



Hydrothermal Synthesis of Chloride Free Nitrogen Doped TiO₂ Nanoparticles

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In this work, the synthesis and characterization of chloride free nitrogen doped TiO₂ nanoparticles have been undertaken. The chloride-free nitrogen doped TiO₂ nanoparticles were hydrothermally prepared by mixing acidic ethylene diamine solution with titanium tetraisopropoxide followed by heating at 120 and 150 °C for 12 h and 180 °C for 6 h. The resulted solid was isolated, dried, grinded and calcined at 450 °C for 3 h. The samples were characterized using powder X-ray diffraction, UV-visible reflectance and SEM-EDAX methods. The results indicated that the samples consist of a major component of rutile and minor anatase types. The hydrothermal temperature does not affect to the composition of the product. The N-doped in TiO₂ decreases the lattice parameters. The crystallite size of rutile is somewhat bigger than anatase. As expected, all samples are free of chloride.

Keywords: N-TiO₂ Nanoparticles, Titanium tetraisopropoxide, chloride free catalysts, band gap energy.

INTRODUCTION

Naturally, titanium oxide (TiO₂) is present in three crystalline forms, namely rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). The rutile phase is the thermodynamically most stable phase, while the anatase and brookite are the metastable phases [1]. The application of TiO₂ is strongly influenced by its form [2]. The rutile phase is commonly used as a pigment material because of its chemical stability [3], whereas anatase is applied widely in photochemical cells due to its high photoactivity [4]. The TiO₂ rutile phase has a band gap energy (E_g) of 3.02 to 3.24 eV, whereas anatase is about 3.23 to 3.59 eV [5]. The band gap energy of TiO₂ corresponds to the maximum absorption wavelength ranging from 365 to 413 nm (UV region). This is the problem in solar-based TiO₂ applications because only 3 to 5 % of the sunlight is emitted in the UV region [6].

Efforts have been made to improve TiO₂ response to visible light [7]. One of those was by nonmetallic doping. Nitrogen performs as the most effective dopant due to the similarity in size with oxygen atom and has small ionization energy, *i.e.* 1402.3 kJ/mol [8]. Therefore, nitrogen-doped TiO₂ becomes an interesting material to be studied in terms of synthesis, characterization and application [9].

Several methods to synthesize TiO₂ have been introduced, such as sol gel [10], solvothermal [11], thermal decomposition [12] and hydrothermal [13]. The hydrothermal method is the most frequently chosen method in the synthesis of TiO₂, because this method facilitates the reaction at low temperature and produces

high uniformity dispersion of metal doping ion. The mesoporous TiO₂ synthesized using hydrothermal method shows high crystallinity, thermal stability, high surface area and photocatalytic activity. The hydrothermal method was then widely used in N-TiO₂ synthesis [14]. The photoactivity of TiO₂ is affected by the response to light and other physico-chemical characters, such as particle size, crystallinity, and porosity [15]. The TiO₂ photoactivity increases with the decreasing crystallite size. The smaller the size of crystallite, the greater will be band gap energy. This is due to the increasing surface area of the material.

Several types of precursors used to synthesize TiO₂ include TiCl₄, TiCl₃, P25, amorphous TiO₂, titanate hydrate and titanium tetraisopropoxide (TTIP) [16]. The precursor types affect the structure and the size of TiO₂. Nitrogen-doped titanium dioxide (N-TiO₂) can be synthesized using various precursors as Ti and N sources. Ethylenediamine as a source of nitrogen has been used to synthesize N-TiO₂ using hydrolysis method [17]. The N-atom in ethylene diamine may provide an optimal ratio to TiO₂. However, chloride containing species are typically most stable, highest availability and low-cost precursors. Thus, its possible that chloride will be present in the resulting catalysts. Chloride ions have been reported to be absorbed at and hence block the active site of catalysts. As such chloride ions can inhibit a number of catalyzed reactions [18]. Removal of such chlorides can be both difficult and time consuming since requires additional processing. This study was conducted to understand the characteristic of chloride-free N-TiO₂ nanoparticles synthesized by hydrothermal method using titanium tetraisopropoxide and

ethylene diamine as Ti and N sources, respectively at various hydrothermal temperatures.

EXPERIMENTAL

Titanium tetraisopropoxide (TTIP), ethylene diamine, ethanol (96 %) and hydrogen chloride (36 %) were purchased from E. Merck. All the chemicals were used without further purification.

