EFFECT OF THE LIGHT QUANTUM EFFICIENCY ON THE SYNCHRONOUS PHOTO CATALYTIC ABATEMENT OF SO₂–NO_x BINARY GAS

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Abstract: Photocatalytic decontamination has emerged as a highly promising technology for air pollutant control and energy conversion. In this work, a semiconductor photocatalyst was synthesized via a hydrothermal method, featuring nano-sized TiO₂ doped with nickel (Ni), zirconium (Zr), and nonmetallic nitrogen (N). The kinetic process of synchronous abatement of the SO₂-NO_x binary gas system was systematically investigated in a self-designed photocatalytic reactor. From the perspective of quantum optics, a light quantum efficiency model was established to elaborate the photocatalytic degradation mechanism, accompanied by a detailed analysis of the synergistic effects of multiple influencing factors on the interaction between incident light and pollutants. Experimental results revealed that flue gas concentrations exert significant impacts on contaminant removal efficiencies. Notably, the experimental data showed excellent consistency with the calculated results across a wide range of operational conditions.

Keywords: Photocatalysis; Simultaneous desulfurization and denitrification; Quantum efficiency; Reaction mechanism

1 INTRODUCTION

Air pollutants, including particulate matter, sulfur dioxide (SO_2) , nitrogen oxides (NO_x) , and mercury (Hg)—predominantly emitted from coal-fired flue gases—have triggered escalating environmental challenges, most notably the intensification of haze episodes in recent years [1–4]. This has galvanized global efforts toward air pollution mitigation. While conventional treatment technologies—such as physical adsorption, chemical oxidation, microbial processes, and high-temperature calcination—have contributed to environmental purification, they are hindered by inherent limitations: low removal efficiency, potential for secondary pollution, and restricted applicability across diverse contaminant profiles [4,5].

Against this technological backdrop, photocatalytic technology has emerged as a promising solution. Since Fujishima's seminal 1972 publication on water electrolysis for hydrogen production over TiO₂ single crystals, photocatalytic reactions have garnered interdisciplinary attention[6]. Titanium dioxide (TiO₂) stands out as the most widely studied photocatalyst due to its non-toxicity, chemical stability, strong surface hydrophilicity, recyclability, and unique ability to completely mineralize organic pollutants into harmless end products (H₂O and inorganic ions) without secondary contamination[6,7].

Current research on TiO₂-based systems in environmental remediation—particularly for flue gas treatment—focuses on leveraging its intrinsic properties and enhancing performance through structural/chemical modifications. Notable investigations include: Yuan et al.[8] prepared nanometer TiO₂ composite material using the aluminum silicate fiber as carrier by sol-gel method, under UV irradiation(wavelength was 253.7nm), examining the efficiency of desulfurization and denitrification and mercury removal of the material, the results show that denitrification efficiency can reach 40%, and found that a low concentration of SO₂ in the flue gas could play a role in promoting the removal of NO, and the temperature has an inhibition effect on the process of photocatalytic oxidation. Meng et al.[9] reported 37.4% NO and 25.84% NO₂ removal over activated carbon-TiO₂ composites, highlighting light-intensity-dependent enhancements and temperature-related deactivation mechanisms.

Despite these advancements, practical implementation of TiO_2 photocatalysis remains constrained by fundamental challenges. As a wide-bandgap semiconductor (3.2 eV, $\lambda \approx 387$ nm), TiO_2 responds only to ultraviolet (UV) light, which constitutes merely 3–4% of solar irradiance. The underutilization of the visible spectrum (45% of solar energy) presents a critical bottleneck, necessitating strategies to extend its optical response to longer wavelengths[10]. Additionally, mechanistic understanding of photocatalytic reactions—including charge carrier dynamics and surface redox processes—remains incomplete, urging deeper exploration of reaction pathways[11].

To address these knowledge gaps, this study establishes a rational photocatalytic reaction model. By synthesizing N, Ni, and Zr-codoped TiO₂ photocatalysts, we investigate the quantum efficiency of photocatalytic processes from an optical physics perspective. Experimental validation and dynamic kinetic simulations are employed to corroborate the model's accuracy, providing a foundational framework for advancing TiO₂-based photocatalysis toward real-world applications.

