

SYNTHESIS, STRUCTURAL CHARACTERIZATION AND APPLICATION OF N-DOPED TiO₂ PHOTOCATALYST UNDER VISIBLE-LIGHT IRRADIATION

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(Received: 15 May 2021; Accepted: 28 June 2021)

Abstract. N-doped TiO₂ nanomaterials were prepared with the sol-gel method. The structure and properties of the materials were characterized by using XRD, UV-Vis, SEM, EDX, and IR techniques. The optimal amount of ammonium chloride in the mixture for doping is 600 mg. The optical absorption edge of N-TiO₂ displays a redshift, and a long tail occurs in the presence of nitrogen in the material. Thereby, N-TiO₂ may exhibit improved absorption properties under visible light and solar irradiation. The photocatalytic activity was investigated in the degradation of rhodamine B and reduction of COD in wastewater from a beer factory. The optimal dose of the photocatalyst is 1.8 g/L under visible light.

Keywords: N-doped TiO₂, photocatalysis, ammonium chloride, visible light

1 Introduction

Recently, different types of pollutants from industrial activities, agriculture, sewage, etc., are directly rejected to water bodies, causing water pollution. Therefore, removing pollutants from wastewaters is one of the major issues in the contemporary world [1]. Numerous methods, such as decomposition and electrochemical and advanced oxidation processes (AOPs), are frequently used to remove toxic compounds from wastewater because of their non-toxicity, chemical stability, ease of processing, low cost, and reusability. Photocatalysis is a promising approach due to its unique advantages, such as low operating costs and easy layout. Among photocatalysts, semiconductor metal oxides, such as WO₃, TiO₂, ZnO, and Fe₂O₃, are promising [2]. TiO₂ is the most attractive because of its high activity, low cost, and reusability compared the other photocatalysts mentioned above. However,

TiO₂ is only active under ultraviolet irradiation ($E_g = 3.2$ eV in the anatase phase), hindering it from various applications [3]. To reduce the bandgap of TiO₂ so that it can be used under the visible light irradiation, researchers have shown that the doping of non-metals, such as N, C, S, P, and halogen, leads to an increase in catalytic activity in the visible region [4, 5].

Among them, N-doped TiO₂ is the most studied because nitrogen doping can modify TiO₂ structure, reduces its bandgap, enlarges light absorption in the visible light spectrum, and does not decrease its UV light absorption [6]. Some reports show that N-doped TiO₂ exhibits a higher degradation activity than pure TiO₂ in wastewater treatment under visible light irradiation [7]. Hence, N-doping is proposed to decrease the bandgap and to improve the photocatalytic activity of TiO₂ in the visible region.

In this work, N-TiO₂ powder was prepared with the sol-gel method; then, it was used to study the photodegradation of rhodamine B and reduction of COD in wastewater from a beer factory under visible light and sunlight.

2 Experimental

2.1 Catalyst preparation

Chemicals: Titanium (IV) isopropoxide (98%), nitric acid (HNO₃ 68%), ethyl alcohol (C₂H₅OH 99,7% PA), and ammonium chloride (NH₄Cl) were purchased from the Merck Company. Rhodamine B (C₂₈H₃₁ClN₂O₃) was purchased from Sigma Aldrich.

Catalyst synthesis: First, two solutions, A and B, were prepared separately. Solution A was obtained after thoroughly mixing 6 mL of titanium isopropoxide in 50 mL C₂H₅OH. Solution B contains a mixture of 28 mL of C₂H₅OH, 0.4 mL of HNO₃, 1.6 mL of distilled water, and x mg of NH₄Cl ($x = 450, 600, \text{ and } 800$ mg). Then, solution A was dropped slowly into solution B, and the mixture was vigorously agitated at ambient temperature for two hours to form a uniform and transparent sol. The sol was aged for two days at ambient temperature to form a gel. Afterwards, the gel was dried at 100 °C for 24 hours and then heated at 550 °C for three hours at a rate of 10 °C/min to obtain the N-TiO₂ catalyst.

Synthesis of pristine TiO₂ for comparison: Pristine TiO₂ was prepared in the same way as above without ammonium chloride.

