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Recent developments in Ti-based nanocatalysts for electrochemical nitrate-to-ammonia conversion

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Recently, electrochemical NO₃⁻-to-NH₃ conversion *via* the nitrate reduction reaction (NO₃⁻RR) has received much attention because it is regarded as an available option for sewage treatment and ammonia synthesis under mild conditions. Exploring promising electrocatalysts with low cost, reduced overpotential, high yield rate and faradaic efficiency toward NH₃, and sufficient stability is the most crucial factor for NO₃⁻-to-NH₃ conversion and energy efficiencies. Considering the advantages of being nontoxic and having wide availability, outstanding stability, hydrogen evolution inertness, and mature fabrication techniques, titanium-based (mainly metallic Ti- and TiO₂-based) nanomaterials have emerged as potential candidates for NO₃⁻-to-NH₃ conversion over a wide pH range. This review summarizes the overview of the NO₃⁻RR and fundamental insights into metallic Ti and TiO₂, and clarifies the relationship among the design strategy, material structure, and performance enhancement. Furthermore, the recent progress in next-generation Ti-based nanomaterials is discussed, including Ti-based MXene and single atomic catalysts. Finally, the challenges and future directions of the NO₃⁻RR and Ti-based nanocatalysts are elucidated. This review aims to provide some inspiration for developing effective electrocatalysts for electrochemical NO₃⁻-to-NH₃ conversion.

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1. Introduction

Ammonia (NH₃) plays an important role in the manufacturing industries such as fertilizers, plastics, pharmaceuticals, $etc.^{1-3}$ Recently, the emerging "hydrogen economy" and "carbon neutralization" have caused NH₃ to be regarded as a carbon-free fuel and a portable energy carrier owing to its high energy density (4.32 kW h L⁻¹); in addition, NH₃ can be used as a "green fuel" to produce electricity via direct ammonia fuel cells. ^{4,5} Importantly, NH₃ is a natural hydrogen carrier with a high H₂ storage capacity of 17.75%, ⁶ making liquid ammonia a safer hydrogen storage medium. Thus, the primary innovation directions of "ammonia = hydrogen 2.0" are derived, ⁷⁻¹⁰ and a new market for NH₃ is estimated to be created soon.

However, NH₃ is still produced by an energy-intensive Haber–Bosch process which requires harsh conditions of high temperature (400–600 °C) and pressure (200–350 atm), resulting in large amounts of global energy consumption and carbon dioxide emission (450 million metric tons). Exploring alternative NH₃ synthetic techniques driven by sus-

tainable energies at room temperature and under an air atmosphere is significant for developing "green ammonia". 16,17 On the other hand, N2, NH3, and NO3 are the key inorganic species for the global nitrogen cycle. Humans utilize the Haber-Bosch process for nitrogen fixation, and as-produced NH₃ is used for chemical fertilizer manufacture or provides nitrates via the Ostwald process for the chemical and ammunition industries. Fertilizer-intensive agriculture generates NO₃⁻containing sewages, 18 and NO₃ is also a major waste byproduct stream of industrial production (for instance, the effluent produced from the ammunition industries contains 65% ammonium nitrate and 20% amine nitrates¹⁹). Extensive nitrogen fixation eventually results in the accumulation of NO₃-, excessive NO3 - cannot be converted naturally in time, interferes with the global nitrogen cycle and pollutes the surface and ground waters.20 Therefore, it's necessary to develop a denitrification technique to establish a closed nitrogen cycle. The electrochemical NO₃⁻ reduction reaction (NO₃⁻RR) for NO_3^- -to- NH_3 conversion $(NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-)$ driven by sustainable energies is regarded as an alternative for "green ammonia" production and an efficient artificial denitrification technique to repair the disturbed global nitrogen cycle, which has received great attention in recent years.21

Electrochemical NO₃⁻-to-NH₃ conversion is an aqueousbased electrochemical strategy for ammonia synthesis using

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water as a hydrogen source, which gets rid of H2 that is needed for NH₃ synthesis. Moreover, the high theoretical potential (0.69 V vs. RHE) of NO₃⁻-to-NH₃ conversion and the high solubility of NO₃ make the efficiency of NH₃ synthesis superior to that of the electrochemical nitrogen reduction reaction (NRR) traditional electrochemical nitrogen technique. 4,8,22 Nevertheless, electrochemical NO₃-to-NH₃ conversion still suffers from the following issues: although electrochemical NO₃-to-NH₃ conversion presents an ideal theoretical potential, it requires a large overpotential (>400 mV) to trigger the NO₃-RR in reality, ^{23,24} due to which the energy conversion efficiency is seriously retarded; the NO₃⁻RR is a complicated multi-electron coupled proton transfer process, in which a series of nitrogen-containing products such as NO2, NO2-, NO, N2O, N2, NH2OH, and NH3 could be generated, and toxic NO2 and low added-value N2 are the major competitive products relative to NH₃. ^{25,26} Studying the reactive mechanisms of the NO3-RR and exploring efficient electrocatalysts are the keys to solving the above bottlenecks.

Recently, Cu- and Co-based electrocatalysts for electrochemical NO₃-to-NH₃ conversion have been intensively developed. 27-35 However, most of them only work in neutral or alkaline electrolytes, as NO₃ exhibits strong oxidability in acid solutions. Although noble metal-based electrocatalysts exhibit a strong resistance to acid corrosion, their NO₃ RR activity is severely compromised by hydrogen evolution. It is desirable to develop efficient electrocatalysts for NO₃-to-NH₃ conversion to treat sewage containing NO₃ over a wide pH range and potential range. Ti-based materials have the inherent advantages of being non-toxic and cost-effective, and having superior stability over a wide pH range and HER inertness, making them ideal candidates. Currently, increasing studies reveal that Ti-based electrocatalysts, typically metal Ti 36-38 and TiO2 composite materials, 39-42 exhibit comparable electrochemical NO₃⁻-to-NH₃ conversion activity. Furthermore, there are a series of low-cost fabrication techniques that enable largescale fabrication of Ti-based materials with various nanostructures under mild conditions. The above superiorities indicate that exploring Ti-based nanomaterials is a crucial development direction for electrocatalysts for NO₃⁻-to-NH₃ conversion. Although some exciting results of Ti-based electrocatalysts have been reported in the literature, there is still a lack of comprehensive evaluation of Ti-based electrocatalysts for NO₃⁻-to-NH₃ conversion, and the fundamentals of compositional and structural features associated with electrochemical NO3-to-NH₃ conversion performances have not been thoroughly summarized.

Herein, brief summaries about the fundamental insights of the NO₃⁻RR and inorganic Ti-based materials are proposed. Ti-based electrocatalysts with various structures and their catalytic performances for NO₃-to-NH₃ conversion have been reviewed in detail. Finally, the challenges and opportunities for further research are also discussed. This review aims to give some new inspiration to develop highly efficient Tibased nanocatalysts for electrochemical NO₃⁻-to-NH₃ conversion.

Brief overview of the NO₃-RR 2.

2.1. Reactive pathway

The NO₃ RR is a complicated process involving multi-electron coupled multi-proton transfer (Fig. 1a). 43 Different NO₃ concentrations, potential ranges and the pH of electrolytes may trigger diverse possible reactive pathways and result in various nitrogen-containing products, including NO₂-, NO_x, N₂, NH₃, etc. Moreover, the exact reactive pathway of the NO₃ RR is still under debate. Niu et al. proposed five possible reactive pathways of the NO₃⁻RR. They can be classified into O-end, O-side, N-end, N-side and NO-dimer pathways based on the adsorption configuration of *NO (* denotes the state of being adsorbed), as depicted in Fig. 1b.44 However, there is still a lack of sufficient experimental evidence to verify the exact reactive pathway. Some of the studies used the N-end pathway of $NO_3^- \rightarrow *NO_3 \rightarrow *NO_2 \rightarrow *NO \rightarrow$ *NOH \rightarrow *NHOH \rightarrow *NH \rightarrow *NH₂ \rightarrow *NH₃ \rightarrow NH₃(g) to perform the density functional theory (DFT) study, while the O-end pathway of $NO_3^- \rightarrow *NO_3 \rightarrow *NO_2 \rightarrow *HNO_2 \rightarrow *NO$ \rightarrow *HNO \rightarrow *H₂NO \rightarrow *HNO \rightarrow *O \rightarrow *OH was often used for Ti-based electrocatalysts.

