Rational design on photo(electro)catalysts for artificial nitrogen looping

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Abstract
Nitrogen, one of the most important elements on the Earth, plays an essential role in shaping the modern society. The natural nitrogen looping, however, is insufficient to satisfy the high demand of the large-scale human activities. To achieve a more sustainable and efficient utilization of nitrogen, artificial nitrogen looping by photo(electro)catalytic processes has been considered as a feasible strategy. In this context, the rational design on the high-performance catalysts for nitrogen looping becomes increasingly important and urgent. On this basis, herein, we provide a timely review on the recent progress, achievements, and essential challenges for the artificial nitrogen looping process, mainly including photo(electro)catalytic transformations among dinitrogen, ammonia, gaseous nitrogen oxides, nitrate, and so on. Especially, the photo(electro)catalysts used in various reactions involved in nitrogen looping, including nitrogen reduction reaction, nitrogen oxidation reaction, ammonia oxidation reaction, ammonia decomposition reaction, etc., are systematically introduced. Finally, we hope that this review will help us deepen the understanding of nitrogen looping-related photo(electro)catalysts, and further pave a way toward the sustainable development on energy and environment.

Keywords
environmental protection, nitrogen looping, photo(electro)catalysis, sustainable energy
As early as the 19th century, some researchers proposed the necessity of artificial nitrogen fixation for meeting the growing need for food. It is not until the early 20th century, however, that Fritz Haber and Carl Bosch developed the efficient method of artificial nitrogen fixation, namely the Haber-Bosch process. In this catalytic process, the conversion from nitrogen gas to ammonia was achieved under the high temperature (300°C-500°C) and the high pressure (200-300 atm), simultaneously assisted by the Fe/Ru-based catalysts. The Haber-Bosch process achieved the large-scale implementation of industrial ammonia synthesis, which laid a solid foundation for the development of modern society.

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The aforementioned Haber-Bosch process, nevertheless, has been regarded as an unsustainable strategy due to its huge energy consumption and high pollution.

Specifically, in order to activate the inert dinitrogen molecules, a high reaction temperature (300°C-500°C) and high pressure (200-300 atm) must be kept in the this process, thus leading to high energy consumption. According to the statistics, the annual energy consumption of the Haber-Bosch process accounts for 1%-2% of the worldwide annual energy generation.

Meanwhile, in order to produce the high-purity hydrogen gas required for this process, a vast amount of CO₂ is also emitted, which contributes to approximately 1.5% of the total greenhouse gas emission.

Obviously, seeking a green and efficient nitrogen fixation technology is necessary for the sustainable development of energy and the environment. Recently, lots of studies have indicated that photo(electro)catalysis processes can achieve effective nitrogen fixation using nitrogen gas and water as raw materials at room temperature and atmospheric pressure. Generally, photo(electro)catalytic processes for nitrogen fixation include nitrogen reduction reaction (NRR) and nitrogen oxidation reaction (NOR). For the former one, nitrogen gas is reduced to ammonia. For the latter, however, dinitrogen molecules are oxidized to nitrate. The reaction not only realizes the efficient utilization of gaseous nitrogen but also produces nitrate, which has a great impact on crops and industrial production.

In contrast to the above nitrogen fixation processes, ammonia decomposition reaction (ADR) and the denitrification reaction can convert the fixed nitrogen back into a molecular state. Specifically, ADR can oxidize ammonia to form nitrogen gas, which has been applied in two important energy-related fields. On the one hand, ADR is the key process for ammonia fuel cells (AFCs). On the other hand, ammonia can also be directly decomposed to produce hydrogen gas in ADR. Because ammonia is much easier to be liquefied than hydrogen, which makes it more facile for storage and transport than hydrogen gas, it has been regarded as an ideal storage medium of hydrogen energy. As for the denitrification reaction, nitrate or gaseous NO₃ can be reduced into nitrogen gas. Eutrophication caused by excessive nitrate or other gaseous nitrogen oxides emission has led to significant difficulties for environment protection in various countries. Consequently, a clean and sustainable environment is desired by the people around the world. Therefore, this
process is frequently used in sewage treatment, which is of great significance for environmental protection.

The above-mentioned processes are the conversions between molecular nitrogen and fixed nitrogen. However, the nitrogen species with different valence states can also be converted to each other by the photo(electro)catalysis way. For example, NO₃ can also be directly reduced to generate ammonia. Producing ammonia by nitrite reduction can be an alternative to the direct ammonia synthesis by nitrogen reduction. Besides, ammonia oxidation reaction (AOR) can also transform NH₃ to nitrogen oxide at a high temperature, which is essential for the ammonia nitrogen treatment in wastewater.

Consequently, the nitrogen-related photo(electro)catalytic reactions, such as NRR, NOR, AOR, ADR, and others, should play a critical role in human production and life, considering its sustainability features (Figure 1). By far, a large number of original works have been reported. For such a research hotspot, a systematic review can help us clarify the development of this field and deepen our understanding of related mechanisms. To the best of our knowledge, however, there are rarely any such reviews available on the nitrogen looping by artificial catalytic reactions. This scenario thus makes it very necessary to provide a comprehensive review to discuss in detail the catalytic reactions involving nitrogen element, especially designing the efficient photo(electro)catalysts.

Herein, we focus on the latest advances in artificial nitrogen element looping, mainly on the photo(electro)catalytic transformations among N₂, gaseous NOₓ, nitrate, and NH₃. The transformation reactions involved in the above artificial nitrogen looping process will be discussed in detail, mainly including NRR, NOR, AOR, ADR, denitrification, etc. In particular, the various photo(electro)catalysts used in the aforesaid reactions will be systematically introduced. Finally, we will point out the development direction for efficient industrial nitrogen fixation and artificial nitrogen looping processes and provide an essential guarantee for the sustainable development of energy and the environment.

2 | CONVERSION BETWEEN NITROGEN AND AMMONIA

The transformation between nitrogen and ammonia have been widely investigated, particularly NRR and AOR. On the one hand, NRR at ambient conditions provides an energy-saving and low-pollution method for the synthetic ammonia industry, which benefits to fertilizer and textile industry. On the other hand, AOR and denitrification show great potentials in AFCs and hydrogen storage, respectively. In this section, we will discuss in detail the above photo(electro)catalytic processes.

2.1 | Nitrogen reduction to ammonia

As above mentioned, although the nitrogen gas in the atmosphere is abundant, it is difficult to directly use nitrogen gas due to its high inertness resulted from the high bond energy of the N≡N triple-bond. The traditional Haber-Bosch process in the industry is accompanied by high energy consumption and a large amount of carbon emission. Thus, for the sustainable development of the ammonia synthesis industry, lots of efforts have been made to explore novel technologies, which can achieve NRR at ambient conditions, such as photo(electro)catalytic nitrogen reduction process.

As shown in Figure 2A, the photocatalytic NRR undergoes three processes: (a) photogenerated electron/hole pairs are generated under the illumination by incident light; (b) photogenerated electrons and holes are separated and further migrated to the surface of photocatalysts, respectively; (c) photogenerated electrons achieved at the surface carry out NRR (N₂ + 2H₂O + 6H⁺ + 6e⁻ = 2NH₃ · H₂O). For the electrocatalytic NRR, however, protons are produced at the interface between the anode and the electrolyte when a voltage is applied to the electrodes. Subsequently, these protons...
will be migrated through the electrolyte to the cathode. Then they react with dinitrogen molecules on the cathode with the help of the reductive electrons, thereby reducing nitrogen gas to ammonia (Figure 2B).

2.1.1 Photocatalytic NRR

Solar-driven NRR (i.e., the photocatalytic NRR) has been regarded as a promising technology for ammonia synthesis due to the inexhaustibility of solar energy and the simple reactants (nitrogen and water), which does not produce harmful species to the environment. However, some issues still impede the goal of efficient and highly selective photocatalytic NRR. On the one hand, the solubility of nitrogen gas in water is low, and its adsorption on the catalyst’s surface is very limited. On the other hand, insufficient NRR active sites on the catalyst surface limit the photocatalytic NRR performance. Besides, the low rate of proton generation and migration, and the high recombination of photoinduced charges is also harmful to the performance of photocatalytic NRR.

Consequently, to explore efficient photocatalysts is a critical step toward high-performance photocatalytic NRR. In recent years, various materials have been investigated in order to develop advanced photocatalysts for solar-driven NRR, including oxides, sulfides, nitrides, polyoxometalates, etc. For example, as a traditional wide bandgap oxide, TiO\textsubscript{2} shows a capacity of NRR due to its suitable band edges for NRR. However, the absence of active sites and insufficient visible light absorption are still the main bottlenecks, which limit its performance enhancement. To solve these problems, oxygen vacancies (V\textsubscript{O}) have been introduced into the TiO\textsubscript{2} matrix. For example, a commercially available TiO\textsubscript{2} with a large number of V\textsubscript{O} delivered a NH\textsubscript{4}\textsuperscript{+} production rate of 0.76 μM/hr after the UV-light irradiation (λ = 280-420 nm, light intensity = 35 W/m\textsuperscript{2}) of 48 hours (Figure 3A). The ammonia yield decreased when the number of V\textsubscript{O} reduced. Besides, Cu\textsuperscript{2+} doping can introduce V\textsubscript{O} into TiO\textsubscript{2} nanosheets (NSs), thus leading to not only more NRR active sites but also enhanced visible light absorption (Figure 3B). As a result, at the optimum doping amount (6 atm%), Cu-doped TiO\textsubscript{2} NSs showed a high NH\textsubscript{3} evolution rate of 78.9 μmol/g/hr under full solar irradiation, which is almost 4.2-fold higher rate than that of pristine TiO\textsubscript{2} NSs.

As an emerging photocatalyst, BiOBr has become a research hotspot due to its good visible light response. Similarly to TiO\textsubscript{2}, nevertheless, the deficiency of active sites is also a significant issue for BiOBr to achieve the excellent photocatalytic NRR. Fortunately, V\textsubscript{O} introduction is also a feasible strategy for BiOBr to improve its photocatalytic activity (Figure 3C). For instance, V\textsubscript{O} defects can greatly enhance the NRR performance of BiOBr NSs from 5.75 to 54.70 μmol/g/hr. Apart from oxides, nitrides and sulfides can also be utilized as photocatalysts for NRR. For example, graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) NSs etched by KOH showed an enhanced photocatalytic performance for NRR. Specifically, the KOH-treatment can bring rich defects to g-C\textsubscript{3}N\textsubscript{4} NSs, which is beneficial to promote the N\textsubscript{2} adsorption, light energy absorption, and charge separation, resulting in a high ammonia production rate of 3.632 mmol/g/hr (Figure 3D). Activation of N\textsubscript{2} is an uphill process involving the generation of high energy intermediates (N\textsubscript{2}H, N\textsubscript{2}H\textsubscript{2} etc.). Fortunately, the thermodynamic barrier of multielectron reactions can be reduced by avoiding the production of high-energy intermediates. As an n-type semiconductor, the ultrathin MoS\textsubscript{2} NSs possessed sufficient free electrons, which can be attracted by the light-induced excitons (electron-hole...
pairs) to form charged excitons (i.e., trions, Figure 3E) under solar light irradiation. These trions have multiple electrons in one bound state, which could accelerate the multielectron transfer reactions. Consequently, the ultrathin MoS2 NSs could reduce the thermodynamic barrier of NRR, thus leading to a relatively high ammonia synthesis rate as 325 μmol/g/hr.41

2.1.2 | Electro catalytic NRR

In addition to the photocatalytic route, the electrocatalytic process can also realize nitrogen reduction to ammonia under ambient conditions. When the electrocatalytic NRR is driven by the electric power generated from renewable energy sources (e.g., solar energy, wind energy, tide/wave energy, biomass energy, etc.), this technology seems to be an attractive and environment-friendly strategy to the ammonia synthesis industry.42,43

For the electrocatalytic NRR, there are two major issues: the low activity and the poor selectivity of electrocatalysts, which reduce the NRR performance.23 On the one hand, the lack of active sites on the surface of electrocatalysts leads to low activity.44 On the other hand, in the process of nitrogen reduction, the competitive hydrogen evolution reaction (HER) decreases the Faradaic efficiency (FE), leading to poor selectivity.1,45 So as to obtain superior NRR performance, the optimization of the electrocatalysts proves distinctly necessary.46

In order to achieve a high activity and selectivity for electrocatalytic NRR, many types of advanced electrocatalysts have been investigated, including metals (e.g., Fe,47,48 Mo,49,50 Cu,51 Ru,52,53 Rh,54 Pd,55 Au,56-58 Pt,59 etc), metal oxides (e.g., TiO2,60 Cr2O3,61 Nb2O5,62 Fe2O3,63,64 etc.), metal nitrides (e.g., VN,65 MoN,66 Mo2N,67 etc.), metal phosphides (e.g., CoP3,68 Cu3P,69 VP,70 etc), and so on.

