# EFFECT OF HEATING TEMPERATURE ON BROOKITE TIO2 SOL-GEL COATING FOR PHOTO-INDUCED HYDROPHILICITY

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**ABSTRACT:** Brookite has been rarely used and always exits as a by-product of TiO2. Until recently, there are limited studied concerned with the preparation of brookite coating. In this paper, the main objective of producing pure brookite coating from a specially synthesized sol without using solvent for photo-induced hydrophilicity is reported. The TiO2 coatings were deposited on a glass substrate via a spin coating method at various temperatures ($200^0$C, $300^0$C, and $400^0$C) and soaked for 3 hours. Coatings characteristic were evaluated using XRD and Raman spectroscopy. For the photocatalytic and photo-induced hydrophilicity performance, a color degradation technique of methylene blue (MB) and water contact angle measurement (CA) was utilized respectively. The test was done under UV light irradiation for 5 hours. The XRD results revealed a single peak denoted to brookite, B (111) with an orthorhombic structure was formed at 31.9° throughout all temperatures with an average crystallite size of 41 nm to 58nm. Further analysis using Raman spectroscopy also indicated that the deposited TiO2 coatings are brookite. Results of the band gap analysis also proved that the obtained values are in agreement with the value of brookite phase. Thus, it can be confirmed that the TiO2 coatings deposited from the synthesized sol are brookite coatings. It is found that the brookite TiO2 coating deposited at $400^0$C is the best to possess well-balanced properties for self-cleaning application.

**KEYWORDS**: *Brookite; Spin-Coating; Photocatalytic; Hydrophilicity; Self-Cleaning*

## 1.0 INTRODUCTION

Titanium Dioxide (TiO2) can exist in three forms of crystalline phases of either anatase (tetragonal), rutile (tetragonal) or brookite (orthorhombic). In nature, anatase and rutile are the most common while brookite is rare. Among these phases, anatase and rutile can be prepared by several synthetic methods and their various properties have been widely studied [1]. However, a comprehensive report on the preparation of a pure brookite sol-gel coating under laboratory conditions is scarce. Despite the difficulty in producing pure brookite coating, there are reports claimed that brookite phase shows high photocatalytic activity and photo-induced hydrophilicity as compared to anatase and rutile. Twong et al. [2] found that the photocatalytic activity of brookite was enhanced as compared to rutile due to the improvement in its band gap energy by being the most efficient photocatalyst in different compounds decomposition. Eshagi et al. [3] reported that crystallinity can be an important factor in enhancing photoinduced hydrophilicity and photocatalytic activity and those two properties can be enhanced when higher brookite crystallinity was formed as compared to anatase and rutile.

In the recent decade, TiO2 has been intensively used in photocatalytic activities due to the excitation of the semiconductor catalyst under UV light irradiation [4]. Another property that can be measured by exposing TiO2 surface under UV light is its hydrophilicity which is known as photoinduced hydrophilicity [5]. Photo-induced hydrophilicity phenomenon is a mechanism when the formation of the hydroxyl group with TiO2 surface interacts with the presence of UV light [6]. Theoretically, photoinduced hydrophilicity efficiency increases as the hydroxyl group (OH-) increases [7]. The more interaction of the hydroxyl group with the TiO2 surface, the more the water droplet will spread out onto the surface. Thus, the mutual action between the hydrophilicity and the photocatalytic activities will reinforce each other and can be used as a self-cleaning application [8].

In reviewing works related to synthesizing brookite TiO2 sol-gel coating, an important parameter that worth to consider is the solvent. Most work-related to synthesizing brookite sol-gel use solvents in its formulation. However, solvents are reported can give influence on the TiO2 characteristic such as its crystal growth, crystallite size as well as surface morphology [9]. Besides, a solvent is a hazardous organic chemical that comprises toxic properties which can affect human health and environmental pollution [10]. Recently, there are works reported of not using solvent during synthesizing TiO2 sol-gel to obtain a specific phase and crystallite size [11-12]. However, the performance of the photocatalyst activity and photoinduced hydrophilicity of pure brookite TiO2 coating has not yet been reported. Therefore, this work aims to deposit pure brookite TiO2 sol-gel coating from specially synthesize sol (without solvent) as a green route approach for a self-cleaning application.

