

The Characteristics and Photocatalytic Activity of Visible Light Driven N-doped TiO₂

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ABSTRACT

We focus on the sol-gel synthesis of N-doped TiO₂ at various ammonia/TTIP molar ratio (0.0 ~ 3.0) and calcination temperatures (400 ~ 800 °C). Samples were analyzed by XRD, UV-Vis, BET and DTA-TG in order to understand the characteristics of N-doped TiO₂. The photocatalytic oxidation reaction activity of N-doped TiO₂ were evaluated for the decomposition of the ethylene under the visible light irradiation. The result indicate the major peak of crystallite plane of anatase and rutile for temperatures showed 400°C and 700°C, respectively. The N-TiO₂ samples revealed the significant red shift of the absorption edges. When the temperature increasing, the percentage of weight (%) displayed decreasing. Lastly, the N-TiO₂ exhibited much higher photocatalytic activity of photodegradation of ethylene than pure TiO₂ under visible light illumination.

Keywords: visible light; N-doped TiO₂; photocatalysts; calcinations; ethylene

1 INTRODUCTION

The semiconductor photocatalyst of titanium dioxide (TiO₂) has been received a great deal of attention due to its chemical stability, lower-toxicity and low cost. It's been employed in self-cleaning, anti-bacteria, and deodorant [1]. Notwithstanding, TiO₂ can only be activated by ultraviolet light (< 387 nm) owing to need high energy and wide band gap [2]. It is known that the UV light of the solar spectrum occupied about 5 % of incoming the solar energy. Many studies have reported that doping of non-metal could narrow the band gap and might drive the response to visible light and catalytic activity, such as S [3], N [4], C [5]. Nevertheless, some researcher mention that the photoactivity of doping with transition metals, such as Cr [6], Mn [7], is poor due to the thermal instability, the need of an expensive ion-implantation facility [8]. Therefore, doping TiO₂ with non-metal elements has received much attention.

Many reports about the modification of N-TiO₂ the mechanism for visible-light activity on this system is still an open question [9]. Asahi claimed that the doped nitrogen atoms narrow the band-gap of TiO₂ [10]. However, Ihara insisted that it is the oxygen vacancies that contributed to the visible light activity [11]. Recently, there are various synthetic routes like sputtering method [12], sol-gel route [13], micro emulsion method [14], homogenous precipitation [15] have been widely studied for nitrogen doped TiO₂. Among these methods, sputtering need expensive and complicated equipment; the micro emulsion need much organic solvent; homogenous precipitation requires a large amount of chemicals and complex procedure, whereas the sol-gel route just need cheap equipment, low cost and easy prepared methods.

In this study, we had focused on the sol gel synthesis of N-doped TiO₂ at various N/Ti molar ratio and reaction temperatures. All samples were characterized using XRD, and UV-Vis, BET and DTA-TG. Eventually, N-doped TiO₂ were evaluated for the decomposition of the ethylene under the visible light irradiation.

2 METHODOLOGY

The sample named for A20T4 that A represents ammonia, 20 illustrates ammonia/TTIP molar ratio 2.0 and T4 symbolizes calcination temperatures at 400 °C.

2.1 Photocatalyst Preparation

The photocatalyst of Nitrogen-doped TiO₂ was synthesized by sol-gel method. Titanium tetraisopropoxide (TTIP) and ammonia was utilized as Ti precursor and N precursor. The ammonia was added dropwise (4.5 ml/min) into the TTIP solution with vigorous stirring until 1 hour in order to ensure mixed uniform at various N/Ti molar ratio (0.0 ~ 3.0). Colloid samples were placed in the hood at room temperature for 24 hours to precipitate and dried at 70 °C for 24 hours so as to remove humidity. Afterword, calcined at the different temperatures (400 ~ 800 °C) for 2 hours.

2.2 Photocatalyst Characterization

X-ray diffraction

The crystalline structure of N-doped TiO₂ photocatalyst was identified using X-ray diffraction with Cu-K radiation at a scan rate of 0.033° s⁻¹ (PANalytical X'Pert Pro MRD, USA) with scanning time at 10 seconds in the range of 20 to 80°.

