THE INFLUENCE OF CARRIERS ON THE PHOTOCATALYTIC ACTIVITY REDUCED NO EMISSION OF THE TNTs/g-C_3N_4/DIATOMITE COMPOSITE

Le Thi Pho[(1)]

(1) Thu Dau Mot University
Corresponding author: pholt@tdmu.edu.vn

DOI: 10.37550/tdmu.EJS/2024.02.556

Article Info

Volume: 6
Issue: 02
June 2024
Received: April 16th, 2024
Accepted: May 5th, 2024
Page No: 283-287

Abstract

Diatomite from Tuy An district, Phu Yen province, with different purities and diatom integrity as catalyst carriers, were adopted to prepare TNTs/g-C_3N_4 composite catalysts by a sol-gel method, with an optimal weight ratio of 1:1 for TNTs/g-C_3N_4 and diatomite. Compared with pure TNTs, g-C_3N_4, and TNTs/g-C_3N_4, the obtained composite photocatalysts exhibited lower photocatalytic performance under the same conditions and NO removal within 30 min under visible light. The NO gas treatment efficiency under the same conditions with different catalyst supports only decreases by approximately 18% at a reaction rate of 0.0950 min-1. This research on composite photocatalysts is a promising step towards practical environmental remediation. The use of diatomite as a carrier for photocatalytic materials is particularly noteworthy, as it is a naturally available and cost-effective source of materials. However, further improvements in the photocatalytic performance of the composite material is necessary to fully realize its potential in environmental remediation, including removing NOx and other pollutants. Overall, this study provides valuable insights into the influence of carriers on the photocatalytic activity of composite photocatalysts and lays the foundation for future research in this field.

Keywords: diatomite, NO removal, photocatalysis, sol-gel technique, TNTs/g-C_3N_4

1. Introduction

Diatomite is a sedimentary rock formed from the remains of microscopic single-cell algae called diatoms. These diatoms have a unique skeletal structure comprising two parts that fit together to create a highly porous and rigid framework of amorphous silica. The frustules of diatoms vary in size, shape, and architecture depending on the species they belong to. This sedimentary rock is soft, brittle, and has a very fine-grained texture. It is typically found on the floors of oceans and freshwater bodies (Janićijević et al., 2014). It's fascinating to learn about the numerous ways in which diatomite can be helpful. Its properties, such as low density, high porosity, large surface area, high absorptive capacity, low thermal conductivity, and chemical inertness, make it incredibly versatile. Diatomite is used in various industries as filter aids, cement additives, fillers, and absorbents. Researchers are also exploring the potential of natural or modified diatomite, chemically or thermally treated, for removing textile dyes, heavy metals, or organic pollutants from wastewater or polluted water by adsorption process and as a carrier in materials to improve their properties (Qian et al., 2015).

Despite its promising properties, using TiO_2 nanotubes (TNTs) has been limited in specific fields due to some intrinsic drawbacks. One of these is its wide band gap, which allows it to capture only a tiny portion (3-5%) of the total solar spectrum. In addition, the fast recombination of photogenerated electron-hole pairs can reduce efficiency in the photo/photoelectron-catalytic activity. To address these limitations, researchers have focused on increasing the photocatalytic active surface, creating Schottky

junctions or heterojunctions, and modifying the band structure to match specific energy levels. These efforts aim to improve the photo-to-energy conversion efficiency by widening the visible light absorption and preventing the recombination of electrons and holes (Roy, Berger, & Schmuki, 2011).

The Carbon nitride (g-C_3N_4) is a metal-free polymer semiconductor with exceptional electric, optical, and structural properties, making it a versatile nano platform for various applications in electronics, catalysis, and energy. The unique properties of g-C_3N_4-based materials have emerged as promising candidates for numerous energy and environmental photocatalytic applications, including photocatalytic water reduction and oxidation, degradation of pollutants, and carbon dioxide reduction. However, the photocatalytic ability of pure g-C_3N_4 is limited by the high recombination rate of photogenerated electrons and holes. Therefore, developing highly active visible-light-driven photocatalytic materials based on g-C_3N_4 for environmental applications has attracted much attention recently (Wen et al., 2017). So, it is interesting to learn about the promising photocatalytic activity exhibited by the TNTs/g-C_3N_4 composite material and its potential for decomposing organic substances under visible light to improve the disadvantages of TNTs and g-C_3N_4 (Fernandes et al., 2023). However, further research is still needed to improve this system's catalytic activity and explore new methods for achieving even better results. Many groups are actively studying this area to find ways to enhance the performance of TNTs/g-C_3N_4 and unlock its full potential for environmental remediation and other applications. The objective of this study was to develop a composite photocatalyst consisting of TNTs/g-C_3N_4/Diatomite that could maintain its photocatalytic performance while incorporating diatomite as a TNTs/g-C_3N_4 nanocarrier for more accessible practical application.

