

Effect of Calcination Temperature on (N, Fe) Doped TiO₂ Nanoparticles

Siti Aida Ibrahim^{1*}, Abdul Hadi Zainal Alam², Rosniza Hussin¹, Zakiah Kamdi², Mohamed Nasrul Mohamed Hatta², Ainun Rahmahwati Ainuddin² and Muhamad Zaini Yunos²

^{1*} Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Hab Pendidikan Tinggi Pagoh, KM 1, Jalan Panchor, 84600 Panchor, Johor Darul Takzim, Malaysia

² Faculty of Mechanical & Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor Darul Takzim, Malaysia.

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Abstract: TiO₂ is one of the most promising photocatalysts that is widely used for environmental clean-up due to its ability to degrade organic pollutants in air or water in the presence of UV light irradiation. In this study, the sol-gel method followed by calcination process was employed to synthesize N, Fe doped TiO₂ nanoparticles. The effect of calcination temperature on the structural, morphology and optical properties of the as-prepared samples was analyzed. Titanium tetra isopropoxide (TTIP) was used as Ti precursor and urea and ferric nitrate nonahydrate were the employed precursors to obtain N and Fe, respectively. X-ray diffraction pattern displayed a transformation of anatase structure to biphasic of anatase and rutile structure as the calcination temperature was increased from 300 to 700 °C. FESEM images indicated an agglomeration of particles with the grain size was estimated at 50-170 nm. UV-Vis analysis revealed that the increment of calcination temperature induced a red shift in the absorption spectra from 485 nm to 664 nm. Hence, the results indicate that N, Fe doped TiO₂ is a highly potential visible-driven photocatalyst to degrade pollutants under the presence of visible light irradiation

Keyword: TiO₂; Sol-gel; Photocatalytic Activity; Optical Property.

1. Introduction

Environmental problem such as water pollution is one of the major issues today due to a substantial population growth which generates more waste products through industries, transportation and households. These pollutants are dangerous to our health as it is soluble in water and easily consumed by human beings and animals. An extensive research work by various researchers have been made in order to improve the water quality including by employing trees and microbial as bio-indicator for heavy metal, filtration and advanced oxidation processes (AOPs) as alternative methods [1,2]. However, the existing technology that has been used to overcome this problem is unable to remove these pollutants completely. A majority of non-degradable organic pollutants in the water are not treatable due to their high chemical stability and/or low biodegradability. Some method is very expensive, high maintenance and applicable only in selective environment or condition. Recent studies have established that the developments of new catalytic and

photocatalytic processes provide great help to address this problem [3,4].

TiO₂ is one of the most promising photocatalysts that can be employed for the purification of water and air [5,6]. It is also proven that TiO₂ can be employed in various environmental applications due to its superior photoreactivity, long term stability, inert and low cost [3,4]. The photocatalytic activity of TiO₂ depends on several factors such as crystallinity, surface area, impurities and density of surface hydroxyl groups [5,7]. In general, TiO₂ required the presence of light to decompose organic pollutant. Due to its large band gap energy (3.0 - 3.2 eV), TiO₂ is only active under UV light irradiation, which limits the light utilization rate of TiO₂ to only 5% of solar energy. Considerable efforts have been made by many researchers to tune TiO₂ with metals and/or non-metal elements that may alter the wavelength absorption of the photocatalyst. Surface modification such as metal ion (i.e. Ag, Fe and Zr) and non-metal doping (i.e. C, F and N), or by coupling with other narrow band gap semiconductors have been adopted to enhance the performance of TiO₂ under visible light irradiation [6,8-10].

*Corresponding author: saida@uthm.edu.my

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More recently, co-doping TiO₂ with two kinds of element has been proposed to promote the photocatalytic performance further benefiting from a synergistic effect of both dopants [11,12]. Study by Ashkarran *et al.* revealed that TiO₂ co-doped with Ag and N improved the photocatalytic efficiency under visible light irradiation due to the generation of two different electronic states acting as electron traps [13].

