



# Influence of nitrogen content levels on structural properties and photocatalytic activities of nanorice-like N-doped TiO<sub>2</sub> with various calcination temperatures

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## ARTICLE INFO

### Keywords:

Interstitial atom  
Restraining phase transformation  
Chemical state  
Photocatalysis  
Paraquat degradation

## ABSTRACT

The purposes of this research were to study the effect of nitrogen content levels on structural properties and photocatalytic activities of catalysts with various calcination temperatures and to test the photocatalytic degradation of paraquat under UV and visible light. The results showed that the effect of calcination temperature was significant on physical properties and amount of nitrogen element, but insignificant on phase structure and oxidation state of titanium (Ti) atom. The N-doped TiO<sub>2</sub> samples demonstrated only anatase phase because nitrogen dopant in TiO<sub>2</sub> restrained the phase transformation from anatase to rutile and displayed nanorice-like morphology. The bandgap energy was about 3.07–3.18 eV. The nitrogen content was only observed at 100, 300 and 400 °C. The nitrogen (N) atom can be incorporated in TiO<sub>2</sub> structural lattice with interstitial site. The specific surface area and nitrogen content level showed the important roles for the photodegradation of paraquat under UV and visible light irradiation.

## 1. Introduction

Ever since Fujishima and Honda who first theoretically overviewed the titanium dioxide (TiO<sub>2</sub>) nanocrystalline material [1], a number of researchers have extremely been interested in this material. Nanoengineering of the TiO<sub>2</sub> photocatalyst is an interesting approach to decompose the environmental organic compounds because of its unique electronic and structural properties. The photocatalytic activity of catalysts is affected by their chemical and physical properties such as the specific surface area, crystallinity, phase and electronic structure as well as the chemical reaction condition including pH, temperature and light intensity [2–7]. Generally, the photocatalytic mechanism is activated by input of super-bandgap energy to the TiO<sub>2</sub> photocatalyst and based on the generation of electron-hole pairs upon irradiation with light [8–11]. Unfortunately, the use of the TiO<sub>2</sub> reveals some key drawbacks that limit their performance for the visible application. Firstly, surface photoactivation cannot be responded and generated electron-hole pairs. Secondly, the visible light activation displays low

quantum yield rate. Finally, the weak separation efficiency of photo-carriers results in low photocatalytic performance. To overcome the existing limitations, many studies have been modified to extend the wavelength range of the photoactivation of TiO<sub>2</sub> photocatalysts towards the visible region of the electromagnetic spectrum as around 43% of solar photons and enhance the utilization efficiency of solar energy. Therefore, it is necessary to develop photocatalyst activity which is more competitive against these some disadvantages in this field and enhances photocatalytic activity, especially under visible light region.

Over the past five years, the pathway to achieve above mentioned goal is represented by several ions doping to improve the photon adsorption such as transition metal [12,13], noble metal [14,15], rare earth metal [16,17] and nonmetal [11,18,19] doping. During recent years, various studies have been carried out by doping with nonmetal element for example carbon, nitrogen, sulfur, fluorine and chlorine into the lattice of TiO<sub>2</sub> to successfully cause the red shift of TiO<sub>2</sub> to the visible light domain. Among these elements, nitrogen is the most popular and most effective doping nonmetal due to its similar size to an

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oxygen atom as well as high electronegativity and high ionization energy. Asahi et al. [20,21] found that doped TiO<sub>2</sub> with nitrogen could enhance its photocatalytic activity. The authors also confirmed that the nitrogen dopant not only shifts absorption toward the longer wavelength but also accelerates the rate of photoreaction. Moreover, many researchers also confirmed that nitrogen doping in TiO<sub>2</sub> easily enables the visible light photocatalytic activity of TiO<sub>2</sub> without reducing its activity under UV light [11,18,19,22,23].

The formation mechanism of N-doped TiO<sub>2</sub> catalyst was obtained via different preparation method such as sol-gel [24,25], hydrothermal [26,27], direct hydrolysis of organic/inorganic salts [28] and calcination of TiO<sub>2</sub> or Ti(OH)<sub>4</sub> under nitrogen atmosphere generated by nitrogen compounds like ammonia [29–31]. The synthesis method demonstrates an important role in identifying the final properties of the materials because different methodologies to incorporate nitrogen lead to system with dopant located in different positions (interstitial or substitutional) of the TiO<sub>2</sub> structure and with different activities. In our study, we focused on the hydrothermal method for the preparation of N-doped TiO<sub>2</sub> because this method is frequently used for the synthesis of N-doped TiO<sub>2</sub> nanoparticles owing to their low cost, good repeatability, perfect crystallinity and unnecessary to calcine. Moreover, it can deliver the appropriate structure and surface properties for photocatalytic application.

Nevertheless, N-doped TiO<sub>2</sub> catalysts with high photocatalytic activity under visible light should present high nitrogen content level, small particle, high specific surface area and small bandgap energy. Similar to the hydrothermal process, the calcination treatment process is the normal way used to improve crystallinity and remove surface organic impurity. On the other hand, more researchers reported that high calcination temperature affects the agglomeration of TiO<sub>2</sub> particles [32,33], phase transformation [34,35] and the loss of the nitrogen dopant in the catalyst [36]. The result of these phenomena can weaken of charge separation resulting in low photocatalytic efficiency. Currently, there are few studies focused on the effect of calcination treatment on the characteristics and visible light driven photocatalytic activity of N-doped TiO<sub>2</sub>. Thus, we were greatly interested in the study of this calcination effect, which was not report in our previous researches [37].

