

## Research Article

# Nitrogen-Doped TiO<sub>2</sub> Photocatalyst Prepared by Mechanochemical Method: Doping Mechanisms and Visible Photoactivity of Pollutant Degradation

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Nitrogen-doped TiO<sub>2</sub> (N/TiO<sub>2</sub>) photocatalysts were prepared using a mechanochemical method with raw amorphous TiO<sub>2</sub> as precursors and various nitrogenous compounds doses (NH<sub>4</sub>F, NH<sub>4</sub>HCO<sub>3</sub>, NH<sub>3</sub>·H<sub>2</sub>O, NH<sub>4</sub>COOCH<sub>3</sub>, and CH<sub>4</sub>N<sub>2</sub>O). The photocatalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric-differential thermal analysis (TG-DTA), and UV-Vis diffuse reflection spectra (UV-Vis-DRS). Their photocatalytic activities were evaluated with the degradation of p-nitrophenol and methyl orange under UV or sunlight irradiation. The catalysts had a strong visible light absorption which correspond to doped nitrogen and consequent oxygen deficient. The results of photocatalytic activity showed the visible light adsorption mechanisms, as the doped nitrogen species gave rise to a mid-gap level slightly above the top of the (O-2p) valence band, but not from the mixed band gap of the N-2p and O-2p electronic levels.

## 1. Introduction

Photocatalysis by titania (TiO<sub>2</sub>) has been demonstrated to be an effective method for removal of pollutants in water or air during the last three decades. Because of its band-gap energy, however, pure TiO<sub>2</sub> can only be activate by short-wavelength UV light below 387 nm, usually only about 4% of the incoming solar energy on the earth's surface utilized [1]. Considerable efforts have been made to extend the photoresponse of TiO<sub>2</sub> further into the visible light region by modifying or using doping technologies in recent years [2–5].

Doping TiO<sub>2</sub> with nonmetal atoms such as nitrogen or carbon has received increasing attention in recent years [6–13]. It was predicted by theory and demonstrated in experiments that nitrogen-doped TiO<sub>2</sub> exhibits improved catalytic activity under visible light irradiation [6, 7]. Asahi et al. [6] reported a nitrogen-doped TiO<sub>2</sub> by sputtering the TiO<sub>2</sub> target in a N<sub>2</sub>/Ar gas mixture, resulting in a significant shift of the absorption edge and exhibited excel visible light

activity. Burda et al. [8] reported a nitrogen-doped TiO<sub>2</sub> with nitrogen concentrations up to 8% by direct amination of 6–10 nm TiO<sub>2</sub> particle using triethylamine, and the doped TiO<sub>2</sub> was catalytically active and was able to absorb well into the visible region up to 600 nm. Usually, the dope of the nitrogen leads to the narrowing of the band gap and improves the photocatalytic activity in the visible light region [14]. The nitrogen doping can be attained by various other methods, such as the heating of TiO<sub>2</sub> powder in an ammonia atmosphere [6, 15, 16], the hydrolysis of titanium compounds with ammonia solution followed by calcination of the resultant precipitates [17], the heating of TiO<sub>2</sub> powder with urea [18], reactive sputtering [19], and the pulsed laser deposition using a TiN target in a nitrogen/oxygen gas mixture [20]. Development of modified N doped TiO<sub>2</sub> photocatalyst with metals, nonmetals, and metal oxides have been reviewed by Zhang et al. [21].

Mechanochemical method is a simple method which can easily realize preparation of nitrogen doping on titania on a large scale. Although the nitrogen-doped TiO<sub>2</sub> prepared

by mechanochemical method had been reported before [22, 23], but little is known about the structural information and activities of the catalyst, especially the doping mechanisms. Yin et al. [22] reported that the nitrogen-doped TiO<sub>2</sub> by a mechanochemical method possessed two absorption edges of 405 and 550 nm. Chen et al. [23] reported a similar nitrogen-doped TiO<sub>2</sub> using the mechanochemical method in the NH<sub>3</sub>·H<sub>2</sub>O solution, but their samples showed a red shift by 20 nm and on one edge only. There should be further research on the structure and visible-light exciting process of the nitrogen-doped TiO<sub>2</sub> prepared by mechanochemical method.

In the present work, nitrogen-doped TiO<sub>2</sub> was prepared by ball milling of amorphous TiO<sub>2</sub> with various nitrogenous substances (e.g., ammoniac salt or ammonium solution) under various prepared conditions. The catalyst was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric-differential thermal analysis (TG-DTA), and UV-Vis diffuse reflection spectroscopy (UV-Vis-DRS). Nitrogen doping mechanism on the amorphous TiO<sub>2</sub> and principle of the electron excitation by visible light irradiation were demonstrated. In addition, its photocatalytic activities were tested using model pollutants under UV or visible light irradiation.

## 2. Experimental

**2.1. Materials and Methods.** TiO<sub>2</sub> (CP) was purchased from Shanghai Qianjin Chemical Reagent Company, China. Ammonia solution, NH<sub>4</sub>F, NH<sub>4</sub>HCO<sub>3</sub>, NH<sub>3</sub>·H<sub>2</sub>O, NH<sub>4</sub>COOCH<sub>3</sub>, and CH<sub>4</sub>N<sub>2</sub>O were from Shanghai Suyi Chemical Reagent Company, China. Methyl orange, p-nitrophenol, and phenol were purchased from Shantou Xilong Chemical Factory and Nanjing Chemical Reagent Factory, respectively. They were used without further purification. All the chemical reagents were of analytical grade except TiO<sub>2</sub>.

