IMPROVEMENT IN PHOTOCATALYTIC ACTIVITY NOx USING N-TiO2 PHOTOCATALYTIC MATERIALS UNDER VISIBLE LIGHT

Le Thi Pho[(1)]
(1) Thu Dau Mot University
Corresponding author: lienhb@tdmu.edu.vn

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Abstract

Improving and exploring the photocatalytic performance of composites for new models continues to pose a challenge. Here, a straightforward thermal dispersion method is achieved by incorporating nitrogen (N) into TiO2 at different weights (1%, 3%, and 5%) to enhance photocatalytic activity. The material properties are analyzed through ultraviolet-visible diffuse reflectance spectroscopy (UV-VIS DRS), and X-ray diffraction (XRD). The results indicate that the NO gas removal efficiency of N-TiO2 photocatalytic materials is higher than that of pure TiO2 after 30 minutes of exposure to visible light. The highest NO gas treatment efficiency of N-TiO2 -1% is 40.4%, with a reaction rate following a first-order kinetic equation of 0.0688 min-1. Successfully fabricating N-TiO2 photocatalytic materials using the thermal dispersion method, with significantly enhanced photocatalytic performance under visible light activation, will benefit practical applications, particularly in the environmental sector.

Keywords: N-TiO2, NOx removal, photocatalysis, TiO2 nanotubes, visible light

1. Introduction

Titanium dioxide nanotubes (TNTs) were studied extensively due to their one-dimensional nanostructure, large internal and external surfaces, ion exchangeability, and photocatalytic activity. These characteristics make TNTs applicable in various fields, such as solar cells, photocatalysis, and electroluminescent devices (Abdullah and Kamarudin 2017). Various methods have been employed to synthesize TNTs, including the sol-gel process (Du, Chen et al., 2001), electrochemical anodic oxidation (Durdu, Cihan et al., 2021), microwave (Wu, Jiang et al., 2005), and hydrothermal treatment (Khan, Lalji et al., 2024). Hydrothermal treatment has garnered significant interest due to its cost-effectiveness and ease of producing TNTs with superior morphology.

However, the high band gap of TNTs, ranging between 3.3eV and 3.87eV, limits their practical use as they can only be excited by UV light, which makes up less than 5% of the solar spectrum. To clarify this limitation, efforts have been made to enhance the absorption of TNTs to visible light. This can be achieved by manipulating particle size, oxygen vacancy, and doping to engineer the TiO_2 band gap (Pang, Lim et al., 2014). Some methods involve using metals like Au, Pd, Ag, and Cu as dopants to improve the photocatalytic efficiency of TiO_2 under visible light (Bai, Ren et al., 2025). Recently, increased efficiency

in photocatalytic degradation of TiO_2 nanotubes through potassium doping in removing methylene blue dyes achieved 70% by Hiba Rahman (Rahman, Nair et al., 2025). However, relatively few studies have focused on reducing the band gap of TNTs.

Adding metal and non-metal elements are being explored as an effective method to create new energy levels within TNTs, allowing for improved visible light absorption, separation of charge carriers, particle size and morphology changes, and enhanced photocatalytic activity. However, the high cost of metal-doped TNTs has limited its commercial potential. Some metal-doped TNTs variants have not been widely used due to their poor photocatalytic performance and reproducibility including $Mn^{2+,}$ Ni^{2+} (Estévez Ruiz, Lago and Thirumuruganandham, 2023). As a result, non-metal elements such as N, S, P, B, C, and F have been investigated for doping TiO_2. Among these, nitrogen-doped TNTs (N-TNTs) has garnered attention for its responsive photocatalytic properties under visible light, attributed to its similar atomic size, low ionization energy, high electronegativity, stability, and cost-effectiveness (Pablos, Marugán et al., 2017).