2.2. Overpotential

Overpotential is a crucial parameter for evaluating the energy conversion efficiency of the NO₃⁻RR. The theoretical potential for NO₃⁻-to-NH₃ conversion is 0.69 V vs. RHE.⁸ In reality, a large overpotential (usually more than 400 mV) is needed for triggering the NO₃⁻-to-NH₃ conversion. The ideal electrocatalyst is still to be developed, and the origin of overpotential should be further clarified. The NO₃-RR is a cathodic reduction reaction in which NO₃ is transferred to a series of nitrogen-containing products by accepting electrons on the electrode surface. The rate-limiting step in the entire reaction is usually the reduction of NO₃⁻ to the intermediate product NO₂* due to the difficulty of breaking the N-O bond. 21,45 It is the process of electron transition from electrodes to the lowest occupied molecular orbital (LUMO) of NO3-, according to the standpoint of frontier orbital theory. This process can be vividly expressed in Fig. 1c for metal and semiconductor electrodes. The molecular orbital diagram of NO₃ shown in Fig. 1d suggests that the high-energy LUMO of the NO₃⁻ ion and the d orbitals of transition metals (except Hg) are hard to match with the LUMO of NO₃⁻, thus extra energy is needed for reducing NO₃⁻ to the intermediate product NO₂*. ⁴⁶ Therefore, exploring electrocatalysts with high energy in the highest occustate (HOS) is essential for reducing overpotential.47,48

2.3. Product selectivity

For NO₃⁻-to-NH₃ conversion, NH₃ is the target product of the NO₃⁻RR. Thus, the selectivity and faradaic efficiency (FE) of NH₃ are crucial parameters. However, NO₃⁻-to-NH₃ conversion involves eight electrons coupled with the transfer of nine protons. Many intermediates with the valence of nitrogen between +5 and -3 may desorb from electrocatalysts to gene-

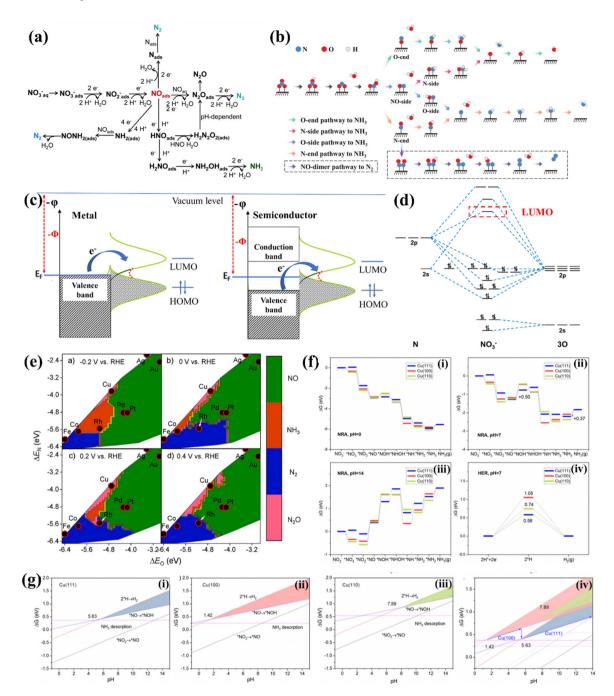


Fig. 1 (a) The possible pathways of the $NO_3^-RR.^{43}$ Reproduced from ref. 43 with permission from The Royal Society of Chemistry, copyright 2021. (b) Detailed pathways of the NO_3^-RR , including O-end, O-side, N-end, and N-side pathways to NH_3 , as well as the NO-dimer pathway to N_2 . Reproduced from ref. 44 with permission from Wiley-VCH, copyright 2020. (c) Electronic band structures of metal- and semiconductor-based electrodes, and the electron transfer from the electrode to the frontier orbitals of the adsorbate. (d) Molecular orbital diagram and the LUMO of NO₃⁻. (e) Theoretical selectivity maps to NO, N₂O, N₂ or NH₃ products from electrocatalytic NO₃⁻ reduction as a function of O and N adsorption energy under different applied voltages. 49 Reproduced from ref. 49 with permission from American Chemical Society, copyright 2019. (f) NO₃-RR pathways at Cu(111), Cu(100), and Cu(110) at (i) pH = 0, (ii) pH = 7, (iii) pH = 14, and (iv) the HER pathway at pH = 7. (g) Competing relationship between the NO₃⁻RR and the HER on (i) Cu(111), (ii) Cu(100), and (iii) Cu(110), and (iv) comparison between different facets. The shaded zones are predominated by the NO₃⁻RR. ⁵⁶ Reproduced from ref. 56 with permission from American Chemical Society, copyright 2021.

rate various by-products, and the coupling reaction between neighboring *N leads to the generation of N₂, N₂H₄ or N₂O as by-products. Liu et al. revealed that the adsorption strengths of O and N atoms ($\Delta E_{\rm O}$ and $\Delta E_{\rm N}$) could be used as descriptors of selectivity on transition metals. As depicted in Fig. 1e, moderate adsorption of O and N prefers NH3 generation, strong adsorption of O and N results in N2 formation, and the weak adsorption intensity of N and O tends to produce NO. They

proposed that Co and Rh are ideal candidates for electrochemical NO₃⁻-to-NH₃ conversion.⁴⁹

Furthermore, the d-band model is commonly used for describing and anticipating the selectivity of the NO₃⁻RR. The d-band center (E_d) is related to the adsorption strengths of intermediates, which increase with the E_d of active sites approaching the Fermi level. NO2- is regarded as a major byproduct of NO_3 -to-NH₃ conversion. A more negative $\Delta(G_{NO^*})$ $-G_{NO_a^*}$) is desired for increasing the preference toward nitrite reduction to nitric oxide. As E_d approaches the Fermi level, $\Delta(G_{NO^*} - G_{NO^*})$ becomes increasingly negative, and *NO₂ tends to be reduced to *NO. 50,51 Subsequently, the adsorbed nitric oxide (*NO) serves as a critical intermediate in determining the selectivity between nitrogen/oxides and ammonium or hydroxylamine.⁵² NH₃ could be generated from *NO via two pathways: one is the so-called Eley-Rideal-like proton-coupled electron transfer, in which *NO was reduced to hydroxylamine (*NH₂OH), ⁵³ and the other involves the dissociation of *NO into *N and *O and the Langmuir-Hinshelwood-like hydrogenation of *N by *H to NH₃. 54,55 The latter has been proposed to favor NH₃ production, namely, dissociative adsorption of nitric oxide is desired for NO₃-to-NH₃ conversion. Theoretical studies revealed that the dissociation activation barriers of *NO decrease with increasing its adsorption strength, suggesting that the E_d of active sites should be close to the Fermi level to activate the dissociation of nitric oxide for NH3 formation.50

On the other hand, the HER is the major competitive reaction of the NO₃⁻RR, which also retards the selectivity and FE of NO₃-to-NH₃ conversion. Hu et al. found that the pH influences the competition between the HER and the NO3-RR on the (100), (111), and (110) facets of Cu. As depicted in Fig. 1f, the Gibbs free energies (ΔG) of intermediates along pathways on Cu(111), Cu(100), and Cu(110) are dependent on the pH of the electrolyte, and the ΔG -pH plots of the potential ratedetermining step of the NO₃⁻RR and HER are shown in Fig. 1g (i-iii). The pH range corresponding to the triangle zone is suitable for the NO₃⁻RR, and the critical pH values of the NO₃⁻RR are 5.63, 1.42 and 7.89 for Cu(111), Cu(100) and Cu(110), respectively. Fig. 1g(iv) suggests that Cu(100) works at pH ranging from 1.42 to 5.63 while Cu(111) works at pH ranging from 5.63 to 14, indicating that Cu(111) works more effectively. Moreover, the product selectivity is highly dependent on the applied potential, and a negative potential is needed for NH₃ generation while the HER tends to retard the FE and selectivity of NH₃.⁵⁶ The above results verify that the NO₃⁻RR is potential-dependent and pH-sensitive; thus, seeking HER inert materials for constructing NO₃⁻RR electrocatalysts which can work in a wide pH and potential range is highly desired.