**2.2. Catalyst Preparation.** The preparation of N/TiO<sub>2</sub> photocatalyst was carried out in a ball mill (QM-1SP2, Nanjing University Instrumental Company). The chemical reagent titanium dioxide was used as a raw material. Raw titanium dioxide (about 16.0 g) and NH<sub>4</sub>F (0.0200 mol, 0.740 g) were mixed in the ball mill tank (100 mL) with 10 mL of deionized water. Twelve agate balls of 10.0 mm diameter and forty agate balls of 5.0 mm diameter were introduced. After grinding for 180 min at a speed of 580 rpm, the wet powder was dried at a temperature of 105°C in air for 5 h. The powder was then calcined at 400°C (or 500, 600, and 700°C) for 2 h at 3°C/min heating rate. During the calcination, the color of the powder changed from white to gray or slightly yellow depending on the ammonia salt and its concentration. In order to evaluate the effect of concentration of ammonia salt on grinding, a series of different NH<sub>4</sub>F concentrations (0.37 g, 1.48 g, and 3.70 g) were used. The catalysts prepared using NH<sub>4</sub>F as the nitrogen source was denoted as the NF series.

For comparison, the NH<sub>4</sub>HCO<sub>3</sub> (0.0200 mol, 1.58 g), NH<sub>3</sub>·H<sub>2</sub>O (m/V28%, 10.0 mL), NH<sub>4</sub>COOCH<sub>3</sub> (0.0200 mol, 1.54 g), and urea (CH<sub>4</sub>N<sub>2</sub>O, 0.0200 mol, 1.20 g) were also

used as nitrogen sources. They were denoted as the NC, NH, AA, and UR series, respectively. As a comparison, a raw TiO<sub>2</sub> ground with 10.0 mL of deionized water, but no nitrogen source was also prepared. This was denoted as WG. A raw TiO<sub>2</sub> was not ground and was denoted as TO.

**2.3. Characterization of N/TiO<sub>2</sub>.** X-ray diffraction (XRD) patterns were obtained using a diffraction spectroscopy with a Ni filter and graphite monochromator (X'Pert Pro model, Philips Inc.) at room temperatures. The X-ray source was Cu K $\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ) and a  $2\theta$  range from 20° to 80°. The crystal size was determined from the diffraction peak broadening using the Scherrer equation. High-purity silicon powder was used as an internal standard to account for instrumental line broadening effects during crystal size estimation. UV-Visible diffuse reflection spectra (UV-Vis-DRS) were recorded by a UV-240 spectrometer (Shimadzu Co., Japan), and the scan range was from 200 to 800 nm with a 150 mm  $\phi$  integral ball. Standard magnesium oxide was used as the reference. X-ray photoelectron spectroscopy data were obtained with an ESCALab250 electron spectrometer (Thermo-VG Scientific Ltd., UK) using 300 W Al K $\alpha$  radiation. The base pressure was approximately  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. The thermogravimetric analysis (TG-DTA) was carried out using a differential scanning calorimeter (DT-250, Shimadzu, Japan) in air atmosphere with a flow rate of 50.0 mL/min. The scanned temperature range was from 100°C to 700°C with a heating rate of 10°C/min.

**2.4. Photocatalytic Activity Measurements.** To evaluate the photocatalytic activities of the nitrogen-doped TiO<sub>2</sub> powders, the photoreactivity experiments were carried out in a circular reactor containing 100 mg catalyst and 140 mL methyl orange of 10.0 mg/L (or p-nitrophenol of 10.0 mg/L). Prior to irradiation, the suspensions were stirred in dark for 15 min to ensure adsorption/desorption equilibrium. After equilibrium, an ultraviolet light lamp with 254 nm wavelength (Jiangyin Lamp Co., China) was used in the photoreactor. At given irradiation time intervals, aliquots of 4.0 mL were sampled and then filtered through a Millipore filter with a pore size 0.45  $\mu\text{m}$  to remove TiO<sub>2</sub> particles. The filtrates were analyzed by recording the adsorption band maximum in the UV-Vis spectra of the substances using a spectrophotometer (751 UV-VIS, Shanghai Instrument Co., China). A UV-light filter was used on the circular reactor to eliminate the ultraviolet when the experiment was carried out under sunlight (outdoor sunlight in spring in eastern of China at northern latitude 31° and irradiation intensity was in the range of 970–1420  $\mu\text{W}/\text{cm}^2$ ).

## 3. Results and Discussion

**3.1. XRD Analysis.** Figure 1 showed the XRD patterns of nitrogen-doped TiO<sub>2</sub> (NF400, ground with 1.40 g of NH<sub>4</sub>F), compared nondoped TiO<sub>2</sub> (WG400, ground with water), and the raw TiO<sub>2</sub> (TO400, raw TiO<sub>2</sub> was not treated by ground). XRD patterns of these samples showed there were

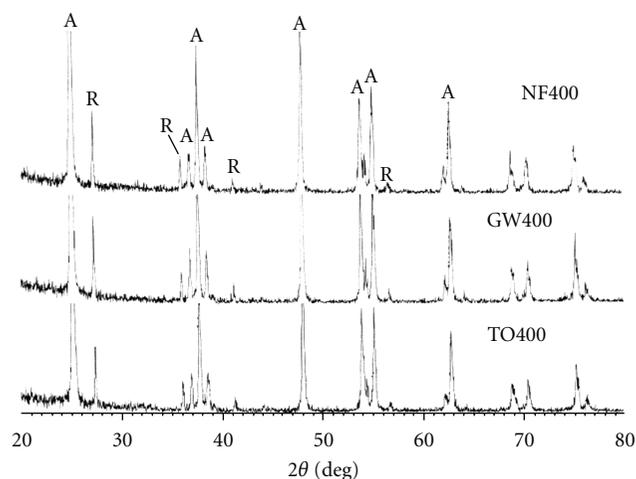


FIGURE 1: XRD patterns of the nitrogen-doped and nondoped  $\text{TiO}_2$  (sample ground with 1.40 g of  $\text{NH}_4\text{F}$  (NF400), ground with water (WG400), and the raw  $\text{TiO}_2$  (TO400); all three samples were calcined at  $400^\circ\text{C}$  for 2 h; A: anatase, R: rutile).

mixed anatase and rutile in all tested samples. The crystal size determined from the diffraction peak broadening using the Scherrer equations was found to be the same, and the crystal phases of the three photocatalysts were identical regardless of the prepared conditions. Comparison between WG400 and TO400 suggested the grinding process did not change the crystal structure of the  $\text{TiO}_2$ . Comparison between WG400 and NF400 also implies that the additional ammonia salt did not affect the crystal structure of  $\text{TiO}_2$  in the grinding process. Comparison between WG400 and TO400 suggested the grinding process did not change the crystal structure of the  $\text{TiO}_2$ . Yin et al. [22] has reported the grinding process can change the crystal structure during the milling of P25 (a commercial  $\text{TiO}_2$ ) in dry condition, but Chen et al. [23] showed a different result in wet condition. Considering our results, these may indicate the grinding process in dry or wet was a crucial factor governing the crystal structure of the  $\text{TiO}_2$  prepared. In the wet process, the high mechanical energy can be readily transferred through water, but, in the dry process, the energy may easily be concentrated in the local region, which accelerates the phase transformation from anatase to rutile as the latter is a thermodynamical stable morphology.

