

SYNTHESIS AND CHARACTERIZATION OF TITANIUM OXIDE (TiO₂) NANOPARTICLES BY CO-PRECIPIATION METHOD

Mya Hnit¹, Zin Min Myat²

Abstract- In this research, the preparation of photo-catalysts titanium oxide (TiO₂) nanoparticles was firstly synthesized by simple and inexpensive co-precipitation method. The synthesis was carried out at room temperature using titanium tetrachloride (TiCl₄), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂) and ammonia (NH₃) as precursors. The as-prepared particles with different pH level were annealed at 500°C for 2 hrs. The crystallographic structure of TiO₂ nanoparticles were tested by X-ray Diffraction (XRD). It was confirmed that the formation of titanium oxide (TiO₂) nanoparticles anatase phase with an excellent crystalline structure. The surface morphology of titanium oxide (TiO₂) nanoparticles were characterized by using Scanning Electron Microscopy (SEM). According to experimental results, TiO₂ nanoparticles can be used as the electron transporting layers for perovskite solar cells.

Index Terms- Titanium tetrachloride (TiCl₄), TiO₂ nanoparticles, XRD, SEM

(1) INTRODUCTION

The science and technology of nanostructured materials is advancing at a very rapid pace. Nano sciences and technology have the ability to see and to control individual atoms and molecules since everything on earth is made up of atoms. Metals oxide nanoparticles are used in many applications due to their high surface to volume ratio and large bandgap^[1]. Nowadays, the preparation and functionalization of one-dimensional nanostructured materials has become one of the most important roles of the nanotechnology. Metal oxide nanoparticles can be made of titanium oxide (TiO₂) by co-precipitation method. In order to obtain these particles, titanium oxide (TiO₂) particles is required and proposed mainly from the titanium tetra chloride, hydrochloric acid and ammonia used as the starting materials^[2,3]. Generally, nanometer sized metal oxide particles such as TiO₂ have a large surface area per unit mass and have the potential of enhancing physical, chemical and electrical properties compared to the equivalent properties manifested in the bulk form of the material. Titanium oxide (TiO₂) is one of the most promising candidate for relatively low cost, simple manufacture and high-performance new generation of solar cells and also has generated a lot of interest because of its

attractive properties such as wide band gap, high refractive index, high dielectric constant, absence of nontoxicity and also it is considerable interest for both scientific and technical applications. The bulk material of TiO₂ is widely nominated for three main phases of Anatase, Rutile and Brookite. Among them, the TiO₂ exists mostly as Rutile and Anatase phases which both of them have a tetragonal structure and also TiO₂ anatase phase is one of the three main crystalline forms of titanium oxide, with the other two forms known as Rutile and Brookite. Experimental evidence suggests that Anatase is the most thermodynamically stable in the nanocrystalline form while the Rutile phase is more stable in the bulk form. Its known to be a better performing photocatalyst compared to brookite or rutile phase because of its improved charge-carrier mobility and the higher number of surface hydroxyl groups.^[4,5] However, Rutile is a high-temperature stable phase and Anatase is formed at a low temperature. The anatase phase has formed in the temperature range between 400°C -700°C and after 700°C the rutile was formed. Structural properties of TiO₂ depend on a large extend on the deposition technique.