Fundamental insights of metallic titanium and titanium oxides

Titanium (Ti) is not only a HER inert element but also one of the most abundant elements in the Earth's crust. Metallic Ti or its alloys and oxides have been widely used in aerospace, photocatalysis, energy storage, and other fields due to their advantages of low cost, superior mechanical strength, unique electronic structure, excellent corrosion resistance and stability, etc.57 Some studies revealed that Ti-based inorganic nanomaterials, majorly, metallic Ti- and TiO2-based nanomaterials exhibited impressive performances of electrochemical NO₃-to-NH₃ conversion. The exploration of lowcost and highly-efficient Ti-based electrocatalysts for the conversion of NO₃-to-NH₃ has attracted much attention. In this part, we systematically review the structure of metallic Ti and TiO₂ to help rationalize the design of Ti-based nanomaterials for electrochemical NO₃⁻-to-NH₃ conversion.

3.1. Metallic Ti

Metallic Ti is a silver-white transition metal with a high melting point of 1660 \pm 10 °C, a low density of 4.506 g cm⁻³, and excellent corrosion resistance. The valence electronic configuration of Ti is [Ar]3d²4s². There are two isomers of titanium: α-Ti and β-Ti; their crystallographic structures are depicted in Fig. 2a and b, respectively. α-Ti belongs to the hexagonal crystal system with an atomic space utilization rate of 74%, while β-Ti presents body-centered cubic dense packing with a utilization rate of 68%. The transition temperature of the above isomers is 882.5 °C, α-Ti is stable below 882 °C, and β-Ti is stable between 882 °C and the melting point; thus α -Ti is the common form in reality. ^{58,59} The work function (Φ shown in Fig. 1c) of metallic Ti is 4.33 eV, lower than those of Co (5 eV), Cu (4.65 eV), Fe (4.5 eV), and Ru (4.71 eV) usually regarded as electrocatalysts for the NO₃-RR,60 suggesting that Ti presents a high-energy Fermi level and may be an ideal candidate with a lower overpotential of the NO₃⁻RR. However, titanium usually forms a stable oxide layer on its surface when exposed to air, and the active sites should be carefully identified while using metallic Tibased materials as catalysts.

3.2. Titanium oxides

TiO₂ belongs to the category of typical semiconductors.⁶¹ There are many kinds of crystallographic structures, including rutile, anatase, brookite and TiO2(B), and several metastable polymorphs, such as TiO2 (H), TiO2 II, and perovskites, have been artificially synthesized.61 Metastable phases are rarely observed as stable electrocatalysts, and the TiO2 (B) phase is less common. Thus, they will not be discussed in this review. Anatase and rutile have more comprehensive applications because they are more stable than brookite,⁵⁷ hence they are emphatically discussed. Generally, rutile is the most stable phase and is usually synthesized by hightemperature deposition or annealing. Anatase-phased nanomaterials are commonly obtained by solution-based or lowtemperature vapor deposition systems.61 Anatase and rutile phases present tetragonal structures (as depicted in Fig. 2c and d) with slightly distorted TiO6 octahedra as a fundamental building block, 57,62,63 and have bandgaps of 3.2 and 2.96 eV, respectively.^{57,64} A large bandgap results in poor

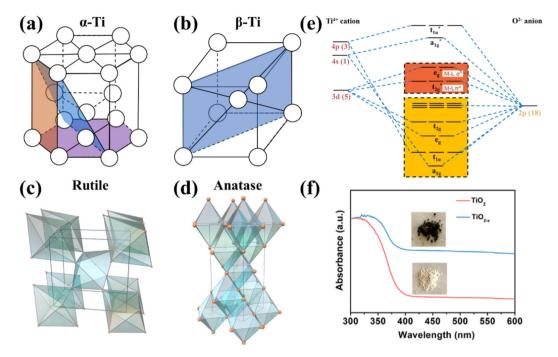


Fig. 2 Unit cells of (a) α -Ti, (b) β -Ti, (c) rutile TiO₂ and (d) anatase TiO₂. ⁶¹ Reproduced from ref. 61 with permission from American Chemical Society, copyright 2014. (e) Molecular orbitals of the octahedral TiO₆ unit. (f) UV-vis absorption spectra (the insets are optical photographs) of TiO₂ and TiO_{2-v}. 65 Reproduced from ref. 65 with permission from American Chemical Society, copyright 2020.

electron conductivity of TiO2. Based on the ligand-field theory, the orbital diagram of the TiO6 octahedral unit is shown in Fig. 2e. Since the valence electronic configuration of ${\rm Ti}^{4+}$ is [Ar]3d⁰4s⁰, the bonding orbitals (a_{1g}, t_{1u}, e_g and t_{2g}) are mainly contributed by the 2p orbitals of O^{2-} , and the unoccupied anti-bonding orbitals (a1g*, t1u*, eg* and t2g*) are mainly contributed by the 3d, 4s and 4p orbitals of Ti⁴⁺. Therefore, the valence band maximum and the conduction band minimum originate from O 2p and Ti 3d, respectively.

Oxygen vacancies (OVs) are easily created on the surface of TiO₂, thereupon leading to the formation of unsaturated Ti³⁺ sites and nonstoichiometric TiO_{2-x} (0 < x < 1). According to the stoichiometry theory for semiconductors, TiO2-x belongs to an n-type semiconductor with a narrow bandgap compared to TiO_2 , ^{57,66} and the electrons in TiO_{2-x} are easily excited from the valence band to the conduction band to form holes and carriers. Therefore, TiO_{2-x} can absorb visible light to show color (Fig. 2f), and the electron conductivity of TiO_{2-x} is strengthened compared to that of intrinsic TiO2.65 Furthermore, the Fermi level could be upshifted by transforming the intrinsic semiconductor to an n-type semiconductor, which is desired for reducing the overpotential of the NO₃⁻RR, as discussed in section 2.2. On the other hand, the electron conductivity of TiO2 can also be modified by heteroatom doping. By controlling the doping pattern, intrinsic TiO2 can be transformed to an n- or p-type semiconductor. 57,67 The bandgap, electron conductivity, and the Fermi level could be regulated subsequently.

Nitrate-to-ammonia conversion performance of Ti-based nanocatalysts

4.1. Metallic Ti-based electrocatalysts

Considering that titanium exhibits a higher Fermi level, poor HER activity and high corrosion resistance, as discussed in section 3, some researchers tried to explore metallic Ti-based electrocatalysts for NO3 -to-NH3 conversion.

Fajardo et al. studied the NO₃ RR on a series of transition metals Ti, Fe, Co, Ni, Cu, Zn, and Sn by electroreduction of 100 mg L^{-1} NO_3^{-} -N in 50 mM Na_2SO_4 at 20 mA cm⁻² and 360 min of treatment time. They found that the NO₃ degradation on the above materials conformed to the pseudo-firstorder characteristic. The selectivity of N₂ for Ti is almost negligible, the FE_{NH}, of Ti is close to those of Co and Fe and higher than those of Ni, Cu, Zn and Sn, and the reaction kinetics of Ti is even comparable to that of Pt. The above results suggest that NH₃ generation on Ti is electrocatalytically preferential over N2 evolution.36 To further reveal the rule of the NO3-RR on Ti, McEnaney et al. systematically studied the effect of pH, nitrate concentration, and applied potential on the FENH3 of the NO₃⁻RR on the Ti electrode. The heatmaps constructed by an entire grid of electrolyte conditions and FE_{NH}, shown in Fig. 3a suggest that (1) more extreme pH values give significantly higher total current densities than those of moderate pH, (2) lower pH generally corresponds to higher FE_{NH}, and (3) in moderate base and moderate acid electrolytes, moderate