The concentration of NO_x in the atmosphere has significantly risen in urban areas worldwide over the last few decades due to industrial and transportation activities. NO_x adversely affects the environment and humans, animals, and plant health. As a result, there is a growing need to address the harmful effects of NO_x in line with sustainable climate policies, leading to increased efforts to improve NO_x reduction methods. Researchers have explored approaches such as direct decomposition, selective catalytic/non-catalytic reduction, solid-liquid adsorption, plasma-assisted catalytic reduction, and photocatalytic oxidation to remove NO_x from the atmosphere effectively. However, these methods are not financially viable for low concentration levels of NO_x and require complex equipment, engineering, or high temperatures. Photocatalysis is an optimal method because this method is simple and easy to perform under atmospheric conditions.

In this study, N-TNTs was synthesized from N (urea) and TiO_2 nanotubes by thermal diffusion. NO_x pollution gas was remediated through a visible light photocatalytic reaction on N-TNTs nanotubes under ambient conditions, and over 40% was achieved at 30 min.

2. Materials and methods

2.1. *Materials*

TiO_2 nanotubes (TNTs) (Le, Cao et al., 2024).

Research chemicals: NaOH (China, 96%), HCl (China, 36%), urea (China, 99%).

2.2. Methods

Add TNTs and urea (%N: 1wt%, 3wt%, and 5wt%, respectively) to a 250ml beaker. Then, stir the mixture for 30 minutes. The resulting product was dried at 80°C for 6 hours. The mixture was burned at 400°C for 2 hours to obtain N-TNTs.

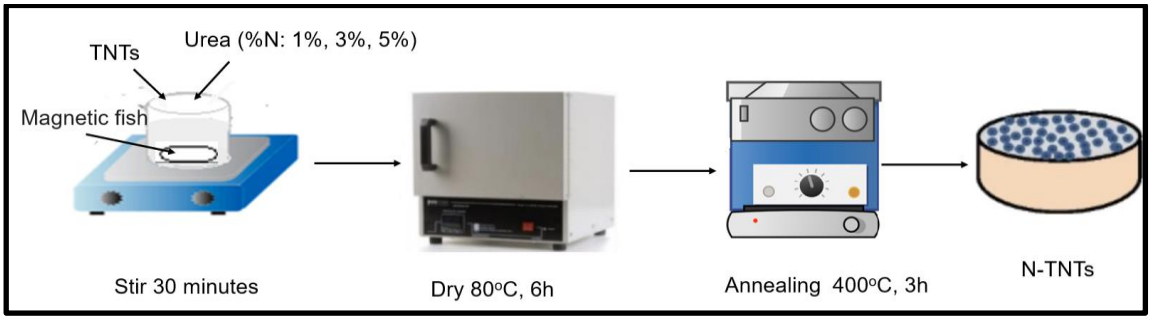

Fig 1. Material synthesis process N-TNTs material

Evaluating the Photocatalytic Activity of materials

A solar simulation lamp (OSRAM 300 W) with a wavelength range from 400 to 800nm was used to investigate the photocatalytic activity of N-TNT materials.

First, 0.2g of N-TNT and 20mL of DI water were placed in a petri dish and were sonicated for 5 minutes. Then, the sample was dried and put into a rectangular stainless-steel vessel environmental chamber for the photocatalysis test. The temperature, relative humidity, and air quality were controlled in the chamber, with the operating temperature and relative humidity being 30°C and 70%, respectively. The chamber was fed nitrogen oxide (NO) via a pneumatic cylinder to provide an initial concentration of 50ppm. The generator then diluted NO gas to 550ppb (Sabio 1001 Generator), and the flow rate was controlled at 3 $L.min^{-1}$. The system was allowed to stabilize for at least one hour to achieve the NO adsorption/desorption equilibrium in the dark before irradiating the N-TNTs. Photocatalytic degradation of NOx was measured using a chemiluminescence NOx analyzer at a sampling rate of 0.6 $L.min^{-1}$ (Environics Series 4000).

