Preparation of N-TiO$_2$ 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 TiO$_2$ lattice making contributions to the visible light absorption of nitrogen-doped TiO$_2$. N-TiO$_2$ material was prepared from K$_2$TiF$_6$ and NH$_3$ as precursors. The N-TiO$_2$ photocatalyst was prepared under the condition of 1 M NH$_3$ solution, 14 % N/TiO$_2$ 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-TiO$_2$ 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-TiO$_2$ showed the absorption maximum at 400 nm with band gap 2.7 eV. The results of photocatalytic experiment proved that, the N-TiO$_2$ exhibited the photocatalytic activity for degradation of methylene blue even under visible light better than that of TiO$_2$.

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

INTRODUCTION

TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ surface, generating reactive oxygen species such as the hydroxyl radical (·OH) and superoxide anion (·O$_2^-$). 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 TiO$_2$ is very weak, the TiO$_2$ exhibits low photocatalytic disinfection activity. Therefore, a large number of studies have been carried out to improve the photocatalytic activity of TiO$_2$ 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 TiO$_2$ 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 TiO₂ 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 K₂TiF₆ and NH₃ to prepare a nonmetal-doped TiO₂ 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. K₂TiF₆ 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) N₂ 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-TiO₂ catalyst**

10 g solid K₂TiF₆ (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 NH₃ 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 TiO(OH)₂. After washing, the TiO(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 TiO₂ and N-TiO₂ materials**

The XRD patterns of the synthesized TiO₂ (T600) and N-TiO₂ (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$^\circ$, 37.78$^\circ$, 38.56$^\circ$, 48.5$^\circ$, 53.9$^\circ$ and 27.34$^\circ$, 55.2$^\circ$ corresponding to component of anatase and rutile phase, respectively. While TiO$_2$ material was synthesized from K$_2$TiF$_6$, it gave anatase form at 600 $^\circ$C. This proved that the modification TiO$_2$ by nitrogen had effects on the phase transformation of TiO$_2$.

Fig. 2. SEM image of N-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.
EDS spectra in Fig. 3A showed that TiO$_2$ sample only contained peaks of Ti and O elements, which could be attributed to the composition of TiO$_2$. The EDS spectra of N-TiO$_2$ material was shown in Fig. 3B. It could be seen that TiO$_2$ 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-TiO$_2$ sample.

Fig. 3. EDS spectra of TiO$_2$ (A) and N-TiO$_2$ (B)

Fig. 4. IR spectra of TiO$_2$ and N-TiO$_2$
TiO$_2$ and N-TiO$_2$ 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 TiO$_2$, the intensities of the two absorption bands in the synthesized N-TiO$_2$ are stronger. This indicated that the N-TiO$_2$ 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 TiO$_2$ lattice [15, 16]. These results clearly demonstrated that the nitrogen had been incorporated into the TiO$_2$ lattice.

![UV–Vis absorption spectra of TiO$_2$ and N-TiO$_2$](image)

**Fig. 5.** UV–vis absorption spectra of TiO$_2$ and N-TiO$_2$

UV–Vis absorption spectra in Fig. 5 showed that after being modified by nitrogen, TiO$_2$ could absorb the radiation in visible region. The spectrum of TiO$_2$ 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-TiO$_2$ 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-TiO$_2$ material were shown in Fig. 6.
Fig. 6. X-Ray photoelectron spectroscopy spectra of N-TiO$_2$: (A) the survey spectra of N-doped TiO$_2$; (B) Ti 2p XPS spectra; (C) O 1s XPS spectra; (D) N 1s XPS spectra.

The whole XPS survey spectrum for N-TiO$_2$ (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 Ti$^{3+}$ in the sample, all Ti was in the Ti$^{4+}$ 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 O$^{2-}$ in TiO$_2$ and the -OH group on the surface of samples.

The N 1s XPS spectrum for N-TiO$_2$ 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 TiO$_2$ 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-TiO$_2$ 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-TiO$_2$ belonged to the mesoporous type. Both materials have type IV curve as classified by IUPAC. N-TiO$_2$ material had the surface area of 24.16 m$^2$/g. From Fig. 7B, the pore size distribution of N-TiO$_2$ were narrow peaks and most pores had size of about 29 nm.
Tests on photocatalytic activity of TiO$_2$ and N-TiO$_2$

The experiments of methylene blue degradation were carried out simultaneously on TiO$_2$ and N-TiO$_2$, 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 TiO$_2$ and N-TiO$_2$ 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 TiO$_2$ and N-TiO$_2$ under different light sources

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion (%)</th>
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<tr>
<td></td>
<td>Compact lamp</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>19.67</td>
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<tr>
<td>N-TiO$_2$</td>
<td>65.27</td>
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</table>

Results in Table 1 showed that the methylene blue conversion decreased insignificantly for experiments in the dark (9.76 % for TiO$_2$ and 11.95 % for N-TiO$_2$). However, when light is on, efficiency of N-TiO$_2$ in the degradation of methylene blue was higher than that of TiO$_2$. That means TiO$_2$ modified by nitrogen can improve the catalytic activity of TiO$_2$ under solar radiation. Data in Table 1 show that after 180 min, methylene blue removal efficiency on N-TiO$_2$ 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$_2$TiF$_6$ 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 oC trong 5 giờ. Vật liệu N-TiO$_2$ thu được tồn tại cả dạng anatas 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 cản 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 khoá: titanium dioxide, pha tạp nitrogen, quang xúc tác, xanh methylene, ánh sáng thấy được

REFERENCES