Among the aforementioned various NRR electrocatalysts, metal elements have been widely studied, especially metallic single-atom catalysts (SACs), due to their super-high atom utilization and excellent NRR performance.71,72 For example, Ru SACs dispersed on nitrogen-doped carbon (Ru SACs/N-C) showed an ammonia yield rate of 120.9 μg NH₃/hr/mg cat and FE of 29.6% at −0.2 V versus reversible hydrogen electrode (RHE),72 respectively (Figure 4A). With the hydrothermal treatment of a precursor solution containing glacial acetic acid, ZrCl₄, H₂BDC, and RuCl₃, UiO-66 (Zr₆O₄(OH)₄(BDC)₆; BDC, 1,4-benzenedicarboxylate) with confined Ru single atoms
was synthesized. After annealing, Ru@ZrO2/NC catalyst was obtained. The Ru sites with oxygen vacancies are claimed to be the major active centers for nitrogen reduction, and the ZrO2 could effectively suppress the hydrogen evolution reaction (HER), resulting in an ammonia generation rate of 3.665 mgNH3/hr/mgcat at −0.21 V versus RHE and FE of 21% at an overpotential as low as 0.17 V versus RHE, respectively (Figure 4B).

Despite of many merits, the rare resource and the high cost still lead to difficulty in the large-scale utilization of noble metal catalysts, such as Ru. Therefore, exploiting non-noble metal catalysts has been regarded as a feasible strategy to realize commercial ammonia synthesis. For instance, Han et al. prepared N-doped porous carbon (NPC) supported single Mo atoms (SA-Mo/NPC) electrocatalyst for NRR. The ammonia yield reached to 34 ± 3.6 μgNH3/hr/mgcat and the FE is 14.6% ± 1.6% at −0.3 V versus RHE, respectively. This superior performance originated from the dispersed single-atom active sites and 3D hierarchical structure of such catalyst (Figure 4C). Very recently, our group developed Fe/Cu atom clusters confined in sub-nanoreactors of g-C3N4 on the surface of carbon nanotubes (CNTs) as efficient NRR electrocatalysts. Due to the synergistic enhancement of Fe and Cu, these Fe/Cu clusters delivered an ammonia production rate of 8.6 μgNH3/hr/mgcat and FE of 18.8% at −0.3 V versus RHE, respectively (Figure 4D).

Apart from metal elements, metal oxides and nitrides also exhibited good performance for NRR. For example, we synthesized Fe-doped W18O49 nanowires on carbon fiber papers through a facile solvothermal route (Figure 5A). This electrocatalyst exhibited a yield rate
of 24.7 μgNH₃/hr/mgcat for ammonia synthesis and FE of 20% at −0.15 V versus RHE. The DFT calculation demonstrated that effective catalytic activity is attributed to the addition of Fe, which not only increases the number of oxygen vacancies and W active sites but also optimizes the adsorption of nitrogen. Besides, Cr₂O₃-based electrocatalysts also achieved a high NH₃ yield of 25.3 μgNH₃/hr/mgcat as well as a high FE (6.78%) at −0.9 V versus RHE (Figure 5B).61

As for metal nitrides, VN nanowires array on carbon cloth (VN/CC) exhibited an ammonia production rate of 2.48 × 10⁻¹⁰ mol/s/cm² and a FE of 2.25% at −0.30 V versus RHE (Figure 5C).65 Through introducing nitrogen vacancies acting as the active sites on two-dimensional (2D) layered W₂N₃ nanosheets (NV-W₂N₃), Jin et al.76 obtained a steady ammonia generation rate of 11.6 ± 0.98 μgNH₃/hr/mgcat and FE of 11.67% ± 0.93% at −0.2 V versus RHE for 12 cycles of 24 hours (Figure 5D).

As for carbon materials, doping has been considered a common method to modify the surface electronic structures of materials.77-80 For instance, carbon nanospheres co-doped by B and N (BNC-NS) obtained a significantly
improved catalytic activity of electrochemical reduction of N2 to NH3. The BNC-NS demonstrated the superior performance of NRR with a FE of 8.1% and ammonia yield rate of 15.7 μgNH3/hr = mgcat, which were attributed to the high N2 adsorption capacity (Figure 5E). Table 1 summarizes the NRR catalysts performance mentioned above.

### 2.2 Ammonia oxidation and decomposition

With high energy density, facile storage and transportation, and carbon-free feature, ammonia is regarded as a feasible carrier for renewable energy sources. In particular, compared with the high-cost liquid hydrogen, ammonia shows facile storage and transport in the forms of the liquid or concentrated aqueous solution. In this field, ammonia oxidation reaction (AOR) and ammonia decomposition play critical roles in AFCs and ammonia-based hydrogen storage, respectively.

#### 2.2.1 Ammonia oxidation reaction for direct ammonia fuel cell

AOR is the half-reaction for direct ammonia fuel cells (DAFCs), which can generate electricity using ammonia and oxygen gas as the electrode materials. Generally, a DAFC is constructed by three parts: an anode, a cathode, and an electrolyte. In its operation, ammonia gas is fed into the anode of DAFC, and reacts with hydroxide (OH−) to produce electrons, nitrogen gas, and water (ie, AOR) (Equation (1)). At the same time, oxygen gas is fed in the cathode and then reacts with water and accepts electrons conducted from the anode to generate OH− (Equation (2)). By this means, the chemical energy stored in ammonia gas and oxygen gas is converted to electricity. Besides, the overall reaction of the DAFC system is also described in Equation (3), indicating that the environmentally friendly nitrogen gas and water are the final products.

Anode: \(2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^-\)  
Cathode: \(\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-\)  
Overall: \(4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}\)

Although DAFCs exhibit excellent potential, the slow kinetics process of AOR hinders the further improvement of DAFCs. For solving this problem, a serial of high-performance catalysts has been designed to accelerate the AOR, mainly including metal elements, binary, and ternary alloy catalysts. For example, with a polycrystalline gold disc electrode (5 mm diameter) acting as the current collector, the preferentially oriented Pt (100) nanoparticles (NPs) were fabricated through a simple colloidal route, exhibiting a higher current density than polycrystalline Pt (Figure 6A). The superior performance of the preferentially oriented Pt NPs can be ascribed to the high sensitivity of AOR to surface sites with square symmetry.

Except for monometal elements, the bimetal catalysts and ternary alloy catalysts are also active for AOR. For example, Pt/Ru (atomic ratio of 90:10) alloy NPs exhibited lower onset potential than Pt (Figure 6B). In another
similar study, Pt/Au (atomic ratio of 70:30) electrocatalysts prepared via borohydride reduction method showed a high power density of 2.64 mW/cm², which was 60% higher compared with single Pt (1.64 mW/cm², Figure 6C). As for the ternary alloys, Pt-Ir-Ni NPs dispersed on the porous silicon dioxide (SiO₂) and carboxyl-functionalized carbon nanotube (SiO₂-CNT-COOH) exhibited high catalytic activity for the AOR, which was evidenced by its low onset potential (~0.40 V vs RHE) at room temperature, which can be attributable to abundant OHad generated by porous SiO₂ and the augmented conductivity by CNTs (Figure 6D). Table 2 Summarizes the AOR catalysts performance mentioned above.

2.2.2 | Ammonia-based electrocatalytic hydrogen storage

As an ideal carbon-free fuel, hydrogen gas has been widely studied as the new energy carrier due to its high energy density of 146 MJ/kg. However, the large-scale utilization of hydrogen is still limited because of the high costs resulting from the transportation and long-term storage of hydrogen. Specifically, the boiling point of hydrogen is as low as −253°C under standard atmospheric pressure and its Carnot efficiency is 7.3%, which means that the liquefaction of hydrogen requires high energy. In addition, the hydrogen is liable to boil off, which leads to the gradual loss of hydrogen with the increase of storage time. Fortunately, ammonia is easier to store and transport and can decompose to hydrogen without carbon emission, which makes it a feasible medium of hydrogen storage. In addition, electrocatalytic ammonia decomposition to generate hydrogen gas can be achieved under low-temperature conditions (<450°C), which facilitates the large-scale implementation of this technology.

As shown in Figure 7A, the process from storing ammonia to release energy from hydrogen contains five steps: ammonia storage, ammonia decomposition,
hydrogen separation and purification, hydrogen storage and compression, as well as last hydrogen use. Among them, the ammonia decomposition process will be mainly discussed in this section. Ammonia decomposition occurs in a series of steps of dehydrogenation reaction (Equations (4)-(7)). The reaction starts from the adsorption of ammonia in the beginning and decomposition to N₂ and H₂ at last (Equation (8)). The same as NRR, nitrogen adsorption is also regarded as the rate-limiting step for ammonia decomposition.

### TABLE 2 Summary of catalysts performance of AOR

| Catalysts                                         | Performance                              | Experimental parameters                                      | Ref. |
|---------------------------------------------------|------------------------------------------|-------------------------------------------------------------|------|
| Pt nanoparticles                                  | 18.7 μA/cm² current density              | 0.2 M NaOH + 0.1 M NH₃, 0.55 V vs RHE                       | 87   |
| Pt₉₀Ru₁₀/C                                        | 84% NH₃ conversion                       | 1 M (KOH + NH₄OH), −0.25 V vs Hg/HgO                       | 88   |
| Pt₇₀Au₃₀/C                                        | 2.64 mW/cm²/g power density, 0.588 V cell potential | 5 M NH₄OH (1 mL/min delivered rate) + 1 M KOH, 150 mL/min oxygen flow rate, 40°C | 89   |
| PtIrNi/SiO₂-CNT-COOH (molar ratio of Pt/Ir/Ni = 9:1:1) | 124.0 A/g peak current density, 0.40 V vs RHE onset potential | 1.0 M KOH + 0.1 M NH₃, 5 mV/s scan rate, 900 rpm RDE rotating speed | 90   |

![Figure 7](image-url)
\[
\text{NH}_3^* + \star \rightarrow \text{NH}_2^* + \text{H}^* \quad (4) \\
\text{NH}_2^* + \star \rightarrow \text{NH}^* + \text{H}^* \\ 
\text{NH}^* + \star \rightarrow \text{N}^* + \text{H}^* \\ 
\text{N}^* + \text{N}^* \rightarrow \text{N}_2 + \text{H}^* \\ 
2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \\
\]

where, \(\text{X}^*\) represents the adsorbed species.