The conversion rate of NO into environmentally friendly products using various photocatalysts was determined using the equation:

$$H\% = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

Where: C_0: initial NO gas concentration

C_t: NO gas concentration at time t

3. Results and Discussion

Fig. 2 displayed the XRD patterns for TNTs and N-TNTs. Both graphs showed peaks at diffraction angles of 25.5°, 36.9°, 37.8°, 38.5°, 48.0°, 53.9°, 55.1°, 62.1°, 62.7°, and 68.7°. These corresponded to various crystal planes (101), (103), (004), (112), (200), (105), (211), (213), (204), and (116) of the anatase TiO_2 phase, respectively (JCPDS No. 21-1272) at 28.68° and 48.23°, which are related to the nanotube structure (Peighambardoust, Asl and Maghsoudi, 2019). No additional peaks were observed during nitrogen doping, and the tetragonal structure of the anatase TiO_2 phase did not change or induce any phase transition. Due to its wide band gap, TNTs absorb UV light, specifically around 388nm (Fig 3a). However, when N atoms are introduced between Ti and O atoms in the TiO_2 crystal structure, the bonding is altered to Ti-O-N, creating additional energy levels near the highest energy level in the valence band (Wang, Li et al., 2014). This modification causes a red shift in the optical absorption or emission spectra, allowing lower energy photons to excite electrons across the modified band gap. As a result, the addition of N atoms causes the redshift phenomenon. Compared to TNTs, the N-TNTs photocatalysts shifted to higher wavelengths, with the N-TNTs-1% sample exhibiting the sharpest increase in absorption at around 396.8nm.

