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# Synthesis of Nano-Sized Titania Particles by Hydrolysis of Titanium Tetrachloride

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**ABSTRACT**

Nano-sized titanium dioxide $TiO_2$ powder was successfully prepared from its precursor titanium (IV) chloride by a simple and new wet chemical method. $TiCl_4$ were used as precursor in hydrogen peroxide, $H_2O_2$ and ethanol. This solution was then peptized using nitric acid and heated under reflux at 80°C. Their physico-chemical properties were then characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-Ray diffraction (XRD). The TEM results showed that the size of as-synthesized $TiO_2$ nanoparticles were in the range of 7-10 nm. The SEM images showed that the size of nanoparticles increased when the nanoparticles prepared in presence of nitric acid. The SEM images showed that the quality of annealed $TiO_2$ nanoaprticles, increased when the nanoparticles synthesized without nitric acid. The crystal structure of the nanoparticles before and after annealing was done by XRD analysis. It was realized that the rutile phase was formed after heat treatment at 600°C. XRD pattern also showed that the size of annealed $TiO_2$ nanoparticles increased from 20 to 50 nm when the nanoparticles prepared with nitric acid.

**Keyword:** Titanium dioxide; Nanoparticles; Chemical synthesis; Crystal structure; Rutile phase; Anatase phase; Characterization.

## 1. INTRODUCTION

Nanocrystalline semiconductor $TiO_2$ particles are of interest due to their unique properties and several potential technological applications such as photocatalysis, sensors, solar cells and memory devices [1-8]. $TiO_2$ exists in three polymorphic phases: rutile (tetragonal density = 4.25 g/cm$^3$), anatase (tetragonal, 3.894 g/cm$^3$) and brookite(orthorhombic, 4.12 g/cm$^3$). Both anatase and rutile have tetragonal crystal structures but belong to different space groups. Anatase has the space group $I4_1$/amd with four formula units in one unit cell and rutile has the space group $P4_2$/mnm with two $TiO_2$ formula units in one unit cell [8-10]. The low-density solid phases are less stable and undergo transition rutile in the solid state. Among the three above mentioned crystal structures of $TiO_2$, anatase owing to its higher photocatalytic activity is commonly used for photocataly-

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sis [11]. This higher photocatalytic activity is related to its lattice structure. Each Ti atom is coordinated to six oxygen atoms in anatase tetragonal unit cell. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distance in anatase is greater whereas the Ti-O distances are shorter than in rutile. In the rutile structures each octahedron is in contact with 10 neighbor octahedrons, while in the anatase structure each octahedron is in contact with eight neighbors. These differences in lattice structures cause different mass densities and electronic band structures between the two forms of $TiO_2$. The low-density solid phases are less stable and undergo transition rutile in the solid state. The transformation is accelerated by heat treatment and occurs at temperatures between 450 and 1200°C [12]. This transformation is dependent on several parameters such as initial particle size, initial phase, dopant concentration, reaction atmosphere and annealing temperature, etc. [13, 14].

$TiO_2$ nanoparticles can be synthesized using various methods such as sulfate process [15], chloride process [15], impregnation [16], co-precipitation [17], hydrothermal method [18, 19], direct oxidation of $TiCl_4$ [20], metal organic chemical vapor deposition method, etc. [1, 21]. Wet chemical method has novel features which are of considerable interest due to its low cost, easy preparation and industrial viability. Anatase phase are commonly obtained by hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$) [22]. In this study, we report the synthesis of $TiO_2$ nanoparticles system by wet chemical route. Anatase and rutile phases of $TiO_2$ are obtained by $TiCl_4$ precursor. The morphology of the nanoparticles has been characterized by XRD, TEM and SEM analyses.

