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Synthesization of Nanostructured Titanium Dioxide at Low Molarity of Sol-Gel Process

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Abstract. Titanium dioxide, TiO₂ is one of the semiconductor materials. The aim of this paper is to determine the production of TiO₂ by sol-gel method. The sol-gel method used because this method is quite simple compare to other methods such as dip-coated and refractive sputtering. The parameter will be used in this paper is the concentration. The sol-gel TiO₂ solution then spin coated on the glass substrate to form homogenous and transparent thin film. The thin film was coated at 8 layers to adjust the refractive index characteristics and to get the clear images during characterize by spin coating technique. Other than that, this work also to get the band gap energy similar to the standard bandgap for TiO₂. The optical properties such as absorption and transmittance of TiO₂ can be done by Ultraviolet-visible Spectroscopy (UV-Vis). The changes on the surface morphology were observed using Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FESEM). Based on the result, higher the molarity of TiO₂, the uniformity of the surface morphology, and the energy bandgap is much better. Higher the molarity, the bandgap will be lower with 0.1M (3.78 eV) and its too large compare to the standard value (3.2 eV).

1. Introduction

TiO₂ is a white powder with maximum whiteness and great opacity. TiO₂ can be crystallizing in two forms which is anatase and rutile [1] while the natural polymorph of TiO₂ includes anatase, rutile and brookite[2]. Great opacity of TiO₂ is because of the refractive index. Higher the refractive index, the opacity will be greater. The refractive index of anatase is 2.55 while rutile is 2.73[3]. TiO₂ is also one of the semiconductor materials with a larger bandgap, approximately 3.2 eV and it can absorb UV-light [4].

TiO₂ nanoparticles has a wide range of application such as antireflection coatings for photovoltaic cells and passive solar collectors[5], photocatalytic purification of polluted air or wastewater because it is nontoxicity, high chemical stability, and excellent degradation for organic pollutants[6]. Akira Fujishima in 1967 discovered the properties of TiO₂ as a photocatalyst, including self-cleaning surfaces, and most recently into the area of photoinduced hydrophilicity, which involves not only self-cleaning surfaces, but also antifogging ones[7].

As mentioned before, one of the application of TiO₂ as a catalyst and can absorb only UV light. When photocatalyst TiO₂ absorbs Ultraviolet (UV)* radiation from sunlight, it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by
light. The excess energy of this excited electron promoted the electron to the conduction band of TiO$_2$ therefore creating the negative-electron (e-) and positive-hole (h+) pair. The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available.

TiO$_2$ thin films can be prepared in several ways such as dip-coating, reactive sputtering, chemical vapor deposition (CVD), sol–gel technique[8]. TiO$_2$ also can be coat by different thermal spray techniques: atmospheric plasma spraying (APS), suspension plasma spraying (SPS), and high-velocity oxygen fuel (HVOF) spray process and liquid phase deposition[9]. The sol–gel process involves the formation of inorganic glass from solution and yields high-purity homogenous ceramic material. The nanostructured materials on the basis of a sol–gel approach have exhibited new optical properties of interest in many areas of application such as electroluminescent devices, optical and chemical sensors. For example, the thin films of anatase from nano-sized TiO$_2$ show a very high photocatalytic activity due to large internal surfaces. Nanocrystalline TiO$_2$ can be prepared by a sol–gel route assisted by a complexing agent-assisted sol–gel route. The advantage of nanostructured particles is an enhancement of the surface area, and related properties. Recently, it was revealed that titanium can be bonded to living bone by treatment with alkali followed by heat [10].

2. Methodology

2.1 Materials

All the solution was prepared using spectroscopic grade solvents. Absolute ethanol (100%) was obtained from Aldrich acts as a solvent. Tetra (IV) Isopropoxide, TTIP as a precursor, Acetic Acid Glacial (GAA) as a stabilizer, Triton-X-100 as a surfactant may act as wetting agent detergents, distilled water. All the reagents were used as received.