2.2 N-TiO₂ catalytic activity

The optimal amount of the catalyst was determined as follows: 100 mL of RhB (20 mg/L) were initially transferred to a 250-mL beaker. Then, an amount (m) of catalyst was added to the RhB solution ($m = 80, 140, 180, 240, \text{ and } 300$ mg). The obtained solution was stirred with a constant

speed for 30 min in the dark to reach the adsorption equilibrium. Finally, the solution was irradiated with a 36-W compact fluorescent lamp. The exposure time was counted from this moment. The RhB concentration during the decomposition was determined with the photometric method. Besides, the decomposition was also performed in the dark and under midday sunlight. We also investigated the effect of irradiation conditions on the RhB decomposition.

2.3 Characterization techniques

The material characteristics were identified by using X-ray diffraction (XRD – D8-Advance 5005), scanning electron microscopy (SEM – Hitachi S4800), and UV-Vis spectroscopy (Tasco-V670 spectrophotometer). The elemental composition of the catalyst was determined via energy-dispersive X-ray spectroscopy (EDX – JEOL-JSM 6490). The functional groups were identified by using IR spectroscopy (IR – Prestige 21). The RhB concentrations were determined by using UV-Vis (UV-vis Novaspec II, Germany) at 553 nm (the maximum absorption wavelength of RhB).

3 Results and discussion

3.1 Characterization of N-doped TiO₂

The XRD diagram (Fig. 1) shows that N-TiO₂ has only an anatase phase with 2θ of 25.26, 37.78, 38.56, 48.00, 53.90, 53.92, and 62.52°, while TiO₂ has a rutile phase besides the anatase phase. The average particle size calculated according to the Debye-Scherrer equation for TiO₂ and N-TiO₂ is 8 and 5 nm.

The scanning electron microscopic image in Fig. 2 shows uniform homogeneous crystalline nanoparticles.

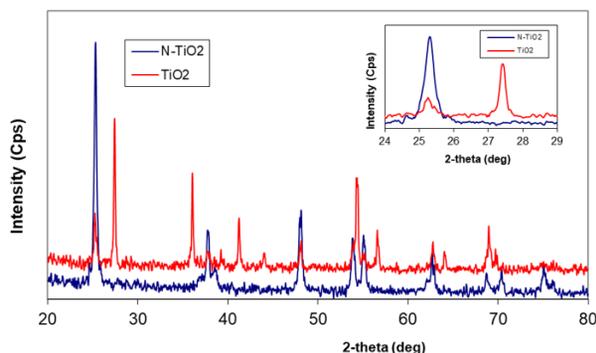


Fig. 1. XRD patterns of TiO₂ and N-TiO₂

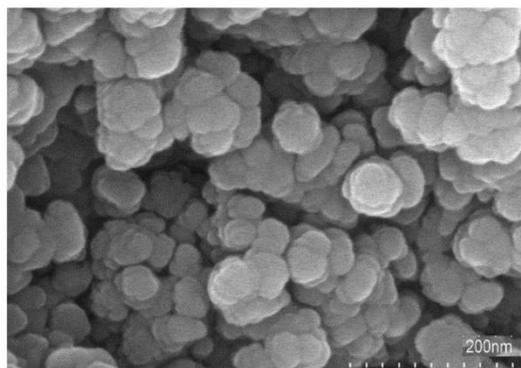


Fig. 2. SEM image of N-TiO₂

The EDX spectrum in Fig. 3 shows the Ti, O, and N elements in the sample, with O and Ti accounting for 35.85 and 60.84%. The Ti/O ratio in N-TiO₂ is lower than that in the pure TiO₂ sample (Ti/O = 6:4) [3]. This decrease might result from the substitution of oxygen in the TiO₂ crystal lattice by nitrogen and is the evidence for the successful N-TiO₂ synthesis with the sol-gel method.