## 2. EXPERIMENTAL DETAIL

The titania nanoparticles were synthesized by drop wise addition of titanium tetrachloride: $TiCl_4$ (5 mL) in ethanol solution (5 mL). The reaction was performed at room temperature while stirring under a fume hood due to the large amount of $Cl_2$ and HCl gases evolved in this reaction. The resulting yellow solution was allowed to rest and cool back to room temperature as the gas evolution ceased. The suspensions obtained were dried in an oven for several hours at 80°C until amorphous and dried $TiO_2$ particles were obtained. After that 10 mL hydrogen peroxide, $H_2O_2$ was added to the solution. The light yellow colored solution changed to red colored. The total volume of the solution was adjusted to 100 mL by adding ethanol solution. This solution was then peptized using nitric acid (10 mL) and heated under reflux at 80°C for 1 hour in a closed vessel. The obtained powder samples were calcined for 3 hours in a box furnace at temperature 600°C in an ambient atmosphere. The morphology of the as-synthesis and annealed $TiO_2$ nanoparticles were done. X-Ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2θ in the range of 4-85° with type X-Pert Pro MPD, Cu-$K_\alpha$: $\lambda = 1.54$ Å. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV.

## 3. RESULTS AND DISCUSSION

X-Ray diffraction (XRD) at 40Kv was used to identify crystalline phases and to estimate the crystalline sizes. Figure 1(a) shows the XRD morphology of $TiO_2$ nanoparticles and indicates the structure of tetragonal anatase phase. The XRD patterns showed this sample have four sharp peaks 2θ angle at the peak position at 25.2°, 37.7°, 47.8°, 54.1°, 62.5°, 69.4° and 75.5° with (101), (004), (200) , (105), 204), (116) and (215) diffraction planes, respectively are in accordance with the $TiO_2$ anatase phase. It can be seen the peak position at 27.5o corresponds to the plane (110) of rutile form. The mean size of the ordered $TiO_2$ nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the X-Ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg an-

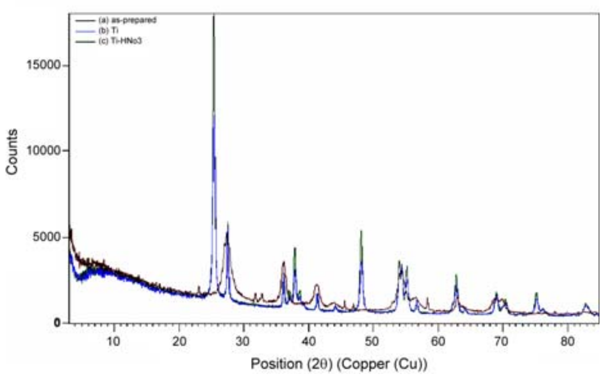


***Figure 1:*** *XRD pattern of $TiO_2$ nanoparticles (a) as-prepared (red line) (b) annealed at 600°C without nitric acid (blue line) (c) annealed at 600°C with nitric acid (green line).*

gle. The mean size of as-prepared $TiO_2$ nanoparticles was 7 nm from this Debye-Sherrer equation.

The crystal structure of the nanoparticles before (red line) and after (blue line) annealing was done by XRD analysis. It is realized that in the rutile phase the size of annealed $TiO_2$ nanoparticles increase from 20 to 50 nm when the nanoparticles prepared with nitric acid (green line).

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of $TiO_2$. These Figures show that high homogeneity emerged in the samples surface by increasing annealing temperature. The results show that with increasing annealing temperature the morphology of the particles changes to the spherical shape and nanopowders are less agglomerated. Figure 2(a) shows the SEM images of the as-prepared $TiO_2$ nanoparticles with sphere-like shaped prepared by wet chemical method. Figure 2(b) shows the SEM images of the annealed $TiO_2$ nanoparticles prepared in presence of nitric acid at 600°C for 3 hours. Figure 2(c) shows the annealed $TiO_2$ nanoparticles prepared in absence of nitric acid. It can be seen that the $TiO_2$ nanoparticles are not agglomerated. In this Figure, the spherical shaped particles with clumped distributions are visible through the SEM analysis. The average crystallite size of annealed nanocrystals increased from 20-50 nm when the particles synthesized in presence of nitric acid.

The transmission electron microscopic (TEM) analysis was carried out to confirm the growth pattern of the particles. Figure 3 shows the as-synthesized TEM image of titanium dioxide prepared by wet synthesis.