In recent years, many materials have been utilized as catalysts for ammonia decomposition, such as metal catalysts (including metal\(^{97,98}\) and alloys\(^{99,100}\)) and alkali metal amides.\(^{101}\) For example, The graphene and defective graphene-supported standing triangular Pt\(_3\) exhibited high reactivity and low activation barriers, which was attributed to the existence of Lewis acid/base pair sites accommodate the adsorption and subsequent dissociation of \(\text{NH}_3^*\) (Figure 7B).\(^{102}\) Apart from Pt, Ru also exhibits a good catalytic activity for ammonia decomposition. Specifically, the mesoporous Ru/MgO composite was fabricated by a deposition-precipitation method. Due to its high surface area and porous structure, this catalyst showed a high electrocatalytic activity of ammonia decomposition. The Ru/MgO catalyst presented the \(\text{H}_2\) evolution rate of 21.2 mmol/min/g, which is higher than that of 14.5 mmol/min/g on Ru/CNTs, meaning that its own an excellent performance of electrocatalytic ammonia decomposition. Further, the catalytic activity of the sample was enhanced to 35 mmol/min/g after a KOH treatment due to the efficient electrons donation of K\(^+\) ions (Figure 7C).\(^{103}\)

In addition, the alloy catalysts are also attractive. For example, Ni-Co bimetallic catalysts were used to decompose ammonia and showed the turnover frequency (TOF\(_{\text{H}_2}\)) as high as 40.57 min\(^{-1}\) at 350°C (Figure 7D).\(^{104}\) The Cs-modified Co\(_3\)Mo\(_3\)N catalysts were synthesized by a facile single-step method, which improves the catalytic activity for ammonia decomposition and promotes the recombinitive desorption of hydrogen and nitrogen atoms (Figure 7E).\(^{105}\)

Apart from metal catalysts, catalyzing the ammonia decomposing process via alkali metal amides is another feasible method. For instance, accelerated decomposition of ammonia was achieved through the synchronous stoichiometric decomposition and sodium amide (NaNH\(_2\)) regeneration. As a result, the decomposition efficiency of 90% was obtained at 500°C using 0.5 g NaNH\(_2\) in a 60 sccm NH\(_3\) flow, which is higher than that of the Ru (82%) and Ni (58%) catalysts.\(^{106}\) Table 3 summarizes the ADR catalysts performance mentioned above.

## 3 | Conversion Between Nitrogen and Nitrogen Oxides

The conversion between N\(_2\) and NO\(_x\) is the key step during the whole process of nitrogen cycling. On the one hand, NOR is another effective way to fix nitrogen, which realizes the conversion from nitrogen to nitrate.\(^{107}\) On the other hand, gaseous nitrogen oxides (eg, NO and NO\(_2\)) are the primary pollutants in the air, which should be removed or converted to nitrogen. Meanwhile, the eutrophication and pollution of water caused by excessive nitrate also should be paid attention to.\(^{108-110}\) For example, waste gas and sewage treatment are very important and attracting widespread attention.\(^{111}\) Consequently, the NOR and reduction of nitrogen oxides are still hot research topics to be further studied.

### 3.1 | Nitrogen oxidation reaction

As mentioned above, NRR is an effective way for nitrogen fixation. In addition to this route, nitrogen oxidation to nitrate (ie, NOR) has also been considered a feasible way to achieve the same goal of fixing nitrogen. Different from NRR, however, the products of NOR are nitrates rather than ammonia, which can not only provide nitrogen sources and nutrition for soil but also play a crucial role in numerous manufactures, for example, making gunpowder, curing coronary heart disease, and so on.\(^{108,112-115}\) It has been suggested that N\(_2\) is oxidized to nitrate by the following two steps: the first step is to activate the N≡N triple-bond, converting the inert N\(_2\) to active NO* intermediates (\(\star\) represents to active sites). The second step is a redox reaction, in which NO* is transformed into nitrate over the active sites.\(^{116}\) In this process, the highly active and selective catalyst materials for NOR are very important.

In order to develop efficient catalysts for NOR, significant efforts have been made. The N≡N triple-bond activation for the direct synthesis of nitrate is very important because no other side effects or by-products, which reduce the energy efficiency, will occur in this process.\(^{117}\) In the photocatalytic NOR process, the valence state of nitrogen is increased due to the oxidation effect of the light-induced hole. Consequently, some typical photocatalysts, such as TiO\(_2\), have been adopted for this purpose.\(^{118}\) However, the activation of nitrogen molecules is extremely difficult.\(^{119,120}\) To tackle with this issue, some researchers have utilized the electron-rich regions on the surface of the catalyst, such as the surface pits or vacancies, to directly absorb nitrogen molecules and promote the charge transfer.\(^{121,122}\) Therefore, catalyst materials for nitrogen oxidation are generally designed to improve
their catalytic performance through structural design, such as the design of atomic configurations. Catalysts with local electron-rich regions and uneven surface structures would produce a synergistic catalytic effect for the adsorption and dissociation of nitrogen molecules, which is expected to overcome the problem of difficult nitrogen activation.

| Catalysts          | Performance                                                                 | Experimental parameters                        | Ref. |
|--------------------|------------------------------------------------------------------------------|-------------------------------------------------|------|
| K-5%Ru/MgO         | 35 mmol/min/g H₂ formation rate, 87% NH₃ conversion                         | 30 mL/min NH₃ flow rate, 450°C                  | 103  |
| Ni₅Co₆/CZY         | 0.71 mmol/min/gcat H₂ formation rate, 40.57 min⁻¹ turnover frequency       | 10 mL/min NH₃ flow rate, 350°C                  | 104  |
| Co₃Mo₃N           | 26.0% NH₃ conversion, 0.7 mol NH₃/gcat/s turnover frequency                | Activation energy: 86.2 kJ/mol, 450°C          | 105  |
| Cs₀.₀₁₈ Co₃Mo₃N    | 48.3% NH₃ conversion, 1.29 mol NH₃/gcat/s turnover frequency               | Activation energy: 70.9 kJ/mol, 450°C          | 105  |
| NaNH₂              | 99.2% decomposition efficiency                                              | 0.5 g of NaNH₂ in a 60 sccm NH₃ flow at 530°C   | 106  |
Currently, the main catalysts are metal oxides and their composites. For example, pothole-rich WO₃ was used to activate the N≡N triple bond, directly synthesizing nitrate at room temperature. The porous structure makes WO₃ have more suspended bonds, activating high-energy electrons to stimulate N≡N triple bond.¹¹⁷ ZnFeₓCo₂₋ₓO₄ spinel oxides were also utilized as catalysts to carry out electrocatalytic NOR,¹²³ which achieved the direct synthesis of nitrate with high yield (130 ± 12 μmol/hr/gMO at 1.6 V vs RHE) by iron catalysts (Figure 8B,C). Besides, modified MXene electrocatalysts have also been utilized as electrocatalyst for NOR, which achieved 2.80 μg/hr/mgcat yield of nitrate (Figure 8D).¹²⁴ In the meantime, Ru-doped TiO₂/RuO₂ has shown a decent catalytic activity for NOR as well, and its FE is 26.1%. Density functional theory calculation showed that Ru⁸⁺ could be the main active center in NOR (Figure 9A).¹¹⁶ Besides, the Fe-doped SnO₂ can also achieve an efficient NOR ability. Specifically, the NO₃⁻ yields and FE of modified SnO₂ at the Fe-doping amount of 3% achieved 42.9 μg/hr/mgcat and 0.84%, respectively. Further, there are two existing forms of Fe element in SnO₂ matrix, Fe single atoms anchored on Vo and lattice doped Fe, which improve the absorption and activation of N₂ and promote the electrical conductivity of SnO₂ (Figure 9B).¹²⁵

3.2 | Denitrification of gaseous nitrogen oxides

Since the first industrial revolution, large-scale human activities, such as fossil fuel combustion, automobile exhaust, industrial nitrate production, and artificial nitrogen fertilizers, have led to a serious imbalance in the global nitrogen cycle.¹²⁶,¹²⁷ The excessive emission of nitrogen oxides, such as NO and NO₂, is not only harmful to the natural environment but also poses a threat to the sustainable development of human society. Therefore, the treatment and control of such nitrogen oxides in the air have become an urgent issue that remained unsolved. In order to solve these issues and alleviate environmental and health problems caused by air pollution, denitrification treatment based on photocatalysis to reduce pollutants in waste gas through catalysis has attracted extensive attention.

Photocatalytic denitrification treatment shows great potential in the reduction of nitrogen oxides in the exhaust gas. In particular, Ti-based materials have been extensively studied due to their high photocatalytic activity and stability.¹¹⁶,¹²⁸-¹³² Titanium alkoxides prepared by the high-temperature hydrolysis method have shown high denitrification activity, with a high absorption rate of 98% for NO photocatalytic oxidation.¹³³ In 2008, TiO₂ nanoparticles coating on woven glass fabric was used as a photocatalyst, which showed a good effect for removing nitrogen oxides and an efficiency of 63.9% upon the steady-state. Two technologies, including photocatalytic oxidation and wet absorption, were jointly utilized to deal with nitrogen oxides in the exhaust gas, which greatly improved NOₓ removal rate up to 75%. They used photocatalytic oxidation convert NO to NO₂ at the first step, then applied a sulfite solution as an absorbent to efficiently absorb nitrogen oxides (Figure 10A); and the main products obtained through this process are nitrite and nitrate, which can effectively reduce air pollution gas.¹³⁴ From 2013 to 2014, based on the selection of photocatalytic materials, researchers conducted relevant model construction and theoretical calculation, controlled and described the photocatalytic oxidation reaction of NO, and deduced the rate law of NO oxidation, providing data support for the control of NO oxidation rate.¹²⁸,¹³⁵ Recently, the composite material based on the novel microporous MIL-100(Fe)/Ti₃C₂ MXene structure could not only increase the material’s thermal stability under visible light but also boost the activity of nitrogen fixation (Figure 10B). The synergistic effect of the Schottky junction makes the photocatalytic activity greatly enhanced, which is expected to treat NO and reduce air pollution efficiently.¹³⁶ From the above discussion, it can be seen that gaseous nitrogen oxides (NOₓ) will be converted into nitrate during the photocatalytic process. Further, with the deepening of research, the performance of the catalysts has been improved to a large extent, including the design of
catalysts structure and the improvement of the activity. It is a feasible method with a very promising prospect for treating large quantities of waste gas. However, there are still very limited studies on the conversion of nitrogen oxides to N$_2$ or nitrate by electrocatalysis. In the future, it might be a very important topic to explore the electrocatalysis route for waste gas treatment.

### 3.3 Nitrate reduction

In the above discussion, the transformation from nitrogen oxides to nontoxic nitrogen gas is necessary. But in fact, more nitrogen oxides are oxidized to produce nitrate so as to reduce pollutants in the air. However, the excessive soluble nitrate species in the water causes severe problems for the water resource. Therefore, it is necessary to reduce the excess nitrates. If the nitrates can be effectively reduced, it will bring a serial of benefits for the environmental sustainability. Effective approaches to reducing nitrate to N$_2$ by photo(electro)catalysis to achieve green and the carbon-free conversion will be discussed in detail.

