

## Research Article

# Facile Synthesis and Characterization of N-Doped $\text{TiO}_2$ Photocatalyst and Its Visible-Light Activity for Photo-Oxidation of Ethylene

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A facile wet chemical method was adopted for preparing highly photoactive nitrogen doped  $\text{TiO}_2$  (N- $\text{TiO}_2$ ) powders with visible responsive capability, which could be achieved by the hydrolysis of titanium isopropoxide (TTIP) in the ammonium hydroxide precursor solution in various concentrations and then calcined at different temperatures. The N- $\text{TiO}_2$  powders were characterized, and the photocatalytic activity was evaluated for the photocatalytic oxidation of ethylene gas under visible light irradiation to optimize the synthesizing conditions of N- $\text{TiO}_2$  catalyst. The N- $\text{TiO}_2$  photocatalytic powders were calcined in a range of temperatures from 300 to 600°C and obviously found to have greater photocatalytic activities than commercial  $\text{TiO}_2$  P25. The strong absorption in the visible light region could be ascribed to good crystallization and adapted sinter temperature of as prepared sample. XPS test demonstrated that the N was doped into  $\text{TiO}_2$  lattice and made an interstitial formation (Ti-O-N), and N doping also retarded the phase transformation from anatase to rutile as well. The N- $\text{TiO}_2$  catalyst prepared with 150 mL ammonium hydroxide added and calcined at 500°C showed the best photocatalytic activity. The experimental results also proved the enhanced photoactivity of N- $\text{TiO}_2$  material depends on the synthesizing conditions.

## 1. Introduction

Recently, the nanomaterial, such as nanoiron, titanium dioxide photocatalysts ( $\text{TiO}_2$ ), has applied for groundwater remediation, degradation of hazardous materials, and environment cleanup [1–3]. However, the wide band gap of  $\text{TiO}_2$  for anatase crystal structure requires UV light and occupied less than 10% energy in solar spectrum for the excitation of electron-hole pairs [4], which restricts the application of  $\text{TiO}_2$  because of low photo quantum efficiency.

Various metals such as Ag have been doped into the  $\text{TiO}_2$  lattice to shift its absorption from UV to visible light, and doping improved their photocatalytic activities [5]. In addition, literatures also fabricated the nanotube array or hybrid structures of element-doped- $\text{TiO}_2$  to enhance

the photocatalytic activity [6, 7]. However, none of them gave satisfactory results due to their thermally instability and increased carrier trapping [8]. Relatively, the doping of anion on  $\text{TiO}_2$  such as nitrogen and carbon element doped and codoped has considerable effect on increasing its photocatalytic activity [9–14], in which, the nitrogen seems to be the most effective dopant due to its similar size to oxygen and metastable defect complex, as well as small ionization energy [15], and N-doped  $\text{TiO}_2$  (N- $\text{TiO}_2$ ) has an advantage on photocatalytic activity [16, 17]. Hence, literatures focused on discussing the structure of N- $\text{TiO}_2$  using the X-ray photoelectron spectroscopy (XPS), electron spin resonance, or X-ray absorption near edge structure. Some reports claim that the band gap of the N- $\text{TiO}_2$  is reduced due to a rigid valence band shift upon doping [18], others attributed the observed

absorption of visible light by N-TiO<sub>2</sub> to the excitation of electrons from localized N-impurity states in the band-gap [8, 19]. In general, the change in banding structure of N-TiO<sub>2</sub> was attributed to the N interstitial doping, N substitution, and O vacancy [20–22]. However, till now the structure of N-TiO<sub>2</sub> is still under debate. The preparatory methods and conditions such as nitrogen precursor and sintering temperature may considerably affect the nitrogen state in the doped TiO<sub>2</sub> [19, 23]. But, only few systematic discussions have been found regarding the dominated factor ratio of N to Ti and calcination temperature for the activity of N-TiO<sub>2</sub>, simultaneously.

In other words, it is necessary to understand the chemical fine-tuning and further optimization of the visible-light photocatalytic activity of N-TiO<sub>2</sub>. The goal of this study is (1) to develop a simple method for the synthesis of N-TiO<sub>2</sub> nanomaterials using facile method at various conditions of nitrogen precursor amounts and composite calcination temperatures, (2) characterization of N-TiO<sub>2</sub> composite materials, (3) carried out the photocatalytic activity of as prepared N-TiO<sub>2</sub> under visible light.

Ethylene is a plant hormone that controls many plant responses, and its higher concentration can affect the food and horticultural product industry [24], safe handling, and the parent compound of important environmental contaminants, and the photocatalytic activity for the degradation was quite different from that of volatile chlorinated organic compounds such as trichloroethylene [25]. Therefore, batch experiments were conducted for the removal of ethylene to evaluate the N-TiO<sub>2</sub> photoactivity under visible light irradiation and have also been compared with that of commercial photocatalysts Degussa P25. Materials characterizations have been performed through specific surface area analysis, X-ray diffraction (XRD), scanning electron microscope (SEM), electron Spectroscopy for Chemical Analysis (ESCA), and diffuse reflectance ultraviolet-visible absorption spectra (DRS UV-vis).

