

Review

Materials Design and Development of Photocatalytic NO_x Removal Technology

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Abstract: Nitrogen oxide (NO_x) pollutants have a significant impact on both the environment and human health. Photocatalytic NO_x removal offers a sustainable and eco-friendly approach to combatting these pollutants by harnessing renewable solar energy. Photocatalysis demonstrates remarkable efficiency in removing NO_x at sub-scale levels of parts per billion (ppb). The effectiveness of these catalysts depends on various factors, including solar light utilization efficiency, charge separation performance, reactive species adsorption, and catalytic reaction pathway selectivity. Moreover, achieving high stability and efficient photocatalytic activity necessitates a multifaceted materials design strategy. This strategy encompasses techniques such as ion doping, defects engineering, morphology control, heterojunction construction, and metal decoration on metal- or metal oxide-based photocatalysts. To optimize photocatalytic processes, adjustments to band structures, optimization of surface physiochemical states, and implementation of built-in electric field approaches are imperative. By addressing these challenges, researchers aim to develop efficient and stable photocatalysts, thus contributing to the advancement of environmentally friendly NO_x removal technologies. This review highlights recent advancements in photocatalytic NO_x removal, with a focus on materials design strategies, intrinsic properties, fundamental developmental aspects, and performance validation. This review also presents research gaps, emphasizing the need to understand the comprehensive mechanistic photocatalytic process, favored conditions for generating desired reactive species, the role of water concentration, temperature effects, inhibiting strategies for photocatalyst-deactivating species, and the formation of toxic NO₂.

Keywords: NO_x removal; photocatalyst; metal oxide; photocatalytic degradation; reactive oxygen species; superoxide radicals; hydroxyl radicals; photogenerated charge; semiconductor



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1. Introduction

Nitrogen oxide (NO_x: 95% NO and 5% NO₂) is a significant contributor to various environmental issues, such as photochemical smog, brown haze, and acid rain. It reacts with volatile organic compounds (VOCs) to form ground-level ozone (O₃), which is a serious pollutant. NO_x is primarily emitted from vehicles (50%) and industrial plants that combust fossil fuels [1–4]. It serves as a major source of PM_{2.5} and PM₁₀ precursors (Group 1 carcinogen), posing serious health concerns, including respiratory irritation, elevated risks of premature death, and the exacerbation of respiratory conditions like emphysema and bronchitis [5–8]. Additionally, NO_x contributes to the acidification of soil, water, and building materials, as well as aquatic acidification and eutrophication, negatively impacting water quality. The deposition of NO_x in oceans provides phytoplankton with nutrients, leading to phenomena such as red tides and harmful algal blooms. The World Health Organization (WHO) recommends a healthy indoor NO_x level of 150 µg m^{−3} (European

limit, $40 \mu\text{g m}^{-3}$ [21 ppb]) [9,10]. Over the years, NO_x removal strategies have been adopted, such as physical adsorption, wet oxidation, chemisorption, biological filtration, thermo-catalytic reduction, photocatalysis, selective catalytic processes, and selective non-catalytic processes [11,12]. The selective catalytic reduction (SCR) process is employed to mitigate high concentrations of NO_x emissions from industrial boilers, typically operating at temperatures of 250°C or higher, by utilizing NH_3 as a scrubber solution. However, this catalytic method often proves economically burdensome, and the use of NH_3 raises environmental concerns while necessitating significant capital investment [13].

The utilization of photocatalysis as an environmentally friendly approach for NO_x removal, employing light-sensitive semiconductor materials to harness solar energy for the conversion of NO_x to nitrate, represents a promising and cost-effective solution [14]. Efficient removal of NO_x at sub-parts per billion (ppb) concentrations from the atmosphere poses a significant challenge for traditional NO_x removal methods. Photocatalytic techniques offer a green and sustainable approach to addressing NO_x levels at ppb levels under ambient conditions, utilizing solar light for pollutant treatment [15,16]. However, many photocatalysts encounter challenges such as limited light absorption capacity, inappropriate band gaps, and rapid recombination of photogenerated charge carriers, resulting in unsatisfactory reaction yields. While the complete removal of NO with conversion to nitrate is anticipated, the generation of more toxic byproducts like NO_2 through unselective oxidation by oxygen species remains a persistent issue [17].

The efficiency of photocatalysts is intricately linked to factors such as microstructure, surface interface properties, band gap tuning to enhance visible light absorption, and charge separation efficiency [18,19]. Research endeavors have been directed towards exploring the potential of a robust and efficient novel catalyst for catalytic conversion or removal of pollutants. In the pursuit of material development, multiple engineering design strategies have been adopted through various synthetic routes. It is imperative to achieve a rich active site that facilitates high accessibility, along with establishing a proper conductive path and the appropriate surface adsorption or desorption energy of reactive species, all in an efficient and selective manner. Surface tailoring techniques such as functionalization and introduction of vacancies have been employed to optimize the adsorption energy of different reactive species [20]. Additionally, morphology engineering plays a pivotal role, ensuring high mass transport and maximizing the exposed surface area of the catalyst. To enhance the light-harvesting capacity within the visible region, molecular-level engineering of the materials is conducted through strain engineering, defect engineering, metal decoration, and innovative heterojunction formation [21,22]. These approaches mechanistically improve charge separation while simultaneously adjusting the band structure of the catalyst, thus enhancing its overall performance. Through these integrated approaches, the catalyst's efficiency and selectivity in catalytic conversion or pollutant removal have progressed to some extent, paving the way for more sustainable and effective environmental remediation strategies. Nevertheless, the photocatalytic removal of NO_x continues to predominantly reside within the realm of laboratory-scale research [23,24]. This status quo is narrowed down through rigorous exploration of diverse fundamental aspects and the application of an extensive array of materials design strategies. This review focuses on recent advancements in photocatalytic NO_x removal, emphasizing materials design strategies, intrinsic properties, fundamental developmental aspects, and performance validation.

2. Photocatalytic NO_x Removal Mechanism and Chemistry

A light-sensitive catalyst, when subjected to solar light irradiation, initiates photocatalytic interfacial reactions. This catalyst generates electron-hole pairs when the energy of the incident light exceeds the band gap (E_g) (Figure 1).

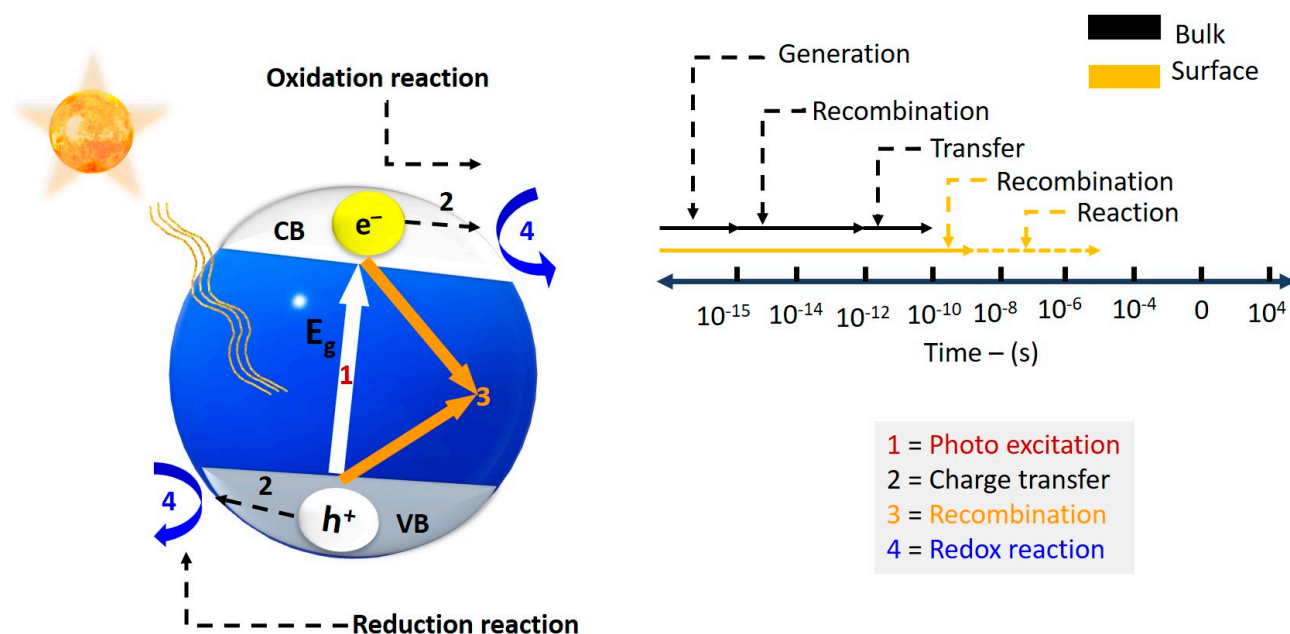


Figure 1. Schematic timescales of photocatalysis process.

The efficient separation of these electron–hole pairs is crucial, as they must overcome Coulomb gravity to achieve long-lasting charge separation, facilitating efficient energy transfer [3,25]. Initially, electron–hole pair generation occurs within femtoseconds, while their migration from the bulk to the surface takes hundreds of picoseconds [26]. Subsequently, migration to the catalyst surface and the occurrence of chemical reactions with adsorbent species happen on a timescale ranging from nanoseconds to microseconds. If there is a mismatch in reaction times, a significant number of charges recombine within the bulk and on the catalyst surface, resulting in the release of light or heat. Only a small fraction of electron–hole pairs successfully reach the catalyst surface to drive redox reactions [27,28]. Additionally, efficient adsorption of reactant species onto the catalyst surface is crucial for utilizing charge carriers effectively in the photocatalytic reaction process.

On the surface of a photocatalyst, photogenerated electrons and holes interact with adsorbed species such as O_2 and H_2O , leading to the formation of reactive oxygen species (ROS) with potent oxidizing properties [29]. These ROS, including superoxide ($\bullet O_2^-$), peroxide (O_2^{2-}), and hydrogen peroxide (H_2O_2), are capable of reacting with nitrogen oxides (NO) to form nitrates and NO_2 (Figure 2) [3,30].