(2) MATERIALS AND METHODS

Experimental Preparation of TiO₂ Nanoparticles

In the present research, titanium tetrachloride (TiCl₄), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl) and ammonia (NH₃) were used as starting materials. All chemical reagents used in our experiments were of analytical grade, commercially purchase from chemical market used as received without purification. Deionized water was used as solvent. TiO₂ nanoparticles have been firstly prepared by using co-precipitation method. Firstly, 20 ml of hydrochloric acid and 80 ml of DIW were dissolved and put in ice-water bath condition. These solutions were mixed together with 20 ml pure solution of titanium tetrachloride (TiCl₄) under 10°C and stirring with magnetic stirrer for 2 hrs at 50°C. Under stirring, the excessive hydrogen peroxide (H₂O₂) was added and it was found that the color of solution was turned from dark red to darker and finally it turned to black liquid. During stirring, ammonia (NH₃) was poured by using drop by drop in the mixture solution until to get a homogeneous solution and adjust pH levels to reach pH 10. When adding ammonia, white sediment is obtained. In the process, with the increase of ammonia, the solution turned dense yellow solution at pH 8 first and finally it changed to bright milky yellow at pH 10. After doing this, the precipitates were put in incubator at 60°C for 24 hrs and then took out and washed with distilled water this sediment to obtain the clear solution. Finally, it was poured the rest of the solution with sediment into micro burette to centrifuge it for 5 mins and then pour out the

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solution from the micro burette and washed distilled water by using ultrasonic dispersion repeat for three times to remove impurities. The sediments were dried at 60°C for 12 hrs and the white powder was obtained. It was heat treated at 500 °C for 2 hrs respectively. Figure 1(a-f) showed the some photographs of sample preparation of titanium oxide nanoparticles. The block diagram of sample preparation was described in Figure 2.