**3.2. UV-Vis Diffuse Reflectance Spectra (UV-Vis-DRS).** The UV-Vis-DRS of the nitrogen-doped  $\text{TiO}_2$  prepared under different conditions are shown in Figures 2–4. All the samples had an obvious visible absorption in the range 400–700 nm, but the absorptive intensities were different, depending on the nitrogen sources used (Figure 2). The highest absorptive intensities were obtained when milled in  $\text{NH}_4\text{F}$  (NF400) and urea (UR400), but weaker in the samples of  $\text{NH}_4\text{OOCCH}_3$  (AA400) and ammonia water (NH400), and the weakest in  $\text{NH}_4\text{HCO}_3$  (NC400). Except for ammonia water, all other nitrogen sources had the same concentration of 2.00 mol/L (0.0200 mol salt in 10.0 mL water). The difference in absorptive intensity, therefore, might not only account for  $\text{NH}_4^+$

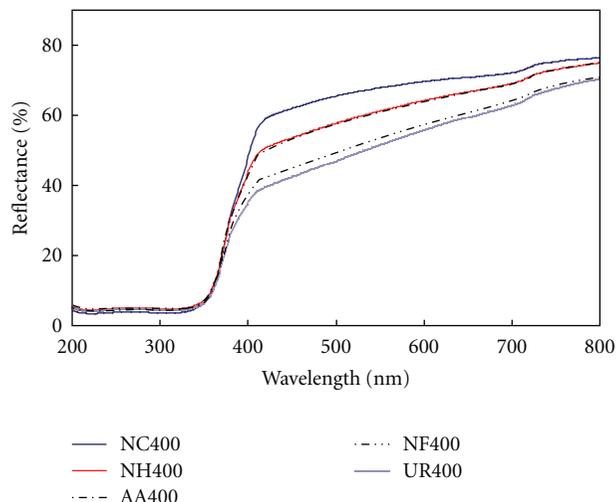
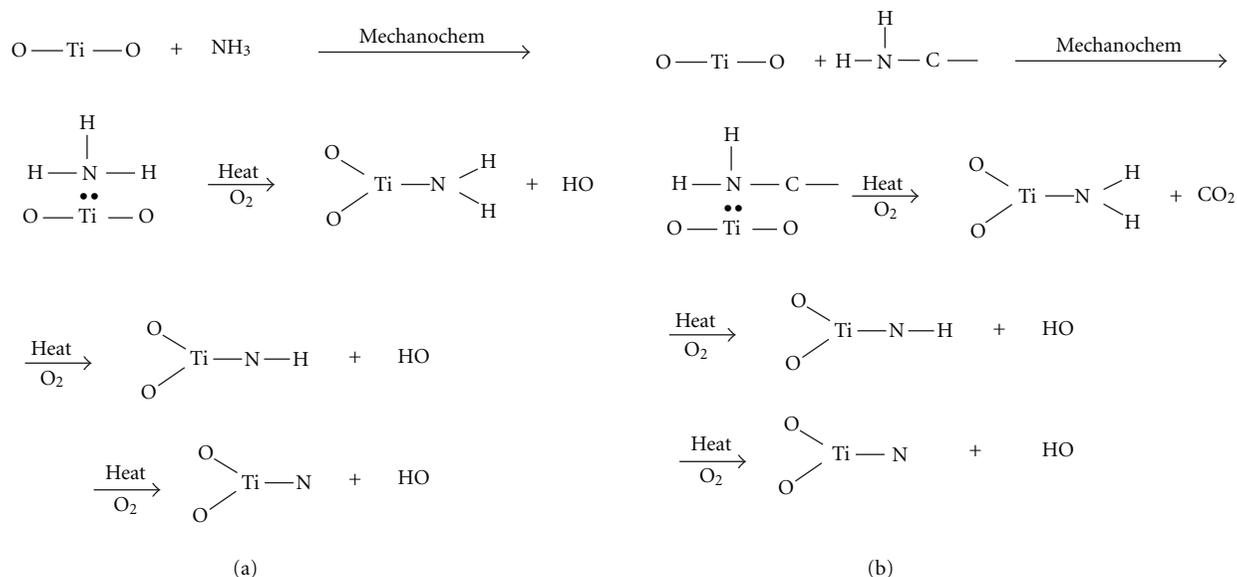


FIGURE 2: UV-Vis-DRS spectrum of the samples prepared in different nitrogen compounds (NF400: $\text{NH}_4\text{F}$ ; NH400: $\text{NH}_3$ ; NC400: $\text{NH}_4\text{HCO}_3$ ; AA400: $\text{NH}_4\text{OOCCH}_3$ ; UR400: $\text{CH}_4\text{N}_2\text{O}$ ).