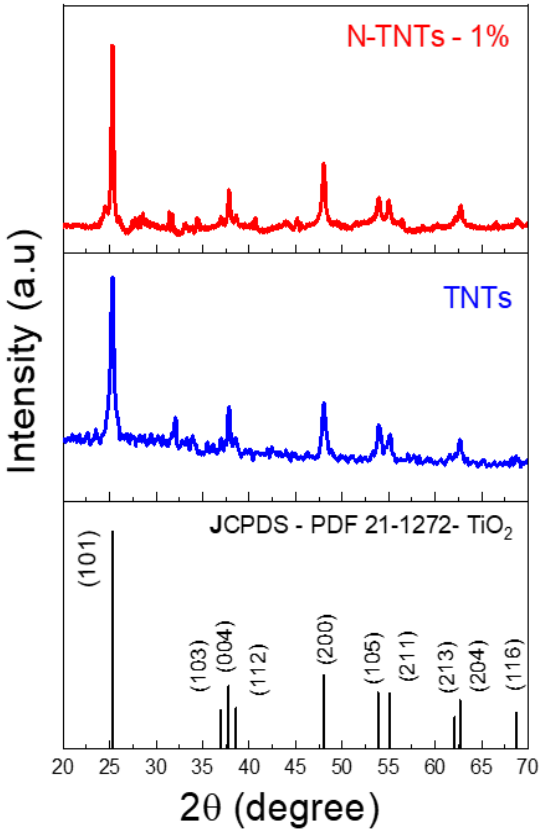

Fig 2. XRD patterns of N-TNTs – 1%

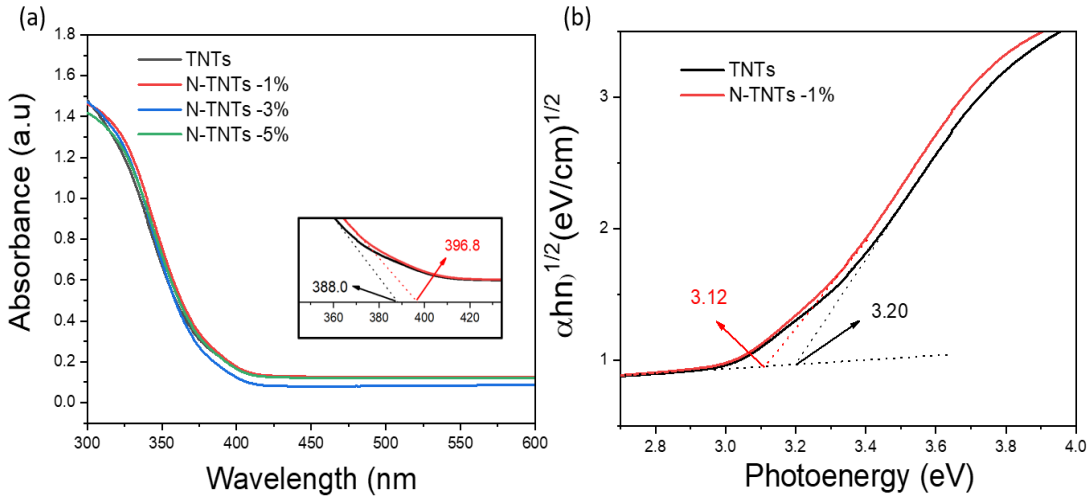

Fig 3. DRS spectra (a), Tauc plots of $(\alpha h\nu)^{1/2}$ vs. energy (b) of TNTs, and N-TNTs -1%

Fig 3b illustrates a distinct shift in the optical absorption edge towards the visible spectrum, showing a change of 0.08eV for N-TNTs-1% at 3.12eV in contrast to 3.20eV. This shift of 0.08 indicated that the nitrogen species are localized within the TNTs lattice. These nitrogen species took up some of the positions generally occupied by oxygen in the lattice structure. Consequently, this finding eliminated the possibility of nitrogen residing in other positions, such as interstitial sites, which would otherwise lead to forming a mid-gap band (Qu, Zhu and Huang, 2021).

