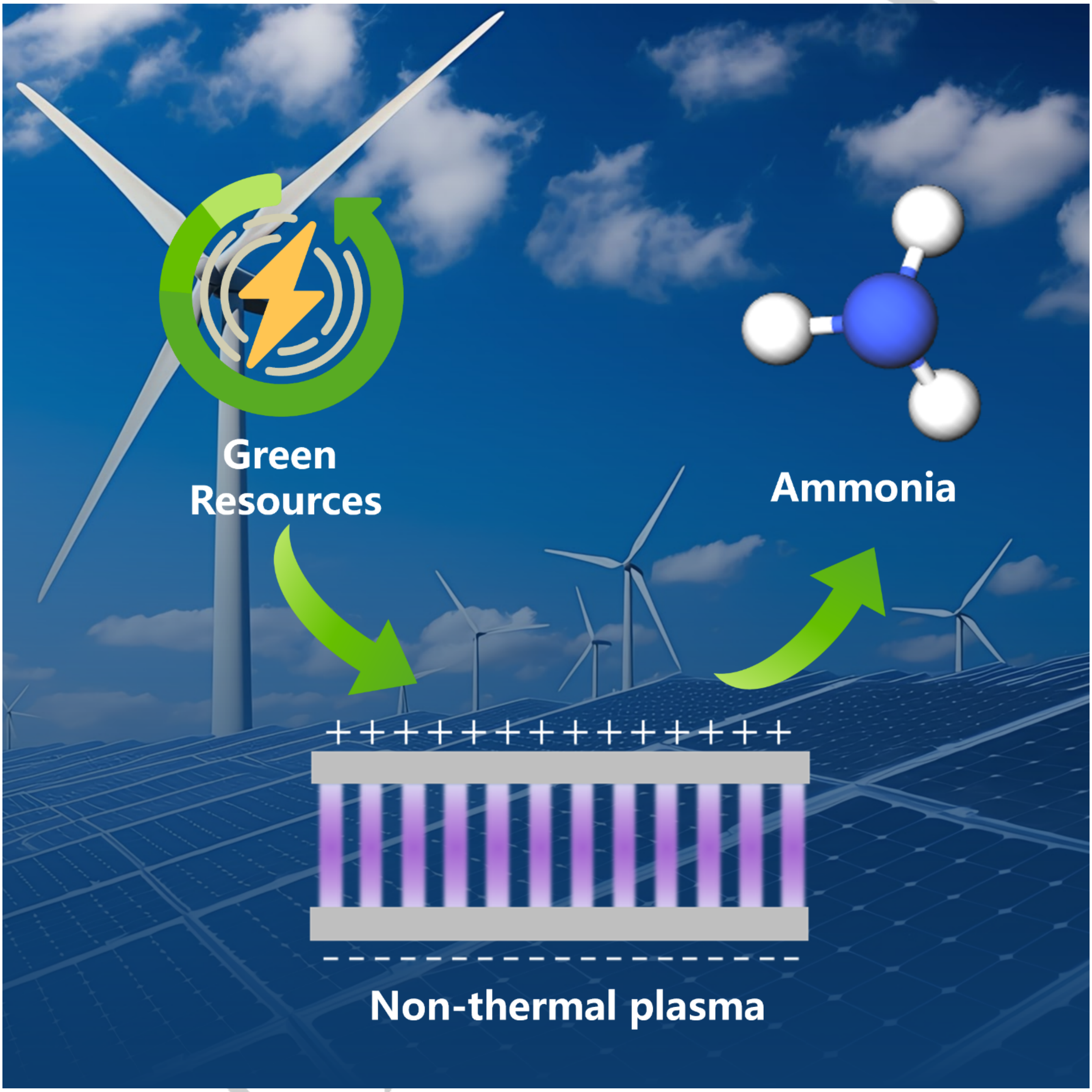

Plasma-Assisted Sustainable Nitrogen-to-Ammonia Fixation: Mixed-phase, Synergistic Processes and Mechanisms

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Abstract: Ammonia plays a crucial role in industry and agriculture worldwide, but traditional industrial ammonia production methods are energy-intensive and negatively impact the environment. Ammonia synthesis using low-temperature plasma technology has gained traction in the pursuit of environment-benign and cost-effective methods for producing green ammonia. This paper discusses the recent advances in low-temperature plasma-assisted ammonia synthesis, focusing on three main routes: N_2 + H_2 plasma-only, N_2 + H_2O plasma-only, and plasma coupled with other technologies. The reaction pathways involved in the plasma-assisted ammonia synthesis, as well as the process parameters, including the optimum catalyst types and discharge schemes, are examined. Building upon the current research status, the challenges and research opportunities in the plasma-assisted ammonia synthesis processes are outlined. The article concludes with the outlook for the future development of the plasma-assisted ammonia synthesis technology in real-life industrial applications.

1 Introduction

Ammonia (NH_3) holds immense global significance as a chemical compound, owing to its versatile applications across diverse industries ranging from agriculture and biomedicine to chemical manufacturing.[1] The chemical industry heavily relies on ammonia as a crucial ingredient for the manufacturing of coatings, plastics, synthetic fibers, and other products. Ammonia also plays a vital role in agriculture as an essential nitrogen source for producing fertilizers that boost crop yield and quality.[2] Apart from its traditional applications, ammonia also holds great potential in sustainable energy storage, particularly as a storage medium and transport vector for clean hydrogen.[3] It is well-known that hydrogen is an efficient and clean energy source, but its storage and transportation present significant challenges. To address these concerns, many efforts have been devoted to develop ammonia-based clean energy solutions. The potential of ammonia to be stored and transported in liquid form makes it an outstanding candidate in this field.[4] This approach involves using renewable energy sources such as solar and wind energy to produce hydrogen, which can be further converted into ammonia for storage and transport.[5]

The Haber-Bosch (H-B) process is the primary method for over 80% of the global ammonia production exceeding 130 million tons annually.[6] The H-B process involves a catalytic reaction that converts nitrogen and hydrogen into ammonia at high pressure and temperature.[7][8] The energy-intensive molecular hydrogen, a crucial feedstock, is typically generated through processes involving fossil fuels, predominantly methane reforming or coal gasification, constituting a notable fraction, around 1-2%, of global energy consumption[9] and resulting in substantial carbon dioxide emissions (~420 million tons annually).[10] Despite these inherent limitations, persistent efforts have been dedicated to the progressive refinement and advancement of the Haber-Bosch process throughout recent decades, culminating in the attainment of its theoretical limits in terms of ammonia energy efficiency.

To overcome the challenges associated with the high energy consumption and excessive greenhouse gas emissions from the H-B process, researchers are actively pursuing sustainable and environment-friendly alternative strategies for ammonia synthesis.[11] Among the emerging solutions, low-temperature plasma technology has garnered strong attention as a promising green and sustainable approach.[12] Plasma, a quasi-electrically neutral medium, consists of abundant ions, free radicals, quasi-stable molecules, electrons, photons, quanta of electromagnetic radiation, and strong electric fields.[13] Of the various types of

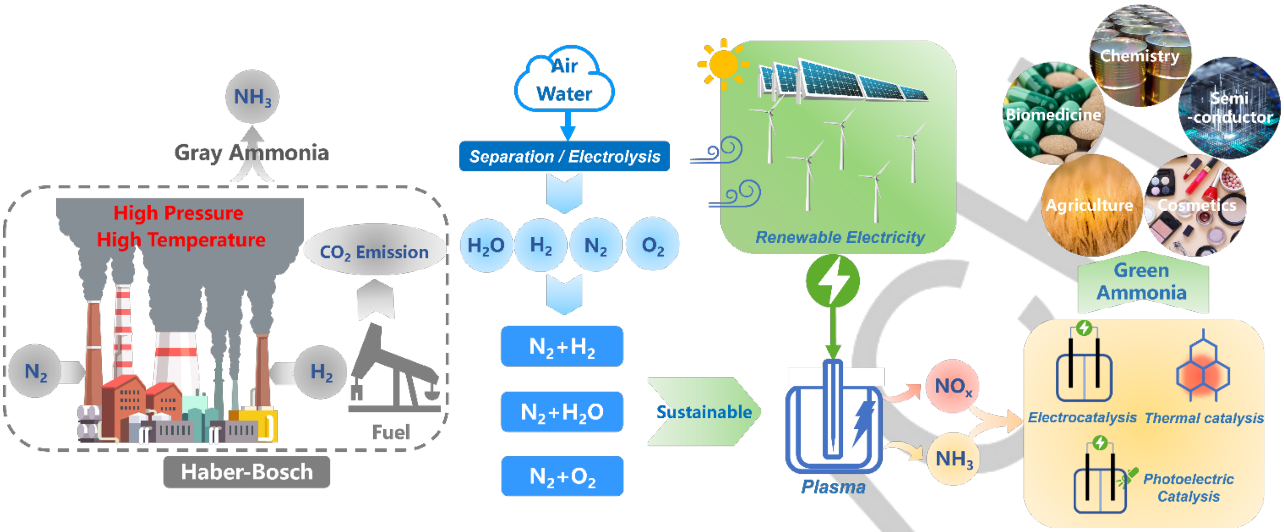

Figure 1. Schematic of the Haber-Bosch process and a sustainable ammonia synthesis process from air and water utilizing renewable energy-driven non-thermal plasma, coupled with various technologies (e.g., electrocatalysis, thermal catalysis, and photoelectric catalysis)

plasmas, low-temperature plasma stands out as a very effective solution for the activation of inert molecules such as N_2. Plasma's unique non-equilibrium characteristics allow normally challenging or slow reactions, to be carried out and accelerated under mild process conditions.[14] Under ambient temperature and pressure, the presence of high-energy electrons in atmospheric-pressure low-temperature plasma can break the triple bonds in nitrogen molecules or excite the nitrogen molecules to the vibrationally excited state, making them more reactive with hydrogen or water, thereby facilitating the formation of ammonia.[15] Furthermore, although plasma technology typically relies on electrical energy for the operation, incorporating new renewable energy sources such as photovoltaic and wind power into plasma generation devices can enhance the sustainability and eco-friendliness of the plasma-enabled ammonia synthesis technology.[16] Overcoming this challenge can enable ammonia production from renewable energy sources, reducing greenhouse gas emissions and promoting sustainable development.[17] Figure 1 shows a schematic of sustainable ammonia production using renewable energy sources with natural raw materials by plasma technology coupled with electrocatalysis, thermal catalysis, and photoelectric catalysis.

The utilization of high-temperature and high-pressure conditions within the H-B process requires extensive, high-capacity ammonia synthesis systems. The slow cooling and heating rates of the H-B process and the required high-pressure conditions make it challenging to initiate and stop ammonia synthesis.[18] Furthermore, the large-scale operation based on centralized production, makes it more difficult to transport and distribute ammonia. On the contrary, low-temperature plasma process is easy to turn on and off, amenable to diverse precursors, and is suitable for localized, intermediate-scale production and subsequent distribution.[19] The three primary techniques for generating low-temperature plasmas, namely dielectric barrier discharge (DBD), plasma jet and gliding arc discharge, have been employed for plasma-assisted ammonia synthesis. Among the above techniques, the DBD produces a filamentary discharge, characterized by its uniformity, stability, and extensive discharge area. Furthermore, DBD plasmas are suitable for coupling with a catalyst and can prevent arc discharges from damaging the catalyst surface.[20] A plasma jet, on the other hand, produces plasma plumes from the reactor nozzle under the influence of electric field and airflow. The plasma jet discharge is mainly used for the reaction of nitrogen with water to produce ammonia, wherein the plasma jet interacts directly with the surface of the liquid phase.[21] Finally, a gliding arc discharge is a non-equilibrium plasma that features an arc generated between electrodes under the influence of a strong electric field. The arc continuously slides along the electrodes under a strong gas flow, giving rise to a plasma with a relatively high emission intensity and macroscopic gas temperature, as well as high energy consumption.[22] Unlike DBD, the gliding arc discharge is generally unsuitable for catalytic ammonia synthesis from nitrogen and hydrogen or water due to its low energy efficiency and the risk of causing damage to catalyst surfaces. Instead, it is more commonly used as a nitrogen fixation strategy in the reaction of nitrogen and oxygen for NO_x production, which can then be electrochemically reduced to produce ammonia.[23]

After nearly a century of intense research, plasma-assisted synthesis of ammonia technology has recently made major advances. Figure 2 summarizes the significant advancements in the field of plasma-assisted ammonia synthesis. The historical timeline of ammonia synthesis reveals that the pioneering work in this field can be traced back to 1877 when William Donkin