#### 3.3.1 Electrocatalytic nitrate reduction

Electrocatalytic nitrate reduction reaction can be regarded as the most promising nitrate conversion route. Specifically, noble metal electrocatalysts, especially alloys, exhibited excellent performance for nitrate reduction. For instance, bi-metallic alloys of Pt/Rh and Pt/Ir have been utilized as catalysts in the electrocatalytic nitrate reduction reaction. Remarkably, the nitrate reduction performance of alloy catalysts (i.e., Pt/Rh and Pt/Ir) was superior to the metal-element catalysts of Pt, Rh, and Ir.

Those above-mentioned expensive materials, however, impose restrictions on the development of electrocatalytic...
nitrate reduction, which limited its industrial deployment. Consequently, those non-noble counterparts have been explored to carry out the efficient and stable nitrate reduction process.\textsuperscript{141,142} For example, a corchorolifolius-structure composite material (Figure 11A), in which Fe nanoparticles were encapsulated in a carbon microsphere with a rough surface, has been developed. The novel materials was used as electrocatalysts for nitrate reduction. Importantly, a high removal ability (1816 mg/N g) and an excellent nitrogen selectivity (98%) were successfully achieved.\textsuperscript{143} In another research, FeN NPs coated by thin-layer carbonized nitrogen (NC) were synthesized (Figure 11B). Importantly, this novel electrocatalyst of NC@FeN possessed a high selectivity (91%) and nitrate removal rate (6004 mg/N g Fe).\textsuperscript{144}

Apart from the iron-containing catalysts, Cu-based composites also demonstrated unique advantages for the nitrate reduction reaction.\textsuperscript{145,146} For example, a nanosized composite that consists of monodisperse Cu nanoparticles and reduced graphene oxide (rGO) has been used as the catalyst for electroreduction of nitrate (Figure 11C). This composite catalyst delivered a nitrate removal rate of approximately 96.8%, which was several times higher than GP (23.27%) and Cu/GP (82.79%) electrodes.\textsuperscript{147}

### 3.3.2 Photocatalytic nitrate reduction

Photocatalytic technology can effectively remove the toxic constituents in the environment, such as organic dyes and bacterias, which has been regarded as an eco-friendly strategy for nitrate reduction.\textsuperscript{148,149} Recently, breakthroughs have been made in the research of nitrate reduction via the photocatalytic route. For example, a novel Pd/GdCrO\textsubscript{3} composite material was prepared and used as the photocatalyst to carry out photocatalytic nitrate reduction reaction (Figure 12A). The Pt content in Pd/GdCrO\textsubscript{3} played an important role on photocatalytic performance. The composite catalyst with 1 wt% of Pt amount owned the highest nitrate removal rate (98.7%) and selectivity for N\textsubscript{2} (100%). This was caused by not only the negative conduction band value of GdCrO\textsubscript{3} but also the catalysis effect of Pd.\textsuperscript{150} Besides, AgCl-modified TiO\textsubscript{2} nanotubes (AgCl/TNTs) also owned good photocatalytic activity of nitrate reduction. Specifically, AgCl/TNTs showed an excellent reduction effect of nitrate (nitrate reduction 94.5% and N\textsubscript{2} selectivity 92.9%) for 30 minutes under 365 nm UV irradiation with the formic acid as hole scavenging agent (Figure 12B).\textsuperscript{129}
The following table mainly combs the performance of catalysts used in nitrogen oxidation reaction and nitrate reduction to nitrogen (Table 4).

4 | CONVERSION BETWEEN AMMONIA AND NITRIC ACID/NITRATE

The conversion between ammonia and nitric acid/gaseous nitrogen oxides mainly involves two redox routes: the ammonia oxidation to nitrogen oxides and the direct reduction of nitrate to ammonia. For the former one, it is a key step in industrial nitric acid production; while, for the latter, it opens a new way to synthesize ammonia route from soluble nitrate instead of inert nitrogen. In this section, we will discuss these processes in detail, with special emphasis on the advanced catalysts used in these two artificial photo(electro)catalytic processes.

4.1 | Ammonia oxidation in the Ostwald process

At present, the production of nitric acid mainly depended on the traditional Ostwald process. This way includes three critical steps: (a) ammonia is oxidized to NO with the help of Pt/Rh catalysts; (b) NO is further oxidized to NO₂; and (c) NO₂ is absorbed by H₂O to produce nitric acid. In these successive steps, ammonia oxidation (ie, steps a and b) is the most critical. Therefore, the ammonia oxidation in the Ostwald route should be paid more attention to.

As mentioned, precious metals, such as Pt and Rh, are frequently used catalysts for ammonia oxidation during the Ostwald process. Therefore, searching for efficient and low-price catalysts to replace these noble metal-based catalysts is necessary for the nitric acid synthesis industry.

In nature, the nitrification of ammonia to NO₂⁻ takes place through the followed steps: (a) the ammonia monooxygenases catalyze ammonia oxidation to hydroxylamine (NH₂OH); (b) the oxidoreductases promote the four-electron oxidation of NH₂OH to produce NO₂⁻. Inspired by microbial route in nature, a biomimetic method of ammonia oxidation to NO₃⁻ can be achieved under the effect of enzymes exiting in ammonia-oxidizing bacteria. Specifically, a microbial biofilm was incubated at 46°C in an ammonium-containing mineral medium to enrich moderately thermophilic AOM. In the mineral media, ammonium acts as the sole source of energy and reductant, and bicarbonate/CO₂ acts as the sole carbon source. And then, the data of near-stoichiometric oxidation ammonium to nitrates is obtained in the enrichment culture ENR4. The nitrospria bacteria can achieve the nearly complete oxidation of the 1 mM ammonium to nitrate (Figure 13A).

4.2 | Direct reduction of nitrate to ammonia

As above-mentioned, the traditional Haber-Bosch process requires a huge energy input as well as leads to significant carbon emissions. To solve this issue, NRR at the ambient condition has been widely studied. However, the low solubility in water and high inertia of nitrogen gas will lead to two serious problems: low yield and poor selectivity. The direct reduction of nitrate to ammonia could provide a more promising strategy for ammonia industry in the future due to higher solubility and activity of nitrate in aqueous solution than that of nitrogen gas.
### TABLE 4 Summary of catalysts performance of NOR and nitrate reduction

| Catalysts          | Electrolyte                  | Potential       | Performance                                      | Ref.  |
|--------------------|------------------------------|-----------------|--------------------------------------------------|-------|
| ZnFeₙCo₂₋ₒ₄       | 1 M KOH                      | 1.6 V vs RHE    | 130 ± 12 μmol/hr/gMO NO₃⁻ yield                 | 123   |
| Fe-doped SnO₂      | 0.05 M H₂SO₄                 | 1.96 V vs RHE   | 42.9 μg/hr/mg-cat NO₃⁻ yields, 0.84% Faradaic efficiency | 125   |
| **Nitrate reduction** |                              |                 |                                                  |       |
| Fe nanoparticles   | 0.1 M Na₂SO₄ + 100 mg/L nitrate | −0.3 V vs RHE  | 1816 mg/N g Fe removal ability, 98% nitrogen selectivity | 143   |
| NC/FeN             | 0.02 M NaCl + 0.1 M Na₂SO₄  | −1.3 V vs RHE   | 6004 mg/N g Fe nitrate removal rate, 91% nitrogen selectivity | 144   |
| Cu/rGO             | 1 mM CuSO₄ 5H₂O + 1 mM Na₂EDTA + 100 mM Na₂SO₄ | −1.4 V vs RHE | 96.8% nitrate removal rate                      | 147   |
| Pd/GdCrO₃          | –                            | –               | 98.7% nitrate removal rate, 100% N₂ selectivity (500 W Hg lamp [365 nm], 30 minutes) | 150   |
| AgCl/TNTs          | –                            | –               | 94.5% nitrate conversion, 92.9% N₂ selectivity (365 nm UV irradiation, 30 minutes) | 129   |

**FIGURE 13**  
A, Near-stoichiometric oxidation of 1 mM ammonium to nitrate with transient accumulation of nitrite in enrichment culture ENR4. (Black: ammonium, blue: nitrite, red: nitrate, green: nitrogen balance.) Reproduced with permission: Copyright 2015, Macmillan Publishers.  
B, The selectivity of reduction products on different electrode materials. Reproduced with permission: Copyright 2013, Taylor & Francis.  
C, Change of NO₃⁻-N removal efficiency and NH₄⁺-N generation efficiency with the initial concentration of nitrate. Reproduced with permission: Copyright 2017, Elsevier.  
D, The adsorption energy of the Cu calculated by DFT. Reproduced with permission: Copyright 2020, Springer Nature.
In this field, the main catalysts include metals (e.g., Al, Cu, Cu-Ni, etc.), metal compounds (Co$_3$O$_4$, Cu$_2$O, etc.), metal composites (e.g., Ni/TiO$_2$, Cu/Cu$_2$O, etc.), and so on. Early research has revealed that Al showed a high selectivity of 12% in the process of direct reduction of nitrate to ammonia (Figure 13B). Apart from metal elements, metal oxides also show great potential in the direct electroreduction of nitrate to ammonia. Specifically, Co$_3$O$_4$/Ti was utilized as electrocatalysts to carry out the above reaction. And it is observed that the NO$_3^-$-N removal and NH$_4^+$-N generation efficiencies are dependent on the initial NO$_3^-$-N concentration. When the initial concentration is 50 mg/L, the NO$_3^-$-N removal efficiency is above 85%; however, becoming lower than 20% when the initial concentration increases to 500 mg/L (Figure 13C).

Very recently, a Cu-containing crystalline (3,4,9,10-perylenetetracarboxylic dihydride [PTCDA]) was synthesized and utilized as the electrocatalyst for direct nitrate reduction to produce ammonia. The FE of PTCDA reached a maximum value of 85.9%, and the rate of NH$_3$ generation was 436 ± 85 μg/hr/cm$^2$ at −0.4 V versus RHE. The outstanding performance of this catalyst can be attributed to two aspects. On the one hand, suppressed HER and enhanced H-N bonding, which originates from Cu electronic structure. On the other hand, the microstructure of PTCDA is favorable for the transport of electrons and protons to Cu active sites (Figure 13D).

The following table mainly summarizes the performance of electrocatalysts used in nitrate reduction (Table 5).

| Catalysts | Electrolyte | Potential | Performance | Ref. |
|-----------|-------------|-----------|-------------|-----|
| Al        | 0.4 M NaHCO$_3$ + 0.4 M Na$_2$CO$_3$ + 0.05 M NaNO$_3$ | –1.8 V vs Ag/AgCl | 15% selectivity of NH$_3$ | 159 |
| Cu-PTCDA  | 0.1 M phosphate buffer solution (pH = 7) | –0.4 V vs RHE | 436 ± 85 μg/hr/cm$^2$ NH$_3$ yield rate, 77% ± 3% Faradaic efficiency | 160 |
| Cu$_{50}$Ni$_{50}$ | 1 M KOH + 100 mM KNO$_3$ | –0.15 V vs RHE | 99% ± 1% Faradaic efficiency for NH$_3$ | 161 |
| Co$_3$O$_4$/Ti | 100 mg/L NO$_3^-$-N + 0.05 mol/L Na$_2$SO$_4$ | – | 3 hours, 99% nitrate-N removal; 3 hours, 66% TN removal at a current density of 10 mA/cm$^2$ | 163 |
| Ni/TiO$_2$ | 50 mg/L of nitrate +0.5 g/L of Na$_2$SO$_4$ | – | 93.4% nitrate removal rate at a current density of 30 mA/cm$^2$ with 90 minutes | 164 |
| Cu/Cu$_2$O | 0.5 m Na$_2$SO$_4$ + 200 ppm nitrate-N | –0.85 V vs RHE | 0.2449 mmol/hr/cm$^2$ NH$_3$ yield rate, 95.8% Faradaic efficiency | 165 |

**Figure 14** The suggestions on improving photo(electro) catalysts for nitrogen looping

**Table 5** Summary of the electrochemical performance of electrocatalysts in nitrate reduction

In this field, the main catalysts include metals (e.g., Al, Cu, Cu-Ni, etc.), metal compounds (Co$_3$O$_4$, Cu$_2$O, etc.), metal composites (e.g., Ni/TiO$_2$, Cu/Cu$_2$O, etc.), and so on. Early research has revealed that Al showed a high selectivity of 12% in the process of direct reduction of nitrate to ammonia (Figure 13B). Apart from metal elements, metal oxides also show great potential in the direct electroreduction of nitrate to ammonia. Specifically, Co$_3$O$_4$/Ti was utilized as electrocatalysts to carry out the above reaction. And it is observed that the NO$_3^-$-N removal and NH$_4^+$-N generation efficiencies are dependent on the initial NO$_3^-$-N concentration. When the initial concentration is 50 mg/L, the NO$_3^-$-N removal efficiency is above 85%; however, becoming lower than 20% when the initial concentration increases to 500 mg/L (Figure 13C).