concentration in the system but also the counterpart anions. In the urea sample, there was almost no free  $\text{NH}_4^+$  or  $\text{NH}_3$ , but it got the similar doped results that suggested that the doping process occurred not just adsorption of  $\text{NH}_4^+$  or  $\text{NH}_3$  on the  $\text{TiO}_2$  surface [22]. In the mechanical process, the high energy could produce the active surface on  $\text{TiO}_2$ , which would react with nitrogenous substance directly to form chemical adsorbed unstable intermediate, and this intermediate could form nitrogen doping in the subsequent thermal treatment. In the ammonia water system, the solution pH was 14.0; therefore, the pH was not a crucial factor when nitrogen-doped  $\text{TiO}_2$  was prepared. Li et al. [24] had reported a  $\text{TiO}_2\text{N}$  photocatalyst prepared by treating  $\text{TiO}_2$  in  $\text{NH}_3$ /Ethanol, and they considered that first doping process was surface adsorption of  $\text{NH}_3$  molecules and that nitridation consequently occurred by replacing the oxygen atom in the  $\text{TiO}_2$  with the nitrogen atom in the  $\text{NH}_3$  and resulting in the formation of the O–Ti–N and the N–Ti–N bond. In the case of  $(\text{NH}_2)_2\text{CO}$ , adsorption of  $(\text{NH}_2)_2\text{CO}$  on surface of  $\text{TiO}_2$  resulting in the formation of the doped nitrogen may demonstrate chemical adsorption occurring between Ti atom and N atom. Nitrogen atom has unpaired electrons which may be easily adsorbed on  $\text{Ti}^{4+}$  by static electricity attraction. The most probably existing bond in the case of  $(\text{NH}_2)_2\text{CO}$  system may be  $\text{O}_2\text{Ti–N–C}$ , and this indicated the chemical adsorption occurring between Ti atom and N atom.

Figure 3 shows the UV-Vis-DRS of the samples milled in  $\text{NH}_4\text{F}$  and subsequently thermally treated at 400, 500, and  $600^\circ\text{C}$ , respectively. When calcined at 500 and  $600^\circ\text{C}$ , the visible absorption was significantly reduced, indicating that the doped nitrogen in  $\text{TiO}_2$  was not very stable under high temperatures. A similar result was reported for the catalyst prepared by other methods [25]. When thermally treated at high temperatures, N, O, and Ti atoms can obtain high energies, and the doped nitrogen (in form of  $\text{O}_2\text{Ti–N–H}$  and/or  $\text{O}_2\text{Ti–N}$ , shown in Scheme 1) will be destroyed and



SCHEME 1: Doping mechanism of nitrogen on titanium dioxide.

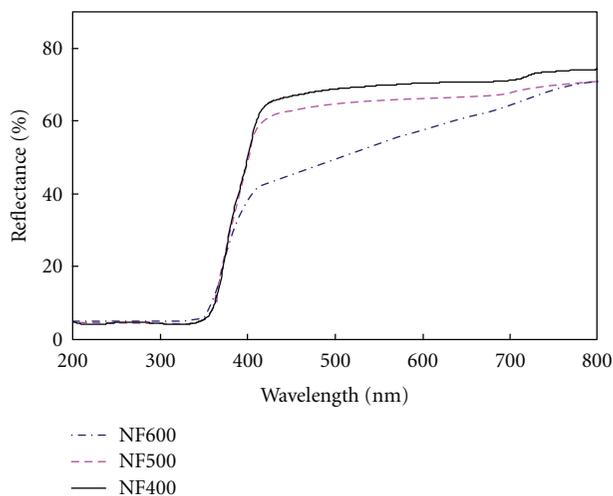
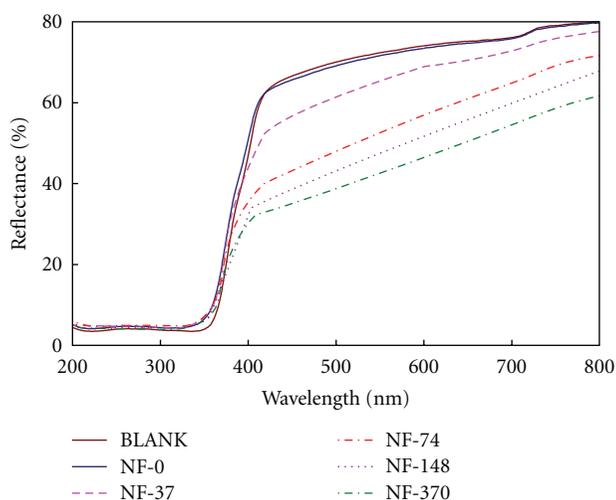


FIGURE 3: Effect of calcined temperature on the UV-Vis-DRS spectrum (NF400, NF500, or NF600 represent the NF series catalyst calcined at 400, 500, or 600°C, resp.).

FIGURE 4: Effect of  $\text{NH}_4\text{F}$  concentration on the UV-Vis-DRS of the NF series catalysts (NF-0, NF-37, NF-74, NF-148, and NF-370 represent the NF series catalyst calcined in the presence of  $\text{NH}_4\text{F}$ ; the dosages of  $\text{NH}_4\text{F}$  were 0, 0.37, 0.74, 1.48, and 3.70 g, resp.; the sample BLANK was the raw  $\text{TiO}_2$  directly calcined without milling (TO400)).

leave unpaired electrons in the lattice of anatase  $\text{TiO}_2$ . As the visible absorption originated from the nitrogen impurity level or nitrogen mixed level [26–28], the absorption was weak when the nitrogen doping was destroyed.

The UV-Vis-DRS of the samples milled at different  $\text{NH}_4\text{F}$  concentrations is shown in Figure 4. A higher absorbance was observed for the greater concentrations of  $\text{NH}_4\text{F}$ . Comparison between the NF400-0 samples and sample BLANK (TO400), which was the raw  $\text{TiO}_2$  directly calcined without milling, found that the UV-Vis-DRS of the two samples were almost the same. This suggested the mechanical treatment of  $\text{TiO}_2$  without nitrogen resources substance would not affect the visible absorbance of  $\text{TiO}_2$ , and this give the firmer evidence that the visible absorbance of nitrogen-doped  $\text{TiO}_2$  originated from nitrogen doping.