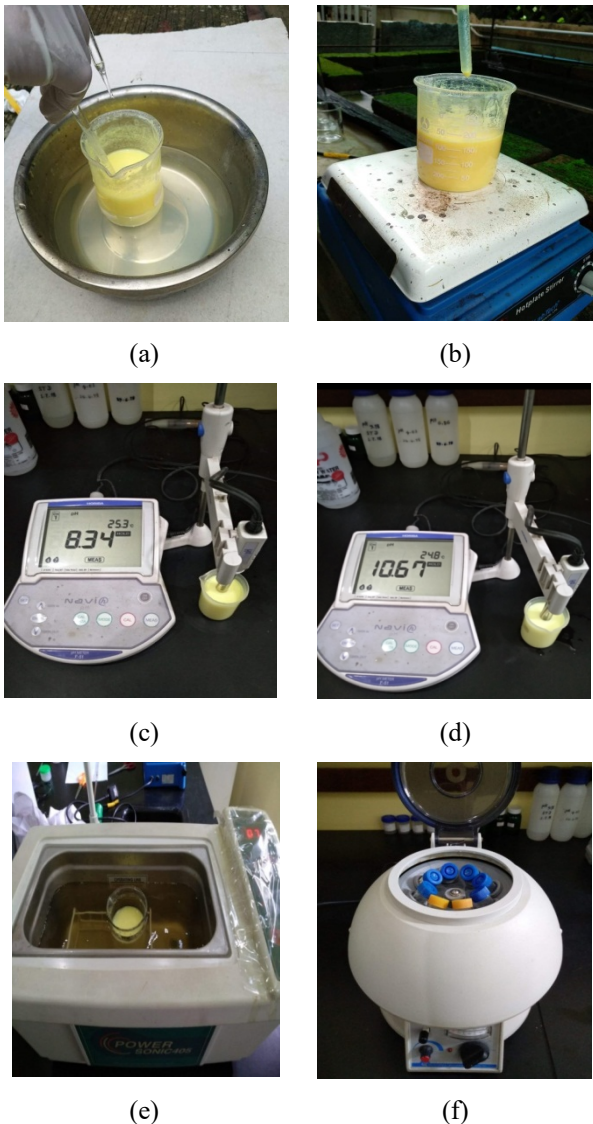


Fig. 1 (a-f) Photographs of sample preparation of TiO₂ nanoparticles at 500°C

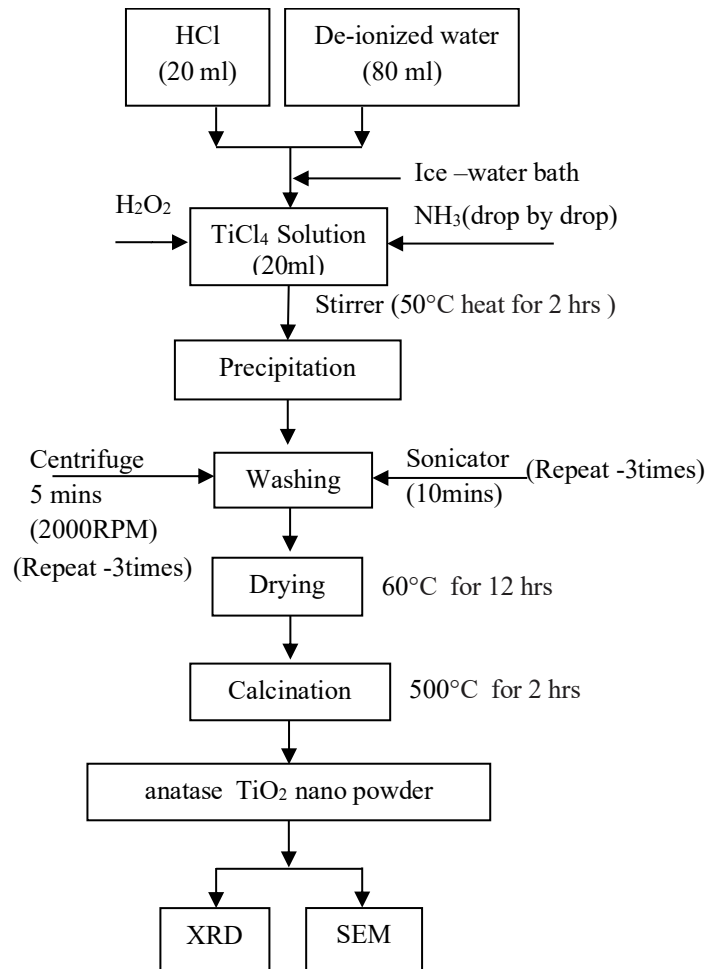


Fig.2 Block diagram of anatase TiO₂ nano powder

(3) RESULT AND DISCUSSION

XRD Analysis of Titanium Oxide (TiO₂) Nanoparticles

The titanium oxide nanoparticles were obtained and XRD technique was used to examine towards studying phase analysis, particle structure, and crystallographic investigation and lattice parameters. The phase analysis of powder was determined by using an X-ray Diffractometer (Rigaku RINT 2000). XRD was performed using monochromatic CuK α radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV (tube voltage) and 20 μA (tube current). Sample was scanned from 10° to 70° in diffraction angle 2 θ with a step-size of 0.02°. The XRD profiles of TiO₂ particles of different temperatures 500°C for pH 8 and pH 10 thus obtained and shown in Figure 3 (a & b). There were extra peaks on pattern of all particles because the results clearly proved the influence of the solvents on the product composition and agreed with the typical TiO₂ pattern of anatase nanoparticles structure. All peaks were found to be well matched with the diffracted of standard. The intensity of (101) reflection was much stronger than that of remaining TiO₂ peaks. The XRD measurement showed that all peaks of TiO₂ were consisted with that TiO₂ standard (JCPDS) file having a tetragonal structure. The broad peaks in XRD patterns indicate fine crystallite size of the TiO₂ particles. The average crystallite size of TiO₂ particles were in the range of 42.39 nm. The

crystallite size was calculated from the XRD peak broadening of peaks using Scherrer's formula.

$$G = \frac{\beta\lambda}{FWHM \cos \theta}$$

where, G = Crystallite size (nm)

β = Scherer's constant ≈ 0.899

λ = Wavelength of copper K_{α} ($\lambda = 1.54056 \text{ \AA}$)

FWHM = Full Width at Half Maximum (rad)

θ_B = Bragg's angle (degree)

By analyzing XRD measurement, all the peak heights and peak positions were in good agreement with library file of XRD machine.

