

Review

TiO₂-Based Photocatalysts for Removal of Low-Concentration NO_x Contamination

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Abstract: The removal of low-concentration NO_x contamination in the urban atmosphere has been regarded as an urgent issue to be solved in the context of urbanization. In the past few decades, TiO₂ photocatalysis has been intensively investigated as an economical, efficient, and environmentally friendly means for the abatement of low-concentration NO_x. Up to now, however, there have been few reviews focusing on TiO₂-based photocatalysts for photocatalytic NO removal. In this review article, we will summarize the latest advances in the photocatalytic removal of NO_x contamination with TiO₂-based photocatalysts, which have been endowed with the reputation of being star catalysts for atmospheric environment remediation. We will begin with a survey of the mechanistic investigations of photocatalytic NO_x removal, focusing on the in situ Fourier Transform Infrared Spectroscopy (in situ FTIR) and Electron Paramagnetic Resonance (EPR) studies and the theoretical calculation of reaction pathways with Density Functional Theory. We will then introduce the test methods and the ISO standards for photocatalytic NO_x removal and discuss the effect of reaction parameters (catalyst mass, irradiation conditions, temperature, and humidity). Meanwhile, we also elaborate the latest modification methods to enhance photocatalytic efficiency and summarize the progress in recent years in modified TiO₂-based photocatalysts applied in NO_x abatement. Lastly, we will put forward some feasible suggestions. In the end, this review may provide some inspiration in designing more effective TiO₂-based photocatalysts for removing NO_x contamination from the ambient atmosphere.

Keywords: TiO₂; photocatalysis; NO_x degradation; air purification; environmental remediation



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1. Introduction

Air contamination existing in the ambient environment has become a serious issue which is being confronted all over the world and may grow exponentially with the rapid development of industrialization [1,2]. The typical contaminants in the atmosphere are nitric oxide (NO_x), sulfur oxide (SO_x), particulate matter (PM 2.5 or PM 10), and the like [3,4]. The air quality index significantly exceeded the limits set by the World Health Organization (WHO) in the countries where the majority of the population lives around the world; thus, numerous studies have shown the connection between the chronic over-exposure to highly polluted air and adverse effects on human health [5–11]. Nitrogen oxide (NO_x, a major form of NO) is one of the major culprits for the seriously polluted air

quality posing serious threats to the environment and human health [12–16]. Until now, the technologies of selective catalytic reduction (SCR) [17–23], non-selective catalytic reduction (NSCR) [24–28], and NO_x storage reduction (NSR) [29–33] have been established for the abatement of NO_x pollution. In the past few decades, a number of reviews have reported the progress in the field of the selective catalytic reduction method using vanadium-based catalysts, layered double-oxide-based catalysts, and zeolite and spinel-oxide-based catalysts under the condition of CO or NH₃ [34–38] as reducing agents to achieve the effect of removing high concentrations of NO in the environment. These technologies could reduce the emission of NO into the air at the source where it is produced; however, they are unable to completely eliminate NO emissions and control low-concentration NO in the atmosphere. What is more, many avoidable drawbacks such as high cost of equipment operation, harsh high-temperature reaction environment, and the potential threat to the environment upon the release of toxic reducing agents has severely limited the widespread use of the above technologies. Therefore, providing an economical, efficient, and widely applicable method which could abate low-concentration NO_x in the ambient atmosphere efficiently is one of the most important research topics in the field of atmospheric contamination remediation.

With the increase in low-concentration NO_x in the environment, the harm to the ecological environment and human health has become increasingly prominent; therefore, photocatalytic degradation of NO_x, as an effective way to repair air pollution, has been widely considered by scientists in recent years. Photocatalytic technology is a suitable alternative to remove NO_x at parts per million (ppm) levels in the air; thus, the photocatalytic process offers an effective solution to degrade gaseous pollutants in the atmosphere [39–42]. More importantly, photocatalysis technology needs merely sunlight, oxygen, and water, which are readily available in nature; no external reagents are required [43–45]. Semiconductor photocatalysts such as TiO₂, BiOX, and g-C₃N₄ have shown potential advantages in photocatalytic NO_x abatement in the ambient environment. In recent years, various reviews have been published on the excellent performance of photocatalyst materials such as 2D bismuth-based nanomaterials, MXenes [46,47], for photocatalytic NO removal as well. Despite the fact that common photocatalysts have revealed a certain application potential in photocatalytic NO removal, some inevitable disadvantages (for instance, their poor photogenerated carrier separation ability, potential physiological toxicity, and complex preparation process) severely hindered the extensive use of the above-mentioned photocatalyst materials. Thanks to the advantages of low cost, strong oxidizing activity, high stability, and nontoxicity compared with other types of photocatalysts, TiO₂ had been considered as the most promising photocatalyst for the abatement of low-concentration NO_x in the atmosphere since the end of the 20th century [48–52]. Meanwhile, modifications including doping, grafting, and composites have been applied to enhance the photocatalytic NO abatement efficiency [53–57]. However, up to now, there are barely any systematic and comprehensive reviews on the study of TiO₂-based photocatalysts applied in the field of photocatalytic NO removal. In recent years, with the deepening of the research on multi-physics coupling technology, especially the coupling of light and heat, thermal-assisted photocatalytic NO removal has gradually become the focus of researchers.

In this review, the fundamentals of photocatalytic NO_x abatement in the ambient environment will first be introduced in a brief way; also, the standards, advanced technologies applied in photocatalytic NO_x removal, factors affecting the photocatalytic performance and optimization of materials, as well as the application in the treatment of NO pollution for the materials will be reviewed in a systematic manner for the first time. The recent research in the field of TiO₂-based photocatalysts for photocatalytic NO_x degradation will be summarized in detail. Lastly, we will put forward some feasible suggestions. This re-

view aims to provide some suggestive inspiration for designing more fantastic TiO₂-based photocatalysts applicable for the efficient removal of NO_x contamination.

2. Mechanistic Studies and Test Methods

2.1. Mechanism of Photocatalytic NO_x Degradation

In general, denitration reactions can be divided into two types, nitrification and denitrification. In the reaction of nitrification, under the action of reducing substances, NO_x is reduced to N₂, which is the main component of the atmosphere. On the other hand, the NO_x may be oxidized to a hypervalent nitrogen compound (NO₂[−], NO₃[−]) when oxidizing species are present in the reaction system. In recent years, photocatalytic oxidation of low-concentration NO_x in the environment has been a focus of attention for researchers. Similar to the conventional photocatalytic oxidation reactions, after being irradiated by a suitably excited exciting light, the TiO₂-based photocatalyst may produce photogenerated electron and hole pairs on the surface of the catalysts, further forming oxygen-containing free groups and forming hydroxyl radicals and superoxide radicals. For a deeper understanding of the photocatalytic mechanism, a schematic representation of the mechanism involved in photocatalytic degradation of inorganic pollutants is displayed in Figure 1.

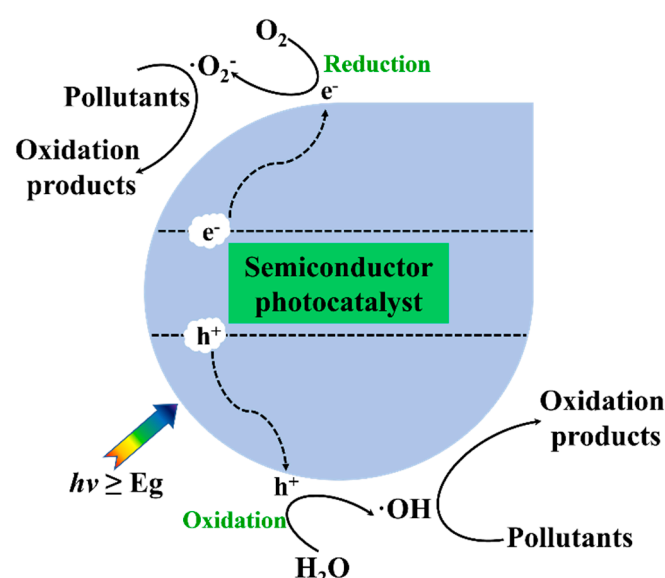
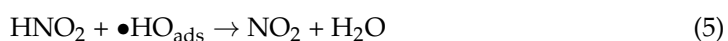
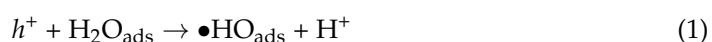
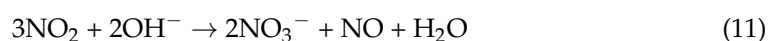


Figure 1. Scheme of photocatalytic degradation of inorganic pollutants.

The photocatalytic NO oxidation degradation mechanism for the usual TiO₂ photocatalysts undergoes the processes of NO → HNO₂ → NO₂ → HNO₃, which are displayed by the reactions exhibited in Equations (1)–(11) [58–61]. Previous research has put forward the corresponding reactions for the photocatalytic NO oxidation mechanism, as demonstrated in Equations (1)–(11) [61,62]





The above equations represent the typical photocatalytic degradation reactions which include the generation of photogenerated carriers and the production of active oxygen-containing radicals (Equations (1)–(3)).

Equations (4)–(7) represent the oxidation reactions of NO_x for the hydroxyl radical and superoxide radical. Nevertheless, as the intermediate toxic by-products of NO₂, there may exist a possibility of competitive adsorption with NO, H₂O, and O₂ in the actual reaction on the surface of the catalysts. On account of the strong polarity of water molecules, they usually occupy the active adsorption sites, which results in the decreased adsorption of reactant and intermediate molecules, exacerbating the incomplete oxidation of NO₂. Furthermore, the lower NO degradation rate during the reaction process is largely due to the weak absorption of the NO molecule as the above-mentioned competitive adsorption effect. Thus, how to increase the adsorption of NO and decrease the desorption of the intermediate NO₂ on the surface of catalysts is of great significance both in theory and in practical experiments. Moreover, the removal of the generated HNO₃ from the surface (catalyst regeneration) is essential for the DeNO_x cycle, as shown in Equation (12) [63].



It is worth noting that how to transform the HNO_{3ads} on the surface of the catalysts into HNO_{3aq} in the actual use of the process is of great significance for the reactivation of the catalysts. Thus, designing and preparing materials with a high-efficiency self-cleaning function is of great practical significance for catalyst regeneration.

