



Recent Advances in Electrocatalytic Nitrogen Reduction to Produce Ammonia Under Ambient Conditions

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ABSTRACT

Ammonia (NH₃) is one of the most widely used chemicals in industry and agriculture, which is very important to the global economy. At present, the Haber Bosch process is adopted for ammonia synthesis in industry. The experimental temperature and pressure used in this process are relatively high, the process energy consumption is high, the one-way conversion of the hydrogen is low, and a large amount of carbon dioxide is discharged into the atmosphere, causing pollution to the environment. To solve its shortcomings, researchers began a new exploration. Electrocatalytic nitrogen reduction (NRR), as a clean and sustainable method of ammonia synthesis, has attracted extensive attention. However, the low activity and selectivity of electrocatalysts are one of the important challenges. Therefore, the search for cost-effective electrocatalysts has become one of the research hotspots of electrochemical ammonia synthesis. For enhancing the catalytic performance and selective performance of catalysts, scientists have carried out a lot of research on electrochemical nitrogen fixation catalysts. In this review article, electrolytic experimental devices, common ammonia detection research methods, and the electrocatalytic NRR mechanism are summarized, and then the research progress in electrocatalysts (precious metals, transition metals, and non-precious metals) is summarized. Then, the research progress of metal-based electrocatalysts is introduced, and the relevant theoretical calculations are given. The discussion of different catalytic systems provides ideas for the development and improvement of subsequent NRR electrocatalysts.

INTRODUCTION

Ammonia (NH₃) is widely used in several industries, such as chemical fertilizer, fiber, dye, explosive resin, and hydrogen carrier. At present, the output of ammonia is increasing year by year (Chen et al. 2018). 78% of the air is composed of N₂. Combined with the nitrogen cycle in the environment, there is great interest in the conversion of N₂ to NH₃. Fig. 1 shows numerous processes of the nitrogen cycle and nitrogen fixation in nature. However, N₂ has stable chemical properties and strong N≡N triple bond energy, so most chemical reactions cannot be carried out directly. Although some prokaryotes can convert atmospheric N₂ into nitrogen by biological nitrogen fixation in nature, the nitrogen fixed by this method is far from meeting the needs of human production and life (Ren et al. 2021, Qi et al. 2021, Ma et al. 2020). In industry, the Haber Bosch process with harsh reaction conditions, high energy consumption, and harm to the environment are still used to obtain ammonia (Hou et al. 2020, Li et al. 2020, Foster et al. 2018, Montoya et al. 2015). The resulting energy consumption is relatively

high (Kibsgaard et al. 2017, Rz et al. 2019). At the same time, the raw materials of the Haber Bosch process need pure hydrogen that does not exist in nature. It is mainly produced by the decomposition of fossil energy (such as natural gas). The natural gas consumed in this process is 3%-5% of the total natural gas consumption in the world. The production of a large number of CO₂ by-products will further aggravate the global greenhouse effect (Dg et al. 2022, Meng et al. 2020). Therefore, to overcome the limitations of harsh conditions and large environmental pollution of Haber Bosch process equipment, it is necessary to develop an environmentally friendly and low energy consumption ammonia production process (Spatzal et al. 2011, Lancaster et al. 2013). Among many ammonia synthesis methods, electrocatalytic nitrogen reduction reaction has the advantages of easy experimental conditions and less environmental pollution (Shipman et al. 2017, Zhu et al. 2020).

In the electrochemical NRR process, catalysts are the key to ammonia synthesis. However, the low reactivity and

selectivity of electrocatalysts are a significant challenge. Therefore, the search for cost-effective electrocatalysts has become one of the research hotspots of electrochemical ammonia synthesis (Zhu et al. 2020). At present, researchers have concluded through theoretical simulations and experimental studies that metal-based catalysts (transition metals, precious metals, and non-precious metals) can achieve the electrochemical NRR (Xu et al. 2020, Chen et al. 2021). Noble metal catalysts have excellent catalytic performance due to their strong binding energy, excellent electrical conductivity, and abundant active polycrystalline surface, and are widely used in electrochemical reactions. In recent years, precious metal catalysts with diverse active sites have been extensively investigated. Meanwhile, non-precious metal catalysts are abundant and inexpensive on earth and have broad application prospects (Yu et al. 2021). In recent years, non-noble metals, especially transient metal compounds were used as electrode materials for electrocatalytic reactions because of their low cost, rich content, and easily regulated catalytic properties (Wang et al. 2018). In this paper, different systems of NRR catalysts (precious metal catalysts and non-precious metal catalysts) are comprehensively reviewed to provide some useful enlightenment for improving the performance of NRR catalysts in the future (Zhao et al. 2019).

