Photocatalytic NO\textsubscript{x} removal and recovery: progress, challenges and future perspectives

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The excessive production of nitrogen oxides (NO\textsubscript{x}) from energy production, agricultural activities, transportation, and other human activities remains a pressing issue in atmospheric environment management. NO\textsubscript{x} serves both as a significant pollutant and a potential feedstock for energy carriers. Photocatalytic technology for NO\textsubscript{x} removal and recovery has received widespread attention and has experienced rapid development in recent years owing to its environmental friendliness, mild reaction conditions, and high efficiency. This review systematically summarizes the recent advances in photocatalytic removal, encompassing NO\textsubscript{x} oxidation removal (including single and synergistic removal and NO\textsubscript{2}\textsuperscript{-} decomposition), NO\textsubscript{x} reduction to N\textsubscript{2}, and the emergent NO\textsubscript{x} upcycling into green ammonia. Special focus is given to the molecular understanding of the interfacial nitrogen-associated reaction mechanisms and their regulation pathways. Finally, the status and the challenges of photocatalytic NO\textsubscript{x} removal and recovery are critically discussed and future outlooks are proposed for their potential practical application.

1 Introduction

Nitrogen oxides (NO\textsubscript{x}, consisting of 95% NO and NO\textsubscript{2}) are pervasive air pollutants which are implicated in various environmental events (acid rain, photochemical smog, and global warming) and cause detrimental impacts on public health.\textsuperscript{1-3} They serve as key precursors for the formation of emerging tropospheric ozone, PM\textsubscript{2.5} as well as secondary organic aerosol pollution.\textsuperscript{4-5} Although there are NO\textsubscript{x} from natural sources, anthropogenic activities, particularly fossil fuel combustion, account for a major contribution to the global NO\textsubscript{x} emissions in the atmosphere.\textsuperscript{6,7}

While NO\textsubscript{x} is a pollutant, it can also be recognized as an energy feedstock. With a high reactivity, NO\textsubscript{x} possesses the potential to be utilized for the synthesis of valuable N-containing chemicals. Ammonia (NH\textsubscript{3}) is indeed an indispensable chemical for fertilizers,\textsuperscript{7} dyes,\textsuperscript{8} polymers,\textsuperscript{9} explosives,\textsuperscript{10} resins,\textsuperscript{11} etc., and can serve as a carbon-neutral energy carrier.\textsuperscript{12}

The industrial production of NH\textsubscript{3} synthesis currently heavily relies on the Haber–Bosch route, which requires harsh conditions (400–500 °C, 150–300 atm), resulting in more than 2% of global energy consumption.\textsuperscript{12,13} This high energy consumption is also largely derived from fossil fuels.\textsuperscript{14} Faced with global energy shortages, recovery of NO\textsubscript{x} to NH\textsubscript{3} gives an alternative route for both environmental control and nitrogen resource utilization.

Photocatalytic technology powered by renewable solar energy has been reckoned as one of the most viable strategies that could convert NO\textsubscript{x} into less harmful or useful products under mild conditions.\textsuperscript{15-17} At present, conventional photocatalytic technologies, including NO\textsubscript{x} oxidation, NO\textsubscript{x} decomposition, and selective NO\textsubscript{x} reduction, have been vigorously developed, spanning from material design to elucidation of the underlying mechanisms.\textsuperscript{6,18-20} Meanwhile, the tendency of photocatalytic removal of NO\textsubscript{x} has been gradually transformed from oxidation, purification, and then to resource utilization. Particularly, the photocatalytic NO\textsubscript{x} reduction for ammonia synthesis has achieved milestone progress in recent years.

The review aims to summarize recent advancements in photocatalytic NO\textsubscript{x} removal and recovery. The cutting-edge developments in photocatalytic removal in terms of NO\textsubscript{x} oxidation, NO\textsubscript{x} reduction to nitrogen, and NO\textsubscript{x} upcycling to ammonia are comprehensively reviewed. We also highlighted the one-step (NO → NH\textsubscript{3}) and two-step (NO → NO\textsubscript{3} → NH\textsubscript{3}) methods as new ideas for simultaneous NO\textsubscript{x} removal and resource utilization. Finally, we discuss the current challenges and provide some perspectives on future directions for NO\textsubscript{x} removal and recovery. The illustration of this review on NO\textsubscript{x} removal and recovery is shown in Scheme 1. We hope that this
review will inspire significant research and essential advancements in the field of photocatalytic NO$_x$ removal.

2 NO$_x$ oxidation

2.1 Single NO$_x$ oxidation

2.1.1 NO$_x$ oxidation mechanisms. Photocatalytic oxidation removal is mainly applied to low-concentration pollutant purification. During the photocatalytic reaction process, electron-hole pairs are generated in the catalyst under light irradiation, initiating the oxidation reactions. These pairs migrate to the surface of the photocatalysts and react with adsorbed H$_2$O and O$_2$ molecules, leading to the generation of reactive oxygen species (ROS) such as 'OH, 'O$_2^-$, and 1O$_2$. These ROS then participate in a series of oxidation reactions with NO, ultimately forming the final product NO$_3^-$. Detailed reaction pathways and intermediates involved in this photocatalytic NO oxidation process can be described using specific equations, which are supported by relevant ref. 21 and 22:

\[
\text{Photocatalysts} + \text{hv} \rightarrow \text{h}^+ + \text{e}^- \quad (1)
\]
\[
\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{'OH} + \text{H}^+ \quad (2)
\]
\[
\text{NO} + \text{'OH} \rightarrow \text{HNO}_2 \quad (3)
\]

\[
\text{HNO}_2 + \text{'OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O} \quad (4)
\]
\[
\text{NO}_2 + \text{'OH} \rightarrow \text{NO}_3^- + \text{H}^+ \quad (5)
\]
\[
\text{O}_2 + \text{e}^- \rightarrow \text{'O}_2^- \quad (6)
\]
\[
\text{NO} + \text{'O}_2^- \rightarrow \text{NO}_3^- \quad (7)
\]
\[
\text{O}_2^- + \text{h}^+ \rightarrow \text{1O}_2 \quad (8)
\]
\[
\text{NO} + \text{1O}_2 \rightarrow \text{NO}_3^- \quad (9)
\]

