

Preparation of N-TiO₂ nanomaterial and evaluation of its photocatalytic activity under visible light

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ABSTRACT

In this study, nitrogen was used as a dopant to defect into the TiO₂ lattice making contributions to the visible light absorption of nitrogen-doped TiO₂. N-TiO₂ material was prepared from K₂TiF₆ and NH₃ as precursors. The N-TiO₂ photocatalyst was prepared under the condition of 1 M NH₃ solution, 14 % N/TiO₂ mass ratio and the calcination temperature of TiO(OH)₂ was 600 °C for 5 hours. The obtained results indicated that the simultaneous existence of both anatase and rutile

phase of pattern of N-TiO₂ and the average particle size was approximately 30 nm. Modification of titania with nitrogen significantly changed the light absorption ability of the catalyst. The UV-vis spectrum of N-TiO₂ showed the absorption maximum at 400 nm with band gap 2.7 eV. The results of photocatalytic experiment proved that, the N-TiO₂ exhibited the photocatalytic activity for degradation of methylene blue even under visible light better than that of TiO₂.

Key words: Titanium dioxide, nitrogen-doped, photocatalyst, methylene blue, visible light

INTRODUCTION

TiO₂ is a popular photocatalyst for degradation of toxic organics owing to the advantages of earth abundance, low toxicity, and chemical stability. It has been well documented that an electron-hole pair is generated when a TiO₂ photocatalyst is excited by UV irradiation, which requires energy that is equal to or higher than its band gap energy. The electron-hole pairs react with water, hydroxyl groups, and molecular oxygen absorbed on the TiO₂ surface, generating reactive oxygen species such as the hydroxyl radical (•OH) and superoxide anion (•O₂⁻). These radical species participate in oxidation reactions with organic compounds. However, in a practical system using light sources, such as a white light fluorescent lamp and solar light whose UV

radiation intensity for photo-exciting TiO₂ is very weak, the TiO₂ exhibits low photocatalytic disinfection activity. Therefore, a large number of studies have been carried out to improve the photocatalytic activity of TiO₂ and to expand photocatalyst applications in practical systems using visible light as the excitation source [1–5]. Most of the reported studies focused on modification of titanium dioxide, using transition metals (Fe, Ag, Cu,...) and non-metals such as N, S, C,... to improve the activity of the photocatalyst to effectively use even under visible light [6–9]. Compared to the other nonmetal elemental doping, N-doped TiO₂ materials exhibit a significant photocatalytic activity and strong absorption in the various reactions performed under visible light irradiation. Most researches indicated that the

substitutional doped N for O in anatase TiO_2 yielded a narrowing of band gap driven by mixing N 2p states with O 2p states. This process leads to enhance the visible light absorbance [10–12].

Therefore, the aim of the study was using K_2TiF_6 and NH_3 to prepare a nonmetal-doped TiO_2 photocatalyst for the degradation of toxic organic pollutants under visible light irradiation.

MATERIALS AND METHODS

Materials and analysis

All the chemical reagents of analytical grade and deionized water were used throughout. K_2TiF_6 used in the present study was prepared from Binh Dinh ilmenite ore (supplied by Binh Dinh Minerals Joint Stock Company, Vietnam) [13].

The phase composition of catalysts was determined by X-ray diffraction (XRD) method (D8-Advance 5005). Material surfaces were characterized by scanning electronic microscopy (SEM) (JEOL JSM-6500F). Oxidation state of elements was revealed using X-ray photoelectron spectroscopy (XPS) (Kratos Axis ULTRA). The specific surface area was measured by Brunauer–Emmett–Teller (BET) N_2 adsorption methods (Micromeritics Tristar 300). Light absorption capability was evaluated by UV–Vis absorption spectroscopy (3101PC Shimadzu). Chemical compositions of catalysts were revealed by Energy-dispersive X-ray spectroscopy (EDS) (Kratos Axis ULTRA). The concentration of *methylene blue* was determined by spectrometric method at 664 nm (UV 1800, Shimadzu).