In this study, we modified the TiO<sub>2</sub> by doped with nitrogen for the photocatalytic degradation. The hydrothermal method was used to prepare the photocatalyst by using ammonia solution (NH<sub>4</sub>OH) as a nitrogen source. Our work demonstrated the effect of calcination temperature on the crystalline structure, optical and textural properties, the state of charge and photocatalytic activity of the N-doped TiO<sub>2</sub>. The crystallite and phase structure of all calcined photocatalysts were investigated by using Wide-angle X-ray scattering (WAXS). The bandgap energy was determined by UV–vis diffuse reflectance spectroscopy (UV–vis-DRS) using the Kubelka-Munk theory. Surface morphology was taken by Focussed ion beam scanning electron microscopy (FIB-SEM). Specific surface area values were computed by using the Brunauer-Emmett-Teller (BET) model. Pore size distributions of the catalysts were determined by using the Barrett-Joyner-Halenda (BJH) theory. The state of charge was investigated by combining two techniques: X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The photocatalytic activity of the synthesized N-doped TiO<sub>2</sub> was evaluated by using the photodecomposition of paraquat under UV and visible light illumination.

## 2. Experimental

### 2.1. Chemicals

All of the chemicals used in this work were of analytical grade. Titanium tetrachloride (TiCl<sub>4</sub>) from Merck Schuchardt OHG was used as a substrate to prepare the TiO<sub>2</sub> amorphous. Hydrogen peroxide (30% H<sub>2</sub>O<sub>2</sub>) and ammonia solution (28% NH<sub>4</sub>OH) were bought from Ajax

Finechem Pty Ltd and QRèc, respectively. The commercially paraquat was purchased from a local market in Thailand (20% w/v) and used as the herbicide organic pollutant in this study. The chemical formula of paraquat is C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub> with a molecular weight of 257.16 g/mol. The paraquat solution was prepared by dissolution with deionized water.

### 2.2. Catalyst preparation

The catalyst synthesis procedure is based on our previous research [2,37–39]. The TiO<sub>2</sub> amorphous was prepared by mixing 6 mL of TiCl<sub>4</sub> dissolved in 400 mL deionized water and then stirred for 30 min. in cooling condition. NH<sub>4</sub>OH solution of 90 mL was then slowly dropped into the mixed TiCl<sub>4</sub> solution. The white suspension appeared and after that, the mixed solution was stirred for another 60 min in an ice bath. Consequently, the white precipitated powder was separated by centrifuge technique and washed with deionized water several times to neutral pH and then dried at 40 °C for 2 h and the temperature increased to 100 °C for 8 h. Next, the N-doped TiO<sub>2</sub> photocatalysts were synthesized via the hydrothermal process. About 2 g of amorphous TiO<sub>2</sub> was dissolved in 40 mL H<sub>2</sub>O<sub>2</sub> solution and stirred for 30 min. in an ice bath. Then, another 200 mL H<sub>2</sub>O<sub>2</sub> was mixed dropwise in the solution. After that, the solution was continuously stirred until it became transparent yellow solution. Thereafter, the transparent yellow solution was transferred to a 300 mL Teflon-lined steel autoclave and aged for hydrothermal process at 150 °C and 13 h, which was optimal condition for aging temperature and time reported in our previous works [2,37]. The suspended solids or N-doped TiO<sub>2</sub> photocatalysts from the autoclave were separated by centrifugal technique and then dried as follows: (1) 40 °C for 4 h and (2) 100 °C for 4 h labeled for uncalcined N-doped TiO<sub>2</sub>. Finally, the photocatalyst was separated into seven parts before calcined in an air muffle furnace at 300, 400, 500, 550, 600, 650 and 700 °C for 4 h with a heating rate of 10 °C/min for calcination step. The white powders of N-doped TiO<sub>2</sub> photocatalysts from every calcination temperature condition were obtained.

### 2.3. Catalyst characterization

The crystallite and phase structure of the N-doped TiO<sub>2</sub> photocatalysts were investigated by using the Wide-angle X-ray scattering (WAXS) at Beamline 1.1 W (BL1.1 W) of Synchrotron Light Research Institute, Thailand. The samples were contained in a solid cell with Kapton windows. Scattering patterns were recorded using an image plate detector (Mar345) with X-ray energy at 10 keV. The recorded patterns were analyzed by using SAXSIT software. The light absorption of the catalysts was estimated from UV–vis diffuse reflectance spectroscopy (UV–vis-DRS, Lambda 950, PerkinElmer, USA) with an integrating sphere using BaSO<sub>4</sub> as the reference. The Kubelka-Munk theory offers great advantages for applying with bandgap energy calculation. The specific surface area of the catalysts was computed from ten-point N<sub>2</sub>-adsorption isotherms by applying the Brunauer-Emmett-Teller (BET) method. Additionally, the pore size distributions of the catalysts were determined by using the Barrett-Joyner-Halenda (BJH) analysis, as applied to the desorption of the nitrogen isotherm. The nitrogen gas (N<sub>2</sub>) was used to the adsorbate and operated at 77 K by using N<sub>2</sub> adsorption-desorption apparatus (ASAP2460, Micromeritics, USA). The surface morphologies of the catalysts were examined by Focussed ion beam scanning electron microscopy (FIB-SEM, Helios NanoLab G3 CX, FEI, USA) with the beam voltage of 5 kV and current of 86 pA under vacuum condition. The surface element atoms of N-doped TiO<sub>2</sub> was observed by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI 500 VersaProbe II) using Al K $\alpha$  radiation as X-ray source at the BL5.3 SUT-NANOTEC-SLRI joint research facility, Synchrotron Light Research Institute, Thailand. The binding energy was calibrated with respect to the C 1s photoelectron line at 284.80 eV. The oxidation state of the titanium atoms in N-doped TiO<sub>2</sub> samples was studied by X-ray absorption spectroscopy (XAS), the spectra focused on Ti K-edge using

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