2. Materials and methods

2.1. Materials

• Diatomite-prepared diatomite material in Phu Yen province

• Research chemicals: NaOH (China, 96%), HCl (China, 36%), pure TiO_2 (China, 98%), melamine (China, 99%).

2.2. Methods

To prepare the diatomite material, it is mixed with 5M HCl acid in a ratio of 1:25 and stirred at 1000 rpm at 75°C for 72 hours. The resulting mixture is then rinsed with deionized water multiple times until the pH value reaches 7 to synthesize the next steps. Finally, the sample is dried at 80°C for five hours. According to Qiong Wu et al. (2019), the synthesis process of TNTs/g-C_3N_4/Diatomite material was as shown in Figure 1.

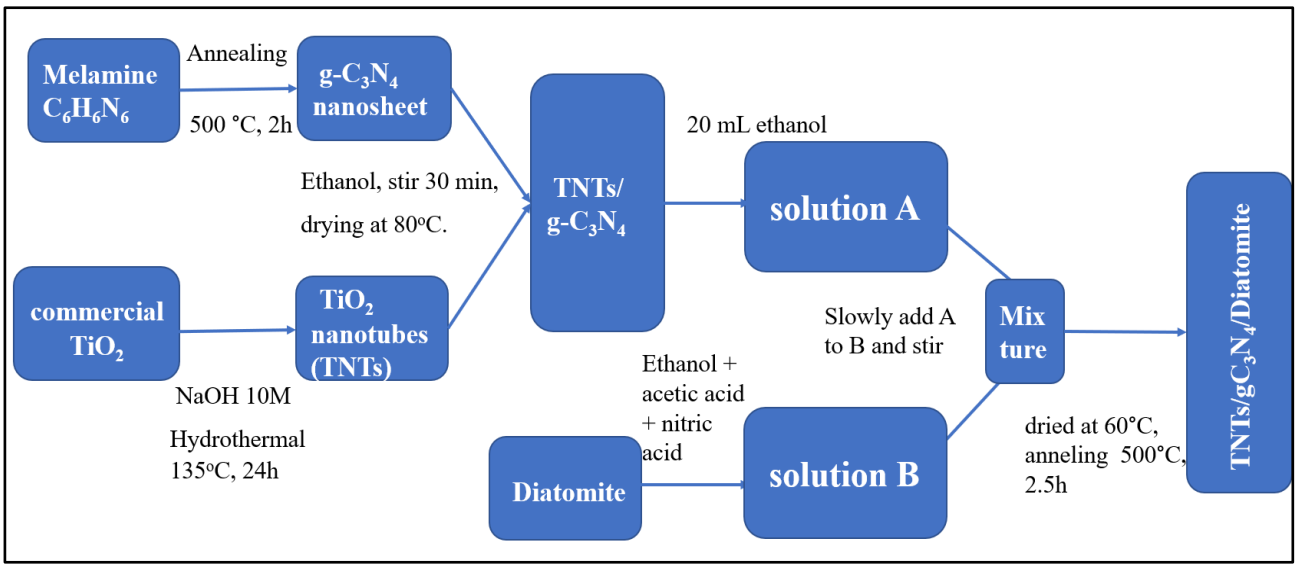

Fig 1. Material synthesis process TNTs/g-C_3N_4/Diatomite material

Investigate the photocatalytic activity of the material

Step 1: To make the mixture homogeneous, 0.2g of material on a 12cm diameter Petri dish and 20mL of DI water sonicated for 10 minutes.

Step 2: Dry the sample mixture at 80°C for 3 hours, then at room temperature.

Step 3: Place the Petri dish containing the sample into a rectangular stainless steel gas measuring chamber (30cm × 15cm × 10cm), illuminate with a solar simulation light (OSRAM 300 W) with a wavelength of 400 to 800nm, operating temperature and relative humidity are 30◦C and 70%, respectively.

Step 4: A compressed air cylinder line supplies the NO gas stream. Nitrogen oxide (NO) with an initial concentration of 50 ppm is diluted by a Sabio 1001 generator with a controlled flow rate of 3 $L.min^{-1}$ to dilute NO to a concentration of 500 ppb.

Step 5: Before the TNTs/g-C_3N_4/Diatomite was irradiated, the system was stabilized for at least one hour to achieve NO adsorption/desorption equilibrium in the dark. A chemiluminescent NOx analyzer measured photocatalytic decomposition NOx at a sampling rate of 0.6 $L.min^{-1}$ (Environics Series 4000).

Step 6: Collect data and calculate results.

The NO removal efficiency (H%) is calculated using the following formula:

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

C_0 and C_t represent the NO concentration in the inlet and outlet streams.

