Recent Advances in Nonprecious Metal Oxide Electrocatalysts and Photocatalysts for N₂ Reduction Reaction under Ambient Condition

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NH₃ plays an indispensable role in agriculture, fertilizer production as well as in the chemical industry. However, its large-scale production still relies deeply on the century-old Haber–Bosch process under high temperature and pressure along with greenhouse gas emission and fossil fuel consumption. The electrocatalytic and photocatalytic N₂ reduction reactions (NRRs) for NH₃ production are favorable approaches to avoid these issues because they are carbon-neutral and energy-saving. Recently, the nonprecious metal oxides (NPMOs) have gathered the most attention due to their ease of synthesis, controllable stability, lower cost, and environmental friendliness. Herein, the recent advances in NPMO electrocatalysts and photocatalysts for the NRR are narrated and the strategies to improve the poor NRR activity of pristine NPMOs by heteroatom doping to engineer their surface-active sites and introduction of oxygen vacancies are highlighted. A brief summary of and the future perspective on this research field are also presented.

1. Introduction

NH₃, which plays an indispensable role in agriculture, fertilizer production as well as the chemical industry,[1,2] is one of the most fundamental constituents of the modern industrial society. More importantly, NH₃ is a carbon-free energy carrier with no CO₂ emission at final decomposition. In consideration of its high energy density and eco-friendly combustion products, NH₃ is promising as a feasible substitute for H₂ for the modern energy economy. Although N₂ accounts for more than 78% of the atmosphere, the usage of N₂ is very painstaking because of the strong triple bond.[3] At present, there are mainly three ways of N₂ fixation (Figure 1): 1) Industrial-scale fixation (N₂ + 3H₂ → 2NH₃) is the century-old Haber–Bosch process under high temperature and pressure along with greenhouse gas emission and fossil fuel consumption;[4,5] 2) biologically, NH₃ is under the excitation of nitrogenase enzymes in the perseverance of H₂O, electrons, and atmospheric N₂ under mild conditions;[6,7] 3) geochemically, it is a high-energy fixation process, such as lightning. However, the NH₃ yields of biological and geochemical ways are subtle and unstable. Large-scale NH₃ synthesis still relies on the energy-intensive Haber–Bosch process. Therefore, it is of great value to develop alternative methods for NH₃ synthesis.

In recent years, there has been ample research on electrocatalytic and photocatalytic reactions, especially the CO₂ reduction reaction (CRR).[7–9] O₂ evolution reaction (ORR).[10,11] O₂ reduction reaction (OER).[12,13] and H₂ evolution reaction (HER).[14,15] Electro catalysis and photocatalysis enable the N₂ reduction reaction (NRR) to make NH₃.[16,17] Compared with the conventional Haber–Bosch process, the electrocatalytic and photocatalytic process under ambient conditions reduces the energy input, simplifies the reaction steps, and eases the pressure on the environment.[18,19] But the process still needs efficient catalysts to break the strong N≡N. Therefore, designing excellent catalysts to boost the electrocatalytic and photocatalytic NRR efficiencies is highly demanded.

Encouragingly, nonprecious metal oxides (NPMOs) have been established as promising materials for a wide variety of applications (such as supercapacitors, sensors, and in the biomedical
fields) because of their ease of synthesis, chemical stability, and low cost. In addition, transition metals in NPMOs show paramagnetic activity and variable oxidation states. Because of these merits, NPMOs have been investigated extensively as NRR catalysts recently. Some reviews on the NRR have been documented, which provide in detail the recent progress on the design of NRR electrocatalysts and photocatalysts. However, few of them focused on NPMOs. Accordingly, a recent review on NPMOs toward the NRR for electrocatalysis and photocatalysis is required. In our review, we summarize the recent progress of NPMO catalysts toward ambient NRR. We highlight the tactics to boost the scanty NRR activity of pristine NPMOs via heteroatom doping to engineer their surface-active sites and introducing oxygen vacancies (OVs). Eventually, we also propose a brief summary of and future perspective on this research field.

2. Basic Understanding of the NRR

2.1. Electrocatalytic N₂ Reduction

Electrocatalytic N₂ fixation is regarded as an auspicious and green means to achieve mild N₂-to-NH₃ conversion with adsorption, activation, and desorption processes. The electrocatalytic NRR process encompasses the following elementary steps: 1) diffusion of N₂ into the surface; 2) activation of N₂ molecules to intermediates via the participation of protons and multiple electron transfer; and 3) desorption of the reduced product from the surface. In the concrete process, the water oxidation and N₂ reduction occur respectively in the anode and cathode three-electrode system. The corresponding reactions are shown as follows.

**Acidic condition**

Anode: \( 3\text{H}_2\text{O} \rightarrow 3/2\text{O}_2 + 9\text{H}^+ + 6\text{e}^- \)  
Cathode: \( 6\text{H}^+ + 6\text{e}^- + \text{N}_2 \rightarrow 2\text{NH}_3 \)

**Alkaline condition**

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

Compared with the Haber–Bosch process, electrocatalytic N₂ fixation is mild because it utilizes electrical energy instead of thermal energy. In addition, water is the hydrogen source, avoiding the use of fossil fuels. To date, electrochemical NH₃ synthesis has been demonstrated on precious metals, including Ru, Au, Pd, and Ag. Although the catalytic performance of noble metal catalysts is good, the high cost and scarcity impose great confinement on large-scale production. Therefore, it is urgent to find more NPMO catalysts for the NRR.

2.2. Photocatalytic N₂ Reduction

The photocatalytic method is deemed to be environmentally friendly and energy-saving for NH₃ production as this process operates mildly and takes advantage of sustainable solar energy. Different from electrocatalysis, the photosynthesis of NH₃ directly produces NH₃ from sunlight, N₂, and H₂O. Since Schrauzer and Guth first published their study on the photo reduction of N₂ in 1977, scientific endeavors on finding effective photocatalysts for N₂ reduction have increased exponentially. Nevertheless, the conversion efficiency is still low due to the recombination of electron–hole pairs and limited active sites.

In general, N₂ photofixation involves the following critical steps: At first, the semiconductor’s conduction band and valence band generate photoinduced holes and electrons to form hole/electron pairs (h⁺/e⁻) after the adsorption of UV light or visible light. Charge separation and photoinduced carrier migration are the second step of N₂ photo fixation. Finally, e⁻ diffuse across the photocatalyst’s surface and reach the active sites, on which the absorption of N₂ molecules and the following conversion processes take place. Meantime, sacrificial agents, such as H₂O, are oxidized by h⁺. The specific reactions are shown as follows.

\[
\begin{align*}
\text{2H}_2\text{O} + 4\text{h}^+ & \rightarrow 4\text{H}^+ + \text{O}_2 \\
6\text{H}^+ + \text{N}_2 + 6\text{e}^- & \rightarrow 2\text{NH}_3 \\
\text{overall: 2N}_2 + 6\text{H}_2\text{O} & \rightarrow 3\text{O}_2 + 4\text{NH}_3
\end{align*}
\]

As recombination of e⁻ and h⁺ and the limited active sites of the photocatalysts hinder the photocatalytic efficiency, developing photocatalysts with enriched active sites and small bandgaps (more generation of h⁺/e⁻) and improving the utilization of charge carriers simultaneously appear to be particularly important for the photosynthesis of NH₃.
2.3. Theoretical Studies of N₂ Reduction

The difficulty in activating N₂ lies in the following aspects. 1) N₂ as a Lewis base shows low proton affinity, nonpolarity, and negatron affinity. 2) The high-energy N≡N bond (941 kJ mol⁻¹) renders the N₂ molecule inert and stable. 3) Also, the energy differences between the lowest vacant molecular orbital (LUMO) and the highest vacant molecular orbital (HOMO) in N₂ do not promote electron transfer. Thus, it is difficult to activate N₂.