In this paper, the catalytic reaction mechanism of NRR, several electrolysis experimental devices for nitrogen reduction synthesis of NH_3 , and different NH_3 detection methods are introduced. On this basis, the latest progress of catalysts in electrocatalytic reactors is reviewed. The research progress of precious metal-based catalysts and non-precious metal transient metal-based catalysts is summarized. Then it is hoped that the research results of this paper can provide useful guidance for the rational design of electrocatalysts for ammonia synthesis, stimulate people's interest in the new research field of ammonia synthesis, and accelerate the green industrialization process of ammonia synthesis.

THE DEVICE OF ELECTROCATALYTIC AMMONIA SYNTHESIS

The electrochemical cell structure is very important for the electrochemical process of N_2 conversion to NH_3 . Electrochemical experimental equipment is generally composed of the following parts: electrolytic cell electrolyte working electrode opposite electrode reference electrode gas pipeline and electrochemical workstation. According to the type and distribution of electrodes and electrolytes, electrolytic cells can be divided into back-to-back type, polymer electrolyte

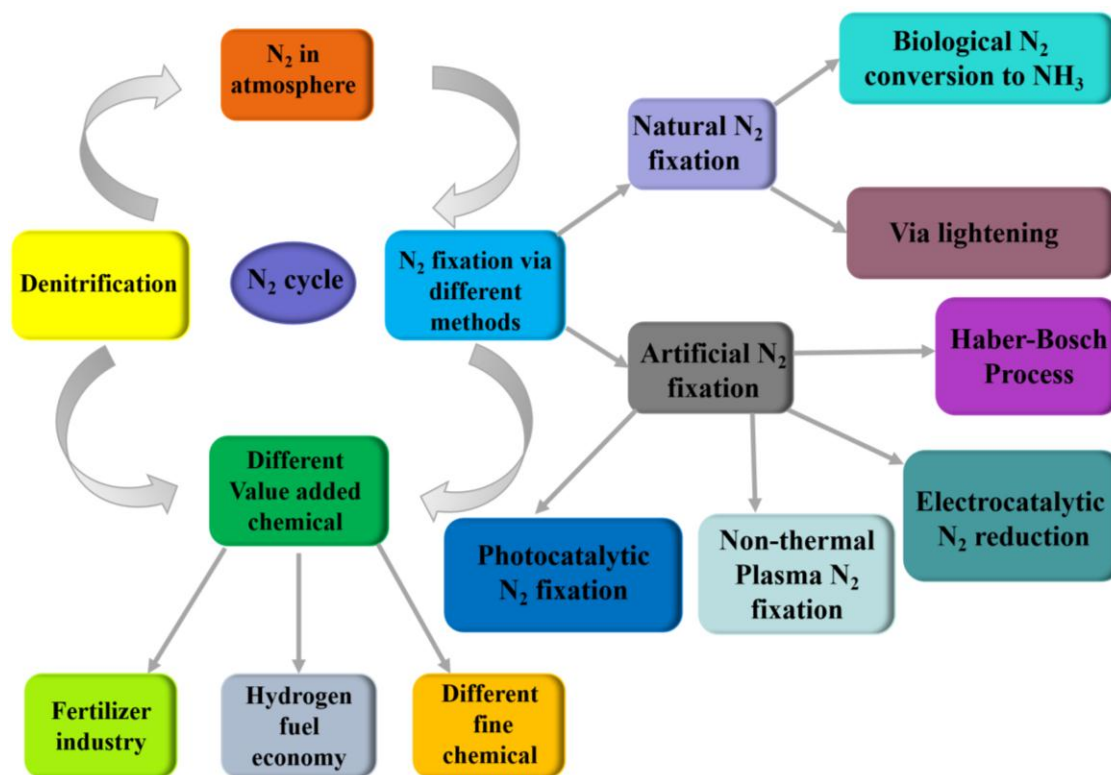


Fig. 1: The numerous processes of the nitrogen cycle and nitrogen fixation in nature.

membrane type, H-type, and single cell type. Among them, single-cell and H-type electrolyzers have been widely used in recent studies (Rostamikia et al. 2019). As shown in Fig. 2a, the cathode and anode of a back-to-back cell are injected with nitrogen and water respectively, the exchange membrane separates the two electrodes. As shown in Fig. 2b, a PEM cell differs from a back-to-back cell in that the electrolyte is injected into the anode, and the protons of the cathode are provided by electrolytic water. In Fig. 2c single-chamber cell, ammonia is oxidized at the anode due to simultaneous cathodic and anodic reactions in the same electrolyte, making

the determination of ammonia inaccurate. H-type cells (Fig. 2d-f) are widely used in the laboratory under current experimental conditions, where the negative and positive reactions are divided with a Nafion membrane in a separate electrolyte. Therefore, in the testing process of ammonia content, ammonia cross-contamination cannot be ignored.