2.1.2 Materials for NO$_x$ oxidation. There are three main factors affecting the catalytic performance of photocatalytic oxidation: light absorption, charge carrier separation and transfer, and active site construction. Based on these factors, various modification methods were conducted on TiO$_2$-based materials, Bi-based materials, g-C$_3$N$_4$-based materials, and perovskite-type materials. Modification methods include but are not limited to metal/non-metal doping, defects, heterojunctions, and sensitization. Single-atom catalysts have attracted much attention in the field of materials due to their unique activity and effective utilization of active atoms. Several studies have confirmed that single atoms can improve the performance of photocatalysts for...
Nitric oxide (NO) and nitrogen dioxide (NO₂) are major pollutants that contribute to air quality degradation and pose health risks. These compounds are released into the atmosphere in various forms, such as from industrial processes, transportation, and natural sources like agricultural activities and wildfires. The efficient removal and provide a convenient way to regulate the generation of reactive oxygen species (ROS) for effective pollutant elimination. Liu et al. achieved the stabilization of Pt on carbon-defective g-C₃N₄ by leveraging its affinity with nitrogen atoms resulting from carbon vacancies. The resulting Pd-Cv-CN catalyst enhances charge transfer efficiency, generating sufficient photoelectrons for the formation of •OH and •O₂⁻ species. This, in turn, facilitates the removal of NO and enhances the selectivity towards NO₃⁻. Hu et al. discovered that single Pt atom bridged within a metal-organic framework (MOF)-derived ZnO/C via carbon atoms (Pt-ZnO/C) exhibits enhanced adsorption energy and charge transfer characteristics for O₂ and H₂O (Fig. 1a and b). In contrast to •OH, •O₂⁻ plays a pivotal role in the conversion of NO₂ to NO₃⁻ on a single atom site at the catalytic surface (Fig. 1c). Zhang et al. incorporated Zn atoms into the interlayer of g-C₃N₄, forming the ZnN₃ structure by linking zinc with three nitrogen atoms. The presence of a single zinc atom facilitated the formation of a Zn–O₂–NO structure upon adsorption of O₂ and NO, thereby promoting the dissociation of O₂ and the direct conversion of NO to nitrate (Fig. 1d). Simultaneously, the formation of the toxic byproduct NO₂ was inhibited. A similar result enhancement was observed upon doping TiO₂ hollow microspheres (TiO₂-HMSs) with single atomic Fe. Particularly noteworthy is the effect of silver atoms loaded onto BiOCl (001)
facet-exposed nanosheets, which constructed triangular Cl-
Ag1–Cl sites on Cl-terminated BiOCl. These sites selectively
activated molecular oxygen to ‘O2’ and enhanced nitrate adsorption by altering the coordination mode of nitrate on the
catalyst, thereby preventing nitrate decomposition (Fig. 1e and f).19 The NO3 removal efficiency of Ag1/BiOCl reached up to 90%,
with 97% selectivity for NO3− and minimal emission of NO2
(Fig. 1g–i).

In summary, the introduction of single atoms can significantly enhance the adsorption of O2 and H2O molecules and the
generation of ‘O2’ and ‘OH, thereby improving both the performance and nitrate selectivity of the photocatalyst. This
provides a facile pathway to manipulate the ROS generation for efficient and selective pollutant removal.

2.1.3 Machine learning as an analysis tool for NOx oxidation. It is well-known that the performance of NO2 removal not
only depends on catalyst properties but also closely relies on preparation methods and reaction conditions. Although catal-

talyst design and optimization of experimental conditions have been fully explored, the dominant factors affecting the NOx
removal rate remain unclear. Machine learning (ML) has achieved remarkable progress over the past few decades and has

become the most potent tool in the field of data mining and analytics.40–41 ML methods leverage algorithms to extract insights from vast, intricate, and multidimensional datasets, enabling rapid and precise predictions. Recently, progress has been made in employing ML methods in the photocatalytic NOx oxidation process. Li et al.42 achieved success in predicting the NO removal rate in the photocatalytic purification of g-C3N4 catalysts using ML methods like gradient boosting decision trees, eXtreme gradient boosting, and random forests. Their findings indicate that catalyst characteristics, reaction process, and preparation conditions are the primary empirical cat-
gories influencing the NO removal rate. They have also unveiled the intricate relationships between the photocatalytic NO removal rate and various influencing factors. This approach, to some extent, mitigates the downsides of traditional experimental work, including high costs, lengthy timelines, and demanding labor.

2.1.4 NO3− decomposition on the photocatalyst. The formation of nitrate is a key process of NOx oxidation, as nitrate
has been considered a permanent sink of NOx.43 However, it undergoes photolysis processes under light irradiation (also
called detoxification), especially on the surface of the photocatalyst, which in turn serves as a source of atmospheric
nitrogenated compounds.44–46 TiO2, the predominant photocatal-
cyst,5,55 has been shown to promote nitrate photolysis processes through photochemical interaction.44 Therefore, exploring the decomposition mechanism of nitrate on the surface of photocatalysts assumes pivotal significance for stabilizing nitrate on the catalyst surface. The enhanced photolysis of nitrate by TiO2 under UV irradiation can be explained using the following reactions52–54 (eqn (10)–(19)):

\[
\text{TiO}_2 + h\nu \rightarrow h^+ + e^- \quad (10) \\
\text{NO}_3^- + h^+ \rightarrow \text{NO}_2^- \quad (11) \\
\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2 \quad (12) \\
\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}. \quad (13) \\
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}(3\text{P}) \quad (14) \\
\text{NO}_2 + e^- \rightarrow \text{NO}_2^- \quad (15) \\
\text{NO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{NO} + \text{H}_2\text{O} \quad (16) \\
2\text{NO} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad (17) \\
\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HO}^- \quad (18) \\
\text{HONO} + h\nu \rightarrow \text{NO} + \text{HO}^- \quad (19)
\]

There are two main factors affecting the nitrate decomposition mechanism on the TiO2, which are co-adsorbed cations and the coexisting atmosphere. It is suggested that the cations on TiO2 could inhibit the decomposition of nitrates. The presence of cations enhanced the adsorption of NO3− by forming ion pairs with NO3− and prevented NO3− from binding with light-induced h+ to generate ‘NO3’.55,56 The decomposition of nitrates is facilitated by co-existing pollutants in the surrounding environment such as SO2 and volatile organic compounds (VOCs). SO2 preferentially reacts with ‘NO3 radicals rather than photoelectrons, resulting in a significant improve-
ment in nitrate decomposition.57,58 Similar to SO2, formaldehyde (HCHO) participated in the transformation of NO3 to
HNO3 through hydrogen abstraction to promote nitrate decomposition. HCHO converts NO3− on particle surfaces into
HNO3 by reacting with ‘NO3, and then HNO3 photolyzes at a faster rate.55 Interestingly, NO produced from nitrate decom-
position may be re-adsorbed on the surface of TiO2 to promote nitrate decomposition.59 The N–O bond of NO3 could be activ-
ated by NO molecules. Subsequently, photogenerated electrons, captured by NO, facilitate the transformation of NO3−
under light irradiation through the NO3− + NO → 2NO2− pathway.59 It is proposed that addressing the photochemical transformation of surface NO3− may entail suppressing the formation of NO− during the photocatalytic NO oxidation process.