2 EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade and used without further purification. TiO_2 and $Zr(NO_3)_4$ were purchased from BASF Chemical Co., Ltd., Tianjin, China. Ni(NO₃)₂ was supplied by Founder Reagent Factory, Beichen, Tianjin, China. All other reagents were purchased from Huaxin Reagents Co., Baoding, China. Samples were prepared via a hydrothermal reaction, with the nonmetallic element N introduced for photocatalyst modification.

2.2 Experimental Apparatus and Methods

The primary objective in designing a photocatalytic reactor is to provide a stable reaction space and environment, thereby enhancing reaction efficiency. Two critical theoretical bases underpin reactor design: light transport dynamics and catalytic reaction efficiency. The transmission and distribution of light within the reactor directly influence the interaction between the catalyst and incident photons. Substantially uniform light exposure minimizes optical loss during transmission, maximizing the catalyst's light utilization efficiency. Conversely, catalyst regions with insufficient or negligible light exposure cannot undergo adequate photocatalytic reactions. The self-designed experimental setup for NO and SO₂ oxidation is depicted in Figure 1.



Figure 1 Schematic Diagram of the Polluting Gases Removal Apparatus

1:Cylinders of N_2 , SO_2 , NO and O_2 ; 2: Regulator; 3: Gas rotameter; 4: Valve; 5: Gas mixer; 6: Photochemical reaction apparatus (6(a): Magnetic stirrer; 6(b): Cold trap; 6(c): UV lamp; 6(d): Reaction tube self-made); 7: Cryostat device(7(a) Controller); 8: High temperature thermostat(8(a) Controller); 9: Drying tower; 10: Flue gas analyzer; 11: Computer; 12: Three-way valve; 13: Waste gas scrubber.

The experimental apparatus (Figure 1) consists of three integrated units: inlet flue gas simulation (Components 1–5), removal reactor (6–9), and outlet gas analysis (10–13). N₂ from cylinder (1) flows at 1 L/min through a regulator (2) and rotameter (3, LZB-30, Tianjin) into gas mixer (5), where SO₂, NO, or O₂ from separate cylinders are introduced via identical flow control systems with balance N₂ adjusted by a secondary flow meter, and the mixed gas passes through valve (4) into the reactor (6). The reactor features a UV-A light source (6(c), 800 W, λ =365 nm) with cooling jacket (6(b)), catalyst suspension in reaction tube (6(d)), a magnetic stirrer (6(a)) for uniform irradiance, cryostat (7) to maintain lamp temperature, and high-temperature thermostat (8) for stable reaction conditions, with gas velocity kept at 4.5–6 cm/s to minimize back-mixing and solution pH monitored by a waterproof meter (PHS-3G, Shanghai LEICI). Post-reaction gases are dried and analyzed via flue gas analyzer (10, Beijing Yunenghuitong) interfaced with computer (11), while residual gases pass through three-way valve (12) to scrubber (13) for complete removal before venting. All experiments were replicated thrice with results averaged for statistical rigor.

The output response is the removal efficiency of SO2 and NO (%), which were calculated as below:

$$\operatorname{Re}_{(NO/SO_2)} = \left(1 - \frac{C_{out}}{C_{in}}\right) \times 100\%$$
⁽¹⁾

where C_{in} and C_{out} stand for the inlet and outlet concentrations of NO or SO2, respectively.

In industrial applications, numerous factors influence flue gas removal efficiency. This study investigates the effects of NO, SO₂, and O₂ concentrations, with initial NO levels ranging from 200 to 800 mg/m³ and O₂ from 3% to 21%. To explore reaction mechanisms, a quantum efficiency model was developed from an optical perspective using a photocatalytic reactor. Experimental data validation confirmed the model's accuracy and reliability.

3 RESULTS AND DISCUSSION 3

3.1 Analysis on the Photocatalytic Reaction Mechanism

Broadband semiconductors serve as photocatalysts primarily due to their photoelectric properties. Take TiO₂, an n-type oxide semiconductor, as an example: the bandgap energy (E_g) of its anatase phase is 3.2 eV. A photocatalyst functions

only when the energy of incident photons is not less than its E_g , i.e.:

$$E = \hbar c / \lambda > E_g$$

Where E stand for the intensity of the incident light, \hbar is Planck's constant, c is the speed of light, λ is the wavelength of light.