UV/Vis spectrometer

The optical absorption response of N-doped TiO₂ was estimated using a UV-Vis spectrophotometer (Hitachi, U-3900H, Japan) equipped with an integrated sphere at the wavelength range of 200-800 nm.

Thermal gravimetric (TG)

The thermal gravimetric and differential scanning calorimetry (TG-DSC) curves were recorded using a STA6000 thermogravimetric analyzer (Perkin Elmer, USA). Powder samples were heated in air at the rate of 50 to 800 °C/min.

Nitrogen Adsorption-Desorption

Specific surface area of samples was obtained by the Brunauer-Emmett-Teller (BET) method. N₂ gas was adsorbed at 77 K using Micromeritics ASAP 2020 system. Surface area was determined at the relative pressure (P/P₀) range of 0.05–0.3.

2.3 Photocatalytic reaction activity

The gases of ethylene, nitrogen and oxygen were mixed by turbulence tube. The mixed gases enter the inner reactor which was placed the photocatalysts of N-doped TiO₂ film, then circulation with airtight system under visible light irradiation. Last, the ethylene concentration analyzed by GC- FID to obtain the data.

3 RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

XRD patterns of different calcined temperature from 400 to 800 °C are shown as Fig.1(a). The major intensity peaks (101) of anatase TiO₂ revealed corresponding with literature that strong peaks showed at 400 to 600 °C, but just a weak major intensity peak (101) of anatase TiO₂ exhibited at 700 °C, and no peak (101) of anatase TiO₂ displayed at 800 °C. Generally, it report that a large amount of transformation of titania from anatase to rutile will occur at 600 °C, however when Nitrogen-doped could retard the phase transformation from anatase to rutile.

3.2 BET analysis

The specific surface area size of all samples is listed in Table 1. Compared to all samples, it is increasing the amount of N, decreasing the surface area. The specific surface area size of all samples is listed in Table 1. Compared to all samples, it is increasing the amount of N,

decreasing the surface area. (1.0 molar ratio)N-TiO₂ and (1.5 molar ratio)N-TiO₂ provided the higher specific surface area. Therefore, N-TiO₂ may be useful degrade the ethylene under the visible light illumination.

Table 1. The characteristics of different content of N-TiO₂ calcined at 400 °C

Sample	Specific surface area(m ² /g)
Pure TiO ₂	93.40
(0.5 molar)N-TiO ₂	107.19
(1.0 molar)N-TiO ₂	119.40
(1.5 molar)N-TiO ₂	118.68
(2.0 molar)N-TiO ₂	97.76
(2.5 molar)N-TiO ₂	97.88
(3.0 molar)N-TiO ₂	85.80

3.3 UV/Vis spectrometer analysis

Photocatalyst of (2.0 molar) N-doped TiO₂ calcined at different temperatures is shown in Fig.1(b). It can be seen that the N-doped TiO₂ sample presents a significant absorption in the visible light region between 400 and 500 nm. The most efficient absorption displayed at calcinations 400 °C, with increasing the temperature, the absorption ability is gradually decreasing. The probably reason might calcinations at 400 °C attain the great anatase phase of TiO₂.

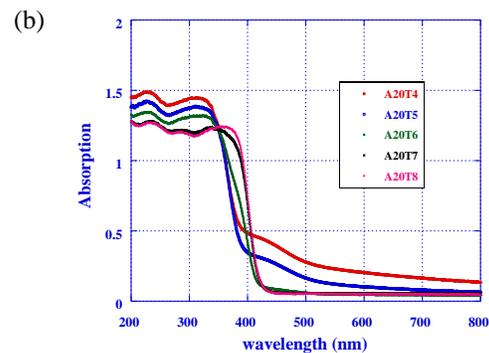
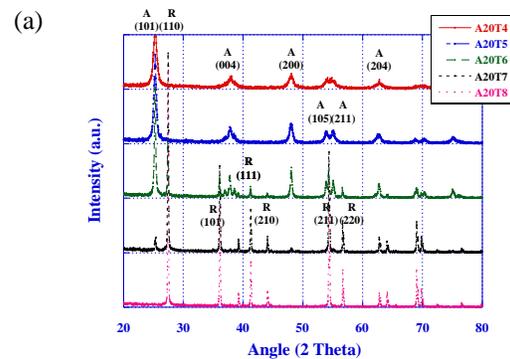


