Short communication

# A novel N-doped TiO$_2$ with high visible light photocatalytic activity

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## Abstract

A novel N-doped TiO$_2$ with high visible light photocatalytic activity was obtained by treating nanotube titanic acid (NTA) in NH$_3$ flow and investigated by means of XRD, TEM, ESR and XPS. The ESR results revealed that the visible light photocatalytic activity is originated from N-doping into TiO$_2$ with the forming of triplet paramagnetic species, the higher triplet paramagnetic species concentration, the better visible light photocatalytic behavior.
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*Keywords:* N-doped TiO$_2$; Photocatalytic activity; Nanotube titanic acid

Although titanium dioxide is the most promising photocatalyst for its low cost, non-toxicity, high stability and high efficiency for degradation of difficult-to-remove pollutants, it can be activated only by irradiating with ultraviolet (UV) light due to the wide band gap energies, 3.0 ev for rutile and 3.2 eV for anatase. Therefore, only a small fraction ($\sim$5%) of the solar energy can be utilized in practical application. To use solar irradiation, many researchers recently have attempted to extend the absorption range of TiO$_2$ from the ultraviolet (UV) to the visible light region by doping nitrogen into TiO$_2$. In 1986, Sato first reported the N-doped TiO$_2$ photocatalyst with visible light photocatalytic activity prepared by annealing of NH$_4$Cl or NH$_4$OH involving titanium hydroxide [1]. Asahi et al. obtained a visible light active TiO$_{2-x}$N$_x$ films by sputtering the TiO$_2$ target in a N$_2$ (40%)/Ar gas mixture in 2001, which rekindled a great attention in TiO$_2$ as a visible light photocatalyst [2]. Afterwards, many preparation methods have been reported to dope nitrogen into TiO$_2$ using different N-doped precursors. Ihara et al. prepared a visible light active photocatalyst by using the hydrolysis product of Ti(SO$_4$)$_2$ with ammonia solution as N-doped precursor, and evaluated the photoactivity by oxidation of acetone to CO$_2$ in gas phase [3]. Also, Wang et al. took the hydrolysis product of tetra-butyl titanate (Ti(OBu)$_4$) with ammonia solution as N-doped precursor and found the visible light photoactivity in

phenol decomposition system [4]. On the other hand, Irie et al. reported a TiO$_{2-x}$N$_x$ powder prepared by annealing anatase TiO$_2$ under an ammonia flow and its photoactivity was evaluated by decomposition of gaseous isopropyl alcohol [5]. Meanwhile, Burda et al. have developed an alternative nanoscale synthesis route that leads to increased nitrogen dopant concentration (up to 8%) in titania [6]. However, the reason for the visible light response is still under discussion.

In this paper, a novel method was reported for nitrogen doping into TiO$_2$ by treating nanotube titanic acid (NTA, H$_2$Ti$_2$O$_5$·H$_2$O) in NH$_3$ flow. The preparing procedure is as follows: (i) NTA was synthesized from nanotube sodium titanate (Na$_2$Ti$_2$O$_5$·H$_2$O) by an ion exchange reaction with 0.1 mol/L HCl solution [7–9]; (ii) NTA was treated in NH$_3$ flow at $T$ = 400–700 °C ($T$ = NH$_3$ treating temperature) for 4 h, while orthorhombic NTA was converted into anatase TiO$_2$ (see Fig. 1) and simultaneously doped with nitrogen (called N–TiO$_2$-I). At $T$ = 700 °C, TiN phase simultaneously generated within anatase TiO$_2$ (Fig. 1, $2\theta$ = 43.27°, 37.29° pointed by arrow). We can obviously see from Fig. 2 that the NTA morphology were broken to form nanoparticles when treated at $T \geq$ 400 °C, while accompanying with the change of crystal form (from orthorhombic to anatase). For comparison, P-25 TiO$_2$ was also treated in NH$_3$ flow at $T$ = 400–700 °C to obtain the other N-doped samples (called N–TiO$_2$-II).

N–TiO$_2$-I samples have higher visible light photocatalytic activity of propylene oxidation than that of corresponding N–TiO$_2$-II samples. Fig. 3 shows the change of visible light photocatalytic activity with $T$. With the increase of NH$_3$

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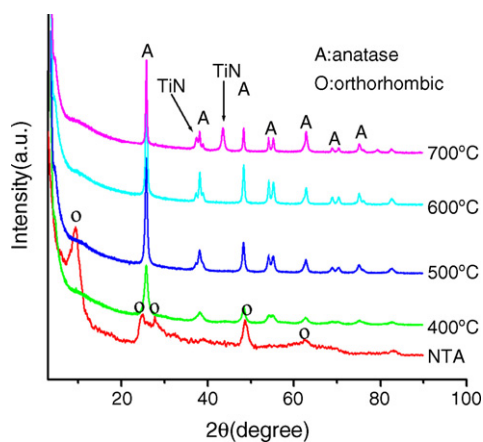*E-mail address:* zhenshengjin@henu.edu.cn (Z. Jin).