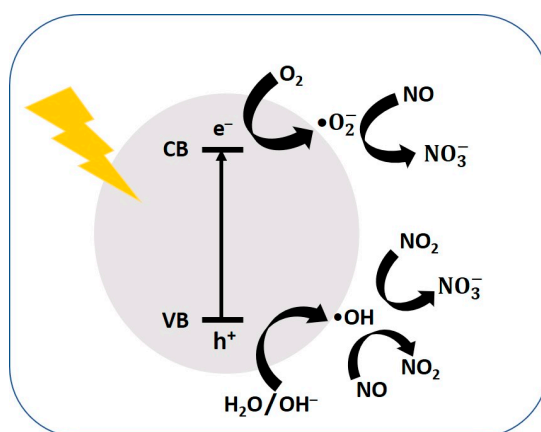
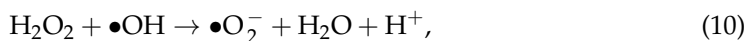
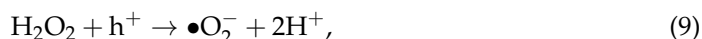
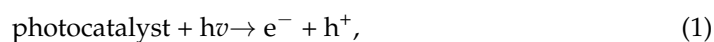


Figure 2. Schematic of the photocatalytic NO oxidation.

Specifically, photogenerated electrons reduce adsorbed O_2 to generate ROS, which subsequently react with NO. Meanwhile, photogenerated holes oxidize H_2O to produce hydroxyl radicals ($\bullet OH$), facilitating the conversion of NO to NO_2 , or NO_2 to nitrate. Oxygen (O_2) can be converted to singlet oxygen ($^1O_2$) through energy transfer pathways or via reactions with ROS. The superoxide radical ($\bullet O_2^-$) may be further reduced to H_2O_2 , which can then decompose into $\bullet OH$ or hydroxide ions (OH^-) [31–33]. Similarly, the $\bullet OH$ radical can be converted back to superoxide radicals or H_2O_2 . It is also feasible for H_2O_2 to react with photogenerated holes, leading to the formation of the superoxide radical and protons (H^+). Additionally, photogenerated holes have the potential to transform hydroxyl radicals back into superoxide radicals. Thus, species such as $\bullet O_2^-$, O_2^{2-} , $^1O_2$, and $\bullet OH$ constitute the ROS instrumental in the oxidation of NO to selectively produce nitrates (Equations (1)–(14)) [3,34,35].



3. Strategic Approaches for Improving Photocatalysis

Traditional visible light-responsive photocatalysts, such as $g\text{-C}_3\text{N}_4$, Bi_2WO_6 , and BiVO_4 , often exhibit low catalytic activity attributable to limitations in light-harvesting capacity, rapid recombination of photogenerated carriers, and scarcity of catalytically active sites on the catalyst surface [36]. Addressing these challenges necessitates a multifaceted materials design strategy, incorporating techniques such as ion doping, defects engineering, morphology control, heterojunction construction, and metal decoration (Figure 3) [37].

Furthermore, optimizing photocatalytic processes involves adjusting band structures, optimizing surface physiochemical states, and implementing built-in electric field approaches. For instance, the formation of reactive species crucial for photocatalysis requires precise band potential alignments, with the valence band potential for hydroxyl radical formation at 1.99 eV and the conduction band potential for O_2 to O_2^- conversion at -0.33 eV. Heterojunction engineering emerges as a promising avenue for enhancing catalytic efficiency by fine-tuning band positions and optimizing charge separation. Various heterojunction architectures, including Z-scheme, S-scheme, and p–n heterojunctions, offer distinct mechanisms for facilitating continuous photocatalytic processes (Figure 4) [38–40].

In Z-scheme configurations, reduction semiconductors absorb light and generate electrons, which are subsequently accepted by oxidation semiconductors, leading to sustained photocatalysis [41–43]. Similarly, S-schemes exploit built-in electric fields at semiconductor

interfaces to facilitate efficient charge carrier migration, enhancing redox capacity [40,42]. p–n heterojunctions, constructed using n-type and p-type semiconductors, provide precise control over band positions, further optimizing photocatalytic performance. This comprehensive approach underscores the potential of advanced materials design strategies in overcoming the limitations of traditional photocatalysts, thereby advancing applications in environmental remediation and sustainable energy conversion [42,44].

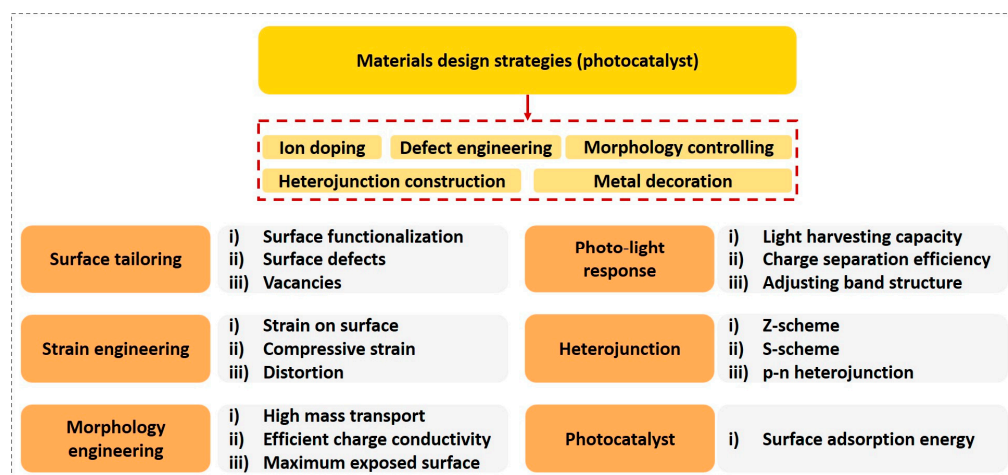


Figure 3. Materials design strategy.

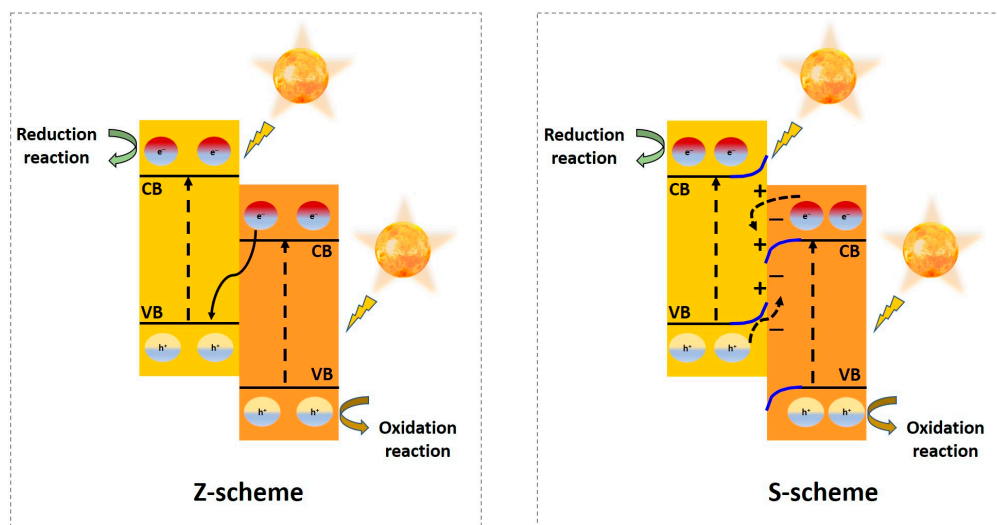


Figure 4. Heterojunction formation (Z-scheme, and S-scheme).

4. Materials Design Strategy

4.1. p–n Heterojunction

The p–n heterojunction is considered an effective strategy for improving photocatalytic activity, as it can effectively resist the recombination of charged carriers. At the interface junction, directional movement of charge carriers occurs due to band bending and band matching by two components, generating built-in electric fields [45]. BiOI, a potential and effective p-type semiconductor with the narrowest band gap (~ 1.9 eV), has the capacity to absorb sunlight below 650 nm [46]. The alternating stacking of $[\text{BiO}]_2^{2+}$ and I^- layers generates built-in electric fields in the 001-orientation facet, inducing the separation and transfer of photogenerated charge carriers. The Liu group designed the photocatalyst of the BiOI/CeO₂ p–n heterojunction, where CeO₂, an n-type photocatalyst, serves as a potential oxygen activation catalyst due to the coexistence of $\text{Ce}^{3+}/\text{Ce}^{4+}$ pairs and O-vacancies (OVs), despite its limited solar light absorption capacity due to its wide band gap (~ 3.1 eV) [47,48].

The p–n heterojunction improves the separation of electron and hole pairs, enhances light absorption, and, at the interface of the p–n junction, the formation of reactive $\bullet\text{O}_2^-$ and hydroxyl radical ($\bullet\text{OH}$) species occur [47]. The Sanchez group employed NiTi–LDH/BiOBr heterojunction type (II) for NO_x removal [49]. Layered double hydroxides (LDHs) contain divalent or trivalent cations within the interlayer space along with molecular water. LDHs containing transition metals are efficient for generating nitrate/nitrite species (>90% yield) during NO_x reduction, although they exhibit poor performance under visible light (Figure 5a,b) [50]. Bismuth oxybromide (BiOBr) is a promising photocatalyst for the photodegradation of contaminants such as CO_2 and DeNO_x [51–53]. The incorporation of BiOBr into NiTi–LDHs increases the electron density of Ti at heterojunctions, thereby enhancing NO adsorption on the catalyst. NiTi–LDH/BiOBr heterojunction photocatalysts exhibit 83–84% NO_x removal efficiency, surpassing that of NiTi–LDHs (66%) and BiOBr (54%) under visible light conditions [49].

4.2. Doping, and Defect Engineering

The utilization of Eu^{3+} with its large cation size (0.95 Å) for doping into the lattice structure of photocatalysts introduces strain or defects, potentially generating energetic states within band gap materials, which in turn can enhance photocatalytic activity through the mitigation of photo-charge recombination [54,55]. Pastor et al. developed Eu^{3+} -doped Zn_2Al –LDHs, observing that an optimal level of Eu^{3+} doping not only reduced photo-charge recombination but also increased the production of radicals [56]. The incorporation of Eu^{3+} into the LDHs' lattice alters the M–O interaction, attributable to the larger cation size of Eu^{3+} compared to Al^{3+} . This doping significantly enhances visible light absorption in the 400–500 nm range, more so than that observed with non-doped LDH catalysts (Figure 5c). Consequently, NO removal efficiency improved to 47.3% with Eu^{3+} -doped LDHs under visible light irradiation, a substantial increase from the 9.3% efficiency of non-doped LDHs (Figure 5d–g) [56].