3. Results and Discussion

The investigation found that diatomite alone does not exhibit photocatalytic activity for removing NO gas with a concentration of 550ppb (Fig 2). However, when diatomite is combined with TNTs/g-C_3N_4 material, the efficiency of NO gas treatment increases significantly, though it is still lower than the efficiency of TNTs/g-C_3N_4 material. The photocatalytic activity increases sharply in the first 5 minutes, likely due to the large contact area and absence of reaction byproducts that could hinder contact between the material and NO gas. After 5 minutes, the efficiency increases slowly up to 30 minutes.

The samples showed the following treatment efficiencies: TNTs (34.21%), g-C_3N_4 (41.91%), TNTs/g-C_3N_4 (45.22%), and TNTs/g-C_3N_4/diatomite (27.81%). The TNTs/g-C_3N_4 material had the highest NO removal efficiency, even higher than the individual TNTs and g-C_3N_4 materials. When diatomite is combined with the TNTs/g-C_3N_4 nanotubes, the nanotubes get attached to the cavities of the diatomite. However, as the diatomite content increases, the surface area of the TNTs/g-C_3N_4 nanotubes decreases, leading to a reduction in photocatalytic activity. The study proposes using diatomite as a carrier for the photocatalytic materials to facilitate practical applications, as the TNTs, g-C_3N_4, and TNTs/g-C_3N_4 materials are all in powder form; this powder form presents some difficulties in practical applications (Li et al., 2014). The appropriate ratio of diatomite to TNTs/g-C_3N_4 needs to be determined to optimize the photocatalytic activity. Other studies are exploring diatomite combined with various materials for environmental treatment applications. This research aims to examine the effectiveness of diatomite in combination with other materials for removing pollutants from different sources, including wastewater and polluted water. Qing Sun et al., 2019 synthesized N-TiO_2/g-C_3N_4@Diatomite material for the application of Cr (VI) degradation under visible light irradiation ($\lambda > 400$ nm) with an efficiency of nearly 100%.

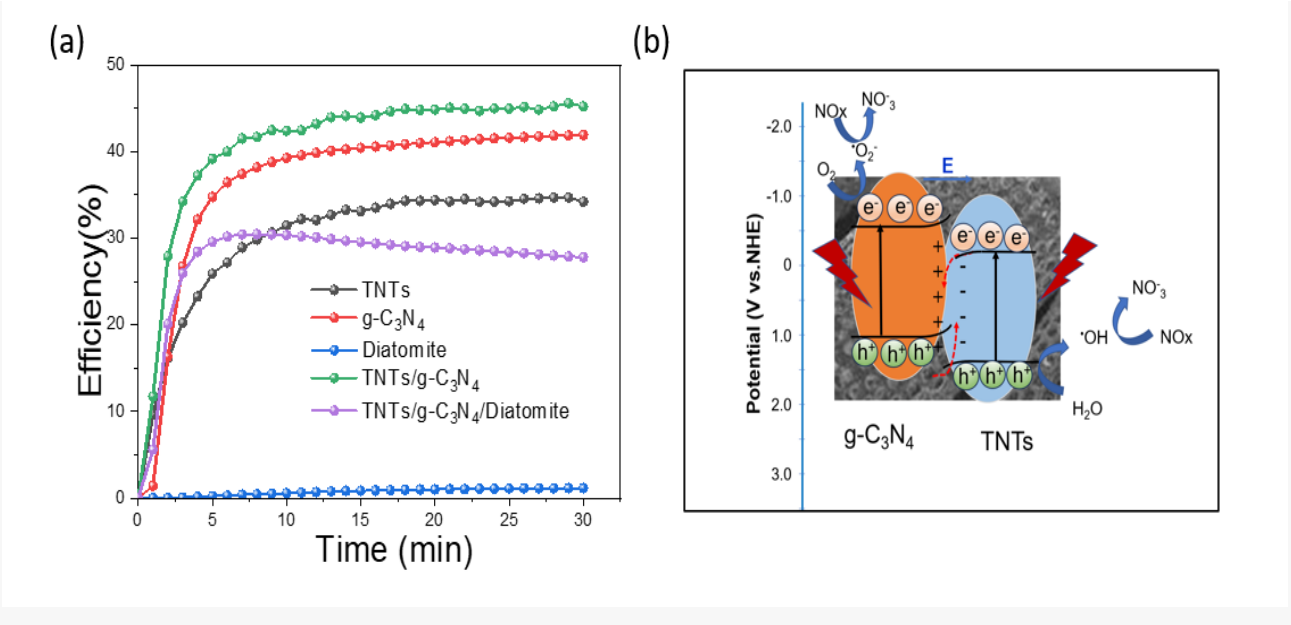

Fig 2. NO gas treatment efficiency depends on time (a), Photocatalytic mechanism illustration of TNTs/g-C_3N_4/Diatomite under visible light illumination (b)