Tafel-type reactions are defined due to H atoms on the electrode surface combination with adsorbed N₂H₄ or NH₃ species, and the combination of adsorbed N₂H₄ or NH₃ species with protons and electrons is called a Heyrovsky-type reaction. Heyrovsky-type reactions include both associative and dissociative mechanisms (Figure 2). In the process, N₂ molecules are first absorbed on the surface of the catalyst and further the N≡N is cleaved. And NH₃ releases with the final N—N bond cleavage, which mainly concerns with Haber–Bosch process. The biological nitrogenase process is related to the associative pathway. The associative mechanism can be subdivided into an alternate pathway and a distal pathway. In the alternating process, the two N atoms are successively hydrogenated till the final N—N bond is broken and NH₃ is released. The N atoms far from the catalyst surface are first hydrogenated and released as NH₃, which leaves an adsorbed N atom on the surface of the catalyst and further hydrogenates to synthesize NH₃ in the distal pathway.[23]

2.4. Selectivity for N₂ Reduction

In the process of electrocatalytic N₂ reduction, the breaking of the strong N≡N requires a reduction potential where the HER readily occurs, leading to a low efficiency and selectivity for NH₃ production. Therefore, current progress in the electrochemical NRR is inhibited by the intense competition from the HER due to the affinity of the H atom with metals. It is imperative to overcome the selectivity challenge to suppress water electrolysis and enhance solid catalyst–gas interactions simultaneously. Slowing down proton transformation to the electrocatalyst surface is the main principle to improve the selectivity. Rational design of catalysts by computational methods makes it possible to prepare new materials that outperform state-of-the-art commercial catalysts.[19] Although there are rare specific theoretical reports on photocatalytic N₂ reduction, it is universal in electrocatalytic N₂ fixation using density functional theory (DFT) calculations to explain concert reaction pathways and mechanisms.[40] As shown in Figure 3, a volcano-shaped plot is obtained by DFT calculations that shows whether the metal surface is overlapped with adsorbed N atoms or H atoms. Rh, Ru, Mo, and Fe are likely to show the highest catalytic activity for N₂ reduction because these metals locate on top of the volcanoes. Nevertheless, these metals’ surfaces are covered with H atoms and the HER will follow when they get negative potentials. The transition metals on the right side of the volcano plots need more negative potentials to conduct the NRR. However, with the negative potential increasing, H atoms are absorbed in these surfaces and the HER becomes the dominant reaction.[23] According to calculations and Figure 3, some transition metals on the left side of the volcano plots probably bind N adatoms more strongly than H adatoms at −1 to −1.5 V versus a standard hydrogen electrode (SHE). Therefore, it gives us suggestions to rationally design NRR catalysts based on these metals with higher selectivity and Faradaic efficiencies (FEs).

To suppress the HER, some external proposals are suggested. 1) Adding alkali metal ions such as Li⁺, Na⁺, and K⁺ into the electrolyte to restrict the H₂ evolution.[41] Hao et al. reported that K⁺ can suppress the HER on bismuth catalysts in aqueous solution due to the prevention of proton migration from the bulk solution to the electrode surface. The FE increased to 66%.[42] 2) Designing a hydrophobic layer to inhibit the access of water molecules to the encapsulated active surfaces. Ling and co-workers used the zeolitic imidazolate framework (ZIF)-71

Figure 2. The general reaction mechanisms of N₂ fixation. a) Dissociative pathway. b) Associative alternating pathway. c) Associative distal pathway. Reproduced with permission.[23] Copyright 2020, American Chemical Society.

Figure 3. Volcano diagrams obtained by plotting the theoretical limiting potential for N₂ reduction via a Heyrovsky-type mechanism against the chemisorption energy of N adatoms on a range of flat (black) and stepped (red) transition-metal surfaces. Reproduced with permission.[23] Copyright 2020, American Chemical Society.
with superhydrophobicity to cover a catalyst surface and used the metal–organic frameworks (MOFs) with high gas sorptivity to absorb N₂.\(^{[43]}\) Zhang and co-workers, inspired by nitrogenases, utilized thiols to form self-assembled monolayers (SAMs) on the surface of Ru. The organic and hydrophobic nature of the SAM limits proton transfer while allowing N₂ transport to the surface of the catalyst.\(^{[44]}\) Inspired by the hydrophobic hairs of aquatic arachnids, Wakerley et al. developed an analogous multiscale hydrophobic surface by modifying dendritic Cu with a monolayer of waxy alkanethiol.\(^{[45]}\) Changing the pH value to improve the FE. The HER can be weakened by decreasing the H⁺ concentration in a weakly acidic electrolyte.\(^{[41]}\)

3. Recent Advances in NPMO Electro catalysts for the NRR

In recent years, an increasing number of researchers have been paying attention to resource-rich elements in the earth. In this section, we sum up the advances in NPMO electrocatalysts based on groups of the period table for the NRR because NPMOs of the same group have similarities.

3.1. Pristine NPMOs

Sc, Y, and La in third subgroup have NRR activity. Our group reported that Y₂O₃ nanosheets and La₂O₃ nanoplates were active for the NRR.\(^{[46,47]}\) Later, Sc and Y as single-atom NRR electrocatalysts with high FEs of 11.2% and 12.1% were investigated.\(^{[48]}\) Although they are rare-earth elements, it is worth taking more efforts to study their catalytic properties toward the NRR because of the following reasons: 1) The abundant electron orbitals are conducive to N₂ activation and 2) their stability is great.

In the fourth subgroup, Ti compounds are stable and low-cost. Pristine TiO₂ (p-TiO₂) achieved an NH₃ yield of 0.17 × 10⁻¹⁰ mol s⁻¹ cm⁻² and an FE of 0.95%.\(^{[49]}\) With the toughness, hardness, and wear resistance properties, more research has been concentrated on ZrO₂. In our group, Xu et al. reported ZrO₂ nanoparticles as efficient electrocatalysts toward the NRR, presenting an NH₃ yield of 24.74 μg h⁻¹ mg⁻¹, with an FE of 5.0% in 0.1 M HCl.\(^{[50]}\) When tested in 0.1 M KOH and 0.2 M phosphate buffer solution (PBS), the FEs are lower than that in 0.1 M HCl. This is because the high H⁺ concentration limits the HER. Over recent years, there has been ample research on TiO₂ in the NRR. However, reports about ZrO₂ in the NRR are limited. Zr-based materials need more dedication to further widen their applications in the NRR.