Although the well-known photochemical activity of nitrate decomposition is excited around 300 nm,60 it has been verified that nitrate decomposition could be induced by visible light (λ > 380 nm) on TiO2. Wang et al.61 investigated the decomposition of surface NO3− on nmTiO2 under visible light exposure. By regulating the reaction atmosphere (dry argon, wet argon, and wet air), distinct production of NO and NO2 is observed (Fig. 2a–c). Through meticulous control of in situ DRIFTS experiments, they uncovered different decomposition pathways stemming from different surface coordination modes of the NO3− (Fig. 2d and e). Nitrates generated on photocatalysts exhibit two coordination modes: monodentate nitrate (m-NO3−) and bidentate nitrate (b-NO3−). The m-NO3− decomposition initiated by photo-induced electrons primarily leads to the production of NO and NO2. It is indicated that H2O and O2 have a remarkable
influence on the decomposition products of NO$_3^−$. The introduction of H$_2$O molecules results in dissociation on nmTiO$_2$, forming surface hydroxyl groups, which then facilitate the conversion of b-NO$_3^−$ to m-NO$_3^−$ through hydrogen bonding interactions. Subsequently, visible-light-driven photocatalytic decomposition led to an enhancement in the concentration of NO$_x$. Although O$_2$ can promote nitrate regeneration through the oxidation process, the effect of H$_2$O on NO$_3^−$ decomposition could not be restrained in the presence of O$_2$.

To sum up, the decomposition of nitrate on the surface of active particulate matter TiO$_2$ under various conditions has been confirmed. Therefore, when exploring the mechanism of oxidative NO$_3$ removal, it is essential to consider the nitrate decomposition process. This perspective offers valuable insights for a more comprehensive understanding of the photocatalytic reaction.

### 2.2 Synergistic NO$_x$ oxidation

In the real scenario, NO$_x$ is typically present alongside other air pollutants. The interaction or combination of NO$_x$ with other pollutants, such as volatile organic compounds (VOCs) and sulfur dioxide (SO$_2$), can lead to the formation of more severe secondary pollutants, especially under sunlight irradiation.

In addition to designing effective photocatalysts, it is crucial to address the complexities arising from these multiple pollutants when implementing photocatalytic NO oxidation technology in real reactors at pilot or larger scales.

#### 2.2.1 Synergistic effect between NO$_x$ and VOCs

It has been revealed that there is a certain synergistic effect between NO$_x$ and VOCs on the specific photocatalysts to inhibit the generation of by-products. Xue et al. proposed an enhanced photocatalytic NO removal through the addition of acetaldehyde to Sr$_5$Sb$_2$O$_7$ to prevent secondary peroxyacetyl nitrate (PAN) formation. The intermediates NO$_3^−$ from NO and CH$_3$ from acetaldehyde tend to bond and further oxidize to CH$_3$ONO$_2$, thus promoting NO removal. Density functional theory (DFT) calculations show that the Gibbs free energy required for the conversion of NO to NO$_3^−$ in the mixed degradation process is lower compared to that in the individual removal pathways, thereby favoring the deep oxidation to NO$_3^−$. Li et al. provided additional details on the synergistic effects between NO$_x$ and VOCs, emphasizing the importance of considering the specific conditions and catalysts for effective removal.
investigated the simultaneous degradation of NO and C7H8 (toluene) mixed pollutants. On the In(OH)3 photocatalyst, NO and toluene exhibit coupling reaction effects and give rise to a new NO conversion pathway, leading to NO deep oxidation to NO3− (Fig. 3a and b). The key intermediate C7H7NOH is favorable for the NO oxidation to NO2 to inhibit O3 formation (Fig. 3c and d). Then NO2 was inclined to bond with toluene to form C7H6NO2. The incorporation of the nitro group alters the charge distribution within the benzene ring, disrupting the typical distribution of electrons within the π–π stacked structure (Fig. 3e). The rearrangement of electrons opens the benzene ring more readily than toluene, allowing further NO3− formation. This synergistic effect of NO and toluene also occurs in InOOH. The increase in humidity could suppress catalyst deactivation and improve the conversion of mixed pollutants, as shown in Fig. 3f. The yield of nitrate is also consistent with the conversion efficiency (Fig. 3g). This finding indicates that the extensive occupation of the catalyst surface by nitrate serves as a deactivation factor in mixed pollutant reactions. Under high humidity conditions, H2O and NO3− indicate similar adsorption configurations on InOOH, but H2O generates more free radicals to directly enhance the conversion of C–N intermediates, thus promoting the conversion of NO to NO3− (Fig. 3h and i). It was also proposed that NO could prevent the deactivation of the photocatalyst due to the incomplete oxidation product NO2 in the process of o-xylene degradation. NO2 ensures the generation of a sufficient amount of TiO2 (‘OL) radicals, allowing for the complete mineralization of o-xylene and inhibiting the deactivation of TiO2.