Fig. 1. XRD patterns of NTA and N–TiO$_2$-I nanoparticles.



Fig. 3. Dependence of visible light photocatalytic activity on NH$_3$ treating temperature ($T$). (Inset) Change of CO$_2$ concentration with $T$. Feed gas = 580 ppm V C$_3$H$_6$ in dried air; flow rate = 100 ml/h; weight of photocatalyst = 32 mg, spread on a 1 cm × 9 cm glass plate which put into a quartz reactor. Light source = a beam of 250 W Xe lamp passed through a water filter and a cut-off filter ($\lambda \geq 420$ nm). Light intensity of $\lambda \geq 420$ nm = 0.4 mW/cm$^2$. C$_3$H$_6$ and CO$_2$ were analyzed by a Shimadzu GAS CHROMATOGRAPH GC-9A equipped with a GDX-502 column, a Ni catalyst reactor for hydrogenation of CO$_2$ and a FID detector.

treating temperature, both have a max propylene removal at $T = 600$ °C, 24.9% and 7.3% for N–TiO$_2$-I(600) and N–TiO$_2$-II(600), respectively. The max photocatalytic activity of former is ca. 3.4 times larger than that of latter. At $T = 700$ °C, the activities of both N–TiO$_2$-I(700) and N–TiO$_2$-II(700) decrease to ca. zero. The inset in Fig. 3 indicates that the dependence of CO$_2$ production on $T$. If C$_3$H$_6$ was completely oxidized, 1 mol C$_3$H$_6$ should produce 3 mol CO$_2$. However, the selectivity of CO$_2$ formation calculated was only to be ca. 80% and 60% for N–TiO$_2$-I and N–TiO$_2$-II samples, respectively, which hints that the photocatalytic oxidation of C$_3$H$_6$ was incomplete.

The ESR spectra of N–TiO$_2$-I samples are shown in Fig. 4. As Fig. 4 displays, the three-g signal ($g = 2.024$, 2.007, 1.987; $H = 64$ G) represents some or other paramagnetic species, which may be NO [10–12] or other types of defects (color centers, oxygen vacancies) formed during nitrogen doping. XPS analyses show $E_b$(N1s) = 400.2 eV [13,14], surface N atomic percent = 0.4–1.4% for N–TiO$_2$-I (400–600). N–doping in TiO$_2$ matrix induces the visible light absorption at $\lambda > 400$ nm [2,15]. Fig. 4 inset indicates that the visible light photocatalytic activity of N–TiO$_2$-I samples is proportional to ESR peak height ($h$) (i.e. proportional to the concentration of paramagnetic species), which evidence that the visible light photocatalytic activity is closely correlated with such paramagnetic species. N–TiO$_2$-
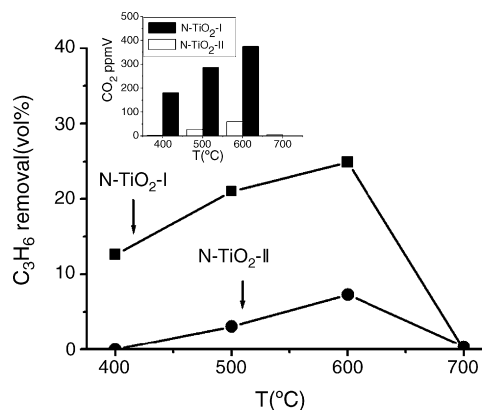
I(700) has a small ESR signal of triplet paramagnetic species (Fig. 4) and an inert TiN phase existed within N–TiO$_2$-I(700) (see Fig. 1), $E_b$(N1s) determined = 396.4 eV [13,16], surface N atomic percent determined = 10.4%. Both interpret the low visible light photocatalytic activity of N–TiO$_2$-I(700) (Fig. 3). Fig. 5 shows the ESR spectra of N–TiO$_2$-I(600) and N–TiO$_2$-II(600) ($h_1/h_2 = 3.3$, corresponding to their activity ratio). It is evident that due to a lower concentration of triplet paramagnetic species involves in N–TiO$_2$-II(600), both its visible light absorption and visible light photocatalytic activity are lower than that of N–TiO$_2$-I(600) (Fig. 5 inset and Fig. 3).