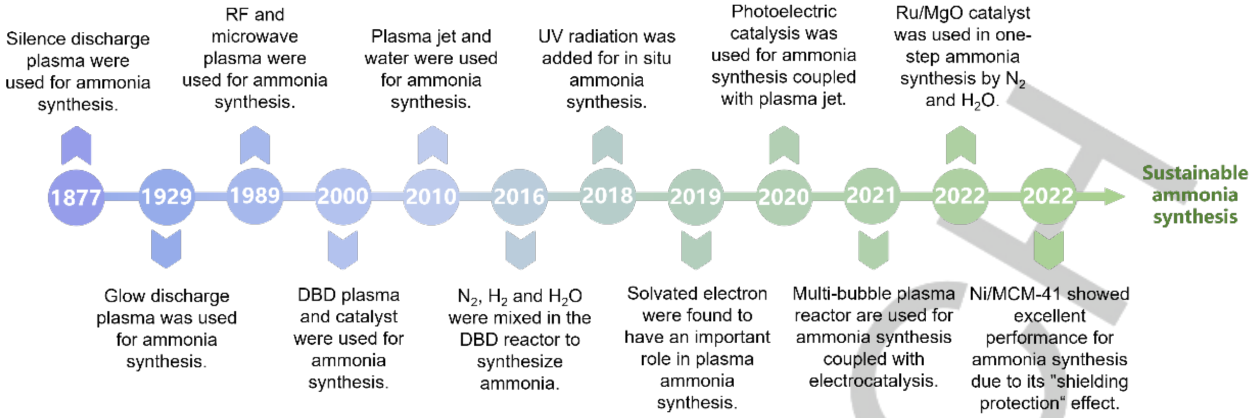

Figure 2. A summary of important developments in ammonia synthesis by the plasma-assisted process. 1877: Donkin et al.[24] ; 1929: Brewer et al. [25] ; 1989: Uyama et al.;[26] 2000: Bai et al.[27]; 2010: KUBOTA et al.[28]; 2016: Xie et al.[29]; 2018: Peng et al.[30]; 2019: Hawtof et al.[31]; 2020: Lamichhane et al.[32]; 2021 Sun et al.[11]; 2022 Zhang et al.[33]; 2022: Wang et al.[34]

conducted ammonia synthesis experiments within a silent discharge configuration. Notably, this milestone predates the formal coining of the term 'plasma' by Irving Langmuir and his colleagues in 1928.[24] The use of glow discharge for ammonia synthesis dates back to 1929,[25] and subsequent decades witnessed the development and utilization of other types of discharges. Specifically, radio frequency and microwave plasma were employed for ammonia synthesis in 1989,[26] followed by the introduction of dielectric barrier discharge (DBD) in 2000,[27] followed by the plasma jet discharges in 2010.[28] Subsequent research efforts have been dedicated to optimizing these systems and deepening the understanding of their mechanisms. In 2016, a hybrid system of N_2, H_2, and H_2O was introduced into plasma-assisted ammonia synthesis,[29] followed by UV radiation in 2018 for *in situ* ammonia synthesis in N_2 and H_2O systems, where UV was shown to enhance the dissociation of H_2O molecules into OH and H. [30] In 2019 the role of solvated electrons in ammonia synthesis in N_2 and H_2O systems was revealed and a new breakthrough in NH_3 selectivity was achieved.[31] In 2020, photocatalysis was introduced into the plasma jet ammonia synthesis system.[32] In 2021, the coupling of electrocatalysis with a multi-bubble plasma reactor achieved great advances in the NH_3 production yield.[11] In 2022, the introduction of Ru/MgO catalysts enabled the plasma-assisted one-step synthesis of ammonia.[33] At the same time, the “shielding protection” effect of Ni/MCM-41 catalysts was revealed, heralding a major step forward in the plasma-catalyzed ammonia synthesis.[34] Currently, low-temperature plasma-assisted ammonia synthesis can be categorized into three main pathways based on the reactants involved: (i) ammonia synthesis from nitrogen and hydrogen; (ii) ammonia synthesis from nitrogen and water, and (iii) ammonia synthesis from air plasma followed by electrocatalytic reduction.[35] All of these pathways require the involvement of hydrogen-containing substances, and they introduce distinct reaction mechanisms, characteristics, and effects into the ammonia synthesis. Nevertheless, to overcome certain limitations that remain in the field of the plasma-assisted ammonia synthesis, such as relatively low yields and selectivity when reacting with water,[36] researchers have introduced other techniques to couple with plasmas and achieve superior ammonia synthesis performances. This hybrid technology represents the current research frontier for sustainable and eco-friendly ammonia synthesis.

In this paper, we aim to provide a comprehensive review of sustainable nitrogen-to-ammonia fixation by low-temperature plasma technology. We will discuss the unique reaction characteristics and mechanisms of each pathway, along with the challenges that need to be addressed to achieve efficient and sustainable ammonia production. Furthermore, we will review the current research status and emerging technologies coupled with plasmas to enhance the efficiency and selectivity of ammonia synthesis. By providing a thorough overview of the current state of low-temperature plasma-assisted ammonia synthesis, this paper seeks to offer insights into the future development of sustainable and eco-friendly ammonia production.

2 Plasma-assisted synthesis of NH_3 from N_2 and H_2

In recent years, studies on the plasma-assisted synthesis of ammonia from N_2 and H_2 have adopted a catalyst-aided plasma approach. The synergy between the catalyst and plasmas is widely discussed in this field. The incorporation of a catalyst can significantly increase the conversion or reaction rates, thus improving the overall ammonia yield. This section will first provide an overview of the fundamental mechanisms and reaction pathways of the plasma-catalyzed synthesis of ammonia from N_2 and H_2, followed by a discussion of the role of the catalyst.

2.1 Basic reaction mechanism

Understanding the mechanism underlying the plasma-catalyzed reactions between nitrogen (N_2) and hydrogen (H_2) is crucial for optimizing the plasma-assisted ammonia synthesis process. The reaction pathway generally involves two main stages: the activation and generation of active species from N_2 and H_2, followed by the combination of these active species to form ammonia (NH_3).[37]

Specifically, the activation of nitrogen and hydrogen molecules occurs in the plasma phase, and the resulting active particles including N_2^+ (Eq. (1)), N_2^* (Eq. (2)), N atoms (Eq. (3)), H atoms, and H_2^+, participate in the subsequent catalytic reactions on the catalyst surface.[38] Nitrogen molecules are typically activated to form N_2* through electron collisional excitation, which results in the formation of excited states that are primarily characterized by both vibrational and electronic excitations.[39] The activation process for H_2 is quite similar to that of N_2, wherein H_2 dissociates into H atoms or is ionized to form H_2^+ in response to the plasma effects, as shown in the reactions described by Eq. (4) and Eq. (5).[40] The plasma-phase activation process provides a unique advantage by enabling reactions that are usually difficult to occur under thermal equilibrium conditions, while massively accelerating them at relatively mild conditions. The generated active particles exhibit high reactivity and can effectively break the triple bond of nitrogen molecules and the strong chemical bonds of hydrogen molecules, which, in turn, promotes the formation of ammonia. In addition to the N_2 activation pathways mentioned in the text, current research indicates that nitrogen molecules activated by plasmas can attach to the catalyst surface and decompose into N atoms. Studies by Peng et al.[41] suggest that electrons can be supplied by Cs to Ru, then transferred to the adsorbed N_2 molecules, leading to the dissociation of nitrogen molecules, as shown in reaction (6):

$$N_2 + e^- \rightarrow N_2^+ + 2e^- \qquad (1)$$

$$N_2 + e^- \rightarrow N_2^* + e^- \qquad (2)$$

$$N_2 + e^- \rightarrow 2N + e^- \qquad (3)$$

$$H_2 + e^- \rightarrow 2H + e^- \qquad (4)$$

$$H_2 + e^- \rightarrow H_2^+ + 2e \qquad (5)$$

$$N_2^*(s) \rightarrow 2N(s) \qquad (6)$$

In the presence of catalysts, the binding of active particles typically occurs through one of two primary mechanisms: the Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) reactions.[11] The E-R reaction involves the individual reaction of active particles with the catalyst surface in the plasma phase, with the resulting products continuing to be adsorbed on the catalyst. In this case, one reactant is activated by the catalyst. In contrast, the L-H reaction occurs when both active particles involved in the reaction are adsorbed on the catalyst, and both reactants are activated in the presence of the catalyst.[42]

The process of combining reactive particles to produce ammonia is the stepwise hydrogenation of N. NH is an important intermediate in the synthesis of ammonia. NH_3 yield is closely associated with the concentration of NH radicals,[40] which are predominantly generated through the direct combination of N atoms and H atoms via the E-R reaction and adsorbed onto the catalyst surface, favored by N atoms adsorbed on the catalyst surface, as shown in reaction (7).[43] It is also possible that certain species, such as N_2^+ and N_2^*, may react with H atoms and H_2 molecules, leading to the production of NH. [44, 45] The NH intermediate can further react with active hydrogen species to generate NH_2 and NH_3. NH_2 free radicals, on the other hand, are formed predominantly through the hydrogenation of NH free radicals, and their generation is governed by the L-H reaction, as shown in the reaction (8).[43]

Ultimately, NH_3 is produced via the hydrogenation of NH_2 or the reaction of NH free radicals with H_2, though the latter reaction is less likely.[46] The hydrogenation of NH_2 can occur through two pathways: L-H reaction (Eq. (9)) and E-R reaction (Eq. (10)), with the gas phase pressure determining the preferred pathway. Shah et al. calculated that at higher pressures, the E-R reaction is more favorable.[43]

However, there are alternative reactions that compete with this process, such as the reverse reaction of NH_3 dissociation and the formation of NH_x and H (or H_2), which will reduce the overall yield of NH_3 (Eqs. (11) and (12)).[37] Therefore, the balance between the formation and decomposition of NH_3 is crucial in the ammonia synthesis process.

The reaction pathways and mechanisms of plasma-catalyzed ammonia synthesis are complex and affected by various factors, such as the plasma parameters, catalyst properties, gas composition, and reaction conditions. Overall, to achieve high yields and selectivity with plasma-assisted ammonia synthesis, it is important to understand the fundamental physio-chemical process and the factors involved in the optimization of the reaction process. Figure 3 shows the plasma synergistic effects with catalysts and the basic pathway of plasma-catalyzed synthesis of ammonia in N_2 and H_2 system.

$$N(s) + H \rightarrow NH(s) \qquad (7)$$

$$NH(s) + H(s) \rightarrow NH_2(s) \qquad (8)$$

$$NH_2(s) + H(s) \rightarrow NH_3(s) \qquad (9)$$

$$NH_2(s) + H \rightarrow NH_3(s) \qquad (10)$$

$$NH_3 + e^- \rightarrow NH_2 + H + e^- \qquad (11)$$

$$NH_3 + e^- \rightarrow NH + H_2 + e^- \qquad (12)$$

In the absence of a catalyst, under the plasma conditions, the synthesis of ammonia from N_2 and H_2 occurs in the gas phase. Ammonia synthesis in the gas phase from N_2 and H_2 involves several key steps. Initially, N_2 and H_2 are initially dissociated into reactive N and H atoms or activated into excited N_2 and H_2 species within the plasma. N_2 molecules can also be ionized to N_2^+ species. These N atoms and N_2^+ then react with H radicals or H_2 molecules in the gas phase to form NH radicals.[47] Subsequent hydrogenation of NH radicals or three-body processes involving N and H atoms, H_2 or N_2 molecules can result in NH_2 formation.[19] NH_2 radicals can also be generated by direct hydrogenation of NH radicals. Further NH_2 hydrogenation or neutral-neutral reactions between NH and H_2 lead to the NH_3 production. In addition, NH_3 can be synthesized from NH_2 radicals with H radicals.[47] The generation of reactive nitrogen species is described by Equation 3, and the ammonia synthesis process is represented by Eqs (1)-(4) and (12)-(18).

$$N + H \rightarrow NH \qquad (13)$$

$$N_2^* + 2H \rightarrow 2NH \qquad (14)$$

$$N + H_2 \rightarrow NH + H \qquad (15)$$

$$N + H_2 + X \rightarrow NH_2 + M \ (X = N_2, H_2) \qquad (16)$$

$$NH + H \rightarrow NH_2 \qquad (17)$$

$$NH_2 + H \rightarrow NH_3 \qquad (18)$$

$$NH + H_2 \rightarrow NH_3 \qquad (19)$$

In the case of metal oxide support (e.g., Al_2O_3), without any metal catalyst, the reaction pathway is similar to that of metal-supported scenarios. However, the absence of the metal catalyst weakens gas-phase radical reactions of N, H, and NH in the plasma and surface reactions on the catalyst. Additionally, it increases the number of strong acidic sites on the surface, reducing the desorption ability of NH_3, ultimately leading to NH_3 adsorption on the catalyst surface and subsequent decomposition under the plasma conditions.[19]