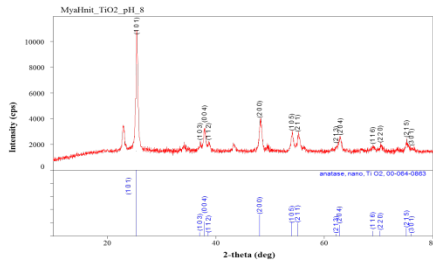


Fig. 3(a) XRD pattern of TiO_2 nano particles (pH 8) at 500°C

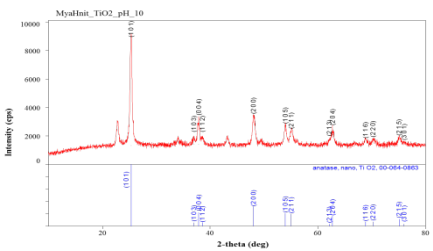


Fig. 3(b) XRD pattern of TiO_2 nanoparticles (pH 10) at 500°C

SEM Analysis of TiO_2 nanoparticles at Different pH values

The microstructural properties of TiO_2 nanoparticles were observed by using Scanning Electron Microscopy (SEM). Materials evolutions were obtained grain size, surface roughness and pore distribution. Figure 4(a-b) showed the SEM photographs of TiO_2 crystalline powder with pH values of pH 8 and pH 10 at process temperatures 500°C . As detail analysis of SEM micrograph, it looked crack-free and little dense. Porosity and grain growth pattern were significantly observed on SEM images. These images were smooth and seemed to be front-oriented and the grain distribution was uniform but some of grain sizes were slightly larger. According to SEM results, these TiO_2 nanoparticles were composed of regular and sphere grains and the average grain size of TiO_2 nanoparticles were found to be $0.15 \mu\text{m}$ with pH 8 and $0.16 \mu\text{m}$ with pH10 at process temperature 500°C .

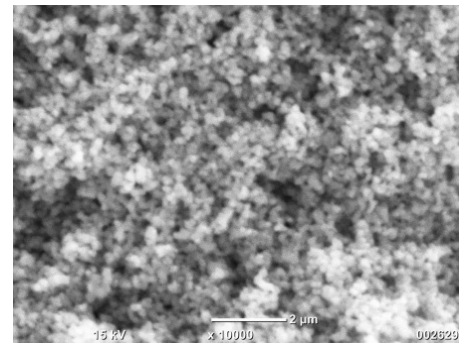


Fig. 4(a) SEM image of anatase TiO_2 nano powder at 500°C (pH 8)

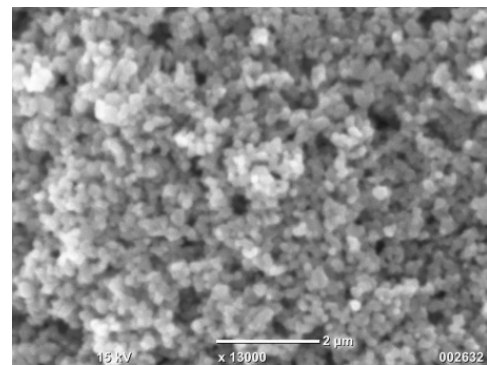


Fig. 4(b) SEM image of anatase TiO_2 nano powder at at 500°C (pH 10)

(4) CONCLUSION

In this research work, the synthesis and characterization of TiO_2 nanoparticles were successfully implemented by co-precipitation method. The average crystallite size of TiO_2 nanoparticles was found to be 42.39 nm . According to XRD analysis, all the peak heights and peak positions were in good agreement with library files of XRD machine. The XRD pattern revealed that these particles were anatase tetragonal structure. From SEM images, SEM analysis was examined to be smooth, uniform, crack free and agglomerated spherical particles of TiO_2 nanoparticles. This suggested that agglomerated grain size decreases with process temperatures. The experimental finding resulted from this research work indicated that the crystal structure, phase formation and surface morphology of TiO_2 particles were influenced by annealing different temperatures. Therefore, these TiO_2 particles can be used as the electron transporting layers for perovskite solar cell.

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