Fig.1.(a) XRD pattern and (b) UV-VIS absorption spectra of N-TiO₂ calcined at different temperatures

3.4 Thermal gravimetric (TG) analysis

The TG pattern of (2.0 molar ratio) N-TiO₂ is shown in Fig.2(a). It can be seen that with increasing the temperature, the weight % is decreasing. It's decreasing rapidly when temperature from 50 to 100 °C and 100 to 200 °C. The former is lost the humidity and the latter is desorption organic compound. The Heat flow is increasing with increasing the temperature. The obscure peak appearance of 451 °C is the phase transformation from amorphous to anatase, and the obvious peak appearance of 730 °C is the phase transformation from anatase to rutile.

3.5 Photocatalytic activity

Photocatalytic active degradation of ethylene for different doped molar ratio calcined at 400 °C are exhibited in Fig.2(b). All samples removal of ethylene are 43.7 % > 36.2 % > 29.7 % > 28.4 % > 24.9 % > 21.4 % > 13.6 % > 1.8 % for A20T4, A15T4, A25T4, A10T4, A30T4, A05T4, A00T4(pure TiO₂) and P25, respectively. A20T4 removal is 3 times high than the pure TiO₂ and 24 times high than the P25 under the visible light irradiation. The probable reason is that the fact that there was an optimum doping content in TiO₂ particles for the most efficient separation of photo induced electron-hole pairs.

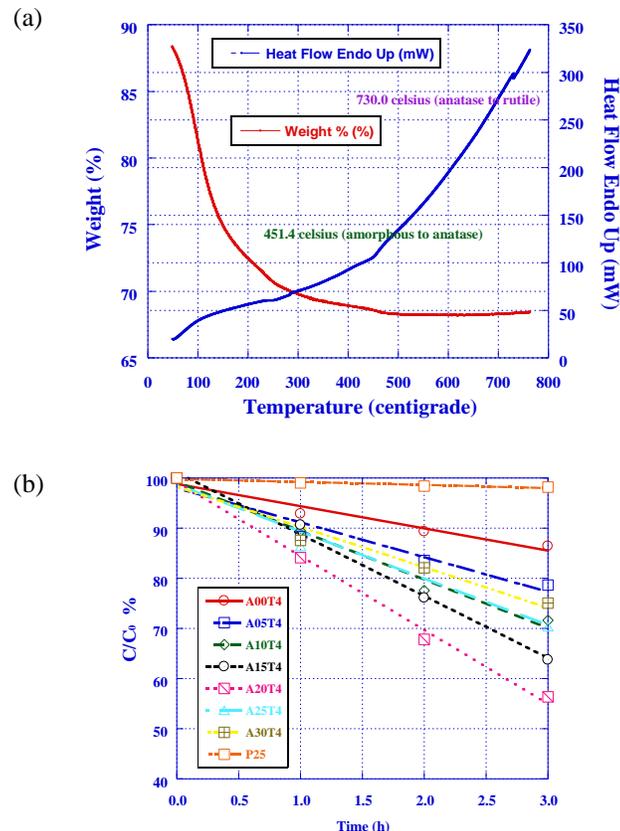


Fig.2.(a) DTA- TG analysis of (2.0 molar ratio)N-TiO₂; (b) Degradation of ethylene for different doped molar ratio calcined at 400 °C

4 CONCLUSIONS

Visible light induced photocatalyst N-TiO₂ was synthesized by sol-gel method, which designed by different N-doped molar ratio (0.0–3.0) and different calcined temperature (400–800 °C). XRD showed that N-doped can retarded the phase transformation from anatase to rutile of TiO₂ calcinations at 600 °C, and UV-vis revealed the significant absorption for A20T4 between 400 and 500 nm. All samples was displayed about 100 m²/g specific surface areas. The optimum photocatalytic activity degradation of ethylene by (2.0 molar ratio)N-doped and calcined at 400 °C due to appropriate doped molar ratio and higher anatase phase of TiO₂.

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