2.2 Synergistic effects with catalysts

Plasma is capable of activating and exciting particles and has been demonstrated to exhibit synergistic effects when combined with catalyst particles.[48] By stimulating the electronic states of reactant molecules, plasma can facilitate their interactions and create additional active sites on the catalyst surface. As a result, integrating plasma with a catalyst for ammonia production holds great potential for achieving more efficient and sustainable ammonia synthesis.[49] The application of low-temperature plasmas to catalytic systems allows for the selective activation of

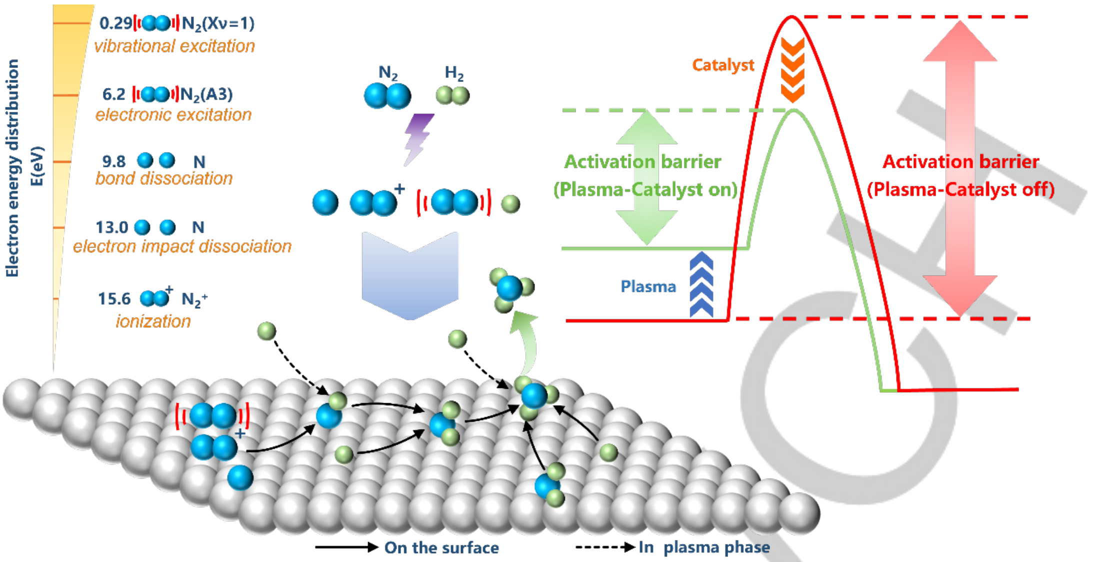

Figure 3. Plasma synergistic effects with catalysts and basic pathway of plasma-catalyzed synthesis of ammonia in N_2 and H_2 system.

certain degrees of freedom of gas molecules, thereby manipulating reaction energetics in ways not possible with conventional thermal catalysis. Using a microkinetic model of nitrogen vibrational excitation in a non-thermal plasma, Mehta et al. predicted that in a plasma-catalyzed reaction environment at low temperature and atmospheric pressure, it is possible to produce NH_3 at a rate that matches the Haber-Bosch process.[39] The effects of the plasma synergy of different catalysts for the synthesis of ammonia from N_2 and H_2 are shown as Table 1.

Active species in the excited state can be adsorbed on the surface of a catalyst, where they will further interact with other molecules, resulting in a variety of chemical reactions.[50] The presence of active sites on the catalyst surface provides a favorable environment for these reactions, lowering the dissociation energy and promoting interactions between reactant molecules.[51] Furthermore, catalysts may modify the reaction pathways and allow specific types of reactions to occur, thereby improving the selectivity of the desired products.[52]

Typically, catalysts that exhibit higher activity have strong binding energies to nitrogen atoms. However, when such a catalyst is used, the products tend to remain adsorbed on the active sites, which somehow lowers the reaction rates.[53] On the other hand, when a catalyst with lower activity is used, the dissociative activation of N_2 becomes the rate-limiting factor,[54] leading to a volcano-shaped activity curve for the catalyst[53] (Figure 4A). In contrast, the presence of plasmas induces the excitation and dissociation of N_2 to occur in the plasma phase rather than on the catalyst surface.[17] This eliminates the limitation of the reaction rate by the dissociation of N_2.

The synergy between the catalyst and plasma thus creates a more favorable environment for ammonia synthesis, leading to higher reaction rates of N_2 and H_2. Figure 3 shows a conceptual representation of the possible mechanism for plasma-catalyzed ammonia synthesis from N_2 and H_2. In the gas phase, non-thermal plasma plays a role in initiating the reaction by activating N_2 molecules into activated reaction species, N_2^*, N atoms, and N_2^+. The increased average electron energy induces electron-induced reactions, leading to the generation of more excited-state radicals (as seen in the "electron energy distribution"). In surface-catalyzed reactions, active particles combine through the E-R and L-H reactions to ultimately produce ammonia molecules. Non-thermal plasma catalysis effectively activates the reactants, largely overcoming the energy barriers of surface reactions (as shown as "plasma-catalyst on" and "plasma-catalyst off").[55]The kinetic model by Mehta et al.[39] shows that the catalysts with the highest rates of ammonia synthesis in plasmas are not the same as in conventional thermal catalysis; instead, the catalysts with the best catalytic performance show weaker bonding to nitrogen. The kinetic model allows for the transition of the active centre of ammonia synthesis from the pedestal site to the ladder site as the high energy state is fully excited, resulting in more atomically efficient catalysis (Figure 4B).[39] For example: the kinetic model introduces the opportunity to follow the step-wise (frequently referred to as the ladder-type in literature) excitations of nitrogen molecules to ultimately achieve atomically- and energy-efficient catalytic synthesis of ammonia.

As mentioned above, an important factor that limits the reaction rate and yield of ammonia synthesis is the reverse reaction, which involves the decomposition of NH_3. Catalyst designs aimed at inhibiting the reverse reaction do so by preventing the target product from being simultaneously exposed to the plasma and the catalytic active sites.[34, 56] Therefore, in plasma catalysis, the selection of a suitable catalyst is crucial in both promoting the synthesis reaction and preserving the products from decomposition. The removal of the products is vital to maintain the reaction conditions and prevent the reverse reaction. By selecting suitable catalysts that interact with various species at specific sites, plasma catalysis can enhance the yield and selectivity of ammonia synthesis.[56]

For example, Liu et al. developed a Co-Ni bimetallic catalyst that can potentially improve the yield and selectivity of the process. The ammonia synthesis rate of Co-Ni/Al_2O_3 catalyst reached 1500·μmol·g^{-1}·h^{-1}. Compared to monometallic catalysis with alumina loading alone, the presence of Co-Ni bimetal reduces the total number and intensity of acidic sites on the catalyst surface on the one hand, which facilitates the desorption of synthetic ammonia gas. On the other hand, the presence of Co-Ni bimetal enhances the plasma discharge observed by the intensified charge-coupled device (ICCD) camera.[57]

Wang et al. used M/Al_2O_3 catalysts for ammonia synthesis studies (M=Ni, Fe, Cu). Among them, the highest ammonia yield of 471 $\mu mol \cdot g^{-1} \cdot h^{-1}$ was obtained with Ni/Al_2O_3, which is 100% higher than the rate of NH_3 synthesis in the plasma-only case. The higher ammonia yield was firstly attributed to the weak acid center on the Al_2O_3 carrier, which had an effect on the performance of the M/Al_2O_3 catalyst. Similar to the findings of Liu et al., the surface acidity of Ni/Al_2O_3 also changed during the reaction, reducing the number of medium to strong acid centers and thus increasing the rate of in situ ammonia synthesis. In addition, the M-N bond strength also affects the catalytic effect. The order of the magnitude of the bond energy of the three catalysts was Ni-N<Cu-N<Fe-N; the weakest Ni-N bond could reduce the energy of ammonia dissociation from the metal center on the catalyst surface, thus inhibiting ammonia decomposition.[58] Similarly, Wang et al. reported the synthesis of a mesoporous Ni/MCM-41 catalyst.[34] The Ni active sites are located on the external surface (Ni/MCM-out), inside the mesopore (Ni/MCM-in) and both inside and outside the mesopore (Ni/MCM-both). For the three types of catalysts, the activities of Ni/MCM-41 catalysts were in the order of Ni/MCM-out (3959 $\mu mol \cdot g^{-1} \cdot h^{-1}$) > Ni/MCM-both (2775 $\mu mol \cdot g^{-1} \cdot h^{-1}$) > Ni/MCM-in (1992 $\mu mol \cdot g^{-1} \cdot h^{-1}$). Ni/MCM-out shows a high NH_3 yield of about 3.7%, which is about 8 times higher than the plasma alone. This high yield can be attributed to the "shielding protection" effect. The "shielding effect" is not related to adsorption but is a result of the porous catalyst structure that facilitates the diffusion of the generated ammonia molecules into the pores of MCM-41. This effect shields the generated species from exposure to the plasma, thus preventing the decomposition of ammonia. Simultaneously, ammonia molecules can diffuse out of the pores of MCM-41, which promotes the synthesis reaction effectively (Figure 4C). [34]

In-situ product removal can also avoid the decomposition of ammonia by plasma and inhibit the reverse reaction. For example, Rouwenhorst et al. utilized zeolite for in-situ adsorption of ammonia molecules generated by plasma. Due to the inability of the plasma to penetrate these pores, the decomposition of ammonia molecules within the plasma was suppressed. After the plasma is turned off, it became imperative to maintain a continuous gas flow in the reactor for purging purposes. This step facilitated the desorption of ammonia adsorbed within the zeolite and allowed for its capture at the outlet of the reactor. The energy yield of ammonia synthesis was increased by a factor of 2, from 1.1 to 2.3 $g \cdot kWh^{-1}$.[56] However, this work shows noticeable differences in results compared to Wang et al. [34], as Rouwenhorst et al. did not detect ammonia at the reactor outlet in the plasma-on process but observed the presence of ammonia after shutting down the plasma system. Therefore, the principles of shielding effects and in-situ adsorption of catalysts in the plasma-enabled NH_3 synthesis need to be further investigated.

Therefore, an optimal catalyst for the plasma-catalytic ammonia synthesis should exhibit several key characteristics, including (i) a high density of active sites for reactive species reactions, (ii) a porous structure to provide shielding for desorbed ammonia molecules from decomposition, (iii) a regulated surface acidity to facilitate rapid ammonia desorption while preventing the recombination of nitrogen or hydrogen atoms and the reverse reactions of NH_3 decomposition. Although promising progress has been made in using the properties of catalysts to inhibit the inverse reactions of ammonia decomposition, further studies are still limited by the reaction conditions, such as the *in-situ* adsorption capacity of zeolites being reduced by plasma-induced heating.[56] The catalytic effect of the relevant catalysts may be greatly reduced in plasma-coupled thermal catalysis for ammonia synthesis (like zeolite4A).[56] Therefore, catalysts that can cope with more stringent reaction conditions are also a direction for future research efforts. In addition, product liquefaction, the use of membranes to separate products or adsorbents may be possible for product separation.[59]

Catalysts are commonly doped on the surface of various carriers such as metal oxides (*e.g.*, Al_2O_3, MgO), zeolites and other materials. These carriers can also contribute to the enhancement of catalyst activity and the acceleration of the ammonia synthesis reactions through either their structural properties, electronic promoters or influence on the plasma discharge characteristics.[60] For example, Shah et al. compared zeolite 5A, zeolite 4A, beta, 13X, and an aluminum phosphate (AlPO-18) catalyst and showed that the highest energy yield of 15.5 $g\text{-}NH_3 \cdot kWh^{-1}$ was achieved using 5A zeolite at equimolar N_2 to H_2 ratio, which was at least 50 times higher than when the plasma acted alone. The presence of zeolites in the DBD reactor promoted the formation of microdischarges and the change of reactor voltage-current characteristics, which improved the catalytic performance.[61] The effect of filled carriers on ammonia synthesis was investigated by Patil et al. They used $\gamma\text{-}Al_2O_3$, $\alpha\text{-}Al_2O_3$, MgO, CaO, quartz wools, TiO_2 and $BaTiO_3$ as catalyst carriers. It was shown that the synergistic effect of loading was not related to the catalytic effect but to the physical properties of the filled carriers. The highest NH_3 yields were found for quartz wool and $\gamma\text{-}Al_2O_3$, with 113% and 95% increases in ammonia yield over the unfilled state, respectively. This finding may be due to the reduction in the width of the air gap in the inter-particle voids, resulting in the electrons in the plasma experiencing a stronger electric field. The average electron energy increases, thus producing higher excited or dissociated state species in the plasma. At the same time, narrow-bandgap materials (TiO_2 and $BaTiO_3$) are more likely (than insulating materials) to emit electrons that contribute to the plasma formation reducing the breakdown voltage at which the plasma is initiated, and thus reducing the electric field and the efficiency of generation of dissociated or excited species in the plasma. However, the porosity and associated specific surface area of the material has a limited effect on the enhancement of ammonia synthesis. This is due to the fact that the plasma does not form within the pores and the active species produced by the plasma do not diffuse into the pores.[62]