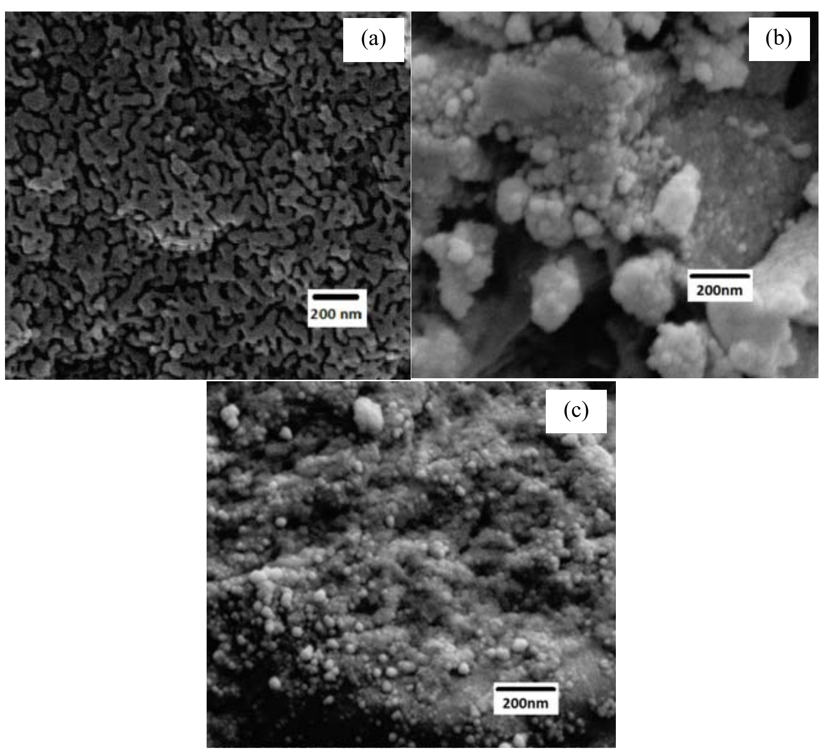


***Figure 2:*** *SEM images of the $TiO_2$ nanoparticles (a) as-prepared (b) annealed at 600°C in presence of nitric acid (c) annealed at 600°C in absence of nitric acid.*

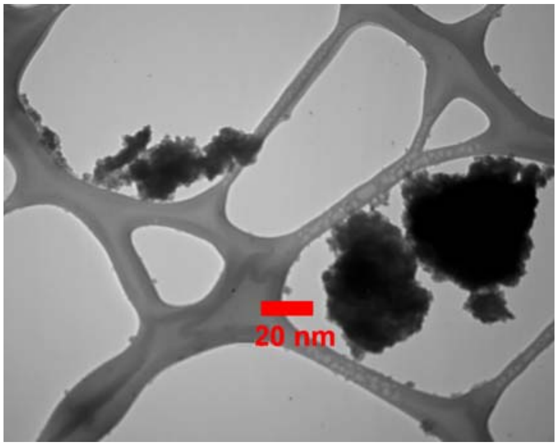


***Figure 3:*** *TEM images of the as-prepared $TiO_2$ nanoparticles.*

The size of as-prepared anatase $TiO_2$ nanoparticles is about 7 nm in diameter.

## 4. CONCLUSIONS

In summary, anatase and rutile $TiO_2$ nanoparticles were successfully synthesized via a simple and new wet chemical synthesis route. Anatase $TiO_2$ was obtained from wet synthesis method. TEM results showed that the size of as-synthesized $TiO_2$ nanoparticles was determined in the range of 7-10 nm. SEM images showed that the size of annealed $TiO_2$ nanoparticles increased from 20-50 nm when the nanoparticles prepared with nitric acid. XRD pattern of $TiO_2$ nanoparticles indicated the structure of rutile phase with annealing process at 600°C. XRD pattern also confirmed the increasing size of $TiO_2$ nanoparticles in presence of nitric acid.

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