## 2. Materials and Methods

**2.1. Chemicals and Synthesis of N-TiO<sub>2</sub> Composite.** All the chemicals were used as procured without further purification. Commercial photocatalyst P25 was purchased from Degussa. Ammonium hydroxide (NH<sub>4</sub>OH, 33 wt%), titanium tetraisopropoxide (TTIP), and absolute ethanol (99.8%) were procured from J. T. Baker. Synthesis procedure of N-TiO<sub>2</sub> composite was modified as reported in literatures [16, 26], and ammonium hydroxide was chosen as a nitrogen precursor. Different amounts of ammonium hydroxide (0–200 mL) and DI water (200–0 mL) were mixed with absolute ethanol (200 mL) in a flask, and then a 400 mL ammonia solution (concentration 0–8.4 M) was obtained. The 10 mL TTIP was added dropwise into the ammonia solution and stirred vigorously for 4 h at 4°C in a water bath. After that the hydrolysis and condensation reaction was kept on stirring for 24 h at room temperature, and then the sol-gel solutions stood to 24 h in aged conditions. The ensuing colloid was then centrifuged and washed thoroughly with distilled water to remove the residual reactants. The final precipitate was dried

at 105°C overnight in air and calcined at various temperatures for 5 h to obtain the final N-TiO<sub>2</sub> composite. The synthesized N-TiO<sub>2</sub> composites were labeled as N<sub>x</sub>T<sub>y</sub>, where *x* and *y* represent the amount (mL) of ammonium hydroxide added during the synthesis procedure and calcinations temperature (unit is 100°C per scale), respectively. For example, the N<sub>150</sub>T<sub>5</sub> catalyst indicates the addition of 150 mL ammonium hydroxide during the sol-gel procedure of amorphous N-TiO<sub>2</sub> catalyst, followed by its calcination at 500°C temperature. Pure TiO<sub>2</sub> catalyst was named as N<sub>00</sub>T<sub>y</sub> (*x* means “zero”), and there was not any addition of ammonium hydroxide during synthesis procedure, such that N<sub>0</sub>T<sub>3</sub> refers to the pure TiO<sub>2</sub> catalyst which was calcined at 300°C temperature.

**2.2. Characterization of Composite.** The composite was characterized by means of XRD, DRS UV-vis, XPS, and specific surface area. XPS were recorded on an ESCA spectrometer (ULVAC-PHI, PHI 5000, Japan) operated at 150 W and were used to investigate the surface properties in the valence band of the composite. The shift of the binding energy due to relative surface charging was corrected using the C 1s as an internal standard. The optical absorption responses of composite were obtained from the pressed disk composite using UV-vis (Hitachi, U-3900H, Japan) equipped with an integrated sphere, and BaSO<sub>4</sub> was used as a reference. Specific surface areas of samples were obtained by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption apparatus (Micromeritics ASAP 2020, USA). Samples were degassed at 150°C for 2 h prior to the measurements. The crystal phases of the composites were analyzed by XRD (PANalytical X'Pert Pro MRD, USA) with Cu-Kα radiation and diffraction angle range of 2θ which is 20° to 80°. The crystal size was determined according to Scherrer's equation and fraction of anatase phase in the mixture was calculated by formula proposed by Spurr [27].

**2.3. Photocatalytic Activity of N-TiO<sub>2</sub>.** During this study, removal ethylene was studied in batch experiment modes to evaluate the photocatalytic activity of N-TiO<sub>2</sub> samples as well as commercial photocatalyst P25. All the powders (0.5 g) were coated onto the flask bottle (catalyst film was kept at 1 mg/cm<sup>2</sup>) and capped with sleeve stoppers. The constant ethylene was injected into the flask to get initial ethylene concentration (about 140 or 85 ppmv in different test); a 150 μL aliquot regularly was withdrawn and injected into gas chromatograph equipment equipped with flame ionization detector (PerkinElmer Clarus 500, USA) to analyze the ethylene concentration. The visible illumination was provided by six three-colored fluorescent lamps (March T5-8W/865), located above the flasks equipped with a filter to cut the UV light region. The visible irradiance 610 nm was determined by detector (international light SED005) and about 0.62 mW/cm<sup>2</sup> at the bottom of flask.

## 3. Result and Discussions

**3.1. BET, XRD, and SEM Analysis.** The characteristics of composites including surface area, anatase phases, and crystallite size are summarized in Table 1 and Figure 1, in which, the

TABLE 1: Characteristics and rate constant of N-doped TiO<sub>2</sub> prepared at various N/Ti ratio and calcinations temperature.