Monometallic catalysts, including wool-like metals, liquid low melting point metals and metal-organic frameworks, are alternatives in the plasma catalysis system. Iwamoto et al. demonstrated that an increase in the number of discharges could lead to a better catalytic performance by introducing wool-like metals into the reactor medium. From the first to the fifth experiment, the catalytic activity exhibited a significant increase, reaching a relatively stable level thereafter. During this period, the reaction rate rose from approximately 20 $\mu mol \cdot min^{-1}$ to around 105 $\mu mol \cdot min^{-1}$, while the ammonia yield increased from approximately 0.5% to 2.5%. Although the type of metal used has a negligible effect on the efficiency of N_2 activation, it does exert a noticeable influence on the reactivity of the activated material in ammonia production. [63] There has been limited research on the synthesis of ammonia using molten metal as a catalyst. While molten metal may show improved performance in ammonia synthesis, its effectiveness strongly depends on the reaction conditions.[64]

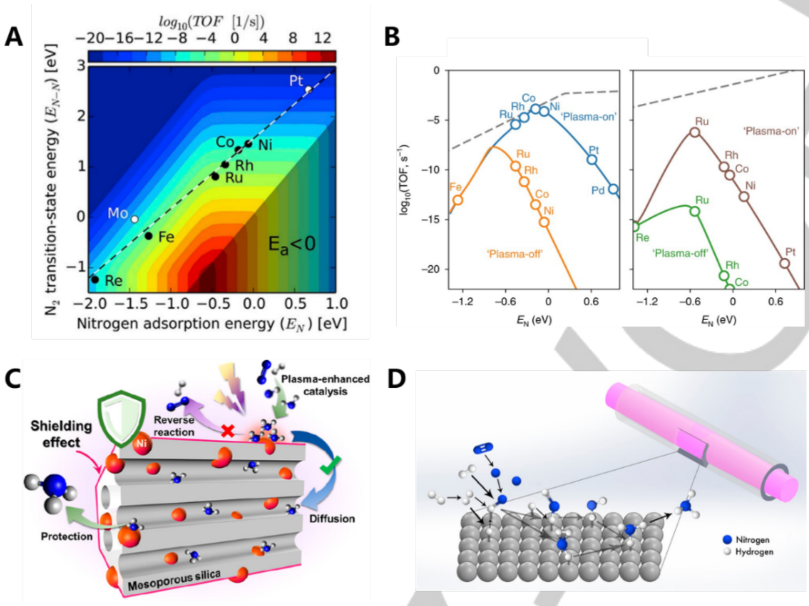

Figure 4. Significant findings of plasma-assisted synthesis of NH_3 from N_2 and H_2. (A) Volcano-shaped activity curve for the catalyst. Reproduced from ref. [65] Copyright (2015), with permission from Elsevier. (B) Comparison of N_2 vibrational-distribution-weighted (plasma-on) and thermal (plasma-off) ammonia synthesis rates on step (left) and terrace (right) sites. Reproduced from ref.[39] Copyright (2018), with permission from Springer Nature. (C) Shielding effect of Ni/MCM-41. Reprinted with permission from ref.[34] Copyright 2022, American Chemical Society. (D) A semimetal, pure gallium was used for the first time as a catalyst for ammonia synthesis. Reprinted with permission from ref.[43] Copyright 2018, American Chemical Society.

Table 1. The effect of plasma combined with different catalysts for the synthesis of ammonia from N_2 and H_2.

Discharge Type	Catalyst	NH_3 production rate (mmol g_{cat}^{-1}·h^{-1})	NH_3 Conversion level	Energy cost (MJ·mol^{-1})	Ref.
Haber-Bosch		-	8%	0.49	[1]
DBD	Ni/Al_2O_3	0.47		437.14	[58]
DBD	Ni/Al_2O_3		6.3%	-	[66]
DBD	Co-Ni/Al_2O_3	1.5		73.73	[57]
DBD	Ni-Mg0.02/SBA-15-IWI	4.4		58.29	[67]
DBD	Ni/MCM-41		>5%	40.8	[34]
RF	Ga		10%	278.18	[43]
RF	Au		19%	-	[43]
RF	Ni-MOF	-		266.09	[68]
RF	Ga-In	-		197.42	[64]
DBD	Zeolite4A	-		26.61	[56]
DBD	ZIF-8、ZIF-67	2.53		-	[69]
DBD	Zeolite5A	-		3.99	[61]
DBD	Rh/Al_2O_3		1.43%	65.11	[70]
DBD	Co-N_2	10.63		-	[71]
DBD	-		0.30%	58.85	[72]
DBD	-		0.18%	-	[73]
DBD	PZT		2.7%	68	[44]
DBD	PZT		7%	-	[45]

Shah et al. conducted studies on ammonia synthesis using RF plasma and molten metal catalysts such as Ga. They achieved a 10% ammonia yield and an energy yield of 0.22 g·kWh^{-1} under mild conditions by employing molten Ga as a catalyst (Figure 4D). However, the performance of Ga, compared to other transition metals, exhibits significant variation within the range of 150-300 W, primarily due to its inclination to form stable nitrides at elevated temperatures. As the power level increases, the catalytic activity of Ga experiences a notable decline, suggesting that molten Ga can only function as a catalyst under specific conditions.[43]

Metal-organic framework (MOF) is another new structured metal-based, highly-porous catalyst with better performance than conventional metal catalysis. Shah et al. developed a Ni-based MOF as a catalyst for ammonia synthesis using RF plasmas. The ammonia yield of Ni-MOF was higher compared to pure nickel metal. The ammonia yield was as high as 0.23 $g \cdot g_{cat}^{-1} \cdot kWh^{-1}$ with an energy consumption of 265 $MJ \cdot mol^{-1}$ using Ni-MOF. The enhanced catalytic activity of Ni-MOF in the presence of plasmas can be attributed to its porous structure, which facilitates the efficient transfer of reactant and product molecules, as well as the presence of open Ni metal sites and reduced surface hydrogen complexation. However, similar to molten metal catalysts, the performance of catalysts with MOF structures is heavily influenced by the conditions of the plasma discharge. At a higher plasma power (300 W), internal stresses within the porous framework can cause amorphization, negatively impacting the catalyst's performance.[68]

From the above discussion, it is evident that there is an need to overcome the limitations imposed by the plasma discharge conditions on catalyst performance, including preventing reactions between metal catalysts and active nitrogen species and mitigating the influence of experimental factors such as electromagnetic fields, micro-discharges, and temperature on catalyst structure. Further development and design of metal catalysts with good performance across various reaction conditions, as well as optimization of their structures, remain crucial objectives.

3 Plasma-assisted synthesis of NH_3 from N_2 and H_2O

In the plasma-assisted N_2-H_2O ammonia synthesis system, water (H_2O) replaces H_2 as the hydrogen source, offering several advantages. Firstly, the use of pure H_2 requires extensive processing, such as methane reforming, which generates large amounts of CO_2 and contributes to global warming.[74] Although electrolysis of water is an alternative method for H_2 production, it requires significant amounts of energy and may not always be a sustainable solution.[75] Furthermore, considering the safety challenges associated with explosive hydrogen gas, using H_2O is a safer and more environmentally friendly option.[76] However, the plasma-assisted N_2-H_2O ammonia synthesis faces several challenges, including improving the yield and selectivity of ammonia synthesis, optimizing plasma-catalyst interactions, and reducing energy consumption. Despite these challenges, this approach holds great potential as an alternative to traditional methods of ammonia production. The effect of plasma-assisted synthesis of ammonia from N_2 and H_2O is shown as Table 2.

3.1 Basic reaction mechanism

The plasma-liquid interaction between N_2 and H_2O involves multiple chemical and physical processes, such as electron transfer, dissociation, recombination, and diffusion. The mechanism depends on the specific reaction conditions, such as the plasma ignition technique, power input, the form of H_2O (gas, mist, droplet, or liquid) and system temperature. Plasma can generate various reactive species, such as electrons, radicals, ions, and atoms, which can interact with H_2O molecules and produce secondary species, such as OH radicals and H atoms. These secondary species can further react with the nitrogen molecules and lead to the formation of ammonia molecules. However, the detailed reaction pathway and kinetics are not yet fully understood, and further research is needed to elucidate the underlying reaction mechanisms.

When reacting with H_2O, N_2 undergoes simultaneous oxidation and reduction reactions, whereby H_2O decomposes into H atoms and OH radicals. Typically, H species participate in the nitrogen reduction reaction (NRR) to produce ammonia, while OH species participate in the nitrogen oxidation reaction, leading to the production of nitrogen oxides (NO_x) as byproducts.[29] Additionally, OH species can recombine to form H_2O_2.[77] The two primary modes of reaction are electron impact and UV interaction, as seen in equations (20) and(21).[11]

$$H_2O + e^- \rightarrow OH + H + e^- \tag{20}$$

$$H_2O + UV/VUV \rightarrow OH + H \tag{21}$$

The plasma-assisted synthesis of NH_3 using H_2O as a hydrogen source shares a similar process to that using H_2. This process generally involves reactive N species reacting with H atoms or H_2O molecules to generate NH radicals, which are then hydrogenated to produce NH_3.[30] These reactive N species including N_2^*, N_2^+, and N atoms, vary in their degree of excitation, and their lifetimes and reaction paths differ. Sakakura et al. utilized UV/VUV assisted irradiation to investigate the reaction paths of these three activated nitrogen species. They found that N atoms exhibit high reactivity and tend to react directly with water molecules. At the same time, N_2^* and N_2^+, which have relatively long lifetimes but low reactivity, are more likely to react with OH and H species.[78]

Due to the importance of the effects of high-energy electrons involved in the main dissociation mechanism of NH_3, it is desirable to maximize the presence of low-energy electrons to minimize the loss rate of ammonia molecules produced in the gas phase. Additionally, the conversion of N_2 and H_2O to ammonia is an endothermic process that requires relatively high temperatures. For example, Peng et al. reported that the efficiency of ammonia generation was significantly influenced by the solution temperature and discharge conditions.[79] Other experimental and simulation results demonstrate that these variables have a more significant impact on the N_2/H_2O plasma system than on the N_2/H_2 plasma system.[80]

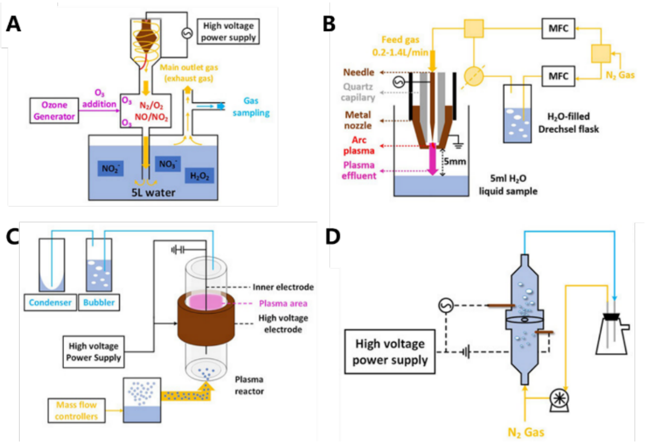

Figure 5. Common reactor configurations of plasma-assisted synthesis of NH_3 from N_2 and H_2O. (A) Gliding arc discharge. (B) Plasma jet discharge. (C) DBD.(D) Multi-bubbles discharge. Reproduced from ref.[36] Copyright(2022), with permission from Wiley-VCH.

3.2 Reactor configurations

The current plasma-assisted ammonia reaction involving N_2 and H_2O can be classified into three distinct types based on the reaction state: continuous gas-liquid phase, continuous gas phase with dispersed liquid phase, and dispersed gas phase with continuous liquid phase. Each type exhibits unique characteristics, which can be summarized as follows.

Continuous gas-liquid phase means that the reaction occurs at the surface of the liquid. Common forms of discharge include the gliding arc (shown as Figure 5A) and the plasma jet (shown as Figure 5B). Continuous gas phase with dispersed liquid phase is the dispersion of liquid in gas, in the form of water droplets or water vapor. The most common discharge form is DBD (shown as Figure 5C). The dispersed gas phase with continuous liquid phase means that the gas is present in the liquid in the form of bubbles. (Shown as Figure 5D).

3.2.1 Continuous gas-liquid phase

The continuous gas-liquid phase reaction typically involves the interaction of the plasma region with the surface of the aqueous solution, leading to the predominant synthesis of ammonia occurring at the liquid surface. As such, the reaction strongly depends on the reaction area, making it crucial to investigate the optimal plasma exposure area of the liquid and the distance between the plasma-generation surface (e.g., a DBD electrode or a nozzle of a plasma jet) to the liquid surface.[36] Common P/L reaction modes associated with continuous gas-liquid phase include electrolysis, jet, and gliding arc, and this reaction mode has been studied the most within the N_2 and H_2O system. However, the mechanism underlying the plasma's interaction with the liquid phase is not yet fully understood. Some researchers propose that the plasma first reacts with water vapor above the liquid phase's surface,[81, 82] while others suggest direct interaction between the plasma and H_2O molecules within the liquid phase.[83] To gain a comprehensive understanding of the reaction mechanism, advanced models incorporating accurate kinetic analysis are necessary.