NRR PRODUCT DETECTION

The commonly used methods for NRR product detection include colorimetry (including Spectrophotometry with

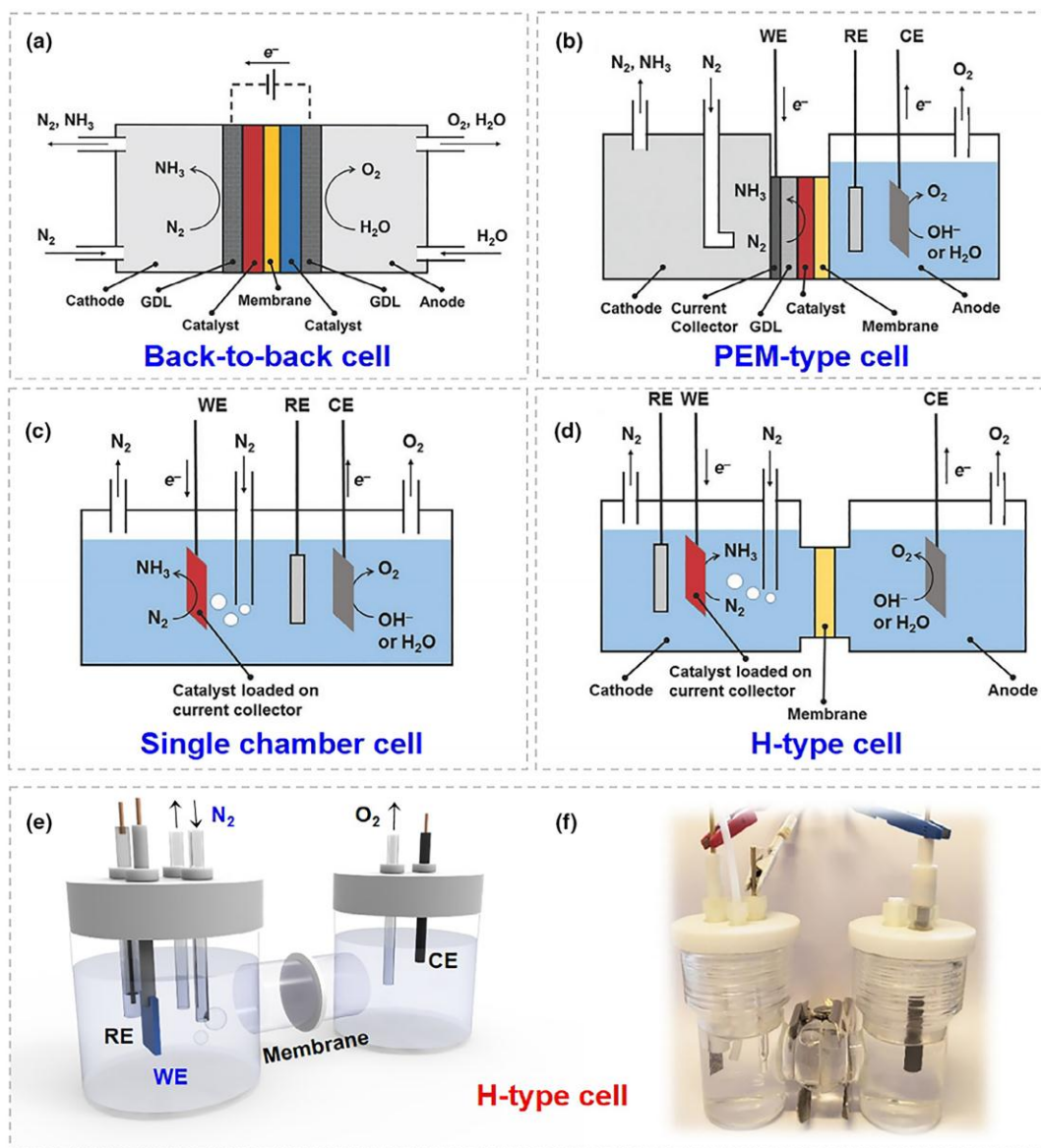


Fig. 2: Diagram of different electrochemical battery devices. Reproduced from Ref. (Rostamikia et al. 2019). (e-f) Installation diagram and photos of H-type electrolytic cell in the experiment (Wan et al. 2019).