In the fifth subgroup, Nb compounds are significant in heterogeneous catalysis. NbO₂ is near the top of the volcano and DFT calculations reveal that NbO₂ with the (110) facet is an excellent NRR electrocatalyst due to the high capability for N₂ reduction to NH₃ while suppressing the competing water reduction. NbO₂ and Nb₂O₃ were recently developed by Huang et al. to catalyze the NRR, and a schematic illustration of their synthesis procedure is shown in Figure 4a.\(^{[51]}\) In their research, they prepared both NbO₂ (Figure 4b) and Nb₂O₃ from a Nb₂O₅(OH) nanorod precursor and then annealed in H₂/Ar and air atmosphere, respectively. After the NRR test, NbO₂ performed brilliantly on average NH₃ yields and FE compared to Nb₂O₃ (Figure 4e). It can be seen that the oxidation state of Nb can result in a different electrocatalytic NRR activity. The excellent NRR performance of NbO₂ is attributed to the partly occupied d orbitals of Nb⁺ that can form π backbonding with N₂. After six recycling tests and 12 h long electrolysis in 0.05 M H₂SO₄, NbO₂ was still stable. Another kind of metal oxide of Nb has been reported. For example, Han et al. prepared crystalline Nb₂O₃ nanofibers (Figure 4c) by electrostatic spinning followed by air annealing and such an electrocatalyst achieved an NH₃ yield of 43.6 μg h⁻¹ mg⁻¹ and an FE of 9.26% (Figure 4f).\(^{[52]}\) In addition, Kong et al. also reported a Nb₂O₃ nanowire array (Figure 4d) on carbon cloth, showing an NH₃ yield of 1.58 × 10⁻¹⁰ mol s⁻¹ cm⁻² and an FE of 2.26% (Figure 4g).\(^{[53]}\) The NRR performance of the same oxides with different morphologies has slight differences. Based on this, when designing the catalyst, we can acquire the best performance by adjusting the morphology. Zhu and co-workers reported a novel flower-like porous Ce₁₋ₓNbO₃ perovskite as an NRR electrocatalyst due to the synergistic effect of the Ce atom.\(^{[54]}\)

In the same subgroup, V has a vital role in the nitrogen enzyme to catalyze N₂ fixation in biology under ambient conditions.\(^{[55]}\) V oxide nanomaterials have been used in the field of batteries and electrolysis. In the NRR field, hollow microsphere VO₂ performed efficaciously and steadily with an NH₃ yield of 14.85 μg h⁻¹ mg⁻¹ and FE of 3.97%.\(^{[56]}\)

In the sixth subgroup, Cr and Mo have attracted much attention. Du et al. synthesized Cr₂O₃ nanofibers by electrospinning of polycrylonitrile/chromium acetate by air annealing.\(^{[57]}\) Figure 5a shows a concrete image of the Cr₂O₃ nanofibers after annealing, the NH₃ yield and FE achieved by which are 28.13 μg h⁻¹ mg⁻¹ and 8.56%, respectively (Figure 5d). In addition, Zhang et al. reported multishelled hollow Cr₂O₃ microspheres (MHCOMs) (Figure 5b) serving as a catalyst for the NRR.\(^{[58]}\) For comparison, Cr₂O₃ microspheres (COMs) and Cr₂O₃ nanoparticles (CONPs) were also prepared in Zhang’s work. Of note, the NRR activity of the multishelled hollow Cr₂O₃ (Figure 5e) was higher than those of COMs and CONPs. This is because the adopted N₂ in the hollow inner surface of the microspheres has higher frequency collisions and the concentration of the species in the rate-determining step increased due to the confined effect of the cage. This further demonstrates that we can get the best performance of catalysts by morphology modulation.

Mo is a significant element in nitrogen enzyme that catalyzes N₂ fixation in biological fields.\(^{[59,60]}\) Recently, Yang et al. reported that in NRR electrocatalysis, Mo nanofilms attached an NH₃ yield of 3.09 × 10⁻¹⁰ mol s⁻¹ cm⁻² and an FE of 0.72%.\(^{[61]}\) Han et al. prepared MoO₃ by a one-step hydrothermal strategy. Figure 5c shows the specific SEM image. Figure 5f shows the NRR property, with the optimal NH₃ yield and FE attained being 29.43 μg h⁻¹ mg⁻¹ and 1.90%, respectively.\(^{[62]}\)

In the seventh subgroup, the Mn element is demonstrated to tremendously boost the catalytic performance of nitrogenases by extraction from the photosynthetic bacterium.\(^{[63,64]}\) As an earth-abundant metal, Mn-based oxides are active for the NRR. Wu et al. reported that MnO nanoparticles, synthesized by hydrothermal reaction at 120 °C for 12 h, attained an NH₃ yield of 11.6 μg h⁻¹ mg⁻¹ and an FE of 3.0%.\(^{[65]}\) Furthermore, Wang et al. demonstrated that MnO particles on Ti mesh (MnO/TM) were also an active NRR catalyst with an NH₃ yield of
1.11 × 10⁻¹⁰ mol s⁻¹ cm⁻² and FE of 8.02%.⁶⁶ The oxidation state of Mn can result in different electrocatalytic NRR activity.

In the eighth group, Fe is one of the most abundant non-noble metals. Moreover, Fe as a natural nitrogenase is capable of catalyzing N₂ fixation in ambient atmosphere. Liu et al. and Xiang et al. reported spinel Fe₃O₄ nanorods on a Ti mesh (NH₃ yield: 5.66 × 10⁻¹² mol s⁻¹ cm⁻², FE: 2.6%)⁶⁷ and Fe₂O₃ nanorods (NH₃ yield: 15.9 μg h⁻¹ mg⁻¹; FE: 0.94%)⁶⁸ as NRR electrocatalysts, respectively. Compared with Fe₂O₃ nanorods, the spinel-type-structure Fe₃O₄ nanorods have higher conductivity, which contributes to enhancement of the electrocatalytic NRR performance.

Apart from transition metals, Bi and Sn in the main group behave as NRR electrocatalysts with weak hydrogen adsorption. Bi nanosheets and Bi nanodendrites are active for the NRR due to the suppression of the HER and the morphology advantage.⁶⁹,⁷⁰ Chang et al. reported that flower-like β-Bi₂O₃ (Figure 6a,b) with a big surface area was an efficient electrocatalyst in neutral solution, of which the optimal NH₃ yield and FE attained were 19.92 μg h⁻¹ mg⁻¹ and 4.30%, respectively (Figure 6d).⁷¹ Cubic submicron SnO₂ particles (Figure 6c) on carbon cloth (SnO₂/CC) with a brilliant NRR property were fabricated via a one-step hydrothermal method. Figure 6e,f shows that such SnO₂ attained an NH₃ yield of 1.47 × 10⁻¹⁰ mol s⁻¹ cm⁻² and FE of 2.17%, severally.⁷²

3.2. Oxygen Vacancy

One of the more attractive advantages of using NPMOs as catalytic materials lies in their OVs. Such point defects can serve as

![Figure 4](https://example.com/figure4.png)

**Figure 4.** a) Schematic for the synthesis procedure of NbO₂ and Nb₂O₅. SEM images of b) NbO₂, c) Nb₂O₅ nanofibers, and d) Nb₂O₅ nanowire array. Average NH₃ yields and FEs for e) NbO₂, f) Nb₂O₅ nanofibers, and g) Nb₂O₅ nanowire array at each given potential. a,b,e) Reproduced with permission.⁶⁶ Copyright 2018, Wiley-VCH. c,f) Reproduced with permission.⁶⁷ Copyright 2018, Elsevier. d,g) Reproduced with permission.⁶⁸ Copyright 2019, Royal Society of Chemistry.
chemisorption and activation sites for gas molecules such as $\text{N}_2$. The electronic properties of NPMOs can be significantly changed by rational engineering of OVs in their lattices and surfaces, achieving a more efficient heterogeneous catalysis process.\[73\] The OV introduction improves their conductivity and structural stability and further affects their performance to a certain extent. OVs can first efficaciously capture the metastable electrons and then deliver them into the antibond of $\text{N}_2$ to recognize the electron receptor–donor process.\[74\] OVs have been universally verified to be effective in activating catalysts, especially on the surfaces of metal oxides. Because it is a promising NRR catalyst, some researchers paid attention to designing $\text{TiO}_2$ by cathodic electrochemical polarization and thermal treatment in an inert gas environment to introduce OVs. Defective $\text{TiO}_2$ on a Ti mesh (d-$\text{TiO}_2$/TM) (Figure 7a) was prepared by cathodic electrochemical polarization of
p-TiO$_2$/TM (Figure 7b). Figure 7d gives the fabrication process of p-TiO$_2$/TM and d-TiO$_2$/TM. The NH$_3$ yield increased from $0.17 \times 10^{-10}$ to $1.24 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$ with an FE boosted from 0.95% to 9.17%.\[^{49}\] Fang et al. reported OV-contained TiO$_2$ (OV-TiO$_2$) nanosheets by a thermal treatment under a H$_2$/Ar atmosphere and reached an NH$_3$ yield of 35.6 $\mu$g h$^{-1}$ mg$_{cat}^{-1}$ and FE of 5.3%.[\(^{76}\)] Figure 7e shows that DFT calculations were conducted on the (010) surface of TiO$_2$
with and without OVs. It also shows the free energy distribution in the process of the NRR on the (101) surface at 0 and −0.8 V versus a reversible hydrogen electrode (RHE). The DFT calculations demonstrated that the existence of OVs in TiO₂ greatly reduced the energy barrier for the NRR. After 12 times electrolysis cycling tests, NH₃ yields and FEs almost have no changes and TEM image still remains good. Another report about a TiO₂ nanosheet array on a Ti plate (TiO₂/Ti) (Figure 7c) with an NH₃ yield of 9.16 × 10⁻¹⁰ mol cm⁻² s⁻¹ and FE of 2.5% demonstrated that OVs in situ magnify the adsorption and activation of N₂.[76] OV formation not only enhances the adsorption and activation of N₂ but exposes more active sites in defective TiO₂.