Sample	Specific surface area m <sup>2</sup> /g	BET		Adsorption type <sup>a</sup> cm <sup>3</sup> /g	Phase content <sup>b</sup> A/R/B (%)	XRD Crystalline size <sup>c</sup> nm	SEM Size nm	UV-vis		Activity Rate constant ×10 <sup>-2</sup> h <sup>-1</sup>
		Pore size nm	Pore volume cm <sup>3</sup> /g					Egl (eV)	Band gap <sup>d</sup> Eg2 (eV)	
N <sub>00</sub> T <sub>2</sub>	258.9	3.4	0.28	IV	78/00/22	14	—	—	—	—
N <sub>00</sub> T <sub>3</sub>	144.7	4.8	0.24	IV	79/00/22	17	—	2.03	2.99	—
N <sub>00</sub> T <sub>4</sub>	70.1	5.3	0.25	IV	82/00/18	24	—	—	3.04	—
N <sub>00</sub> T <sub>5</sub>	65.8	6.2	0.17	IV	86/00/14	55	22	—	3.05	0.63 <sup>*</sup>
N <sub>00</sub> T <sub>6</sub>	19.5	9.6	0.08	IV	92/08/00	113	—	—	2.91	—
N <sub>00</sub> T <sub>7</sub>	0.5	18.3	0.01	V	28/72/00	138	—	—	2.87	—
N <sub>00</sub> T <sub>8</sub>	0.2	25.9	0.00	V	06/94/00	155	—	—	—	—
N <sub>50</sub> T <sub>3</sub>	144.8	4.8	0.24	IV	100/00/0	31	—	2.51	3.18	1.72 <sup>#</sup>
N <sub>100</sub> T <sub>3</sub>	231.7	3.9	0.28	IV	100/00/0	28	—	2.51	3.06	1.09 <sup>#</sup>
N <sub>150</sub> T <sub>3</sub>	186.1	4.0	0.27	IV	100/00/0	27	—	2.46	3.12	1.93 <sup>#</sup>
N <sub>200</sub> T <sub>3</sub>	260.4	3.5	0.27	IV	100/00/0	25	—	2.52	3.05	0.87 <sup>*</sup>
N <sub>150</sub> T <sub>2</sub>	319.9	3.2	0.22	IV	— <sup>e</sup>	— <sup>e</sup>	—	—	—	1.29 <sup>*</sup>
N <sub>150</sub> T <sub>4</sub>	61.0	6.6	0.16	IV	100/00/0	36	—	2.38	3.10	1.50 <sup>*</sup>
N <sub>150</sub> T <sub>5</sub>	45.3	6.9	0.13	IV	100/00/0	37	21.3	2.39	3.13	1.76 <sup>*</sup>
N <sub>150</sub> T <sub>6</sub>	34.2	9.3	0.11	IV	100/00/0	62	—	—	3.01	1.54 <sup>*</sup>
N <sub>150</sub> T <sub>7</sub>	0.8	29.5	0.03	V	78/22/00	108	—	—	2.92	0.01 <sup>*</sup>
N <sub>150</sub> T <sub>8</sub>	1.6	39.7	0.04	V	58/42/00	113	—	—	2.92	0.00 <sup>*</sup>
P25	51.2	18.7	0.25	IV	82/18/00	62	—	—	3.04	0.47 <sup>*</sup>

<sup>a</sup> Adsorption isotherm type and hysteresis loop were based on the IUPAC manual; <sup>b</sup> A, R, and B denote anatase, rutile, and brookite, respectively; <sup>c</sup> from XRD data using Scherrer formula; <sup>d</sup> the band gap is determined by the plot of  $(\alpha h\nu)^{1/2}$  versus photon energy, as shown in Figure 4; <sup>e</sup> no obvious characteristic pattern of crystal to calculate the size; <sup>\*</sup> experimental conditions: reaction temp. = 20 °C, R.H. = 63%,  $[C_2H_4]_{\text{initial}} = 140$  ppmv, light intensity = 0.62 mW/cm<sup>2</sup>; <sup>#</sup> experimental conditions: reaction temp. = 20 °C, R.H. = 53%,  $[C_2H_4]_{\text{initial}} = 85$  ppmv, light intensity = 0.62 mW/cm<sup>2</sup>.

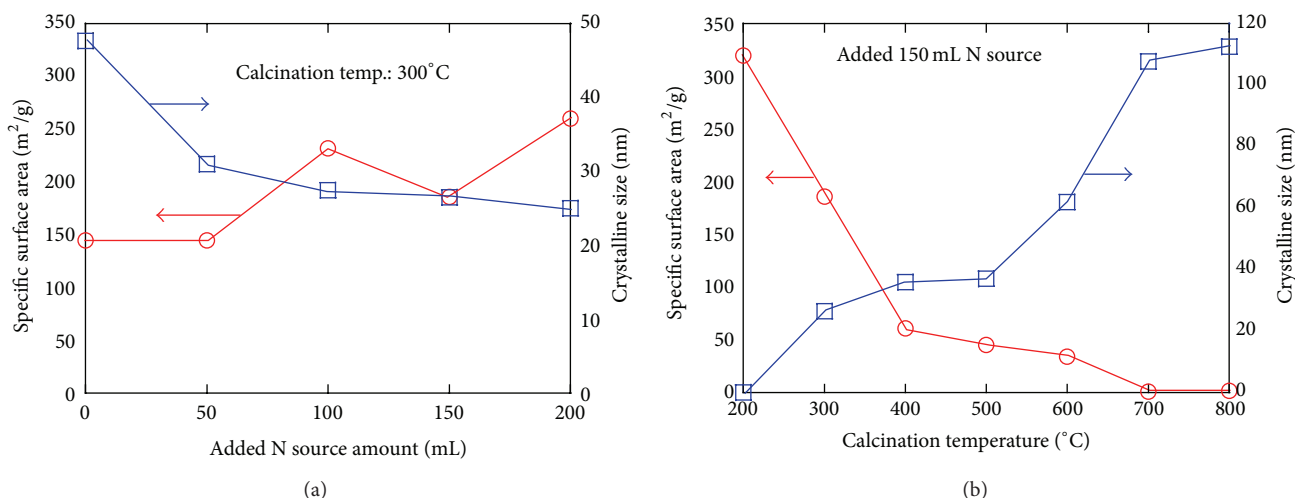


FIGURE 1: The specific surface area of N-TiO<sub>2</sub> samples as a function of (a) the various ammonium hydroxide amounts added and (b) calcinations temperature.

crystallite size and phase content of sample is calculated using the Scherrer equation from XRD peak position and full width half maximum [27]. Comparing Figure 1(a) with Figure 1(b), the unobvious change in the BET surface area and crystalline size of samples were observed after the addition of N precursor amounts. However, the clear changes in composites at different calcination temperatures depicted that the dominant factor for surface area and crystalline size of catalysts are calcination temperature, not the addition of N amounts. The pore size and pore volume of composite relative to surface area decreased with the increase of the calcination temperature, and this result is attributed to the pores collapsed and bigger crystallites aggregation of catalyst [28].