Nessler's reagent colorimetric method and salicylic acid-hypochlorite spectrophotometry), ion-chromatography, ^{15}N isotope labeling-nuclear magnetic resonance NMR method and so on.

The spectrophotometric method uses iodide ions and mercury ions to coordinate with NH_4^+ under strongly alkaline conditions. The characteristic peaks of the complex can be found at 420 nm, and the concentration of NH_4^+ can be reflected by the intensity of the absorption peak. The detection range of NH_4^+ is 0.025-5.0 $\text{mg}\cdot\text{L}^{-1}$. Salicylic acid-hypochlorite spectrophotometry is in an alkaline medium, NH_4^+ in turn with the salicylate, hypochlorite ion, and sodium nitroferrocyanide (nitropuna) reaction to produce blue compounds. The characteristic absorption peak was at 664 nm, and the range of NH_4^+ detected by this method was 0.01-1.0 $\text{mg}\cdot\text{L}^{-1}$ (Zhou & Boyd 2019).

Ion chromatography is also widely used in the detection of NH_4^+ , with a detection range of 0.02-40 $\text{mg}\cdot\text{L}^{-1}$. The experiment has high reproducibility, high sensitivity, and a short detection time. However, when using ion chromatography to determine the content of NH_4^+ , it is noteworthy that the close position of NH_4^+ and Na^+ ion peak results in a low separation degree. If the content of Na^+ ions in the electrolyte is too high, the concentration of NH_4^+ cannot be accurately determined (Thomas et al. 2002, LeDuy & Samson 1982).

To obtain relatively reliable results, in addition to colorimetry and ion chromatography, ^{15}N isotope-nuclear magnetic resonance NMR was used to verify the experimental results (Hodgetts et al. 2020). The source of ammonia formation can be traced directly through isotope calibration to determine catalyst activity. The detection range is 5-10 $\mu\text{mol}\cdot\text{L}^{-1}$. The results of ^{15}N isotope-nuclear magnetic resonance (NMR) should be similar to those of colorimetry or ion chromatography, and the ammonia yield of the catalyst should be determined by mutual verification of various detection results.

REACTION MECHANISMS OF NRR

The reaction mechanism of NRR is very complex and mainly depends on the catalytic surface and application potential. The reaction principle of electrocatalytic NRR ammonia synthesis is shown in Fig. 3a. As can be seen from Fig. 3b, according to kinetics, there is a gap of 10.8 eV energy gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) in nitrogen molecules (Zheng et al. 2019). The sorption and activation hydrogenation process of nitrogen is the most critical step. The sorption and activation process of nitrogen mainly includes a dissociative pathway, associative pathway (alternative pathway, distal pathway), enzymatic pathway, and Mars-van Krevelen (MvK) pathway, as shown in Fig. 3c (Zheng et al. 2019). The first three are more common, and