2.2. Efficacy Evaluation Methods

At the laboratory scale, the photocatalytic nitrogen oxide removal reaction is made to complete the catalytic oxidation reaction by placing the catalyst sample in a flow reactor. For the evaluation of air contamination remediation, many standards have been established for the utilization of the photocatalytic materials, such as ISO 22197-2 [64], ISO 22197-3 [65], ISO 22197-4 [66], and ISO 22197-1 [67]. The design of these standards aimed to evaluate the performance of the photocatalysts by a basic method. Detailed descriptions of the NO_x degradation equipment based on the ISO standards that was employed to test the NO_x abatement capacities of different photocatalysts have been presented elsewhere [68]. Although the ISO standard was widely used in the study of photocatalytic NO removal, the ISO standard creates a strong discrimination between the different samples because its experimental configuration is affected by a strong resistance to gas->solid mass transfer, which makes it unsuitable for samples with surface roughness [66]. In addition to the standard of ISO 22197-1, many standards (for instance, EN 16980-1 [69] and JIS R 1701-1 [70]) also provide important guidance for catalyst performance testing in the photocatalytic NO_x removal process [69,70]. It is worth noting that under the system of the EN 16980-1 standard, the reaction system provided the measurement of the photocatalytic abatement rate in grams m⁻²s⁻¹, which is a very important engineering parameter that should be paid attention to during the testing process. Thus, to accurately evaluate the photocatalytic nitric

oxide removal performance of materials, it is necessary to select the appropriate standard according to the property of the sample to obtain accurate test results. In this review, we selected the ISO standard as an example to discuss the effect of different photocatalyst materials on photocatalytic nitric oxide removal performance.

Briefly, an inert flat-bed photoreactor which could hold two pieces of $5 \times 5 \text{ cm}^2$ test samples under UVA light illumination (central wavelength 365 nm, intensity = $1 \text{ mW}/\text{cm}^2$) was utilized to complete the test, as shown in Figure 2a [71]. The 1 ppm target reaction NO gas was supplied by a gas cylinder with compressed NO which was diluted by a pure air stream with the total airflow of $3 \text{ L}/\text{min}$ and fed into the reactor. The humidity in the reactor was always controlled at 50% (room temperature 25°C). After reacting with the photocatalyst sample, the residual gas that outflowed from the reactor outlet was tested through a valve attached to a chemiluminescence air pollution monitor.

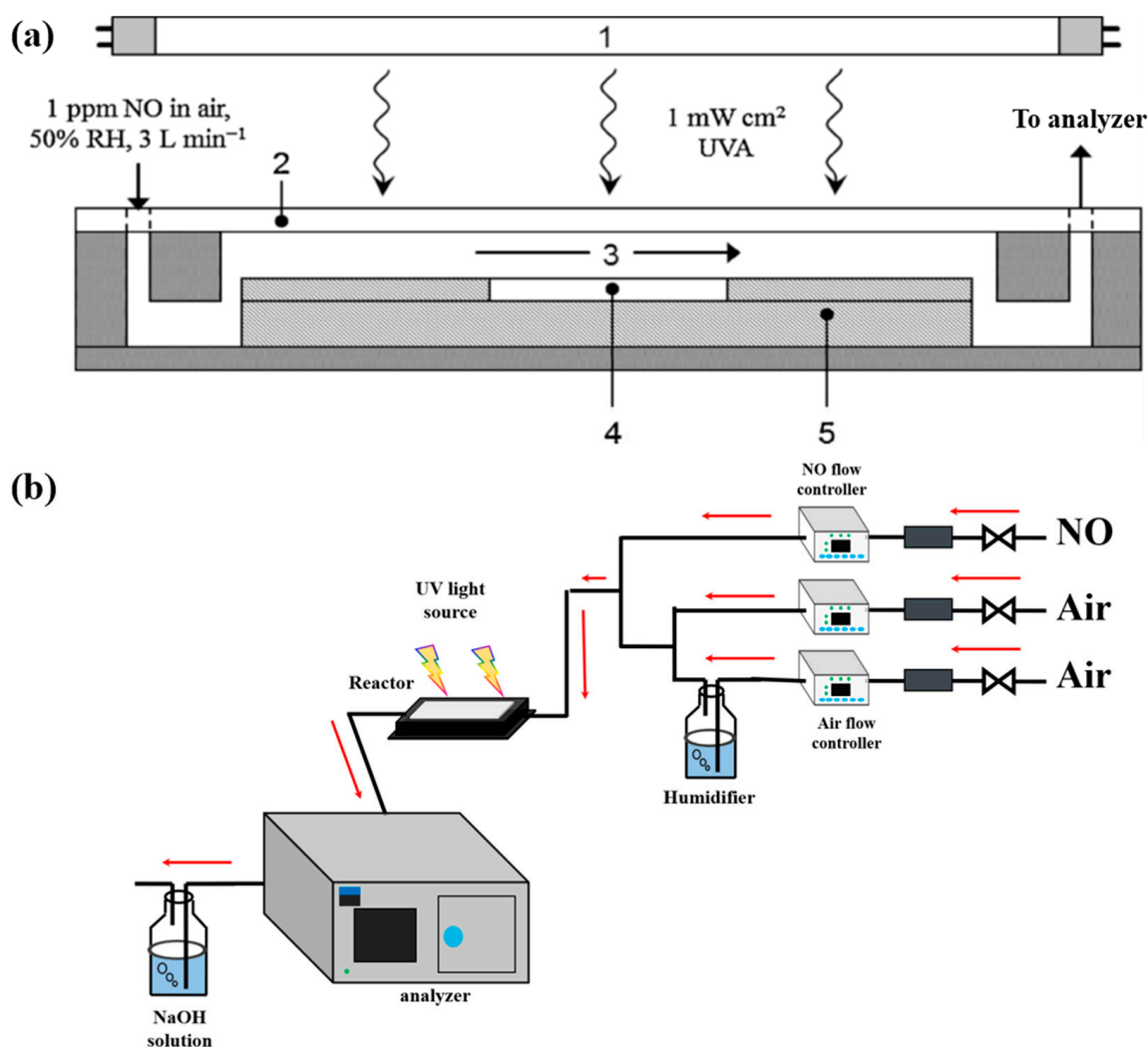


Figure 2. (a) Cross-sectional view of the NO_x degradation photoreactor based on the ISO standards [71]; (b) schematic diagram of the photocatalytic NO_x abatement system [72].

Before the light source was switched on, the concentration of NO and NO₂ was monitored during the dark adsorption process; then, the monitor was also maintained for 5 h after switching on the UV light at regular intervals, and for 0.5 h after the photocatalytic reaction. For the different reactions, the operation may have exhibited slight differences compared to the ISO standards; nonetheless, the target gas mixed with pure air was switched to the carrier gas (which merely contained pure air) at the end of the photocatalytic reaction,

and the light source was switched off at the same time. Based on the ISO standards, many researchers have carried out these photocatalytic reactions using a similar system [73–75], and an example schematic diagram of the photocatalytic NO_x abatement system is shown in Figure 2b [72]. The establishment of the ISO standard for photocatalytic NO_x degradation provides a consistent testing protocol which helps in the comparison of photocatalytic activity for different catalysts and promotes the development of new catalyst materials.

The photocatalytic oxidation of NO_x has been extensively studied, and researchers have systematically investigated its reaction mechanisms using various methods. These investigative techniques include in situ spectroscopy analysis methods such as in situ Fourier Transform Infrared Spectroscopy (DRIFTS), in situ Electron Paramagnetic Resonance (in situ EPR), and Density Functional Theory (DFT), which is utilized to analyze and predict possible reaction paths in the reaction process, among others. The research techniques have clearly revealed the intermediates, reactive species, and free energies at various stages during the whole reaction process. Researchers have used these technologies to gain a deeper understanding of the mechanisms of photocatalytic NO_x oxidation, providing a theoretical basis for the development of efficient photocatalysts.

2.3. Advanced Technologies for Deeper Understanding of Photocatalytic NO_x Removal

2.3.1. In Situ FTIR

In situ Fourier Transform Infrared Spectroscopy (in situ FTIR) is a method that allows for real-time monitoring of structural changes and the formation and transformation of reaction intermediates during a chemical process. It combines the high sensitivity of infrared spectroscopy with the dynamic characteristics of in situ experiments, making it an important tool for gaining a deep understanding of the reaction mechanisms in NO photocatalytic oxidation.

As early as 2006, Wu et al. used in situ FTIR spectroscopy to analyze the intermediates of NO on the surface of TiO₂ [76]. They found that NO reacted with a large number of surface peroxide species and OH groups present on the TiO₂ surface, adsorbing as bidentate nitrite and nitrate species. Under the irradiation of UV light, the bidentate nitrite on the catalyst surface was oxidized by superoxide species, which were generated from the oxidation of peroxide species by photogenerated holes, forming monodentate or bidentate nitrates. These findings have been significant for a deeper understanding of the reaction mechanisms in NO photocatalytic oxidation.

2.3.2. In Situ Electron Paramagnetic Resonance (EPR)

Electron Paramagnetic Resonance (EPR) technology can provide information about the local environment of unpaired electrons, such as local geometric configuration, ligand field strength, and interactions with other atoms or molecules. What is important is that in situ EPR is an important technique for identifying the dynamic evolution of active sites and defects in gas–solid photocatalytic reactions at the electronic level.

Ren et al. used in situ EPR technology to monitor and study the dynamic oxygen vacancies (OVs) on a BiOCl catalyst under various reaction conditions [77]. The authors found that the number and state of oxygen vacancies changed under light irradiation, and these oxygen defects participated in the photocatalytic reaction, which acted as genuine active sites (Figure 3). Combining in situ FTIR spectroscopy, they demonstrated that these dynamically photo-excited oxygen vacancies could promote the conversion of reaction intermediates to final products. This work elucidated the mechanism by which light-induced OVs may act as active centers in the NO oxidation reaction and introduced the new concept that dynamic defects were the truly active sites in catalytic reactions.