The XRD patterns of N-TiO<sub>2</sub> samples in different conditions are shown in Figure 2. The diffraction peaks marked with letters “A” and “R” on the figure corresponds to the anatase and rutile phase, respectively. In Figure 2(a), the major peak of 2 theta at about 25.5° corresponding to crystal plane (101) of anatase, which became thinner and the relative intensity was increased with calcination temperature. Such stronger crystalline flair of catalyst would enhance its photoactivity. The XRD patterns of N-TiO<sub>2</sub> synthesized with different nitrogen precursors presented in Figure 2(b) have also shown the similar results. It was also depicted that the nitrogen precursor amount did not significantly affect the N-TiO<sub>2</sub> crystal phase and crystal size.

The N-TiO<sub>2</sub> catalyst (N<sub>150</sub>T<sub>3</sub>) shows great effect on the photoactivity and also prevents the conversion of N-doped amount into nitrogen gas during calcination process. This sample synthesized with 150 mL N precursor was tested to investigate the effects of calcination temperature and the result is presented in Figure 2(c).

In Figures 2(a) and 2(c), the anatase phase on pure and N-doped TiO<sub>2</sub> sample started to appear at 200°C and 300°C calcination temperatures, respectively. The phase transformation from anatase to rutile was observed after the 600°C and 700°C calcination temperatures. This result can be implied that the nitrogen-doped catalyst retarded the phase transformation [10]. Such higher thermal stability could elevate the

anatase crystallinity and promoted the photo-induced charge separation and transportation [29]. The interesting brookite phase was only observed in pure TiO<sub>2</sub> (see Figure 2(a)) and disappeared as the beginning of rutile phase, and further the inhibited form of the brookite phase in the N-TiO<sub>2</sub> was implied (Figure 2(c)), since the addition of nitrogen in N-TiO<sub>2</sub> catalyst. Figures 2(b) and 2(c) showed that the N-doped TiO<sub>2</sub> samples had typical peaks of polycrystalline anatase structure and rutile without any detectable dopant related peaks, such as TiN, which was possibly due to the movement of dopant ions either into interstitial positions or substitutional sites of the TiO<sub>2</sub> structure or ion concentration, was detected to be too low [30].

The morphology and particle size of the N-TiO<sub>2</sub> (N<sub>150</sub>T<sub>5</sub>) and pure TiO<sub>2</sub> (N<sub>00</sub>T<sub>5</sub>) samples can be obtained from an examination of the SEM image (Figure 3). Single particle in agglomerates in both of them exhibited uniform spherical shape; the size was in range from 20 to 25 nm and a narrow size distribution appeared. Both of these sizes were slightly smaller than the crystallite sizes determined from the XRD in Figure 1(b). The results of similar size and morphology also indicated that the N precursor did not have significant effect on the particle size and shape of TiO<sub>2</sub> catalyst.

**3.2. DRS UV-Vis and ESCA.** In this study, the N-TiO<sub>2</sub> powders sintered below 600°C, all exhibited a pale yellow color which suggests its ability to absorb light in the visible region [31]. However, Qiu and Burda infer that the obtained UV-vis spectra that localized defect states may also play a role in providing visible light activity [32]. Optical absorption spectra of the N-TiO<sub>2</sub> and Degussa P25 samples are shown in Figure 4, and the absorption at wavelengths shorter than 400 nm can be assigned to the intrinsic band gap absorption of TiO<sub>2</sub>. A significant shift of the absorption edge to a lower energy in the visible-light region was observed for N-doped TiO<sub>2</sub>. This result indicates that band-gap narrowing has successfully been achieved by the doping of N into the TiO<sub>2</sub> lattice, presumably due to the modification of the band structure