2.2.2 Inhibition effect between NOx and SO2. In contrast to VOCs, research indicates that SO2 tends to hinder the removal of NOx. According to the studies of Ao et al., the presence of

Fig. 3  (a) The removal of NO and C7H8 at different mixing ratios. (b) The nitrogen-containing products identified by IC. (c) The generation of O3 without and with the photocatalyst under light irradiation. (d) In situ DRIFTS spectra for the photocatalytic reaction of NO and C7H8. (e) Charge distribution of C7H8 and C7H8NO2 on the In(OH)3 photocatalyst; blue and yellow clouds represent charge depletion and accumulation, and the isosurface level is set to 0.0007 eV Å−3. (f) Conversion of mixed pollutants at different relative humidities. [NO] = [C7H8] = 30 ppm. (g) NO3− production in mixed and single systems at different relative humidities. (h) Simulation of reactant and product binding on the catalyst. (i) Illustration of the synergistic interaction between NO and C7H8 and the promoting effect of H2O.
SO₂ resulted in an 8% decrease in NO conversion and a 10% increase in NO₃ generation. The formation of sulfate ions on the catalyst surface obstructed the adsorption sites of TiO₂ for converting NO₂ to HNO₃, consequently increasing the exit concentration of NO₃. Chen et al.⁴ further validated this deactivation mechanism through DFT calculations. The result showed that surface hydroxyls on the (101) facet of TiO₂ create unsaturated coordination of adjacent Ti or O atoms, promoting the adsorption of NO and SO₂. However, there is a competitive adsorption between NO and SO₂, as evidenced by the decreasing adsorption energy and charge density. In the oxidation process, SO₂ significantly competes with NO for reaction with ‘O⁻’. More valence electrons are involved in the oxidation of SO₂, resulting in higher binding energy between *O–SOO* than *O–NOO*.

3 NOₓ reduction to nitrogen

Contemporary research in photocatalytic NO abatement predominantly centers on oxidizing NO to NO₃⁻. Nevertheless, concerns arise from the production of the more toxic by-product, NO₂, catalyst deactivation resulting from the obstruction of reaction sites by nitrate products, and the denitrification of NO₃⁻. These challenges impede the practical application of photocatalysts. An alternative approach for NO₂ removal involves the reduction of NO to N₂ without causing deactivation or secondary pollution. This can be achieved through two approaches: direct reduction of NO to N₂ and O₂ under oxygen-free conditions (NO₄ decomposition), and selective reduction of NO to N₂ in a reducing atmosphere (NOₓ photo-selective reduction).

3.1 NO₂ decomposition

The decomposition of NO into harmless N₂ and O₂ represents one of the most desirable pathways of NO removal, as it eliminates the need for additional reductants. Transition metal oxides have emerged as typical photocatalysts for NO₂ decomposition.⁷²-⁸² Utilizing zeolite supports allows for the production of highly dispersed powders, enhancing the performance of NO decomposition.⁸¹ Previous studies have demonstrated the significant contribution of transition metal ions to the photocatalytic NO decomposition. As shown in eqn (20), highly dispersed and isolated transition metal oxides form the charge-transfer excited states under irradiation, which involve electron transfer from O₂⁻ to M⁻:

\[
[M^{n+} - O^2-)_{n} + h\nu \rightarrow [M^{(n-1)+} - O^2+]_{n}] \quad M = Ti, V, Cr, Mo, W
\]  

(20)

The selectivity of N₂ increases as the coordination number of the M–O bond decreases, which triggers the photocatalytic decomposition of NO.⁸³ It was shown that the Ti-oxide/Y-zeolite catalysts with tetrahedral coordination exhibit higher reactivity and selectivity for N₂ generation and lower selectivity for N₂O formation than those with octahedral coordination.⁸³ The performance of the photoreduction reaction could also be improved by oxygen vacancies and doping the catalyst with transition metals.⁸⁵-⁸⁷ van de Krol et al.⁸² doped TiO₂ nanoparticles with Fe³⁺, which changed the photocatalytic NO removal route from oxidation to reduction (Fig. 4a). The Fe³⁺ substituted Ti⁺ in the lattice, and the negative charge of this acceptor-type dopant contributed to the stabilization of positivity-charged oxygen vacancies. The oxygen vacancies could act as active sites to capture the molecular O of the NO molecule and provide light-induced electrons (Fig. 4b). Besides, Ag⁺ and Agтр coexist on the TiO₂ surface, which both play different roles in the enhancement of N₂ selectivity: the Ag⁺ nanoparticles enhance the light absorption of the material, while Agтр can decompose the attachment product N₂O into N₂.⁸² A recent study shows that layered structured perovskite SrBi₂Nb₂O₉ with ultrathin nanostructure and oxygen vacancies (SBNO-UT) is capable of decomposing NO into N₂ and O₂ at the close-to-stoichiometric ratio (Fig. 4e).⁸³ As can be seen from Fig. 4d, N₂O intermediates were formed by NO reduction during the photocatalytic process. The in situ formed N₂O bounds to the defective surface, ensuring further reduction (Fig. 4e). Finally, the breakage of the N≡O bond completes the reduction of NO to N₂.

3.2 NOₓ photo-selective reduction

The method of selectively converting NO to N₂ by introducing reducing agents such as NH₃, CO, H₂, and hydrocarbons into the system is known as selective catalytic reduction (SCR). Despite extensive study,⁸⁵-⁸⁷,⁸⁸-⁹⁰ the technology typically operates at high temperatures (300–400 °C),⁸⁷,⁸⁸ leading to relatively high energy consumption and potentially excessive CO₂ emissions. In addressing these challenges, photo-assisted SCR (photo-SCR) of NOₓ with NH₃ using photocatalysts under light irradiation and low-temperature conditions has been developed as an alternative for NO reduction.