Powder XRD pattern was recorded on Miniflex600 Rigaku XRD using CuK α radiation ($\lambda = 1.54060$ Å). The particle size was determined by using the Debye-Scherrer equation [19]. Anatase (A), rutile (R) lattice parameters and phase ratio were determined by using Rietica suite of program running in LeBail method [20]. The spectrophotometer UV Pharnaspec specular reflectance equipped with halogen light sources was used to study the electronic transition and the band gap energy (E_g) of chloride free N-TiO₂ nanoparticles. The absorption was recorded in the range of 200 to 800 nm with scanning speed of 2 nm/s. The band gap energy was determined by plotting the photon energy (hv) to $(F(R'_{\infty})hv)^{1/2}$. The band gap energy is the magnitude of hv at $(F(R'_{\infty})hv)^{1/2} = 0$, obtained from the linear regression equation of plot. SEM-EDAX was performed using COXEM EM-30AX to determine the surface morphology of chloride free N-TiO₂ nanoparticles and to trace the presence of chloride ion in the samples.

The chloride-free N-TiO₂ nanoparticles was prepared by hydrothermal method as reported in literature [21]. The mixture of titanium tetraisopropoxide and ethylenediamine was heated hydrothermally at 120 °C for 12 h. The obtained solid was isolated and calcined at 450 °C for 3 h. The hydrothermal temperatures (150 and 180 °C) were used to collect another chloride free N-TiO₂ nanoparticles samples.

RESULTS AND DISCUSSION

The powder XRD patterns of chloride free N-TiO₂ nanoparticles indicate a higher degree of crystallinity (Fig. 1). In general, all the sample consist of anatase and rutile type of N-TiO₂. The existences of anatase and rutile are indicated by XRD strong lines positioned at $2\theta = 25.13^\circ$, 25.16° and 25.03° and $2\theta = 27.24^\circ$, 27.24° and 27.15° , respectively. The mol percentage of rutile and anatase phases are presented in Table-1. The presence of anatase phase in the samples remains same at about 18.60 %.

TABLE-1
PERCENTAGE OF RUTILE AND ANATASE
PHASES IN THE CHLORIDE-FREE N-TiO₂ NPs

Hydrothermal temperature (°C)	Rutile (mol %)	Anatase (mol %)
120	81.36(3)	18.64(0)
150	81.44(1)	18.56(0)
180	81.45(1)	18.55(0)

The chloride free N-TiO₂ nanoparticles crystallite size of the calcined sample was calculated based on the full width at a half of the maximum height (FWHM) with the Debye-Scherrer formula (Table-2). The crystallite sizes of chloride free N-TiO₂ nanoparticles samples are increased with the increasing hydrothermal temperature, except for the crystallite size of anatase

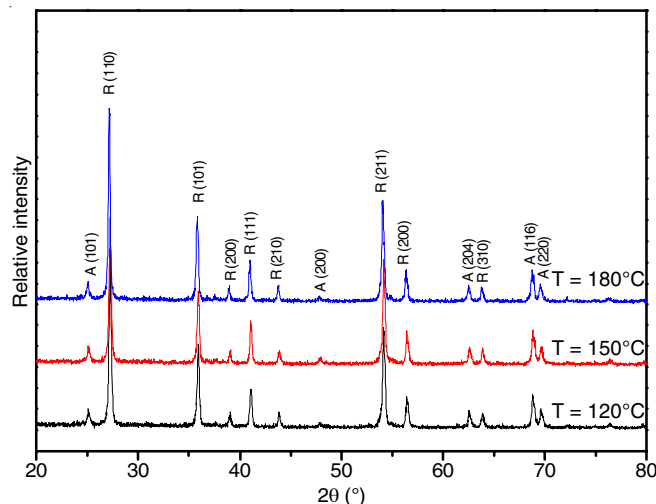


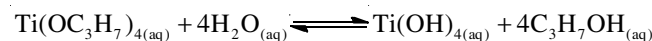
Fig. 1. Powder XRD patterns of chloride-free N-TiO₂ NPs (T = hydrothermal temperature, A = anatase, R = rutile)

TABLE-2
CRYSTALLITE SIZE OF CHLORIDE-FREE N-TiO₂ NPs

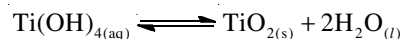
Hydrothermal temperature (°C)	Rutile (nm)	Anatase (nm)
120	38.18	38.20
150	39.58	37.59
180	42.92	37.88

which remain the same. The formation of TiO₂ is resulted by two processes; namely hydrolysis and condensation reactions. In general, the two stages of the reaction can be written as follows:

Hydrolysis:



Condensation:



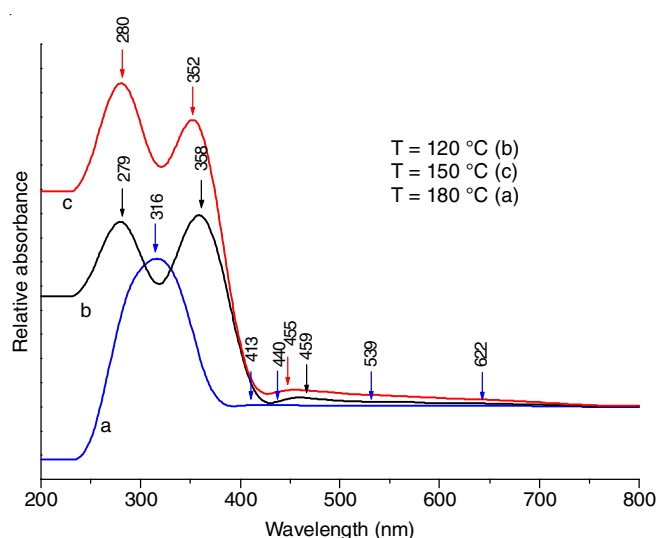
The hydrolysis reaction leads to the formation of nucleus, while the condensation reaction the formation of the nucleus network [22]. The formation of TiO₂ anatase and rutile is determined by both hydrolysis and condensation reactions. If condensation begins before the hydrolysis reaction completed, amorphous TiO₂ and anatase would be formed. All samples indicate the presence of crystalline anatase phase. This means that condensation runs simultaneously with hydrolysis reaction.

The lattice parameters of chloride free N-TiO₂ nanoparticles are listed in Table-3. The lattice parameters determination for rutile were based on the standard JCPDS No. 01-076-0322 with $a = 4.6344$ Å and $c = 2.9919$ Å for rutile, and JCPDS No. 01-083-2243 with $a = 3.7850$ Å and $c = 9.5100$ Å for anatase. The presence of N in the phases is denoted by the smaller value of the lattice parameters compare to standard TiO₂.

The UV-visible method was used to study the shift of absorption area at the visible wavelength. Fig. 2 depicted the relationship between absorbance to wavelength. The shift of electronic transition in chloride free N-TiO₂ nanoparticles synthesized at 120, 150 and 180 °C and calcined for 3 h at 450 °C, where the shift in the sample synthesized at hydrothermal temperature of 150 °C is the largest.

The band gap energy of chloride free N-TiO₂ nanoparticles was determined using the Tauc equation [23]. The plot between

Hydrothermal temperature (°C)	Rutile		Anatase	
	a (Å)	c (Å)	a (Å)	c (Å)
120	4.6140(3)	2.9650(2)	3.8014(6)	9.5326(18)
150	4.5935(4)	2.9627(2)	3.8076(3)	9.4600(9)
180	4.6002(3)	2.9629(2)	3.8121(3)	9.4717(6)
TiO ₂ (JCPDS)	4.6344	2.9919	3.7850	9.5100