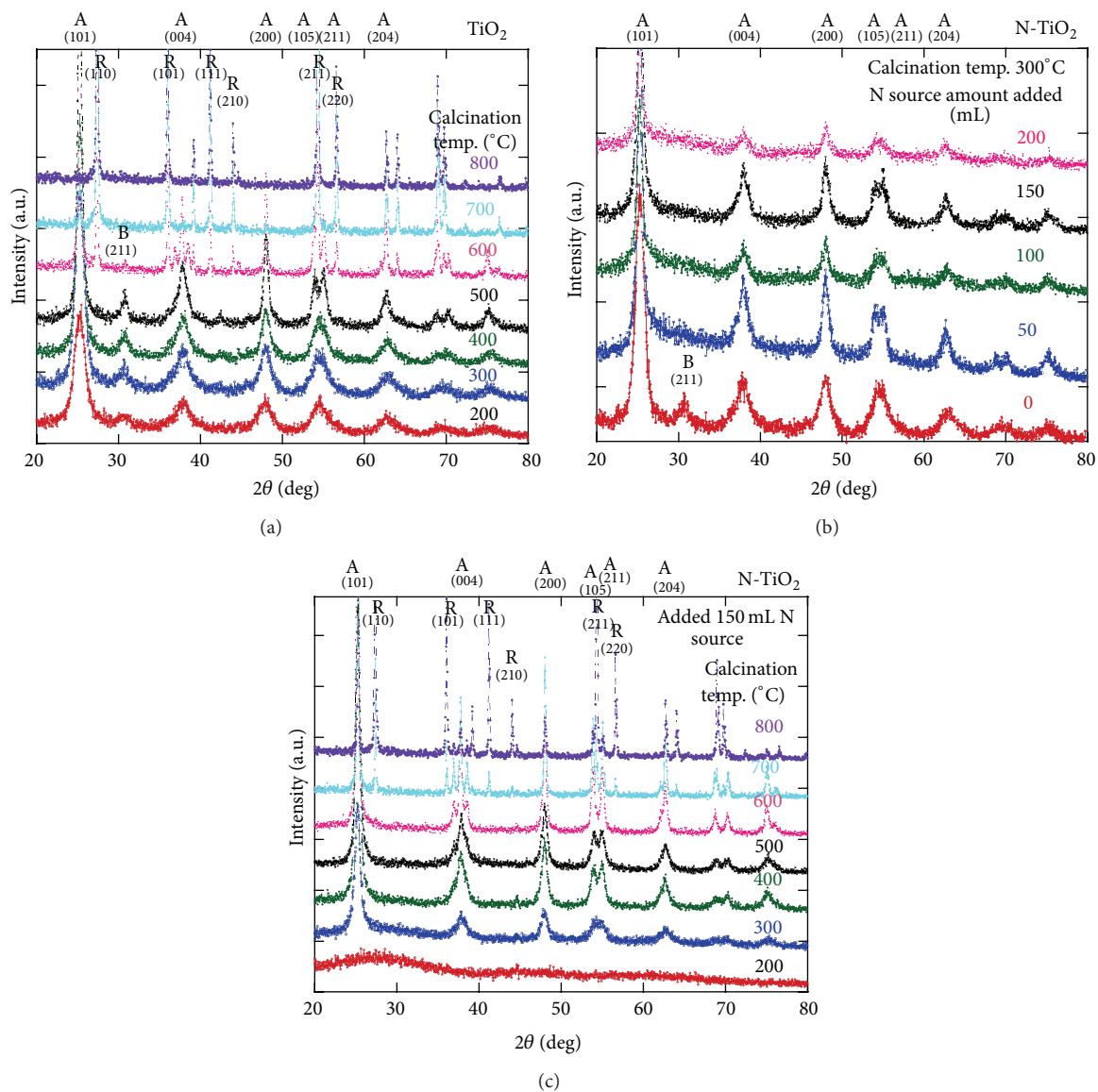


FIGURE 2: XRD pattern of (a) pure  $\text{TiO}_2$  calcined at different temperature, (b)  $\text{N-TiO}_2$  samples synthesized in different loading of ammonium hydroxide amounts, and (c)  $\text{N-TiO}_2$  samples calcined at different temperature.

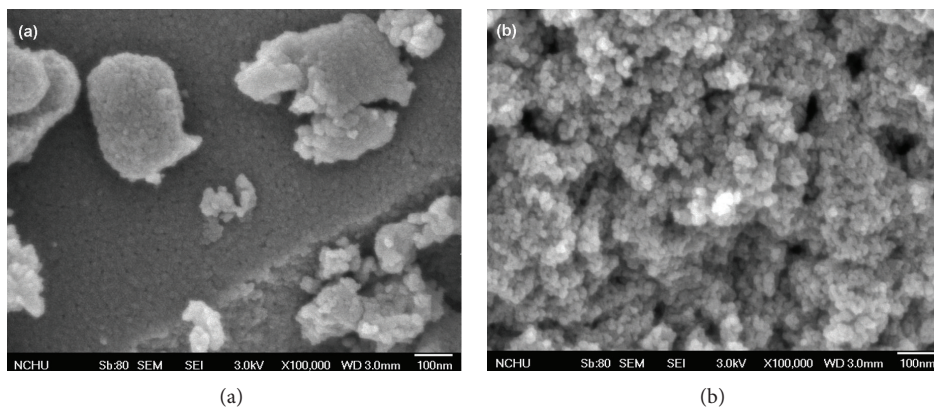


FIGURE 3: SEM images of (a) pure  $\text{TiO}_2$  and (b)  $\text{N-TiO}_2$  catalyst.

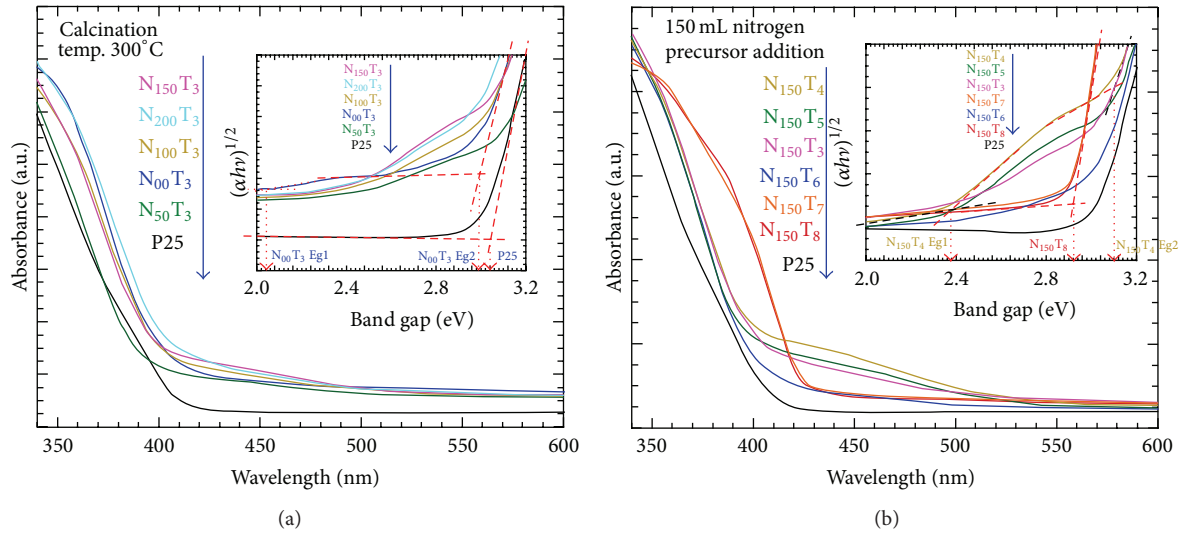


FIGURE 4: The UV-vis adoption pattern of N-TiO<sub>2</sub> (a) prepared with various ammonium hydroxide amount added and (b) calcined at different temperature.