NH₃ serves as a common reductant for NOₓ removal by photo-SCR, with TiO₂ being the most extensively utilized catalyst in this system. The reaction mechanism of NO photo-SCR with NH₃ on TiO₂ is depicted in Fig. 5a.⁹³ There are numerous TiO₂-based materials for photo-SCR, e.g., TiO₂/SiO₂,⁹⁳ TiO₂ nanotube arrays,⁹⁴ Bi₂WO₆/TiO₂ Z-scheme heterojunctions,⁹⁵ g-C₃N₄/TiO₂ (ref. 93) and Pd-loaded TiO₂,⁹⁶ and Si/TiO₂.⁹⁷ Tanaka et al.⁹⁷ reported achieving the photocatalytic selective reduction of NO with NH₃ using TiO₂ under xenon lamp illumination at conversion temperatures as low as 50 °C. They also investigated the activity of TiO₂ surfaces loaded with 1 wt% of various transition metal oxides.⁹⁷ Their findings revealed that Nb, Mo, and W oxides promoted the photo-SCR activity of TiO₂ with WO₃/TiO₂ exhibiting the highest activity (Fig. 5b). The number of acidic sites on TiO₂ as active sites for the photo-SCR reaction determines the reactivity of the photocatalyst.⁹⁸ Modification of TiO₂ with WO₃ resulted in increased polarizability, enhancing the surface acidity and thus facilitating the reduction of NO.⁹⁸,¹⁰⁰ Subsequent studies concluded that agglutination occurs with increasing WO₃ addition, with isolated W species enhancing the chemical reduction activity of NO, while agglutinated W species remain inactive.¹⁰¹
Perovskite (ABO$_3$) structured materials with flexible structures have recently garnered scientific interest for their application in photo-SCR. Researchers have synthesized Ce–Fe–Mn doped CaTiO$_3$ perovskite from titanium-containing solid waste using the molten salt method.$^{103}$ Fig. 5c–e illustrate that CaTiO$_3$ showed no photocatalytic activity for NO removal at temperatures ranging from 100 to 300 °C. However, (Ca, Ce) (Ti, Mn, Fe) O$_3$ demonstrated almost 100% NO conversion under light irradiation at 135 °C (GHSV $= 72,000$ h$^{-1}$). Both Mn and Fe are incorporated into the B-site of CaTiO$_3$, while Ce occupies the A-site. Mn doping enhances material light absorption and the capacity to capture NO. After Fe doping, the oxidation center for NO-to-NO$_3^-$ shifts from the five-coordinated Mn$_{2p}$ site to the Fe$_{3c}$ site, significantly altering the reaction pathway of conventional SCR. Furthermore, Pr doping of LaCoO$_3$ supported on a natural palygorskite (Pal) surface eliminates over 95% of NO$_x$ within the low-temperature range of 150–250 °C.$^{104}$ Appropriate Mn doping into LaFeO$_3$ to form LaFe$_{1-x}$Mn$_x$O$_3$/attapulgite (ATP) nanocomposites extends its visible light absorption range, resulting in increased NO conversion, reaching a maximum of 83%, with N$_2$ selectivity close to 100%. Ni-doped LaFeO$_3$ nanocomposites exhibit a higher NO$_x$ conversion rate of 92%.$^{105}$ Moreover, nitrogen-doped carbon quantum dot modified PrFeO$_3$/Pal, with abundant acid sites, demonstrate 93% NO removal and 100% N$_2$ selectivity under visible light illumination, showing considerable tolerance to SO$_2$ and H$_2$O.$^{106}$

4 NO$_x$ upcycling to ammonia

The upcycling of NO$_x$ to ammonia presents an environmentally friendly opportunity for both NO$_x$ pollutant elimination and
sustainable ammonia production. While electrocatalytic synthesis of ammonia has garnered considerable attention, photocatalytic reduction of NO to ammonia remains in its nascent stage. Nevertheless, recent years have seen significant advancements in photocatalytic ammonia synthesis. The authors outline two potential approaches for NOx resource utilization via photocatalysis. One method involves the use of a chelating agent with the dissolution of NO in water, followed by a one-step reduction to ammonia via photocatalysis (one-step method). Another approach entails oxidizing NO to the highly water-soluble NO₃⁻ initially, followed by its reduction to ammonia through an eight-electron reduction process (two-step method).

4.1 One-step method (NO → NH₃)

The direct one-step synthesis of NH₃ from NO is an ideal strategy for transforming waste into valuable resources. While research efforts in NOx reduction reactions (NOxRR) have predominantly focused on enhancing NH₃ synthesis rates, achieving high NOx conversion efficiency remains a crucial yet less explored objective. Typically, NOxRR experiments necessitate efficiency tests with high concentrations (>10,000 ppm) of NO to ensure an adequate feedstock for enhancing ammonia production. However, limited NO conversion persists as a key challenge for the sustainability of the NO-to-NH₃ reduction pathway.

The ultra-low solubility of NO in water (1.94 mmol L⁻¹) is one of the primary reasons for limited NO conversion. To address this challenge, a novel one-step NOx photoreduction pathway, referred to as the on-site coupling system, has been recently developed. This system enables NO direct upcycling under ambient conditions (Fig. 6a). Specifically, the solution was supplemented with Fe(II)EDTA as a NO chemical absorbent, generating Fe(II)EDTA-NO chelates, while formaldehyde (HCHO) served as an antioxidant to prevent the Fe(III) formation from Fe(II) oxidation. This simultaneous chemical absorption and photocatalytic reduction system enabled continuous NO adsorption, NO reduction, and Fe(II)EDTA regeneration on-site. TiO₂ decorated with 11.6 mg L⁻¹ Au nanoparticles could provide ample active sites to facilitate charge separation, thereby enhancing NH₃ generation. Using this on-site coupling system, the performance of AuₙNOₓ-TiO₂ is shown in Fig. 6b and c, demonstrating exceptional NO conversion efficiency (89.0%), ammonia production selectivity (95.6%), and ammonia recovery efficiency (>90%). Virtually no other side products are detected. Subsequently, the generated ammonia was recovered via.

Fig. 5 (a) Proposed reaction mechanism of the photo-SCR over a TiO₂ photocatalyst under UV-light irradiation. (b) Conversion of NO in the photo-SCR over various metal oxide-promoted TiO₂ photocatalysts. (c–e) NH₃-SCR activity of single- and multi-element doped CaTiO₃.
a simple ion exchange method, with recovery rates still exceeding 90% within 50–200 mg L\(^{-1}\) ammonia production (Fig. 6d). Moreover, the NO conversion efficiency and the NH\(_4^+\) selectivity remained unaffected even in the presence of resistance factors such as H\(_2\)O, SO\(_2\), and metal ions (K\(^+\), Ca\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\)) (Fig. 6e). These high recovery efficiencies and anti-poisoning capacities underscore the environmental practicality of NO\(_x\) removal in flue gas. The on-site coupling strategy achieves significant efficiency milestones for sustainable NO

Fig. 6  (a) Illustration of the on-site coupling system of continuous chemical absorption and catalytic reduction. (b) NH\(_4^+\) synthesis rate between the pristine and Au-decorated TiO\(_2\). (c) Selectivity test. (d) Ammonia recovery evaluation after the continuous absorption and photoreduction of NO. (e) Poisoning resistance against vapor, SO\(_2\), and metals.\(^{111}\)
removal and also offers insights into NO upcycling for the future of carbon neutrality.