Synthesis of N- TiO_2 catalyst

10 g solid K_2TiF_6 (was prepared from Binh Dinh ilmenite ore) [13] and the required amount of deionized water were first charged into a reactor. Then the reactor was heated in the condition of continuous stirring. When the temperature reached up to 80 °C, kept stable. A certain amount of 1 M NH_3 solution was added to the reactor up to pH 9. Then, the mixture of the reactants was stirred at a specific stirring speed under atmospheric pressure. Finally the obtained solution was filtrated to separate titanium as titanic acid $\text{TiO}(\text{OH})_2$. After washing, the $\text{TiO}(\text{OH})_2$ *precipitate* was dried at 80 °C and calcinated at 600 °C for 5 hours.

Methylene blue degradation experimental set-up

600 mL of 10 mg/L methylene blue solution in 1000 mL beaker. For each test, 0.20 g catalyst was added. Before reaction, the solution was stirred in the dark for 2 hours to ensure the establishment of an adsorption equilibrium of methylene blue on the surface of the catalyst. Light sources in this experiment were natural solar light (from 08.00 am to 11 am in summer, the days had an *equivalent light intensity*) and the light of a compact lamp (60 W). After 3 hours, 2 mL samples were taken and centrifuged at 6000 rpm for 20 min. Then, 1.5 mL of the supernatant was put in a cuvette and analysed.

RESULTS AND DISCUSSION

Characterization of TiO_2 and N- TiO_2 materials

The XRD patterns of the synthesized TiO_2 (T600) and N- TiO_2 (TN600) were shown in Fig. 1.

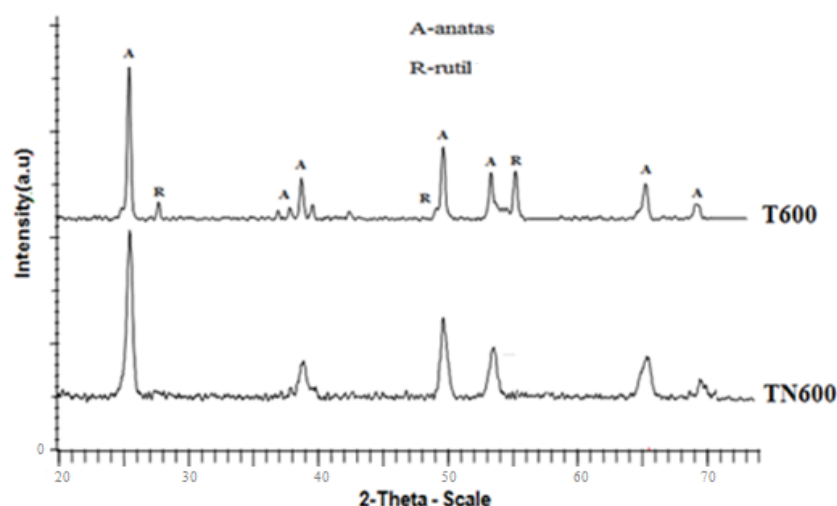


Fig. 1. XRD pattern of TiO_2 and N-TiO_2

The XRD pattern in Fig. 1 showed that the simultaneous existence of both anatase and rutile phase of pattern N-TiO_2 of with peaks at 25.26° , 37.78° , 38.56° , 48.5° , 53.9° and 27.34° , 55.2° corresponding to component of anatase and rutile phase, respectively. While TiO_2 material was synthesized from K_2TiF_6 , it gave anatase form at 600°C . This proved that the modification TiO_2 by nitrogen had effects on the phase transformation of TiO_2 .

The N-TiO_2 material was characterized by SEM to reveal its material surface. From Fig. 2, it could be clearly seen that the sample exhibited a quite unique nanoporous spherical structure and the average size of particles were about 30 nm.

To prove the presence of nitrogen, EDS analysis was employed. The EDS spectra of N-TiO_2 material was shown in Fig. 3.