## 2.0 METHODOLOGY

### 2.1 Preparation of TiO2 Sol

TiO2 sol was prepared by using titanium (IV) isopropoxide (TTiP 97%, Sigma Aldrich), hydrochloric acid (37% HCl) and deionized water. 4ml of TTiP and 64ml of deionized were mixed under continuous stirring for 30 minutes. During the hydrolysis reaction, HCl was added into the solution. The solution was mixed and stirred constantly at room temperature ($25^0$C) using hot plate stirrer for 3 hours. Then, the TiO2 sol was kept for 2 days for the aging purpose.

### 2.2 Preparation of TiO2 Coating

During the deposition, a drop of the TiO2 solution was placed on the upper glass substrate under a centrifugal force with a spin speed of 1800rpm and a dwell time of 30 seconds. After each coating, the glass substrates were dried in air for 30 minutes. Then, the spin coated glass substrates were dried in an oven another 30 minutes at $110^0$C. The TiO2 coatings were heated at various temperatures in the range of $200^0$C to $400^0$C with a heating rate of $5^0$C/min for 3 hours in the furnace.

### 2.3 Material Characterization

XRD (Philips pro PAN Analytical XRD model X pert x-ray diffractometer) was performed to analyze the structural and phase obtained using over a scan range $20^0$-$80^0$ at a rate of $5^0$ per min using Cu K$\alpha$ radiation. Raman spectroscopy (UniRAM-3500) was used to investigate the phase formation and confirm the XRD analysis. The absorbance of TiO2 coating was performed using UV-Vis spectrophotometer (Perkin/Lambada 35). The TiO2 coating was subjected to water contact angle measurement using a contact angle meter. The value of water angle was measured 20 s after droplet is touched the surface of theTiO2 coating.

### 2.4 Measurement of Photoactivity Performance

The brookite TiO2 coating was evaluated through the degradation of methylene blue. The photocatalytic activity of TiO2 materials was evaluated through the removal efficiency of methylene blue. A germicidal UV-C 100 Watt lamp was used as a light source. The distance from the UV light source applied to the surface of the TiO2 coating was fixed at 15cm. The degradation of methylene blue upon UV irradiation was determined by a UV–V is spectrophotometer. The absorbance of residual methylene blue was detected for every 1 hour, 3 hours and 5 hours. The degradation efficiency was calculated using the following equation [11]:

$$n\% = \frac{A_0 - A}{A} \times 100\% = \frac{C_0 - C}{C} \times 100\% \tag{1}$$

where

$A_0$ represents an initial absorbance of methylene blue solution, A represents the changed absorbance of methylene blue solution, $C_0$ represents the initial concentration of methylene blue solution and C represents the reaction concentration of methylene blue solution.

As concern of the study to its hydrophilic properties, the contact angle of water on the surface of the brookite TiO2 coating was examined using a contact angle meter. The experiment was performed at room temperature and a germicidal UV-C 100 Watt lamp was used as UV light irradiation. Then, the water droplet change on the surface TiO2 coating was observed for 1, 3 and 5 hours.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Analysis on Phase and Crystallite Size

The XRD data were analyzed for its phase presence and crystallite size. Figure 1 shows the XRD pattern of the deposited TiO2 coating at various temperatures ranging from $200^0$C to $400^0$C. As seen, only a single peak emerges at 31.9° and can be implied to the characteristic of a brookite phase B (111) (JCDPS No: 00-029-1360). The XRD result indicates that the deposited coatings are consist of pure brookite coating. The effect of temperatures on the brookite intensity is insignificant. This finding is also in agreement with the work of Komariah et al. [13], which had also produced TiO2 thin film with a single phase orthorhombic brookite B (111) via spin coating.

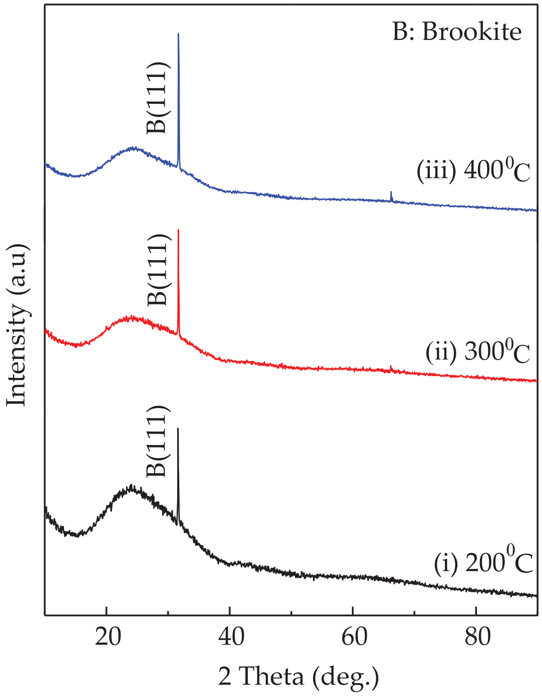


Figure 1: XRD pattern of the deposited TiO2 coating at temperatures ranging from 200⁰C to 400⁰C