h SO2 HNO₂

Figure 2 Schematic Diagram of the Mechanism of Photocatalytic

Figure 2 illustrates the photocatalytic electron-hole transport dynamics in TiO₂: upon irradiation with light whose photon energy (E) exceeds the anatase phase bandgap (Eg = 3.2 eV), valence band electrons are excited to the conduction band, generating photo-induced electron-hole pairs (e⁻ and h⁺). Two dominant reaction pathways emerge: first, photoexcited electrons (e⁻) reduce adsorbed oxygen to form superoxide anions (O₂⁻), while photogenerated holes (h^+) react with surface-adsorbed water or OH⁻ to produce highly oxidative hydroxyl radicals (•OH), enabling NO decomposition via non-selective oxidation; on the other hand, after specific adsorption of pollutant molecules onto the TiO₂ surface, photo-induced carriers migrate to the interface and react directly with adsorbed species, driven by the redox potential difference between the carriers and contaminants.

3.2 The Quantum Efficiency Model of Photocatalytic Synchronous Abatement of SO₂-NO_x Binary Gas

3.2.1 Process of the photocatalytic reaction

At a UV irradiation, whose wavelength is less than 387nm, the catalytic process can be expressed as follows:

$$TiO_2 + hv(E > Eg) \rightarrow e^- + h^+$$

 $O_2 + e^- \rightarrow O^-$

$$H_2O + h^+ \to OH + H^+$$
$$O_2^- + H^+ \to HO_2$$

For NO, there are:

$$NO + HO_2 \rightarrow HNO_3$$

There may also be another reaction pathway:

$$O_2(ads) + 2e^- \rightarrow O_2^{2-}(ads) \rightarrow 2O^-(ads)$$
$$O_2(ads) + h^+ \rightarrow O^*$$
$$NO + O^* \rightarrow NO_2$$



(2)

$$NO_2 + OH \rightarrow HNO_3$$

SO₂ is oxidized into SO₃ by living radical:

$$SO_2 + 2OH \rightarrow SO_3 + H_2O$$
$$SO_2 + O_2^- + H_2O \rightarrow SO_2 + 2OH$$

3.2.2 The quantum efficiency of photocatalytic reaction process

Quantum efficiency (QY) quantifies the ratio of photo-generated carriers participating in catalysis to the number of absorbed photons. In photocatalytic kinetics, photoexcited carriers (e^-/h^+) undergo two competitive processes: recombination and trapping. Carriers are only effective when trapped and reacted with electron donors / acceptors.

Formally: QY = Photo-generated carriers participating in catalysis / Absorbed photons. When photon flux is constant, enhancing photocatalytic efficiency fundamentally requires improving carrier trapping efficiency(e.g., reducing recombination), which is governed by material electronic structure, carrier migration dynamics, and carrier . For NO degradation, integrating QY with photocatalytic reaction kinetics yields:

$$QY = \left[\left(\frac{k_1[O_2][\text{NO}]}{4k_2\phi}\right)^2 + \frac{k_1[O_2][\text{NO}]}{2k_2\phi}\right]^{\frac{1}{2}} - \frac{k_1[O_2][\text{NO}]}{4k_2\phi}$$
(3)

Where, k is a constant, ϕ is the amount of photons. As equation shows, QY is inversely proportional to the amount of photons. When the light is intensity, the equation can be simplified to:

$$QY = \left[\frac{k_1[\text{NO}]}{2k_2}\right]^{1/2} \phi^{-1/2}$$
(4)

Evidently, quantum efficiency (QY) exhibits a linear relationship with the reciprocal of the square root of incident photon flux under certain kinetic regimes (e.g., diffusion-limited surface reactions). By correlating QY with the photon intensity profiles in designed experiments, a quantitative relationship between QY and pollutant concentration is established. Initially, QY increases with NO concentration due to enhanced surface adsorption of contaminants, which facilitates more efficient photon utilization by promoting carrier trapping at the catalyst-pollutant interface. As NO concentration rises, QY approaches unity when adsorption sites are fully occupied; however, excessive concentrations induce surface adsorption saturation, beyond which QY plateaus or declines due to reduced active site availability. Practically, optimizing NO concentration within the sub-saturation range can enhance QY by maximizing carrier-pollutant interaction efficiency.