The simultaneous presence of NO and SO2 in flue gas poses significant challenges for their concurrent removal and recovery. Since SO2 is easily dissolved and oxidized, it can serve as a potential reductant in the NO photoreduction reaction. Furthermore, the on-site coupled system demonstrated the synergistic removal and recycling of NO and SO2 without the need for scavengers. The formation of the SO2–NO redox pair facilitates high conversion rates of both NO and SO2 in continuous flow. Achieving a remarkable selectivity for both NO-to-NH3 upcycling (97%) and SO2-to-SO4$^{2-}$ purification (92%) simultaneously underscores the practicability of value-added conversion of air pollutants (Fig. 7a and b). Maintaining the efficiency of NO conversion and reduction crucially depends on preventing the oxidation of Fe(II) to Fe(III) in Fe(II)EDTA. Through verified in situ ATR-FTIR experiments, it was revealed that SO2 exhibited a promoting effect on Fe(II) maintenance, while no interaction was observed between SO2 and EDTA (Fig. 7c and d).

The chemical redox pair of SO2–Fe(III) is illustrated in eqn (21)–(23).

\[
\text{Fe(II)} \rightarrow \text{Fe(III)} \text{ (spontaneous oxidation)} \quad (21)
\]

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \text{ (dissolution)} \quad (22)
\]

\[
2\text{Fe(III)} + 2\text{SO}_4^{2-} + \text{O}_2 \rightarrow 2\text{Fe(II)} + 2\text{SO}_4^{2-} \text{ (chemical redox pair)} \quad (23)
\]

As depicted in Fig. 7e and f, compared to h$^+$-induced 'OH production, the h$^+$-induced SO2 oxidation reaction to 'SO3$^-$ promotes charge separation, thereby generating more e$^-$, and enhancing the efficiency of the nitrogen oxide reduction reaction to produce NH3. The overall mechanism for synchronous NO and SO2 conversion is illustrated in eqn (24)–(26):

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \text{ (dissolution)} \quad (24)
\]

\[
5\text{SO}_3^{2-} + \text{NO} + 5\text{h}^+ + 5\text{e}^- + 5\text{H}^+ \rightarrow 5\text{SO}_4^{2-} + \text{NH}_4^+ + \text{OH}^- \text{ (photocatalytic redox pair)} \quad (25)
\]

\[
5\text{SO}_3^{2-} + \text{NO} + 5\text{h}^+ + 5\text{e}^- + 5\text{H}^+ + 9\text{OH}^- \rightarrow 5\text{SO}_4^{2-} + \text{NH}_4^+ + 5\text{H}_2\text{O} \text{ (photocatalytic redox pair)} \quad (26)
\]

Thus, a one-step NO reduction method has been devised by concurrently absorbing and converting NO. This system also exhibits great resistance to toxicity, including resistance to K$^+$, Ca$^{2+}$, and Cd$^{2+}$ metal ions, respectively. The effective separation and retrieval of reaction products provide this system with sustainable stability and potential economic viability. Continuous NO removal and upcycling under ambient conditions with high conversion efficiencies were achieved, marking significant advancements in photocatalytic NO removal and recycling compared to SCR and chemical absorption technologies.

4.2 Two-step method (NO → NO$_3^-$ → NH$_3$)

Among the redox products of NO$_2$, NO$_3^-$ is the dominant and accessible substance on the surface of the photocatalyst.
Significant quantities of NO$_3^-$ are released into the environment through processes such as the combustion of fossil fuels and agricultural activities, driven by the progress of urbanization and industrialization. The surface of the photocatalyst is the overlooked storage site for NO$_3^-$, where the generated nitrate could be easily removed from the catalyst and subsequently concentrated in liquid form. However, excessive amounts of NO$_3^-$ in water can pose a pollution concern. To address this issue, photocatalytic technologies have been employed to convert excess nitrate into valuable NH$_3$.

Photocatalytic reduction of NO$_3^-$ to ammonia via multiple electron transfer (eqn (27)), could emerge as a potent method for ammonia production under ambient conditions of room temperature and atmospheric pressure. $\text{N}_2$ and H$_2$ formation reactions are two side reactions that consume photoexcited electrons (eqn (28) and (29)). Therefore, it is necessary to enhance not only the ammonia yield but also the ammonia selectivity. A summary of studies on the reduction process of nitrate to ammonia by various photocatalysts is presented in Table 1.

$$\text{NO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O} \quad (27)$$

$$\text{NO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow 1/2\text{N}_2 + 3\text{H}_2\text{O} \quad (28)$$

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (0.00 \text{ V vs. NHE}) \quad (29)$$

It can be inferred from Table 1 that TiO$_2$-based materials are prominently utilized as catalysts for NO$_3^-$-to-NH$_3$ reduction, particularly highlighting metal-modified TiO$_2$ nanosheets (TNSs). Recently, as shown in Fig. 8a, alkaline-earth oxide clusters constructed on TiO$_2$ nanosheets (MO$_{x}$NCs-TNSs, M = Mg, Ca, Sr or Ba) were reported to enhance NO$_3^-$-to-NH$_4^+$ production, among which BaO$_{x}$NCs-TNSs achieve both exceedingly high NH$_4^+$ selectivity (97.7%) and high NH$_4^+$ yield (89.8 mmol g$_{\text{cat}}^{-1}$ h$^{-1}$). To the best of our knowledge, this is the highest production of ammonia by the photocatalytic reduction reaction. Remarkably, there’s an incremental rise in the rate of ammonia synthesis throughout the reaction, attributed to the concurrent Operando formation of BaO$_{x}$NCs and the ammonia synthesis reaction (Fig. 8b and c). Upon achieving stabilization of BaO$_{x}$NCs on TNSs, a notable and consistent production of ammonia on BaO$_{x}$NCs-TNSs composites was realized.

Chen et al. further elucidated the criticality of the on-site formation of authentic active sites under realistic catalytic conditions. They engineered Cu$_{x}$O$_{x}$NCs-TNS materials, wherein dynamic Cu$_x$O sub-nanoclusters were on-site constructed on TNSs using CuCl$_2$ solution through a photoinduced pseudo-Fehling’s route. Different from BaO$_{x}$NCs-TNS which remains stable once it has been constructed, the morphology and chemical state of Cu$_x$O exhibit dynamic evolution, as the actual reaction cannot progress over preformed Cu$_x$O sites (Fig. 8d and e). Numerous in situ experiments revealed a photoswitchable reversible conversion pattern between Cu$^{2+}$ and Cu$^+$ in the photosynthesis reaction, aligning with the performance of ammonia synthesis by nitrate reduction (Fig. 8f and g). NH$_3$ photosynthesis was directly attributed to the enhanced charge separation and transformation capacity from the Cu$_x$O active sites. Consequently, the establishment of a genuine structure-activity correlation was achieved by uncovering the synchronous formation of the Cu$_x$O active site and catalytic reaction (Fig. 8h).