Fu et al. reported that Ta₂O₅ nanorods with rich OVs achieved an NH₃ yield of 15.9 μg h⁻¹ mg⁻¹ and an FE of 8.9%.[77] The vapor hydrolysis–synthesized Ta₂O₅ nanorods further generated OVs in the process of hydrolysis by ethylene glycol at a high temperature. DFT calculations disclosed that N₂ can be absorbed at the OV sites due to the coordination with two Ta atoms contiguous to the OVs. It is easier for the step of N₂ adsorption on the surface of defective Ta₂O₅ than defect-free Ta₂O₅ in the NRR process.

Zhang et al. designed OV-MoO₃ nanosheets using a modified chemical vapor deposition (CVD) process at an atomic level, achieving an NH₃ yield of 12.20 μg h⁻¹ mg⁻¹ and FE of 8.2%.[78] DFT calculations disclosed that OVs in MoO₃ layers were beneficial for the proton transfer step via selective stabilization of N₅H⁺ and destabilizing N₂H₂ via a distal or alternating hybrid path, thereby lowering the activation energy barrier from 1.49 to 0.36 eV with respect to the OV-free one. DFT calculations suggest that inert N≡N triple bond could be activated by a single tungsten atom anchored on N-doped graphene. Inspired by this, Kong et al. demonstrated that 2D WO₃ nanosheets OVs-richness (OVs-WO₃) achieve an NH₃ yield of 17.28 μg h⁻¹ mg⁻¹ and a FE of 3.0%, outstripping the defect-free WO₃ nanosheets (6.47 μg h⁻¹ mg⁻¹ and 1.02%).[79]

MoO₂ with a OV nanowires array on a Ti mesh (OV-MoO₂) obtained an NH₃ yield of 1.63 × 10⁻¹⁰ mol cm⁻² s⁻¹ and a FE of 11.4%, superior to its pristine MoO₂ counterpart (2.3 × 10⁻¹⁰ mol cm⁻² s⁻¹ and 1.96%).[80] DFT calculations manifested that the N₂ adsorption enhanced on the OV-MoO₂ surface because of the stronger electronic interaction between the Mn₆c atoms and N₂. Due to the favorable modulation of the electronic structure, Ni-based materials have attracted considerable attention. Li et al. used the plasma technique, with its characteristics of being versatile, rapid, and energy-saving, to engineer NiO nanosheets with enriched OVs, exhibiting an NH₃ yield of 29.1 μg h⁻¹ mg⁻¹ and FE of 10.8%.[81]

Because of the adaptable transition between Ce⁴⁺ and Ce³⁺, CeO₂ has brilliant electronic or ionic conductivity and is considered an excellent material for investigating defect-rich catalysts.[82] Xu et al. utilized hydrogen-reduced CeO₂ nanorods, achieving an NH₃ yield of 16.4 μg h⁻¹ mg⁻¹ and FE of 3.7%, which is 2.8 times higher than that of the CeO₂ nanorod precursor.[83] According to these specific research works, we can summarize that OVs were generated by thermal treatment in an inert atmosphere, chemical reduction, and ion doping. We choose the most appropriate method to design catalysts based on their characteristic properties.

### 3.3. Heteroatom Doping

Heteroatom doping has been widely regarded as another valid approach to form coordination with the environment and modulate the electronic structure, accelerating the mobility of charge carriers and creating more active sites to boost the electrocatalytic activity.[84] Heteroatom doping can be divided into metal element doping and nonmetal element doping.

#### 3.3.1. Metal Atom Doping

Metal doping is an effective pathway to design the compound material, enhance conductivity, and optimize absorption of the intermediates. DFT calculations manifest that metal sites with low chemical valence have the potential to enhance the electron-donating ability to the π* antibonding orbitals of the N₂ molecule.[85] Consequently, the electrocatalytic activity will increase to a certain extent.

The electrocatalytic performance of TiO₂ can be improved by metal atom doping, including Fe, V, Cu, Mn, and Zr. Previously, we explained that Fe and V were crucial for biological N₂ fixation and VO₂.[56] Fe₂O₄[67] and FeO[68] were reported as electrocatalysts for the NRR. Wu et al. reported Fe-doped TiO₂ nanoparticles (Figure 8a) and V-doped TiO₂ nanorods (Figure 8b), achieving an NH₃ yield of 25.47 and 17.73 μg h⁻¹ mg⁻¹ and FE of 25.6% and 15.3%, respectively.[86,87] DFT calculation results revealed that the doping of Fe into TiO₂ (101) increased the number of OVs. But the enhancement by V doping is caused by the synergistic effect of Ti and V. Figure 8c shows the free energy of the NRR process on the TiO₂ (110) surface at U = −0.50 V. In Wu et al.’s work, the FE is higher than that of other research results and the electrolyte is LiClO₄ because of which alkali metal ions suppress the HER to some extent. In addition, Cao et al. reported Zr⁺ doping of anatase TiO₂, achieving an NH₃ yield of 8.90 μg h⁻¹ mg⁻¹ and FE of 17.3%.[88] The schematic illustration of N₂ fixation is shown in Figure 8d. It suggests that Zr doping generates more OVs and bi-Ti³⁺⁺, which has a lower activation barrier as the most effective catalytic center of chemisorption and polarization N₂. Ti³⁺⁺ plays a significant role in TiO₂ but what kinds of Ti³⁺⁺ defect states improve the NRR activity in TiO₂ is not clear. Cu ions with mixed valences of Cu¹⁺ and Cu²⁺ can spontaneously modulate the OV concentration, which can induce different electronic defect states in transition-metal oxides.[89] Inspired by this, Wu et al. demonstrated that mixed-valent Cu-doped TiO₂ behaved as an efficacious dopant to attenuate the OV concentration and Ti³⁺⁺ formation, which is beneficial for generating different Ti³⁺⁺ 3d⁵ defect states localized below the Fermi energy.[90] The synergistic effects of Cu¹⁺–Ti³⁺, Ti¹⁺–Ti⁴⁺, and Ti³⁺–Ti³⁺ all contribute to the enhanced NRR performance. Similarly, the typical dopant element Mn has the same effect on TiO₂ by generating bi-Ti³⁺⁺. Zhang and co-workers uncovered that Ti₄c⁺⁺ was the active site for N₂ binding and activation.[91]