For a nitrogen-doped  $\text{TiO}_2$  sample prepared by other methods and calculated by the spin-polarized plane wave pseudopotential method, its absorption in the visible light region was primarily located between 400 and 500 nm, but  $\text{TiO}_2$  with the oxygen deficient was above 500 nm [29]. The photoabsorption above 500 nm for the milled and thermally treated  $\text{TiO}_2$  samples might be originated from oxygen deficiency. For the milled  $\text{TiO}_2$  (NF400), the active surface on  $\text{TiO}_2$  prepared in the mechanical process could react with nitrogen source substances (in most cases  $\text{NH}_4^+$  or  $\text{NH}_3$ , except  $(\text{NH})_2\text{CO}$ ) to form a reductive intermediate, which would inevitably be oxygen deficient on titania in the thermal

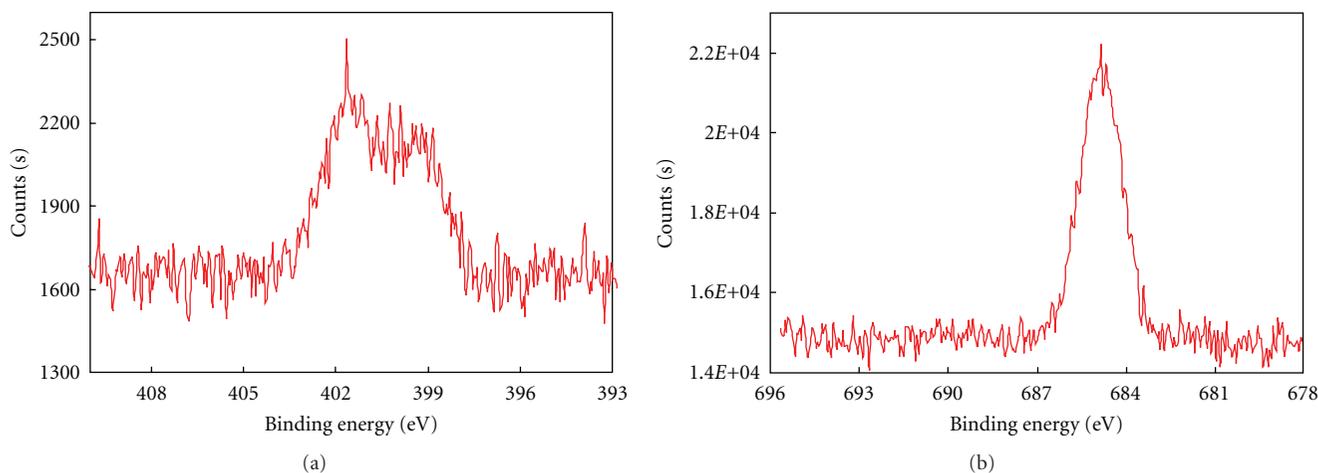


FIGURE 5: XPS spectra of NF400, (a) N1s and (b) F1s.

process. This might account for the visible light absorption above 500 nm. It is noticed that there were no clear onset of visible light absorption for most samples, and this may indicate that the light absorption in the visible range may be mixed with the function of nitrogen doping and oxygen deficient.

**3.3. XPS Measurement.** The X-ray photoelectron spectroscopy of NF400, which was calcined for 2 h at 400°C after milled for 3 h in  $\text{NH}_4\text{F}$ , is shown in Figure 5. Except for the titanium and oxygen, a small fraction of nitrogen was located at 402.0 eV and 399.5 eV, respectively. This confirms that after mechanochemical treatment nitrogen was doped into  $\text{TiO}_2$ . The binding energy of 402.0 eV is attributed to molecular chemical-adsorbed N [6, 29]. It was previously reported there were two peaks of chemisorbed  $\text{N}_2$  molecule on the  $\text{TiO}_2$  surface around 400.0 eV and 402.0 eV [6, 26]. Previous studies had demonstrated that the binding energy of N1s is located at about 396.0 eV and is attributed to substitutional doped nitrogen ( $\text{N}^-$  or  $\text{N}^{2-}$ ), which is in the proximity to the typical binding energy of Ti–N [9, 26, 30–32]. The absence of this peak suggests that there was little substitution doped nitrogen in the sample in the formation of N–Ti–N but that other nitrogen-doped forms must exist [33]. Diwald et al. reported the binding energy of 399.6 eV was found in the  $\text{NH}_3$  gas-thermal-treated  $\text{TiO}_2$  and it was attributed to the N–H bond [34]. However, the binding energy of 399.6 eV of NF400 in our work may be attributed to the N in form of interstitial nitrogen either in N–H or bare N atom form. For the NF400, the precursor had N–H bond and the subsequent thermal treatment temperature was sufficiently high to form Ti–N–H bond and can break N–H bond at even high temperature. The binding energy of 399.5 eV of NF400, therefore, might be attributed to the interstitial nitrogen bond to Ti, and the structure of the doped nitrogen in the  $\text{TiO}_2$  might be as  $\text{O}_2\text{Ti–N–H}$  or  $\text{O}_2\text{Ti–N}$  corresponding to treated temperature. We also monitored binding energy of N1s of the sample UR400 and found it also located at 399.5 eV (Figure 6). These suggested the doping

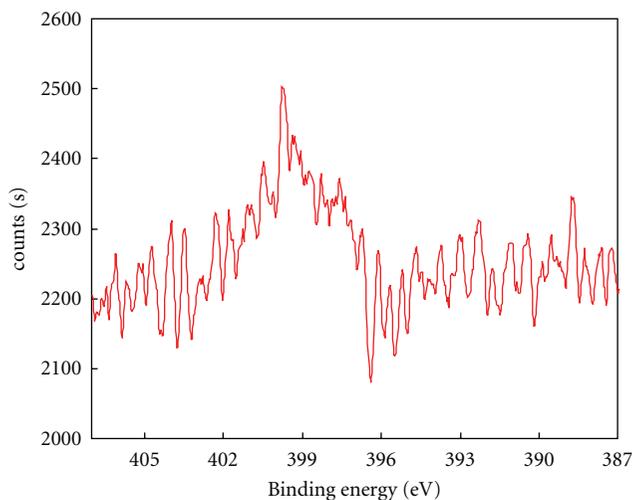


FIGURE 6: XPS spectra of N1s of UR400.

mechanism and the existing nitrogen in the titania doped by various nitrogen substances were the same. These results further confirmed the doping process of mechanochemical method was initiated between Ti and N, and the existing formation of nitrogen had no relation with the nitrogen substances.