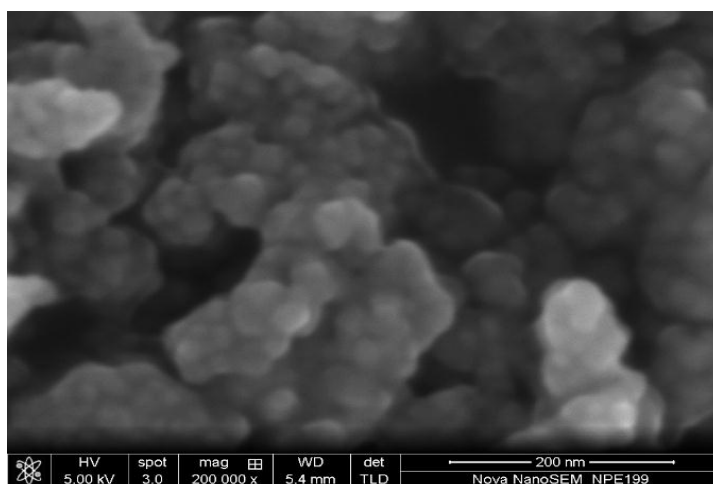


Fig. 2. SEM image of N-TiO_2

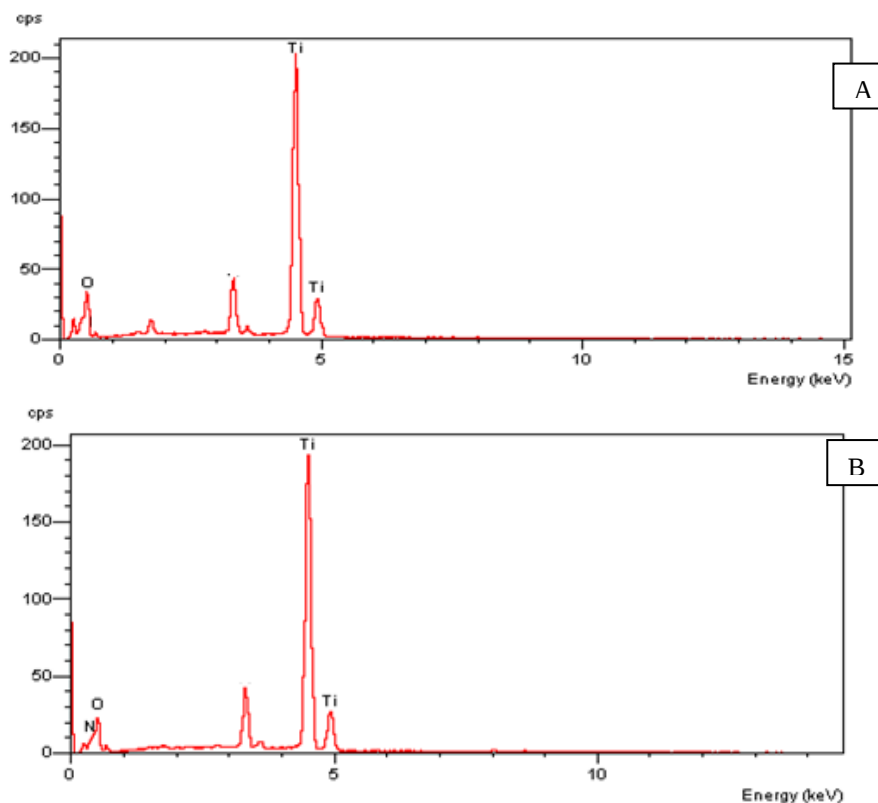


Fig. 3. EDS spectra of TiO₂ (A) and N-TiO₂ (B)

EDS spectra in Fig. 3A showed that TiO₂ sample only contained peaks of Ti and O elements, which could be attributed to the composition of TiO₂. The EDS spectra of N-TiO₂ material was shown in Fig. 3B. It could be seen

that TiO₂ was modified by nitrogen containing peaks of Ti, O and N elements, and there were no peaks of other elements on the EDS spectra. This proved the presence of nitrogen in the N-TiO₂ sample.