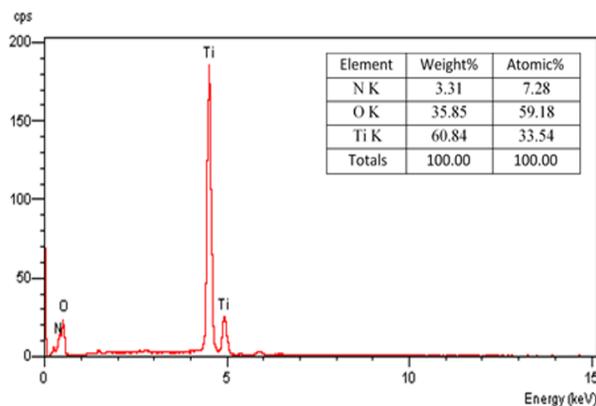


Fig. 3. EDX analysis of N-TiO₂

The IR spectra (Fig. 4) show that the N-TiO₂ sample has more functional groups than the undenatured TiO₂ sample. Specifically, a peak at 484.2 cm⁻¹ represents the oscillation of the Ti–O bond. A characteristic peak at 1647 cm⁻¹ corresponds to the vibration of the H–O–H group of H₂O molecules adsorbed on the material. In addition, a high-intensity peak at 3447 cm⁻¹ could represent the vibration of the –OH group attached to the TiO₂ surface. The presence of –OH groups on the TiO₂ surface might increase the catalytic activity of N-TiO₂ in the decomposition of organic compounds. In addition, a new peak appears at about 1420 cm⁻¹, representing the valence oscillation of the N–H bond. This peak indicates the presence of N in the nitrogen-modified TiO₂ sample [8]. The IR spectrum, together with the EDX spectrum, once again confirms the success of TiO₂ modification by nitrogen, and nitrogen may have participated in the structure of TiO₂, making the structure of the material change, thereby changing its photocatalytic activity.

The UV-Vis spectra (Fig. 5) show that after nitrogen denaturing TiO₂, the absorption region of TiO₂ extends towards the visible-light region. The increase of wavelength from 365 to 425 nm reveals that E_g shifts to lower E'_g energy of 2.9 eV. The bandgap is narrowed after doping, enabling N-TiO₂ to have high activity in the visible region.

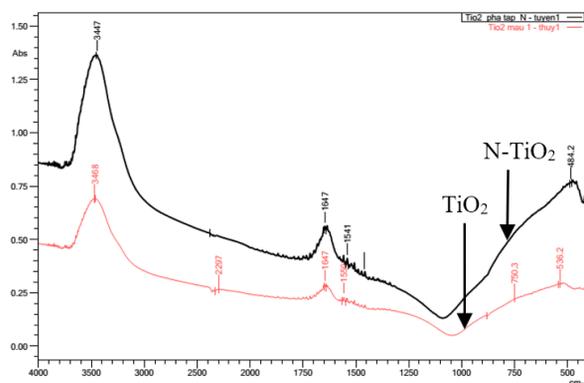


Fig. 4. IR spectra of TiO₂ and N-TiO₂

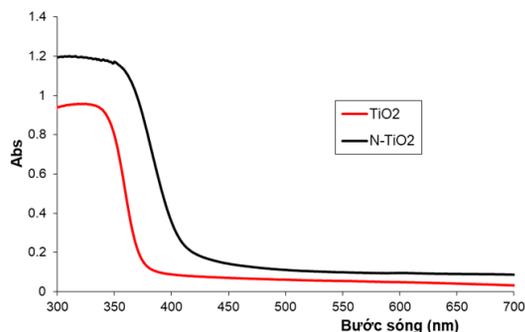


Fig. 5. UV-Vis spectra of TiO₂ and N-TiO₂

The broadening of the absorption spectrum of TiO₂ towards the visible light region upon N doping might result from the replacement of oxygen from the TiO₂ lattice by nitrogen (Fig. 6a). This replacement causes the bandgap to reduce, and the absorption spectrum shifts to the visible region [6].

3.2 Investigation of the photocatalytic activity of TiO₂ and N-TiO₂ in the decomposition of rhodamine B under visible light

Fig. 7 shows that N-TiO₂ has a higher ability to decompose RhB than pristine TiO₂. After 150-minute exposure, N-TiO₂ decomposes RhB up to 96% instead of 69.86% for pristine TiO₂. This increase results from the oxygen atoms replacement by nitrogen atoms (Fig. 6b), causing a decrease in bandgap energy [6, 9].