Apart from defect-rich CeO₂, researchers also designed CeO₂ by metal atom doping to improve the NRR activity. Theoretical calculation studies exposed that single atomic Cu substitution on the CeO₂ (110) surface could augments to three OVs around each Cu site. Zhang et al. designed Cu-doped CeO₂ nanorods
(Cu-CeO$_2$) attaining an NH$_3$ yield of $5.3 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$ and FE of 19.1%.$^{[92]}$ It was the Cu doping that effectively facilitated the concentration of multiple OVs in CeO$_2$ and significantly boosted the NRR activity. In CeO$_2$, Cu doping was apt to replacing Ce$^{3+}$ sites by Cu$^{2+}$. This rendered a decrease of Ce$^{3+}$ ratio in the Ce$^{4+}$, resulting in a decrease of oxygen vacancies around Ce$^{3+}$ sites. But the increasing Cu content led to great increase of oxygen vacancies around Cu$^{2+}$ sites, which were the real active centers. Xie et al. reported Cr-doped CeO$_2$ nanorods achieving an NH$_3$ yield of 16.82 μg h$^{-1}$ mg$_{cat}^{-1}$ and an FE of 3.84%.$^{[93]}$ It was a Cr atom that increased the OVs in CeO$_2$. But different from Cu-CeO$_2$, there was an increase of Ce$^{3+}$ sites due to the Cr$^{3+}$ reducibility, meaning a great increase of OVs around Ce$^{3+}$ sites. In addition, Chu et al. reported that Fe doping could cause a morphology change form crystalline CeO$_2$ nanoparticles to partially amorphous Fe–CeO$_2$ nanosheets, filling with OVs. $^{[94]}$ The NH$_3$ yield and the FE achieved were 26.2 μg h$^{-1}$ mg$_{cat}^{-1}$ and 14.7%, respectively.

In addition, a commercial indium-tin oxide glass (ITO/G) has been reported as a NRR electrocatalyst.$^{[95]}$ Due to the In doping, the conductivity of SnO$_2$ increases, leading to enhanced charge transfer to improve the NRR performance.

### 3.3.2. Nonmetal Atom Doping

Apart from metal atom doping, nonmetal atom doping has become a research concentration as well. The most generally used nonmetal dopants are B, F, and N. By introducing different negative-charge dopants and adjusting the electron acceptor–donor behavior of NPMOs, the charge transfer of NPMOs can be improved and the adsorption energy of reaction intermediates can be optimized, which favor the catalytic activity and reaction kinetics.

Zheng and co-workers reported that B is an important doping element that induces electron deficiency, which is beneficial for the NRR performance.$^{[96]}$ Wang et al. reported B-doped TiO$_2$ microparticles (Figure 9a) with the interstitial B serving as a three-electron donor, and the NH$_3$ yield and FE attained were 14.4 μg h$^{-1}$ mg$_{cat}^{-1}$ and 3.4%, respectively.$^{[97]}$ Chu et al. reported the structural engineering of MnO$_2$ nanosheets by B doping, which was found to effectively enrich OVs on the MnO$_2$ nanosheets.$^{[98]}$ It was B that induced lattice distortion predominantly and removed adjacent lattice oxygen to generate OVs. Such an electrocatalyst reached an NH$_3$ yield of 54.2 μg h$^{-1}$ mg$_{cat}^{-1}$ with an FE of 16.8%.

SnO$_2$ has a wider bandgap at the Fermi level and is typical semiconductor. Due to its dissatisfied conductivity, Chu and co-workers prepared F-doped SnO$_2$ (F-SnO$_2$) mesoporous nanosheets (Figure 9b) grown on carbon cloth to reinforce its conductivity, achieving an NH$_3$ yield of 19.3 μg h$^{-1}$ mg$_{cat}^{-1}$ and FE of 8.3%.$^{[99]}$ After F doping, there was a negative shift of the conduction band of SnO$_2$ toward the Fermi level, meaning metallic characteristics of F-SnO$_2$.

The N element has a higher electronegativity, which is favorable for the adsorption of N$_2$. Chu and co-workers also synthesized a N-doped NiO (N-NiO) nanosheets array (Figure 9c) on
carbon cloth, achieving an NH₃ yield of 22.7 \( \mu \)g/C₀⁻¹ mg⁻¹ and FE of 7.3%.\(^{[100]}\) DFT calculations disclosed that the N doping enhanced the surface conductivity, increased the \( d \)-band center, and promoted NNH stabilization. Figure 9d shows that N-NiO changed the potential-determining step (\( *N_2 \rightarrow *NNH \)) of NiO from the first hydrogenation step to the last NH₃ release step (\( *NH_2 \rightarrow NH_3 \)).

### 3.4. Carbon Hybridization

In general, the unsatisfactory conductivity of NPMOs greatly confines their potentially brilliant NRR performance. Combining catalysts with conductive substrates is a forceful method to solve this problem. Synergetic effects are commonly induced by hybridization, which lead to generate more active sites, advanced charge transfer, and ameliorated intermediate adsorption.

The low electronic conductivity of V₂O₅ handicaps its application in the field of electrocatalysis. MOFs are known as appropriate self-templates for metal oxides/carbon with conductivity compound materials.\(^{[103]}\) Therefore, Zhang et al. prepared shuttle V₂O₅/C by Ar annealing of a solvothermally synthesized V MOF precursor, with the NH₃ yield and FE of 12.3 \( \mu \)g h⁻¹ mg⁻¹ and 7.28%, respectively.\(^{[102]}\) Compared with V₂O₅, the NH₃ yield increased from 2.0 to 12.3 \( \mu \)g h⁻¹ mg⁻¹ due to the faster charge transfer.

Reduced graphene oxide (rGO) is a brilliant 2D conductive substrate due to its high conductivity, chemical stability, and high surface area.\(^{[103,104]}\) Chu and co-workers did a series of studies on metal oxides supported on rGO or graphene, including CuO,\(^{[105]}\) SnO₂,\(^{[106]}\) MoO₂,\(^{[107]}\) NiO,\(^{[108]}\) CoO,\(^{[109]}\) and ZnO.\(^{[110]}\) According to the DFT calculations, SnO₂/defect graphene exhibited a smaller work function of 4.831 eV than SnO₂ (6.128 eV), which demonstrated that SnO₂/defect graphene had a higher Fermi level energy and could stimulate the donation of more valence electrons to the absorbed N₂. Consequently, the strongly electronically coupled SnO₂/defect graphene brought about enhanced conductivity and decreased work function, which was expected to enhance the NRR activity by accelerating the reaction kinetics and promoting the N₂ adsorption and activation.\(^{[106]}\) TiO₂-supported by rGO (TiO₂–rGO) showed higher conductivity and Zhang et al. reported that TiO₂–rGO was active for NRR, reaching an NH₃ yield of 15.13 \( \mu \)g h⁻¹ mg⁻¹ and FE of 3.3%.\(^{[111]}\) Due to the wide bandgap of Cr₂O₃, it was an efficacious strategy to hybridize it with rGO, which enhanced the electron transfer.\(^{[112]}\)

### 4. Recent Advances in NPMO Photocatalysts for the NRR

NPMOs are widely studied in heterogeneous photocatalysts because of their favorable electronic structure, excited lifetimes, and light adsorption properties. Many efforts have been dedicated to optimize the dynamic behavior of photogenerated carriers, such as introducing vacancies, regulating the

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**Figure 9.** SEM images of a) B-TiO₂ microparticles, b) F-SnO₂ nanosheets, and c) N-NiO nanosheets array. d) Adsorption of *NNH on N-NiO and free energy diagrams of distal NRR pathway on NiO and N-NiO at zero applied energy. a) Reproduced with permission.\(^{[97]}\) Copyright 2018, American Chemical Society. b) Reproduced with permission.\(^{[99]}\) Copyright 2019, American Chemical Society. c,d) Reproduced with permission.\(^{[100]}\) Copyright 2019, Wiley-VCH.
nanostructure, and doping heteroatoms. In this section, we discuss the advances of TiO$_2$-based materials and other NPMO-based materials for photocatalysis N$_2$ reduction.