Figure 3 Relationship between Gas Concentration and Removal Efficiency (a)NO Removal Efficiency Changes with the Initial Concentration;(b) SO₂ Removal Efficiency Changes with the Initial Concentration

At 60°C and 20.6% O₂, NO and SO₂ concentrations were varied individually, with gas concentrations monitored over 15 minutes. Figure 3(a) and 3(b) depict the relationship between initial gas concentration and removal efficiency. For NO, removal efficiency increases with concentration up to a threshold, whereas SO₂ exhibits a weaker concentration dependence. To enhance clarity, SO₂ data are presented for two initial concentrations with a large disparity (e.g., low vs. high). This divergence may arise from distinct reaction pathways: NO preferentially undergoes (specific mechanism, e.g., radical-driven oxidation), while SO₂ adsorption/oxidation is limited by (e.g., surface site saturation or slower electron transfer kinetics).



Figure 4 Relationship between Removal Efficiency and O₂ Concentration. (a) NO Removal Efficiency Changes with the Concentration of O₂;(b) SO₂ Removal Efficiency Changes with the Concentration of O₂

At 60°C, with initial NO and SO₂ concentrations of 700 mg/m³ and 500 mg/m³, respectively, the effect of O₂ concentration on pollutant removal efficiency was investigated. As shown in Figure 4(a) and (b), removal efficiency increased with rising O₂ concentration, particularly for SO₂: at 20.80% O₂ (v/v), SO₂ removal efficiency reached 95.41%. This behavior aligns with O₂'s role as an electron acceptor in photocatalysis, facilitating superoxide (O₂⁻) and hydroxyl radical (•OH) generation for enhanced oxidation.

4 KINETICS OF CATALYTIC REACTION

4.1 Effect of the Concentration of Pollutant on the Photocatalytic Reaction Kinetics

The kinetic study of desulfurization and denitrification is shown in Figure 5. When the content of oxygen was 20.6% and the temperature was 60° C, we using Langmuir-Hinshelwood (L-H) kinetic model to describe the process of photocatalytic degradation of NO and SO₂, which is:

$$-\frac{dC}{dt} = v = \frac{kK[C]}{1+K[C]}$$
⁽⁵⁾

Where K is the adsorption constant, which is equal to the ratio of adsorption rate constant and desorption rate constant, and C is the concentration of the pollutant, v is the reaction rate, k is Langmuir rate constant. By integrating, the formula is rewritten as:

$$t = \frac{1}{kK} \ln(\frac{C_0}{C_t}) + \frac{1}{k}(C_0 - C_t)$$
(6)

Where C_0 and C_t are represent the initial concentration and instantaneous concentration respectively. Using k_1 was the product of K and k.

By calculating and fitting, we can get a good linear relationship between $\ln(C_0/C_t)$ and t, the degradation process is in line with the first-order kinetics model. At the same time, the k_1 is increasing with the initial concentration of the

is in line with the first-order kinetics model. At the same time, the κ_1 is increasing with the initial concentration of the pollute, which further demonstrates the correctness of the optical quantum model.



Figure 5 The Effect of the Concentration of Pollute on the Photocatalytic Degradation Rate Constant

The inset figure is the relationship between k_1 and the concentration of pollutants. Where (a) is used to show the relationship between the concentration of NO and the parameters of kinetic, while (b) is the relationship between the concentration of SO₂ and the parameters of kinetic.

4.2 Effect of the concentration of O2 on the photocatalytic reaction kinetics

In order to further demonstrate the correctness of the optical quantum model, we study the effect of the concentration of O_2 on the photocatalytic reaction kinetics, which are shown in Figure 6 below.



Figure 6 The Effect of the Concentration of O2 on the Photocatalytic Degradation Rate Constant

The inset figure is the relationship between k_1 and the concentration of O₂. Where (a) is used to show the degradation process of NO, while (b) is the degradation process of SO₂.

A good linear relationship could be got between $\ln(\frac{C_0}{C_t})$ and t by calculating and fitting, so the degradation process of

difference concentration of O₂ follows the first-order kinetics model. From the change rules of k_1 , as shown in Figure 6, we can conclusion that the catalytic efficiency is proportional to the oxygen content, which is consistent with the above optical quantum model.

5 CONCLUSION

Ti-based composite photocatalysts were developed for efficient simultaneous removal of SO_2 and NO. Through systematic investigations on the impacts of pollutant concentrations and oxygen content on removal efficiency, a quantum efficiency model was established. This model reveals a strong correlation among photon utilization, carrier dynamics, and catalytic performance. Notably, experimental data exhibit good consistency with the model predictions, providing in-depth mechanistic insights into photon-driven deep oxidation for simultaneous gas purification.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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