TiO_2 is recognized as a promising material due to its low cost, non-toxicity, and stable physical and chemical characteristics. However, its wide band gap (~3.6 eV) limits its ability to absorb only ultraviolet light, which constitutes merely 4% of solar light, rendering it inefficient for visible light applications [23,57]. To address this limitation, a combination of 0D carbon quantum dots (CQD) with 1D TiO_2 has been explored for photocatalytic NO removal under visible light. The Yang group has enhanced the photocatalytic performance by inducing oxygen vacancies in the TiO_2 component of the CQD/ TiO_2 composite, reducing its band gap to 2.70 eV (Figure 6a) [58]. This modification has significantly improved the efficiency of visible light-driven photocatalytic NO removal by up to 57%. The introduction of CQDs and the creation of oxygen vacancies are key to narrowing the band gap. This defect engineering through oxygen vacancies enhances the separation and transfer of electrons and holes, facilitating the generation of active radicals such as superoxide ($\bullet\text{O}_2^-$) and hydroxyl ($\bullet\text{OH}$), which are crucial for the photocatalytic process (Figure 6b) [58].

In alternative approaches, the Young–Si group has introduced nitrogen doping to TiO_2 , thereby narrowing the band gap from 3.25 to 3.18 eV [23]. This process increases visible-light absorption and enhances the separation and transfer of photoexcited charge carriers. The adjustment primarily tunes the positions of the conduction and valence bands through the ratio of nitrogen doping. Surprisingly, achieving an even narrower band gap of 3.10 eV, which enhances light absorption, does not lead to higher NO removal efficiency (20%). However, tuning the positioning of the conduction band at -0.73 eV and the valence band at 2.45 eV does result in higher NO removal efficiency (51%) [23].

Stucchi et al. employed wastewater enriched with Ag^+ ions to decorate TiO_2 photocatalysts [59]. Other studies indicate that the stability of Ag nanoparticles (NPs) on TiO_2 is enhanced when coupled with other noble metals such as Pt and Au. The synergistic effects between Ag/Au and Ag/Pt enhance localized surface plasmon resonance (LSPR), resulting in enhanced electron trapping compared to Ag/ TiO_2 monometallic photocatalysts [59]. Bianchi and colleagues synthesized metal-modified TiO_2 (Au@Ag/TiO_2) photocatalysts utilizing

metal-enriched wastewater for the photocatalytic abatement of NO_x (90%) (Figure 6c) [60]. The beneficial effects of decorated Au NPs on NO_x removal are attributed to the absorption of visible light and the high tolerance of Au NPs to HNO_3 , which is produced on the surface of the photocatalyst (Figure 6d) [61].

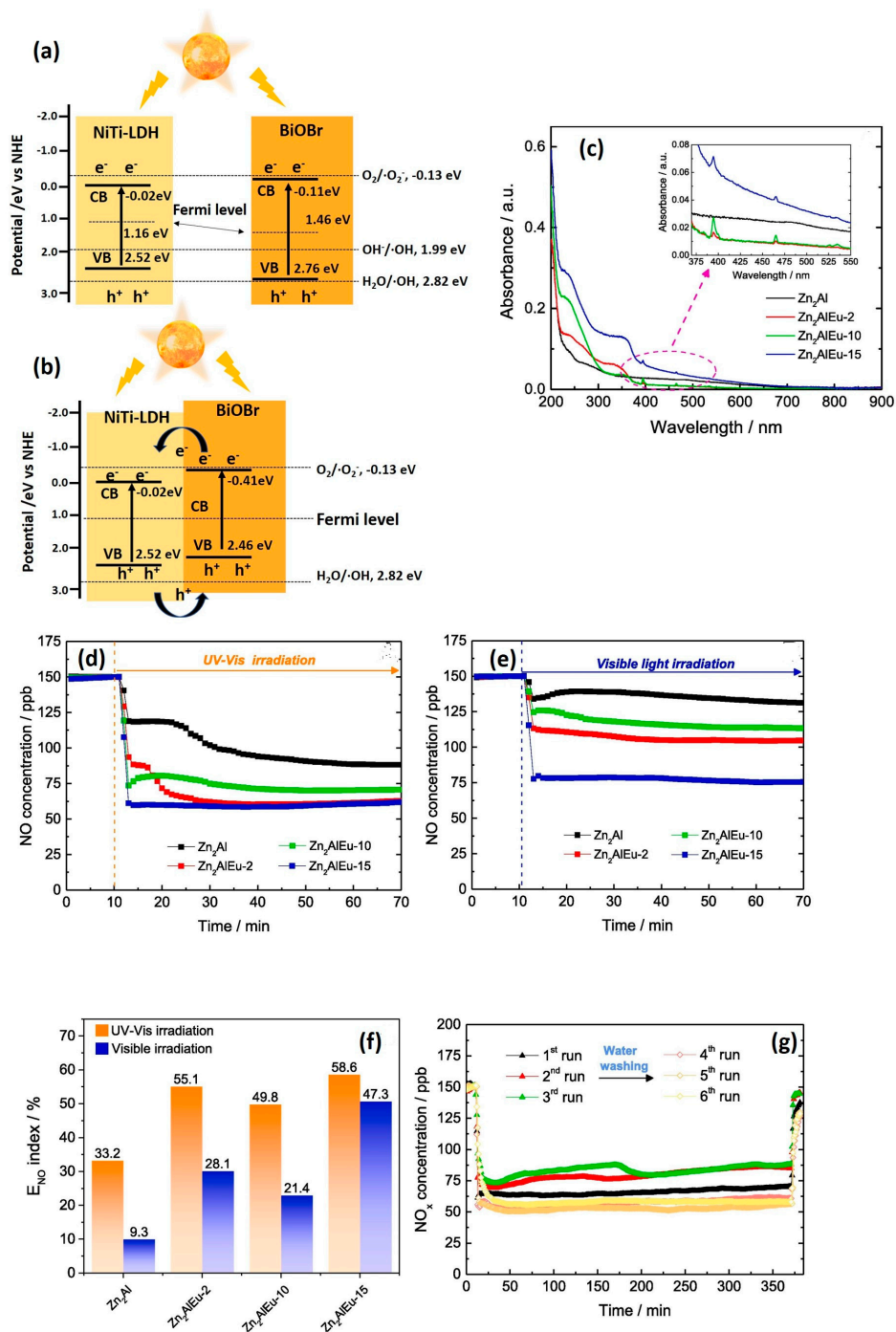


Figure 5. Schematic of band diagram of NiTi-LDHs (layered double hydroxides) (a) before and (b) after photocatalytic test of Eu-doped LDH; NO concentration profile of (c) UV-Vis (ultraviolet-visible) absorption spectra, (d) UV light, (e) visible light, (f) NO removal efficiency, and (g) cycle run of De NO_x process of $\text{Zn}_2\text{AlEu-15}$ LDH under UV-Vis light irradiation. (Adapted with permission from Ref. [56], Copyright © 2023 Elsevier Ltd.)

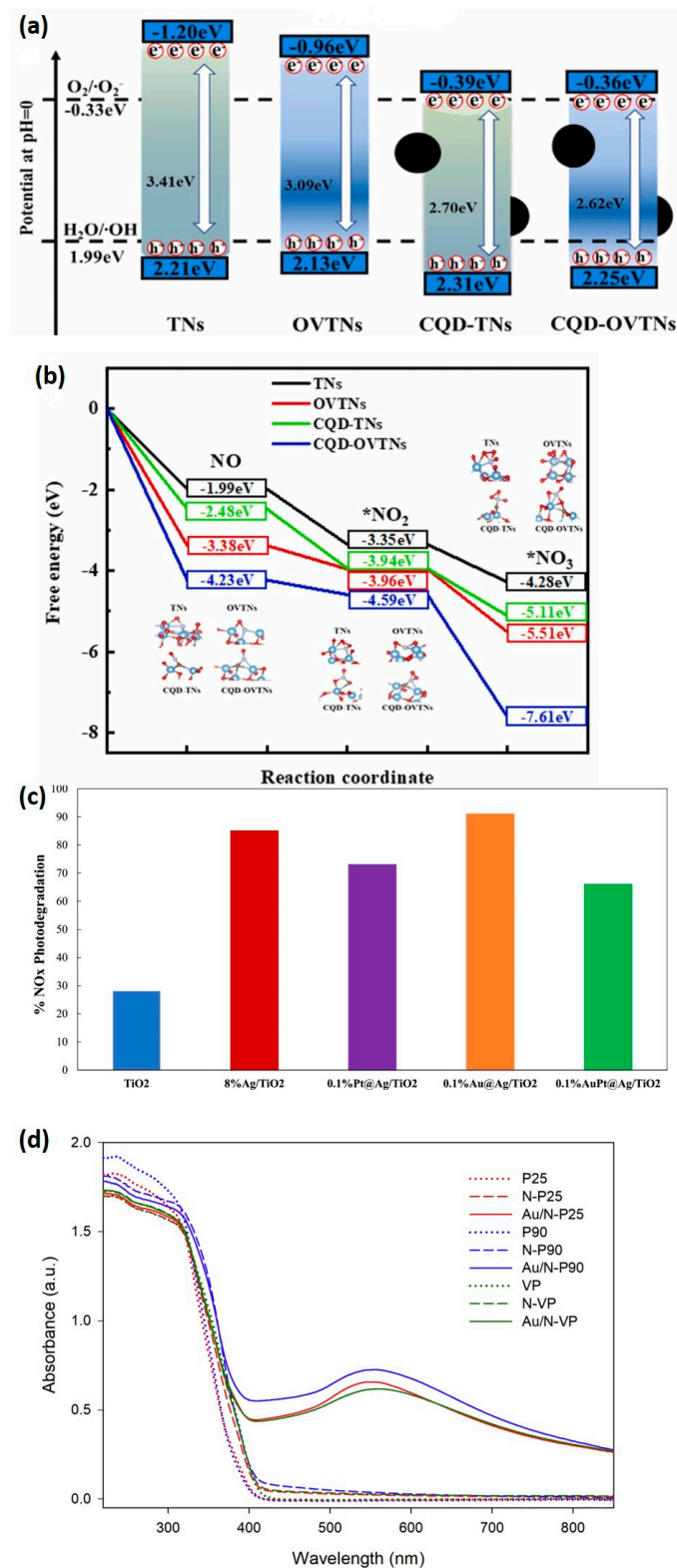


Figure 6. (a) Schematic of band structure of TiO_2 with creating OV and introducing CQDs, (b) free energy changes NO-to-* NO_3 photocatalytic process for different modified photocatalyst catalyst (adapted with permission from Ref. [58], Copyright © 2023 Elsevier Ltd.), (c) comparison of NO_x photodegrading performance by TiO_2 modified with different noble metals (adapted with permission from Ref. [60], Copyright © 2023 Elsevier Ltd.), and (d) comparison of light absorption capacity of UV-to-visible region by different modified photocatalysts (adapted with permission from Ref. [61], Copyright © 2019 Elsevier Ltd.).