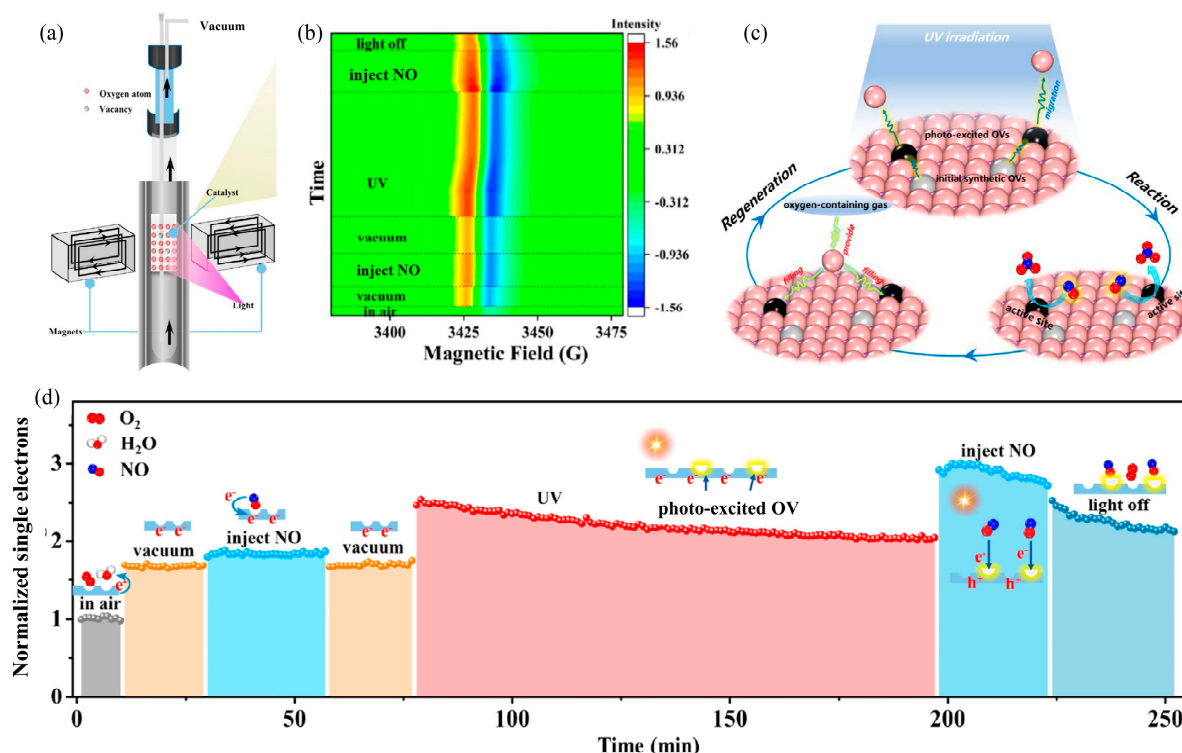


Figure 3. (a) Reactor configuration for the in situ EPR system. (b) Visualization map for in situ EPR on the BOC-OV sample in a H₂O (gas) atmosphere. (c) Schematic illustration of photocatalytic NO oxidation in which PE-OVs serve as real active sites under UV irradiation and the reversible creation of PEOVs. (d) The trend in the number of single electrons [77].

2.3.3. Theoretical Calculations

DFT describes the properties of a system based on the electron density. DFT calculations have been widely used not only to analyze the electronic structure of catalysts, helping to understand the behavior of photogenerated electrons and holes, but also to predict the energies of intermediates and transition states by simulating reaction pathways, thereby revealing the reaction mechanisms. Currently, there is a growing tendency to combine in situ FTIR spectroscopy with DFT to gain a deeper understanding of the reaction mechanisms in NO_x photocatalytic oxidation.

Wang et al. used a combination of in situ FTIR spectroscopy and DFT to reveal the possible chemical reaction pathways of surface NO₃[−] under light illumination and the reasons for its instability [78]. They first monitored, using time-resolved in situ FTIR spectroscopy, the process of NO being oxidized to nitrate on the surface of a TiO₂ catalyst under UV light and the subsequent accumulation of nitrate (Figure 4a,b). After prolonged light exposure, the NO₃[−] on the surface of the catalyst decomposed when NO was continuously introduced. Based on this observation, they hypothesized that NO, under the influence of photogenerated electrons, could promote the conversion of NO₃[−], primarily through the pathway NO₃[−] + NO → 2NO₂[−]. Subsequently, the authors used Density Functional Theory (DFT) to elucidate the decomposition mechanism of surface NO₃[−] in the presence of NO. As shown in Figure 4c,d, when NO and NO₃[−] were simultaneously adsorbed on the P25 surface, NO gradually approached NO₃[−], causing the N–O bond length in NO₃[−] to increase from 1.26 to 1.42 Å. This indicated that the surface NO₃[−] was activated by NO, leading to an unstable state.

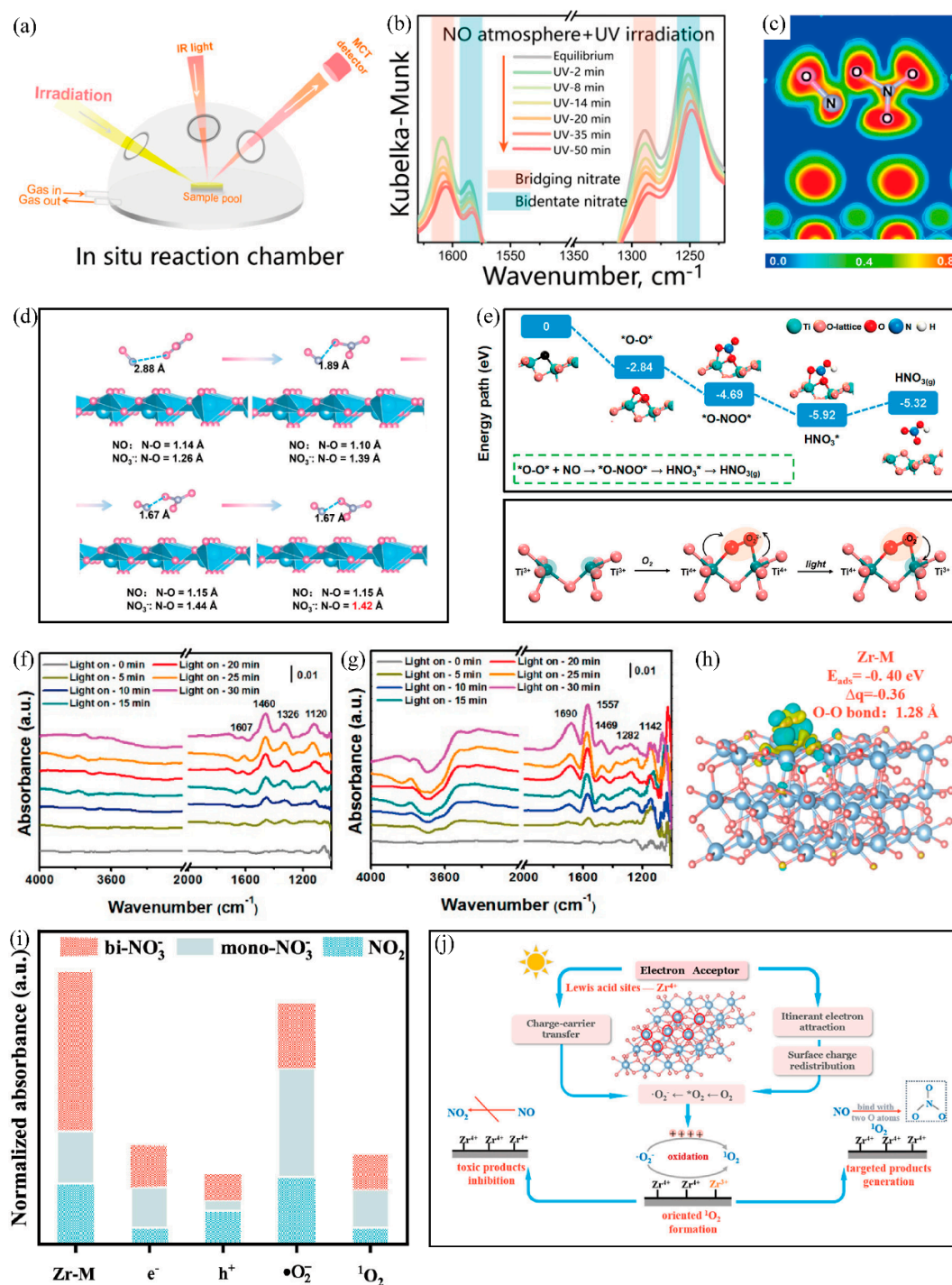


Figure 4. (a) Schematic illustration of the reaction cell for the in situ FTIR instrument. (b) In situ FTIR spectra of surface NO₃⁻ on TiO₂ surface exposed in NO atmosphere under UV irradiation conditions. (c) ELF calculations for NO and NO₃⁻ adsorbed on the TiO₂ surface. (d) Calculated interaction process of the coexistence of NO and NO₃⁻ on the TiO₂ surface. (e) Free-energy change against the reaction coordinate for the NO oxidation on the TiO₂(101) defective surface. Schematic illustration of the interfacial charge transfer path on the TiO₂-OV. The red and green ellipses represent the electron clouds, respectively. The oxygen vacancy with two localized electrons is essentially two unsaturated titanium ions (Ti³⁺). In situ FTIR spectra of (f) TiO₂-OV and (g) TiO₂ during photocatalytic NO oxidation. (h) Charge density difference of Zr-M (the yellow electronic cloud represents the loss of electrons, and the blue electronic cloud represents the gain of electrons; the isosurface is set to 0.005 eV). (i) In situ ROS-quenching DRIFTS of the normalized absorbance of end products over Zr-M with different scavengers in the first 10 min. (j) Possible ROS evolution and NO oxidation process over Zr-M [78–80].

The gradual accumulation of nitrite as reaction intermediates on the catalyst surface not only occupied active sites, hindering the adsorption and conversion of new reactant molecules, but also led to the formation of more by-products, significantly reducing the selectivity of NO photocatalytic oxidation. To address this issue, researchers have attempted to modify the surface properties of the catalyst to precisely control the types of reactive oxygen species (ROS). This approach could promote the efficient conversion of NO and simultaneously suppress the formation of intermediate products. Shang et al. reported a study on enhancing the 99% selectivity of NO to NO_3^- conversion under visible light by introducing oxygen vacancies (OVs) into TiO_2 semiconductor photocatalytic materials [79]. To elucidate the electronic interaction mechanisms of OVs in aerobic NO removal, the authors first performed theoretical modeling of the adsorption and reaction of NO and O_2 on the (101) lattice plane of TiO_2 . By analyzing the adsorption energies and charge transfer characteristics of NO and O_2 , they found that OVs with localized electrons can serve as adsorption and activation sites for both NO and O_2 . The calculation of charge difference showed that bonded O_2 could accumulate electrons from the localized electrons of two unsaturated Ti atoms near the OVs on the TiO_2 surface, while O_2 was activated to $\cdot\text{O}_2^-$ via a single-electron transfer pathway. Combining experimental results from NO-TPD, O_2 -TPD, and EPR spectroscopy, the authors inferred that O_2 may preferentially adsorb on oxygen vacancies, promoting its conversion to $\cdot\text{O}_2^-$. The reactive $\cdot\text{O}_2^-$ could directly oxidize NO to NO_3^- (Figure 4e). Subsequently, the authors used in situ FTIR spectroscopy with stepwise gas introduction (Figure 4f,g) and conducted photocatalytic oxidation experiments on NO using H_2O_2 -filled TiO_2 with surface oxygen vacancies. The generated intermediate species and catalytic data during the reaction process further confirmed that oxygen vacancies not only promoted the activation of molecular oxygen to superoxide but also facilitated the annihilation of photogenerated holes, thereby achieving highly efficient and selective conversion of NO to NO_3^- .