2.2 Preparation of glass substrate

In this experiment the substrate will be use is microscope glass. The glass substrate is cutting in dimensions of 2 cm x 2 cm. Then, it is treating with acetone two times, methanol two times and distilled water in ultrasonic bath for 10 minutes each. Lastly, the substrate was blow with N$_2$ gas for drying purpose [11].

2.3 Synthesis of pure TiO$_2$ solution by sol–gel method.

Using a sol–gel technique, TiO$_2$ thin film was prepared by mixing tetra (IV) isopropoxide, glacial acetic acid, ethanol, deionized water and triton x-100. In order to investigate the influence of amount of precursor, the amount of tetra (IV) isopropoxide was varies in the molarity for 0.01M, 0.05M and 0.10M. In this technique, tetra (IV) isopropoxide was used as precursor, glacial acetic acid as a stabilizer or chelating agent, ethanol as a solvent and deionised water as a function of adding the oxygen (O$_2$). Triton X-100 used acts as a surfactant to avoid precipitation in solution and at the same time used to increase the conductivity of films. The hydrolysis and the polycondensation of titanium alkoxides proceeds according to the following scheme:

\[
\text{Ti (OR)}_4 + \text{H}_2\text{O} \rightarrow \text{Ti(OR)}_3(\text{OH}) + \text{ROH}
\]

\[
\text{Ti (OR)}_4 + \text{Ti(OR)}_3(\text{OH}) \rightarrow \text{Ti}_2\text{O(OR)}_6 + \text{ROH}.
\]

The reaction stops with the inclusion of two water molecules: Ti (OR)$_4$ + 2H$_2$O → TiO$_2$ + 4ROH.

0.01 Molar equal to 10 ml divided by 1000 ml. To find the value of molar mass of TTiP in 1 ml is by the division of molar mass of TTiP by 1000 ml. To prepare 0.01 Molar in 50 ml TiO$_2$ solution, the amount of TTiP must be multiply by 50ml and then divided by 1000. Since the amount of TTiP was
found, the value of solvent then can be calculated. The amount of solvent comes from the equation below:

Amount of solvent = 50 ml (TiO\textsubscript{2}) – TTiP – GAA – DI water

Since the first chemical is put into the Schott Blue Cap Bottle, the solution will be starting to stir and heat. The time for heating is 1 hour, since the times up heating must be switch off and solution are left in continuous stirring for another 23 hours. The purpose for heating is to break the carbon chain, while continuous stirring is to avoid from agglomeration.

2.4 TiO\textsubscript{2} Thin Films
The TiO\textsubscript{2} solution was coated onto a glass substrate by spin coating method. The spin coating was done in 6000 rpm at 30 seconds. The spin coated was done in 8 layers. Every layer will be heated at 100 °C for 5 minutes. The purpose of heated the thin film is to vaporize the solvent or volatile material and to remove the contamination. The process repeated represents the number of layer of TiO\textsubscript{2} thin film. As prepared, sample was carried to annealing process at 450 °C in 2 hour to restructure the lattice through deformation of atoms.

2.5 Characterization
UV-Vis spectroscopy was measured with spectrophotometer in the range of 300 nm – 800 nm. Particle morphology and composite structure were examined by field-emission scanning electron microscope (FESEM) equipped with an energy–dispersive spectroscopy (EDS). Atomic force microscope (AFM) was used to observe the morphology and measure the roughness of the thin films on glass substrate.

3. Results and discussion

a. Optical properties by UV-Vis.