In addition, a groundbreaking perspective has emerged regarding the interplay between single atoms and oxygen vacancies (OVs) (Fig. 9). The incorporation of single-atom Cu into TiO$_2$ nanosheets (Cu-TNSs) resulted in a 62-fold increase in ammonia production compared to pristine TiO$_2$, with a selectivity of 97.6%. The introduction of Cu atoms, replacing Ti sites, induces the generation of OVs and lattice strain. NO$_3^-$ preferentially adsorbs onto Ti atoms neighboring Cu atoms. The near-isolated Cu atoms and OVs facilitate multiple NO$_3^-$ adsorptions at a single site, effectively inhibiting the release of NO$_2^-$.  

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Hole scavengers</th>
<th>Light source</th>
<th>pH</th>
<th>NO$_3^-$ conversion (%)</th>
<th>NH$<em>4^+$ production (mmol g$</em>{\text{cat}}^{-1}$ h$^{-1}$)</th>
<th>NH$_4^+$ selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>2$O$</em>{x}$NCs-TNS</td>
<td>Formaldehyde</td>
<td>300 W Xe lamp</td>
<td>N/A</td>
<td>94.2</td>
<td>42.6</td>
<td>98.6</td>
<td>119</td>
</tr>
<tr>
<td>CuO$_x$@TNS</td>
<td>Ethylene glycol</td>
<td>300 W Xe lamp</td>
<td>8.3</td>
<td>100</td>
<td>16</td>
<td>96.1</td>
<td>120</td>
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<tr>
<td>Cu-TNS</td>
<td>Formic acid</td>
<td>300 W Xe lamp</td>
<td>3.5–3.6</td>
<td>&gt;99</td>
<td>0.1</td>
<td>97.6</td>
<td>118</td>
</tr>
<tr>
<td>BaO$_{x}$NCs@TNS</td>
<td>Ethylene glycol</td>
<td>300 W Xe lamp</td>
<td>7</td>
<td>~3.5</td>
<td>89.8</td>
<td>97.7</td>
<td>121</td>
</tr>
<tr>
<td>Photo-reductive TiO$_2$</td>
<td>N/A</td>
<td>450 W medium pressure UV</td>
<td>7</td>
<td>~71</td>
<td>N/A</td>
<td>60</td>
<td>122</td>
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<tr>
<td>LaFeO$_3$/HTCC nanocomposites</td>
<td>Acetic acid</td>
<td>300 W Xe lamp</td>
<td>2</td>
<td>94.6</td>
<td>N/A</td>
<td>88.7</td>
<td>123</td>
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<tr>
<td>LaFeO$_3$/biochar nanocomposites</td>
<td>Formic acid</td>
<td>300 W Xe lamp</td>
<td>2</td>
<td>98</td>
<td>N/A</td>
<td>97</td>
<td>124</td>
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<tr>
<td>Ni/H$<em>2$WO$</em>{4}$ hybrids</td>
<td>Ethylene glycol</td>
<td>300 W Xe lamp</td>
<td>N/A</td>
<td>~92</td>
<td>10.5</td>
<td>98.3</td>
<td>125</td>
</tr>
<tr>
<td>Carbon/bismuth/Bi$_2$O$_3$</td>
<td>Ethylene glycol</td>
<td>Simulated sunlight</td>
<td>N/A</td>
<td>N/A</td>
<td>0.4</td>
<td>95</td>
<td>126</td>
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<tr>
<td>CuAg/TiO$_2$</td>
<td>Methanol</td>
<td>Black light</td>
<td>6</td>
<td>96</td>
<td>N/A</td>
<td>85</td>
<td>127</td>
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<tr>
<td>Ni$_2$P/Ta$_2$N$_5$</td>
<td>N/A</td>
<td>Fluorescent lamps</td>
<td>2</td>
<td>79</td>
<td>0.2</td>
<td>68</td>
<td>128</td>
</tr>
<tr>
<td>Pd$_2$Sn/Ni@NaTa$_2$O$_6$</td>
<td>Formic acid</td>
<td>125 W high pressure UV</td>
<td>N/A</td>
<td>100</td>
<td>N/A</td>
<td>72</td>
<td>129</td>
</tr>
<tr>
<td>JRC-TIO-6 (rutile TiO$_2$)</td>
<td>Formic acid</td>
<td>2 kW Xe lamp</td>
<td>2.4–3</td>
<td>79</td>
<td>0.02</td>
<td>97</td>
<td>117</td>
</tr>
<tr>
<td>CuPd/TiO$_2$</td>
<td>Methanol</td>
<td>UV</td>
<td>N/A</td>
<td>&gt;95</td>
<td>N/A</td>
<td>78</td>
<td>130</td>
</tr>
</tbody>
</table>
intermediates and minimizing N-to-N interactions, thus ensuring high NH₃ selectivity.

Furthermore, CuOₓ@TNS was designed for NO₃⁻ reduction with a 100% NO₃⁻ conversion rate and 96.1% ammonia selectivity by coupling the nitrate reduction reaction with a glycol oxidation reaction system. The active site for improving ammonia formation is identified as the CuOₓ species with an amorphous Cu–O–Ti bimetallic oxide cluster structure.