Figure 2 displays the Raman spectrum of the deposited TiO2 coatings ranging from 100cm$^{-1}$ to 800cm$^{-1}$ at various temperatures (200⁰C to 400⁰C). It can be seen that the Raman bands of brookite appear at 245cm$^{-1}$, 322cm$^{-1}$ and 364cm$^{-1}$. This observation agrees with Zhao et al. [14], findings where Raman bands of brookite appear at ~245cm$^{-1}$, ~320 cm$^{-1}$, and ~366 cm$^{-1}$. It can be observed that the Raman band of brookite is slightly shift due to size-induced phonon confinement [15]. Also, the intensity of the Raman band of brookite was observed to be higher as heating temperature increased. This can be attributed to the increasing crystallite size produced resulted in improving the crystalline quality of brookite [16]. Thus, further characterization with Raman spectra also proved the existence of pure TiO2 brookite phase throughout all temperatures

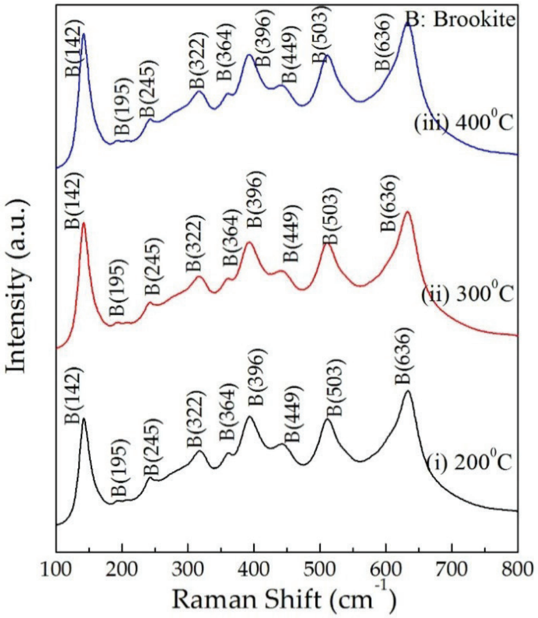


Figure 2: Raman spectrum of TiO2 coating at temperatures ranging from200$^0$C to 400$^0$C

Figure 3 shows the optical band gap graph of the deposited TiO2 coating at various temperatures ranging from 200$^0$C to 400$^0$C. The band gap values are determined by plotting a straight line from the curve line until it reached the x-axis. The value of the band gap, can be obtained by taking the intersection of the extended line with the x-axis and calculated using Tauc's plot equation [13]:

$$(\alpha hv)^n = \mathrm{B}(\mathrm{hv} - \mathrm{Eg}) \qquad (2)$$

where

$\alpha$ is the absorption coefficient (cm$^{-1}$), B is the gradient of the Tauc curve and the exponent n is referred on transition whether 1/2 for indirect transition or 2 for a direct transition. Therefore, as seen in Figure 3, the energy band gap of the deposited TiO2 coatings are found to be 3.44 eV, 3.38 eV, 3.3 eV for temperatures of 200$^0$C, 300$^0$C and 400$^0$C respectively. Interestingly, these values are also aligned to the band gap energy of brookite TiO2 as it falls within the range of 3.3 to 3.48 eV [13].