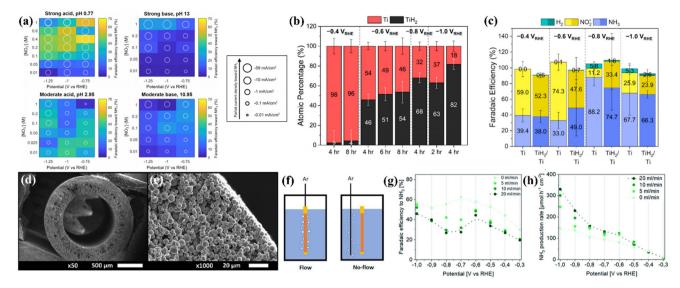


Fig. 3 (a) Heatmap plots at four distinct pH values showing faradaic efficiency to NH₃ by varying applied potentials and nitrate concentrations. Each grid block displays the data from a 30 min potentiostatic experiment performed at the indicated pH, nitrate concentration, and applied potential.¹³ Reproduced from ref. 13 with permission from American Chemical Society, copyright 2020. (b) Ti atomic percentages of the Ti foil cathode after the NO₃⁻RR obtained from the EXAFS modeling. (c) Faradaic efficiencies toward the production of ammonia, nitrite, and hydrogen gas on unamended Ti and TiH_2/Ti electrodes.³⁸ Reproduced from ref. 38 with permission from American Chemical Society, copyright 2022. (d) SEM images the cross section of a Ti hollow fiber electrode at different magnifications; (e) gas flow configurations of the working electrode compartment; (f) performance of Ti hollow fiber electrodes for the electrochemical reduction of NO₃⁻ to NH₃ in 0.1 M HClO₄ using 50 mM KNO₃; potential- and Ar flow ratedependent (g) faradaic efficiency and (h) production rate toward ammonia.³⁷ Reproduced from ref. 37 with permission from the Royal Society of Chemistry, copyright 2022.

nitrate concentrations (between 0.025 and 0.2 M NO₃⁻) generate higher FE_{NH}. According to the above results, the authors used an electrolytic cell constructed by using a Nafion membrane divider with 0.1 M HNO₃/0.3 M KNO₃ electrolyte for the NO₃⁻RR, and achieved the highest FE_{NH₂} of 82%. Importantly, the authors first revealed that titanium hydride (TiH_x) is generated on the Ti electrode after the reaction. 13 Subsequently, Liu et al. focused on this issue and utilized highly surface-sensitive techniques such as ex situ grazing-incidence X-ray diffraction (GIXRD) and total electron yield X-ray absorption spectroscopy (TEY XAS) to deeply elucidate the self-reconstruction of metallic Ti foil. The GIXRD result suggests that α -Ti was the primary phase of unamended Ti foil; the diffraction patterns for TiH_x appeared after the NO₃⁻RR was performed at -0.6 V vs. RHE in 0.1 M HClO₄ + 0.8 mM KNO₃. The quantitative analysis of Ti K-edge TEY XAS measurements further suggested that more negative applied potential and longer applied durations promoted near-surface TiH2 enrichment, as depicted in Fig. 3b. The electrochemical NO₃⁻RR performance of unamended Ti and preformed TiH2/Ti electrodes was assessed with 30 min chronoamperometry experiments at -0.4, -0.6, -0.8, and -1.0V vs. RHE in 1 M NaClO₄ + 10 mM HNO₃, GIXRD of unamended Ti electrodes after such a short-time chronoamperometry showed that self-reconstruction could not be observed, and the NO₃-RR performance of unamended Ti could be attributed to the intrinsic Ti foil. Surprisingly, the FE_{NH}, FE_{NO₂}- and FE_{H₂} of unamended Ti and preformed TiH₂/Ti electrodes depicted in Fig. 3c followed a similar trend with almost identical partial current densities of NH₃.³⁸ Thus, the mystery of whether the active species of the metallic Ti electrode for the NO₃⁻RR is Ti, Ti hydride, or a combination of species remains under debate, and the above two studies remind us that the self-reconstruction during the NO₃⁻RR cannot be neglected, even if Ti-based materials are usually regarded as stable components. It should be highlighted that the near-surface structure is important for the NO₃⁻RR.

A representative study about electrochemical NO₃⁻-to-NH₃ conversion on metallic Ti-based nanomaterials reported by Krzywda et al. suggested that a tubular porous Ti electrode prepared by dry-wet spinning exhibited interesting catalytic behaviors. The as-prepared Ti electrode exhibited uniform pore distribution over the entire length of the fiber (Fig. 3d and e). They introduced a flow of inert gas exiting the wall of the hollow fiber electrode (Ar flow through the hollow fiber electrode from the inside to the outside, denoted as flow-through conditions), as illustrated in Fig. 3f. The current density of tubular porous Ti electrodes with flow-through conditions is higher than that with no-flow (Ar was introduced through an external sparging line next to a hollow fiber electrode) and vigorous magnetic stirring conditions. This result excluded the possibility that enhanced current density originated from the bubbling induced convective flow. Although the flow-through conditions decreased the FE_{NH}, (Fig. 3g), the yield rates and partial current densities of NH₃ eventually improved (Fig. 3h). The authors suggested that the flow-through conditions promote the transport of protons and nitrate towards the electrode, thus increasing the catalytic current density. However, the flow-through conditions take NO and N2O away from the solution, promote the homogeneous reaction of NO2 and NH₂OH to NO and N₂O, hinder the consecutive electrochemical reduction of NO2- and NH2OH towards NH3, and eventually result in a decrease of FENH, 37 Furthermore, Tarpeh et al. constructed a representative flow-cell configuration with a polycrystalline titanium electrode for the NO₃⁻RR and revealed that NO2- and NH3 accounted for almost all NO₃⁻RR products, the selectivity was flow rate dependent, and NH₃ was favored at the lowest flow rate. The above results suggested that the NO₃ RR was subject to mass transport limitations.68

4.2. TiO₂-based electrocatalysts

TiO₂ is suitable as a substrate for loading active materials due to its low cost, non-toxic nature and corrosion resistance. The electrons in TiO2 can be excited from the valence band to the conduction band, and the electrons and holes are able to diffuse to the semiconductor surface for participating in the reaction; thus, modulating the valence electronic structure is an alternative for narrowing the bandgap and improving the electron conductivity of intrinsic TiO2. In this section, three common strategies for modulating the NO₃⁻-to-NH₃ conversion performances of TiO₂based nanomaterials including heteroatom doping, creating oxygen vacancies and heterostructures will be introduced.