In this work, nanocrystalline N, Fe doped TiO₂ was synthesised by using sol-gel method and subsequently followed by a calcination process. Titanium (iv) isopropoxide was used as Ti precursor while iron (iii) nitrate and urea act as the sources of Fe and N dopant, respectively. The calcination temperatures were varied from 300 to 700 °C. The characteristics of the as-prepared samples were investigated using XRD, FESEM and UV-Vis. The effects of calcination temperature towards N, Fe doped TiO₂ characteristic were investigated and discussed.

2. Experimental Method

All chemicals used in this study were analytical reagent without further purification. Distilled water was used in all experiments. The preparation of N, Fe doped TiO₂ was a modification method from Teck and Ibrahim (2016) [14]. In a typical synthesis, 20 ml titanium isopropoxide (TTIP) and 80 ml isopropanol were added dropwise into a hydrolysis medium which contains 8 ml of acetic acid, 6 ml of distilled water iron (III) nitrate (0.15 wt%) and urea (0.3 wt%). The resulting mixture was stirred slowly for 3 hours at room temperature and centrifuged at 3000 rpm for 20 minutes in order to obtain the white precipitate. The white precipitate was dried at 80 °C for 12 hours in a drying oven. The precipitate was granulated by using agate mortar to get fine granules. Finally, the sample was calcined at 300, 500 and to 700 °C for 2 h, respectively.

The as-prepared samples were characterised by x-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and ultraviolet-visible spectrophotometer (UV-VIS). The XRD was performed on a D8 Advanced Bruker System with Cu α radiation as the x-ray source. Morphologies of the samples were observed by using a high-resolution field emission

environmental scanning electron microscope (FESEM, JSM-7600F). Optical properties of samples were measured on a Shimadzu UV-VIS spectrometer (UV-1800) in the wavelength of 300-800 nm.

3. Results and Discussion

X-ray powder diffraction (XRD) testing is used to determine the structure and crystallite size of N, Fe-TiO₂ samples. Fig. 1 shown XRD patterns for N-Fe-TiO₂ samples at different calcination temperatures of 300 °C, 500 °C and 700 °C. The anatase and rutile phase used were similar to the Joint Committee on Powder Diffraction Standard (JCPDS) file no. 08-2082 and file no. 03-6142, respectively. The results shown that N, Fe doped TiO₂ samples were anatase at temperature 300 °C and 500 °C while rutile phase occurred at 700 °C. It was observed that with increasing temperature from 300 to 500 °C, the peak intensities of anatase and rutile increased gradually, implying improvement of crystallization and growth of crystallites [15,16]. Generally, the transformation of anatase to rutile occurs when the temperature was increased from 400 to 800 °C [16]. This can be attributed to the fact that when sufficient thermal treatment is provided, the phase transformation of meta-stable anatase to a more stable rutile phase in the TiO₂ specimen can be achieved [14]. It is noted that all samples did not show the presence of iron or nitrogen compound. This may be due to two reasons, one is the limitation of XRD to detect low concentration foreign atoms in the composition and the other is the similarity of ionic radii of Ti⁴⁺ (0.68 Å) and Fe³⁺ (0.64 Å) [17].

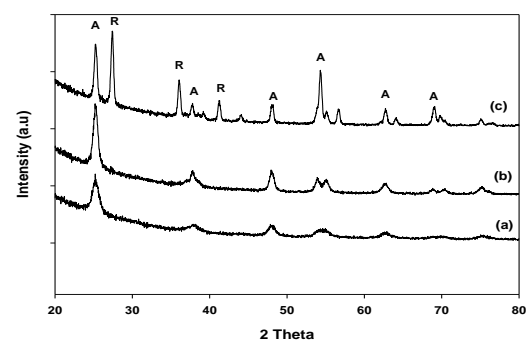


Fig. 1 XRD patterns of N, Fe-TiO₂ at (a) 300 °C, (b) 500 °C and (c) 700 °C. (A: Anatase, R: Rutile)

The average crystallite size was calculated according to Scherrer's equation as shown in Eq (1). Table 1 shown the summary table of XRD analysis for all samples. Based on the result, the crystallite size of N, Fe-TiO₂ was in the range of 14 to 46 nm. The crystallite size of N, Fe doped TiO₂ at 700 °C which consist of biphasic phase of anatase and rutile is larger than the single phase samples. The trend shows that the crystallite size was increased with the increment of calcination temperature. Li *et al.* [18] reported similar behaviour as the increment calcination temperature accelerated the crystallite growth due to high-phase transformation heat.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where D denotes the average crystallite size (nm); K is the Scherrer constant, somewhat arbitrary value that falls in the range 0.8–1.0 (it has been assumed to be 0.9 in present work); λ is wavelength of X-ray radiation (0.154 nm); θ is the diffraction angle and β is full width at half maximum (FWHM).