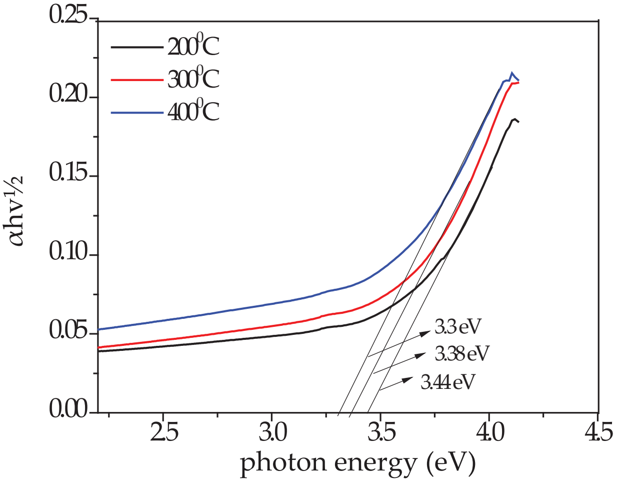


Figure 3: The optical band gap of brookite TiO2 coating heated at temperatures ranging from 200⁰C to 400⁰C

The crystallite size of the brookite TiO2 coating is calculated using Scherrer's equation [11]:

$$L = \frac{0.94\lambda}{\beta \cos(\theta)} \tag{3}$$

where

$\lambda$ is the wavelength of X-ray (Cu K$\alpha$ = 0.154056 nm), $\theta$ is the diffraction angle and $\beta$ is the half peak of maximum intensity which is recognized as FHWM values. Table 1 shows the crystallite size of brookite TiO2 heated throughout all temperature ranging from temperatures of 200⁰C to 400⁰C produced crystallite sizes of 41.07 nm, 46.92 nm and 58.44 nm, respectively. The crystallite size is found to increase as the temperature increase. The influence of temperature on promoting the growth of crystallite size has been reported by Lin et al. [17].

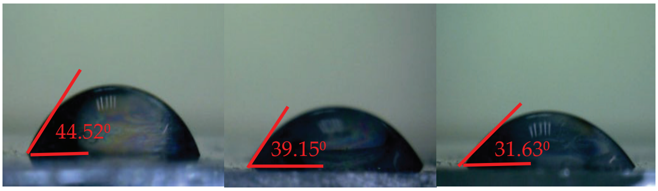
Table 1: Crystallite sizes for TiO2 coating heated in the range of 200⁰C-400⁰C

| Heat Treatment (⁰C) | Position 2 Theta (deg.) | FHWM [⁰2Th.] | Crystallite size, d (nm) |
|---|---|---|---|
| 200 | 31 | 0.2 | 41.07 |
| 300 | 31 | 0.18 | 46.92 |
| 400 | 31 | 0.14 | 58.44 |

Based on the above findings, it can be concluded that all results from the XRD, the Raman and the optical band analyses, confirmed that the deposited sol-gel coatings are pure brookite coatings. The band gap value of the brookite TiO2 coatings, however, were found to decrease inversely with the brookite crystallite size. The lower band gap energy of the deposited brookite TiO2 coatings can be attributed to the quantum size effect [18] as well as temperature effect. This finding is also in agreement with the work of Arier and Tepehan et al. [19] in which increasing temperature caused the band gap values to decrease.

## 3.2 Hydrophilic Property

Figure 4 shows the water contact angle (CA) values of the deposited brookite TiO2 coating at various temperatures from 200$^0$C to 400$^0$C. As seen in the figure, the CA decrease from 44.5$^0$ to 31.63$^0$ as the temperature increase from 200$^0$C to 400$^0$C. The value of CA obtained is dependent with increasing crystallinity of brookite [20]. The higher crystallinity of brookite gave the lowest value of CA. Interestingly, all CA's values obtained are below 90$^0$ indicating that the deposited brookite coatings are hydrophilic [21]. The lowest CA is found for the brookite TiO2 coating deposited at 400$^0$C.



(a) (b) (c)

Figure 4: Image of the CA on the deposited brookite TiO2 at various temperatures of (a) 200°C, (b) 300°C and (c) 400°C

## 3.3 Brookite Photoactivity Performance

### 3.3.1 Photocatalytic Activity

Figure 5 shows the percentage of the methylene blue degradation (MB) of the brookite TiO2 coating measured at various temperatures from 200$^0$C to 400$^0$C. As seen in the figure, the percentage values of the MB increase as the temperatures increase. At 200$^0$C, the MB degradation rate is 88.78% while at 300$^0$C the MB degradation rate is 90.56%. At 400$^0$C, the MB degradation rate is the highest which is 93.94%. The higher photocatalytic efficiency for the brookite TiO2 coating deposited at 400$^0$C can be related to its larger crystallite size. Nandiyanto et al. [22], also suggested in his work that the rapid degradation of the methylene is observed for the largest crystallite size.