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The following table mainly summarizes the performance of electrocatalysts used in nitrate reduction (Table 5).

5 | SUMMARY AND PERSPECTIVE

The photo(electro)catalytic reactions during artificial nitrogen looping play a crucial role in many aspects of modern society, including the chemical industry, environmental protection, clean energy source, and so on. Advanced catalysts involved in the above processes are essential for realizing efficient, stable, and low-cost artificial nitrogen looping. In this review, we have summarized the latest progress in this hot spot, and further provided an in-depth discussion on the rational design of these state-of-the-art photo(electro)catalysts.

As abovementioned, the development of photo(electro) catalysts used in the artificial nitrogen looping can bring a great breakthrough in the fields of energy and the environment. However, there are still a series of key challenges remaining unsolved, such as low efficiency, high cost, poor stability, and absence of in-depth theoretical understanding. Thus, more efforts should be made on some key
points in order to further promote the development of these catalysts, and finally achieve the practical application, as following (Figure 14):

1. High-performance photo(electro)catalysts. The high efficiency and good selectivity are two important aspects of a high-performance photo(electro)catalytic reaction. In the field of artificial nitrogen looping, however, the current researches focus more attention on designing and conceptual demonstration of novel catalysts. The efficiency and selectivity of these catalysts are still relatively low, especially for the emerging NRR. In order to achieve the goal of practical application, the efficiency and the selectivity of these photo(electro)catalysts should be further improved by means of some feasible strategies, such as exposing more active sites, regulating the electronic structure of catalysts, designing electrode materials with highly ordered nanoarray architectures, and so on.

2. Low-cost and stable photo(electro)catalysts. Low cost and good stability are also crucial points for the commercial application of photo(electro)catalysts in artificial nitrogen looping. At present, noble metals are still mainly used as catalysts in artificial nitrogen looping. However, the rarity and the high value of noble metals will limit the large-scale implementation of artificial nitrogen looping by means of photo(electro) catalytic routes. Consequently, searching the earth-rich and cheap alternatives, such as transition metal elements/alloys/oxides, carbon-based materials, etc, is an urgent task in the future. Meanwhile, enhancement on the durability of catalysts in full life-cycle is equally important as an improvement in their performance.

3. In-depth theory research. Assisted by some theoretical calculations (eg, density functional theory), the catalytic mechanisms can be well understood at the atomic scale. For instance, kinetic study (eg, Langmuir-Hinshelwood-type rate law) can reveal the process and the intermediates of photocatalytic oxidation of NO, which can help us to optimize the reaction. Besides, kinetic and thermodynamic processes of photo(electro)catalysis can also be clearly manifested by some theoretical study. All of these are very helpful for us to deeply understand the mechanisms of artificial nitrogen looping and design the high-performance photo(electro)catalysts.

To sum up, the photo(electro)catalytic artificial nitrogen looping and corresponding catalysts have attracted increasing attention due to great potentials in the future industry, agriculture, environmental protection, and sustainable energy source. Although there are still many obstacles on the road toward the goal of commercialization, we believe that artificial nitrogen looping will play a key role in the future and will help pave the way for the sustainable development of society.

ACKNOWLEDGMENTS
This work was supported by the Natural Science Foundation of China (No. 21905202), Innovative Research in the University of Tianjin (TD13-5077), Developed and Applied Funding of Tianjin Normal University (135202XK1702), the Australian Research Council (ARC) through the Discovery Project (No. DP200100365), and Discovery Early Career Researcher Award (DECRA, No. DE170100871) program.

CONFLICT OF INTEREST
The authors declare no conflicts of interest.

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REFERENCES
1. Suryanto BHR, Du HL, Wang D, et al. Challenges and prospects in the catalysis of electrodereuction of nitrogen to ammoxia. Nat Catal. 2019;2(4):290-296. https://doi.org/10.1038/s41929-019-0252-4.
2. Li CZ, Zhang M, Yang YC. Leaching characteristics of big spherical coated controlled-release fertilizer in soil columns. J Soil Water Conserv. 2013;27(3):72-76. https://doi.org/10.13870/j.cnki.sjtkxb.2013.03.047.
3. Rong L, Irvine JTS, Tao S. Ammonia and related chemicals as potential indirect hydrogen storage materials. Int J Hydrogen Energy. 2012;37(2):1482-1494. https://doi.org/10.1016/j.ijhydene.2011.10.004.
4. Schueth F, Falkovits R, Schloegl R, Su DS. Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition. Energy Environ Sci. 2012;5(4):6278-6289. https://doi.org/10.1039/c2ee02865d.
5. Huang ZZ, Li HE, Hu YL, Wu XF. Process optimization of breaking cyanogens by oxidation for treatment of electroplating effluent. J Cent South Forest Univ. 2006;26(2):96-99. https://doi.org/10.1016/S1005-9040(06)60038-X.
6. Yu YC, Li N, Gao P, et al. Technology for cyanogen-free electroplating of magnesium alloy castings. Mater Prot. 2009;42(4):27-29. https://doi.org/10.1360/972009-1551.
7. van der Ham CJM, Koper MTM, Hetterscheid DGH. Challenges in reduction of dinitrogen by proton and electron transfer. Chem Soc Rev. 2014;43(15):5183-5191. https://doi.org/10.1039/c4cs00085d.
8. Knobloch DJ, Lobkovsky E, Chirik PJ. Dinitrogen cleavage and functionalization by carbon monoxide promoted by a hafnium complex. Nat Chem. 2010;2(1):30-35. https://doi.org/10.1038/nchem.477.
9. Kitano M, Inoue Y, Yamazaki Y, et al. Ammonia synthesis using a stable electrode as an electron donor and reversible hydrogen store. Nat Chem. 2012;4(11):934-940. https://doi.org/10.1038/nchem.1476.
10. Lan R, Irvine JTS, Tao SW. Synthesis of ammonia directly from air and water at ambient temperature and pressure. Sci Rep. 2013;3(1):1145. https://doi.org/10.1038/srep01145.

11. Banerjee A, Yuhas BD, Margulies EA, et al. Photochemical nitrogen conversion to ammonia in ambient conditions with FeMoS-chalcogels. J Am Chem Soc. 2015;137(5):2030-2034. https://doi.org/10.1021/ja512491v.

12. Liu J, Kelley MS, Wu WQ, et al. Nitrogenase-mimic iron-containing chalcogels for photochemical reduction of dinitrogen to ammonia. Proc Natl Acad Sci U S A. 2016;113(20):5530-5535. https://doi.org/10.1073/pnas.1605512113.

13. Jiao F, Xu BJ. Electrochemical ammonia synthesis and ammonia fuel cells. Adv Mater. 2019;31(31):1805173. https://doi.org/10.1002/adma.201805173.

14. Adli NM, Zhang H, Mukherjee S, Wu G. Review-ammonia oxidation electrocatalysis for hydrogen generation and fuel cells. J Electrochem Soc. 2018;165(15):J3130-J3147. https://doi.org/10.1149/2.019181jes.

15. Mukherjee S, Devaguptapu SV, Sviripa A, Lund CRF, Wu G. Low-temperature ammonia decomposition catalysts for hydrogen generation. Appl Catal B. 2018;226:162-181. https://doi.org/10.1016/j.apcatb.2017.12.039.

16. Lamb KE, Dolan MD, Kennedy DF. Ammonia for hydrogen storage: a review of catalytic ammonia decomposition and hydrogen separation and purification. Int J Hydrogen Energy. 2019;44(7):3580-3593. https://doi.org/10.1016/j.ijhydene.2018.12.024.

17. Bao D, Zhang Q, Meng F-L, et al. Electrochemical reduction of N2 under ambient conditions for artificial N2 fixation and renewable energy storage using N2/NH3 cycle. Adv Mater. 2017;29(3):1604799. https://doi.org/10.1002/adma.201604799.

18. Tanaka H, Nishibayashi Y, Yoshizawa K. Interplay between theory and experiment for ammonia synthesis catalyzed by transition metal complexes. Acc Chem Res. 2016;49(5):987-995. https://doi.org/10.1021/acs.accounts.6b00033.

19. Muhler M, Hinrichsen O, Bielawa H, Jacobsen CJH. Process for ammonia ammonia production-preparation and recovery of ammonia synthesis catalyst. US Patent Application. 20030158036.

20. Kyriakou V, Garagounis I, Vourros A, Vasileiou E, Stoukides M. An electrochemical Haber-Bosch process. Joule. 2020;4(1):142-158. https://doi.org/10.1016/j.joule.2019.10.006.

21. Chen JG, Crooks RM, Seefeldt LC, et al. Beyond fossil fuel-driven nitrogen transformations. Science. 2018;360(6391):eaar6611. https://doi.org/10.1126/science.aar6611.

22. Li Y, Wang H, Priest C, Li S, Xu P, Wu G. Advanced electrocatalysis for energy and environmental sustainability via water and nitrogen reactions. Adv Mater. 2020;33:2000381. https://doi.org/10.1002/adma.202000381.

23. Qing G, Ghazfar R, Jackowski ST, et al. Recent advances and challenges of electrocatalytic N2 reduction to ammonia. Chem Rev. 2020;120(12):5437-5516. https://doi.org/10.1021/acs.chemrev.9b00659.

24. Guo CX, Ran JR, Vasileff A, Qiao SZ. Rational design of electrocatalysts and photo(electro)catalysts for nitrogen reduction to ammonia(NH3) under ambient conditions. Energy Environ Sci. 2018;11(1):45-56. https://doi.org/10.1039/C7EE02220D.

25. Ye LQ, Han CQ, Ma ZY, et al. Ni3P loading on Cd0.5Zn0.5S solid solution for exceptional photocatalytic nitrogen fixation under visible light. Chem Eng J. 2017;307:311-318. https://doi.org/10.1016/J.CEJ.2016.08.102.

26. Medford AJ, Hatzell MC. Photon-driven nitrogen fixation: current progress, thermodynamic considerations, and future outlook. ACS Catal. 2017;7(4):2624-2643. https://doi.org/10.1021/acscatal.7b00439.

27. Chen XZ, Li N, Kong ZZ, Ong WJ, Zhao XJ. Photocatalytic fixation of nitrogen to ammonia: state-of-the-art advancements and future prospects. Mater Today. 2018;5(1):9-27. https://doi.org/10.1016/j.mattod.2017.12.039.