In the milling process, the active  $\text{TiO}_2$  surface was able to react with N atom, but the O atom could not be substituted by the N atom directly. The unstable nitrogenous intermediate can be transformed by thermal treatment. At high temperature, the hydrogen can react with oxygen and left  $\text{O}_2\text{Ti–N}$  between the inter lattice of  $\text{TiO}_2$ . When treated at very higher temperature, Ti–N bond would break and oxidation of nitrogen by  $\text{O}_2$  happened. The probably doping mechanism of nitrogen on titanium dioxide under experimental conditions was shown in Scheme 1.

A small fraction of fluorine located at 684.8 eV was also found. It was originated from surface fluoride formed by ligand exchange between  $\text{F}^-$  and surface hydroxyl group on

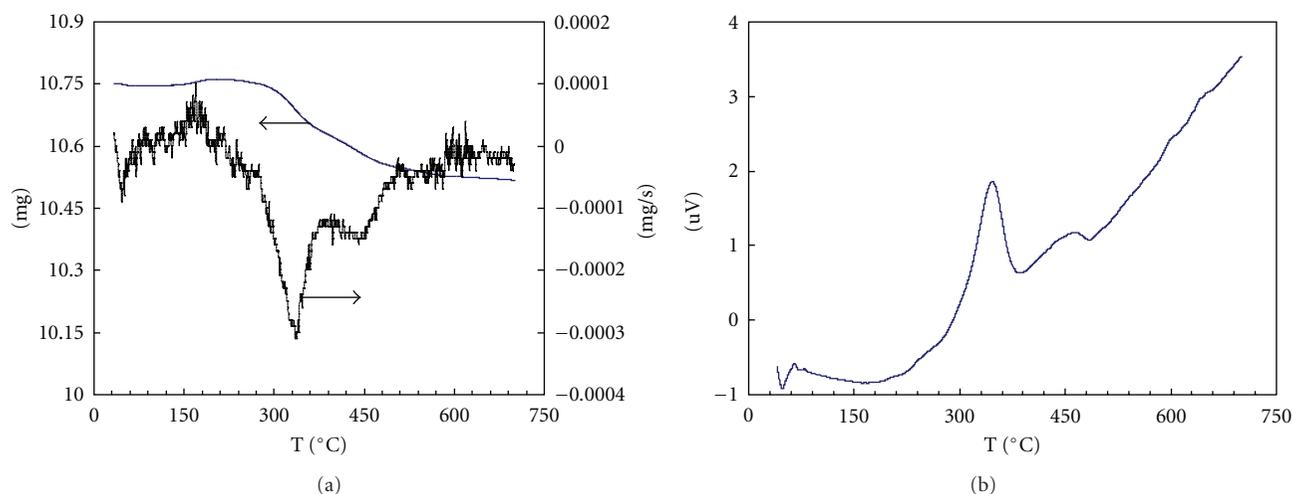


FIGURE 7: TG (a) and DTA (b) of the nitrogen-doped TiO<sub>2</sub> (NH400).

TiO<sub>2</sub>:  $\equiv\text{Ti}-\text{OH} + \text{F}^- \rightarrow \equiv\text{Ti}-\text{F} + \text{OH}^-$  [35]. No sign of doped fluorine in the lattice of TiO<sub>2</sub> was found with binding energy corresponding to 688.5 eV [35, 36]. This suggests the fluorine ion could react with Ti<sup>4+</sup> through ligand exchange to form a surface fluorinated substance, but not lattice substitution or interstitial doping. It was also observed that the binding energy of Ti and O in the NF400 was 459.0 eV and 530.3 eV, respectively, (not shown). These values were substantially different from those for pure TiO<sub>2</sub>, that is, 458.3 eV and 531 eV, respectively. The binding energy of Ti<sup>4+</sup> in the UR400 corresponding to 458.3 eV was very close to that for pure TiO<sub>2</sub>. This implies the form of Ti and O in the NF400 was significantly changed by the chemadsorbed fluorine ion, rather than by the doped nitrogen ion. As the most reactive atom, the fluorine ion had a considerable effect on the electrical chemical environment of Ti<sup>4+</sup> through electrostatic action and increasing the binding.

**3.4. TG-DTA Analysis.** Figure 7 showed the results of DT-TGA measurement of the nitrogen-doped TiO<sub>2</sub> (using the precursor of NH400). Significant weight loss appeared in the range of 300–500°C, this indicate chemadsorbed unstable intermediate can be destroyed under high temperature. The strongest weight loss appeared in the range of 340–360°C, and an exothermic band appears at which coincidentally. This means that the exothermic effect was because intermediate oxidation on TiO<sub>2</sub> and water escape from matrix. Ihara et al. [17] reported exothermic reaction start at about 380°C could be due to the oxidation reaction of NH<sub>3</sub> or NH<sub>2</sub> which are bonded coordinately onto Lewis acid site with the oxygen released from amorphous grain-boundaries by forming oxygen deficient sites. A weak weight loss peak appears in the range of 440–450°C, and a weak exothermic band appears, at which coincidentally again, this indicate the hydrogen can be destroyed under this temperature and formed in a gaseous substance. In the heating process, doped nitrogen substance can react with oxygen (oxygen in air but in the lattice of

TiO<sub>2</sub>) to form oxidative substance and escape from TiO<sub>2</sub> surface.

**3.5. Photocatalytic Activity.** The photocatalytic degradation results of p-nitrophenol under ultraviolet and sunlight using NF400, NF500, NF600, and NF700 as catalysts are shown in Figure 8. The NF400 gave a little higher activity regardless of the irradiation light treatment. In order to understand how the doped-nitrogen and oxygen deficiency affected the photocatalytic activity of the catalyst, a comparison was made for the activities under the identical reaction conditions, also using the raw TiO<sub>2</sub> catalysts which were calcinated at 400, 500, 600, and 700°C but not milled. A comparison among the four raw TiO<sub>2</sub> catalysts (without nitrogen doping) showed the same activities (data not shown). This suggests the heating temperature did not affect the photo activity of the catalysts and that the higher activity of NF400 was attributed to the doped nitrogen, rather than treatment temperature. Since the doped nitrogen was not stable, the high temperature treatment resulted in the loss of nitrogen in TiO<sub>2</sub>. The NF400 was able to absorb visible light efficiently, but its visible light activity was very low, when considering the same performance of the catalyst under UV light. This indicates the absorbed visible light by the doped nitrogen or (and) oxygen deficiency could not be efficiently used in the photocatalytic reaction under the experimental conditions. These results also imply that the visible light absorbance mechanisms may be associated with the doped nitrogen species, which could give rise to a mid-gap level slightly above the top of the (O-2p) valence band, rather than the mixed band gap by N-2p and O-2p [37]. The electron excited on the mid-gap level has a lower oxidative ability as compared to that excited on O 2p [9, 15, 31, 38]. If the visible light absorbance is excited on the mixed band gap, the excited electron would have same oxidative ability, regardless from UV light or visible light. The NF400 should have photocatalytic activity under sunlight, as it had a great visible light absorptive ability.