$g\text{-}C_3N_4\ (hv) \rightarrow g\text{-}C_3N_4(e^- + h^+)$ (1)

$TNTs\ (hv) \rightarrow TNTs\ (e^- + h^+)$ (2)

$TNTs/g\text{-}C_3N_4/Diatomite\ (hv) \rightarrow TNTs/g\text{-}C_3N_4/Diatomite\ (e^- + h^+)$ (3)

$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$ (4)

$e^- + O_2 \longrightarrow {}^{\bullet}O_2^-$ (5)

$NO + 2H_2O + 3\ h^+ \rightarrow NO_3^- + 4\ H^+$ (6)

$NO_2 + H_2O + h^+ \rightarrow NO_3^- + 2\ H^+$ (7)

$NO + {}^{\bullet}OH \rightarrow HNO_2$ (8)

$NO + 2{}^{\bullet}OH \rightarrow NO_2 + H_2O$ (9)

$NO_2 + {}^{\bullet}OH \rightarrow HNO_3$ (10)

$H^+ + {}^{\bullet}O_2^- \longrightarrow {}^{\bullet}HO_2$ (11)

$NO + {}^{\bullet}HO_2 \rightarrow HNO_3$ (12)

TNTs/g-C_3N_4 and TNTs/g-C_3N_4/Diatomite are S-scheme heterojunction, so they promote the recombination of electron-hole pairs at low redox potentials to prevent the recombination of electron-hole pairs with high redox potentials and provide excellent photocatalytic performance (Du et al., 2020). The photocatalytic mechanism of TNTs/g-C_3N_4 S-scheme could be described, as shown in Fig. 2b. Firstly, the photocatalysts will be irradiated to excite the electrons from VB to CB as shown in Equations (1-3). Secondly, the electrons from CB of TNTs will recombine with holes of g-C_3N_4 with the support of an internal electric field to prevent the self-recombination of electron-hole pairs at high redox potential, as shown in Equation (4). Thirdly, these electrons and holes will react with O_2 and H_2O to produce $\bullet O_2^-$ and •OH radicals, as shown in Equations (4) and (5), respectively. Fourthly, these charge carriers will transfer within the materials to enhance the lifetime of photogenerated electron-hole pairs. Finally, the charge carriers and radicals will degrade NO into NO_2, HNO_2, and HNO_3, as shown in Equation (6-12).

4. Conclusion

This study aimed to improve the photocatalytic performance and enhance the ease of use of the TNTs/g-C_3N_4/Diatomite composite material for practical environmental remediation applications. To achieve this, further research is needed to optimize the material's morphology, structure, and recyclability. Additionally, exploring new methods for enhancing the composite material's catalytic activity may be helpful. With continued research and development, the TNTs/g-C_3N_4/Diatomite composite can potentially become a highly effective and cost-efficient solution for removing environmental pollutants.

References

Du, X., Bai, X., Xu, L., Yang, L., & Jin, P. (2020). Visible-light activation of persulfate by TiO2/g-C3N4 photocatalyst toward efficient degradation of micropollutants. *Chemical Engineering Journal*, 384, 123245.

Fernandes, Y. L., Silva, M. C., Raimundo, R. A., Cavalcante, J., Tomaz, J. B., Mashhadikarimi, M., Morales, M. A., da Motta, F. V., Acchar, W., & Gomes, U. U. (2023). Development of mesoporous ceramic membranes of Diatomite/TiO2/Nb2O5 nanocomposites for the treatment of contaminated water. *Journal of Environmental Chemical Engineering*, *11*(6), 111161.

Janićijević, J., Krajišnik, D., Čalija, B., Dobričić, V., Daković, A., Krstić, J., Marković, M., & Milić, J. (2014). Inorganically modified diatomite as a potential prolonged-release drug carrier. *Materials Science and Engineering: C*, 42, 412-420.

Li, Y., Li, S., Wang, J., Li, Y., Ma, C., & Zhang, L. (2014). Preparation and solar-light photocatalytic activity of TiO 2 composites: TiO 2/kaolin, TiO 2/diatomite, and TiO 2/zeolite. *Russian Journal of Physical Chemistry A*, 88, 2471-2475.

Qian, T., Li, J., Min, X., Deng, Y., Guan, W., & Ning, L. (2015). Diatomite: A promising natural candidate as carrier material for low, middle and high temperature phase change material. *Energy Conversion and Management*, 98, 34-45.

Roy, P., Berger, S., & Schmuki, P. (2011). TiO2 nanotubes: synthesis and applications. *Angewandte Chemie International Edition*, *50*(13), 2904-2939.

Wen, J., Xie, J., Chen, X., & Li, X. (2017). A review on g-C3N4-based photocatalysts. *Applied Surface Science*, 391, 72-123.