To obtain deeper insights into the mechanisms underlying the interaction between liquid-phase H_2O and N_2 in the presence of plasma, and to explore the disparities in the products resulting from gas-liquid reactions and the discharge properties of nitrogen gas under the varying levels of humidity, experiments involving the introduction of H_2O vapor into nitrogen gas through plasma jet and electrolysis methods were conducted. Gorbanev et al. utilized a plasma jet reactor situated at the interface between the plasma and water, where they introduced water vapor into N_2 gas to investigate the reaction mechanism between H_2O and N_2 in the presence of plasmas. It was concluded that the primary source of NH_3 production was the addition of H_2O vapor to N_2.[84] Similarly, Pattyn et al. employed a DC electrolytic cathodic jet reactor, also incorporating water vapor into nitrogen. Their study revealed that the supply of oxidizing substances (O_2, OH) and reducing substances (H_2, H) involved in the reaction primarily depended on the gas phase, with higher levels of water vapor favoring the vibrational excitation of N_2 and strongly correlating with the production of NO and H_2 species. Moreover, the discharge characteristics were influenced in intricate ways by the water vapor content due to the disparate ionization energies of nitrogen (15.58 eV) and water (12.62 eV). This influence can be due to the inelastic collision mechanism, electron density, and electron energy distribution function.[85]

To enhance the efficiency of ammonia synthesis, researchers have explored the incorporation of metals into the liquid phase. Lamichhane and colleagues conducted studies on ammonia synthesis using a plasma jet reactor, in which they introduced 5 grams of metals including Zn, Mg, Al, and Cu into the liquid phase.[86] These metals acted as reducing agents, facilitating the conversion of H^+ ions, produced through the dissolution of NO_x in water, into H atoms. The generated H atoms were subsequently employed in the reduction reaction of nitrogen.[86] Additionally, metals can also influence pH levels and enhance the reaction rate of NH_3 synthesis. Among the various metals tested, Mg demonstrated the best ammonia synthesis performance.[86]

In addition to the aforementioned electrolysis and jet models, researchers are actively exploring new approaches for the continuous gas-liquid phase reaction between N_2 and H_2O. Indumathy et al. utilized a gliding arc to discharge at the the liquid interface, resulting in the formation of a plasma plume. They observed significant vibrational and rotational excitation at the tip of the plasma plume in contact with water. While this method achieved a high yield of 0.68 $mg \cdot h^{-1}$, its energy efficiency was relatively low, in the range of 0.0249~0.0268 g-$NH_3 \cdot kWh^{-1}$.[87] Further investigation and development of more efficient and effective reaction methods are required in future research endeavors.

3.2.2 Continuous gas phase with dispersed liquid phase

In the continuous gas phase reaction with a dispersed liquid phase, the interaction between H_2O and N_2 plasma takes place when H_2O is in the form of droplets or aerosols within the gas phase. As the dispersion of H_2O increases, this reaction can be expanded to include the reaction between plasma-assisted water vapor and N_2 plasma. Among the various discharge methods employed, dielectric barrier discharge (DBD) remains a commonly utilized approach.

The effectiveness of plasma-assisted ammonia synthesis is significantly influenced by the design of DBD reactors. Zhang et al. compared different DBD reactor designs and concluded that DBD-W (single medium-water-cooled) configuration demonstrated notable enhancements in the ammonia production rates. This specific design resulted in 1.4-1.6 times higher current and electron density compared to the other three reactor designs. The improved performance can be attributed to the generation of high-density vibrational excitation of $N_2(v)$ and $H_2O(v)$, leading to dissociation and rapid rates of adsorption, thus facilitating efficient production of N(s) and H(s). When incorporating catalysts, noble metals are typically required for N_2 dissociative adsorption, as DBD plasma tends to exhibit a relatively low degree of dissociation and a high degree of excitation. Consequently, experiments were conducted utilizing different oxides (Al_2O_3, SiO_2, MgO) as supports of Ru catalysts. The findings revealed that MgO, which possesses strong basicity, enhanced the rate of ammonia synthesis by providing additional surface electrons, thereby reducing the dissociation potential of N_2 and H_2O (Figure 6B).[33]

To explore the impact of introducing H_2O into the reaction system using a DBD, Toth and colleagues conducted investigations involving both atomized water droplets and water vapor forms (Figure 6C). Their findings indicate that the primary pathway for ammonia synthesis occurs through the utilization of water vapor, while the liquid droplets undergo evaporation within the DBD discharge filament, contributing to the overall reaction. Interestingly, the physical state of H_2O has a minimal effect on the ammonia synthesis process, indicating that the reaction is largely independent of it. The concentration of water vapor in the reactor is notably influenced by the temperature, necessitating high temperatures to prevent H_2O condensation. Conversely, the reaction system involving liquid droplets requires relatively milder reaction conditions, making it a feasible alternative to using water vapor.[88]

Furthermore, Muzammil and colleagues employed an interesting approach in which a N_2 rotating gliding arc reactor was used in conjunction with liquid water in the form of a thin film, allowing nitrogen to be introduced from the reactor wall to cool the reactor without affecting the arc stability (Figure 6D). Energetic electrons and reactive nitrogen species generated in the arc plasma collide with the water film, resulting in the ionization and dissociation of H and OH/O radicals. These radicals then react with the nitrogen radicals to form NO_x. The NO and H_2 species produced in the reaction are then injected into the Pd/γ-Al_2O_3 catalyst distributed within the plasma reactor. The co-produced H_2 completely reduces the NO_x to produce NH_3 with a selectivity of up to 95%. This approach differs from the previous methods in which ammonia reacts with NO_x through nitrogen disproportionation. Instead, this method utilizes nitrogen and water to produce NO and H_2, which are subsequently reduced to produce ammonia. As a result, the selectivity of ammonia production is significantly improved compared to other typical plasma catalyst methods.[89]

In continuous gas phase with dispersed liquid phase reaction system, gas flow rate and water vapor content are critical reaction conditions that can affect the energy consumption and yield of plasma-catalyzed ammonia synthesis. Typically, the water vapor content is controlled by adjusting the water bath temperature. The work by Zhang and colleagues indicates that an increase in the water vapor input flow rate leads to an enhancement in the NH_3 production rate. [33] Furthermore, when the gas flow rate increased from 0.2 standard liters per minute to 1.0 standard liters per minute, the synthesis rate increased from 1.53 $\mu mol\ h^{-1}$ to 65.4 $\mu mol\ h^{-1}$. However, the findings of Nguyen and co-workers differ from those of Zhang et al. When the N_2 input flow rate exceeded 6.1 sccm (specific cubic centimeters per minute), specifically at 12.5 and 25.0 sccm, the ammonia synthesis rate from N_2 and seawater vapor decreased with increasing N_2 input flow rate.[90] Additionally, Feng and his team's research suggests that the water vapor content significantly impacts energy efficiency and yield. When the water bath temperature increased from 30°C to 90°C, energy efficiency increased from approximately 4.4 $mg\cdot kWh^{-1}$ to about 7.5 $mg\cdot kWh^{-1}$, and NH_3 production rate rose from around 2.6 $\mu mol\cdot g_{cat}^{-1}\cdot h^{-1}$ to approximately 4.3 $\mu mol\cdot g_{cat}^{-1}\cdot h^{-1}$.[91]

Water vapor serves as the sole hydrogen source in plasma catalysis ammonia synthesis from nitrogen and water. Consequently, an adequate supply of water can contribute to the generation of more active H atoms, thereby promoting the ammonia synthesis reaction and enhancing energy efficiency.[33, 90]

3.2.3 Dispersed gas phase with continuous liquid phase

Currently, the research in the plasma-assisted synthesis of ammonia utilizing nitrogen and water predominantly focuses on the two previously discussed reaction forms. However, there has been a relatively limited exploration of the gas-phase dispersion liquid-phase continuous form, specifically underwater bubble discharges. Underwater discharges primarily occur at the interface between the gas and liquid, in the form of spark discharges. This type of reaction system places higher requirements on the conductivity of the liquid phase, which essentially serves as an electrode within the discharge system.[79] The conductivity of the liquid determines the power consumption and the intensity of the discharge, ultimately affecting the nitrogen fixation performance. Further investigation into this area is necessary to better understand and optimize the potential of underwater bubble discharge in the plasma-assisted ammonia synthesis.

Peng et al. conducted a study where N_2 bubbles were introduced into an aqueous solution within a reactor, and a high-voltage electrode, along with a ground electrode in the liquid phase, was employed to generate plasmas through underwater discharge. Although this approach achieved a rate of 11.2 $\mu mol\cdot min^{-1}$, the selectivity for ammonia was low, and the majority of the products generated were nitrogen oxides.[79] In another investigation, Sun et al. developed a multi-bubble reactor utilizing underwater discharges. In this approach, air was initially introduced into the reactor to generate NO_x intermediates through spark discharges. Then, electrochemistry was employed to reduce the intermediate products to ammonia, which provided a sustainable approach to produce ammonia under mild conditions. These studies highlight the potential of underwater discharges in the production of ammonia, with Sun et al.'s approach particularly promising for achieving green ammonia production under mild reaction conditions.[11]

Reviewing the literature, it becomes evident that underwater discharges exhibit high intensity but relatively low selectivity for ammonia production, making them more suitable for generating NO_x. Nevertheless, their potential for nitrogen fixation at high rates offers an opportunity for sustainable ammonia synthesis under mild conditions by coupling them with complementary techniques such as electrochemical catalysis to convert NO_x to ammonia.[92] Furthermore, there is a crucial need to explore the incorporation of catalysts in this type of reactions. The selection of suitable catalysts, their optimal placement and supports, as well as the understanding of the reaction mechanisms involved in the interaction between catalysts and plasma in the liquid phase require further research.

Feed humidity has different effects on ammonia synthesis in different reactor setups. Discussing the impact of humidity on ammonia synthesis in different reaction setups is indeed essential. In DBD reactor, as mentioned earlier, Zhang and colleagues showed that an increase in the water vapor input flow rate led to an increase in the NH_3 generation rate.[33] In addition, the synthesis rate increased from 1.53 $\mu mol\ h^{-1}$ to 65.4 $\mu mol\ h^{-1}$ when the gas flow rate was increased from 0.2 to 1.0 L/min.

When the reactor was a plasma jet, the work of Gorbanev et al.[84] showed that the introduction of a small amount of H_2O vapor produced higher NH_3 yields and higher selectivity. Large amounts of water vapor can further increase the productivity but with lower selectivity. Ammonia selectivity is 70-80% when the feed gas is dry N_2. When the H_2O vapor content is higher (50-100%) ammonia production is higher but selectivity to NH_3 decreases to 60-70%, however, when a small amount of H_2O vapor content (about 2-10% saturation) is involved in the reaction, selectivity increases compared to dry N_2 feed gas and is more selective at any N_2 flow rate. However, when a small amount of H_2O vapor content (about 2-10% saturation) is involved in the reaction, the selectivity increases compared to dry N_2 feed gas and is around 90% at any N_2 flow rate. (It is interesting to note that at 0.2 L/min of N_2 gas and 5% H_2O vapor saturation, the selectivity for NH_3 is about 96%).[84]

Under DC conditions, the humidity of the feed gas has a significant impact on the efficiency and energy consumption of ammonia synthesis. Pattyn et al. conducted experiments comparing dry nitrogen gas with humidified nitrogen gas and examined the gas-liquid phase products, electron temperature, and energy consumption during the DC-electrolysis plasma-assisted ammonia synthesis process[85]. The results indicated that introducing water vapor into nitrogen gas increased the content of NO and NH_3 in the gas phase, possibly due to the participation of H atoms dissociated from water vapor and OH radicals in gas-phase reactions. Additionally, under higher current conditions, mixing reactants with water vapor led to increased selectivity for NH_3 and NH_4^+, although the precise mechanism behind this phenomenon remains unclear. The introduction of water vapor into the system resulted in a noticeable increase in vibrational temperature (T_{vib}) within the plasma, accompanied by the higher energy efficiency. Thus, in this reaction system, the amount of water vapor significantly affects discharge characteristics, and increasing the quantity of water vapor in the gas phase enhances the vibrational excitation of N_2 molecules.[85]

Table 2. The effect of plasma-assisted synthesis of ammonia from N_2 and H_2O.