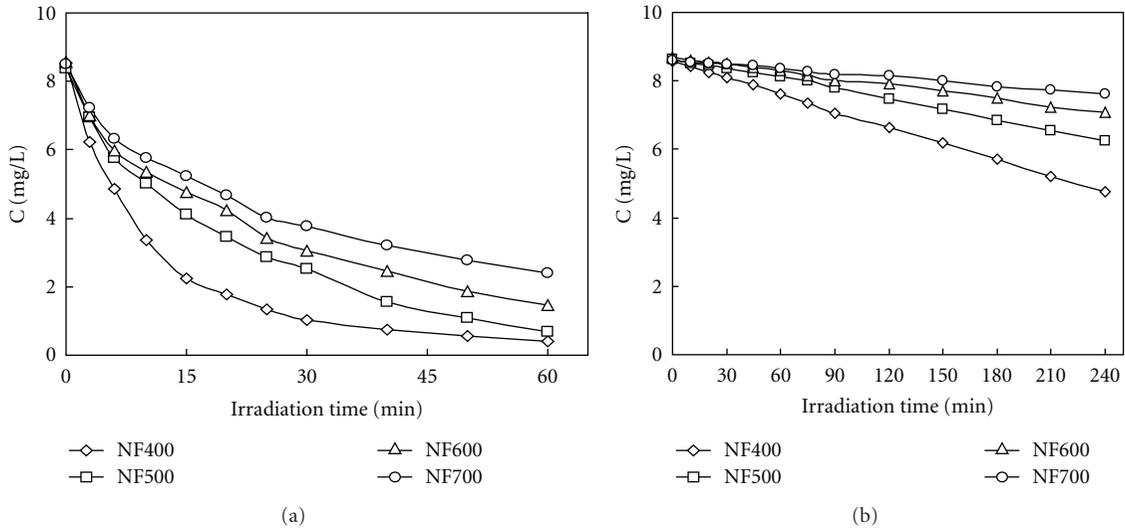


FIGURE 8: Photocatalytic degradation of p-nitrophenol (PNP) using NF400, NF500, NF600, and NF700 as catalysts under (a) ultraviolet and (b) sunlight.

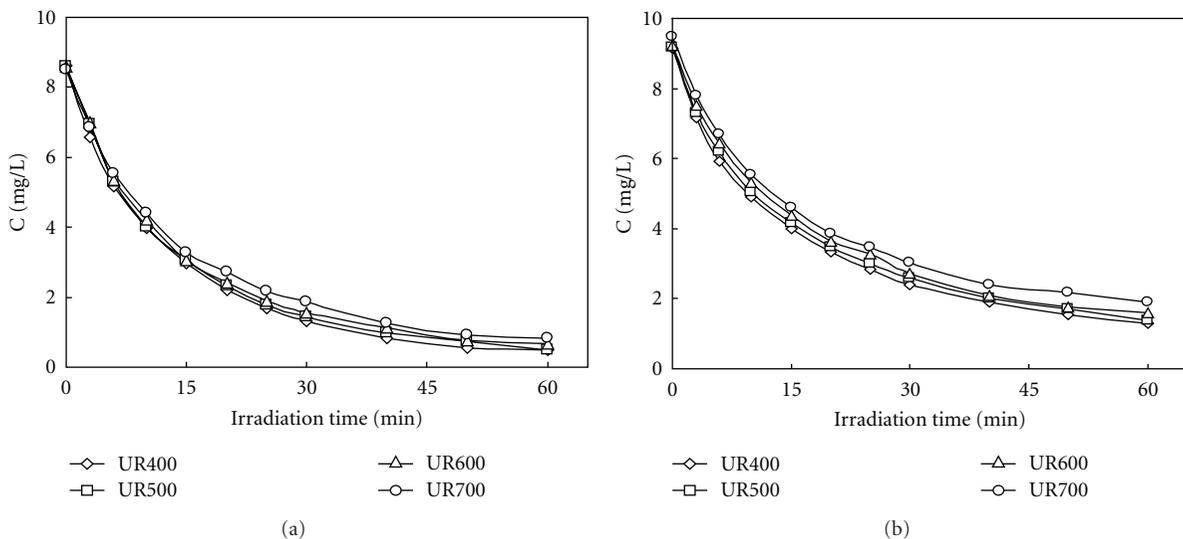


FIGURE 9: Photocatalytic degradation of (a) p-nitrophenol and (b) methyl orange under ultraviolet using UR400, UR500, UR600, and UR700 as catalysts.

The photocatalytic degradation results of p-nitrophenol and methyl orange under ultraviolet using UR400, UR500, UR600, and UR700 as catalysts are shown in Figure 9. The photocatalytic activities of the four catalysts were of almost the same levels, when either p-nitrophenol or methyl orange was used as the model pollutant. These results suggest that the photo activity of the nitrogen-doped TiO<sub>2</sub> was related to the prepared conditions.

Figure 10 shows the photocatalytic degradation of methyl orange under ultraviolet light using NF400, NF500, NF600, and NF700 as catalysts. The photoactivities of the NF series catalysts for methyl orange degradation were very similar to those of the NF series catalysts for p-nitrophenol degradation under UV light. The activities of the NF series catalysts

were in order of NF400 > NF500 > NF600 ≈ NF700, for methyl orange or p-nitrophenol degradation. A comparison between this result and those for the UR series catalysts showed a very different activity order. This indicates that the photo activities of the nitrogen-doped TiO<sub>2</sub> prepared using the mechanochemical methods were highly related to the nitrogen sources. In milling process, the active surface of the TiO<sub>2</sub> might react with the nitrogen sources. This was confirmed by the UV-Vis-DRS data shown before.