### 4.1. TiO$_2$-Based Materials

TiO$_2$ has been regarded as a candidate photocatalyst due to its light absorption, charge transport, and surface adsorption, and research of TiO$_2$-based materials for photocatalysis NRR is flourishing.

In 1977, Schrauzer and Guth first reported photocatalytic N$_2$ to NH$_3$ by TiO$_2$.[161] Later, there has been more and more research on TiO$_2$ toward the photocatalytic NRR. In 1988, Bourgeois et al. reported that pristine TiO$_2$ displayed photocatalytic N$_2$ fixation performance by air annealing. The thermal pretreatment generated surface defects, introducing a defect or impurity state into the semiconductor bandgap.[113] Later, Xie et al. probed the precise NRR process on the TiO$_2$ (100) surface.[116] The initial N$_2$ adsorption, the activation of the N≡N, and the N–N cleavage were all efficiently promoted by TiO$_2$ photogenerated electrons, surface hydroxilation, and their synergistic effects.

Similar to electrocatalysts, introducing OVs is favorable for enhancing the photocatalysis performance.[117] Hirakawa et al. reported that a commercial TiO$_2$ with many surface OVs successfully produced NH$_3$ by irradiating UV light and inlleting N$_2$.[118] Interestingly, OVs can produce substantial strain in photocatalysts. Recently, it was demonstrated that ultrathin CuCr layered double hydroxide (LDHs) nanosheets containing abundant OVs improved the N$_2$ adsorption and activation of the photocatalysts. The introduction of OVs and a strain effect contributed to the electron density around Ti or O atoms becoming larger (Figure 10c,d). Therefore, the OVs and strain in transition metal oxides enhance catalytic activity synergistically. Gong and co-workers reported a plasmon-enhanced amorphous TiO$_2$ photoelectrode by atomic layer deposition (ALD) with surface OVs, offering higher carrier concentration and more active sites.[120] Due to the ALD, OVs could be confined at the very surface region of TiO$_2$ without affecting the bulk properties, which not only facilitated surface reaction between excited electrons and adsorbed N$_2$ but also avoided recombination from undesired bulk defects.

With appropriate heteroatom doping, including Fe, Mg, Ce, and V, there are more defects in TiO$_2$, resulting in modified adsorption properties.[120] Metal ion doping also contributes to the absorption spectrum shifting to the visible region.[120] Zhao et al. prepared Fe-TiO$_2$ nanoparticles by a two-step hydrothermal method, contributing to a 3.84 times higher quantum yield than pristine TiO$_2$.[121] The dopant of Fe$^{3+}$ on the TiO$_2$ surface boosted the trapping of e$^-$ and h$^+$ by forming Fe$^{2+}$ and Fe$^{4+}$ to impede charge recombination and holes. The unstable Fe$^{3+}$ and Fe$^{4+}$ transferred e$^-$ and h$^+$ to Ti$^{3+}$ and •OH, respectively. The surfacial Ti$^{3+}$ provided an amount of active sites for N$_2$ fixation by behaving as an electron donor, leading to dissociation of the triple bond. The N$_2$ reduction scheme is shown in Figure 10e.

Ileeperuma et al. studied Mg-doped TiO$_2$ with enhanced photocatalytic activity compared with pristine TiO$_2$.[122] In their research, the optimum doping level is 2–4%. By doping with Mg, there is a narrower depletion layer width in TiO$_2$, affecting the rate of band bending. This could facilitate the electron tunneling to proceed more easily at the interface, consequently enhancing electron transfer. Later, they performed research about Ce- and V-doped TiO$_2$.[123] The V-doped TiO$_2$ catalyst shows n-type semiconductor behavior at pH=3, whereas the Ce-doped TiO$_2$ possesses p-type behavior at pH=12.5.

### 4.2. Other NPMO-Based Materials

Recently, there have been various catalytic applications of Bi-based materials.[124,125] Sun et al. focused on low-valent Bi (II) and demonstrated that BiO without additional reducing agents is an ideal model for the NRR due to its empty 6d orbitals and high electron donating power for N$_2$ adsorption and activation.[126] As shown in Figure 11a, N$_2$ was activated by supplying electrons to the 6d orbital of Bi and accepted the lone pair electrons from three Bi atoms to its antibonding orbit.

ZnO is another excellent semiconductor material optics due to its wide bandgap. Janet et al. used the wet chemical etching method to prepare ZnO and the N$_2$ photofixation yielded around 86 μmol h$^{-1}$ g$^{-1}$.[127] A schematic shows the whole process of water splitting at the semiconductor metal interface along with the N$_2$ activation through the insertion of N$_2$ to the Pt–H bond (Figure 11b).

Zhao et al. reported that mesoporous β-Ga$_2$O$_3$ nanorods, a wide-bandgap semiconductor, were used in N$_2$ photoreduction.[128] The photoactivity of β-Ga$_2$O$_3$ was operated in the presence of different alcohols, including tert-butanol (TBA), methanol, and ethanol, which formed •CO$_2$ in situ. The performance of N$_2$ to NH$_3$ was enhanced by reducing ability of •CO$_2$ dramatically. In addition, the presence of O$_2$ in the N$_2$ accelerated the formation of •CO$_2$+, which boosted the reducing energy (Figure 11c).

As an n-type semiconductor, WO$_3$ is also a promising photocatalyst because of its brilliant electron and proton conductivity. Li et al. reported WO$_3$ with carbon decoration as a photocatalyst with an NH$_3$ yield of 205 μmol h$^{-1}$ g$^{-1}$.[129] Pothole-rich WO$_3$ nanosheets are also a photocatalyst for direct nitrate synthesis.[130]

Mo is a typical doping element for the NRR.[131,132] Moreover, Xiong’s group reported Mo-W$_{18}$O$_{46}$ nanowires and revealed the doping of Mo species contributed to multi-synergetic effects on N$_2$ activation and dissociation.[133] The active sites of Mo–W not only polarized the adsorbed N$_2$, but also enhanced metal–oxygen covalency in the lattice. Mo doping facilitated the photocatalytic NRR by raising the defect-band center to preserve the energy of photoexcited electrons.

Fe is universally in the nitrogenase and Haber–Bosch process ascribed to its good interaction with dinitrogen. Both Fe$_2$O$_3$ and Fe$_2$O$_4$ have N$_2$ photocatalytic activity. Khader et al. synthesized α-Fe$_2$O$_3$ that was effective in photoactivating N$_2$.[134] Recently, Lashgariand and Zeinalkhani reported that the 1:1 ratio...
nanocomposite of Fe$_2$O$_3$–TiO$_2$ and Pd-loaded Fe$_2$O$_3$–TiO$_2$ were active for photofixation.$^{[115]}$ Thus, as Fe$_2$O$_3$ was incorporated into TiO$_2$, due to the extended light absorption of visible light in Fe$_2$O$_3$, the coupled heterojunction nanocomposite materials played a key role in the N$_2$ photoreduction process.