![Figure 1. UV-Vis spectroscopy for different molarity of TiO\textsubscript{2}](image)

UV–Vis absorption study was carried out in order to characterize the optical absorbance of pure TiO\textsubscript{2} for different molarity. The absorption spectrums of the synthesized pure TiO\textsubscript{2} with different molarity are shown in figure 1. The optical band gap can be estimated by plotting (α*hν\textsuperscript{2}) versus photon energy (hv) based on the relation αhv = A (hv - Eg)n/2 where α is the absorption coefficient, A is a constant, Eg is the band gap and n is the exponent depending on quantum selection rule for a particular material, n = 1 for a direct and n = 4 for indirect bandgap. According to the above relation, the intercept of the
tangent on the photon energy axis corresponds to optical band gap [12]. From the \((\alpha*h\nu)^2\) versus photon energy \((h\nu)\) plots, the optical band gaps \(E_g\) for all the three synthesized samples were estimated and tabulated in Table 1.

\textit{b. Surface Morphology}

Figure 2. AFM result for a. 0.10M, b. 0.05M and c. 0.10M.

Figure 2 shows the AFM results of TiO\(_2\) for different molarity. At low molarity, which is 0.01M the thickness of TiO\(_2\) is only 8.483 nm. The thickness for 0.05M and 0.10M are 58.139 nm and 178.755 nm respectively. The roughness also shows the difference for every molarity. At low molarity, roughness is 1.331 nm, followed by 9.292 nm for 0.05M. At the higher molarity, roughness is 32.264 nm.

The top view for low molarity (0.01M) in figure 2a is not uniform. The gap is very obvious between higher peak and the lower peak. For figure 2b, the top view of the surface is uniform where the gap between higher and lower peak is almost same. For figure 2c, it’s quit uniform because the gap is low between higher and lower peak.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Molarity & Thickness, nm & Roughness, nm & Band gap, eV \\
\hline
0.01M & 8.483 & 1.331 & 3.90 \\
0.05M & 58.139 & 9.292 & 3.84 \\
0.10M & 178.755 & 32.264 & 3.78 \\
\hline
\end{tabular}
\caption{Summarize for AFM and optical bandgap result.}
\end{table}
c. **Surface morphology by FESEM**

![FESEM images](image_url)

**Figure 3.** FESEM result for a. 0.10M, b. 0.05M and c. 0.01M with a magnification x 200,000 at 5 kV power.

FESEM is one of the characterizations to found the particle morphology and the diameter of the particles. Figure 3 shows the detailed FESEM studies on the material indicated that the mean diameter of the nanoparticles, their diameter distribution and tendency to agglomerate are strongly correlated to the experimental parameters, due to the mixing technique by using magnetic. When the solution was not continuously stirred the nanoparticles were irregular in shape and easily formed agglomerates. The temperature of the process strongly influenced the mean diameter of the TiO\(_2\) nanoparticles. Higher temperature of the process resulted in the preparation of TiO\(_2\) nanoparticles with lower mean diameter. It was already investigated that more energy delivered through increase of the temperature influences the reaction rate and more nuclei particles are formed[11]. As a consequence this leads to the preparation of higher number of TiO\(_2\) nanoparticles with smaller diameter.

Figure 3a shows some agglomeration of the particles because the molarity is higher than figure 3b and 3c. The morphology for figure 3b and 3c doesn’t give much comparison because the molarity for both figures is only slightly different. In this study used TiO\(_2\) nanoparticles produced at 60°C with continuous magnetic stirring for 2h. Statistical analysis of the nanostructures revealed a mean diameter of 11nm with the diameter distribution ranging between 10 and 12 nm [12].

### 4. Conclusion

Sol-gel is the simple method to produce pure TiO\(_2\) nanostructured at nano-scale. This solution then coated onto a glass substrate by do the spin coating at 6000 rpm in 30 seconds. For UV-Vis result, it
can be concluded that higher the concentration of the solution, lower the bandgap as shown in Table 1. For AFM, higher the molarity of the solution, the roughness and the thickness will be higher. Lastly, based on the result of FESEM, higher the molarity of the solution, the mean diameter of the particle will be lower. This is might be initial result for future research direction and it’s a part for optimization TiO$_2$ to hybrid TiO$_2$ with metal, to modified the bandgap become wider and can absorb other than UV light.

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