Discharge Type	Yield/Synthesis rate (μmol·h⁻¹)	Energy cost (MJ·mol⁻¹)	Selectivity	Ref.
APPJ	NH_3: 3.75	95−118	NH_3: 96%	[84]
DBD	NH_3+NO_x: 60	1 900	-	[88]
APPJ	-	61	-	[85]
GA	NH_3: 39.9	2 358	-	[87]
APPJ	NH_3: 25.8	139	-	[31]
Spark	NH_3+NO_x: 672	-	NO_3^-: 55%	[79]
RGA	NH_3: 432000		NH_3: 95%	[89]
DBD	NH_3: ~2670(per g_{cat})	-	-	[33]
Theoretical thermodynamic minimum		0.04		[16]
H_2O electrolyzer + air separation+ HB		0.67	NH_3: 100%	[16]
Electocatalysis		0.46	NH_3: 100%	[16]

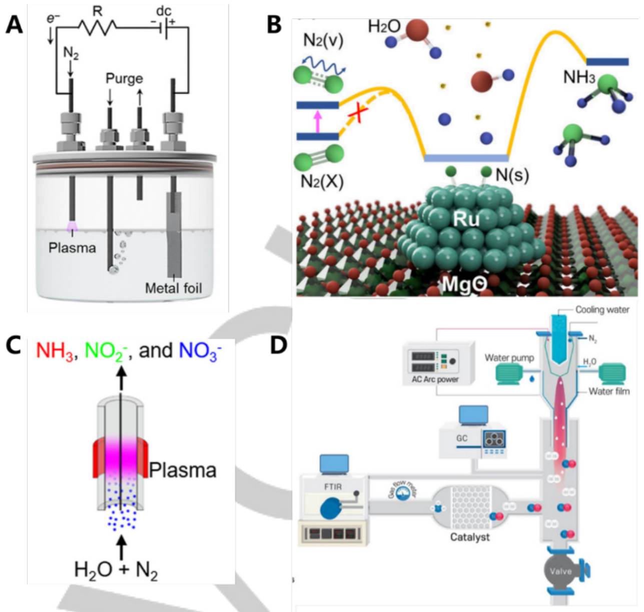

Figure 6. Significant findings of the plasma-assisted synthesis of NH_3 from N_2 and H_2O. (A) Solvated electron were found to have an important role in N_2 and H_2O system. Reproduced from ref.[31] Copyright (2019), with permission from American Association for the Advancement of Science. (B) Ru/MgO catalyst was used in one-step ammonia synthesis by N_2 and H_2O. Reproduced from ref.[33] Copyright (2023), with permission from Wiley-VCH. (C) Water droplets and water vapor are passed into the DBD reactor for ammonia synthesis performance comparison. Reprinted with permission from ref.[88] Copyright 2020, American Chemical Society. (D) Synthesis of ammonia with H_2 and NO as intermediates in plasma synergy. Reprinted with permission from ref.[89] Copyright 2021, American Chemical Society.

3.3 Reaction selectivity

As previously stated, when nitrogen and water interact in a plasma reaction system, the decomposition of H_2O inevitably leads to the generation of OH radicals. These radicals then react with reactive nitrogen species, resulting in the production of nitrogen oxides that dissolve in water and ultimately form nitrate and nitrite species through a series of reactions. While this type of reactions is acceptable for nitrogen fixation purposes, it presents a challenge for the plasma-assisted ammonia synthesis as it competes with the desired reaction, utilizing reactive nitrogen species and generating byproducts that reduce the ammonia yield.[93] Therefore, improving the selectivity of the plasma nitrogen-water system has become a key objective in the ammonia synthesis research. Researchers are currently exploring various strategies to enhance selectivity, including modifying the electrical characteristics of the reaction, adjusting reaction conditions, and designing reactors to introduce new reaction modes that can suppress nitrogen oxide generation and improve ammonia yield.[31] As a result, current research in the field of nitrogen-water reactions is primarily focused on optimizing selectivity to maximize ammonia production.

Understanding the reaction pathway and mechanisms in plasma-assisted nitrogen-water reactions is crucial for controlling reaction conditions and enhancing ammonia synthesis. However, the current understanding of the reaction mechanism remains incomplete, and different explanations for selectivity based on experimental findings have been proposed. Therefore, further studies are necessary to comprehensively understand the reaction mechanisms and optimize reaction conditions for maximizing ammonia synthesis.

Solvated electrons (e-(aq)) are recognized as potent reducing agents and play a significant role in the reduction process of nitrogen species. In the study conducted by Hawtof et al., an electrolysis jet reactor utilizing sulfuric acid as the liquid phase was employed.[31] Sulfuric acid, in addition to enhancing the electrical conductivity of the liquid phase and promoting the fixation of ammonia in the liquid phase, also provides an ample supply of protons (H^+) for plasma-assisted ammonia synthesis (Figure 6A). The results revealed that a considerable number of solvated electrons were generated at the plasma-liquid interface, which reduced protons to H atoms. These H atoms then participated in the ammonia synthesis process, resulting in an exceptional selectivity of nearly 100%. The high selectivity observed in this study can be attributed primarily to the reaction of solvated electrons with hydrogen ions in the liquid phase, facilitating the direct formation of NH_3 from H atoms and N species.[31]

Moreover, the efficient transport of ions within the liquid phase remains a critical concern, particularly the transfer of H^+ from the liquid phase to the plasma-liquid interface for subsequent reactions, as it significantly affects the reaction selectivity. Lamichhane's study has demonstrated that dissolved NO_x, which exhibits high reactivity with e-(aq), can effectively regulate NH_3 formation. This is primarily due to the electron absorption rate of NO_x being 500 times faster than the rate at which electrons bind to protons.[32]

Ongoing research also focuses on controlling reaction conditions to enhance the selectivity. The dissociation of hydrogen, which converts H atoms in the liquid phase into hydrogen gas, is the primary competing reaction for ammonia synthesis. Hawtof et al. have demonstrated that reducing the discharge current can effectively suppress the occurrence of hydrogen precipitation reaction, thereby leading to improved selectivity in ammonia production.[31]

Under continuous gas-liquid phase conditions (DC, jet et al.), plasma catalysis is not commonly employed, in contrast to separated liquid-phase systems. Nevertheless, the critical role of the catalyst must be recognized when the discharge mode is DBD. In the context of plasma-catalyzed ammonia synthesis using nitrogen and water vapor, the deliberate exclusion of hydrogen usage, which mitigates transportation and reaction risks, presents the challenge of unwanted byproduct formation. This, in turn, rises the downstream separation costs. A thoughtful catalyst design can partially mitigate these challenges. Catalysts characterized by well-developed pore structures and high surface areas are favored, as they enhance the adsorption and capture of excited state particles within the plasma phase.[91]

Research conducted by Zhang et al.[33] and Nguyen et al.[90] collectively underscores that, within the framework of plasma collectively revealed that in plasma catalysis, byproducts generated from the reaction between N_2 and water vapor predominantly manifest as N_2O, while other forms of NOx remain below detectable thresholds. Notably, N_2O production primarily occurs in the gas phase. Due to the distinctive attributes of the Dielectric Barrier Discharge (DBD) reactor, N_2 is more activated than dissociated within the plasma. Consequently, the effective dissociation of N_2 with weak intermediate bonding can be achieved by either enhancing the catalytic activity of oxyphilic metals or augmenting the electron density on the catalyst's surface. Furthermore, the selection of active metals with a greater affinity for oxidative oxygen species can immobilize these species, impeding the formation of nitrogen oxides and thereby enhancing ammonia selectivity. Given the limited availability of hydrogen in H_2O, it is imperative to develop catalysts that lower the energy barrier for H_2O dissociation, ensuring a sufficient supply of H(s).

Nguyen conducted ammonia synthesis from nitrogen using seawater vapor via the wet method under low-temperature plasma conditions.[90] They employed M/SiO_2 catalysts, with M representing Ag, Cu, and Co. Remarkably, even at a relatively modest input power of 2 watts, the Co/SiO_2 catalyst exhibited a noteworthy ammonia synthesis rate of 3.7 $mmol\cdot g_{cat}^{-1}\cdot h^{-1}$, with an energy yield of 3.2 $g\cdot kWh^{-1}$. Despite the impressive performance of the Co/SiO2 catalyst in ammonia synthesis, the detection of the most intense N_2O-related spectra implies a strong competitive formation of N_2O. On the other hand, the Ag/SiO_2 catalyst did not exhibit OES spectra related to NOx species but had a lower yield. This suggests that there might be a synergistic interaction between Ag or Ag/SiO_2 and active species, potentially restricting N_2O formation and consequently enhancing NH_3 selectivity. In a related study, Zhang and colleagues explored the use of Ru as the catalytic metal and tested MgO, SiO_2, and Al_2O_3 as carriers for synthesizing ammonia.[33] The results indicated that, irrespective of the carrier used, there was little variation in N_2O production. However, the NH_3 yield was significantly higher when MgO was the carrier. This can be attributed to the strong basicity of MgO, which provides a high surface charge density to activate dinitrogen molecules by providing electrons during the ammonia synthesis process.

Future research on plasma-assisted ammonia synthesis from nitrogen and water should emphasize increasing yield, energy efficiency, and ammonia production selectivity. To achieve this goal, researchers must continuously explore novel reactor designs, discharge types, and catalyst formulations that allow high-energy particles to participate optimally in the reaction.[90] To enhance selectivity, progress in kinetics is essential to elucidate the mechanism of the nitrogen-water reaction in the presence of plasma, enabling better control of reaction conditions to steer the process toward nitrogen reduction.[31] Building upon existing research, future investigations may focus on inhibiting reactions between oxidative species (such as OH radicals and O atoms) and nitrogen species, as well as suppressing hydrogen evolution reactions, to further enhance ammonia synthesis selectivity.[93] Research into the generation of different reactive nitrogen species and their respective reactivity with oxidants and reductants could lead to breakthroughs.[94] This exploration can provide insights into adjusting reaction conditions to promote the formation of active nitrogen species favorable for ammonia synthesis.

4 Plasma coupled with other technologies for ammonia synthesis

As mentioned earlier, plasma-assisted ammonia synthesis from nitrogen and water encounters several challenges that must be overcome to enhance the overall process. These challenges include optimizing experimental conditions, discharge parameters, and reactor design to improve ammonia selectivity and ensure predominant reduction of N_2 rather than its oxidation to nitrogen oxides. However, the complex interaction between the plasma and liquid phases, along with the inherent difficulties in controlling the plasma, pose significant obstacles in advancing plasma-assisted ammonia synthesis. Consequently, researchers have explored alternative technologies that can be combined with low-temperature plasma technology to achieve more efficient and sustainable ammonia synthesis.[95] In this context, the coupling of low-temperature plasma with electrocatalysis, photoelectric catalysis, and UV radiation technologies has shown promising potential in enabling greener and more sustainable ammonia synthesis processes. These alternative approaches offer new avenues to address the challenges associated with the plasma-assisted ammonia synthesis, allowing for significantly improved control and efficiency while maintaining environmental sustainability.

4.1 Plasma-coupled electrocatalysis for ammonia synthesis

The N_2 plasma generates a considerable amount of activated nitrogen species. Although high-energy nitrogen species can directly produce NH_3 in the presence of water or hydrogen, theoretical studies suggested that vibrational excitation is relatively weaker in milder plasmas, making this reaction difficult to occur. To overcome this limitation, the nitrogen reduction reaction can be accelerated by delivering a high flux of active nitrogen species to the catalyst surface of the cathode in an electrolyzer.[96] Furthermore, plasma and electrocatalysis can mutually enhance each other. Plasma can supply active species that facilitate the electrocatalytic reaction, while electrocatalysis can provide electrons and protons that assist the plasma reaction.[95] The plasma activation of reactive species has been found to have minimal effects on the charge transfer at the cathode and does not immediately impair the functioning of the electrochemical workstation.[97] As a result, the hybrid process combining plasma and electrocatalysis leads to a higher production of NH_3 compared to either process employed individually. The effect of plasma coupled with electrocatalysis for ammonia synthesis is shown as Table 3. Sharma et al. used a plasma-activated proton-conducting solid oxide electrolyzer for the sustainable production of ammonia from N_2 and H_2O (Figure 7B). Water on the anode is oxidized to produce hydrogen, which is transported through a proton conduction membrane to the cathode where they react with plasma activated nitrogen to produce ammonia. Ammonia yields and Faraday efficiencies of 26.8 $nmol{\cdot}s^{-1}{\cdot}cm^{-2}$ and 88% were achieved, respectively.[98]

The use of air as a feed gas in the plasma-assisted ammonia synthesis has become more feasible with the integration of electrocatalysis. Wu et al. found that the introduction of air into the system allows for the formation of oxygen-containing reactive nitrogen species (RNOS) that are crucial for the subsequent electrocatalytic reactions. In comparison to N_2 plasmas, air plasma demonstrated higher activity, further supporting the importance of RNOS in promoting electrocatalytic reactions. The synthesis of ammonia involving oxygen involves a two-step process: firstly, the reaction between nitrogen, oxygen, and water in the presence of plasma generates nitrogen oxides in liquid phase, and secondly, these nitrogen oxides are electrochemically reduced to ammonia. The two-step ammonia synthesis process yields significantly higher amounts of ammonia compared to plasma-assisted synthesis using only nitrogen and water.[99] Consequently, enhancing the yield of ammonia when using air as a feedstock can be achieved by promoting both the generation of nitrogen oxides and the electrochemical reduction of nitrogen oxides.