Wang et al. achieved the effective activation and electron transfer of O_2 molecules by regulating the acidic sites on the ZrO_2 catalyst surface, thereby generating highly selective singlet oxygen radicals ($^1\text{O}_2$) for the efficient oxidation of NO and the suppression of toxic NO_2 formation [80]. In that study, the authors used DFT to simulate the interaction between O_2 molecules and the catalyst to investigate the adsorption and activation processes of O_2 at the optimal adsorption sites (Figure 4h). They employed charge difference density (CDD) to study the role of Lewis acid sites in interfacial charge separation and transfer. It was confirmed that the presence of Lewis acid sites as active sites facilitated effective charge separation and transfer, thus promoting the adsorption and activation of O_2 molecules. Subsequently, the dynamic evolution of ROS during the photocatalytic process and the crucial role of $^1\text{O}_2$ in this reaction system were confirmed through in situ ROS-quenching DRIFTS experiments (Figure 4j). This led to the inference of the direct reaction pathway between NO and $^1\text{O}_2$. The possibility of this pathway was further supported by calculating the relevant energy profiles for the NO conversion reaction (Figure 4j). The integration of in situ FTIR spectroscopy and DFT calculations has gradually become an important approach for analyzing the mechanisms of NO photocatalytic oxidation. This combined method is significant for advancing the development of photocatalytic NO treatment technologies.

In situ Infrared Spectroscopy (in situ IR), Density Functional Theory (DFT), and in situ Electron Paramagnetic Resonance (in situ EPR) are all very important tools in the fields of materials science and catalysis. Each of these techniques has unique advantages, and when used in combination, they can provide a deep understanding of reaction mechanisms and material properties. The future trend is to integrate multiple characterization techniques to obtain comprehensive information about catalytic behavior. For example, in situ IR can be used to track bond breaking and formation during the reaction process, while DFT

simulations can be employed to explain the physicochemical principles behind experimental observations. Additionally, other in situ techniques such as EPR, X-ray Photoelectron Spectroscopy (XPS), and Raman spectroscopy can be combined to provide a more complete picture. Through continuous technological innovation and interdisciplinary collaboration, we expect to see more innovative applications of these advanced techniques in the future study of photocatalytic NO_x oxidation.

3. Factors Influencing the Removal Performance of Photocatalytic NO_x

The process parameters such as mass of the photocatalysts, wavelength, irradiation intensity, and humidity in the reaction are the important factors which may influence the photocatalytic NO_x removal efficiency.

3.1. Mass of the Photocatalysts

The mass of the photocatalysts which participated in the photocatalytic reaction could influence the activity during the whole process. In general, the photocatalytic reactions for the materials were tested on laboratory scales; thus, powder photocatalysts were the most commonly used target materials. Under such conditions, many factors such as the penetration depth of excited light into the catalyst powder and the necessary adsorption of the reaction gas must be considered in the selection of the mass of photocatalysts. For a $5 \times 5 \text{ cm}^2$ film sample whose thickness was tens of microns to a few millimeters, although the penetration depth of UVA was in the micron scale, considering the factors such as gas adsorption and desorption, the mass of the catalysts ranged from 10 mg to 50 mg. It is worth noting that the specific catalyst quality needs to be determined based on factors such as the dispersion of the material and the particle size under the particular circumstances [81]. Nevertheless, when the catalyst material is applied to a practical application, the photocatalysts are always fixed on the surface of a substrate and the impact of the mass of the photocatalysts on the production process, economy, and environmental protection become factors that have to be considered.

3.2. Irradiation Conditions

For most of the photocatalytic reactions, the reaction rate was a function of the wavelength which the materials may absorb after irradiated, with a close relationship to the optical band gap of the photocatalysts. As is well-known, most semiconductor photocatalysts are wide-band gap materials ($>3.0 \text{ eV}$), which can only absorb excitation light less than 340 nm (UVA). In the natural environment, due to the influence of the geographical environment and other factors, the UV light which occupies merely 3% in the full spectrum has significant differences in intensity across different regions. Thus, researchers use 1 mW/cm^2 as a measure of light intensity. In recent years, various methods have been tried to improve the light absorption capacity of the catalysts. However, it is worth noting that the photothermal phenomenon after the photocatalyst absorbs infrared light will become more obvious with the increase in absorption wavelength, which has a significant effect on the photocatalytic activity.

3.3. Temperature

The photocatalytic NO_x degradation reactions are conducted under the ambient environment at room temperature without external heat source. Once the reaction temperature changes, the adsorption properties of the adsorbent on the catalyst surface will be significantly affected. Due to the increase in temperature, the adsorption of material on the catalyst surface decreases with the increase in temperature. However, raising the reaction system temperature, the coverage of water molecules on the catalyst surface can be weakened significantly, enhancing the competitive adsorption capacity of oxygen and nitric

oxide [82]. On the other hand, when the reaction temperature was increased during the photocatalytic process, the lattice oxygen atoms could be activated in the semiconductor photocatalysts, boosting the sluggish reaction thermodynamics and kinetics. The activated lattice oxygen atoms could play an important role in enhancing the chemical adsorption of NO on the surface of photocatalysts. Meanwhile, a cocatalyst with thermal catalytic activity will also play its unique role after increasing the temperature, which may markedly activate the lattice oxygen of the substrate as well and finely tune the adsorption strength of reaction intermediates [83]. Thus, the selection of the optimal reaction temperature could not only inhibit the recombination of a photogenerated carrier to a great extent but also promote the activation of surface lattice oxygen atoms, contributing to the promotion of deep oxidation of NO.

3.4. Humidity and Light Absorption Capacity

NO₂, an intermediate product that is several times more toxic than NO, may easily be desorbed from the surface of the TiO₂ photocatalyst to the ambient environment unless the parameters are adjusted the optimum status. Folli et al. elaborated the mechanism of the photocatalytic oxidation path of NO to nitrate via the generation of NO₂ and emphasized the important role of relative humidity in photocatalytic NO oxidation upon anatase [84]. Zhang et al. [82] indicated that a change in the humidity may strongly influence the efficiency of photocatalytic NO_x degradation. As can be seen in Figure 5a,c, when the relative humidity decreased from 80% to 20%, both P25 and TiO₂(B) exhibited NO degradation capacity and less generation concentration of intermediate NO₂. This phenomenon indicated that lower RH is beneficial for a lower NO₂ generation rate and higher non-NO₂ selectivity.

Despite the fact that P25 exhibits no obvious change in the NO conversion ratio with the relative humidity being increased gradually, as shown in Figure 5c, the concentration of NO₂ drastically increased which led to the non-NO₂ selectivity decreasing significantly. Consistent with previous research, the photocatalytic capacity of materials decreased with an increase in the relative humidity [84]. As we all know, the light absorption range of the material is closely related to its photocatalytic activity, as can be seen from Table 1, and the commercial P25 had a larger light absorption edge of 405 nm compared to that of TiO₂(B) microsphere which displayed a slight sign of redshift. The larger the light absorption edge of the materials, the more photons could be absorbed, and the expanded light absorption range may promote the separation of photogenerated charge carriers. Thus, the commercial P25 demonstrated a better NO conversion rate under high humidity compared to that of the TiO₂(B) microsphere. It is worth noting that the specific surface area of TiO₂(B) was 220.3 m²/g, which was four times greater than that of P25. Such a high specific surface area endows TiO₂(B) with greater adsorption capacity, so that it can adsorb more target molecules during the reaction. The detailed data for the NO conversion rate, non-NO₂ selectivity, and NO₂ released ratio under different relative humidities for the TiO₂(B) microsphere and commercial P25 are summarized in Table 1 [82].

Table 1. Comparison of NO conversion rate, non-NO₂ selectivity, and NO₂ released ratio under different relative humidities for the TiO₂(B) microsphere and commercial P25.

	TiO ₂ (B)	P25
specific surface area	220.3 m ² /g	50.1 m ² /g
morphology	microsphere	nanoparticle
absorption edge	392 nm	405 nm

Table 1. Cont.

	TiO ₂ (B)			P25		
	20%	60%	80%	20%	60%	80%
relative humidity						
NO conversion ratio (%)	73.76	18.68	7.52	71.69	70.25	69.6
NO ₂ released ratio (%)	0.36	8.6	3.42	1.87	23.78	19.56
non-NO ₂ selectivity ratio (%)	99.54	56.01	57.21	97.38	67.78	72.77