[33]. The absorption spectra of the N-doped TiO<sub>2</sub> samples show a stronger absorption than undoped TiO<sub>2</sub> as well as P25 in the UV-vis light region and a red shift in the band gap transition except N<sub>50</sub>T<sub>3</sub> sample. The red shift is ascribed possibly to the oxygen vacancy [34] or the fact that N doping can narrow the band gap of the TiO<sub>2</sub> [35, 36]. Generally, the photocatalytic activity is proportional to the photo numbers absorbed by photocatalyst per second and the efficiency of the band gap transition [28], the N doping expand the wavelength response range of TiO<sub>2</sub> into the visible region and also increased the number of photo-generated electrons and holes to enhance the photocatalytic performance of N-TiO<sub>2</sub>. The enhanced activity in N-TiO<sub>2</sub> catalysts also was demonstrated in Figure 6. Figure 4(a) revealed that the absorbance increases with increasing added nitrogen precursor amounts of N-TiO<sub>2</sub> synthesized condition.

Unfortunately, such absorbance is not proportional to its photoactivity. Further, the UV-vis absorbance spectra of appropriate samples with different calcined temperature are shown in Figure 4(b). The absorbance of all N-TiO<sub>2</sub> samples in the visible region is higher than that of P25 and may be ascribed to the fact that the narrowing of band gap as well as localized defect resulted from N doping and calcination. Higher than 700°C calcination, the N-TiO<sub>2</sub> powders show a significant red shift in the band gap transition due to the formation of rutile phase and growth of TiO<sub>2</sub> crystallite. However, interestingly, amorphous N<sub>150</sub>T<sub>2</sub> powders also showed a greatest red shift. As the calcination temperature increased from 300°C to 600°C, the intensive absorption of N<sub>150</sub>T<sub>4</sub>, N<sub>150</sub>T<sub>3</sub>, and N<sub>150</sub>T<sub>5</sub> were observed in the visible region between 400 and 500 nm, which is the typical absorption feature of nitrogen doped TiO<sub>2</sub> [10], whereas it was not observed on N<sub>150</sub>T<sub>6</sub> sample even if N<sub>150</sub>T<sub>6</sub> appeared better photoactivity than N<sub>150</sub>T<sub>3</sub>. However, the aforementioned result could not possibly provide a definite relation between absorbance and photoactivity of as-prepared sample, which is due to that the absorption features in the visible range

originated from color centers through doping processes or posttreatments rather than by narrowing of the band gap [32, 37]. Literature also reports the intensive absorption of ion doped TiO<sub>2</sub> that can be assigned to oxygen vacancies produced by thermal treatment, which form localization levels within the band gap [34]. Moreover, the origin of visible light absorption originated from N and O vacancies suggested that the N dopants can only affect the absorption below 500 nm wavelength, while the O vacancies are responsible for the induced absorption at wavelengths above 500 nm [38].

ESCA analyses of N 1s and Ti 2p were performed on pure TiO<sub>2</sub>, P25, and N-TiO<sub>2</sub> catalysts and results are shown in Figure 5. In Figure 5(a), the binding energy (BE) peaks corresponding to N 1s core-levels for N-TiO<sub>2</sub> samples prepared with various amounts of N precursor and calcined at 300°C are observed one major peak at 398–402 eV. However, sometime the binding energy observed at 400 eV is ascribed to N atoms which are incorporated into the TiO<sub>2</sub> lattice as N<sub>2</sub> molecules [33]. Saha and Tompkins investigated the N 1s ESCA spectra during the oxidation of TiN and assigned the peaks as atomic β-N (396 eV) and molecularly chemisorbed γ-N<sub>2</sub> (400 eV and 402 eV) [31]. Those different N 1s spectral features are still debated and dependent on different preparation methods and conditions [35]. Further, the Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> spin-orbital splitting photoelectrons for anatase TiO<sub>2</sub> were located at binding energies of about 464.0 and 458.2 eV, respectively, which were assigned to the presence of typical Ti<sup>4+</sup>. Same Ti 2p peaks are located at same binding energy and distribution (Figure 5(b)), because the N precursor amount was not a dominating factor in the electronic structure of N-TiO<sub>2</sub>, although the different activity of N-TiO<sub>2</sub> synthesized in N precursor amount is shown in Figure 6(a).

The content of nitrogen were maintained in all the composites smaller than 1% and found decreased with increasing calcination temperature as shown in Figure 5(c), which may be due to the replacement of N in the matrix by O and