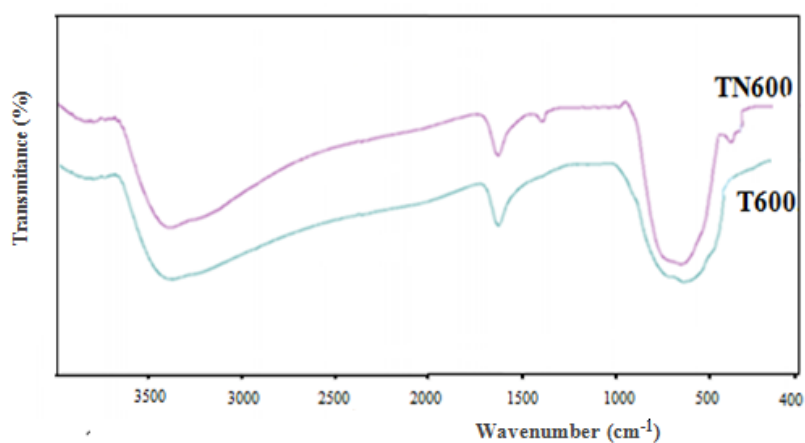


Fig. 4. IR spectra of TiO₂ and N-TiO₂

TiO₂ and N-TiO₂ materials were characterized by IR spectroscopy. The results were shown in Fig. 4. In the IR spectrum of both samples in Fig. 5, two peaks located at 3400 cm⁻¹ and 1620 cm⁻¹ assigned to the stretching vibration of the hydroxyl group on the surface and O–H bending of dissociated or molecularly adsorbed water molecules, respectively [14]. Noticeably, compared with that of pure TiO₂, the intensities of the two absorption bands in the

synthesized N-TiO₂ are stronger. This indicated that the N-TiO₂ sample had more surface-adsorbed water and hydroxyl groups, which played an important role in the photocatalytic reaction. The presence of the band at 1417 cm⁻¹ could be attributed to the nitrogen atoms embedded in the TiO₂ lattice [15, 16]. These results clearly demonstrated that the nitrogen had been incorporated into the TiO₂ lattice.

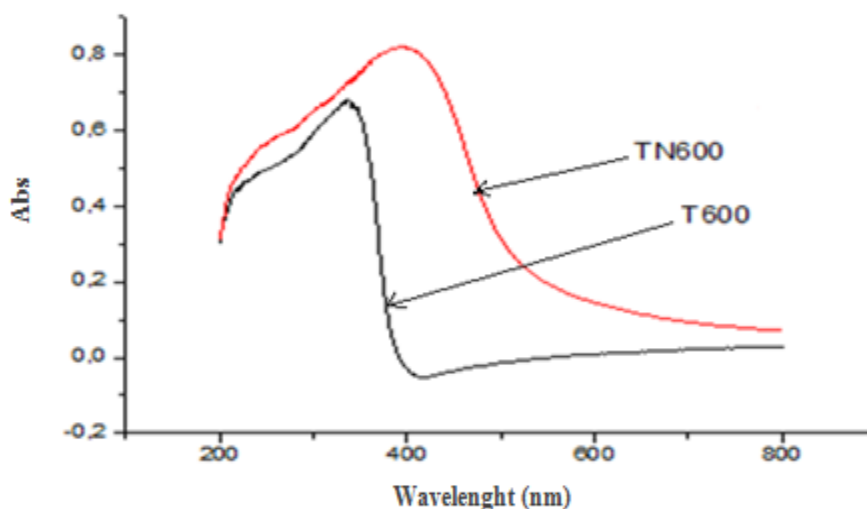


Fig. 5. UV-vis absorption spectra of TiO₂ and N-TiO₂

UV-Vis absorption spectra in Fig. 5 showed that after being modified by nitrogen, TiO₂ could absorb the radiation in visible region. The spectrum of TiO₂ showed a relatively weak absorption at about 400 nm. It totally agrees with the fact that the band gap energy of titania in the anatase form is 3.2 eV, which is equivalent to photon with the wavelength about 382 nm. Modification of titania with nitrogen had significantly changed the light absorption ability of the catalyst. It could be seen that the

absorption of N-TiO₂ was at the larger wavelength and had the absorption maximum at 400 nm with band gap 2.7 eV. Absorption spectrum successfully proved that the modification of titania with nitrogen can shift the working region of the catalyst into the visible one.