28. Li MQCO, Huang H, Low JX, Gao C, Long R, Xiong Y. Recent progress on electrocatalyst and photocatalyst design for nitrogen reduction. Small Methods. 2019;3(6):1800388. https://doi.org/10.1002/smtd.201800388.

29. Wang ZH, Hu X, Liu ZZ, et al. Recent developments in polymeric carbon nitride-derived photocatalysts and electrocatalysts for nitrogen fixation. ACS Catal. 2019;9(11):10260-10278. https://doi.org/10.1021/acscatal.8b03418.

30. Alka K-i. Role of alkali promoter in ammonia synthesis over ruthenium catalysts-effect on reaction mechanism. Catal Today. 2017;286:14-20. https://doi.org/10.1016/j.cattod.2016.08.012.

31. Connor GP, Holland PL. Coordination chemistry insights into the role of alkali metal promoters in dinitrogen reduction. Catal Today. 2017;286:21-40. https://doi.org/10.1016/j.cattod.2016.08.014.

32. Comer BM, Liu YH, Dixit MB, et al. The role of adventitious carbon in photocatalytic nitrogen fixation by titania. J Am Chem Soc. 2018;140(45):15157-15160. https://doi.org/10.1021/jacs.8b08464.

33. Hirakawa H, Hashimoto M, Shiraishi Y, Hirai T. Photocatalytic conversion of nitrogen to ammonia with water on surface oxygen vacancies of titanium dioxide. J Am Chem Soc. 2017;139(31):10929-10936. https://doi.org/10.1021/jacs.7b06634.

34. Zhao YX, Zhao YF, Shi R, et al. Tuning oxygen vacancies in ultrathin TiO2 nanosheets to boost photocatalytic nitrogen fixation up to 700 nm. Adv Mater. 2019;31(16):1806482. https://doi.org/10.1002/adma.201806482.

35. Li HP, Liu JY, Liang XF, Hou WG, Tao XT. Enhanced visible light photocatalytic activity of bismuth oxybromide lamellas: facile hydrolysis preparation and selective visible-light photocatalytic activity of bismuth oxybromide lamellas with decreasing lamella thicknesses. J Mater Chem A. 2014;2(23):8926-8932. https://doi.org/10.1039/C4TA00236A.

36. Zhang D, Li J, Wang QG, Wu QS. High-facets dominated BiOBr lamellas: facile hydrolysis preparation and selective visible-light photocatalytic activity. J Mater Chem A. 2013;1(30):8622-8629. https://doi.org/10.1039/C3TA11390F.

37. Wang XJ, Zhao Y, Li FT, et al. A chelation strategy for in-situ constructing surface oxygen vacancy on [001] facets exposed BiOBr nanosheets. Sci Rep. 2016;6(1):24918. https://doi.org/10.1038/srep24918.

38. Zhang X, Ai ZH, Xue XL, et al. Generalized one-pot synthesis, characterization, and photocatalytic activity of hierarchical BiOBr (X = Cl, Br, I) nanoplate microspheres. J Phys Chem C. 2008;112(3):747-753. https://doi.org/10.1021/jp077471t.

39. Xue XL, Chen RP, Chen HW, et al. Oxygen vacancy engineering promoted photocatalytic ammonia synthesis on ultrathin two-dimensional bismuth oxybromide nanosheets. Nano Lett.
18. 2019;39(4):8474-8477. https://doi.org/10.1039/c8cc03627f.
45. Liu AM, Yang YN, Ren XF, et al. Current progress of electrocatalyst development and performance improvement. J Mater Chem A. 2020;8(4):1545-1556. https://doi.org/10.1039/C9TA13044F.
46. Liu AM, Yang YN, Ren XF, et al. Current progress of electrocatalyst development and performance improvement. J Mater Chem A. 2020;8(4):1545-1556. https://doi.org/10.1039/C9TA13044F.
47. Sclafani A. Dinitrogen electrochemical reduction to ammonia over iron cathode in aqueous medium. J Electrochem Soc. 1983;130(3):734-736. https://doi.org/10.1149/1.2119794.
48. Ma BY, Zhao HT, Li TS, et al. Iron-group electrocatalysts for ambient nitrogen reduction reaction in aqueous medium. Nano Res. 2021;14(3):555-569. https://doi.org/10.1007/s12274-020-3049-5.
49. Yang DS, Chen T, Wang ZJ. Electrochemical reduction of aqueous nitrogen (N2) at a low overpotential on (110)-oriented Mo nanofilm. J Mater Chem A. 2017;5(36):18967-18971. https://doi.org/10.1039/C7TA06139K.
50. Wang T, Liu Q, Li TS, et al. A magnetron sputtered MoSi thin film: an efficient electrocatalyst for N2 reduction under ambient conditions. J Mater Chem A. 2021;9(2):884-888. https://doi.org/10.1039/D0TA1231C.
51. Ji XQ, Wang T, Liu Q, et al. Oxidation-etching induced morphology regulation of Cu catalysts for high-performance electrochemical N2 reduction. EcoMat. 2020;2(2):e12026. https://doi.org/10.1002/ecom.2012026.
52. Geng ZG, Liu Y, Kong XD, et al. Achieving a record-high yield rate of 120.9 for N2 electrochemical reduction over Ru single-atom catalysts. Adv Mater. 2018;30(40):1803498. https://doi.org/10.1002/adma.201803498.
53. Tao HC, Choi C, Ding LX, et al. Nitrogen fixation by Ru single-atom electrocatalytic reduction. Chem. 2019;5(1):204-214. https://doi.org/10.1002/chem.201810067.
54. Liu HM, Han SH, Zhao Y, et al. Surfactant-free atomically ultrathin rhodium nanosheet nanoassemblies for efficient nitrogen electroreduction. J Mater Chem A. 2018;6(7):3211-3217. https://doi.org/10.1039/C7TA0866D.
55. Wang J, Yu L, Hu L, Chen G, Xin H, Feng X. Ambient ammonia synthesis via palladium-catalyzed electrohydrogenation of dinitrogen at low overpotential. Nat Commun. 2018;9(1):1795. https://doi.org/10.1038/s41467-018-04213-9.
56. Zheng JY, Lyu YH, Qiao M, et al. Tuning the electron localization of gold enables the control of nitrogen-to-ammonia fixation. Angew Chem Int Ed Engl. 2019;58(51):18604-18609. https://doi.org/10.1002/anie.201909477.
57. Yao Y, Zhu SQ, Wang HJ, Li H, Shao MHA. Spectroscopic study on the nitrogen electrochemical reduction reaction on gold and platinum surfaces. J Am Chem Soc. 2018;140(4):1496-1501. https://doi.org/10.1021/jacs.7b12101.
58. Nazemi M, Panikkanvalappil SR, El-Sayed MA. Enhancing the rate of electrochemical nitrogen reduction reaction for ammonia synthesis under ambient conditions using hollow gold nanocages. Nano Energy. 2018;49:316-323. https://doi.org/10.1016/j.nanoen.2018.04.039.
59. Lv JL, Tian ZF, Dai K, Ye YX, Liang CH. Interface and defect engineer of titanium dioxide supported palladium or platinum for tuning the activity and selectivity of electrocatalytic nitrogen reduction reaction. J Colloid Interface Sci. 2019;553:126-135. https://doi.org/10.1016/j.jcis.2019.05.105.
60. Wu TW, Zhao HT, Zhu XJ, et al. Identifying the origin of Ti3+ activity toward enhanced electrocatalytic N2 reduction over TiO2 nanoparticles modulated by mixed-valent copper. Adv Mater. 2020;32(30):2000299. https://doi.org/10.1002/adma.202000299.
61. Zhang Y, Qiu WB, Ma YL, et al. High-performance electrohydrogenation of N2 to NH3 catalyzed by multishelled hollow Cr2O3 microspheres under ambient conditions. ACS Catal. 2018;8(9):8540-8544. https://doi.org/10.1021/acscatal.8b02311.
62. Han JR, Liu ZC, Ma YJ, et al. Ambient N2 fixation to NH3 at ambient conditions: using Nb2O5 nanofiber as a high-performance electrocatalyst. Nano Energy. 2018;52:264-270. https://doi.org/10.1016/j.nanoen.2018.07.045.
63. Li Y, Kong Y, Hou Y, et al. In situ growth of nitrogen-doped carbon-coated γ-Fe2O3 nanoparticles on carbon fabric for electrochemical N2 fixation. ACS Sustain Chem Eng. 2019;7(9):8853-8859. https://doi.org/10.1021/acssuschemeng.9b00852.
64. Xiang XI, Wang Z, Shi XF, Fan MK, Sun XP. Ammonia synthesis from electrocatalytic N2 reduction under ambient conditions using Fe2O3 nanorods. ChemCatChem. 2018;10(20):4530-4535. https://doi.org/10.1002/ccct.201801208.
65. Zhang XP, Kong RM, Du HT, Xia L, Qu FL. Highly efficient electrochemical ammonia synthesis via nitrogen reduction reactions on a VN nanowire array under ambient conditions. Chem Commun. 2018;54(42):5323-5325. https://doi.org/10.1039/C8CC00459E.
66. Ling Z, Ji XQ, Xiang R, et al. Efficient electrocatalytic N2 reduction to NH3 on MoN nanosheets array under ambient conditions. ACS Sustain Chem Eng. 2018;6(8):9550-9554. https://doi.org/10.1021/acssuschemeng.8b04138.
67. Xiang R, Guanwei C, Liang C, et al. Electrochemical N2 fixation to NH3 under ambient conditions: Mo2N nanorod as a highly efficient and selective catalyst. Chem Commun. 2018;54(61):8474-8477. https://doi.org/10.1039/c8cc03627f.
68. Gao JJ, Lv X, Wang FY, et al. Enabling electrochemical conversion of N₂ to NH₃ under ambient conditions by a CoP₃ nanoneedle array. *J Mater Chem A*. 2020;8(35):17956-17959. https://doi.org/10.1039/D0TA07720H.

69. Zhao RB, Geng Q, Chang L, et al. Cu₆P nanoparticle-reduced graphene oxide hybrid: an efficient electrocatalyst to realize N₂-to-NH₃ conversion under ambient conditions. *Chem Commun*. 2020;56(65):9328-9331. https://doi.org/10.1039/D0CC04374E.

70. Wei FP, Geng Q, Channa AI, et al. Electrocatalytic N₂ reduction to NH₃ with high faradaic efficiency enabled by vanadium phosphide nanoparticle on V foil. *Nano Res*. 2020;13(11):2967-2972. https://doi.org/10.1007/s12274-020-2956-9.

71. Peng W, Feng YY, Yan X, Hou F, Wang L, Liang J. Multiammonium catalysts for energy-related electrocatalysis. *Adv Sustain Syst*. 2020;2000213. https://doi.org/10.1002/adss.202000213.

72. Yan X, Liu DL, Cao HH, Hou F, Liang J, Dou SX. Nitrogen reduction to ammonia on atomic-scale active sites under mild conditions. *Small Methods*. 2019;3(9):1800501. https://doi.org/10.1002/smtd.201800501.

73. Han LL, Liu XJ, Chen JP, et al. Atomically dispersed molybdenum catalysts for efficient ambient nitrogen fixation. *Angew Chem Int Ed Engl*. 2019;58(8):2321-2325. https://doi.org/10.1002/anie.201811728.

74. Wang XW, Qiu SY, Feng JM, et al. Confined Fe-cu clusters as sub-nanometer reactors for efficiently regulating the electrochemical nitrogen reduction reaction. *Adv Mater*. 2020;32(40):2004382. https://doi.org/10.1002/adma.202004382.