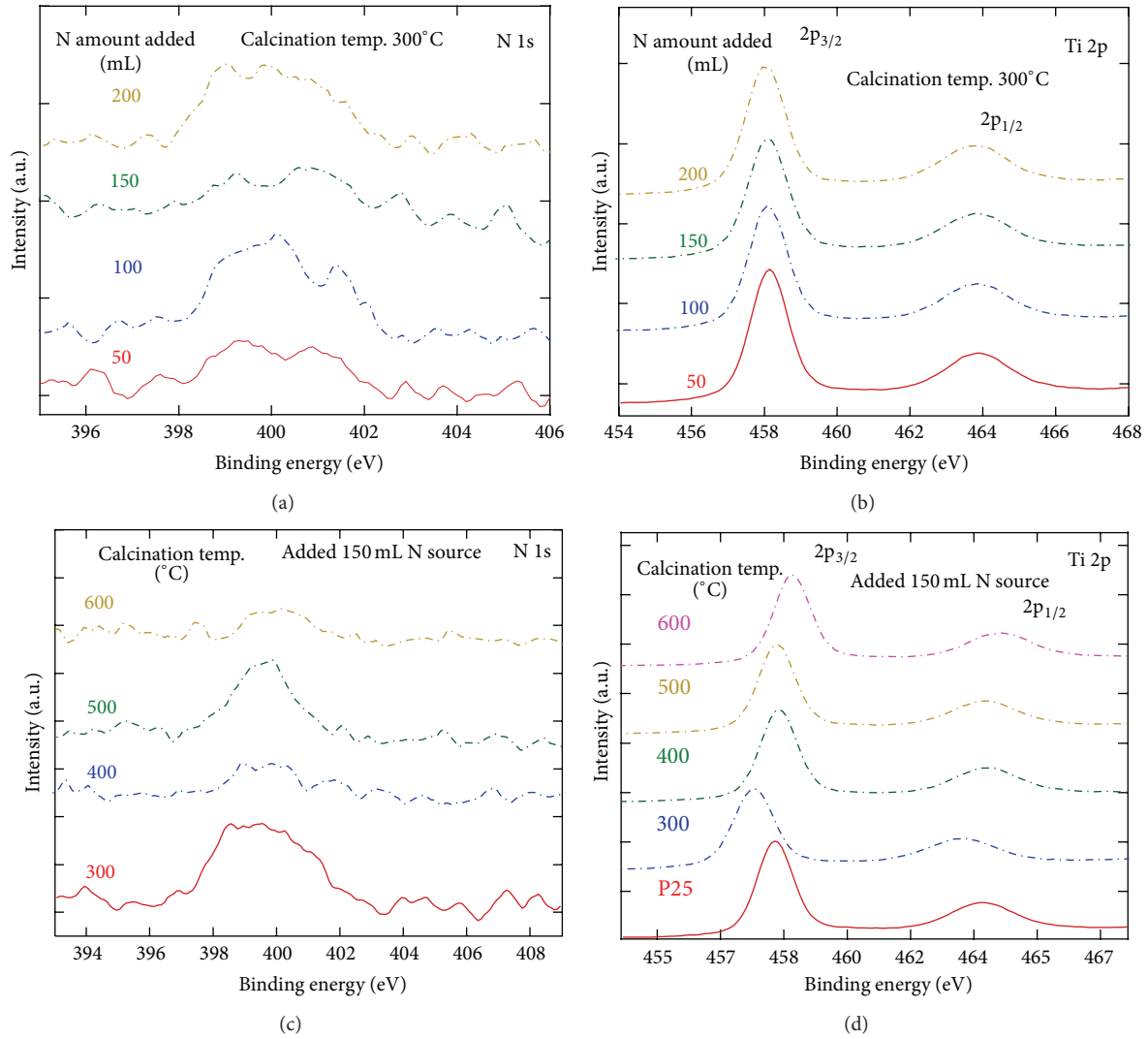


FIGURE 5: The XPS spectra for N-TiO<sub>2</sub> samples, ((a) and (c)) N 1s and ((b) and (d)) Ti 2p.

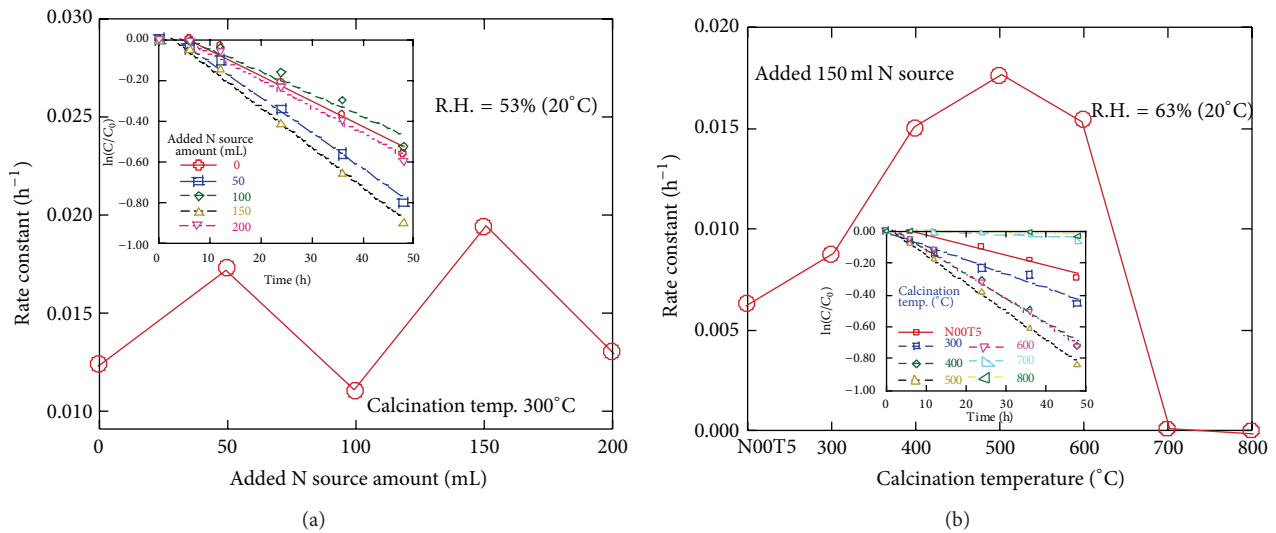


FIGURE 6: Photocatalytic reaction of N-TiO<sub>2</sub> samples as a function of (a) the various ammonium hydroxide amount added and (b) the various calcination temperature.