In addition, hydrous oxides Cu$_2$O·xH$_2$O, WO$_3$·xH$_2$O, and Sm$_2$O$_3$·xH$_2$O/V$_2$O$_5$·xH$_2$O were also studied as photocatalysts in the NRR.$^{[116–118]}$

5. Conclusion

Highly efficient NH$_3$ production at ambient conditions is an urgent research duty for the continuous development of contemporary society. Low-voltage electricity and solar energy can act as alternative energy sources for NH$_3$ production, whereas the Haber–Bosch process exhausts massive energy and releases greenhouse gases. Electrocatalytic and photocatalytic artificial N$_2$ fixation have fascinated rising research attention due to the following virtues: 1) The reactive materials (N$_2$ and H$_2$O) are infinite and the reactive conditions are moderate, leading to lower cost and 2) electricity and solar are clean and renewable sources; therefore, the artificial NRR process alleviates environmental issues with no carbon emission. The reported studies and the performance of electrocatalysts and photocatalysts are summarized in Table 1 and 2. According to these reports, NPMO catalysts show good stability, which refers to the change of catalysts’ activity and selectivity with time. Most of the catalysts display chemical and structural stability. The NH$_3$ yields and FEs almost have little change after long tests and repeated experiments.
In addition, the components and morphologies remain greatly after cycle tests. Nevertheless, the current researches are still superficial and defective. The NRR still faces grand challenges. In our Review, we describe the recent progress in NPMO electrocatalysts and photocatalysts for the NRR and highlight the approaches to overcome the poor NRR activity of pristine NPMO by heteroatom doping to engineer its surface-active sites and introduction of OVs. Eventually, a brief summary of and future perspective on this research field are also proposed.

1) It is worth engineering catalysts rationally to overcome their lower intrinsic catalytic reactivity and selectivity for the NRR. Herein, previously, we talked about the pristine NPMO catalysts first. Then, we narrated OV introduction and heteroatom doping, which both enrich the active sites and enhance the catalytic performance apparently.

OVs in NPMOs play a critical role in boosting the catalysis performance. Strategies to create such OVs differ but generally lack fine control over OVs’ concentration and location (bulk or surface). In addition, surface OVs in NPMOs suffer from oxidation, thus leading to activity decay. Practical strategies for stabilizing surface OVs are therefore expected. Qiu et al. designed p-n heterojunction CeO$_2$/Co$_3$O$_4$ and OVs were generated by the coupled heterojunction interface, which rendered rapid interfacial charge transfer from CeO$_2$ to Co$_3$O$_4$. Note that characterization to verify and elucidate OVs such as electron paramagnetic resonance (EPR), X-ray absorption fine structure spectroscopy (XAFS), and scanning tunneling microscopy (STM) should be performed. DFT is also a powerful method that constructs theoretical models at the atomic and molecular level to analyze changes in electronic structure and assess the catalytic mechanism of materials bearing OVs. For photocatalysts, DFT calculations could help estimate bandgap changes, charge separation, as well as adsorption and activation of the substances involved in catalytic reactions. The energy barrier for the rate-limiting step of a catalytic reaction can also be calculated to evaluate how OVs impact the efficiency and selectivity of the catalysis. Therefore, there will be a promising future for metal oxides with OVs by DFT calculation forecasting, regulating rationally, and verifying precisely.

The role of dopants is to change the NPMO’s surface chemical bonds to render oxygen atoms close to the dopants. Therefore, the active centers may be the oxygen atoms near the dopant or the dopant itself. The main synthesis methods for doped oxides include solid-state synthesis, coprecipitation, sol–gel synthesis, and electrochemical synthesis. However, no matter which method is used, we could not know if the doped oxides and the dopants are homogeneous or even make sure whether the dopants are small oxide clusters on the surface or not. Therefore, advanced and precise characterization methods using photons, electrons, or chemical behaviors are needed for further demonstration. Generally, XRD is not a precise method because the doped oxide has the same structure as the pristine oxide. Moreover, it is clear whether the subtle lattice parameter shift is to be ascribed to the dopant or the small size of crystallites. Extended X-ray absorption fine structure (EXAFS) could locate the dopant in the solid exactly. Another efficacious technique is X-ray photoelectron spectroscopy (XPS), which presents the surface concentration of the dopant and oxidation states of atoms on the surface. Electron microscopy, including SEM and electron stimulated X-ray emission spectroscopy (EDX), provides morphological information. In addition, spectroscopy, including UV optical spectroscopy (UV–vis), Raman spectroscopy, and
Table 1. Comparison of NRR performance of NPMO electrocatalysts.

| Catalyst         | Electrolyte         | NH₃ yield (µg h⁻¹ mg⁻¹) | FE  | Potential (V) versus RHE | Ref.  |
|------------------|---------------------|--------------------------|-----|--------------------------|-------|
| Y₂O₃             | 0.1 M Na₂SO₄        | 1.06 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 2.53% | −0.90V                  | [46]  |
| p-TiO₂           | 0.1 M HCl           | 0.17 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 0.95% | −0.15V                  | [49]  |
| d-TiO₂           | 0.1 M HCl           | 1.24 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 9.17% | −0.90V                  | [49]  |
| OVs-TiO₂         | 0.005 M H₂SO₄       | 35.6                     | 5.30% | −0.80V                  | [75]  |
| Ti/TiO₂          | 0.1 M Na₂SO₄        | 9.16 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 2.50% | −0.70V                  | [76]  |
| Fe-TiO₂          | 0.5 M LiClO₄        | 25.47                    | 25.60% | −0.40V                  | [86]  |
| V-TiO₂           | 0.5 M LiClO₄        | 17.73                    | 15.30% | −0.40V                  | [87]  |
| Cu-TiO₂          | 0.5 M LiClO₄        | 21.31                    | 21.99% | −0.55                    | [90]  |
| Zr-TiO₂          | 0.1 M KOH           | 8.90                     | 17.30% | −0.45V                  | [88]  |
| Mn-TiO₂          | 0.1 M Na₂SO₄        | 20.05                    | 11.93% | −0.50V                  | [91]  |
| B-TiO₂           | 0.1 M Na₂SO₄        | 14.4                     | 3.40%  | −0.80V                  | [96]  |
| TiO₂/RGO         | 0.1 M Na₂SO₄        | 15.13                    | 5.30%  | −0.80V                  | [111] |
| CuO/RGO          | 0.1 M Na₂SO₄        | 1.8 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 3.90%  | −0.75V                  | [105] |
| SnO₂/RGO         | 0.1 M Na₂SO₄        | 25.6                     | 7.10%  | −0.50V                  | [106] |
| MoO₃/RGO         | 0.1 M Na₂SO₄        | 37.4                     | 6.60%  | −0.35V                  | [107] |
| NiO/RGO          | 0.1 M Na₂SO₄        | 18.6                     | 7.80%  | −0.70V                  | [108] |
| CoO/RGO          | 0.1 M Na₂SO₄        | 21.5                     | 8.30%  | −0.60V                  | [109] |
| ZnO/RGO          | 0.1 M Na₂SO₄        | 17.7                     | 6.40%  | −0.65V                  | [110] |
| ZrO₂             | 0.1 M HCl           | 24.74                    | 5.0%   | −0.45V                  | [50]  |
| Nb₂O₅            | 0.05 M H₂SO₄        | 11.6                     | 32.0%  | −0.65V                  | [51]  |
| Nb₂O₅            | 0.1 M HCl           | 43.6                     | 9.26%  | −0.55V                  | [52]  |
| Nb₂O₅            | 0.1 M Na₂SO₄        | 1.58 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 2.26%  | −0.60V                  | [53]  |
| VO₂              | 0.1 M Na₂SO₄        | 14.85                    | 3.97%  | −0.70V                  | [56]  |
| V₂O₅/C           | 0.1 M Na₂SO₄        | 12.3                     | 7.28%  | −0.60V                  | [102] |
| Cr₂O₃            | 0.1 M HCl           | 28.13                    | 8.56%  | −0.90V                  | [57]  |
| Hollow Cr₂O₃     | 0.1 M Na₂SO₄        | 25.3                     | 6.78%  | −0.90V                  | [58]  |
| Ta₂O₅            | 0.1 M HCl           | 15.9                     | 6.9%   | −0.60V                  | [77]  |
| MoO₃             | 0.1 M HCl           | 4.80 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 1.9%   | −0.40V                  | [62]  |
| MoO₂             | 0.1 M HCl           | 12.2                     | 8.20%  | −0.15V                  | [78]  |
| WO₃              | 0.1 M HCl           | 17.28                    | 7.00%  | −0.30V                  | [79]  |
| MnO              | 0.1 M Na₂SO₄        | 1.11 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 8.02%  | −0.39V                  | [66]  |
| MnO₂             | 0.1 M Na₂SO₄        | 2.3 × 10⁻¹⁰ mol s⁻¹ cm⁻²  | 1.96%  | −0.50V                  | [80]  |
| B-MnO₂           | 0.5 M LiClO₄        | 54.2                     | 16.80% | −0.20V                  | [98]  |
| Mn₃O₄            | 0.1 M Na₂SO₄        | 11.6                     | 3.00%  | −0.80V                  | [65]  |
| Fe₂O₃            | 0.1 M Na₂SO₄        | 5.6 × 10⁻¹⁰ mol s⁻¹ cm⁻²  | 2.6%   | −0.40V                  | [67]  |
| Fe₂O₃            | 0.1 M Na₂SO₄        | 15.9                     | 0.94%  | −0.80V                  | [68]  |
| NiO              | 0.1 M Na₂SO₄        | 29.1                     | 10.8%  | −0.50V                  | [81]  |
| N-NiO            | 0.5 M LiClO₄        | 22.7                     | 7.30%  | −0.50V                  | [100] |
| Ce₂O₃            | 0.1 M Na₂SO₄        | 16.4                     | 3.70%  | −0.40V                  | [83]  |
| Cu/CoO₂          | 0.1 M Na₂SO₄        | 5.3 × 10⁻¹⁰ mol s⁻¹ cm⁻²  | 19.1%  | −0.45V                  | [92]  |
| Cr/CoO₂          | 0.1 M Na₂SO₄        | 16.82                    | 3.84%  | −0.70V                  | [93]  |
| Fe/CoO₂          | 0.5 M LiClO₄        | 26.2                     | 14.70% | −0.50V                  | [94]  |
| Bi₂O₃            | 0.1 M Na₂SO₄        | 19.92                    | 4.30%  | −0.80V                  | [71]  |
| Sn₂O₃            | 0.1 M Na₂SO₄        | 1.47 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 2.17%  | −0.70V                  | [72]  |
| ITO/G            | 0.5 M LiClO₄        | 1.06 × 10⁻¹⁰ mol s⁻¹ cm⁻² | 6.17%  | −0.40V                  | [95]  |
| F/SnO₂           | 0.1 M Na₂SO₄        | 19.3                     | 8.60%  | −0.45V                  | [99]  |
Table 2. Comparison of NRR performance of NPMO photocatalysts.