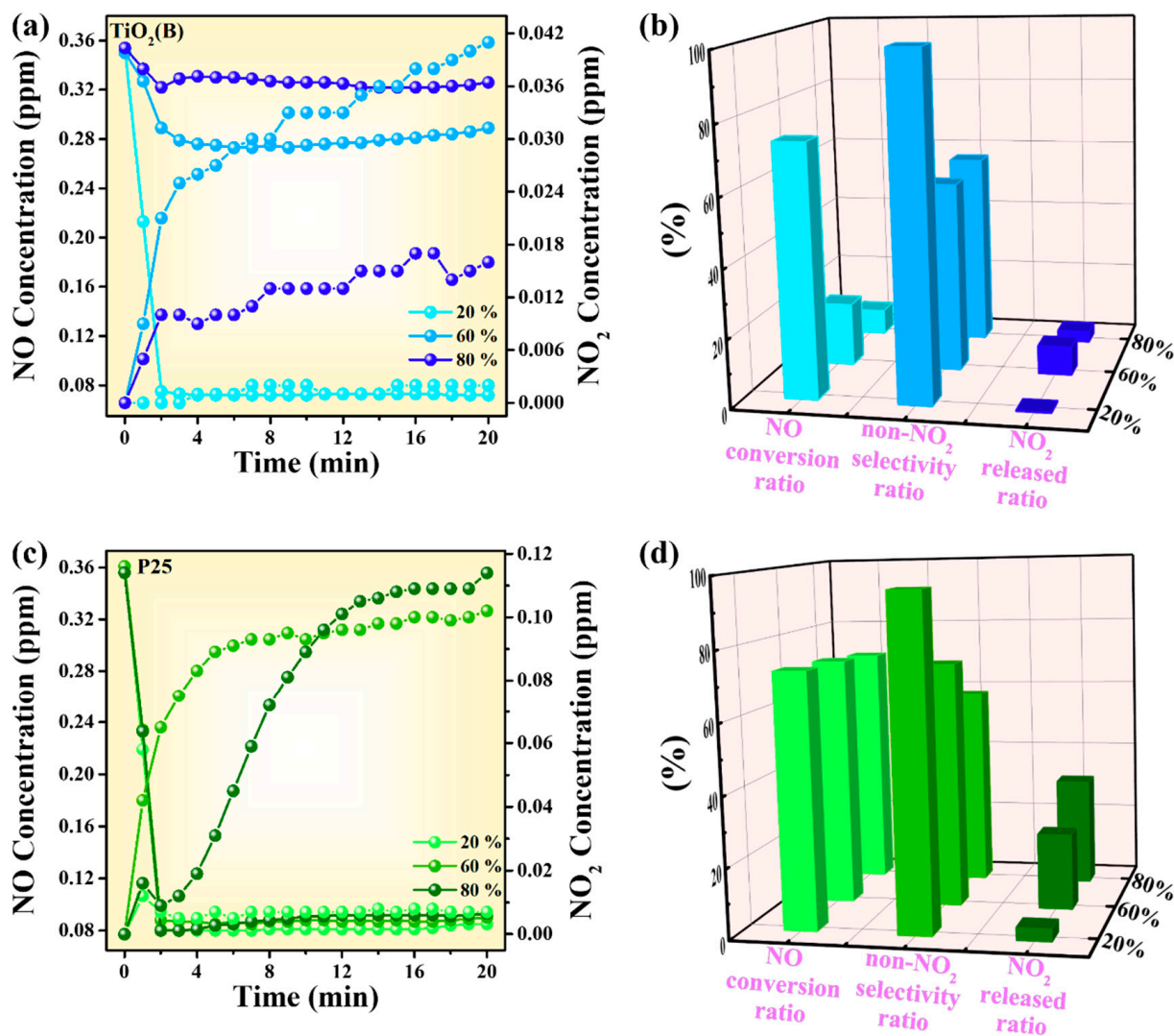


Figure 5. Photocatalysis experimental concentration curves of NO and NO₂ under 1 mW/cm² irradiation for different relative humidities; NO conversion, non-NO₂ selectivity, and NO₂ released ratios for the TiO₂(B) microsphere (a,b) and P25 (c,d) [82].

3.5. Crystallinity, Phase, and Nanomorphology

Beside the above factors, many factors such as the crystallinity, nanomorphology, and nanomorphology could also affect the photocatalytic NO_x degradation activities significantly. As can be seen in the previous research reported by Zhang et al. [82], when the crystal phase of the material is fixed as TiO₂(B), however, the morphology is microsphere, nanosheet, and nanotube, respectively. Thanks to the larger specific surface areas

of the microsphere and nanosheet samples, which were $220.3 \text{ m}^2/\text{g}$ and $334.5 \text{ m}^2/\text{g}$, which were almost 4 and 6 times larger than that of the nano tube sample, the microsphere and nanosheet samples exhibited much lower intermediate products than that of nanotube sample during the whole reaction. In addition, the difference in the specific surface area of different samples may as well be an important factor for the surface reaction efficiency. As is well-known, the size of the specific surface area has great influence on the adsorption quantity of reactants and intermediates. Compared to the nanotube sample, the microsphere sample not only had the better NO oxidation capacity but also revealed a lower NO_2 generation rate rather than a gradual upward trend over time, due to the larger specific surface area which endowed a better surface reaction efficiency to the microsphere sample. Meanwhile, the crystallinity was also an important factor in determining the photocatalytic NO removal performance even if the materials had the same crystal phase. Although the nanosheet sample had the highest specific surface area of $334.5 \text{ m}^2/\text{g}$, it had the poorest crystallinity, leading to the lowest NO conversion rate. Hence, high crystallinity was directly related to the photocatalytic performance of the material to some extent. Furthermore, different crystal phases gave the material different lattice structures, which led to the differences in the selective adsorption of molecules. Obviously, the samples with different crystal phases exhibited different photocatalytic NO degradation performance even though under the same test conditions. Thus, it is necessary to comprehensively evaluate the photocatalytic nitrogen oxide removal performance of catalyst materials by considering various internal and external influencing factors.

4. Design of TiO_2 -Based Catalysts for Enhancing Photocatalytic NO_x Degradation Efficiency

4.1. TiO_2 -Based Composite Materials

Among the numerous common photocatalysts, due to its properties of strong redox ability, physicochemical stability, abundance, and non-toxicity, TiO_2 was selected as the most common material applied to photocatalysis [85,86]. Unfortunately, the shortcomings inherent in TiO_2 severely restrict its wide application. On the one hand, the original TiO_2 can absorb merely the ultraviolet region, which occupies 3–5% of sunlight, owing to the broad band gap of 3.2 eV. On the other hand, the majority of photogenerated carriers prefer to recombine on the surface of catalysts, rather than effective separation, leading to low quantum efficiency. Hence, it is very necessary to exploit the photocatalysts with broad spectral response and highly reactive activity in the photocatalysis research field. To accomplish this goal, modification has become the focus of scientific research workers, using various methods such as noble metal cocatalysts, doping, sensitizing, and semiconductor complexes which can improve the photocatalytic activity of the original TiO_2 greatly [60,87–92].

Pham et al. prepared palladium nanoparticle (Pd NP)-modified TiO_2 nanotubes (TNTs) by gamma-ray irradiation. As the authors explained, the as-prepared Pd/TNT with a 14 kGy dose had the best photocatalytic NO_x degradation activity, achieving as high as a 53.30% NO_x abatement rate, which was 1.6 times higher than that of the original TNTs under atmospheric environment [92]. As can be seen in Figure 6a, compared to the TNTs, the photocatalytic NO oxidation efficiency was obviously promoted when the Pd NPs were modified onto the surface of TNTs. The reason why the Pd NPs could enhance the photocatalytic activity of the TNTs may be summarized as (i) by playing an important role in collecting the photogenerated electrons to hinder the recombination of the carriers and (ii) effectively boosting the effective light absorption area [93]. As is well known, during the whole photocatalytic NO oxidation reaction, the more the concentration of intermediate NO_2 generated, the lower the selectivity for the target product (nitrate or nitrite). As

demonstrated in Figure 6c, the as-prepared Pd/TNT with a 14 kGy dose expressed the best selectivity of 47.3%, which was 1.33 times greater than that of the unmodified TMT sample. What is important is that the 14 kGy Pd/TNT heterostructure sample exhibited the highest apparent quantum efficiency (AQE) of $10.8 \times 10^{-2}\%$, which is one order of magnitude higher than that of the original TNT ($6.14 \times 10^{-2}\%$). Thus, in consideration of the above excellent characteristics of the 14 kGy Pd/TNT sample, the superior photocatalytic capacity for NO oxidation should unquestionably be highlighted.

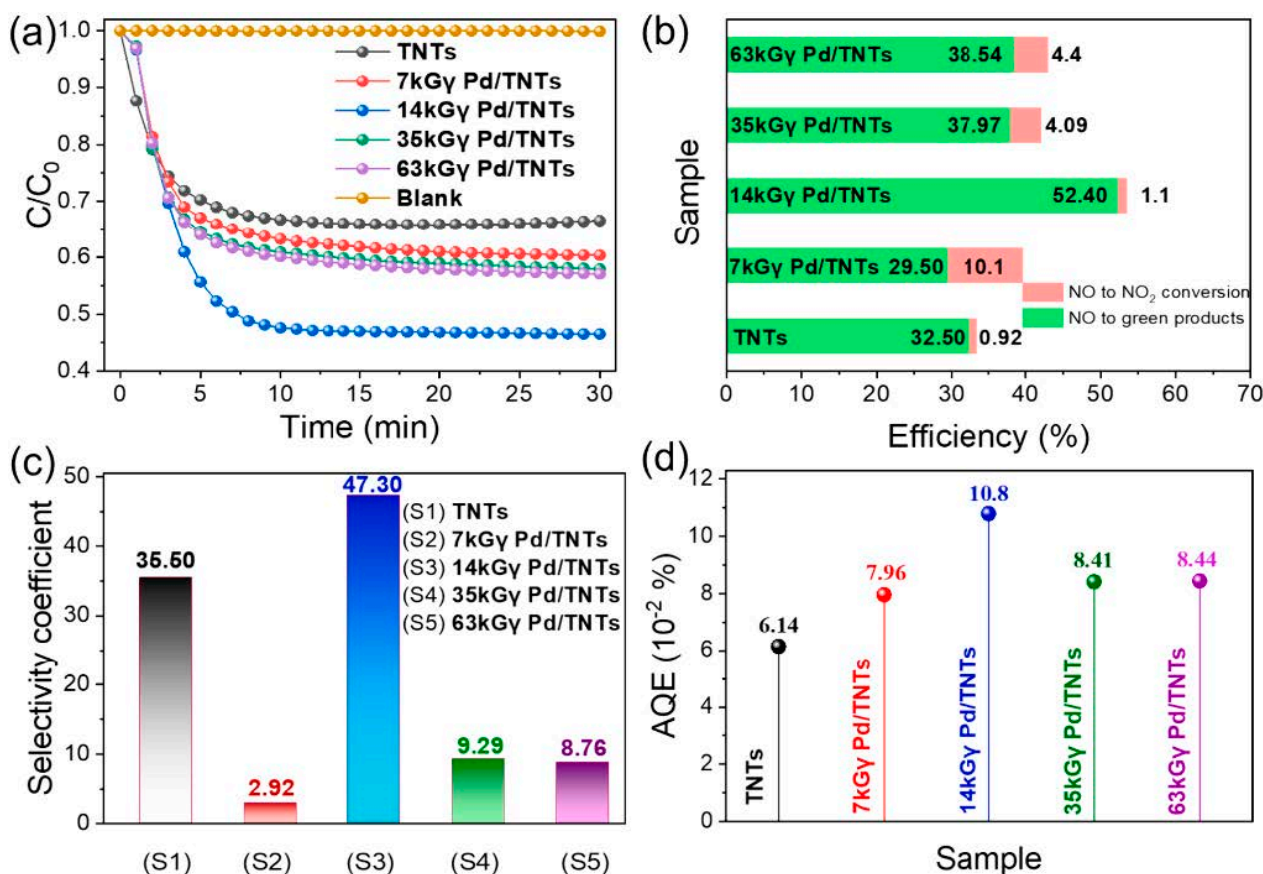


Figure 6. (a) Photocatalytic NO oxidation degradation rate, (b) NO conversion efficiency into nitrate or nitrite or byproduct NO_2 , (c) selectivity coefficient, and (d) apparent quantum efficiency of original TNT and the as-prepared Pd/TNT materials [92].