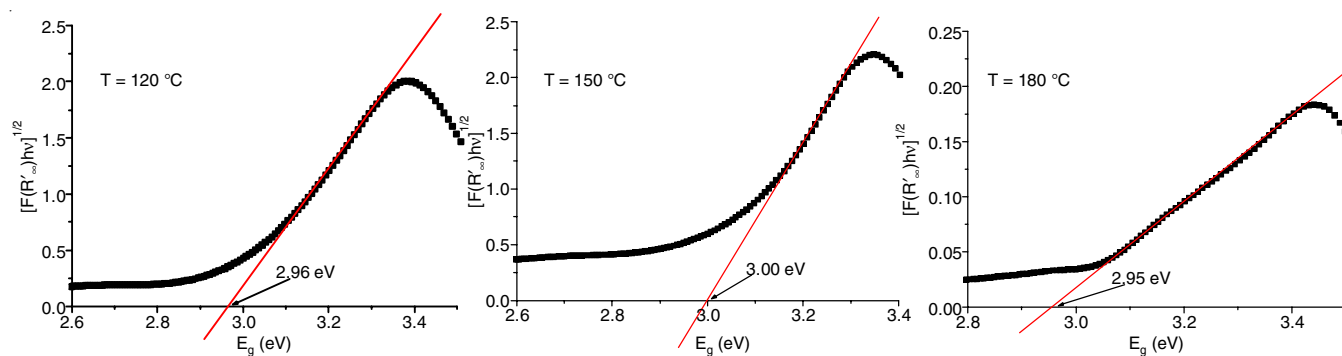
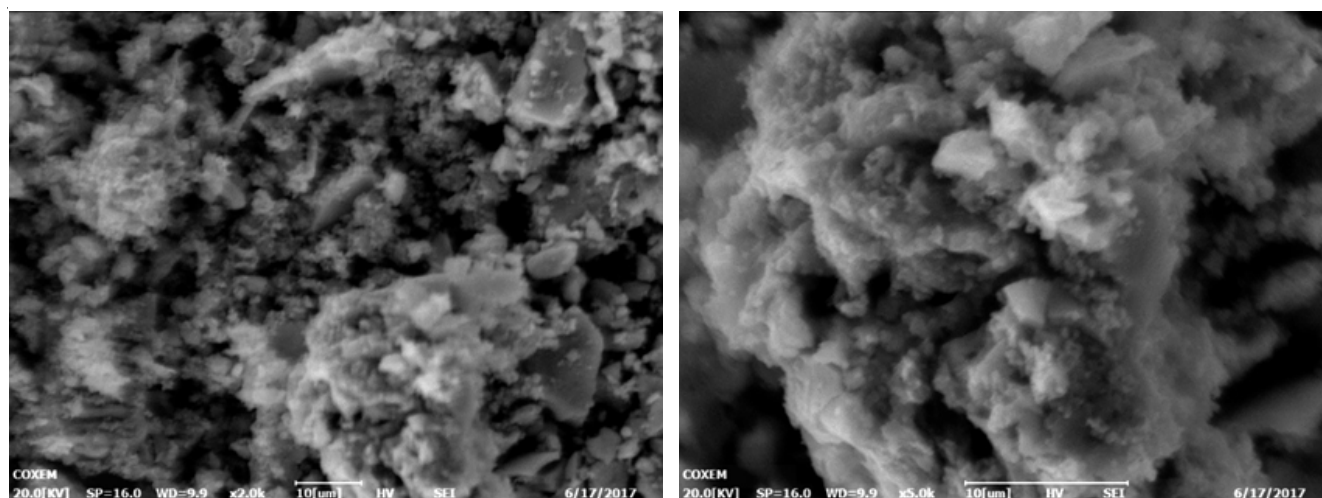
Fig. 2. UV-visible absorption spectra of chloride-free N-TiO₂ NPs

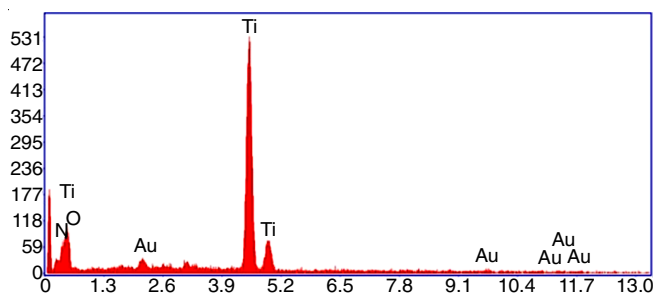
$h\nu$ (eV) versus $[F(R'_{\infty})h\nu]^{1/2}$ (Fig. 3) was used to figure out the band gap energy of chloride free N-TiO₂ nanoparticles. The E_g of chloride free N-TiO₂ NPs are listed in Table-4. The N-doping and the increase hydrothermal temperature lower the band gap energies and suitable for visible absorption.

Hydrothermal temperature (°C)	E_g (eV)
120	2.96
150	3.00
180	2.95

SEM-EDAX measurements provide topographical information on the surface and element composition of chloride free N-TiO₂ nanoparticles. The samples have irregular form with the particle size is in the range of 1 to 10 μm (Fig. 4). The rutile is unable to be distinguished from the anatase based on SEM-EDAX data.

The qualitative elemental analysis on the particle surface of sample was undertaken using EDAX method. The spectra (Fig. 5) confirms the presence of N, O, Ti and Au elements in the sample. With the exception of Au, all the elements is the elements consisting N-TiO₂. The existence of Au is due to Au coating on the surface of sample to improve the conductivity [24]. As expected, the sample is chloride-free.

Fig. 3. Plot of $h\nu$ versus $[F(R'_{\infty})h\nu]^{1/2}$ Fig. 4. Typical SEM micrographs of N-TiO₂ NPs

Fig. 5. EDAX spectra of the chloride-free N-TiO₂ NPs

Conclusion

The chloride free nitrogen doped TiO₂ nanoparticles can be prepared by using hydrothermal method. The products consist of rutile (81.40 %) and anatase (18.60 %) types of N-TiO₂ nanoparticles, which is suitable for working under visible light. The lattice parameters of N-TiO₂ NPs are smaller than TiO₂.

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