Table 1 Summary table of XRD analysis

Samples	Phase	Crystallite size (nm)
N, Fe-TiO ₂ (300 °C)	Anatase	14
N, Fe-TiO ₂ (500 °C)	Anatase	20
N, Fe-TiO ₂ (700 °C)	Anatase & Rutile	46

Fig. 2 shows the morphology of N, Fe-TiO₂ calcined at temperatures of 300 °C, 500 °C, and 700 °C. It is found that all samples have rough surface and agglomerated. The grain size of all samples were estimated in the range of 50 to 170 nm. According to Brinker and Scherer, small particles incline to agglomerate due to high surface energy and draws other particles to coalesce together to form bigger particle size [19].

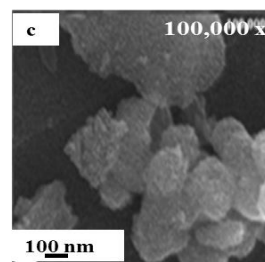
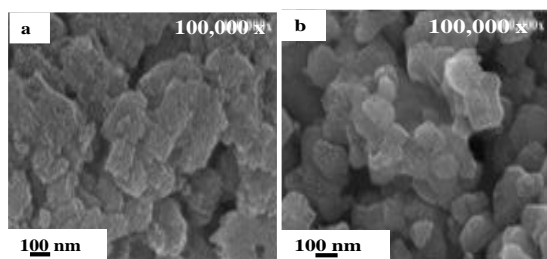


Fig. 2 FESEM image of TiO₂ powders: a) N-Fe-TiO₂ (300 °C), b) N-Fe-TiO₂ (500 °C), c) N-Fe-TiO₂ (700 °C)

Fig. 3 shows the optical properties of N, Fe doped TiO₂ using UV-Vis Spectrophotometer. The values of the light absorption were obtained by extrapolating the steepest slope of the UV-Vis spectra. The intersection point between X-axis and extrapolation line shows the excitation wavelength of the as-prepared samples. Based on the figure, an intense absorption of all samples found at wavelengths from 485 nm to 664 nm which can be assigned to the band gap absorption of N, Fe-TiO₂ due to the electronic transition from the valence band to the conduction band. The extension of absorption wavelength in visible light region may attribute to the increment of calcination temperature from 300 to 700 °C, resulting from crystal growth and crystallinity of N,Fe-TiO₂. Thus, the synthesis parameter such as the calcination temperature is important for optical characteristics as these aspects increase the ability of TiO₂ to work under broader spectrum of light.

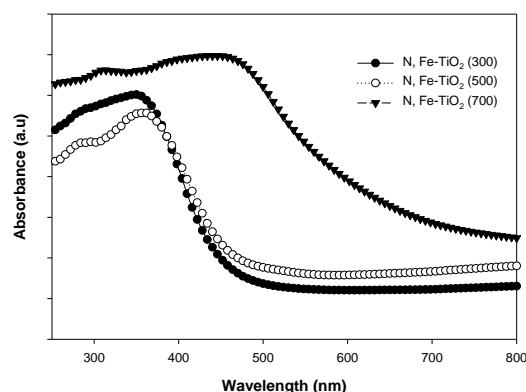


Fig. 3 UV-Vis Spectral of N, Fe-TiO₂ calcined at varies temperature of 300 to 700 °C.

4. Conclusion

In conclusion, N, Fe-TiO₂ were successfully synthesised by using sol-gel method. The XRD pattern shown that calcination

temperatures plays a centre role for phase transformation from anatase to rutile as the temperature increased from 300 to 700 °C. The grain size is also affected when the calcination temperature was increased. Based on UV-Vis result, the increment of calcination temperature broadened the range of response of visible light. Therefore, it is found that the temperature plays an important role towards TiO₂ characteristic.

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