Graphitic carbon nitride ($g-C_3N_4$)-based materials are an important alternative which can also effectively achieve the reaction of photocatalytic NO oxidation. He et al. successfully synthesized graphitic carbon nitride–titanium dioxide ($g-C_3N_4$ - TiO_2) through a facile annealing path using the common P25 and melamine as the precursors [94]. Due to the fact that the photocatalytic activity of the compounds was highly dependent on the content of $g-C_3N_4$, as the authors demonstrated, the incorporation of $g-C_3N_4$ could efficiently increase the photocatalytic NO conversion rate. When $g-C_3N_4$ was optimized to the optimum content (~ 15 wt%, M400), the photocatalytic NO_x conversion rate reached as high as 27%, which was much higher than that of commercial P25 (17%) and the obtained $g-C_3N_4$ (7%) under the irradiation of visible light. Moreover, when irradiated under UV light, compared to P25 and the pure $g-C_3N_4$, the photocatalytic NO_x conversion was also obviously promoted. Unfortunately, when P25 and $g-C_3N_4$ were mixed, although the same content of the M400 sample was maintained through a simple mechanical mixing method, the photocatalytic NO_x conversion rate could not be improved under either visible light or UV light irradiation. This phenomenon showed the importance of the interaction between

g-C₃N₄ and P25 for boosting the photocatalytic NO_x degradation activity. On account of the perfect interfacial interaction of M400, compared to that of the mechanically mixed sample, more photogenerated-electrons could transfer from the conductive band of g-C₃N₄ to the conductive band of TiO₂, resulting in more superoxide radicals being generated under visible light, which was indicated by the results of EPR. The more superoxide radicals that were generated, the more NO that could be oxidated to nitrate directly. Therefore, constructing the appropriate interface interaction between semiconductors may enhance the photocatalytic NO_x abatement activity effectively. A brief summary of photocatalytic NO conversion for different TiO₂-based composite materials is provided in Table 2 [92,94–104].

Table 2. A brief summary of photocatalytic NO conversion for different TiO₂-based composite materials.

Samples	Pd/TNT	g-C ₃ N ₄ -TiO ₂	B-TiO ₂ /MgAl-CLDH	ZnFe ₂ O ₄ /TiO ₂	TiO ₂ /CNTs	TiO ₂ /Graphene	Metal-Ion-Modified Sepiolite/TiO ₂
method of synthesis	impregnation	calcination	hydrothermal and calcination	hydrothermal	ball-milling	hydrothermal	hydrothermal
structure	heterojunction	heterojunction	heterojunction	heterojunction	heterojunction	heterojunction	heterojunction
morphology	nanotube	nanoparticle and 2D lamellar	hexagonal platelet and nanoparticle	nanoparticle	nanotube and nanoparticle	nanosheet and nanoparticle	nanofiber and nanoparticle
absorption edge	423 nm	~440 nm	446 nm	in the visible-light region of 400–600 nm	392 nm	403 nm	401 nm
light source	AM 1.5 solar light	35.8 mW/cm ² 420–700 nm	55 mW/cm ² λ > 420 nm	LED lights 450 < λ < 460 nm	Xenon lamp λ > 420 nm	UV-A light 1 mW/cm ²	UV-A/visible light 1 mW/cm ² / d 7000 lx
NO conversion rate	53.5%	27%	23.4%	54%	41.2%	42.68%	38% and 10.2%
Ref.	[92]	[94]	[95]	[96]	[97]	[98]	[99]

4.2. Doped TiO₂-Based Materials

Due to the characteristics of strong photocatalytic oxidation ability and chemical stability, TiO₂ has been considered as a promising candidate for environmental remediation application. Unfortunately, on the one hand, the inherent band gap (3.0–3.2 eV) of TiO₂ hinders the utilization of visible light (400 nm–750 nm); on the other hand, the rapid recombination of the photogenerated carriers seriously decreases the photocatalytic activity, which severely limits wide application in the environmental field for TiO₂. Thus, metal/nonmetal elements doping, coupling narrow-band-gap semiconductors, etc., are the efficient path to improve the photocatalytic reactivity for TiO₂-based materials [105–107]. Among the numerous strategies, element doping is the expedient way to extend the visible light absorption region effectively and facilitate the separation of photogenerated carriers to some extent. In general, halides, nitrogen, carbon, phosphorus, and sulfur are the common nonmetal doping elements; on the other hand, some transition metal elements such as Fe, Co, Ni, Cu, Mn, Mo, Cr, and V have been selected as the dopant to elevate the photocatalytic efficiency of TiO₂-based materials [108–117].

Huang et al. fabricated a functionalized transparent film on glass which contained Ti³⁺ self-doped TiO₂ nanoparticles using a facile method [116]. As described by the authors and shown in Figure 7a, the as-prepared films covered the surface of the glass substrate uniformly; beyond that, the T/C-1/5 films exhibited perfect light transmittance, which nearly reached 90%, as demonstrated in Figure 7b. Under the condition of 3D angle view mode

with AFM, the films displayed a hill–valley surface with a roughness of 7.16 nm, which may prolong the contact time to the reaction gas flow coming to enhance the photocatalytic activity. After the photocatalytic reaction started, except for the pCN film sample, all the samples exhibited visible-light activity without any inactivation in 30 min, as shown in Figure 7c. The self-doping Ti^{3+} film sample showed a NO abatement conversion rate of 13.4%, whereas the pure pCN film had hardly any NO conversion during the whole reaction. It is worth noting that while the ratio of TiO_2 and pCN was optimized at 1/5, the NO abatement conversion rate could reach as high as 25.8%, which can be seen in Figure 7c. In addition to this, the photocatalytic activity of NO abatement remained basically unchanged, with an inappreciable inactivation after five cycles of testing. Consequently, in a continuous-flow reaction mode, the T/C-1/5 films exhibited the fascinating photocatalytic NO removal activity under visible-light irradiation and meanwhile maintained perfect stability.

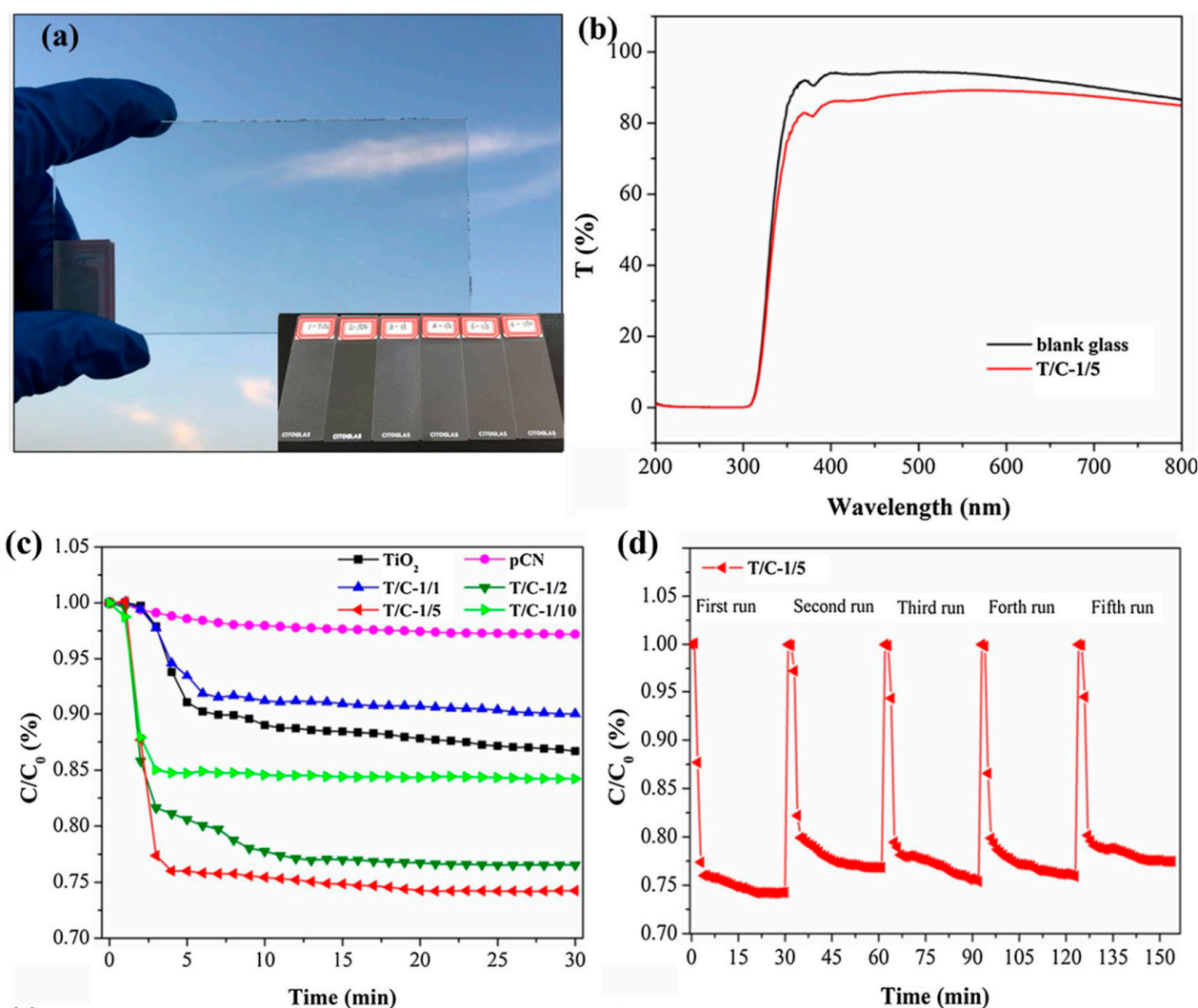


Figure 7. (a) Photograph of the as-prepared pCN/ TiO_2 films, (b) transmittance comparison of the pure glass and T/C-1/5 films, (c) photocatalytic activities of the T/C films for NO degradation under visible light irradiation ($\lambda > 420$ nm), and (d) cyclic stability test for photocatalytic abatement of NO upon T/C-1/5 films [116].