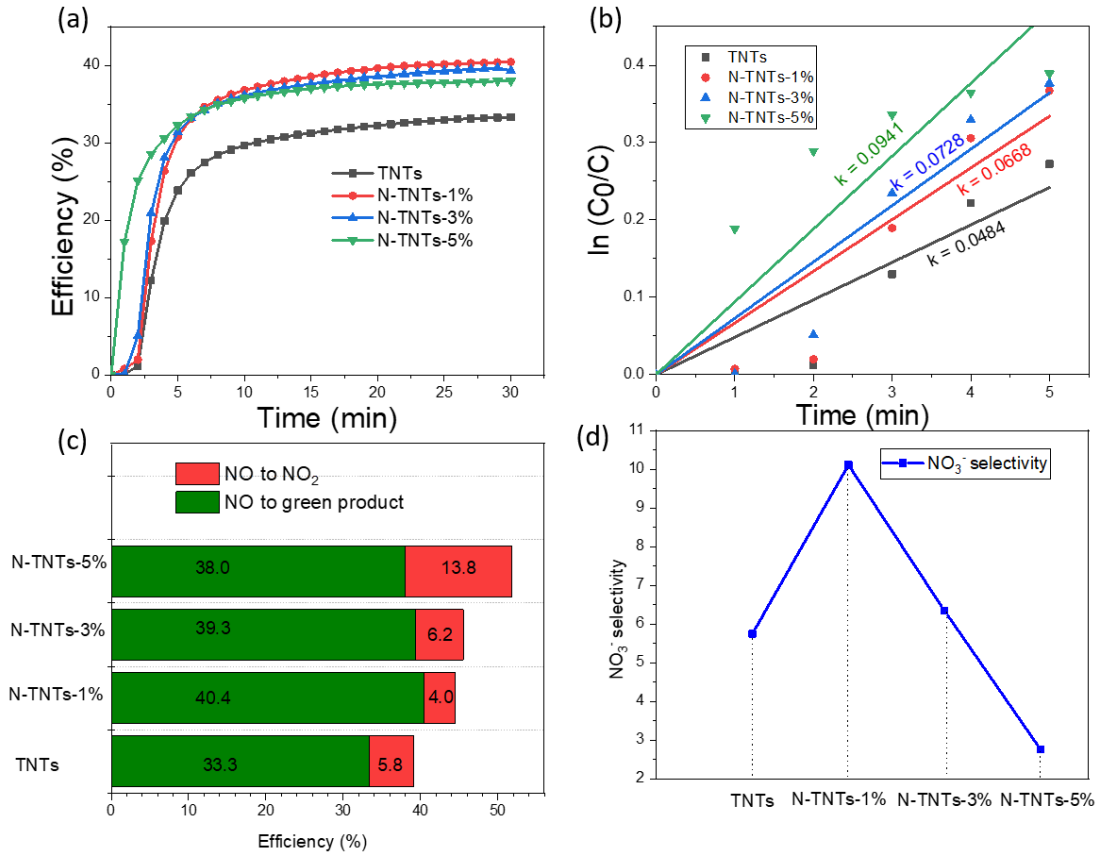

Fig 4. Time-dependent photocatalytic degradation of NO (a) and corresponding pseudo first order kinetic curves (b), NO degradation performance into the green product, NO-to-NO_2 conversion (c), and NO_3^- selectivity (d)

Under visible light irradiation (Fig. 4a), all synthesized N-doped TNTs materials demonstrated significantly improved photocatalytic performance in removing both NO and NO_x compared to the TNT sample. However, the generation of NO_2 in the N-TNTs - 3% and N-TNTs - 5% samples was relatively higher than that in the TNTs sample (Fig. 4c). Among all the samples, N-TNTs - 1% exhibited the highest NO removal rate at 40.4% under visible light for 30 minutes, while also producing the lowest NO_2 generation at just 4%. Compared to the findings of Tamal et al., who reported a conversion efficiency of 51% for NO gas under visible light irradiation over 1 hour, our results highlight that N-TNTs-1% achieved a notable NO removal efficiency of 40.4% in just 30 minutes. This suggests that our approach may offer a more rapid solution for NO reduction under similar conditions (Khan, Bari et al., 2021). N-TNTs initiate a process of photoinduced electron (e^-) and hole (h^+) separation upon exposure to appropriate photon energy. A portion of the generated electrons (e^-) migrate to the surface of the photocatalyst, where they interact with absorbed O_2 molecules, reducing them to form superoxide radicals ($^{\bullet}O_{2-}$). These $^{\bullet}O_2^-$ radicals then undergo a series of intermediate reactions with water (H_2O), leading to additional hydroxyl radicals ($^{\bullet}OH$). Collectively, these reactive oxygen species-comprising $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals - exhibit a solid capability for decomposing nitrogen oxide (NO) gas. The Langmuir-Hinshelwood model was used to analyze the NO photocatalytic reaction rates of N-TNTs materials, which aligns with a first-order kinetic equation (Fig. 4b). A linear plot of $\ln(C_0/C)$ against the photocatalytic reaction time (t) allowed for a comparison of the reaction rates among TNTs, N-TNTs-1%, N-TNTs-3%,

and N-TNTs-5%. The observed rates were 0.0484 min^{-1}, 0.0668 min^{-1}, 0.0728 min^{-1}, and 0.0941 min^{-1}, respectively. Notably, the N-TNTs-5% exhibited the highest constant, 1.9 times greater than that of the TNTs nanotubes.

Nitrogen doping within the TNTs lattice enhanced the ability of a material to absorb visible light, narrowed the energy bandgap, and resulted in more negative conduction band potentials. This improvement facilitated the formation of superoxide radicals, thereby increasing NO oxidation. For practical applications, the aim is to develop materials with high selectivity for NO_3^-. As shown in Fig. 4d, the selectivity for NO_3^- in N-TNTs varied significantly and was much higher under visible irradiation. This observation can be attributed to the differences in the energy band structure of TNTs compared to N-TNTs.

4. Conclusion

In summary, N-TNTs were synthesized from TiO_2 nanotubes and urea precursors using thermolysis processes. The NO removal efficiency of the N-TNTs composite material is 1.2 times greater than that of pure TNTs. As a result, N-TNTs present significant potential for widespread applications in environmental remediation. Further research is essential to investigate its morphology, structure, and recycling capabilities to optimize the practical use of N-TNTs as a photocatalytic material.

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