In order to examine the chemical states of elements involved in the as-prepared samples, XPS measurements were performed. The XPS spectra of N-TiO₂ material were shown in Fig. 6.

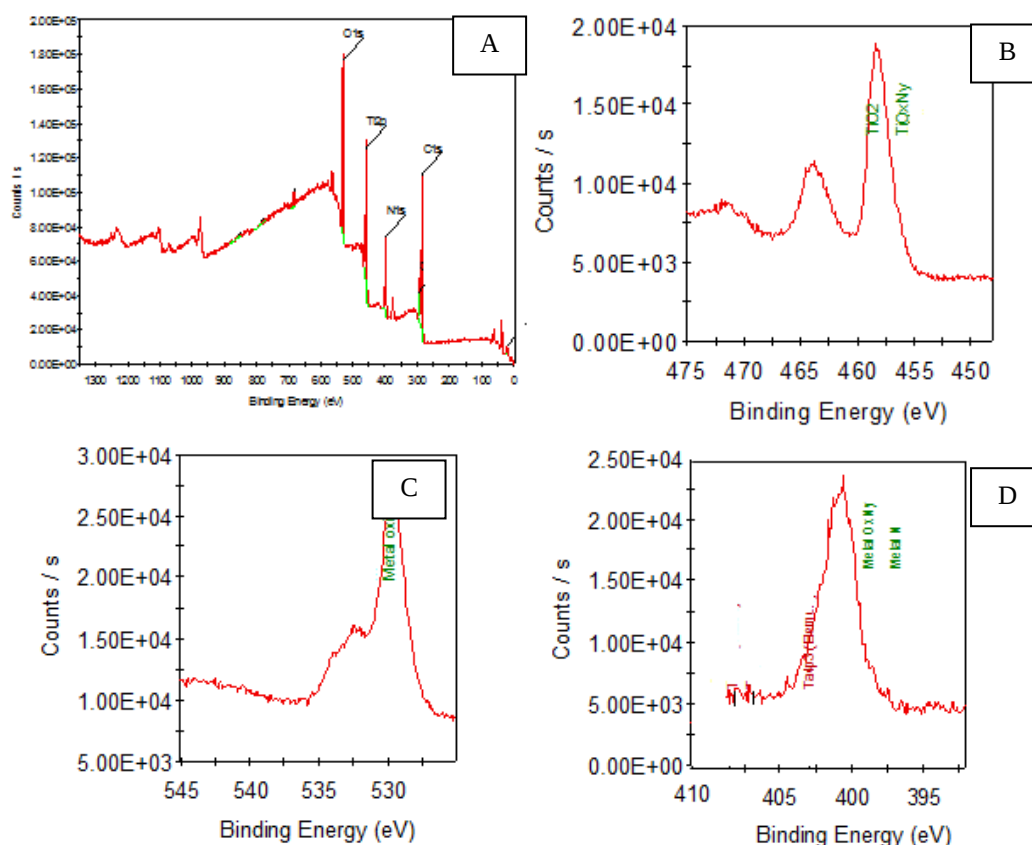


Fig. 6. X-Ray photoelectron spectroscopy spectra of N-TiO₂: (A) the survey spectra of N-doped TiO₂; (B) Ti 2p XPS spectra; (C) O 1s XPS spectra; (D) N 1s XPS spectra

The whole XPS survey spectrum for N-TiO₂ (Fig. 6A) indicated that it contained predominantly Ti, O and N elements. From Fig. 6B, Ti 2p peaks could be observed at the binding energy of 464.1 (Ti 2p_{1/2}) and 458.4 eV (Ti 2p_{3/2}). This showed that there was no Ti³⁺ in the sample, all Ti was in the Ti⁴⁺ form. In the XPS spectrum of O 1s (Fig. 6C), two peaks of the binding energy were at 529.8 and 531.5 eV, which were associated with the O²⁻ in TiO₂ and the -OH group on the surface of samples.