4.3. Microstructure, Crystal Facet, and Morphology Engineering

Modification of TiO_2 for effective visible light-activated photocatalysis represents a crucial avenue in enhancing the utilization of visible light for photocatalytic applications [62]. One promising approach involves the utilization of photonic crystal structures with an opal-like arrangement, which presents a highly potent strategy. This involves shaping the catalyst into a periodic photonic structure capable of manipulating the flow of light (Figure 7a). The incorporation of photonic crystals in semiconductor photocatalysis serves to improve light harvesting by the catalyst materials and enhances light–matter interactions [63,64].

Photonic nanostructures featuring optical microcavities confine light at the nanometer scale, thereby improving the efficiency of solar energy conversion through enhanced interaction with the semiconductor material [65,66]. In this context, the Fu research group has utilized TiO_2 –PC for NO removal, demonstrating a remarkable 2.3-fold increase in NO removal efficiency in the visible region compared to pristine TiO_2 films (32% vs. 13%) [67]. The phenomenon of slow photon effects further amplifies photon–matter interactions, consequently enhancing solar utilization in the UV–visible light region and leading to higher NO removal performance (Figure 7b–d). However, further development of photocatalysts is imperative, particularly in terms of stability, as evidenced by a decrease in performance from 32% to 20% within 30 min of application [67].

Graphitic carbon nitride (CN) is considered one of the potential non-metallic semiconductor photocatalysts due to its biocompatibility, response to visible light, excellent stability, and non-toxic nature. It offers versatile synthesis methods to achieve various characteristic properties depending on the application area [68]. However, its photocatalytic activity is hindered by inherent limitations such as low light absorption capability, fast charge recombination, and a lower specific surface area. Efforts have been made to enhance the photocatalytic activity or adjust the catalytic performance through methods such as heteroatom doping, heterojunction construction, crystallinity improvements, and supporting co-catalysts. To increase the surface area of catalytic reactive sites, exfoliation of 2D nanosheets is carried out using techniques like ultrasound, ball milling, and oxidation exfoliation strategy. A higher surface area and pore structure facilitate mass diffusion and separation of photogenerated charge carriers by exposing new edge sites.

However, such nano-sized structures increase the band gap of the semiconductor photocatalyst due to quantum confinement effects, resulting in decreased light absorption capability [68–70]. In a recent study conducted by the Lv group, sulfur-doped holey carbon nitride nanosheets were synthesized and evaluated as a photocatalyst for the removal of nitrogen oxides (NO) [71]. The incorporation of sulfur (S) into the carbon nitride matrix was found to significantly attenuate the recombination rates of electron–hole pairs, a pivotal factor in augmenting the NO oxidative capabilities of the photocatalyst by facilitating the generation of a higher concentration of reactive oxygen species, including superoxide and hydroxyl radicals. Notably, the S-doping strategy led to a reduction in the band gap of carbon nitride from 0.98 to 0.87 eV, accompanied by a discernible negative shift in the positions of the energy bands. The electronic structure of carbon nitride plays a crucial role in its photocatalytic performance. Prior to doping, the valence band of carbon nitride is predominantly constituted by C 2p and N 2p orbitals, whereas the conduction band is composed of N 2s and N 2p orbitals. The introduction of sulfur introduces a minor proportion of S 3p orbitals into the system, which is instrumental in the observed narrowing in the band gap. Furthermore, S-doping induces a charge redistribution mechanism wherein carbon atoms gain electrons from sulfur atoms (Figure 8a,b). This phenomenon is attributed to the elevated electron density and the expansion of the π -conjugated system, which, in turn, promotes the separation of charge carriers. The enhanced separation facilitates an increased abundance of photoelectrons, thereby significantly bolstering the photocatalytic efficiency of the carbon nitrides (Figure 8c) [71]. The Lu research group has successfully achieved the in situ growth of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ lead-free perovskite (CBB) on a three-dimensional flower-like structure of graphitic carbon nitride (CN) [72]. This innovative configuration

capitalizes on the advantageous properties of the perovskite, which demonstrates high absorption energy, low exciton binding energy, and superior carrier mobility (Figure 8d–f). Notably, the establishment of a heterojunction between CBB and CN within this framework serves to impede the recombination of electrogenerated electron–hole pairs. This effect is primarily facilitated by the directed transfer of charge carriers, with holes migrating from the CN valence band (1.91 eV) to the CBB valence band (1.37 eV), and electrons transferring from the CBB conduction band (−1.13 eV) to the CN conduction band (−0.83 eV). As a result of these mechanisms, the efficiency of NO degradation is markedly enhanced within the CBB/CNN heterojunction, exhibiting a notable improvement from 20 to 54% when compared to the performance of CBB in isolation [72].

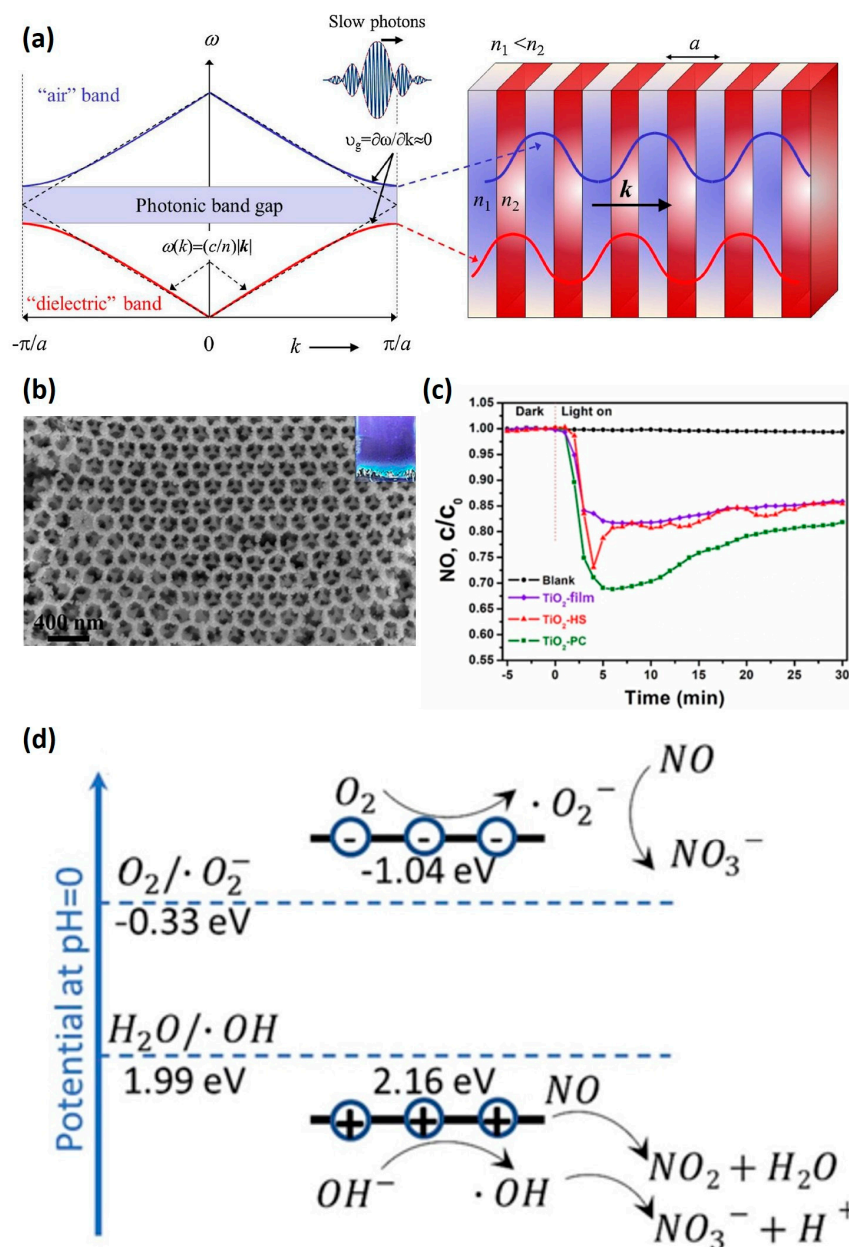


Figure 7. (a) Photonic band gap formation in a 1D periodic stack consisting of alternating dielectric layers with different refractive indexes ($n_2 > n_1$) (adapted with permission from Ref. [66], Copyright © 2018 Elsevier Ltd.), (b) SEM image of TiO₂-PC, (c) NO removal rate comparison, and (d) NO conversion mechanism (adapted with permission from Ref. [67], Copyright © 2023 Elsevier Ltd.).