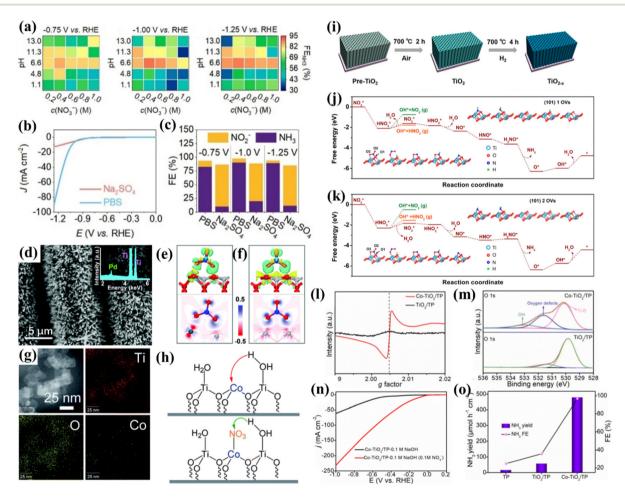


Fig. 4 (a) Heatmaps of FE_{NH}, in electrolyte solution with different NO₃⁻ concentrations and pH values under three applied potentials; comparison of NO₃⁻RR activities in 1.0 M PBS and 1.0 M Na₂SO₄ with 0.4 M KNO₃, (b) LSV curves, (c) FE_{NH.}; ³⁹ reproduced from ref. 39 with permission from Wiley-VCH, copyright 2022; (d) SEM images and the EDX spectrum (inset) of Pd/TiO2 nanoarrays; (e and f) 3D and 2D electron density difference mappings for the optimized (e) Pd/TiO₂-NO₃⁻ and (f) TiO₂-NO₃⁻ structures;⁴⁰ reproduced from ref. 40 with permission from the Royal Society of Chemistry, copyright 2021; (g) EDS elemental mapping images of Co/TiO₂ NSs; (h) proposed hydrogen-activated routes and the corresponding hydrogen acceptors in the HER and NO₃-RR processes; ⁴¹ reproduced from ref. 41 with permission from the Royal Society of Chemistry, copyright 2022; (i) schematic illustration for TiO_{2-x} synthesis; calculated free energy changes of the nitrate reduction reaction on the TiO₂ (101) surface with (j) one, and (k) two oxygen vacancies in one 1 x 3 slab at 0 V vs. RHE;⁶⁵ reproduced from ref. 65 with permission from American Chemical Society, copyright 2020; (I) EPR spectra and (m) O 1s regions of Co-TiO₂/TP and TiO₂/TP; (n) LSV curves of Co-TiO₂/TP in 0.1 M NaOH with and without 0.1 M NO₃⁻; (o) NH₃ yields and FEs of Co-TiO₂/TP, TiO₂/TP, and bare TP at -0.5 V vs. RHE. 42 Reproduced from ref. 42 with permission from The Royal Society of Chemistry, copyright 2022.

Firstly, the electrochemical NO₃⁻-to-NH₃ conversion behavior of intrinsic TiO2 must be clarified. Xu et al. synthesized anatase TiO2 and systematically studied its NO3-RR behavior affected by electrolytic conditions, including pH values, nitrate concentration, and the type of electrolyte. The heatmap in Fig. 4a shows that the relationship between FE_{NH}, and the NO₃ concentration exhibits an approximate volcano shape, and the relationship between FE_{NH}, and the pH of the electrolyte also obeys a similar tendency. According to the heatmap, higher FE_{NH}, could be achieved in neutral media of 0.4 M $KNO_3 + 1.0 M PBS (pH = 6.6)$, unlike metallic Ti, which is more inclined to produce NH₃ in acidic electrolytes (Fig. 3e). This phenomenon demonstrates that NO₃-RR behaviors on both metallic Ti and TiO2 are pH-sensitive. To further understand the insightful effect of the electrolyte, the electrolyte was switched into another neutral solution of 0.4 M KNO₃ + 1.0 M Na_2SO_4 (pH = 6.7). Fig. 4b and c suggest that TiO_2 displayed a much lower catalytic current density, FE_{NH}, and partial current density of NH₃ in an electrolyte of 0.4 M KNO₃ + 1.0 M Na₂SO₄. To reveal the essence of this phenomenon, the authors tested the pH values of two electrolytes after 30 min electrolysis. Consequently, PBS only increased 0.3 pH units while in Na₂SO₄ solution the pH drastically increased from 7 to 13. Therefore, the pH of the electrolyte could be maintained in a suitable range for NH3 formation in the buffer. However, the pH of Na₂SO₄ quickly ascended to an inferior area shown in Fig. 4a, which inhibited the NH₃ formation. Moreover, the authors proposed that faster proton transport in PBS is responsible for the larger catalytic current density. This effect could increase the proton concentration on the electrode surface and facilitate the hydrogenation of NO₃⁻ to NH₃.³⁹ This study preliminarily revealed the NO₃⁻RR behavior on TiO₂ and demonstrated optimal electrochemical conditions for electrochemical NO₃⁻-to-NH₃ conversion using TiO₂ as an electrocatalyst.

4.2.1. Heteroatom doping. Heteroatom doping modifies the valence electronic structure of TiO2 by elemental interaction, which is a straightforward strategy for modulating the electrochemical performances.

A representative study of heteroatom doping is presented by Guo et al., who successfully doped Pd atoms into TiO₂ (Fig. 4d) for NO₃⁻-to-NH₃ conversion. They proved that the lattice stress caused by doping Pd atoms into the TiO2 phase creates dislocations and distortions forming the active sites of the catalytic reactions. DFT studies revealed that the HOMO of NO₃⁻ is located at the O atoms. Fig. 4(e and f) further illustrate that the introduction of Pd atoms makes the electrons of TiO2 transfer to Pd atoms, forming an electron-rich accumulation on Pd, promoting electron transfer to the oxygen atoms of nitrate ions, and eventually accelerating the dissociation of the N-O bond. Meanwhile, a novel Zn-nitrate cell system was assembled for the first time based on the Pd/TiO₂ catalyst as the cathode and metal Zn as the anode. The battery delivers remarkable dual functions, i.e., it generates electricity and produces NH3 at the same time with a peak power density of 0.87 mW cm^{-2} and a high FE_{NH₂} of 81.3%. This study demonstrated the feasibility of the galvanic nitrate-based cell, which

broadens the field of Zn-based batteries. 40 Xu et al. synthesized Co(II)-decorated TiO2 nanosheets (Fig. 4g) exhibiting excellent nitrate performance with an FE and NH3 yield of 97.4% and 0.348 mmol cm⁻² h⁻¹ respectively in 1.0 M phosphate buffer solution (PBS, pH = 6.53). The inhibited HER mechanism was also investigated. They demonstrated a proton pumping mechanism for thermodynamically facilitating proton transfer in the presence of nitrate as follows: in the HER, the hydrogen/ proton acceptor should be the Co atoms on Co/TiO2 NSs, while the hydrogen/proton acceptor switches into the N/O atoms of nitrate adsorbed on the Co sites in the NO₃⁻RR, and Ti serves as active sites for water dissociation, as depicted in Fig. 4h. Due to the negative charge and delocalized conjugated π electron cloud on NO₃⁻, the barrier of proton transportation from H_2O to NO_3^- (0.508 eV) is much lower than that to Co^{2+} (0.805) eV), thus the HER could spontaneously switch to the NO₃⁻RR and the energy input for the NO3-RR could be lowered simultaneously.41

4.2.2. Oxygen vacancy. The OVs, as an anionic defect, provide electrons to the catalyst surface and endow the lattice oxygen with a higher electron density, making it easier to participate in the catalytic reaction. OVs are easy to form on TiO₂ and they can vary the coordinative structure and the valence state of Ti on the surface (as discussed in section 3.2). Creating OVs is also a common strategy for optimizing the electronic structure of TiO2. Moreover, the increase of OVs in TiO₂ is closely related to the NO₃⁻RR activity.

Jia et al. synthesized oxygen vacancy-enriched TiO_{2-x} nanotubes by hydrogen reduction (Fig. 4i) and the as-prepared TiO_{2-x} nanotubes were regarded as an efficient electrocatalyst for NO₃-to-NH₃ conversion. DFT calculations suggested that introducing OVs on the surface of TiO2 resulted in the occupation of excess 3d electrons of Ti, and the Fermi level could be moved into the conduction band minimum, eventually giving rise to the metallic behavior of TiO_{2-x} and then improving the electron conductivity. This study revealed that OVs are the adsorption sites filled by the oxygen atoms in nitrate, which weaken the N-O bonding. By comparing the Gibbs free energy diagram of TiO2 (101) with one and two vacancies, the latter needed a higher reaction barrier for the formation of HNO2 (Fig. 4j and k), thus suppressing the generation of byproducts.65

The enhancement of oxygen vacancies by metal doping has also received much attention. Song et al. utilized electrochemical anodic oxidation and electrodeposition to synthesize a highly dispersed Cu-doped TiO2 nanotube array (Cu/TNTA) cathode with a high electrocatalytic NO3-RR efficiency and long-term stability. They discovered that just doping trace amounts of Cu into TiO2 could activate more OVs during the NO₃ RR process. The OVs highly promoted charge transfer between the NO₃ and the electrocatalyst, thus reducing the energy barrier of the NO₃⁻RR, eventually reducing the overpotential required for triggering the NO₃-RR and improving the yield rate of NH₃ and FE_{NH₃}.⁶⁹ Similarly, Yu's group synthesized a unique structure of Cu clusters homogeneously supported on TiO_2 nanosheets with abundant OVs (10Cu/ TiO_{2-x}).