The N 1s XPS spectrum for N-TiO₂ was shown in Fig. 6D. The high binding energy of around 401.6 eV could be attributed to the nitrogen in the form of an Ti-N-O linkage, and the low bonding energy component located at 397.5 was generally known as the N atom

replacing the oxygen atoms in the TiO₂ crystal lattice to form an N-Ti-N bond. Results obtained from this method agreed with reports of other authors [17, 18].

To determine the surface area of N-TiO₂ material and pore size, the catalyst was characterized by BET. Results were shown in Fig. 7. From Fig. 7A, the sharp decline in the desorption curve and the hysteresis loop at high relative pressure meant that N-TiO₂ belonged to the mesoporous type. Both materials have type IV curve as classified by IUPAC. N-TiO₂ material had the surface area of 24.16 m²/g. From Fig. 7B, the pore size distribution of N-TiO₂ were narrow peaks and most pores had size of about 29 nm.

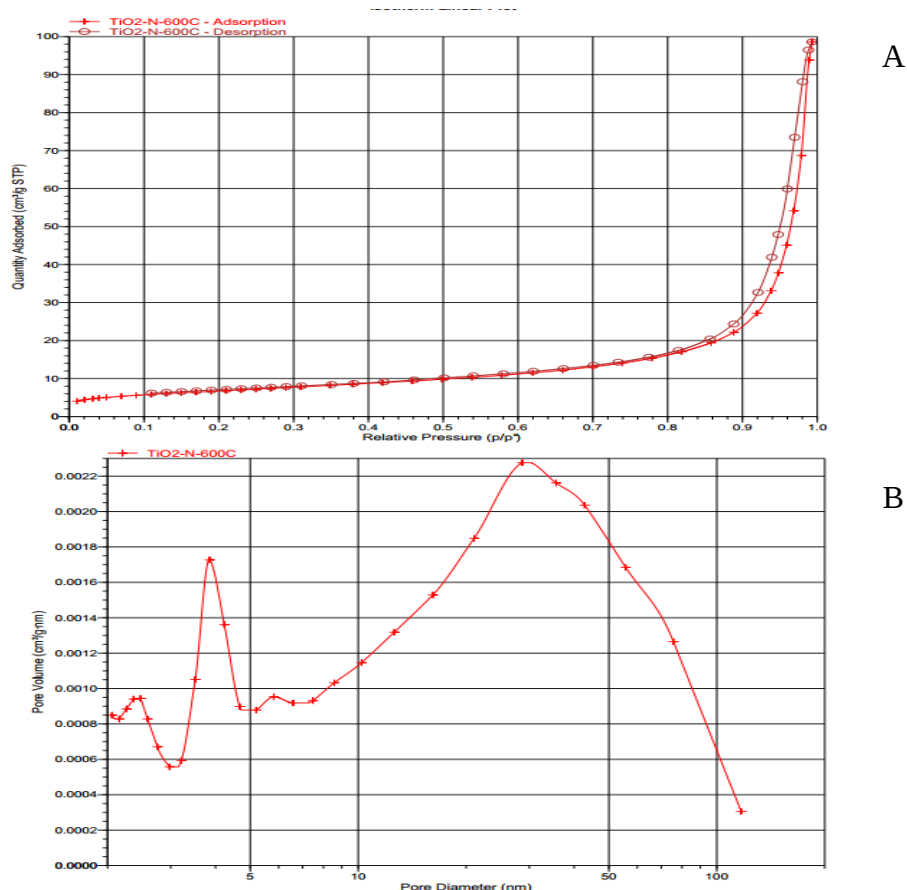


Fig. 7. Adsorption - deabsorption isotherms diagram (A) and pore size distribution (B) of N - TiO₂

Tests on photocatalytic activity of TiO₂ and N- TiO₂

The experiments of methylene blue degradation were carried out simultaneously on TiO₂ and N-TiO₂, one with solar light (from 8–11 am per day) and compact lamp light and one in the dark. All other conditions (600 mL of 10 mg/L methylene blue solution, 0.20 g TiO₂ and N-TiO₂ catalysts and 3 hours for the reaction) were kept the same. Results were shown in Table 1.