transform to nitride result in lower N concentrations [32]. Literature reports that the N dopant was adsorbed NO or bond to oxygen vacancy site in interstitial formation (Ti-O-N), especially at such low N doping concentrations [39]. The N 1s peaks also shifted towards higher binding energy with increasing calcination temperature level and appeared as different distribution. However, high sintering temperature can also cause the loss of dopants from N-TiO<sub>2</sub> catalyst. Therefore, an appropriate sintering temperature would be more important to the activity of N-doped TiO<sub>2</sub> [32]. At the same time, in Figure 5(d), the Ti 2p peaks undergone a shift towards higher binding energy with increasing calcination temperatures. This indicates the lowering of electronic density around the central Ti ion by introducing more O next to Ti [32]. The above mentioned binding energy shift pointed out that the calcination temperature may be a dominating factor in the electronic structure of N-TiO<sub>2</sub>, and this is found consistent with XRD and BET analyses, and thus the calcination temperature would be key factor for the characteristics of N-TiO<sub>2</sub> based on synthesized method of this study.

**3.3. Photoactivity of N-TiO<sub>2</sub> under Visible Light Illumination.** Figure 6 shows the photocatalytic performances for ethylene removal over the various N-TiO<sub>2</sub> and pure TiO<sub>2</sub> in batch reactions under the visible light irradiation. The rate of photocatalytic oxidation has been described by a pseudo-first-order equation, as presented in (1) [24] and the rate constant values are given in Table 1. Consider

$$\ln\left(\frac{C_0}{C_t}\right) = -kt, \quad (1)$$

where  $C_0$  is the initial concentration of ethylene,  $C_t$  is the ethylene at time  $t$ , and  $k$  is the apparent pseudo first photocatalytic oxidation rate constant. Examination of (1) suggests that the apparent pseudo first photocatalytic oxidation rate constant  $k$  can be determined experimentally from a plot of  $\ln(C_0/C_t)$  versus time, which has a slope of  $-k$ . All the photocatalytic oxidation rate constants ( $k$ ) of catalysts are summarized in Table 1. Figure 6(a) shows the effect of N-TiO<sub>2</sub> synthesized at different nitrogen precursor with 300°C calcination temperature, and the order of the reaction rates (Table 1) was N<sub>150</sub>T<sub>3</sub>, N<sub>50</sub>T<sub>3</sub>, N<sub>200</sub>T<sub>3</sub>, N<sub>00</sub>T<sub>3</sub>, and N<sub>100</sub>T<sub>3</sub>. Then, the N-TiO<sub>2</sub> catalyst was synthesized at 150 mL nitrogen precursor and sintered from 300°C to 800°C temperatures to investigate the effects of sintering temperature on N-TiO<sub>2</sub> photoactivity. In Figure 6(b), the activity of N<sub>00</sub>T<sub>5</sub> (Pure TiO<sub>2</sub> sintered at 500°C temperature) was found better than commercial TiO<sub>2</sub> P25 under visible light irradiation due to the transfer of electron and hole between two phases (mix phase of anatase with few fraction of brookite) which is ascribed to the oxygen vacancy resulted from the calcination at 500°C [40].

Moreover, the optimized N<sub>150</sub>T<sub>5</sub> photocatalyst has shown better ethylene degradation than undoped N<sub>00</sub>T<sub>5</sub> and others. Based on the experimental results, the nitrogen doping would improve the photoactivity of undoped TiO<sub>2</sub> under visible light irradiation. Both N<sub>150</sub>T<sub>7</sub> and N<sub>150</sub>T<sub>8</sub> showed less photoactivity due to the existence of rutile phases and the tiny

BET surface area as shown in Figure 1(b). However, the largest specific surface area of N<sub>150</sub>T<sub>3</sub> should have theoretically better photoactivity for the removal of ethylene due to the abundance of active sites. More effectiveness of N<sub>150</sub>T<sub>5</sub> was also observed for visible region of solar illumination and there are some other facts that may affect photoactivity of TiO<sub>2</sub> under visible illumination such as O vacancy resulted from calcination and N impurity acted as light sensitization [41, 42]. We have found that not only is the N-TiO<sub>2</sub> sample oxygen-deficient but also it involves a small amount of N-doped. N doping in TiO<sub>2</sub> was in interstitial formation (Ti-O-N) and that function retarded the reoxidation of oxygen deficient TiO<sub>2</sub>, which is essentially indispensable for visible light sensitization [36].

## 4. Conclusions

N-TiO<sub>2</sub> nanocatalysts can be developed directly by so-gel method under the conditions: 150 mL ammonium hydroxide precursor added and 500°C calcination temperature. The ethylene removal efficiency was dependent on the optimal contents of nitrogen precursor, surface area, and oxygen vacancy and good crystallization resulted from the adapted calcination temperatures [32, 43]. The N-TiO<sub>2</sub> powders showed a stronger absorption in the visible light region from 400 to 500 nm wavelength, which was possibly due to narrow band gap by mixing of N 2p states with O 2p states on the top of the valence band or a creation of N-induced mid-gap level. Other more intensive absorption in the visible light region longer than 500 nm wavelength is ascribed to oxygen vacancy resulted from the calcination and N doping. The N-doping wet-method has an advantage on photocatalytic activity as compared to metal ion doping (thermally instability). In addition, the doped TiO<sub>2</sub> enhanced the photoactivity may be further investigated in depth [32], such as use of first principle calculations, origin of the enhanced visible light absorption in N-doped anatase TiO<sub>2</sub> [44], or approaches to combine TiO<sub>2</sub> with another mineral such as schorl.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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