To further prove the effectiveness of doping, Hu et al. reported that their group successfully synthesized numerous Pt-doped TiO_2 samples with various doping amounts by a facile sol–gel method [117]. In the results of UV-Vis diffuse reflectance spectroscopy (DRS), due to the doped Pt in TiO_2 , all the as-prepared samples exhibited extended absorption

within the visible light region while the crystallinity had hardly changed, maintaining the anatase phase observed in X-ray diffraction. The chemical state of Pt is one of the important types of evidence for successful doping; as revealed by the X-ray photoelectron spectra (XPS), Pt had been doped into the lattice of anatase in the form of Pt^{4+} cations favorably accompanied by a fraction of PtO loaded on the surface of TiO_2 . Serving as an impurity level, the Pt^{4+} cations existing in the crystal lattice of TiO_2 could suppress the recombination of the photogenerated electron–hole pair, which obviously gave a high-efficiency carrier separation rate; meanwhile, the fraction of PtO loaded on the surface of the catalyst favored a good visible-light response. Thanks to the structure containing two Pt species, the synergistic effect of lattice-doped Pt^{4+} and surface-loaded PtO played an important role in the improvement of the photocatalytic oxidation of NO_x performance under irradiation by UV light, simulated sunlight, and visible light compared to those of pure TiO_2 and P25. Consequently, a suitable kind and amount of metal or nonmetal doping could not only obviously extend the light absorption region but also promote the carrier separation rate, which in turn enhances the photocatalytic NO oxidation abatement efficiency. A brief summary of photocatalytic NO conversion for different doped TiO_2 -based materials is displayed in Table 3 [116–126].

Table 3. A brief summary of photocatalytic NO conversion for different doped TiO_2 -based materials.

Samples	pCN/ Ti^{3+} - TiO_2 Films	Pt- TiO_2	N- TiO_2	NF- TiO_2 Films	Fe-doped TiO_2	Au/N- TiO_2	NHL+5 wt% Ag- TiO_2
method of synthesis	sol–gel	sol–gel	sol–gel and calcination	sol–gel	precipitation	sol–gel and calcination	sol–gel and calcination
structure	Ti^{3+} -doped TiO_2	Pt-doped TiO_2	N- TiO_2	NF- TiO_2	Fe-doped TiO_2	Au/N- TiO_2	Ag-doped TiO_2
morphology	thin film	nanoparticle	spherical nanoparticle	thin film	nanoparticle	nanoparticle	nanoparticle
absorption edge	440 nm	~450 nm	390 nm	--	423 nm	400–450 nm	419 nm
light source	visible light $\lambda > 420$ nm	visible light $\lambda > 420$ nm	UV light 0.1 mW/cm ²	UV light 0.28 mW/cm ²	420–700 nm 35.8 mW/cm ²	UV-A light 1 mW/cm ²	solar-light AM 1.5
NO conversion rate	25.8%	25.9%	51%	38.6%	60%	41.6%	21.01%
Ref.	[116]	[117]	[118]	[119]	[120]	[121]	[122]

4.3. Ultradispersed-Cocatalyst-Modified TiO_2 -Based Materials

Single-atom catalysts (SACs) or atomically dispersed catalysts are well-defined materials where the atomic-size materials are highly dispersed on the surface of the substrate [127]. Studies in recent years have shown that SACs, atomically dispersed catalysts, and subnanometer-sized metal clusters own the characteristics of homogeneous single active centers, high conversion and high selectivity, stable structures, and almost 100% metal utilization that could minimize the use of expensive noble metals and give them unique functions of adsorption, charge transportation, and activation of reactants [128]. Once the metal materials are set at ultrasmall scale on the substrates, the low coordination number and quantum size effect can enhance the photocatalytic performance and the interaction between metal and substrate, preventing the aggregation of the SACs, atomically dispersed catalysts, and subnanometer-sized metal clusters [129–133]. In recent years, SACs, atomically dispersed catalysts, and subnanometer-sized metal clusters have played

an important role in photocatalytic air contamination remediation and they have promising application prospects in the degradation of NO under specific ppm levels [134–138].

Pratsinis et al. found that when the size of platinum-group metals (PGMs) was reduced sharply to single-atom scale, this could not only maximize the photocatalytic ability of the catalysts but also minimize the amount of precious metal materials which were used [135]. Thus, their group prepared Pd/TiO₂ particles by strictly controlling the Pd content, utilizing flame spray pyrolysis technology. The theoretical content of the Pd element was 0.025–1 wt.% evaluated by leaching; 40–70% of the Pd atoms which loaded on the surface of the TiO₂ distinctly promoted the solar-light-driven photocatalytic NO abatement property. It is important to note that the authors employed diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to quantify the fraction of isolated Pd atoms on the surface of the TiO₂ and used NO as the probing molecule. Compared to the Pd species (0.1 and 1 wt.%) photoinduced deposition on the surface of TiO₂, for which no linear NO adsorption peak was detected even if the theoretical Pd content increased to 0.1 wt.%, the linear NO adsorption peak on cationic single Pd atoms could still be detected clearly on the flame-made Pd/TiO₂, proving the existence of isolated Pd atoms. As the author explained in the article, regardless of the content of Pd on the surface of the material, during the whole test, the photocatalytic NO abatement performance linearly increased with the proportion of isolated Pd atoms for the FSP-made Pd/TiO₂ samples, whether there existed trace amounts of Pd clusters or particles or not. What is more surprising, the FSP-made Pd/TiO₂ samples showed high resistance to nitrate poisoning and high selectivity for the conversion of NO to nitrate rather than NO₂ due to the ultradispersed isolated Pd atoms on the surface of the TiO₂.

Recently, Zhang et al. reported that their group had synthesized the atomically dispersed MnOx cocatalyst on TiO₂(B) microspheres through a mild hydrothermal process [72]. In previous studies, most of the current single-atom cocatalysts were noble metals, which severely restricted their large-scale application and development. Finding and applying the proper non-noble-metal single atom as the cocatalyst may be the key to promoting the performance of the catalysts in NO_x abatement. As can be seen from the EDS mapping of the Mn element in Figure 8c, the loaded Mn species was uniformly distributed on the surface of the substrate. No characteristic lattice of MnOOH was observed in the HRTEM image, proving that the atomically dispersed MnOx cocatalysts were ultra-small and highly dispersed. High Angle Annular Dark Field (HAADF) was employed to further investigate the dispersed state of the Mn species. As shown in Figure 8e,f, the HAADF images of the MT-0.5 samples indicated that most of the Mn species existed in an atomically dispersed state and very few in clusters. The atomically dispersed MnOx-modified TiO₂(B) microsphere samples could dramatically promote the deep oxidation of NO_x under mild photocatalytic conditions (1 mW/cm² UV-A light). During the photocatalytic process, the target pollutant of NO could be degraded approximately 67.15% on the atomically dispersed MnOx-modified TiO₂(B) microsphere samples, which is 2.76 times greater than for the pristine TiO₂(B) sample. What is more notable is that the more toxic intermediate NO₂ was significantly inhibited, 2.11 times more than in the case of the unmodified sample. Thus, constructing appropriate non-noble-metal-based atomically-dispersed-cocatalyst-modified semiconductor photocatalysts was not only a perfect alternative for the noble metal single-atom cocatalysts but also provided new insights into developing effective photocatalysts to eliminate NO effectively.

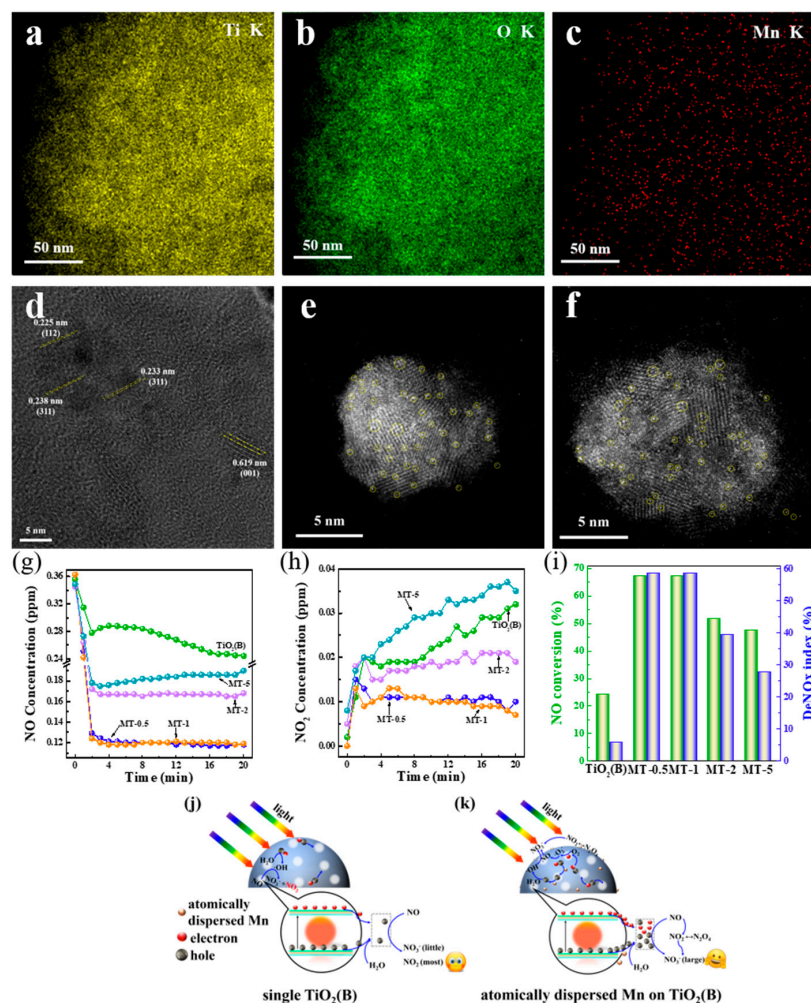
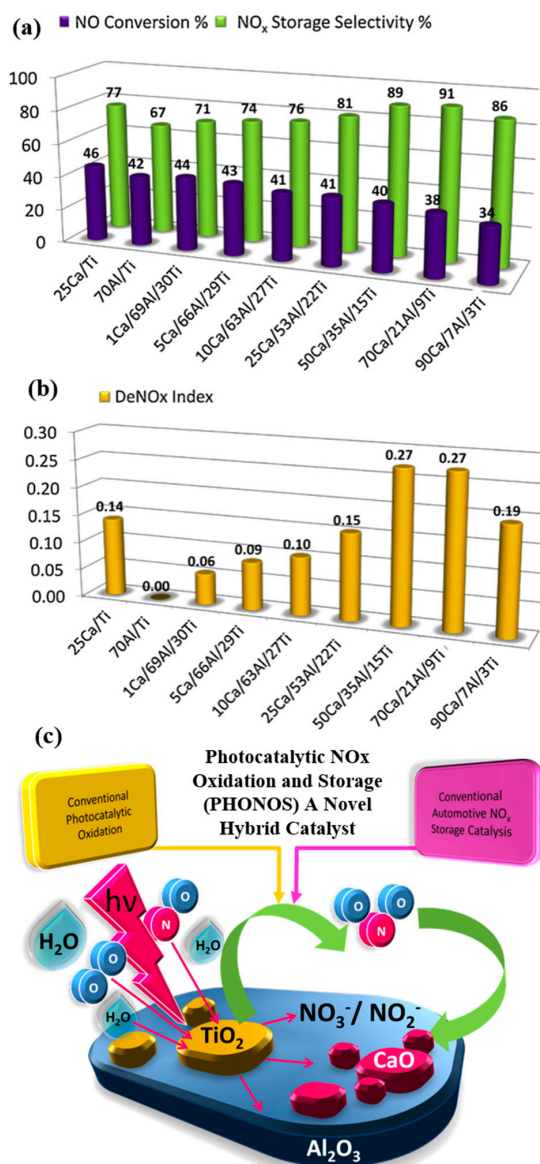