Table 1. The degradation of methylene blue using TiO₂ and N-TiO₂ under different light sources

Catalysts	Conversion (%)		
	Compact lamp	Solar	Dark
TiO ₂	19.67	30.55	9.76
N-TiO ₂	65.27	87.74	11.95

Results in Table 1 showed that the methylene blue conversion decreased insignificantly for experiments in the dark (9.76 % for TiO₂ and 11.95 % for N-TiO₂). However, when light is on, efficiency of N-TiO₂ in the degradation of methylene blue was higher than that of TiO₂. That means TiO₂ modified by nitrogen can improve the catalytic activity of TiO₂ under solar radiation. Data in Table 1 show that after 180 min, methylene blue removal efficiency on N-TiO₂ reached 87.74 % when using solar as light source, while it was only 65.27 % if experiments were carried out with the compact lamp light. This observation was understandable because photon in solar light is stronger than that in compact lamp light.

CONCLUSION

Modification of titania with nitrogen had significantly changed the light absorption ability of TiO_2 leading to effective use of the synthesized materials even under visible light region. The obtained results indicated that the nitrogen had been incorporated into the TiO_2 lattice resulting the decrease of the band gap energy of titania in the anatase form from 3.2 eV

to 2.7 eV, more surface-adsorbed water. Most pores had the size of about 29 nm and the average particle size was approximately 30 nm. The experimental results indicated that the photocatalytic degradation of blue methylene by the N- TiO_2 material was higher than that by the TiO_2 material under visible light. This will open a new era to apply the semiconductor for the treatment of organic pollutants.

Điều chế vật liệu nano N- TiO_2 và đánh giá hoạt tính quang xúc tác trong vùng ánh sáng thấy được

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TÓM TẮT

Trong nghiên cứu này, titanium dioxide biến tính bởi nitrogen được điều chế từ tiền chất ban đầu potassium hexafluorotitanate (IV) và dung dịch ammoniac vừa là dung dịch thủy phân tạo kết tủa hydroxide titan vừa là nguồn cung cấp nitrogen cho quá trình biến tính. Việc pha tạp nitrogen vào mạng TiO_2 sẽ làm cho vật liệu có khả năng hoạt động trong vùng ánh sáng thấy được. N- TiO_2 được điều chế trong điều kiện: thủy phân K_2TiF_6 bằng dung dịch NH_3 1 M đến pH 9, tỉ lệ % khối lượng N/ TiO_2 là 14% và xử lý mẫu ở nhiệt độ 600 °C trong 5 giờ. Vật liệu N- TiO_2 thu

được tồn tại cả dạng anatase và rutil, có kích thước hạt trung bình khoảng 30 nm. Sự biến tính TiO_2 bởi nitrogen đã cải thiện đáng kể khả năng hấp thụ bức xạ khả kiến của vật liệu. Phổ UV-Vis của N- TiO_2 cho thấy cực đại hấp thụ ở bước sóng 400 nm và mở rộng về vùng ánh sáng khả kiến, ứng với mức năng lượng vùng cấm tương ứng là 2,7 eV. Kết quả thí nghiệm chỉ ra rằng, vật liệu N- TiO_2 có hoạt tính quang xúc tác phân hủy xanh methylene dưới ánh sáng thấy được cao hơn nhiều so với TiO_2 .

Từ khóa: titanium dioxide, pha tạp nitrogen, quang xúc tác, xanh methylene, ánh sáng thấy được

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