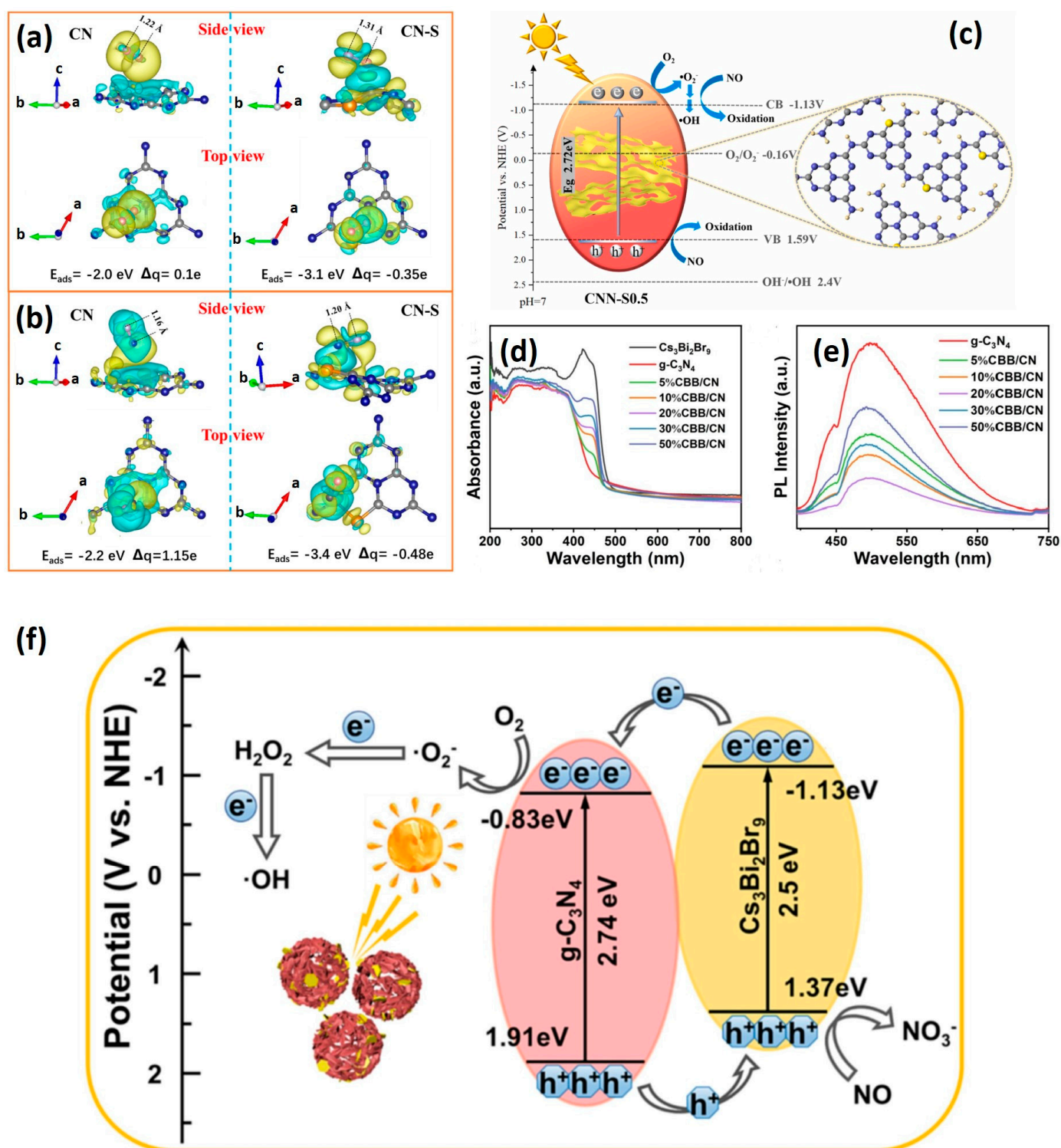


Figure 8. The distribution of charge difference in pure CN and S-doped CN is shown for (a) adsorbed O_2 and (b) adsorbed NO, where yellow represents charge depletion and blue signifies charge accumulation. E_{ads} and Δq denote the adsorption energy and the Bader charge, respectively, (c) NO oxidation mechanism of S-doped CN (adapted with permission from Ref. [71], Copyright © 2023 Elsevier Ltd.), (d) light-harvesting capacity (aible DRS spectra), (e) charge separation efficiency (photoluminescence spectra), and (f) NO removal mechanism by CBB/CN heterojunction (adapted with permission from Ref. [72], Copyright © 2023 Elsevier Ltd.).

A restricted surface area contributes to inadequate absorption of visible light and rapid rates of charge recombination. Dong et al. present a method for enhancing the surface area (31 to $288\text{ m}^2\text{ g}^{-1}$) of carbon nitride by exfoliating and splitting layers (35 nm to 15 nm). By reducing layer thickness, they effectively shorten the charge transfer distance and mitigate charge recombination. Their study demonstrates that increasing pore volume (0.09 to $1.41\text{ cm}^3\text{ g}^{-1}$) and achieving a high specific surface area enhance the diffusion rate of intermediates. Consequently, the likelihood of photooxidation of NO_2 to nitrate is heightened (26 to 32% NO removal ratio in comparison to pristine) [73]. In another study, a similar group produced ultrathin carbon nitride, creating carbon vacancies on the ultrathin surface [74]. These vacancies efficiently trap photogenerated electrons and intensify the reduction of NO to N_2 (48% improved) under visible light.

4.4. Heterojunction

Ferroelectric-type materials with oppositely polar surfaces tune catalytic activity and maintain the separation efficiency of photogenerated charge [75]. The Wang group enhanced the light absorption and charge separation efficiency of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ferroelectric perovskite nanosheets by decorating them with the noble metal Au. This modification leverages the localized surface plasmon resonance (LSPR) and interface effects of the photocatalyst, resulting in improved efficiency in removing NO [76]. The Lu group has ingeniously designed a triphasic Z-scheme heterostructure ($\text{TiO}_2/\text{Ti}_3\text{C}_2\text{ MXene}/\text{CN}$) photocatalyst, utilizing electrostatic self-assembly for the effective removal of NO gas [77]. In this configuration, the 2D $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{ MXene}$ component plays a pivotal role in enhancing the adsorption and subsequent removal of NO gas. It is important to note that, in isolation, $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{ MXene}$ does not exhibit photocatalytic activity, nor does it generate reactive species such as superoxide or hydroxyl radicals under visible light irradiation; these functions are exclusively performed by the CN component. However, when integrated into the triphasic Z-scheme heterostructure, the combined effects of these components significantly amplify the NO removal efficiency, achieving a rate of 56% compared to the 32% efficiency observed with CN alone. This enhancement underscores the critical role of both the adsorption and removal processes of NO gas at the catalyst surface. Furthermore, $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{ MXene}$ contributes to this system by facilitating electron transport and reducing the recombination of photogenerated charges, thereby improving the overall photocatalytic performance of the heterostructure in NO removal applications [77]. The Amama group has developed a $\text{TiO}_2\text{-gCN}$ photocatalyst Z-scheme heterojunction characterized by significant visible light absorption, enhanced reaction kinetics, and robust reduction and oxidation capabilities, thereby promoting improved charge carrier dynamics (Figure 9a–d) [78]. The research underscores the critical role of NO_x adsorption capacity in achieving efficient NO_x oxidation. Nevertheless, the $\text{TiO}_2\text{-gCN}$ composite exhibits limited NO_x adsorption capacity. Water (H_2O) assumes a pivotal role in NO_x oxidation by sequestering photoexcited holes to generate active $\bullet\text{OH}$ radicals, essential for NO_x oxidation. Moreover, the higher polarity of water compared to NO and NO_2 may displace the latter from the catalyst surface, thereby impeding oxidation. The study explores NO conversion under differing relative humidity conditions—low (10% RH) and high (50% RH) levels—under blue light illumination. Results indicate superior NO conversion rates at lower humidity levels, with no detectable NO_2 formation compared to higher humidity conditions [78].

Pyrazinoquinoxaline-based graphdiyne (PQ-GDY) serves as a pivotal substrate in photocatalysis, owing to its pronouncedly augmented generation of photogenerated charge carriers, attributable to its larger conjugated cross-linked heterocyclic aromatic ring structure [79,80]. Concurrently, $\text{NH}_2\text{-UiO-66 (Zr)}$, a base metal–organic framework (MOF), emerges as a promising counterpart characterized by its expansive surface area, exceptional thermal and aqueous stability, and superior gas molecule absorption capabilities. Nonetheless, the efficiency of MOF photocatalysts is often hindered by their limited electron utilization capacity, a consequence of the swift recombination of photogenerated charge

carriers [81,82]. In a technical endeavor, the Zhang group has synthesized well-dispersed $\text{NH}_2\text{-UiO-66 (Zr)}$ on the PQ-GDY surface via microwave irradiation (Figure 9e,f) [83].

This innovative approach harnesses microwave energy to induce hot spots, thereby facilitating the dispersion of $\text{NH}_2\text{-UiO-66 (Zr)}$ with exquisite crystallinity across the PQ-GDY substrate. Within this composite architecture, PQ-GDY expedites hole transport to $\text{NH}_2\text{-UiO-66 (Zr)}$, markedly amplifying the separation efficiency of photogenerated charge carriers. The resultant heterojunction photocatalyst, comprising PQ-GDY and $\text{NH}_2\text{-UiO-66 (Zr)}$, establishes a robust heterostructure through $\pi\text{-}\pi$ stacking interactions. Notably, the slender morphology of the catalyst minimizes transmission distances, while the inherent rapid hole mobility properties of PQ-GDY further augment charge separation efficiency. Under visible light irradiation, the synergistic effects of the PQ-GDY/ $\text{NH}_2\text{-UiO-66 (Zr)}$ heterojunction culminate in a notable NO_x removal efficiency of 74%, representing a substantial enhancement over the 44% efficiency attained with $\text{NH}_2\text{-UiO-66 (Zr)}$ as a standalone catalyst [83].

Photocatalysis using semiconductor materials is a promising method for environmental remediation. Cubic perovskite SrTiO_3 (STO) has attracted attention as a photocatalyst due to its superior redox potential compared to TiO_2 [84]. Additionally, co-catalysts such as SrCO_3 (SCO) have been explored to enhance pollutant degradation [85,86]. Han et al. investigate the photocatalytic degradation of indoor air pollutant NO using the STO/SCO heterojunction under solar light [9]. The heterojunction exhibited a 44% degradation of NO with a reaction rate of 0.078 min^{-1} . Mechanistic insights reveal the formation of an internal electric field due to disparate potentials of STO and SCO, promoting charge separation. Under solar light, O-vacancies in SCO induce electron transfer, enhancing photocatalytic activity. Accumulated holes on the VB of SCO react with water molecules, forming hydroxyl radicals. The study sheds light on the enhanced photocatalytic activity of the STO/SCO heterojunction under solar light irradiation. Mechanistic insights into the photocatalytic activity of the STO/SCO heterojunction elucidate its enhanced performance. The formation of an internal electric field due to the disparate potentials of STO and SCO in the insulator heterojunction facilitates charge separation. Under solar light irradiation, O-vacancies are generated in SCO, leading to a direct transition of electrons from the valence band (VB) to an intermediate level and subsequent transfer to the conduction band (CB) of SCO, promoting photocatalytic activity. Moreover, the accumulated holes on the VB of SCO react with water molecules, generating hydroxyl radicals that further contribute to the degradation of pollutants. These mechanistic insights underscore the significance of the STO/SCO heterojunction as an efficient photocatalyst for environmental remediation applications [9].