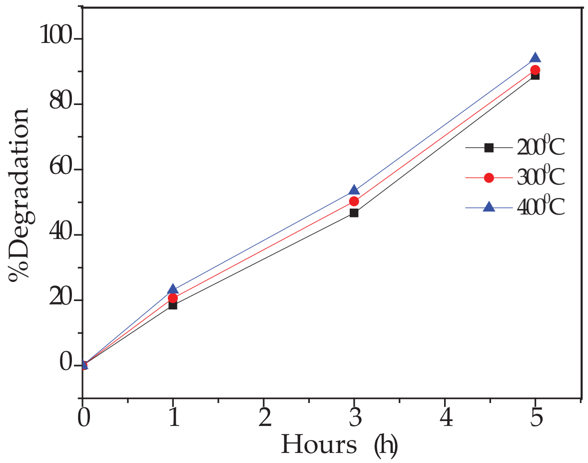


Figure 5: Percentage of MB degradation of the deposited brookite TiO2 coating at temperatures ranging from 200⁰C to 400⁰C

### 3.3.2 Photo-Induced Hydrophilicity Activity

Figure 6 displays the values of the CA as a function of UV light irradiation time for the brookite TiO2 coating at temperatures ranging from 200⁰C to 400⁰C. It can be seen that all values decrease as the irradiation time and the temperatures increase. At 200⁰C, the CA value is 23.85⁰ while at 300⁰C its value is 20.30⁰. At 400⁰C, the value obtained is 15.21⁰. The higher photoinduced hydrophilicity efficiency of brookite TiO2 heated at 400°C due to its higher hydroxyl group content (OH) of brookite TiO2 coating obtained. This result is in same agreement by research from Simonsen et al. [23], who reported that increase in the hydroxyl content on the surface of TiO2 films enhances photoinduced hydrophilicity activity. Thus, it can be concluded that the hydrophilic of brookite TiO2 coating heated at 400⁰C reduced more quickly than brookite TiO2 coating heated at 200⁰C and 300⁰C. As a result, the water contact angle of brookite TiO2 coating also became lower. Yu et al. [24], also reported that increase in the amount of OH groups influences not only the photocatalytic activity but also the polar properties and hydrophilicity of the surface. Therefore, the brookite TiO2 coating deposited at 400⁰C possesses higher photo-induced hydrophilicity activity due to the lowest value of the CA [25].

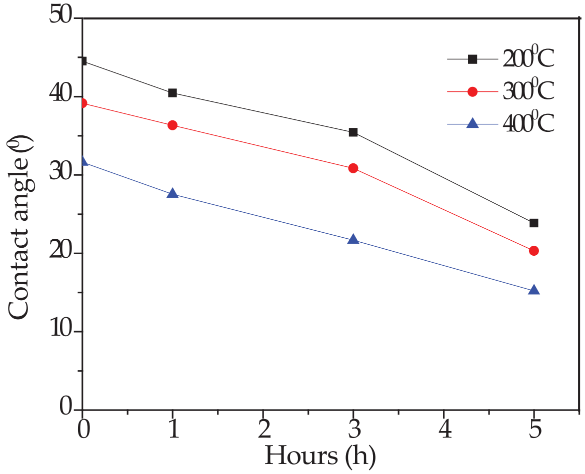


Figure 6: The CA values under UV irradiation of brookite TiO2 coating heated at temperatures ranging from 200⁰C to 400⁰C

## 4.0 CONCLUSION

Pure brookite TiO2 coatings were successfully fabricated from specially synthesize sol using green route approach via spin coating. XRD analysis showed the coating was a single phase of orthorhombic brookite structure. Raman spectroscopy analysis also indicated that the deposited TiO2 coatings are brookite. The band gap analysis also shown that the values obtained are within the brookite range of 3.3 eV to 3.4 eV. Thus, it can be concluded that the deposited TiO2 coatings produced are pure brookite of B(111). The average crystallite sizes obtained for the brookite TiO2 coating heated at 200⁰C, 300⁰C, and 400°C are 41.07nm, 46.92nm and 58.44nm, respectively. The lowest value of the contact angle is 31.63° for the brookite coating deposited at 400⁰C. The brookite TiO2 coating produced at 400⁰C also showed the highest photocatalytic and photo-induced hydrophilicity activity. Thus, the brookite coating deposited at 400⁰C is preferable for self-cleaning application due to its superior photocatalytic and photo-induced hydrophilicity activity.

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