DFT calculations suggested that OVs should be the strong adsorption sites of NO₃⁻. The N-O bond of NO₃⁻ breaks automatically during the adsorption process, and the by-products of NO2 or HNO2 are suppressed by OVs with higher reaction barriers, suggesting that the positive effect of interfacial OVs optimized the NO₃⁻RR on 10Cu/TiO_{2-x}. ⁷⁰ Zhao *et al.* skillfully utilized Na₂Ti₂O₅ grown on a Ti plate as a precursor to prepare CoTi₂O₅ by an ion exchange strategy, and then the Co-doped TiO₂ nanoribbon array grown on the Ti plate (Co-TiO₂/TP) was achieved by Ar-annealing of CoTi₂O₅. XRD patterns suggested that Co in the lattice of TiO₂ reduced the crystal quality. Moreover, the EPR and XPS results verified that OVs were introduced into TiO2 after Co doping (Fig. 4l and m). DFT calculations revealed that Co-TiO2 shows a higher impurity level near the Fermi level compared to TiO2, which facilitates charge transfer at the interface. Co doping and OVs also reduced the Gibbs free energy barrier from *NO to *N, which was regarded as a potential determining step in these systems. These advantages enabled Co-TiO2/TP to attain an improved onset potential compared to TiO2/TP, a large NH3 yield of 1127 μ mol h⁻¹ cm⁻² at -0.9 V and a high FE_{NHa} of 98.2% at -0.5 V vs. RHE (Fig. 4n and o).42

The above Cu/Co induced OVs generated in TiO2 could be attributed to the charge difference between Cu^{2+/}Co²⁺ and Ti⁴⁺. Doping Cu^{2+/}Co²⁺ into the TiO₂ lattice must create OVs to compensate for the missing positive charge while remaining charge neutral.⁷¹

4.2.3. Heterostructure. Stacking any two dissimilar materials with different Fermi levels (work functions, Φ shown in Fig. 1c) to form a heterostructure could form a built-in electric field (BEF). As shown in Fig. 5a, the Fermi level (or work function) represents the electrochemical potential of electrons in the materials, and the difference in Fermi levels results in electrons crossing the heterostructure from the material with a higher Fermi level to the other to form a BEF until their Fermi levels reach equilibrium. Therefore, the electronic interaction that originated from the rectifying effect can also effectively modify the valence electronic structure of TiO2-based materials. Based on the above discussions, a series of studies achieved impressive results.

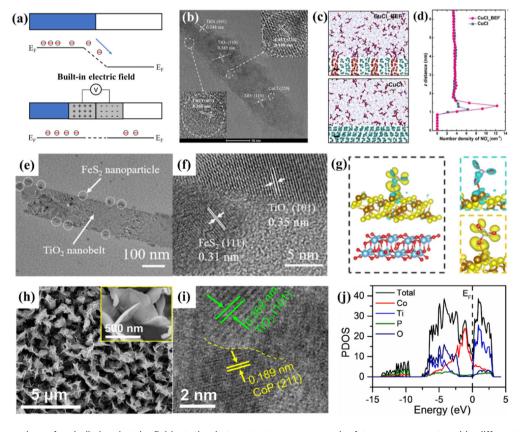


Fig. 5 (a) The formation of a built-in electric field at the heterostructure composed of two components with different Fermi levels. (b) Representative HRTEM image of CuCl_BEF. (c) Molecular dynamics simulation of CuCl and CuCl_BEF in KNO₃ (100 mg L⁻¹) solution. Scale bar, 0.5 nm. (d) Distribution of NO_3^- along the z-axis electrode distance based on the molecular dynamics simulation. ⁷² Reproduced from ref. 72 with permission from Wiley-VCH, copyright 2022. (e) TEM and (f) HRTEM images of FeS2@TiO2/TP. (g) Charge density difference of FeS2@TiO2 with adsorbed NO₃⁻, where yellow and cyan color indicate electron accumulation and depletion, respectively, and the isosurface values are set to 0.000213 Å⁻³.73 Reproduced from ref. 73 with permission from The Royal Society of Chemistry, copyright 2022. (h) SEM images and (i) HRTEM images of CoP/TiO₂. (j) Calculated PDOS of CoP/TiO₂. ⁷⁶ Reproduced from ref. 76 with permission from Elsevier, copyright 2022.

Sun et al. stacked CuCl (111) and rutile TiO₂ (110) layers together (Fig. 5b), a BEF could be induced by electron transfer from TiO2 to CuCl due to the difference in their Fermi levels, and the BEF strength was roughly estimated to be 8×10^8 V m⁻¹. Molecular dynamics simulation and finite element analysis suggested that the BEF accumulated NO₃ in the diffusion layer near the surface of the electrocatalyst (Fig. 5c and d). This study demonstrated that the BEF increased the free energy of *ON, resulting in a great decrease of ΔG of the potential determining step. This phenomenon could be elucidated as the BEF resulted in electron richer Cu(1), which suppressed the electron donation from *NO but facilitated the back donation to the π^* anti-bonding orbital of *NO, thus, destabilizing the N-O bond of *NO. The above advantages endowed the heterostructure with an NH3 selectivity of 98.6% and a yield rate of 1.82 mg h⁻¹ cm⁻² at -1.0 V vs. RHE in $100 \text{ mg L}^{-1} \text{ NO}_{3}^{-} + 0.5 \text{ M Na}_{2}\text{SO}_{4}^{-72}$

Wang et al. reported a heterostructure of an FeS2 nanoparticle-decorated TiO₂ nanobelt array supported on a titanium plate (FeS2@TiO2/TP), as depicted in Fig. 5e and f. They proved that the abundant heterostructures endowed FeS₂@TiO₂/TP with excellent electrocatalytic performance with an NH₃ yield of 860.3 mmol h⁻¹ cm⁻² and a FE_{NH₃} of 97% at -0.4 V vs. RHE in 0.1 M NaOH + 0.1 M NO₃. Furthermore, they elucidated the positive effect of the FeS2@TiO2 heterostructure by DFT studies. The charge density difference and partial density of states suggested that the electrons were spontaneously transferred from TiO2 to FeS2 (Fig. 5g). The corresponding charge accumulation and depletion endowed the FeS₂@TiO₂ interface with local nucleophilic and electrophilic regions, thus favoring the adsorption of targeted species. Moreover, such a heterostructure achieves the targeted adsorption of molecules by electrostatic interaction, promoting the charge transfer between the active site and the O atom of NO₃⁻, resulting in the activation of the N-O bond.⁷³ Similar results are obtained for the CoS2@TiO2/TP heterostructure synthesized by Zhao et al. They utilized XPS to prove the electron transfer from TiO₂ to CoS₂, and the heterostructure eventually resulted in an improved electrocatalytic performance of CoS₂@TiO₂/TP with a high FE_{NH}, and NH₃ yield rate of 92.80% and 538.21 mmol h⁻¹ cm⁻², respectively.⁷⁴

Based on the conclusion that CoP is proven to be an effective and stable electrocatalyst for NO₃-to-NH₃ conversion, ⁷⁵ Deng et al. designed a heterostructure of CoP/TiO₂@TP, as depicted in Fig. 5h and i. Interestingly, XPS proved that the BEF of the CoP/TiO2 heterostructure was established by the electrons transferring from CoP to TiO2, which is reversed for the heterostructures mentioned above. This phenomenon should be attributed to the fact that CoP exhibits the metallic character of a continuous electron occupation state at the Fermi level, and the work function of CoP should be lower than that of TiO₂ with semiconductor properties. Moreover, the heterostructure displayed an impurity level near the Fermi level compared with CoP and TiO2, indicating that more charge carriers were created (Fig. 5j), thereby enhancing the electron conductivity of CoP/TiO₂. The Gibbs free energy

diagram suggested that the potential-determining step of conversion of NO₃⁻ to *NO₃ presented a lower energy barrier in the CoP/TiO₂ heterostructure. Therefore, such CoP/TiO₂@TP attained an excellent FENH, of 95.0% with a large NH3 of 499.8 μmol h⁻¹ cm⁻².⁷⁶

4.3. New generation Ti-based MXene and single atomic catalysts

In addition to the traditional metallic Ti- and TiO2-based nanomaterials, MXene attracts much attention in electrocatalysis. Moreover, single atomic catalysts (SACs) are emerging as fantastic materials due to their ultra-high active site utilization and outstanding catalytic activity. Therefore, developing Tibased MXene and SACs for electrochemical NO₃-to-NH₃ conversion could be a prevailing trend, although related studies are still rarely reported. In this section, we summarized some preliminary experimental and theoretical achievements of Tibased MXene and SACs for the NO₃-RR and hope to provide inspiration for designing novel Ti-based electrocatalysts.