The heterojunction employing the S-scheme demonstrates enhanced reduction and oxidation potentials compared to the isolated reduction photocatalyst (RP) and oxidation photocatalyst (OP), which are composed of two distinct semiconductors possessing differing Fermi levels. This configuration induces a built-in electric field at the interface of the RP and OP semiconductors due to charge reorganization. This occurs as the Fermi levels align, causing band bending and facilitating accelerated charge transfer [87,88]. The Zhang group successfully synthesized the $\text{CeO}_{2-x}/\text{gC}_3\text{N}_{4-x}$ heterojunction, incorporating both nitrogen and oxygen defects through a singular calcination step (Figure 10a–e) [45]. CeO_2 , characterized by the coexistence of Ce^{4+} and Ce^{3+} ions, introduces oxygen defects and presents a highly active lattice plane that favors interfacial electron transfer. The presence of dual nitrogen and oxygen defects offers additional active sites. Moreover, the intrinsic electric field within the CeO_2 and gC_3N_4 heterojunction not only aids in generating more active species but also promotes exciton to carrier conversion, facilitated by well-regulated band bending. This, in turn, enhances carrier separation and accelerates the surface reduction semi-reaction. This study underscores the S-scheme $\text{CeO}_{2-x}/\text{gC}_3\text{N}_{4-x}$ photocatalyst's efficacy in NO removal, attributing its performance to the synergistic effects of the built-in electric field, co-activation by nitrogen–oxygen dual defects, and the efficient conductivity of CeO_2 [45].

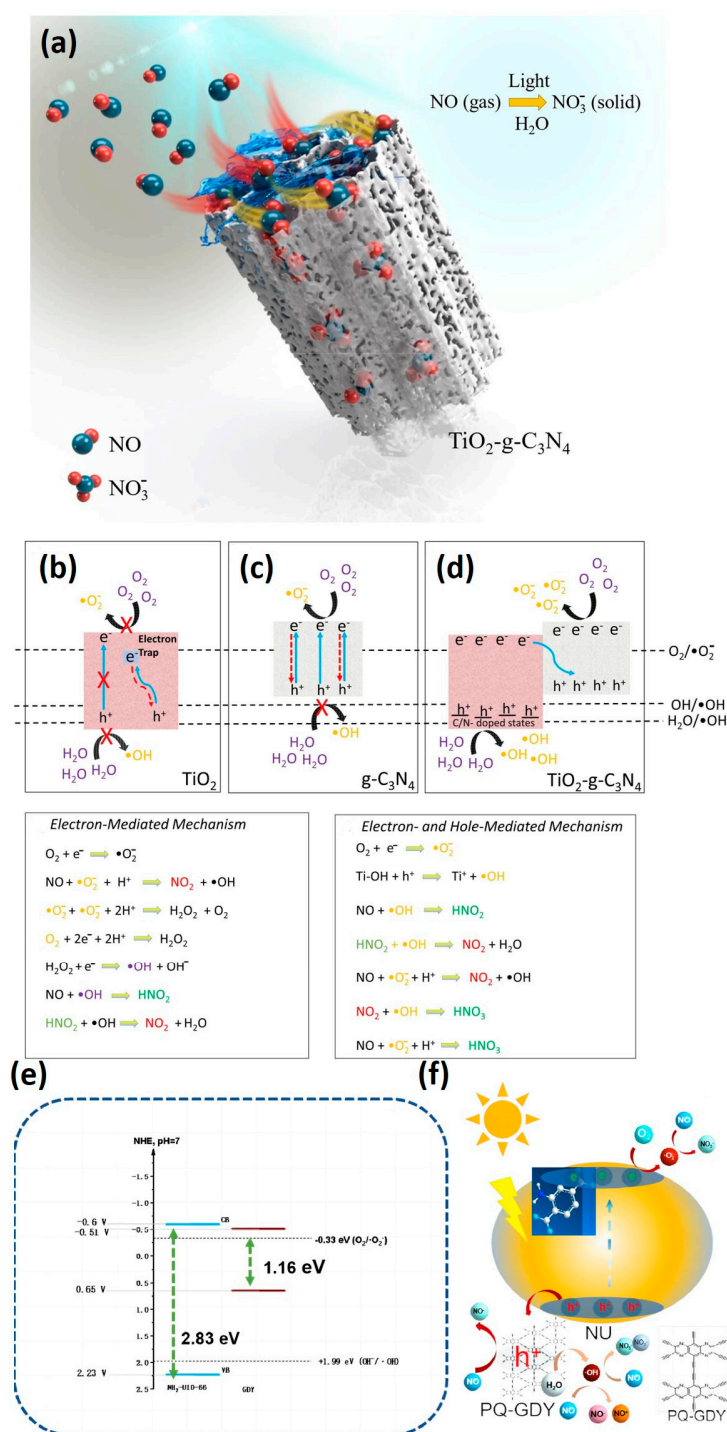


Figure 9. (a) Schematic of $\text{TiO}_2\text{-gCN}$ photocatalyst, (b–d) schematic diagrams of photo-induced charge carrier formation and subsequent active radicals formed in under cyan lights with reaction mechanism (adapted with permission from Ref. [78], Copyright © 2023 Elsevier Ltd.), (e) energy band gap diagram, CB and VB edge potentials of PQ-GDY and $\text{NH}_2\text{-UiO-66(Zr)}$, and (f) schematic of photocatalytic mechanism of $\text{PQ-GDY@NH}_2\text{-UiO-66(Zr)}$ (adapted with permission from Ref. [83], Copyright © 2023 Elsevier Ltd.).

Metal–organic frameworks (MOFs) are recognized as promising materials for tackling air pollution challenges owing to their large surface area for catalysis and abundant adsorption sites for active species. UiO-66, a MOF-based light-responsive photocatalyst, boasts significant surface area and is predominantly known for its chemical and thermal

stability [89]. However, its photocatalytic responsiveness is confined to ultraviolet light due to its wide band gap (4.0 eV) [90]. Modification of the UiO-66 structure through ligand grafting ($X = -NH_2, -COOH, -OH, -NO_2$, and $-H$) and partial substitution of Zr nodes with metals such as Ti can effectively narrow the band gap, rendering the photocatalyst responsive to visible light [91]. In a recent study, Liu et al. engineered (Zr/Ti) UiO-66- NH_2 with a core-shell structure via microwave-assisted post-synthetic modification (Figure 10f–h) [92].

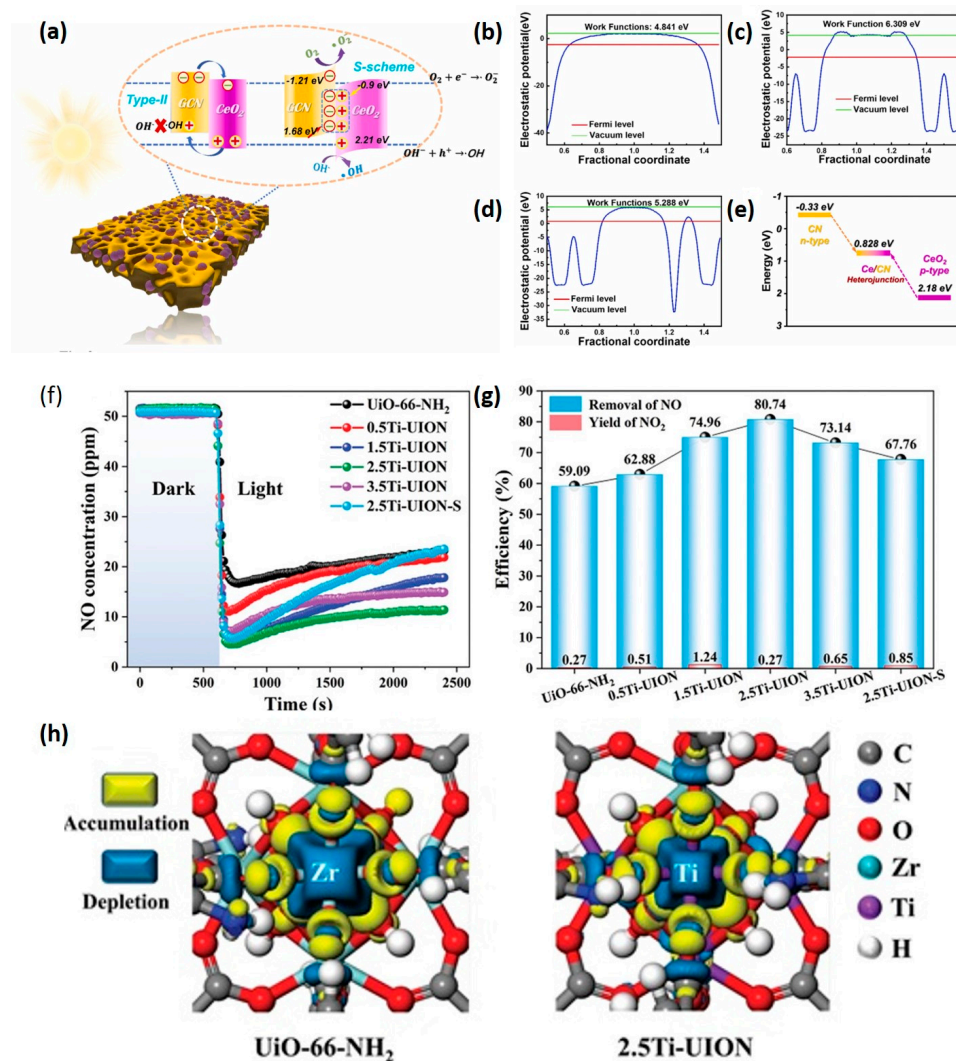


Figure 10. (a) Schematic of S-scheme heterojunction of $CeO_{2-x}/g-C_3N_{4-x}$; work function of (b) $g-CN$, (c) CeO_2 , (d) $/CN$, (e) Fermi level position (adapted with permission from Ref. [45], Copyright © 2023 Elsevier Ltd.); (f) NO concentration profile photocatalytic process and (g) NO removal efficiency; (h) represents charge density difference of metal cluster (adapted with permission from Ref. [92], Copyright © 2023 Elsevier Ltd.).

The introduction of Ti enhances the separation and migration of photogenerated charge carriers, with Ti–O units in metal clusters expediting their migration. Concurrently, the improved gas molecule adsorption capacity enhances NO oxidation and impedes the escape of NO_2 from catalyst surfaces. This culminates in a notable NO removal efficiency of 80.7% under visible light irradiation. However, catalytic activity diminishes to 70% after five cycles, underscoring stability concerns that remain unaddressed in current strategies [92].