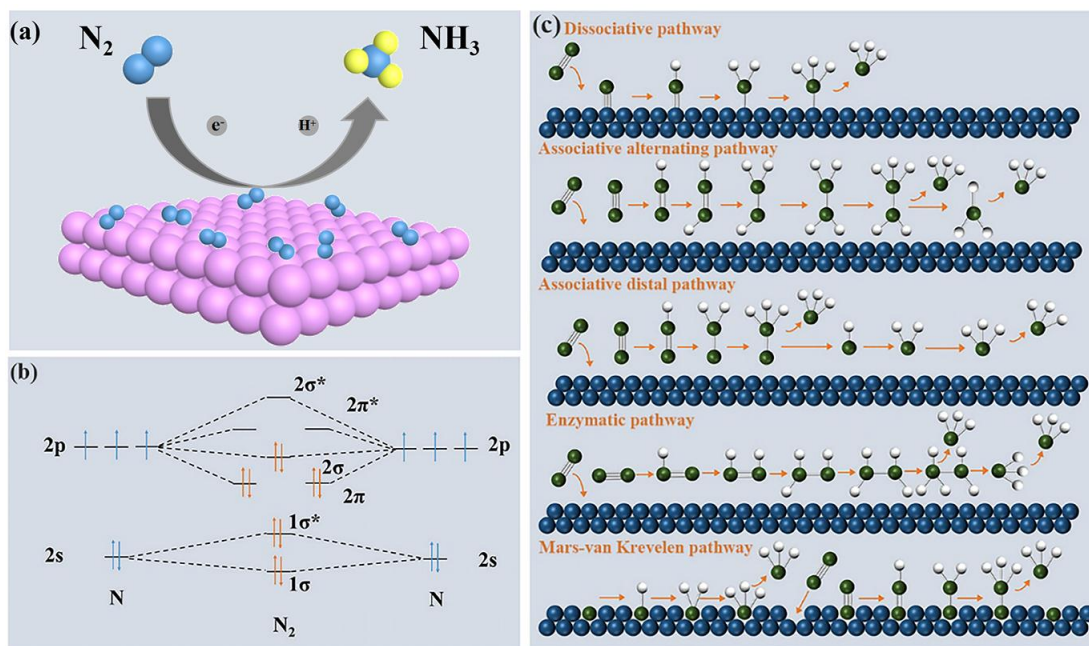


Fig. 3: Diagrammatic sketch of (a) NRR electrocatalysis and mechanisms. (b) Graphs of N orbitals and N_2 orbitals. (c) Reaction pathway of catalyst for nitrogen reduction (Adapted from Ref. (Zheng et al. 2019)).

the detailed process is shown in Fig. 3c. The dissociative mechanism process is that N_2 is first dissociated into N atoms adsorbed on the surface, each N atom is hydrogenated to form NH_3 and desorbed from the surface to complete the catalytic process, and the H-B process belongs to the dissociative mechanism. In the associative mechanism (distal pathway), N_2 is adsorbed on the surface in molecular form, and the chemical bond connection between the two nitrogen atoms is maintained. Hydrogenation first occurs on the nitrogen atom far from the surface. After hydrogenation, the N-N bond breaks, a molecule of NH_3 is removed from the outside, and the inner N atom begins hydrogenation to form a molecule of NH_3 and then desorbs from the surface. The preliminary process of the associative mechanism (alternative pathway) is similar to the distal pathway mechanism, but in the alternative pathway mechanism, two nitrogen atoms carry out the hydrotreating process alternately, the hydrogenated nitrogen atoms are the first to form NH_3 and desorb from the surface, and the remaining nitrogen atoms continue the hydrogenation process. In the two association mechanisms, with the progress of hydrogenation, the chemical bond between two N atoms will weaken, and the fracture of the N-N bond is relatively easy. Therefore, compared with the dissociative mechanism, the associative mechanism consumes less energy and is easier to carry out. When the catalyst type, structure, and reaction conditions are different, the reaction process experienced by nitrogen reduction to synthesize ammonia is also different, and the application mechanism needs to be analyzed in detail.

In addition, there are two mechanisms: the enzymatic pathway and Mvk. The former mainly occurs in the nitrogen reduction reaction of nitrogenase. In this mechanism, N_2 is still adsorbed in the form of molecules, but the two N atoms are not far from each other and are adsorbed on the surface side by side (Niu et al. 2021). The hydrogen process is the same as the alternative pathway mechanism. The Mvk mechanism appears more often in the catalytic process of transient metal nitrides (Abghoui & Skúlason 2017).

ELECTROCATALYSTS FOR NRR

Noble Metal-based Catalyst

At present, precious metal materials such as Pt, Rh, Au, Ru, Pd, Ag, and Ir Noble (Li et al. 2021) have been widely studied as catalysts for NRR because of their abundant surface active sites, unfilled d-electron orbitals, and superior conductivity. As mentioned earlier, precious metal materials have excellent HER properties and form fierce competition with nitrogen reduction reactions. Therefore, reasonable improvement and hybridization can improve its selectivity and yield. In recent years, many scholars have done a lot of research on

precious metal catalysts including (Au catalyst, Ru catalyst, Rh, and Pd catalysts). Experiments have shown that precious metal catalysts have obvious catalytic effects on NRR. This article uses the Au catalyst as an example to introduce the utilization of precious metal catalysts in nitrogen reduction reaction (NRR) and the performance achieved.