Fig. 8 (a) Catalytic efficiency tests showing the enhancement of Operando construction of alkaline-earth oxide clusters on TNS surfaces. (b) Quasi in situ high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images showing the evolution course from isolated Ba single atoms (BaSAs) to subnanometric (BaONCs) at the irradiation time of 5 min (up) and 10 min (down). (c) Variation of Ba²⁺ concentration during the Operando construction of BaOONCs detected by ion chromatography. (d) NH₃ photosynthesis rate of the dynamic process. (e) Efficiency comparison between the different composites of Cu species and the TNS substrate. (f) The evolution process of the different chemical states of Cu²⁺ and Cu⁺ under the catalysis conditions. (g) Snapshots of the photosynthesis reactor along with the photosynthesis reaction time for the observation of the dynamic evolution of Cu species. (h) Schematic illustrations for the synchronous Cu₂O NCs construction and NH₃ photosynthesis in the realistic catalysis condition.
Given that redox reactions occur concurrently, it’s evident that the oxidation half-reaction also significantly influences NH₃ production. To explore the impact of various oxidation half-reactions on NO₃⁻ reduction, oxidative reactants including deionized water (DI), methanol (CH₃OH), ethylene glycol ((CH₂OH)₂), and acetic acid (HCOOH) are introduced into the reaction system (Fig. 10b and c). It is revealed that the NO₃⁻ reduction process is hindered by the formation of potent oxidizing ·OH radicals (Fig. 10d). The presence of ethylene glycol expedites the consumption of h⁺ during the formation of alkoxy radicals (·R), thus mitigating ·OH production. Moreover, the Cu–O–Ti sites could promote the preferential oxidation of ethylene glycol, thereby enhancing both the efficiency and selectivity of ammonia production (Fig. 10e). These findings underscore the pivotal role of the oxidation half-reaction. The deliberate design of the oxidation half-reaction not only enhances the effective utilization of electrons and holes but also modulates the reaction pathway, thus promoting the progress of the NO₃⁻ reduction half-reaction.

In summary, the photocatalytic performance of NO₃⁻-to-NH₃ photocatalytic reduction highly relies on the strategic construction of active sites and the coordination of redox reactions. This offers an innovative perspective on experimental design aimed at achieving high NH₃ selectivity and production.

Recent studies have shown that NO₃⁻ originating from NO oxidation has achieved nearly 100% NH₃ selectivity. It is desired to employ a two-step process (NO → NO₃⁻ → NH₃) to achieve a highly selective conversion of NO to NH₃.

5 Conclusions and perspectives

5.1 Conclusions

Table 2 summarizes and compares the application scenarios, reaction conditions, photocatalysts, and reaction activity for NOx removal under the different reaction pathways. It is found that the application of photocatalytic technology has transcended indoor NOx treatment and is now addressing challenges posed by complex pollutant compositions and industrial flue gases. Interestingly, TiO₂ remains the most extensively studied photocatalyst in both NOx oxidation and NOx reduction, probably due to its outstanding carrier separation capability. Besides, the overall redox properties also depend on catalyst modification or adjustment of environmental atmospheres in different systems. The photocatalytic performance showed that the NOx conversion and product selectivity have exceeded 90% for most of the redox pathways except NOx decomposition. This marks a significant advancement towards the future application of photocatalytic NOx removal and recovery.
In conclusion, photocatalytic technology is a promising method for NO\textsubscript{x} removal and recovery, owing to its mild reaction conditions and eco-friendliness. In recent years, significant strides have been made in the field of photocatalytic NO\textsubscript{x} removal, spanning from the optimization of photocatalysts to the exploration of mechanisms and the modulation of reaction pathways, resulting in unprecedented performance in NO\textsubscript{x} removal. The emerging photocatalytic reduction of NO\textsubscript{x} to ammonia offers a viable alternative for NO\textsubscript{x} recovery. This review summarizes the latest advancements in photocatalytic removal, encompassing NO\textsubscript{x} oxidation (both single and synergistic removal, as well as NO\textsubscript{3}\textsuperscript{-} decomposition), NO\textsubscript{x} reduction to nitrogen, and the upcycling of NO\textsubscript{x} into ammonia. Furthermore, we highlight photocatalysis-based NO\textsubscript{x} recovery, including one-step and two-step methods, as a promising approach to tackle existing environmental and energy challenges.

5.2 Future outlook
The utilization of photocatalytic technology for the removal and recovery of NO\textsubscript{x} is currently in the research phase, with the practical application still a considerable distance away. We recommend that future studies systematically address the following issues:

(1) Comparing the performance of photocatalysts across different studies in the realm of NO\textsubscript{x} oxidation proves...
Challenging due to the diverse array of reaction conditions such as light source, gas flow rate, initial NO\textsubscript{x} concentration, mass of the photocatalyst, reactor design, and others. To comprehensively evaluate photocatalyst performance and identify truly efficient photocatalysts, there is a pressing need to establish uniform performance standards.

(2) Despite notable advancements in the performance of photocatalytic NO\textsubscript{x} removal in recent years, a gap persists when compared to thermal catalytic NO\textsubscript{x} removal. One of the primary reasons for this gap is the insufficient exploration of the interfacial reaction mechanism governing photocatalytic NO\textsubscript{x} removal. To address this, in situ detection methods with higher resolution, such as in situ EPR, DRIFTS, and Raman spectroscopy, should be more extensively employed. These techniques can unveil the intricacies of the photocatalytic reaction mechanism, subsequently informing catalyst design and modification efforts.

(3) In the one-step method, the yield of ammonia is significantly influenced by the solubility of NO\textsubscript{x}, thus necessitating further enhancement of NO solubility in water. Introducing chemical absorbents to adsorb NO suggests the need for additional methods to separate the resulting ammonia, thereby increasing costs and rendering it less favorable for practical applications. An absorbent-free approach is preferable to augment the solubility of high concentrations of NO in water and to develop photocatalysts capable of achieving an ammonia yield that meets recovery criteria. Moreover, photocatalysts can be selectively designed to further reduce NO\textsubscript{x} to N\textsubscript{2} instead of ammonia, offering an alternative solution to address current environmental challenges.

(4) In the two-step process, the primary challenge lies in effectively collecting the nitrates produced from NO\textsubscript{x}. During the photocatalytic NO\textsubscript{x} oxidation process, nitrates gradually accumulate on the catalyst surface. However, due to the limited availability of adsorption sites on the surface and the simultaneous decomposition of nitrates, only a small portion of nitrates remains on the photocatalyst surface. It is imperative to enhance the thorough oxidation of NO\textsubscript{x} and suppress the decomposition of nitrates. Additionally, nitrates are commonly found in relatively high concentrations in wastewater, presenting an opportunity to enhance ammonia production.

(5) Machine learning offers a potent tool for predicting catalytic reaction performance accurately, aiding chemists in tasks like material screening, experiment optimization, and mechanistic studies. Nonetheless, it’s crucial to emphasize that machine learning should be applied judiciously. While it’s a valuable tool, it’s not a universal solution and cannot substitute well-considered experimental designs. In practice, a combination of expertise is still vital to ensure that machine learning and traditional methods work together harmoniously to achieve broader environmental science objectives.

**Author contributions**

All of the authors contributed to the literature search, writing and editing of this review.
Conflicts of interest
There are no conflicts to declare.

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