Sun et al. employed an underwater multi-bubble reactor to generate air plasma, which was then combined with an electrochemical workstation using a copper nanowire electrocatalyst to convert nitrogen oxides to ammonia (Figure 7A). The multi-bubble reactor offers the advantage of enabling the adjustment of glow/spark reaction mode and bubble kinetics to optimize NO_x production and consequently enhance ammonia yield.[11] In a two-electrode system, where both the plasma and electrochemical workstation share electrodes, typically leads to low energy efficiency due to the high voltage required to generate the plasma. Therefore, a more appropriate voltage range for the nitrogen reduction reaction can be achieved by utilizing a four-electrode configuration, with two electrodes allocated for plasma generation and the remaining two dedicated to electrochemical workstations.[97] Moreover, the use of plasma-assisted proton exchange membranes (PEM) is crucial in facilitating particle transport and exchange in the liquid phase.[32, 97]

The primary objective of electrocatalytic materials is to enhance the rate of chemical reactions through the electron transfer process in electrochemical reactions. Generally, an electrocatalytic material possesses superior electrical conductivity and catalytic activity, including metals, alloys, metal oxides, carbon materials, and various other substances. In electrochemical reactions, these materials function as electrodes by adsorbing reactant molecules and supplying electrons to facilitate the chemical reactions occurring between these molecules.

Electrocatalysts play a critical role in the plasma-coupled electrocatalysis for ammonia synthesis by enhancing both the selectivity and production rate of ammonia. By modifying the adsorption and dissociation energy of surface H atoms and active nitrogen species, electrocatalysts improve the efficiency of reducing nitrogen molecules, thereby increasing the yield and purity of ammonia. Furthermore, certain electrocatalysts are specifically designed to suppress competing reactions such as the hydrogen evolution reaction (HER), thus enhancing the selectivity towards ammonia synthesis. Additionally, electrocatalysts can promote the dissociation and adsorption of ammonia molecules, further increasing the yield and selectivity of the process. Electrocatalysts exhibit an active volcano curve that can be shifted towards Co metal by electrocatalysis. Moreover, the activity and stability of electrocatalysts need to be carefully considered after multiple uses. [97]

The catalytic activity of electrocatalysts depends on several factors, including their chemical properties and surface structure, such as the lattice structure, defects, surface energy, and electron affinity. Efficient catalytic and selective control of electrochemical reactions can be achieved by modulating the surface structure and chemical properties of electrocatalytic materials. For instance, Cui et al. conducted a study utilizing air as the feedstock for plasma-coupled electrocatalytic ammonia synthesis. They found that Cu-MOF-400 as the electrocatalyst achieved the highest ammonia synthesis rate of 3.0 $mg{\cdot}h^{-1}{\cdot}cm^{-2}$ with a Faraday efficiency of 83.2%. In comparison, Cu-MOF-300 exhibited a rate of 1.43 $mg{\cdot}h^{-1}{\cdot}cm^{-2}$ with an efficiency of 77%, while Cu-MOF-500 demonstrated a rate of 1.75 $mg{\cdot}h^{-1}{\cdot}cm^{-2}$ with an efficiency of 75.5%. The results indicated that Cu-MOF-400 had both Cu^0 and Cu^+ states on its surface, whereas the other two catalysts predominantly exhibited a single state of Cu^+ or Cu^0. The presence of Cu^+/Cu^0 in Cu-MOF-400 significantly suppressed hydrogen evolution, and the higher specific surface area of MOF-400 improved mass transfer and exposed more active sites.[100]

Gao et al. employed a dual-functional catalyst composed of $CuCo_2O_4$ nanosheets loaded onto nickel foam ($CuCo_2O_4$/Ni) to simultaneously promote plasma-assisted conversion of NO_x^- and electrochemical reduction (eNO$_x$RR). This catalyst exhibits the capacity to generate a substantial amount of adsorbed oxygen (O_A), enabling favorable activation of O_2 and thereby enhancing the oxidative activity of N_2, leading to increased NO_x production, reaching a notable yield of 159.1 mmol h^{-1} of NO_x^-. Furthermore, density functional theory (DFT) calculations indicate that the introduction of Cu in $CuCo_2O_4$/Ni lowers the energy barrier for the rate-determining step (RDS) in the eNOxRR process. Ultimately, under a high global current density of 1384.7 mA cm^{-2}, impressive results were achieved, including a 96.8% Faradaic efficiency and the highest reported NH_3 production rate to date at 145.8 mg h^{-1} cm^{-2}. Furthermore, the researchers successfully scaled up the application of this catalyst, achieving large-scale NH3 synthesis at 3.6 g h^{-1}. They also transformed the generated NH_3 into solid magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4·6H_2O$, MAP) using a precipitation method, which offers significant advantages in terms of NH_3 storage and transportation.[101] Wu et al. investigated cobalt-based single-atom electrocatalysts, which possess unique electronic properties and isolated active sites that enhance the efficiency of proton/electron transfer to the active site. These monatomic electrocatalysts offer highly controllable surface structures that provide more reaction sites. Coordination modulation of Co SAs/N-C promoted the desorption of NH_3 and enhanced the adsorption of H. At -0.33 V / RHE, the ammonia water yield (~1.43 mg·cm^{-2}·h^{-1}) reached almost 100% Faraday efficiency. At -0.63 V / RHE, the ammonia water yield reached ~3.0 mg·cm^{-2}·h^{-1} with a Faraday efficiency of ~62%.[99] Similarly, Meng et al. introduced a Ti bubbler to generate nitrate/nitrite (NO_x^-) during plasma activation of air at a maximum rate of 55.29 mmol·h^{-1}. The resulting aqueous solution of NO_x^- was used directly as a cathode for electroreduction using oxygen-vacancy-rich Co_3O_4 nanoparticles as a catalyst. The introduction of oxygen vacancies increased the activity of adjacent Co atoms and promoted the adsorption and hydrogenation of NO_x^-, while inhibiting the hydrogen precipitation reaction. Since the energy of adsorption (EAD) for the most probable adsorption configuration of NO_2^- on O_V-Co_3O_4 (with oxygen vacancies) is -2.98 eV when considering only NO_2^- as a reactant. In contrast, the EAD of NO_2^- on the surface of single crystalline Co_3O_4 is -2.44 eV, indicating that the Co atoms around O_V become more active, thus achieving stronger adsorption and easier separation of NO_2^- on the surface of O_V-Co_3O_4. easier separation. Thus, the oxygen-vacancy-rich Co_3O_4 NPS had a significant NH_3 yield of 39.60 mg·h^{-1}·cm^{-2}, a Faraday efficiency of 96.08%, and a current density of 376.48 mA·cm^{-2}. [102]

Table 3. The effect of plasma coupled with electrocatalysis for ammonia synthesis

Discharge Type	Catalytic mode	Yield/Synthesis rate (mg·h^{-1})	Faraday efficiency	Energy cost (MJ/mol)	Ref.
APPJ	Electrocatalysis	~1.43	~100%	3.17	[99]
APPJ	Electrocatalysis	~3.0	~62%	-	[99]
DBD	$LaFeO_3$+ Electrocatalysis	~3.0	83.2%	-	[100]
RF	Electrocatalysis	1.64	88%	-	[98]
APPJ	Co_3O_4 + Electrocatalysis	39.6	96.08%	-	[102]
Spark	$Ni_3B@NiB_{2.74}$ + Electrocatalysis	3.37	~100%	4.6	[92]
Spark	Electrocatalysis	23.2	-	13.7	[11]

Currently, the transfer of excited active nitrogen species to the catalytic sites poses a challenge when integrating plasma into the electrochemical processes. Consequently, the concentration of energetic species near the electrocatalyst is diminished, thus reducing the efficiency in ammonia synthesis. Nevertheless, the utilization of microwave or gliding arc discharge plasma shows promise in increasing the density and energy of vibrationally excited nitrogen species.[23, 103] This enhancement facilitates plasma-coupled electrocatalysis, thereby resulting in higher yields for ammonia synthesis.

4.2 Plasma-coupled ultraviolet radiation for ammonia synthesis

The utilization of UV radiation to excite water molecules on the plasma-exposed surface can create a distinctive reaction environment that enhances the production of ammonia. This phenomenon occurs as UV light induces the dissociation of water molecules on the plasma-liquid reaction surface, resulting in the formation of hydrogen atoms and hydroxyl radicals.[30, 78, 94] The active nitrogen species in the plasma can then react with these hydrogen atoms to generate ammonia. Furthermore, UV light can excite and enhance the reactivity of water molecules. Plasma-coupled UV radiation enables the synthesis of ammonia with efficient control over its yield, conversion, and selectivity, even in the absence of a catalyst. This approach provides a promising pathway for catalyst-free ammonia production, highlighting its potential as an innovative and sustainable method in ammonia synthesis.

UV radiation can induce water decomposition, resulting in the generation of reactive species and ammonia through reactions with nitrogen oxides. This process is reasonably selective towards ammonia synthesis. In a study conducted by Peng et al. (Figure 7D), it was demonstrated that UV irradiation significantly increased the synthesis rates of NO_2 and NH_4^+ by approximately threefold and twofold, respectively, while the synthesis rate of NO_3^- only increased by approximately 1.3 times.[30] This finding provides a viable approach for enhancing the selectivity of ammonia synthesis. By incorporating UV/VUV irradiation equipment to take advantage of the selectivity of UV radiation towards ammonia, the reaction conditions can be tailored to promote the reduction of nitrogen and improve the overall efficiency of the process.

The impact of various UV radiation wavelengths on ammonia synthesis varies significantly. Sakakura et al. explored the use of different UV radiation wavelengths to irradiate the plasma-liquid interface and found that the highest ammonia yields were achieved using 185 nm and 254 nm UV radiation, while 248 nm UV radiation led to lower ammonia production rate. Additionally, wavelengths below 200 nm were found to be the most effective in promoting ammonia synthesis.[78] Nevertheless, the authors did not detail the underlying reasons behind this phenomenon. It is evident that further research is necessary to attain a more comprehensive understanding.

Moreover, vacuum ultraviolet (VUV)/UV radiation exhibits selectivity for reactions involving various reactive nitrogen species within the plasma. According to the findings of Sakakura et al., the contributions of UV irradiation to the reactions of distinct reactive nitrogen species, such as N atoms, N_2^+, and N_2^*, with water were very different.[94] As mentioned above, the principles, pathways, and resulting products generated by the reactions of different reactive nitrogen species with water exhibit differences. Exposed to VUV/UV radiation, N_2^* and N_2^+ exhibit the higher reactivity towards water molecules, leading to an enhanced pathway for ammonia production in combination with other nitrogen oxides. This finding highlights the potential of VUV/UV radiation in selectively promoting specific reactions and optimizing the yield of ammonia in plasma-assisted processes.

Therefore, the combination of UV/VUV radiation with plasma-assisted ammonia synthesis offers a promising pathway for the sustainable production of green ammonia. By implementing this approach with varying wavelengths, it becomes possible to optimize the selectivity and yield of the ammonia synthesis by modifying the reaction environment of the plasma-liquid reaction and controlling the production of active species. This method presents an opportunity to advance the efficiency and sustainability of ammonia production while reducing the reliance on conventional catalysts.

4.3 Plasma-coupled photocatalytic for ammonia synthesis

In addition to electrocatalysis, the potential synergy of photocatalysis is another promising avenue for plasma-assisted technologies. In this process, the photoelectrochemical water decomposition can provide the required electrons and holes, while the nitrogen plasma can provide the active species needed for the reaction. Since commercially available membrane electrode assembly (MEA) electrolyzers can be used for water electrolysis, direct plasma exposure can lead to a gradual degradation of MEA performance with problems such as sputtering mechanisms, electrode dehydration, and difficulties in current stability after the plasma exposure. In contrast, photoelectrochemical coupling can help avoid such problems.

Lamichhane et al. conducted an experimental study by employing a jet device and UV light irradiation on a titanium dioxide semiconductor photoanode to synthesize a hydrogen donor for the nitrogen reduction reaction in photoelectrochemical hydrolysis (Figure 7C). Their results showed that the amount of ammonia produced by the synergistic process of the photoelectrochemical hydrolysis and nitrogen plasma was sixfold higher than that achieved by the nitrogen plasma alone. To improve the selectivity and yield of ammonia, the researchers employed a proton exchange membrane to prevent oxygen, a byproduct of hydrolysis, from entering the plasma and affecting NO_x production, which would otherwise reduce the ammonia Faraday efficiency and selectivity.[32]

Therefore, despite the challenges faced by low-temperature plasma ammonia synthesis, the synergistic combination of plasma with other technologies offers the opportunity to address these challenges. However, this field remains largely unexplored, and future research could explore further combinations to leverage the strengths of different technologies. Therefore, the coupling of plasma with other technologies is a highly promising pathway for sustainable and green ammonia synthesis, with significant potential to impact the future of this field.