Gold (Au) is considered an ideal nuclear reactor material because, for the unfilled electron orbital, the reactant is easy to be adsorbed on the surface, has appropriate strength, and is conducive to the formation of intermediate “active compounds”. It can be obtained from Fig. 4a, the average particle size of Au nanoclusters in the TiO_2 lattice is 0.5 nm. Fig. 4b shows that the use of this catalyst greatly improves the ammonia yield, and its NH_3 yield can reach $21.4 \mu g h^{-1} mg^{-1}$. The electrolysis experiments of three different catalysts showed that TA-reduced Au/ TiO_2 (TA-Au/ TiO_2) showed the best nitrogen reduction performance compared with sodium borohydride reduction Au/ TiO_2 and Photoreduction Au/ TiO_2 (Fig. 4c). As shown in Fig. 4d, to investigate the stability of the nitrogen reduction performance of the catalyst TA-reduced Au/ TiO_2 , 10 electrolysis cycle experiments were carried out. It was found that there was no obvious change in the NH_3 yield and Faradaic efficiency. In addition, nitrogen reduction was also applied at the same potential and different temperatures. In recent years, many researchers have found that the Faraday efficiency of Au in nitrogen reduction reaction needs to be improved, and have carried out a lot of research on it. Xue et al. have successfully loaded Au and Ni nanoparticles on an N-doped C supporter (Xue et al. 2019). HAADF-STEM (Fig. 4e) test was carried out on the catalyst. The results showed that an N-doped C supporter with gold nanoparticles was deposited on adjacent Ni particles. As shown in Fig. 4f, electrolytic experiments were conducted on several catalysts with different Au contents. Through comparison, it was found that the Faraday efficiency of Au₆Ni was the highest among the catalysts, reaching 67.8% at -0.14 V (vs. RHE). Fig. 4g shows that the turnover rate (TOF) of the nitrogen reduction reaction on the Au catalyst continuously increases with the decrease of the Au content, which is similar to the electron enrichment of the Au component. By summarizing the previous density functional theory (DFT) calculation and experimental results and combined with the standard free energy spectrum of nitrogen reduction (Fig. 4g) in this work, we obtained the association mechanism on Au, in which the decomposition of adsorbed nitrogen ($*N_2$) into $*NNH$ is the rate-limiting step. As can be seen from Fig. 4i, the electron interaction between Au and Ni makes the electrons in Ni particles can be absorbed by Au, which is beneficial to the adsorption and dissociation of N_2 . Therefore, higher Faraday efficiency of image pairs is obtained.