The photocatalytic activities of NF400, NC400, NH400, AA400, and UR400 under ultraviolet light using p-nitrophenol as a model pollutant are illustrated in Figure 11. The photo activities of the NF400, AA400, and UR400 were of similar levels, but the NH400 had the lowest photocatalytic

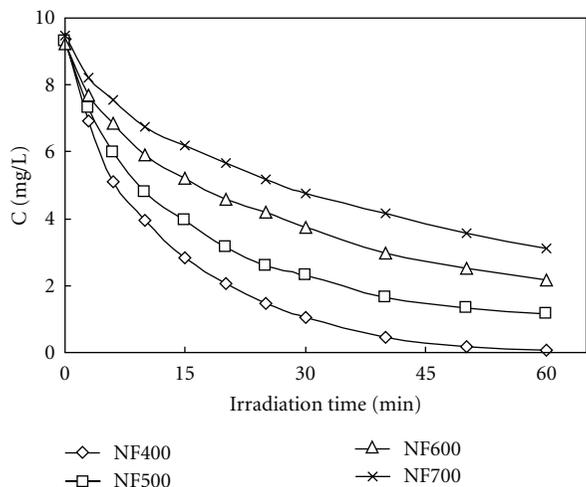


FIGURE 10: Photocatalytic degradation of methyl orange under ultraviolet light using NF400, NF500, NF600, and NF700 as catalysts.

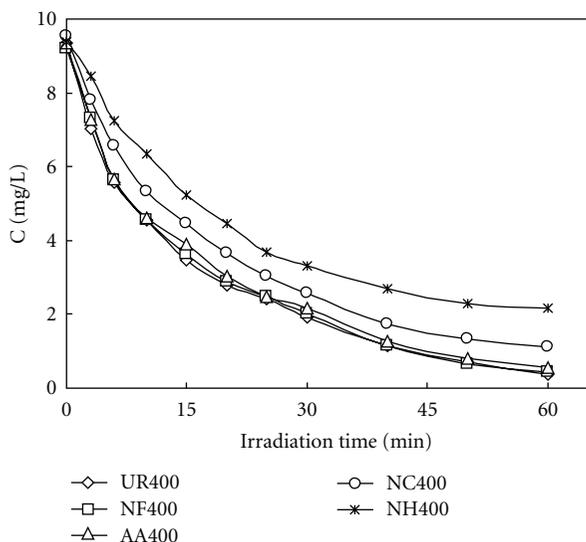


FIGURE 11: Comparison of photocatalytic activities of NF400, NC400, NH400, UR400, and AA400 under ultraviolet light using p-nitrophenol as model pollutant.

activity, attributed to the alkaline conditions in the ball milling process. The lower photoactivity of NC400 was likely to be associated with the strong adsorption of  $\text{HCO}_3^-$  onto the active site on  $\text{TiO}_2$  surface.  $\text{HCO}_3^-$  had very strong adsorptive ability on the  $\text{TiO}_2$ , causing a blocking of the active site and decreasing the photocatalytic activity of degradation stearic acid [39].

The photocatalytic degradation of methyl orange under ultraviolet shown in Figure 12 indicates that after the mechanochemical process, the activity of all the nitrogen-doped catalysts was reduced. Comparison between the activities of NF400-0 and the BLANK suggests that the ball milling treatment was the reason for the decreased activity. This implies that the  $\text{TiO}_2$  surface structure was destroyed by ball

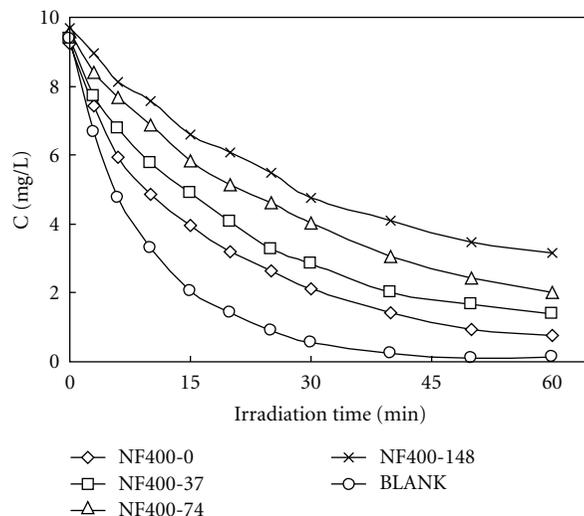


FIGURE 12: Effect of  $\text{NH}_4\text{F}$  concentration on photocatalytic degradation activity of methyl orange under ultraviolet light. (NF400-0, NF400-37, NF400-74, and NF400-148 which represent the qualities of  $\text{NH}_4\text{F}$  in milling process were 0, 0.37, 0.74, and 1.48 g, resp.; BLANK represents the raw titania directly calcined at  $400^\circ\text{C}$  without milling (TO400).)

milling treatment. Although the visible light absorption was achieved through the ball milling method, the photocatalytic activity of the  $\text{TiO}_2$  was reduced.

#### 4. Conclusions

The nitrogen-doped  $\text{TiO}_2$  was prepared with mechanochemical methods using wet ball milling of raw amorphous  $\text{TiO}_2$  in different nitrogen compounds. Characterization of the catalysts demonstrated that the nitrogen-doped  $\text{TiO}_2$  could improve visible light adsorption efficiency. Such an improvement was attributed to the fact that the mixed function of the doped nitrogen and oxygen deficient, and the former species gave rise to a mid-gap level slightly above the top of the (O-2p) valence band of  $\text{TiO}_2$  and latter absorbed the light wavelength above than 500 nm. However, the  $\text{TiO}_2$  surface structure was destroyed by ball milling treatment, resulting in a reduced photocatalytic activity.

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