5 Summary and Outlook

After several decades of persistent research and significant advances, atmospheric-pressure low-temperature plasma has emerged as a promising approach for ammonia synthesis. The plasma-assisted processes have gained popularity due to its eco-friendliness, mild reaction conditions, and potentially low energy requirements. In recent years, researchers have focused on exploring the reaction mechanisms, kinetic models, and kinetic analysis of the plasma-assisted ammonia synthesis. They have also integrated catalysts and catalytic methods with distinct features to enhance the process efficiency, selectivity, and yield. Additionally, researchers have conducted experiments and numerical simulations with various discharge reactors and configurations to identify the most effective approaches for ammonia synthesis.

This paper provided an analysis of the current state of research on atmospheric pressure low-temperature plasma ammonia synthesis approach. The focus has been on the plasma-assisted reactions involving N_2 with H_2, N_2 with H_2O, and plasma coupled with other technologies. We have summarized the different reaction routes, mechanisms, and pathways associated with these reactions, as well as the impact of commonly used catalysts and various forms of catalyst action combined with other catalytic methods on ammonia synthesis effectiveness. Despite its potential, atmospheric pressure low-temperature plasma ammonia synthesis technology faces several challenges, including:

(1) The ammonia synthesis system involving N_2 and H_2 is a complex multi-phase and multi-scale reaction process that includes gas-solid interface exchange by mass, energy, reactive species and products. This is further complicated by the presence of catalysts and multiple physical fields, such as electromagnetic, density, temperature, airflow fields, among others. These factors make theoretical analysis particularly challenging, and the design and optimization of the reactor and its parameters even more demanding. Furthermore, the interactions and synergistic effects between the plasma and catalysts are not yet fully understood, hindering the generalization of their combined effect. The use of diagnostic methods is imperative for revealing the pathways and mechanisms of the plasma-catalyzed ammonia synthesis. NTP diagnostic techniques provide key parameters such as electron density, electron temperature, vibrational temperature, and rotational temperature. The crux of mechanistic exploration

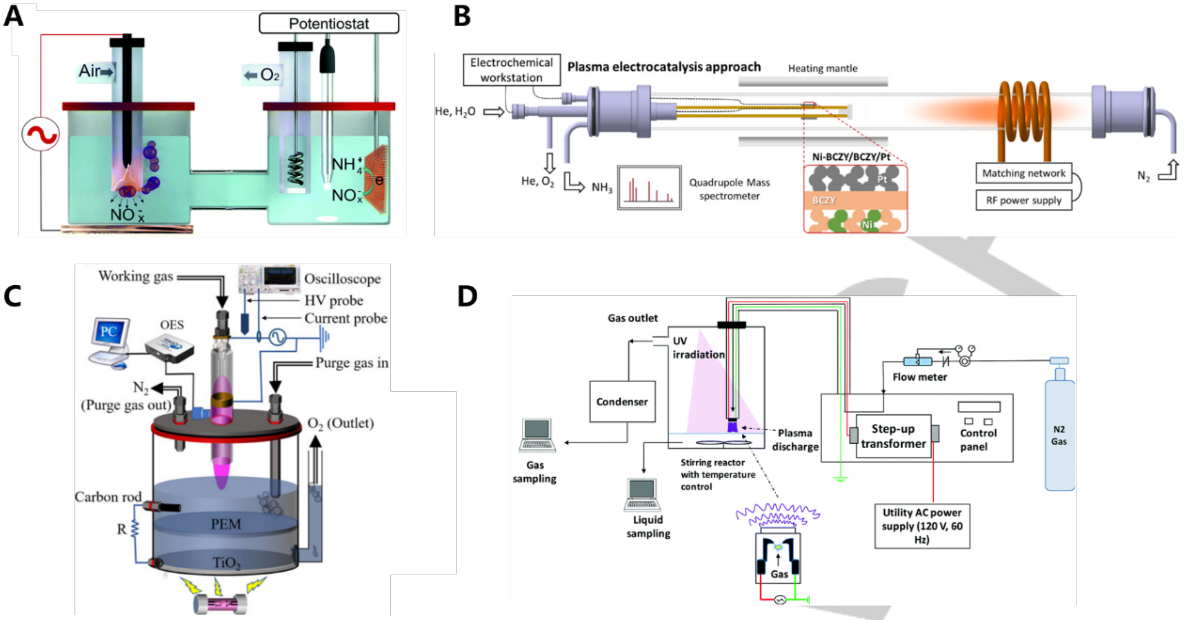

Figure 7. Significant findings of plasma-coupled electrocatalysis for ammonia synthesis. (A) The multi-bubble plasma reactor is used for ammonia synthesis coupled with electrocatalysis. Reproduced from Ref.[11] Copyright (2021), with permission from The Royal Society of Chemistry. (B) Hybrid plasma electrochemical reactor. Reprinted with permission from ref.[98] Copyright 2020, American Chemical Society. (C) Photoelectric catalysis was used for ammonia synthesis coupled with plasma jet. Reproduced from ref.[32] Copyright (2020), with permission from IOP Publishing. (D) UV radiation was added for in situ ammonia synthesis. Reproduced from ref.[30] Copyright (2014), with permission from The Royal Society of Chemistry.

predominantly resides in the realm of surface-catalyzed reactions within the presence of plasma. Leveraging state-of-the-art in-situ diagnostic techniques facilitates the revelation of intermediate reaction species. Optical Emission Spectroscopy (OES) proves instrumental in capturing vital reactants within the plasma phase, with the crucial particle wavelengths for ammonia synthesis reactions duly delineated.[104] Furthermore, certain pivotal diagnostic techniques, such as diffuse reflectance infrared spectroscopy and laser-induced fluorescence, encounter challenges in their application to plasma-catalyzed processes. This is primarily due to the plasma generation, strong electric fields, making real-time detection of active species on catalyst surfaces during discharge processes a formidable endeavor. Hence, the introduction and utilization of advanced characterization and diagnostic techniques is crucial for plasma catalysis.

(2) In the N_2 and H_2O reaction system, it is difficult to separate gas-phase reaction products, such as N_2O and other species with lower valence states of nitrogen, from ammonia for further use. The plasma or coupled catalytic reaction pathway in gas-liquid reactions is more complicated and typically occurs in the form of a jet discharge with relatively slow reaction rates. To enhance the reaction, catalysts and UV light are often utilized, but their effectiveness is limited by the possibility of catalyst passivation or dissolution upon interaction with water, leading to a decline in catalyst activity. Moreover, nitrogen and water interaction produce byproducts, such as H_2O_2, necessitating additional steps for product separation. Despite its potential, the high energy consumption associated with the N_2 and H_2O reaction system remains a challenge, and its economic feasibility is relatively low.

(3) Plasma coupled with other technologies, a new hybrid approach for ammonia synthesis, combines plasma discharges with electrocatalysis and photoelectric catalysis to make up for the disadvantages of the plasma ammonia synthesis processes, such as the frequently reported lower yields and selectivity. In addition, plasma coupled with other technologies for ammonia synthesis extends the feedstock from pure nitrogen to air, reducing the cost of nitrogen separation. However, the technology is in its infancy and the principles of synergy are still not well studied, while the optimum experimental conditions still need to be explored. More catalytic methods are expected to emerge in the near future.

Table 4. The wavelength of reactive species

Reactive species	Wavelength(nm)
N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$, 0-0)	337.1
N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$, 0-1)	357.6
N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$, 0-2)	380.4
N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, 0-0)	391.4
N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, 0-1)	427.87
N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, 0-2)	470.89
N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$, 0-3)	522.7
OH ($A^2\Sigma^+ \rightarrow X^2\Pi$, 0-0)	306~315

Atmospheric pressure low-temperature plasma ammonia synthesis technology, as a novel sustainable and environment-friendly ammonia synthesis technology, has a broad future development prospect. In view of its current research status, the future outlook for this technology is very positive and can be summarized as follows:

(1) To improve the energy efficiency and conversion rate of the plasma-assisted ammonia synthesis, it is essential to continually optimize the reactor structure, and explore various reaction conditions for better outcomes. In the current context of plasma-assisted ammonia synthesis, the utilization and selection of suitable catalysts are crucial. The search for high-performance catalysts, as well as the exploration of the synergistic effects between catalysts and plasma, offer new horizons for research. Employing advanced diagnostic techniques to monitor the synergistic processes in real time for in the plasma-catalysis system becomes imperative to elucidate reaction pathways, thereby providing valuable insights for the future development of novel catalysts with unique structures and functionalities. Notably, the research at the intersection of photocatalysts and plasma-assisted ammonia synthesis remains relatively nascent, thus holding promising prospects. Furthermore, the introduction of catalysts into the plasma-liquid water ammonia synthesis system may yield unforeseen synthetic outcomes. Moreover, the coupling of renewable power and ammonia synthesis needs to be gradually explored to address the energy and environmental challenges of ammonia production. The adoption of renewable energy sources is crucial not merely for the operational viability of plasma processes but, more importantly, for addressing broader environmental and climate concerns. Using renewable energy is an absolute prerequisite to be environmentally sound and practical. Although the Plasma process's energy efficiency is currently not on par with that of established methods, the plasma process is designed to utilize inexpensive excess renewable energy.

In comparison to the challenges (i.e., poor production rate, low selectivity) faced by electrocatalysis, plasma-assisted ammonia synthesis demonstrates more effective breakthroughs in overcoming the high energy barrier of N_2 activation, facilitating better activation of nitrogen. The plasma processes uniquely enable on-site, small-scale ammonia production, operating under ambient conditions. On the other hand, the well-established Haber-Bosch process, while efficient and mature, necessitates large, centralized plants for economic viability due to its thermodynamic limitations, particularly concerning pressure requirements. Such constraints make it incompatible with localized, on-site ammonia production, which the plasma process actively addresses. However, it is of importance to clarify that the application of plasma does not aim to replace the Haber-Bosch process but to offer a supplementary, environmentally friendly pathway for nitrogen fixation, especially where small-scale, decentralized production is desirable. This decentralized approach not only can eliminate the need for large-scale synthesis but also prevent issues related to ammonia storage and transportation, each carrying significant safety and economic challenges. By establishing a network of small-scale plants powered by excess renewable electricity, we envision facilitating on-site ammonia production, thereby reducing distribution costs and dependency on fossil fuels significantly.

(2) To elucidate the mechanism of the plasma catalysis, it is crucial to establish *in situ* characterization techniques. Additionally, catalysts with better synergistic effects under plasma working conditions should be explored, and the impact of catalysts on the physicochemical properties of plasma requires further investigated. Furthermore, the role of plasma and reaction products in modifying the surface characteristics and active sites of catalysts should be studied. Lastly, there is a need to develop new catalytic materials with lower N binding energy and dissociation potential barriers for their application in ammonia synthesis technology.

(3) The integration of the plasma technology with other catalysis techniques presents significant potential for further advancements. Current research has shown that coupling plasma with other catalytic methods is a crucial approach to reducing energy consumption and increasing the efficiency of ammonia synthesis technology. This promising avenue warrants continued exploration to achieve more economical and efficient ammonia synthesis processes.

Finally, the plasma-assisted ammonia synthesis is an emerging technology in sustainable energy conversion, opening new exciting opportunities for cleaner industry and a greener future. More disciplines are expected to be involved and there will be more cross-disciplinary collaborations in the plasma-assisted sustainable nitrogen-to-ammonia synthesis. Significant discoveries and technological advances are expected in the near future with the efforts from relevant researchers worldwide.

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Conflict of interest declaration

Author PJ Cullen is CTO of PlasmaLeap Technologies, a company with commercial interests in plasma driven ammonia synthesis.

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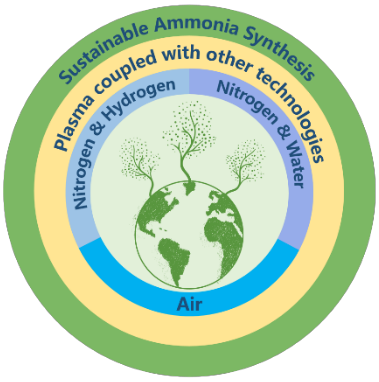

This review summarizes the different technical routes for plasma-assisted ammonia synthesis in recent years and the key points: mixed-phase, synergistic processes and mechanisms. The advantages and existing problems of the different routes are also discussed. Finally, we make an outlook on the future direction of plasma-assisted ammonia synthesis.

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