5. Secondary Pollutant Control Strategy

N_2O , a secondary pollutant produced catalytically during the removal of NO_x , poses unforeseen detrimental environmental concerns, surpassing those associated with NO itself. In the context of photocatalytic NO_x reduction, the generation of N_2O is a significant obstacle, attributed to its chemical inertness, high kinetic stability, and a decomposition half-life exceeding 100 years. Its role in stratospheric ozone depletion and as a potent global warming agent underscores the urgency in addressing N_2O formation [93,94]. A promising strategy to mitigate this involves harnessing a high concentration of photogenerated electrons to activate reductants effectively. The Zhou research group has innovatively developed a $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ heterojunction photocatalyst, showcasing a strategic approach to inhibit N_2O formation (Figure 11a–d) [95]. Their findings indicate that N_2O is stably adsorbed on the TiO_2 (110) plane, a site where photogenerated electrons are accumulated, thus facilitating the reduction of N_2O . The adsorption energy of N_2O on TiO_2 is significantly higher (-1.75 eV) compared to that on Bi_2WO_6 (-0.63 eV), confirming more stable adsorption on the TiO_2 (110) plane. When TiO_2 is used as a standalone photocatalyst, the quantity of photogenerated electrons proves insufficient for the prompt reduction of N_2O , primarily due to the rapid recombination of electron–hole pairs. However, the introduction of a Z-scheme heterojunction significantly increases the electron availability on the TiO_2 surface, enhancing the adsorption energy of N_2O on the TiO_2 (110) planes and consequently promoting more effective N_2O reduction [95].

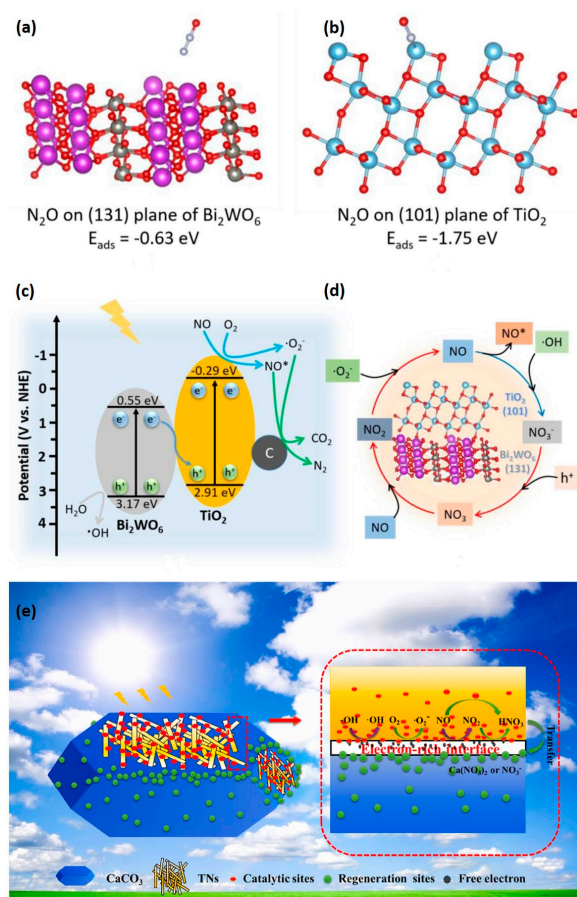


Figure 11. Adsorption energy of N_2O (a) Bi_2WO_6 , (b) TiO_2 , (c) schematic of Z-scheme of $\text{Bi}_2\text{WO}_6/\text{TiO}_2$, (d) catalytic dynamic process of NO consumption and formation (adapted with permission from Ref. [95], Copyright © 2023 Elsevier Ltd.); and (e) schematic of the NO degradation mechanism, a degradation–regeneration double site, which inhibits NO_2 formation (adapted with permission from Ref. [96], Copyright © 2023 Elsevier Ltd.).

6. Stability Development Approach

The stability of photocatalysts is pivotal in crafting an effective NO removal strategy. Observations from cyclic photocatalytic tests reveal a 5–15% decline in the efficiency of photocatalytic NO removal. This decrease in efficiency is primarily due to the accumulation of nitric acid on the catalyst's surface, a byproduct that either damages the photocatalyst's properties or leads to its deactivation towards NO degradation [97,98]. As a result, the long-term utility of photocatalytic materials in practical applications is significantly compromised. Although a water wash process has been suggested to restore the degraded photocatalyst, this method is considered impractical because it leads to increased maintenance costs and contributes to the production of wastewater and pollution [99–101]. The mechanism of photocatalytic NO degradation is a multi-step process. Initially, NO is converted into nitric acids, NO_2 , or nitrite through oxidation by superoxide and hydroxyl radicals, which are subsequently oxidized to nitrate [102,103]. It has also been identified that NO can be directly oxidized to nitrate by superoxide radicals [98]. These fundamental theoretical insights underline the necessity of developing a design strategy aimed at improving the durability of photocatalysts for NO_x removal. Implementing such a strategy would not only enhance the performance of NO_x removal technologies but also their sustainability and practical viability. In an effort to enhance photocatalyst durability, Li et al. have engineered a WO_3 – TiO_2 nanorod composite with CaCO_3 (Figure 11e). The CaCO_3 reacts with nitric acid to form calcium nitrate, thereby providing regeneration sites for the photocatalytic process and ensuring its durability [96]. Furthermore, calcium carbonate acts as an insulating heterojunction, creating an electron-rich region on the photocatalyst surface, which contributes to its enhanced performance and durability. Furthermore, subsurface oxygen vacancies near the defect-free surface, within TiO_2 (101), exhibit high photocatalytic activity. Anatase TiO_2 predominantly harbors subsurface oxygen vacancy defects beneath the defect-free oxygen vacancies, thereby facilitating chemical activity in the nearby surface region [104]. These subsurface defects significantly enhance visible light-harvesting and exhibit inertness toward reactive oxygen species, thereby maintaining high stability near catalytic sites. Conversely, surface defects related to oxygen vacancies easily trap oxygen intermediates and hinder their release or further progression of reactions. Consequently, this process fails to generate O_2 products and may even deteriorate oxygen defects. Subsurface defects on metal oxide sites represent a strategic approach to enhancing the stability of the photocatalyst [104,105].

7. Comparative Recent Review on Photocatalytic NO_x Removal Process

The focus of research on photocatalytic NO removal has encompassed various reviews, placing significant emphasis on the efficacy of removal techniques. Kumar et al. conducted a specific investigation into the S-scheme heterojunctions formed by binary composites, with a particular focus on potential enhancements should the dual S-Scheme be developed [106]. They underscored the superiority of S-scheme heterojunctions compared to other photocatalytic systems, attributing this advantage to their capacity for tailored, targeted actions facilitated by an understanding of charge transfer principles. Kumar et al. directed their efforts towards modifying S-scheme heterojunctions through diverse synthesis methodologies including hydrothermal, solvothermal, precipitation, solid-phase, and sol–gel techniques, while simultaneously establishing criteria for optimizing their performance [106].

In a similar vein, other researchers concentrated on reviewing Z-scheme photocatalyst systems, categorizing them into first, second, and third generations [107]. Their review emphasized the synthesis pathways involved in material development, including hydrothermal, ball milling, impregnation, and solvothermal methods. In contrast, our present review takes a comprehensive approach to material development in photocatalysis, focusing on fundamental design strategies and modifications grounded in a deep understanding of mechanistic cores.

8. Technology Readiness Levels (TRLs)

Technology readiness levels (TRLs) are a framework used to evaluate the development and maturity of technologies in general (Figure 12) [108]. The TRLs framework consists of nine stages, providing a systematic way to measure the overall maturity and monitor research progress in the respective field. These stages range from TRL 1, representing the inception of basic principles, to TRL 9, which denotes the stage of commercialization. The TRLs spectrum is further segmented into three sub-categories to provide a more granular understanding of progress. Levels 1 to 4 are dedicated to initial research and development efforts at the laboratory scale. Levels 5 to 6 encompass prototype testing, indicating a transition from theoretical research to practical application. Finally, levels 7 to 9 are associated with the final development phase and subsequent commercialization, marking the readiness of the technology for market introduction. In the context of this review article's evaluation and findings, the current progress in photocatalytic NO_x removal technology is positioned at TRL 3. This indicates that the technology is in the experimental proof of concept stage, where the basic technological principles are actively being explored and validated in a controlled environment.

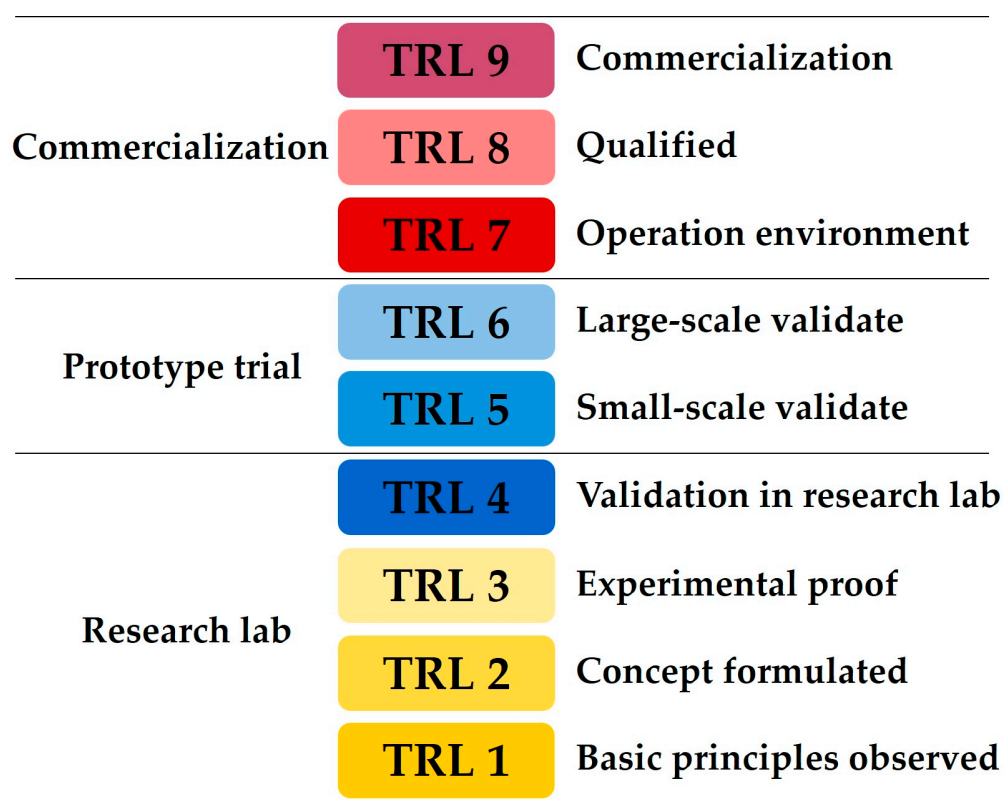


Figure 12. Schematic representation of technology readiness levels (TRLs).