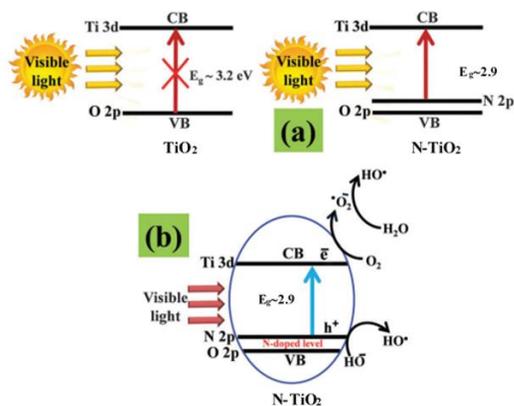


Fig. 6. (a) Energy level diagrams for undoped and N-doped TiO₂ and (b) possible reaction mechanism for the photocatalytic degradation of organic pollutants by N-doped TiO₂ under visible-light irradiation

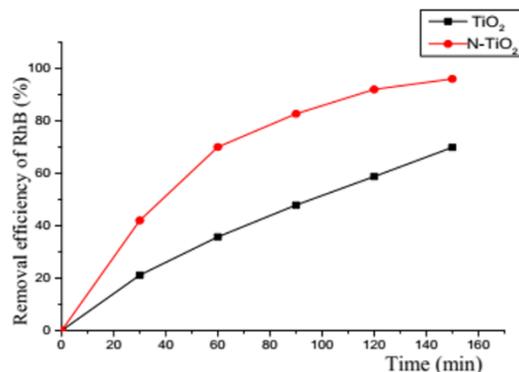


Fig. 7. Comparison of RhB degradation efficiency on TiO₂ and N-TiO₂

3.3 Effect of ammonium chloride content on the photocatalytic activity of N-TiO₂

The XRD spectra (Fig. 8) show that all samples have high crystallinity with the anatase phase. The particle size of the 450-, 600-, and 800-mg-NH₄Cl samples calculated from the Debye-Scherrer equation is 4.7, 3.15, and 4.8 nm, respectively. In general, the particle size of the material is within the nanoscale [10].

The results show that RhB decomposition with N-TiO₂ is optimal when 600 mg of NH₄Cl is added to the synthesising solution. When the amount of NH₄Cl is 800 mg, it causes the photogenerated electrons and the hole to recombine, therefore reducing the photocatalytic efficiency.

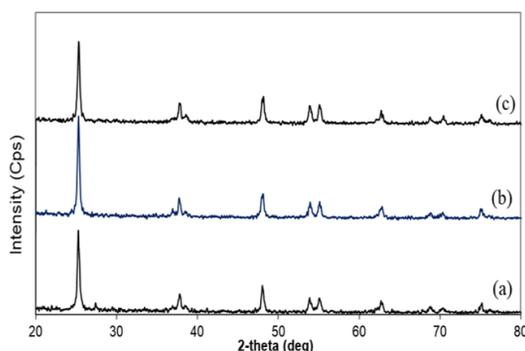


Fig. 8. XRD pattern of N-TiO₂ samples with NH₄Cl amount of 800 mg (a); 450 mg (b); 600 mg (c)

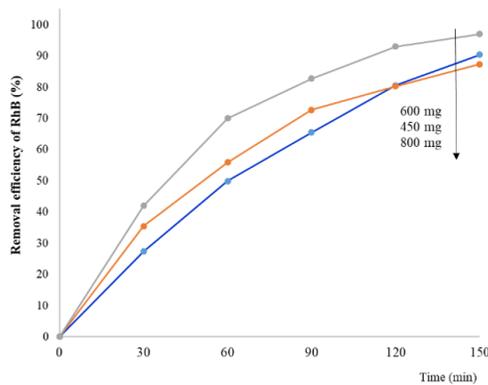


Fig. 9. RhB degradation efficiency of N-TiO₂ samples with different NH₄Cl amounts over time