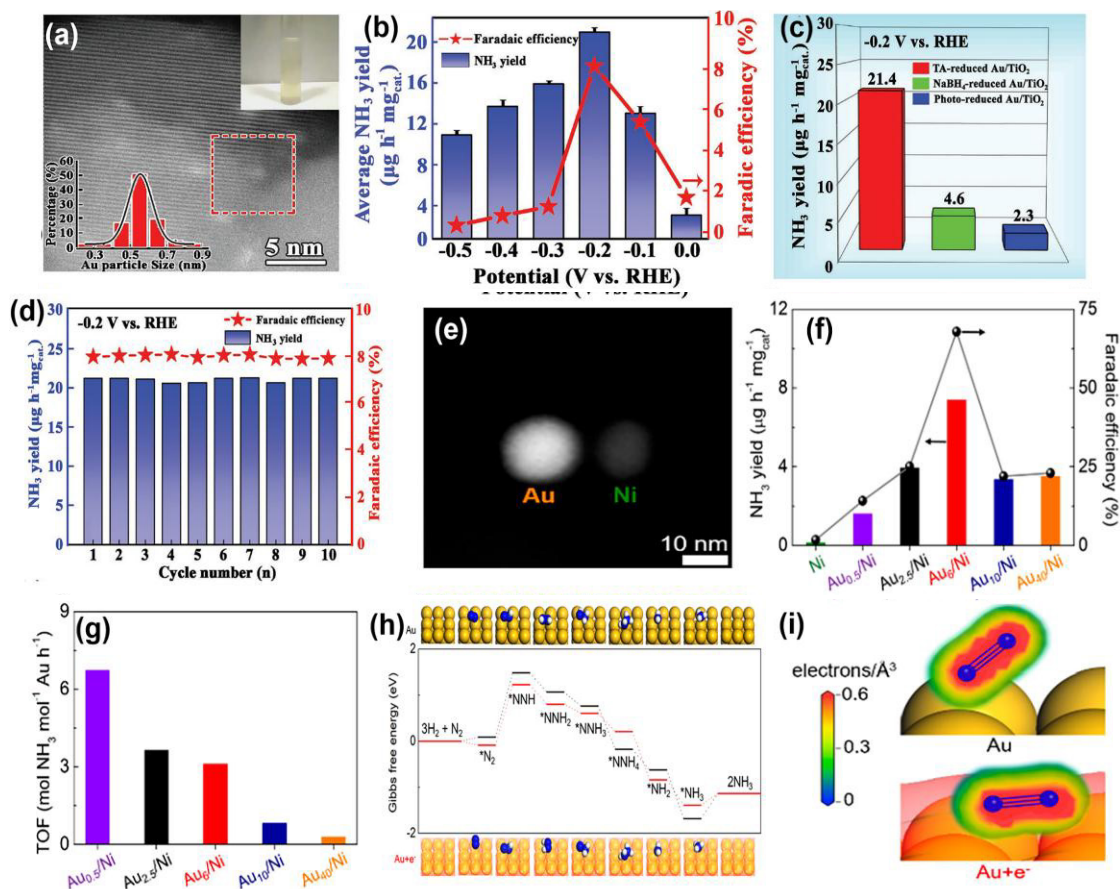


Fig. 4: (a) HAADF-STEM image of the TA-Au/TiO₂ (the picture of TA-Au/TiO₂ floated in the water, and the diameter distribution of Au). (b) Variation diagram of ammonia production rate and Faradaic efficiency. (c) Variation chart of the ammonia production rate of different catalysts. (d) Variation diagram of ammonia production rate and Faradaic efficiency of catalysts with different Au contents. (e) HAADF-TEM image. (f) Ammonia production rate and Faradaic efficiency of catalysts with different Au contents. (g) TOF values of the ammonia production rate based on the Au content. (h) The energy spectrum of nitrogen reduction. (i) The electron density map of N₂ adsorption was obtained by calculation. Reproduced with permission from Ref. (Xue et al. 2019).

Non-precious Transient Metal-based Catalyst

Precious metal catalysts usually have low ignition temperatures and high efficiency. Its catalytic efficiency is unmatched by other catalysts at low temperatures, but due to limited resources and high prices, it cannot be applied on a large scale (Zhang et al. 2018). Therefore, many scholars have shifted their research focus to non-precious transient metals as substitutes. Compared with noble metal catalysts, non-precious metal transient metals have the advantages of cheap and easy availability, abundant resources, and relatively good catalytic activity. Therefore, they are widely used as ideal electrocatalysts. At present, there are many kinds of transient element materials, mainly including their phosphides (Chu et al. 2019), chalcogenides (Zhang et al. 2018), borides (Yu et al. 2019), oxides (Yao et al. 2019), nitrides (Liu et al. 2020), metal single atoms (Guo et al. 2020), and carbides (Yang et al. 2020) have been widely

studied as valid electrocatalysts for the nitrogen reduction reaction.

Experiments have shown that non-precious transient metal-based catalysts have obvious catalytic effects on NRR. This article uses Fe-based electrocatalysts as an example to introduce the application of precious metal catalysts in NRR and the performance achieved. Fig. 5a is a schematic diagram of single-atom Fe supported on an n-doped carbon framework. In 0.1 M PBS, the electrolysis experiment of ISAS-Fe/NC catalyst shows that its ammonia production rate can reach $62.9 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$ and Faraday efficiency can reach 18.6%. Fig. 5b depicts the variation of current density and Faraday efficiency, implying that the catalyst has a FE of $18.6 \pm 0.8\%$ at the highest NH₃ production rate. To explore the nitrogen reduction property of the ISAS-Fe/NC catalyst, we studied its three possible reactions, including the distal pathway, the alternative pathway, and enzymatic mechanisms (Liu et al.