4.3.1. Ti-based MXene for the NO₃ RR. Transition metal carbides, nitrides, and carbonitrides with 2D structures, known as MXenes, were first reported in 2011 and received much attention due to their advantages of large surface area, structural flexibility, and surface tunable chemistry.⁷⁷ MXenes are commonly synthesized by top-down etching of layered ternary MAX phases with the formula $M_{n+1}AX_n$ (n = 1-4) as precursors. Here, "M" represents early transition metals, "A" is the elements of group 13-14, and "X" is C or/and N. In the MAX precursors, the edge-sharing octahedron of $[MX_6]$ extends laterally to form an "M-X" layer, while "A" layers are located on both sides of the "M-X" structures to form a sandwich-like structure. By removing the "A" layers from the MAX phase, 2D MXenes with alternately arranged structures "M" and "X" were formed. Moreover, -F, -OH, -Cl could also be coordinated to the surface of the M layer to form abundant surface terminations (denoted as Tx). Therefore, MXene is always written as $M_3C_2T_x$. ⁷⁸ $Ti_3C_2T_x$ is the most widely studied MXene.

Li's group investigated the possible mechanism and catalytic activity of electrochemical NO3-to-NH3 conversion on Ti₃C₂ MXene by theoretical calculations. They proposed that the reactive pathway of $NO_3^- \rightarrow *NO_3 \rightarrow *NO_2 \rightarrow *NO \rightarrow *N \rightarrow *NO_3 \rightarrow$ *NH \rightarrow *NH₂ \rightarrow *NH₃ \rightarrow NH₃(g) is thermodynamically preferable to that of $NO_3^- \rightarrow *NO_3 \rightarrow *NO_2 \rightarrow *NO \rightarrow *NOH \rightarrow$ *NHOH \rightarrow *NH \rightarrow *NH₂ \rightarrow *NH₃ \rightarrow NH₃(g). *NO₃ and *NO₂ prefer to adsorb on Ti₃C₂ MXene in parallel adsorption modes due to the O atoms of *NO3 and *NO2 being inclined to bond with Ti, resulting in drastic distortion of *NO3 and *NO2 (Fig. 6a). Moreover, the Gibbs free energy suggests that the NO₃⁻RR prefers to occur on the basal plane rather than the edge plane of Ti₃C₂ MXene because basal plane sites present lower energy barriers for the potential determining step (Fig. 6b). The termination effects of $Ti_3C_2T_2$ (T = O, OH, H, Cl, F, representing the terminal atoms located at the surface of Ti₃C₂ MXene) for NO₃⁻-to-NH₃ conversion were also elucidated in detail. As illustrated in Fig. 6c, the NO₃⁻RR is more competitive than the HER on the O-terminated Ti₃C₂O₂ with OVs

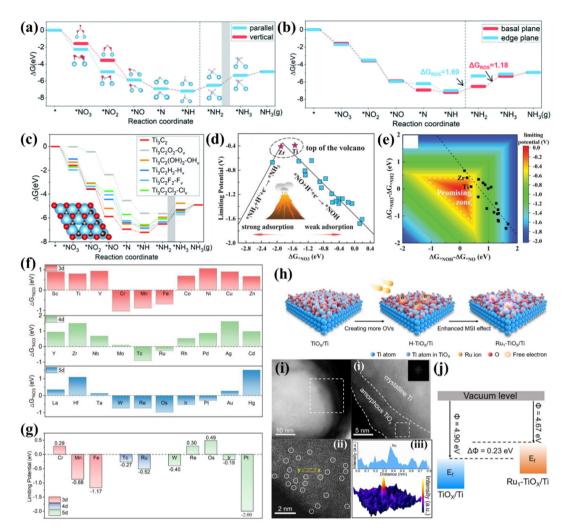


Fig. 6 (a) Gibbs free energy diagram of NO_3^- -to- NH_3 on Ti_3C_2 in vertical and parallel * NO_3 adsorption modes. The grey zone means that * $NH_2 \rightarrow NO_3$ and the grey zone means that * NO_3 and * NO_3 *NH₃ is the RDS. (b) Gibbs free energy diagram of NO₃⁻-to-NH₃ on the basal plane and edge plane of Ti₃C₂. (c) Gibbs free energy diagram of the reaction pathway of $Ti_3C_2T_2$ - T_v , and the grey zone highlights the step *NH₂ \rightarrow *NH₃ as the RDS. ⁷⁹ Reproduced from ref. 79 with permission from The Royal Society of Chemistry, copyright 2022. (d) NO₃⁻RR volcano plot of TM/g-CN with a descriptor of $\Delta G_{^{+}NO_{3}}$. (e) Contour plot of limiting potential as a function of two potential-determining steps (*NO + H $^+$ + e $^ \rightarrow$ *NOH and *NH $_2$ + H $^+$ + e $^ \rightarrow$ *NH $_3$). The promising zone is highlighted. Reproduced from ref. 44 with permission from Wiley-VCH, copyright 2020. (f) Gibbs free energy change of NO_3^- absorption on $Ti_3C_2O_2$ - TM_{SA} . (g) Summary of limiting potentials on Ti₃C₂O₂-TM_{SA}.⁸¹ Reproduced from ref. 81 with permission from Springer Nature, copyright 2023. (h) Schematic illustration of preparing the Ru₁-TiO_x/Ti electrode via an inherent surface oxide anchoring strategy. (i) (i and ii) Low-magnified HAADF-STEM images of Ru₁-TiO_x/Ti. (iii) Atomic-resolution HAADF-STEM image of Ru₁-TiO_x/Ti; Ru single atoms are indicated by white circles. (iv) Line intensity profile (inset) taken along the yellow dashed rectangle in HAADF-STEM and the corresponding 3D surface intensity profile. (j) Schematic illustration of the work functions of Ru₁-TiO_x/Ti and TiO_x/Ti.⁸² Reproduced from ref. 82 with permission from Wiley-VCH, copyright 2022.

(denoted as Ti₃C₂O₂-O_v), and all free energy changes of NO₃⁻to-NH₃ on the Ti₃C₂O₂-O_v are negative, signifying that the termination effect of oxygen promotes the hydrogenation of nitrogen-containing intermediates. 79 Another study utilized Ti₃C₂T_x nanosheets as a promising molecular catalyst substrate. CuPc can be spontaneously dispersed on delaminated $Ti_3C_2T_x$ to overcome their large π -conjugated stacking. The prepared CuPc@MXene exhibited a high yield rate and selectivity for NH₃, which is superior to other counterparts of FePc@MXene, NiPc@MXene, and CoPc@MXene. DFT calculations suggested that NO₃-to-NH₃ conversion tends to obey the ONH pathway

because the Gibbs free energy required only 0.27 eV to form *ONH.80

4.3.2. Ti-based SACs for the NO₃⁻RR. Recently, SACs have become a frontier of research due to their outstanding catalytic performance and relatively simple coordinative structure. A typical structure of SACs denoted as M-N_x/C is a transition metal atomic site singly separated on nitrogen (N)-doped carbon (C)-based substrates. 83-86 Moreover, metallic oxides, 87 phosphides, 88 and sulfides 89 could also be used as substrates for anchoring the atomic metal sites. Recently, significant advances in SACs were achieved in water splitting and CO₂

reduction. However, Ti-based SACs designed for NO₃⁻-to-NH₃ conversion are currently rare. In this section, we summarized a theoretical prediction of the catalytic activity of Ti SAs and Tibased substrates for anchoring the noble metal SAs, to provide some inspiration for the design of Ti-based SACs for the NO₃⁻RR.