Figure 8. Images of (a–c) EDS mappings; (d) HRTEM; (e,f) HAADF of single particle for the atomically dispersed MnOx cocatalyst on TiO₂(B) microsphere sample; concentration curves of (g) NO and (h) NO₂ under UV light irradiation (central wavelength 365 nm, 1 mW/cm²); (i) histogram of NO Conversion and DeNOx Index for Mn-species-loaded TiO₂(B) microsphere samples; scheme of photocatalytic reaction for (j) single TiO₂(B) and (k) atomically dispersed Mn on TiO₂(B) under UV light irradiation [72].

4.4. Acid and Basic Oxides Co-Modified System

Previous studies have shown that the relative surface acidity for metal oxide materials is an extremely important factor which may influence their interaction strength with gaseous NO_x species. When NO₂ was adsorbed or generated on the surface of alkaline earth metal oxides, nitrites had been already formed, which led to the formation of nitrite–nitrate ion pairs [139,140]. In addition to this, due to its properties of excellent chemical and thermal stability, large specific surface area, and suitable surface acid/base, γ -Al₂O₃ was widely selected to be the support material for the photocatalytic NO_x oxidation and storage [141]. During the whole reaction, γ -Al₂O₃ could promote the total NO_x storage ability for the whole catalytic system through the generation of surface nitrites and nitrates. When the photocatalytic reaction was started, the TiO₂ photocatalysts provided the ability to oxidize NO into NO₂, nitrites, and nitrates under ambient environment; meanwhile, the components of CaO or Al₂O₃ provided the additional surface sites for non-catalytic storage of oxidized NO_x. Ozensoy et al. reported that among different ternary-mixed-oxide samples of CaO/ γ -Al₂O₃/P25, as shown in Figure 9a,b, the sample of 50Ca/35Al/15Ti obtained the highest DeNOx index of 27%, which was much higher than that of the best binary-mixed-oxide sample of 25Ca/Ti (14%) and the unary P25 (–32%) [142]. In the

entire catalyst system, the overall basicity of the oxide mixture was increased through increasing the relative content of CaO; thus, the number of the NO_x adsorption sites for non-catalytic storage was increased simultaneously. As the author assumed in the article, the whole reaction system utilized the property of the strongly binding adsorption for the basic oxide to provide more surface sites for non-catalytic storage of oxidized NO_x. Hence, constructing and optimizing polybasic metal-oxide photocatalysts to be applied in NO_x degradation may greatly improve photocatalytic performance.



schematic of photocatalytic NO_x oxidation assisted by acidic- and basic-oxide co-modified system.

Figure 9. (a) NO conversion rate (%) and NO_x storage selectivity (%); (b) DeNO_x index values for different CaO/ γ -Al₂O₃/P25 photocatalyst samples under the irradiation of UVA light; (c) schematic of photocatalytic NO_x oxidation assisted by acidic- and basic-oxide co-modified system [142].

5. Progress in the Field of Thermal-Assisted NO Removal

As is well known, the introduction of appropriate heat into the photocatalytic reaction system may effectively improve the local temperature of the catalyst and subsequently help the electrons detrapp to the surface of photocatalysts, which could accelerate the separation of photogenerated carriers [143–146]. Meanwhile, coupling thermal to the traditional

photocatalytic reaction system can efficiently decrease the activation energy of lattice oxygen, which may promote oxidation reactions on the surface of photocatalysts [147]. Thus, it is highly desired to couple thermal field synergy with the photocatalytic reaction system for NO degradation. To achieve this goal, many strategies such as external heat source assistance, infrared thermal conversion, and localized surface plasmons have been attempted to enhance the efficiency of NO degradation [148,149].

Under the premise of trying to expand the TiO_2 -based photocatalyst materials to a wider range of Ti-based photocatalysts, Lu and Kou et al. reported C/PVDF-BaTiO₃ (polyvinylidene fluoride, PVDF) photocatalytic films with bi-pyroelectric effect which could boost the full-spectrum solar photocatalytic conversion of NO_x [148]. Under the irradiation of a Xenon lamp, the surface temperature of PVDF-BaTiO₃ can reach $\sim 57^\circ\text{C}$ within 20 min, which is similar to pristine BaTiO₃. Nevertheless, the surface temperature of C/PVDF-BaTiO₃ rises rapidly after the addition of carbon black, and as the content of carbon black increases, the surface temperature experiences a corresponding enhancement, as shown in Figure 10a. These results can be attributed to the excellent photothermal conversion capability of carbon black. The removal rate of NO on bi-pyroelectric material PVDF-BaTiO₃, which is obtained by compounding PVDF and BaTiO₃ with pyroelectricity, can reach 45%. Furthermore, carbon is incorporated into the PVDF-BaTiO₃ films to enhance its denitrification efficiency. Specifically, as demonstrated in Figure 10b, the 0.5 wt% C/PVDF-BaTiO₃ film achieves a denitrification efficiency of 60%, surpassing both BaTiO₃ and PVDF-BaTiO₃ samples by 25% and 15%, respectively. The incorporation of carbon black can elevate the temperature of the entire system, leveraging its light-to-heat conversion capability, while its high electrical conductivity also aids in efficiently transporting photogenerated carriers to the material surface for enhanced reaction participation.

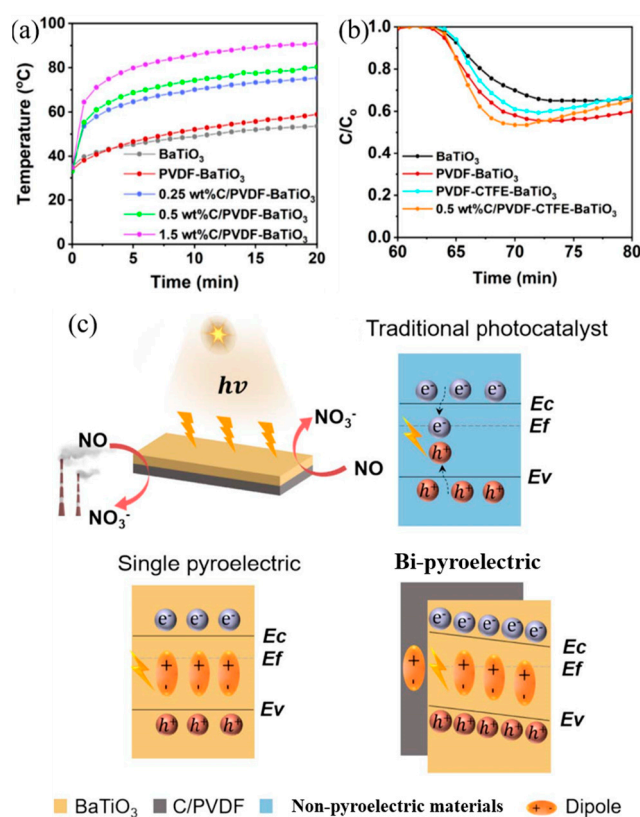


Figure 10. (a) Surface temperature profiles for pristine BaTiO₃, PVDF-BaTiO₃, and x wt% C/PVDF-BaTiO₃ (x = 0.25, 0.5, 1.5); (b) photocatalytic activity of samples for the removal of NO in air: BaTiO₃, PVDF-BaTiO₃, PVDF-CTFE-BaTiO₃, and 0.5 wt% C/PVDF-CTFE-BaTiO₃; (c) plausible mechanism of NO removal by C/PVDF-BaTiO₃ [148].

6. Conclusions and Outlook

Research in the past few decades has evidenced the effectiveness of TiO₂-based photocatalysts in the removal of low-concentration NO_x and their potential in the maintaining of air quality in urban areas. Mechanistic investigations by means of in situ spectroscopic methods and DFT theoretical calculation have advanced the understanding of the pathways of photocatalytic NO_x oxidation and offered hints to the design of high-performance photocatalysts. Strategies including heterojunction, doping, cocatalysts, and composites with basic compounds have performed effectively in enhancing the NO_x removal efficiency and stability of TiO₂-based photocatalysts. However, achieving both high efficiency in NO conversion and high selectivity for NO₃[−] currently remains a significant challenge on the basis of existing conditions. This difficulty has hindered the practical application of photocatalytic oxidation technology for NO_x removal. Additionally, limited research on NO removal under real-world conditions has greatly restricted practical applications. Factors such as catalyst temperature increases caused by intense sunlight irradiation during the summer and autumn seasons, the presence in real air of other interfering gases (VOCs, CO, O₃, etc.) that have not been adequately considered, and maintaining the stability of catalyst performance over multiple usage cycles further complicate the issue. Therefore, in future research, attempts to modify material structures (such as specific surface area, crystal facets, size, and micro-porous structure) or construct heterostructures and alter surface electronic properties to specifically regulate catalytic reaction pathways may be an effective approach to achieve efficient conversion and high selectivity. Moreover, attention should also be paid to the photothermal catalytic processes and their mechanisms under real reaction conditions, as well as the synergistic catalytic processes involving other air pollutants (VOCs, CO, etc.) with NO_x.

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