75. Tong YY, Guo HP, Liu DL, et al. Vacancy engineering of iron-doped W₁₈O₄₉ nanoreactors for low-barrier electrochemical nitrogen reduction. *Angew Chem Int Ed Engl*. 2020;59(19):7356-7361. https://doi.org/10.1002/anie.202002029.

76. Jin HY, Li LQ, Liu X, et al. Nitrogen vacancies on 2D layered W₂N₂: a stable and efficient active site for nitrogen reduction reaction. *Adv Mater*. 2019;31(32):1902709. https://doi.org/10.1002/adma.201902709.

77. Xiao SL, Luo F, Hu H, Yang ZH. Boron and nitrogen dual-doped carbon nanospheres for efficient electrochemical reduction of N₂ to NH₃. *Chem Commun*. 2020;56(3):446-449. https://doi.org/10.1039/c9cc07708a.

78. Xia L, Yang JI, Wang HB, et al. Sulfur-doped graphene for efficient electrocatalytic N₂-to-NH₃ fixation. *Chem Commun*. 2019;55(23):3371-3374. https://doi.org/10.1039/c9cc00602h.

79. Wang J, Wang S, Li JP. S-doped three-dimensional graphene (S-3DG): a metal-free electrocatalyst for the electrochemical synthesis of ammonia under ambient conditions. *Dalton Trans*. 2020;49(7):2258-2263. https://doi.org/10.1039/c9dt04827h.

80. Wu TW, Li XY, Zhu XJ, et al. P-doped graphene toward enhanced electrocatalytic N₂ reduction. *Chem Commun*. 2020;56(12):1831-1834. https://doi.org/10.1039/c9cc0917c.

81. Wang YH, Yang J, Wang JX, et al. Low-temperature ammonia decomposition catalysts for direct ammonia solid oxide fuel cells. *J Electrochem Soc*. 2020;167(6):064501. https://doi.org/10.1149/1945-7111/a7b75b.

82. Mônica HMTA, GDS S, FBDS R, et al. Direct ammonia fuel cell performance using PtIr/C as anode electrocatalysts. *Int J Hydrogen Energy*. 2014;39(10):5148-5152. https://doi.org/10.1016/j.ijhydene.2014.01.053.

83. Xu W, Lan R, Du DW, et al. Directly growing hierarchical nickel-copper hydroxide nanowires on carbon fibre cloth for efficient electrooxidation of ammonia. *Appl Catal B*. 2017;218:470-479. https://doi.org/10.1016/j.apcatb.2017.07.005.

84. Chan YT, Siddharth K, Shao MH. Investigation of cubic Pt alloys for ammonia oxidation reaction. *Nano Res*. 2020;13(7):1920-1927. https://doi.org/10.1007/s12274-020-2712-1.
97. Fujitani T, Nakamura I, Hashiguchi Y, Kanazawa S, Takahashi A. Effect of catalyst preparation method on ammonia decomposition reaction over Ru/MgO catalyst. *Bull Chem Soc Jpn.* 2020;93(10):1186-1192. https://doi.org/10.1246/bcsj.20200103.

98. Bell TE, Ménard H, Carballo JMG, Tookie R, Torrente-Murciano L. Hydrogen production from ammonia decomposition using Co/γ-Al2O3 catalysts-insights into the effect of synthetic method. *Int J Hydrogen Energy.* 2020;232:124-134. https://doi.org/10.1016/j.ijhydene.2020.07.090.

99. Köpke KG, McAulay K, Bell TE, et al. CO2-free hydrogen production from ammonia-mimicking the activity of Ru catalysts with unsupported co-re alloys. *Appl Catal B.* 2020;280:119405. https://doi.org/10.1016/j.apcatal.2020.119405.

100. Xie PF, Yao YG, Huang ZN, et al. Highly efficient decomposition of ammonia using high-entropy alloy catalysts. *Nat Commun.* 2019;10:4011. https://doi.org/10.1038/s41467-019-11848-9.

101. Branwell PL, Lentink S, Ngene P, Jongh PE. Effect of pore confinement of LiNH2 on ammonia decomposition catalysis and the storage of hydrogen and ammonia. *J Phys Chem C.* 2016;120(48):27212-27220. https://doi.org/10.1021/acs.jpcc.db10688.

102. Cui CN, Luo ZX, Yao JN. Enhanced catalysis of Pt3 clusters supported on graphene for N-H bond dissociation. *CCS Chem.* 2019;1(2):215-225. https://doi.org/10.31635/ccschem.019.20180031.

103. Ju XL, Liu L, Yu P, et al. Mesoporous Ru/MgO prepared by a deposition-precipitation method as highly active catalyst for producing CO2-free hydrogen from ammonia decomposition. *Appl Catal B.* 2017;211:167-175. https://doi.org/10.1016/j.apcatal.2017.04.043.

104. Huang CQ, Li RX, Yang JM, et al. Ce0.5Zr0.5Y0.1O2 solid solutions-supported Ni co bimetal nanocatalysts for NH3 decomposition. *Appl Surf Sci.* 2019;478:708-716. https://doi.org/10.1016/j.apsusc.2019.01.269.

105. Srida A, Okura K, Okanishi T, Muroyama H, Matsui T, Eguchi K. Hydrogen production by ammonia decomposition over Cs-modified CoMo3N catalysts. *Appl Catal B.* 2017;218:1-8. https://doi.org/10.1016/j.apcatal.2017.06.034.

106. David WIF, Makepeke JW, Callear SK, et al. Hydrogen production from ammonia using sodium amide. *J Am Chem Soc.* 2014;136(38):13082-13085. https://doi.org/10.1021/ja5042836.

107. Han S, Wang C, Wang Y, Yu Y, Zhang B. Electrodeposition of nitrate via the oxidation of nitrogen on dinitrogen-preserved palladium porous Nanosheets, *Angew Chem Int Ed.* 2021;60(9):4474-4478. https://doi.org/10.1002/anie.202014017.

108. Wei L, Liu DJ, Rosales BA, Evans JW, Vela J. Mild and selective hydrogenation of nitrate to ammonia in the absence of noble metals. *ACS Catal.* 2020;10(6):3618-3628. https://doi.org/10.1021/acscatal.9b05338.

109. Davis DM, Gowda PH, Muller DJ, Randall GW. Modeling nitrate nitrogen leaching in response to nitrogen fertilizer rate and tile drain depth or spacing for southern Minnesota, USA. *J Environ Qual.* 2000;29(5):1568-1581. https://doi.org/10.2134/jeq2000.00472425002900050026x.

110. Gheysari M, Mirlatifi SM, Homaei M, Asadi ME, Hoogenboom G. Nitrate leaching in a silage maize field under different irrigation and nitrogen fertilizer rates. *Agric Water Manag.* 2009;96(6):946-954. https://doi.org/10.1016/j.agwat.2009.01.005.

111. Zeng YC, Priest C, Wang GF, Wu G. Restoring the nitrogen cycle by electrochemical reduction of nitrate: Progress and prospects. *Small Methods.* 2020;4(12):2000672. https://doi.org/10.1002/smtd.202000672.

112. Xie P, Ho SH, Xiao QY, et al. Revealing the role of nitrate on sulfide removal coupled with bioenergy production in chlamydomonas sp.ta1-03: metabolic pathways and mechanisms. *J Hazard Mater.* 2020;399:123115. https://doi.org/10.1016/j.jhazmat.2020.123115.

113. Hackett D, Davies G, Maseri A. Coronary constriction in acute myocardial-infarction-role of nitrates. *Eur Heart J.* 1988;9:151-153. https://doi.org/10.1093/eurheartj/9.suppl_A.151.

114. Abrams J. The role of nitrates in coronary heasy-disease. *Arch Intern Med.* 1995;155(4):357-364. https://doi.org/10.1001/archinte.155.4.357.

115. Ning X, Xiong ZB, Yang B, Lu W, Wu SM. The role of nitrate on the sol-gel spread self-combustion process and its effect on the NH3-SCR activity of magnetic iron-based catalyst. *Catal.* 2020;10(3):314. https://doi.org/10.3390/catal10030314.

116. Yuan S-J, Li W, Cheng Y-Y, et al. Efficient nitrate synthesis via ambient nitrogen oxidation with Ru-doped TiO2/RuO2 electrocatalysts. *Adv Mater.* 2020;32(26):2002189. https://doi.org/10.1002/adma.202002189.

117. Liu YW, Cheng M, He ZH, et al. Pothole-rich ultrathin WO3 nanosheets that trigger N≡≡N bond activation of nitrogen for direct nitrate photosynthesis. *Angew Chem Int Ed.* 2018;58(3):731-735. https://doi.org/10.1002/anie.201808177.

118. Yuan S-J, Li W-W, Cheng Y-Y, et al. A plate-based electrochromic approach for the high-throughput detection of electrochemically active bacteria. *Nat Protoc.* 2014;9(1):112-119. https://doi.org/10.1038/nprot.2013.173.

119. Vetraino M, Trudeau M, Lo AYH, Schurko RW, Antonelli D. Room-temperature ammonia formation from dinitrogen on a reduced mesoporous titanium oxide surface with metallic properties. *J Am Chem Soc.* 2002;124(32):9567-9573. https://doi.org/10.1021/ja020313p.

120. Zhu D, Zhang L, Ruther RE, Hamers RJ. Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction. *Nat Mater.* 2013;12(9):836-841. https://doi.org/10.1038/nmat3696.

121. Li H, Shang J, Ai Z, Zhang L. Efficient visible light nitrogen oxidation by a well-dispersed Pd on MXene electrocatalyst. *ACS Catal.* 2020;10(6):3618-3628. https://doi.org/10.1021/acscatal.9b05338.

122. Liu Y, Zhou T, Zheng Y, et al. Local electric field facilitates high-performance Li-ion batteries. *ACS Nano.* 2017;11(8):8519-8526. https://doi.org/10.1021/acsnano.7b04617.

123. Dai CC, Sun YM, Chen G, Fisher AC, Xu ZJ. Electrochemical oxidation of nitrogen toward direct nitrate production on spinel oxides. *Angew Chem Int Ed.* 2020;59(24):9418-9422. https://doi.org/10.1002/anie.202002923.

124. Fang W, Du CF, Kuang M, et al. Boosting efficient ambient nitrogen oxidation by a well-dispersed Pd on MXene electrocatalyst. *Chem Commun.* 2020;56(43):5779-5782. https://doi.org/10.1039/d0cc01759k.

125. Zhang LL, Cong MY, Ding X, et al. A Janus Fe-SnO2 catalyst that enables bifunctional electrochemical nitrogen fixation.
Islam MT, Dominguez A, Turley RS, et al. Development of \( \text{NO}_2 \) and \( \text{NO} \) land use regression models for estimating air pollution exposure in 36 study areas in Europe—The escape project. *Atmos Environ.* 2013;72:10-23. https://doi.org/10.1016/j.atmosenv.2013.02.037.

Winxwartier W, Kliment Z. The role of N-gases (\( \text{N}_2\text{O}, \text{NO}, \text{NH}_3 \)) in cost-effective strategies to reduce greenhouse gas emissions and air pollution in Europe. *Curr Opin Environ Sustain.* 2011;3(5):438-445. https://doi.org/10.1016/j.cosust.2011.08.003.