Niu et al. established several transition metal atoms from Ti to Au supported on graphitic carbon nitrides (g-CN) as representatives (TM/g-CN) to study the NO3-RR rule of SACs. They found that the adsorption energies of NO₃⁻ (ΔG_{*NO_3}), protons (ΔG_{*H}) , and the N₂ molecule (ΔG_{*N_2}) on TM/g-CN exhibited periodic regulations. Furthermore, they proposed that the N-end pathway is the most reasonable on TM/g-CN because the N-end adsorption of NO presents the lowest energy. Based on the above reactive pathway, the performance criteria of limiting potential on TM/g-CN were evaluated. A volcano plot of limiting potential vs. ΔG_{*NO} on TM/g-CN was proposed. As shown in Fig. 6d, too strong adsorption of NO₃⁻ results in a larger energy barrier in the step from *NH2 to *NH3. In contrast, too weak adsorption leads to a sluggish step from *NO to *NOH, and Ti/g-CN and Zr/g-CN stand exactly near the top of the volcano. Regarding selectivity, the large energy barriers prevented the formation of NO₂, NO, N₂O, and N₂ on Ti/g-CN, guaranteeing a high FE_{NH_3} of Ti/g-CN. In addition, the linear scaling relationship between $(\Delta G_{*NH_3} - \Delta G_{*NH_2})$ and (ΔG_{*NOH_3}) $-\Delta G_{*NO}$) hinders the exploration of more effective electrocatalysts (Fig. 6e), hence, a critical strategy to break such a scaling relationship is desired.44 Another study that predicts TM/ g-C₃N₄ (TM = Sc to Au, except Tc, Cd, and Hg) for the NO₃⁻RR also proposes a similar volcano plot and suggests that Ti/ g-C₃N₄ should be an ideal candidate with outstanding limiting potential and FE_{NH}, 90

Recently, Ti-based MXene and oxides are also predicted to be suitable substrates for anchoring SAs. Wang et al. screened out 30 single transition metal atoms (3d: Sc-Zn, 4d: Y-Cd, and 5d: La-Hg) anchored on Ti₃C₂O₂ by means of first principles calculations. They found that SAs with half-filled d orbitals (around d⁵) are favorable for NO₃⁻ activation due to high electronic states at the Fermi level (Fig. 6f). Further screening suggested that Cr, Re and Os SAs anchored on Ti₃C₂O₂ present negative free energy changes in the whole NO₃⁻-to-NH₃ conversion process and thus exhibit positive limiting potentials (Fig. 6g); hence, they are recognized as the most efficient candidates.66

An experimental study utilized Ti foil as a substrate to binder-free monolithic single-atom electrodes (MSAEs). Metallic Ti inevitably undergoes oxidation in air to form a thin metal oxide layer (TiO_x) with abundant dangling bonds and defects, thereby providing unique on-site hosts for the dispersion of SACs. A two-step annealing approach depicted in Fig. 6h was employed to successfully anchor Ru atoms into the TiO_x layer (Fig. 6i). The as-prepared MSAEs were named Ru₁-TiO_x/Ti. Anchoring of Ru atoms upshifted the Fermi level, as proven by the lower work function of Ru₁-TiO_x/ Ti compared to TiO_x/Ti, as shown in Fig. 6j. This characteristic endowed Ru₁-TiO_x/Ti with much improved catalytic current

density and FE_{NH}, at various applied potentials. The highest FE_{NH_2} and NH_3 yield rate of 87.6% and 22.2 mol g^{-1} were respectively achieved at −0.3 V vs. RHE for Ru₁-TiO_x/Ti.⁸²

Although DFT studies predicted Ti-based SACs to be outstanding candidates as electrocatalysts for NO₃-to-NH₃ conversion, there is still a lack of experimental achievement to fulfill the above results. Further synthesis strategies and performance studies should be conducted.

Conclusion and perspective

Emerging "hydrogen economy" and "carbon neutralization" have caused NH3 to be regarded as a carbon-free fuel and a portable energy carrier, endowing the electrochemical nitrate reduction reaction for NO₃-to-NH₃ conversion with a new opportunity for "green ammonia" synthesis. Compared to noble metal-based electrocatalysts, Ti-based electrocatalysts mainly composed of metallic Ti- and TiO2-based nanomaterials are attractive due to their inherent advantages of being nontoxic and cost-effective and having outstanding stability and HER inertness. Fundamental studies revealed that metallic Ti and TiO2 are more suitable for NO3-to-NH3 conversion over a wide pH range. Many strategies including morphological design, heteroatom doping, creation of OVs, and the construction of heterostructures have been developed for reducing the overpotential while improving the FE_{NHa}. To sum up, regulating the work function (for metallic Ti) or ionizing energy (for TiO2) to reduce the gap between the HOS and the LUMO of nitrogen-containing intermediates is essential for reducing the overpotential, modulating the d-band structure to optimize the binding energy of O- and N-containing intermediates is crucial for regulating the reactive route and faradaic efficiency of NH3, and designing secondary active sites for splitting H2O on Ti-based nanomaterials is also crucial for the hydrogenation of NO₃ and consequent intermediates in neutral and alkaline electrolytes. In particular, since potential induced self-reconstruction exists for Ti-based electrocatalysts, the use of in situ characterization techniques is encouraged to reveal the real active sites for the NO₃⁻RR.

Finally, the difficulties and opportunities of Ti-based nanocatalysts for electrochemical NO₃-to-NH₃ conversion are discussed.

The large bandgap of TiO₂ (~3 eV) results in poor electronic conductivity which is the major reason for low electrochemical activity. Narrowing the bandgap of TiO2 is an essential strategy to solve the problem of electronic conductivity. Therefore, characterizing the bandgap by UV-Vis spectroscopy, UPS, or DFT calculations is suggested to be performed for TiO2-based nanomaterials. Moreover, constructing metal/TiO2 heterostructures (such as Ti/TiO₂) and in situ compositing the TiO₂based nanomaterials with electronic conductive additives such as graphene, carbon nanotubes or acetylene black are effective strategies for solving the electronic conductivity issue. Recently, novel Ti-based MXenes with a large specific area and outstanding electron conductivity have been proposed as ideal

candidates for nitrate-to-ammonia conversion; thus developing Ti-based MXene electrocatalysts is an important development direction in the future.

The effect of lattice facets is rarely considered for Ti-based nanomaterials for the $\mathrm{NO_3}^-\mathrm{RR}$. Different lattice facets present unique atomic arrangements, signifying that the nanostructure with different exposed lattice facets exhibits disparate catalytic performance. Typically, high-index facets represent better catalytic activity. Therefore, exploring the effect of the lattice facets of Ti-based nanomaterials on the catalytic performance of the $\mathrm{NO_3}^-\mathrm{RR}$ is important for designing Ti-based nanomaterials with desired exposed lattice facets, reducing the overpotential and improving the $\mathrm{FE_{NH_3}}$.

Although heteroatom doping is a common modification strategy for inorganic materials, OVs in ${\rm TiO_2}$ could also be simultaneously formed by doping metallic atoms with lower valence than ${\rm Ti}^{4+}$. Therefore, doping-induced OVs should be considered but unfortunately, they are often neglected.

In addition to NH₃, producing high value-added organic molecules with deeply reduced nitrogen functional groups (such as urea, 91,92 methylamine, 93 formamide, 94 glycine, 95 etc.) by electrochemical reduction of NO₃⁻ is also an emerging direction. Since TiO₂-based nanomaterials exhibit profound reduction ability of NO₃⁻, some preliminary studies successfully coupled the CO₂ reduction reaction and the NO₃⁻RR on TiO₂-based nanomaterials to produce urea. 91 Zhang et al. revealed that constructing secondary active sites on TiO₂ for adsorbing carbon-containing intermediates is a feasible strategy for the gC–N coupled reaction. 92

We hope that this review will shed light on the exploration of Ti-based nanocatalysts and pave the way for low-cost and efficient Ti-based nanocatalysts to realize large-scale industrial applications.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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