| Material     | Light source | Scavenger | NH$_3$ yield | Ref. |
|--------------|--------------|-----------|--------------|------|
| OVs-TiO$_2$  | >280 nm      | 2-Propanol | 35.0 μmol h$^{-1}$ g$^{-1}$ cat. | [115] |
| OVs-TiO$_2$  | 200-800 nm   | /         | 78.9 μmol h$^{-1}$ g$^{-1}$ cat. | [116] |
| Fe-TiO$_2$   | =254 nm      | Ethanol   | 400 μmol h$^{-1}$ g$^{-1}$ cat. | [121] |
| Mg$_2$TiO$_4$| UV light     | /         | 10.3 μmol h$^{-1}$ g$^{-1}$ cat. | [122] |
| V$_2$TiO$_5$ | UV light     | /         | 28 μmol h$^{-1}$ g$^{-1}$ cat.  | [123] |
| Ce$_2$TiO$_7$| UV light     | /         | 30 μmol h$^{-1}$ g$^{-1}$ cat.  | [123] |
| BiO          | Full spectra | Methanol  | 1226 μmol h$^{-1}$ g$^{-1}$ cat. | [126] |
| ZnO          | UV light     | EDTA-2Na  | 35 μmol h$^{-1}$ g$^{-1}$ cat.  | [127] |
| β-Ga$_2$O$_3$| λ = 254 nm   | TBA       | /             | [128] |
| WO$_3$       | Full spectra | /         | 205 μmol h$^{-1}$ g$^{-1}$ cat. | [129] |
| Mo$_2$W$_8$O$_{33}$| Full spectra | Na$_2$SO$_3$ | 195.5 μmol h$^{-1}$ g$^{-1}$ cat. | [131] |
| Fe$_3$O$_4$  | UV light     | /         | 100 μmol h$^{-1}$ m$^{-2}$      | [134] |
| Cu$_2$O+H$_2$O/CuCl | UV light | / | 70 mM h$^{-1}$te/f | [136] |
| Sm$_2$O$_3$/V$_2$O$_5$ | UV light | / | 44 μmol h$^{-1}$te/f | [138] |

The DFT method has been widely used as a practical tool to predict and forecast the possible active sites, adsorption energies, catalytic pathways, intermediates, and rate-determining step of the reaction. It is a powerful and effective tool to combine experimental results and theoretical analysis, which has contributed to disclosing the molecular-scale reaction mechanisms of the NRR. Thus, more focus should be paid to establish sound models closer to factual reaction systems. 5) NO$_x$ contaminants and other N-containing substances exist in the process of the NRR. To prevent misjudgment of the tested catalyst, accurate detection of the source of the produced NH$_3$ based on an isotopic labeling test via NH$_3$-selective electrodes, ion chromatography, and/or a quantitative NMR method is a necessity. Moreover, eliminating pollution from nitrogen sources before the NRR process is also important.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

ambient conditions, electrocatalysis, N$_2$ reduction reaction, nonprecious metal oxides, photocatalysis

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Fourier transformed infrared spectroscopy (FTIR) also could identify the presence of dopants.30 2) Amorphous metal oxides (AMOs) will offer us a new direction in the field of NRR as most of the catalysts we discussed before are crystals and the research of AMOs in the NRR is limited. AMOs with highly disordered 3D arrangement present high catalytic performance in energy electrocatalysis.31,32 Rich defects in AMOs also bestow higher catalytic activity. In contrast, crystalline materials only provide surface catalysis. With these merits of amorphous materials, further and deep research in NRR fields are needed to take more efforts. For photocatalysts, amorphous structures have a smaller bandgap and more defects, which enhance visible light absorption and promote the migration and separation of photogenerated charge carriers.33 3) Stability is an essential criterion of whether a catalyst can be used in practice. In fact, metal oxides dissolve more or less in acidic media. Although NPMOs show good stability for acidic NRR in previous reports, these research works34,35 lack reliable characterizations (such as in situ electrochemical quartz crystal microbalance and inductively coupled plasma) to describe the leaching rate of oxide ions. Indeed, the stability of NPMOs can be demonstrated by cycling/long-term stability tests. But for accurate quantification of this critical criterion, we need more details concerning NPMOs’ mass change during electrocatalysis. Meanwhile, the duration of stability testing in the NRR should be extended. Apart from these, strategies such as engineering special heterojunctions to improve NPMOs’ stability also count. For instance, the stability of Pt nanoparticles can be much enhanced by constructing a Pt–ITO–graphene triple junction.36 Likewise, preparing NPMOs on suitable substrates may also stabilize them for N$_2$ reduction. 4) Theoretical calculations and computational methods have made it feasible to investigate catalysts at the atomic level. Furthermore, there are many factors remaining unclear because the NRR is a greatly complex multistep reaction.
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