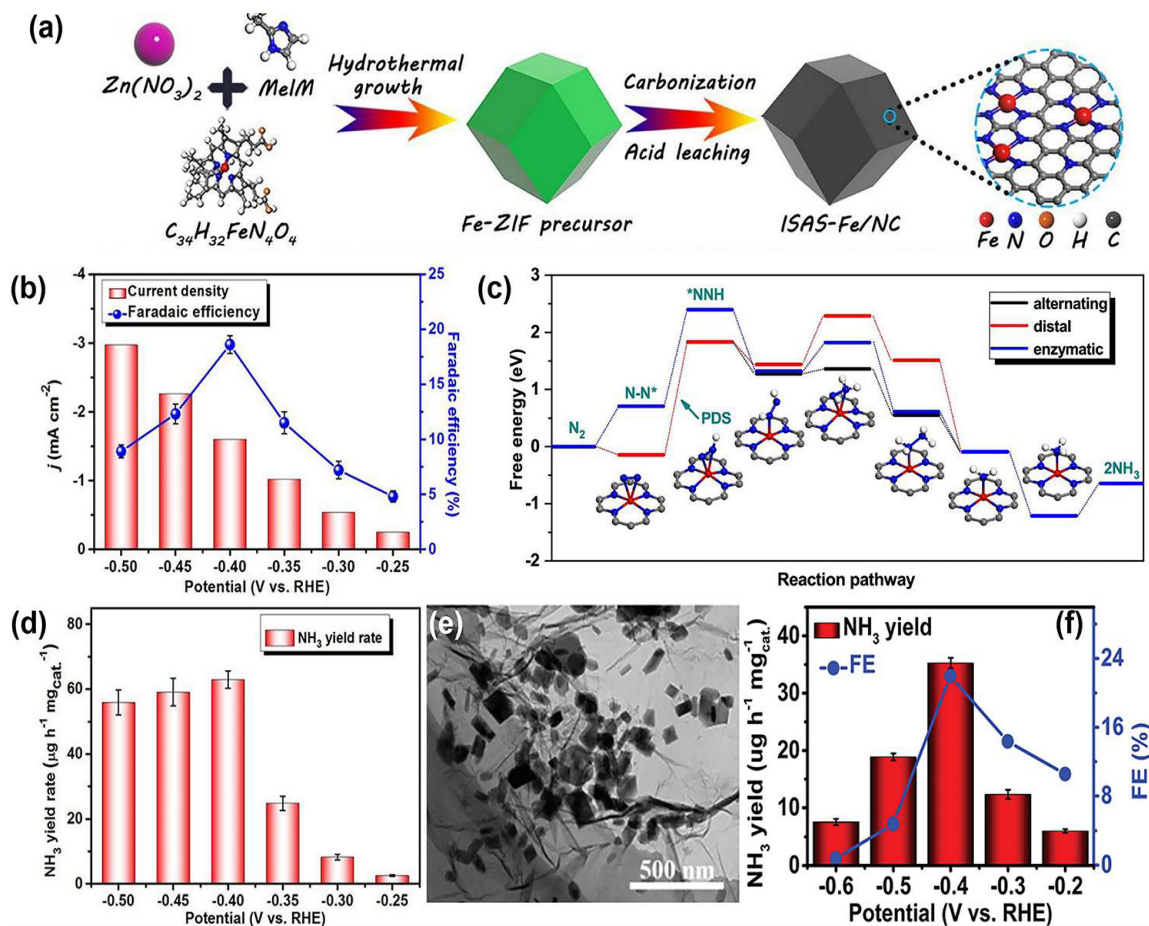


Fig. 5: (a) Composite diagram of ISAS-Fe/NC. Reproduced with permission from Ref. (Lü et al. 2019). (b) Variation diagram of current density and Faraday efficiency. (c) The calculation shows that nesting is the most stable of the three reaction mechanisms (d) Variation diagram of NH_3 yield and different potentials. (e) TEM images of FeP_2 -rGO. (f) Ammonia yields and Faraday efficiency of FeP_2 -rGO/CP. Reproduced with permission from Ref. (Zhu et al. 2020).

2018). As shown in Fig. 5c, the first hydrogenation step is a potential determining step. Compared with distal and alternative PDS (1.98 eV), the PDS of the enzymatic mechanism (1.69 eV) is lower, indicating that the enzymatic mechanism of ISAS-Fe/NC catalyst in nitrogen reduction is better (Zhao et al. 2017). Fig. 5d shows the variation of ammonia yield under different potentials. Under this catalyst, the NH_3 yield is $62.9 \pm 2.7\ \mu g\ h^{-1}\ mg_{cat}^{-1}$. From the TEM image of FeP_2 -rGO in Fig. 5e, it can be seen that FeP_2 nanoparticles have been successfully loaded on rGO. Fig. 5f depicts the variation of ammonia yield and Faraday efficiency at different potentials after electrolysis of the FeP_2 -rGO/CP catalyst. FeP_2 -rGO/CP has significant nitrogen reduction activity, the NH_3 yield is $7.06\ \mu g\ h^{-1}\ cm^{-2}$, and the FE value is 21.99%.

CONCLUSIONS AND PERSPECTIVES

At present, the development of low-cost and high-activity

catalysts is the key to optimizing the NRR process. To enhance the efficiency of the NRR process and promote the industrialization of electrocatalytic ammonia synthesis, the following aspects need to be considered.

- (1) Combine theory with experiment. Through the calculation of adsorption activation energy and reaction thermodynamic energy barrier, the overpotential and corresponding speed-limiting steps required to drive the reaction can be obtained, which plays a major role in revealing the catalytic mechanism and guiding the development of catalysts.
- (2) Enhance the catalytic activity of existing material systems. Material design and regulation strategies are applied to improve NRR reaction activity, such as lattice defect regulation strategies such as doping and vacancy construction, as well as surface and interface design such as morphology and size regulation to raise the active

points of the reaction, improve the adsorption performance of materials to nitrogen molecules, tuning the electron structure of catalysts, accelerate $\text{N}\equiv\text{N}$ fracture, and regulate the adsorption and desorption performance of intermediates in the reaction process.

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