9. Evaluation Criteria in Field Studies

Table 1 presents a comprehensive comparison of various photocatalyst performances for NO_x removal at the lab scale. It is important to note that performance analyses conducted at this scale are influenced by variations in light source conditions, posing challenges in accurately evaluating, interpreting, or comparing the efficacy of different photocatalytic materials. Hence, the establishment of a universally accepted protocol with standardized measurement techniques is imperative for ensuring a fair assessment of photocatalyst performance in NO_x removal at the laboratory scale.

The studies' results require proper evaluation, which necessitates comparison with a standardized protocol to maintain the quality of individual studies. Jensen's group suggests an evaluation scheme based on various criteria, including laboratory tests, test site area,

monitoring distance, reference data, blank data, study duration, monitoring frequency, durability testing, and supplementary data [109]. The criteria for evaluation purposes are outlined in Table 2. Although many paint industries advocate for outdoor applications and employ TiO₂ for photocatalytic NO_x removal efficiency, several model field applications reveal minimal differences in atmospheric NO_x concentration removal. The outcomes of these applications and evaluations on the TRLs scale can be quantified at level 5 in the case of outdoor paint applications [110,111].

Table 1. Comparison of various photocatalysts' performances.

Materials	Light Source	NO _x /NO Removal Performance	Ref.
BiOI/CeO ₂	300 W Xe lamp ($\lambda > 420$ nm)	NO removal rate: 45.5% (30 min in light irradiation)	[47]
SnO ₂ /CNT *	300 W Xe lamp ($\lambda > 420$ nm)	NO removal efficiency: 9.3%; selectivity: NO-to-green 24.72	[17]
CQD *-OVTNs	500 W Xenon lamp ($\lambda > 420$ nm)	NO removal efficiency: 57.8%	[58]
N-doped TiO ₂	LED lamp 6000 lux	NO removal efficiency: 51% (1 h in light irradiation)	[23]
Au@Ag/TiO ₂	16.8 W LED lamp (λ : 400–700-nm)	NO _x removal efficiency: 90% (30 h light irradiation)	[60]
TiO ₂ -PC *	300 W Xe lamp, visible light	NO _x removal efficiency: 32% (10 min light irradiation)	[67]
NiTi-LDH/BiOBr	510 W LED lamp ($\lambda = 420$ nm)	NO _x removal efficiency: 83–84%	[49]
Zn ₂ AlEu	580 W LED lamp ($\lambda = 420$ nm)	NO removal efficiency: 47.3%	[56]
S-doped CN *	150 W LED lamp ($\lambda > 400$ nm)	NO removal rate: 53%	[71]
Cs ₃ Bi ₂ Br ₉ /g-C ₃ N ₄	300 W Xe lamp ($\lambda > 420$ nm)	NO removal rate: 54%	[72]
PQ-GDY */NH ₂ -UiO-66 (Zr)	300 W Xe lamp ($\lambda \geq 420$ nm)	NO _x removal efficiency: 74% (12 h light irradiation)	[83]
TiO ₂ /Ti ₃ C ₂ MXene/CN	300 W Xe lamp ($\lambda \geq 420$ nm)	NO removal efficiency: 56% (10 min light irradiation)	[77]
Bi ₄ O ₅ Br ₂ -SnS ₂	Visible light	NO _x removal efficiency: 33% (15 min light irradiation)	[112]
ZnCr-LDH	500 W Xe lamp UV-visible light	NO removal efficiency: 67% (20 min light irradiation)	[113]
ZnO	300 W Xe lamp UV-visible light	NO removal efficiency: 55.4%	[113]
SrTiO ₃ -Ag	Energy saving lamp ($\lambda > 420$ nm)	NO removal rate: 70%	[114]
TiO ₂ /Ca ₁₂ Al ₁₄ O ₃₃	10 W UV light	NO removal 8.5 μ mol (300 min)	[115]
β -Bi ₂ O ₃ /Bi/g-C ₃ N ₄	LED lamp	NO removal rate: 88%	[116]
TiO ₂ /gCN	Cyan light	NO removal efficiency: 37% (30 min light irradiation)	[78]
SrTiO ₃ /SrCO ₃	300 W Xe lamp	NO degradation rate 44% (10 min light irradiation); reaction rate: 0.078 min ⁻¹	[9]
CeO _{2-x} /gC ₃ N _{4-x}	300 W Xe lamp Visible light	NO removal rate 73.8%	[45]
(Zr/Ti) UiO-66-NH ₂	300 W Xe lamp ($\lambda > 380$ nm)	NO removal efficiency 80.7% (12 min light irradiation)	[92]
TiO/ZnO	Visible light	NO _x removal efficiency 70%	[117]
Ag/ZnO/Zn-Al-LDH	Visible light	NO _x removal ratio 80%	[118]
Bi/BiOBr	300 W Xe lamp ($\lambda > 420$ nm)	NO _x removal efficiency 63%	[119]
Bi ₂ WO ₆ /TiO ₂	1.1 mW (Rayonet UV) $\lambda = 350$ nm	100% inhibited N ₂ O formation	[95]
Ni-C ₃ N ₅	LED light	NO removal ratio 54% (25 min light irradiation)	[13]
Au/Bi ₅ Ti ₃ FeO ₁₅	Simulated sun light	NO removal efficiency 45%	[76]
0.5 Ca-CN	LED lamp ($\lambda > 420$ nm)	NO removal rate 51.8%	[5]
Bi ₁₂ TiO ₂₀ -TiO ₂	300 W Xe lamp Simulated solar light	NO removal efficiency 42.6%	[11]

* CNT: carbon nanotube; CQD: carbon quantum dots; CN: carbon nitride; PQ-GDY: pyrazinoquinoline-based graphdiyne; PC: photonic crystal.

Table 2. Evaluation criteria of field studies for photocatalytic NO_x removal.

Evaluation Criteria	Comments/Purpose
Laboratory tests	To verify if the product is actually performing as expected.
Test site area (250 m ²)	A larger area provides more reliable results.
Monitoring distance (0.5–3 m)	The monitoring height should reflect realistic human exposures to assess ambient air quality.

Table 2. Cont.

Evaluation Criteria	Comments/Purpose
Reference data	Comparison of test site data with reference data and blank data is necessary to quantify potential changes over time in NO _x emissions. Include light-on/light-off data (for tunnels) and day/night measurements.
Blank data	Blank data should be collected at both the reference site and test site for a similar duration to establish a baseline for comparison.
Duration of study	The study duration should be long enough to account for fluctuations in NO _x levels, meteorological parameters, and seasonal variations (e.g., winter/summer) in the local climate.
Monitoring frequency	Sampling should be conducted at a frequency sufficient to ensure an adequate number of data points. Ensure that measurements at the test site, reference site, and blank data are taken with a similar time gap.
Durability testing	Periodic activity testing of photocatalytic active materials in the lab is necessary during the trial study to ensure the product's potential to remove NO _x is maintained.
Supplementary data	Supplementary data, such as meteorological data and traffic counts, are essential, especially in cases where a reference site is unavailable.

10. Summary and Future Research Perspective

The findings reveal that light-sensitive catalysts, when exposed to solar irradiation, initiate photocatalytic interfacial reactions by generating electron–hole pairs if the incident light's energy surpasses the catalyst's band gap. The efficient separation and migration of these pairs are vital for achieving prolonged charge separation, essential for effective energy transfer. Electron–hole pair generation is swift, but their migration to the surface, where they drive chemical reactions, can take significantly longer, leading to potential recombination losses in the form of light or heat.

On the catalyst surface, photogenerated electrons and holes react with adsorbed molecules like O₂ and H₂O, forming reactive oxygen species (ROS) that have powerful oxidizing properties. These ROS play a crucial role in converting nitrogen oxides into nitrates and NO₂ through a series of reactions, highlighting the importance of efficient adsorption of reactants for effective photocatalysis.

Photocatalysts face challenges such as limited light absorption, quick recombination of photogenerated carriers, and a lack of active sites, which diminish their catalytic activity. To overcome these obstacles, involving ion doping, defect engineering, morphology control, heterojunction construction, and metal decoration, these techniques aim to optimize the photocatalytic process by adjusting band structures, enhancing surface physiochemical states, and employing built-in electric fields for better charge separation and efficient redox reactions. Heterojunction engineering, including Z-scheme, S-scheme, and p–n junctions, emerges as a promising solution to enhance catalytic efficiency by fine-tuning band positions and facilitating efficient charge carrier migration. This multifaceted approach demonstrates the potential of advanced materials design to surpass the limitations of conventional photocatalysts.

Future studies should not only aim to narrow the band gap of photocatalysts but also focus on the appropriate positioning of the valence and conduction bands. This approach is crucial for enhancing photocatalytic efficiency beyond merely adjusting the band gap. There is a critical need for a more comprehensive mechanistic understanding of photocatalytic processes. Researchers have yet to fully elucidate the pathways and interactions at play, highlighting a significant gap in fundamental knowledge that needs to be addressed.

The specific roles of reactive species in photocatalysis, based on materials design, have been nearly omitted in existing research. Future work must concentrate on elucidating the main mechanisms of species formation, particularly focusing on the conditions that favor the generation of desired reactive species. The influence of pH on photocatalytic reactions has not been adequately explored. Future research should specify and investigate the impact of pH on the mechanistic pathways of photocatalysis. While much research

has focused on NO_x removal, there is a gap in studies specifically aimed at the selective formation of nitrates. Understanding the conditions that favor nitrate formation over other nitrogen dioxides (NO₂) is essential for advancing photocatalytic applications in environmental remediation.

The role of water concentration in photocatalytic processes remains unclear and underexplored. Identifying how water concentration affects the generation of reactive species and photocatalytic efficiency is crucial for optimizing reaction conditions. Strategies to inhibit N₂O formation are scarcely researched and need significant attention. Identifying stable catalytic planes, such as the TiO₂ (110) plane known for N₂O adsorption, and exploring further reduction mechanisms by photogenerated electrons are critical areas for future exploration.

The formation of toxic NO₂ poses a great challenge. There is a need for material designs that not only prevent NO₂ formation but also address the deactivation of photocatalysts caused by degradation products such as nitric acid. Incorporating tail gas (NO₂) absorbers like NaOH could significantly enhance NO removal, improve transport, and generate hydroxyl radicals more efficiently. This strategy requires further investigation to optimize photocatalytic processes for environmental applications. By addressing these focused areas, future research can significantly advance our understanding and application of photocatalytic technologies for environmental remediation and beyond.

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