Dillert R, Engel A, Grosse J, Lindner P, Bahnemann DW. Light intensity dependence of the kinetics of the photocatalytic oxidation of nitrogen(II) oxide at the surface of TiO\(_2\). *Phys Chem Chem Phys.* 2013;15(48):20876-20886. https://doi.org/10.1039/c3cp54469a.

Geng Z, Chen ZT, Li ZY, et al. Enhanced photocatalytic conversion and selectivity of nitrate reduction to nitrogen over AgCl/TiO\(_2\) nanotubes. *Dalton Trans.* 2018;47(32):11104-11112. https://doi.org/10.1039/c8dt01915k.

Park KH, Lee SM, Kim SS, Kwon DW, Hong SC. Reversibility of Mn valence state in MnOx/TiO\(_2\) catalysts for low-temperature selective catalytic reduction for NO with \( \text{NH}_3 \). *Catal Lett.* 2013;143(3):246-253. https://doi.org/10.1007/s10562-012-0952-8.

Işıklı MT, Domínguez A, Turley RS, et al. Development of photocatalytic paint based on TiO\(_2\) and photopolymer resin for the degradation of organic pollutants in water. *Sci Total Environ.* 2020;704:135406. https://doi.org/10.1016/j.scitotenv.2019.135406.

Papoulis D, Kordouli E, Lampropoulou P, et al. Synthesis, characterization and photocatalytic activities of fly ash-TiO\(_2\) nanocomposites for the mineralization of azo dyes in water. *J Surf Interfaces Mater.* 2014;2(4):261-266. https://doi.org/10.1166/jsim.2014.10171.

Hashimoto K, Wasada K, Toukai N, Kominami H, Kera Y. Photocatalytic oxidation of nitrogen monoxide over titanium(IV) oxide nanocrystals large size areas. *J Photochem.* 2000;136(1-2):103-109. https://doi.org/10.1016/s1010-6030(00)00329-4.

Wu ZB, Wang HQ, Liu Y, Jiang BQ, Sheng ZY. Study of a photocatalytic oxidation and wet absorption combined process for removal of nitrogen oxides. *Chem Eng J.* 2008;144(2):221-226. https://doi.org/10.1016/j.cej.2008.01.025.

Dylla H, Hassan MM, Thibodeaux LJ. Kinetic study of photocatalytic degradation of nitrogen monoxide with titanium dioxide nanoparticles in concrete pavements. *Transp Res Rec.* 2014;2441(1):38-45. https://doi.org/10.3141/2441-06.

Wang HM, Zhao R, Qin JQ, et al. MIL-100(Fe)/\( \text{Ti}_2\text{C}_2 \) MXene as a Schottky catalyst with enhanced photocatalytic oxidation for nitrogen fixation activities. *ACS Appl Mater Interfaces.* 2019;11(47):44249-44262. https://doi.org/10.1021/acsami.9b14793.

Barrabés N, Sa J. Catalytic nitrate removal from water, past, present and future perspectives. *Appl Catal B.* 2011;104(1-2):1-5. https://doi.org/10.1016/j.apcatb.2011.03.011.

Horold S, Vorlop KD, Tacke T, Sell M. Development of catalysts for a selective nitrate and nitrite removal from drinking water. *Catal Today.* 1993;17(1-2):21-30. https://doi.org/10.1016/0920-5861(93)80004-k.

Berndt H, Monnich I, Lucke B, Menzel M. Tin promoted palladium catalysts for nitrate removal from drinking water. *Appl Catal B.* 2001;30(1-2):111-122. https://doi.org/10.1016/s0926-3373(00)00225-3.

Duca M, Sarel N, Wang A, Garbarino S, Guay D. Enhanced electrocatalytic nitrate reduction by preferentially-oriented (100) PtRh and PtIr alloys: the hidden treasures of the 'miscibility gap'. *Appl Catal B.* 2018;221:86-96. https://doi.org/10.1016/j.apcatb.2017.08.081.

Teng W, Fan J, Zhang WX. Iron-catalyzed selective denitrification over N-doped mesoporous carbon. *ACS Appl Mater Interfaces.* 2020;12(25):28091-28099. https://doi.org/10.1021/acsami.0c03953.

Chen X, Zhang T, Kan M, et al. Binderless and oxygen vacancies rich FeNi/graphitized mesoporous carbon/Ni foam for electrocatalytic reduction of nitrate. *Environ Sci Technol.* 2020;54(20):13344-13353. https://doi.org/10.1021/acs.est.0c05631.

Su L, Han DD, Zhu GJ, et al. Tailoring the assembly of iron nanoparticles in carbon microspheres toward high-performance electrocatalytic denitrification. *Nanotechnology.* 2019;19(8):5423-5430. https://doi.org/10.1016/j.analecta.9b01925.

Wang J, Ling L, Deng ZL, Zhang WX. Nitrogen-doped iron for selective catalytic reduction of nitrate to dinitrogen. *Sci Bull.* 2020;65(11):926-933. https://doi.org/10.1016/j.scib.2020.02.015.

Shih YJ, Wu ZL, Lin CY, Huang YH, Huang CP. Manipulating the crystalline morphology and facet orientation of copper and copper-palladium nanocatalysts supported on stainless steel mesh with the aid of cationic surfactant to improve the electrochemical reduction of nitrate and \( \text{N}_2 \) selectivity. *Appl Catal B.* 2020;273:119053. https://doi.org/10.1016/j.apcatb.2020.119053.

Yang MX, Wang JT, Shuang CD, Li A. The improvement on total nitrogen removal in nitrate reduction by using a prepared CuO-Co\(_3\)O\(_4\)/Ti cathode. *Chemosphere.* 2020;255:126970. https://doi.org/10.1016/j.chemosphere.2020.126970.

Yin D, Liu YY, Song P, et al. In situ growth of copper/reduced graphene oxide on graphite surfaces for the electrocatalytic reduction of nitrate. *Electrochim Acta.* 2019;324:134846. https://doi.org/10.1016/j.electacta.2019.134846.

Wang B, An B, Su Z, Li L, Liu Y. A novel strategy for sequential reduction of nitrate into nitrogen by CO\(_2\) anion radical: experimental study and DFT calculation. *Chemosphere.* 2020;128754:128754. https://doi.org/10.1016/j.chemosphere.2020.128754.

Zazo JA, García-Muñoz P, Pliego G, Silveira JE, Jaffe P, Casas JA. Selective reduction of nitrate to \( \text{N}_2 \) using ilmenite as a low cost photo-catalyst. *Appl Catal B-Environ.* 2020;273:118930. https://doi.org/10.1016/j.apcatb.2020.118930.

Hou Z, Chen F, Wang J, François-Xavier CP, Wintgens T. Novel Pd/GdCrO\(_3\) composite for photo-catalytic reduction of nitrate to \( \text{N}_2 \) with high selectivity and activity. *Appl Catal Environ.* 2018;232:124-134. https://doi.org/10.1016/j.apcata.2018.03.055.

Salman AR, Enger BC, Aurvay X, et al. Catalytic oxidation of NO to \( \text{NO}_2 \) for nitric acid production over a Pt/Al\(_2\)O\(_3\) catalyst.
Appel Catal A. 2018;564:142-146. https://doi.org/10.1016/j.apcata.2018.07.019.

152. Hooper AB, Vannelli T, Bergmann DJ, Arciero DM. Enzymology of the oxidation of ammonia to nitrite by bacteria. Antonie Van Leeuwenhoek. 1997;71(1):59-67. https://doi.org/10.1023/A:1000133919203.

153. Walker CB, de la Torre JR, Klotz MG, et al. Nitrosopumilus maritimus genome reveals unique mechanisms for nitification and autotrophy in globally distributed marine cyanobacteria. Proc Natl Acad Sci U S A. 2010;107(19):8818-8823. https://doi.org/10.1073/pnas.0913533107.

154. Caranto JD, Vilbert AC, Lancaster KM. Nitrosomonas europaea cytochrome P460 is a direct link between nitrification and nitrous oxide emission. Proc Natl Acad Sci U S A. 2016;113(51):14704-14709. https://doi.org/10.1073/pnas.1611051113.

155. Daims H, Lebedeva EV, Pjevac P, et al. Complete nitrification by Nitrospira bacteria. Nature. 2015;528(7583):504-509. https://doi.org/10.1038/nature16461.

156. Hao D, Chen Z-G, Figiela M, Stepniak I, Wei W, Ni BJ. Emerging alternative for artificial ammonia synthesis through catalytic nitrate reduction. J Mater Sci Technol. 2021;77:163-168. https://doi.org/10.1016/j.jmst.2020.10.056.

157. Li K, Chen C, Bian X, Sun T, Jia J. Electrolytic nitrate reduction using CoO rod-like and sheet-like cathodes with the control of (220) facet exposure and Co2+/Co3+ ratio. Electrochim Acta. 2020;362:137121. https://doi.org/10.1016/j.electacta.2020.137121.

158. Fu X, Zhao X, Hu X, et al. Alternative route for electrochemical ammonia synthesis by reduction of nitrate on copper nanosheets. Appl Mater Today. 2020;19:100620. https://doi.org/10.1016/j.apmt.2020.100620.

159. Dortsiou M, Katsounaros I, Polatides C, Kyriacou G. Influence of the electrode and the pH on the rate and the product distribution of the electrochemical removal of nitrate. Environ Technol. 2013;34(3):373-381. https://doi.org/10.1080/09593330.2012.696722.

160. Chen GF, Yuan YF, Jiang HF, et al. Electrochemical reduction of nitrate to ammonia via direct eight-electron transfer using a copper–molecular solid catalyst. Nat Energy. 2020;5(8):605-613. https://doi.org/10.1038/s41560-020-0654-1.

161. Wang Y, Xu A, Wang Z, et al. Enhanced nitrate-to-ammonia activity on copper-nickel alloys via tuning of intermediate adsorption. J Am Chem Soc. 2020;142(12):5702-5708. https://doi.org/10.1021/jacs.9b13347.

162. Gao J, Jiang B, Ni C, Qi Y, Bi X. Enhanced reduction of nitrate by noble metal-free electrocatalysis on P doped three-dimensional Co3O4 cathode: mechanism exploration from both experimental and DFT studies. Chem Eng J. 2020;382:123034. https://doi.org/10.1016/j.cej.2019.123034.

163. Su LH, Li K, Zhang HB, et al. Electrochemical nitrate reduction by using a novel Co3O4/Ti cathode. Water Res. 2017;120:1-11. https://doi.org/10.1016/j.watres.2017.04.069.

164. Liu F, Liu K, Li M, et al. Fabrication and characterization of a Ni-TNTA bimetallic nanoelectrode to electrochemically remove nitrate from groundwater. Chemosphere. 2019;223:560-568. https://doi.org/10.1016/j.chemosphere.2019.02.028.

165. Wang Y, Zhou W, Jia K, Yu Y, Zhang B. Unveiling the activity origin of a copper-based electrocatalyst for selective nitrate reduction to ammonia. Angew Chem Int Ed Engl. 2020;59(13):5350-5354. https://doi.org/10.1002/anie.201915992.

166. Maksimova YG, Maksimov AY, Demakov VA. Biofilms of nitrite-hydrolyzing bacteria: dynamics of growth, resistance to toxic substances, and biotechnological potential. Appl Biochem Microbiol. 2016;52(8):739-749. https://doi.org/10.1134/s0003683816080068.

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How to cite this article: Li M, Liu X, Wang L, Hou F, Dou SX, Liang J. Rational design on photo (electro)catalysts for artificial nitrogen looping. *EcoMat*. 2021;3:e12096. [https://doi.org/10.1002/eom2.12096](https://doi.org/10.1002/eom2.12096)