In our previous work [9,17], we have found that during the dehydration of NTA with the conversion into anatase TiO$_2$ at $T = 400$–600 °C in air, a lot of single-electron-trapped oxygen vacancies ($V_O^\bullet$) formed. We suggest that when NTA is treated at $T = 400$–600 °C in NH$_3$, the dehydration and N-doping reactions will take place in sequence:

$$H_2Ti_2O_5 \cdot H_2O \rightarrow 2H_2O + 2TiO_2(V_O^\bullet) \tag{1}$$
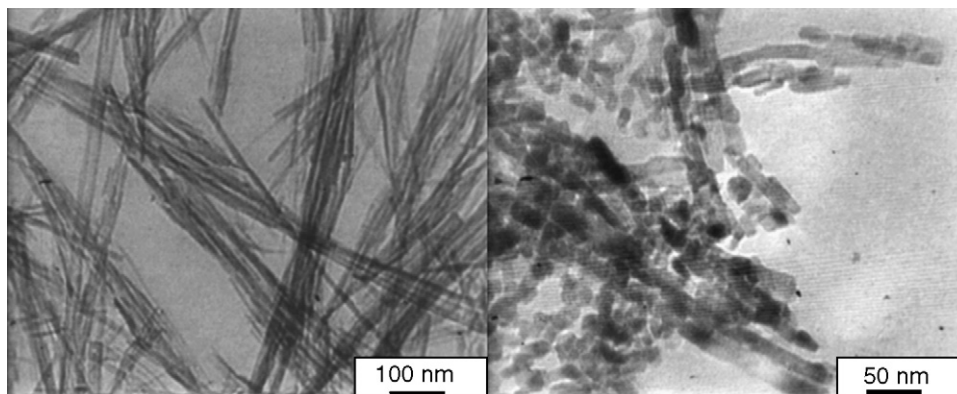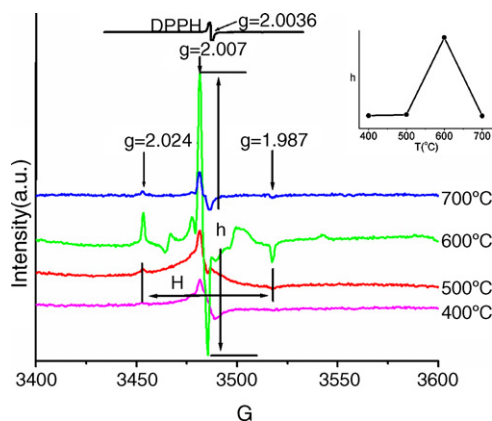


Fig. 2. TEM images of NTA and N–TiO$_2$-I(400).

Fig. 4. ESR spectra of N–TiO$_2$-I(400–700), $h$ = ESR peak height ($g$ = 2.007), $H$ = width between two ESR peaks ($g$ = 2.024–1.987). ESR were obtained on a Brüker ESP 300E spectrometer which was operated in the X band (ca. 9.80 kHz) with 100 kHz field modulation and 10 mW microwave power. Values $g$ were measured by taking diphenyl picryl hydrazyl (DPPH, $g$ = 2.0036) as a reference at room temperature (ca. 20 °C).
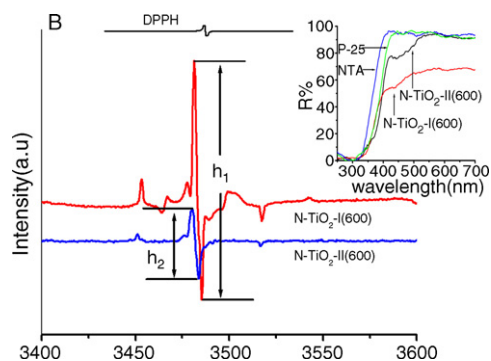


Fig. 5. ESR spectra of N–TiO$_2$-I(600) and N–TiO$_2$-II(600).

$$TiO_2(V_O{}^\bullet) \xrightarrow{NH_3} N–TiO_2 \qquad (2)$$

Due to TiO$_2$($V_O{}^\bullet$) is more active than P-25 TiO$_2$, the paramagnetic species formation should be easier in former than in latter. The results shown in Fig. 5 proved that this inference is correct. At $T$ = 700 °C, TiN phase becomes the main N-containing product:

$$TiO_2(V_O{}^\bullet) \xrightarrow{NH_3} TiN \qquad (3)$$

In summary, using NTA as the precursor, we obtained a novel N-doped TiO$_2$ with higher visible light photocatalytic activity than that obtained from P-25 TiO$_2$. The ESR results proved that the formation of triplet paramagnetic species in TiO$_2$ matrix formed during nitrogen doping is responsible for the visible light photoactivity. By comparison, this study could give us a novel idea to prepare efficient visible light-responsible photocatalyst by using NTA as precursor.

## Acknowledgments

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