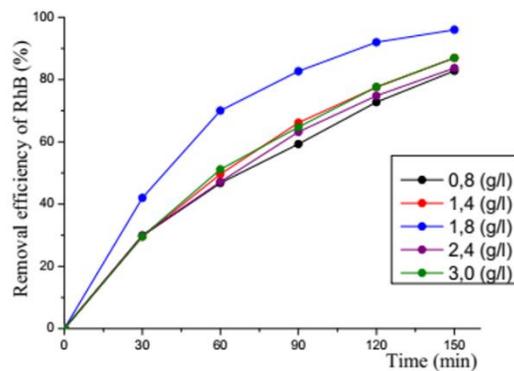


Fig. 10. RhB removal efficiency with different N-TiO₂ concentrations under visible-light irradiation

3.4 N-TiO₂ performance in RhB photo-degradation

Effect of N-TiO₂ concentration on RhB degradation efficiency

The results of rhodamine B degradation (Fig.10) show that the degradation efficiency increases from 82.81% to 97.01% when the mass concentration of the catalyst increases up to 1.8 g/L, while the degradation efficiency of RhB decreases from 96.00% to 86.99% when increasing the concentration of the catalyst from 1.8 g/L to 3.0 g/L. This may be due to the increase in the turbidity of the solution when increasing the content of catalyst, causing photo-resistance and scattering of light, thus reducing the degradation efficiency. The optimal mass concentration of N-TiO₂ catalyst for the degradation of rhodamine B is 1.8 g/L.

Effect of different conditions of irradiation on RhB degradation efficiency

Fig. 11 shows that N-TiO₂ is highly active under visible light. The compact lamp provides a slightly higher photodegradation efficiency (96%) than sunlight irradiation (93.54%). This difference might result from the discrepancy in the stability of the light sources. Therefore, the N-TiO₂ catalyst can be applied to the treatment of organic compounds under sunlight irradiation and visible light.

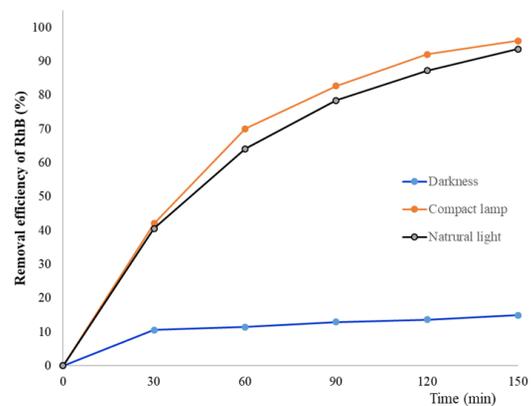


Fig. 11. RhB degradation efficiency of N-TiO₂ under different conditions of irradiation

3.5 Application of N-TiO₂ photocatalyst to treatment of beer-production wastewater

The results show that COD decreases from 612 to 92 mg/L after six hours of treatment with the N-TiO₂ photocatalyst under natural-light irradiation (Table 1). The COD value meets the allowed values applied to industrial processes. This result opens up a great prospect for the practical application of N-TiO₂ catalyst in the treatment of stable organic compounds in the aqueous medium.

Table 1. COD removal with N-TiO₂ catalyst under visible-light irradiation

Time (hour)	0	1	2	3	4	5	6
COD (mg/L)	612	462	332	282	232	212	92

4 Conclusion

N-TiO₂ was successfully synthesized with the sol-gel method. The results show that TiO₂ doped with nitrogen exists in the anatase phase and has an extended absorption margin towards visible light. N-doped TiO₂ presents a higher photocatalytic activity in the visible region in the decomposition of rhodamine B compared with undoped TiO₂. The optimal amount of ammonium chloride in the doping process is 600 mg. Under optimal conditions, almost 100% RhB is degraded after 150 min of exposure. When N-TiO₂ catalyst is applied to actual wastewater, it can remove COD concentration from over 600 mg/L to under 100 mg/L after six hours. This could open up the prospect of catalyst applications in practice.

Acknowledgement

The authors would like to thank ROHAN Catalysis and OEPAC programs at VNU Key Laboratory of Advanced Materials Applied in Green Development, Hanoi, for equipment support.

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