HEAT TREATMENT TEMPERATURE INFLUENCE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF BROOKITE TiO_2 THIN FILM SYNTHESIZED USING GREEN SOL-GEL ROUTE

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ABSTRACT: Alcoholic solvents have disadvantages for the environment and the human body. Brookite film was deposited via green sol-gel route (without the use of any alcoholic solvent), in combination with different heat treatment temperatures, in order to study the effect of heat treatment temperature on structural and optical properties. Different heat treatment was studied at 200°C and 300°C. Brookite film formation was evaluated with X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), UV-Vis spectrometer and water contact angle measurement. X-ray diffraction (XRD) analysis revealed the formation of brookite (111) and (023) at 200°C and 300°C with a crystallite size of 47 nm and 58 nm, respectively. FTIR analysis also revealed Ti-O-Ti bonding at 400–800 cm^{-1}. The band gap energy was 3.40 eV (200°C) and 3.37 eV (300°C). The water contact angle was 19.64° at 200 °C and 13.50° at 300°C, respectively. Therefore, via this green sol–gel route, a lower heat treatment temperature of 200°C was more preferable for the formation of single brookite compared to the common TiO_2 sol formulation (with solvent) that required a high heat treatment temperature. Brookite was produced with a lower band gap and contact angle that contributed to better photocatalytic activity.

KEYWORDS: *Brookite Thin Film; Heat Treatment Temperature; Sol-Gel; Spin Coating; Alcoholic Solvent*

1.0 INTRODUCTION

Brookite is one type of titanium dioxide, TiO_2 polymorph besides anatase and rutile. Brookite is now gaining more interest in the photocatalytic sector because of its excellent results. In previous, considerable attention has been mostly focused on anatase and rutile which are historically known as good candidates for photocatalytic activity. Brookite is the least reported and is tough to synthesize in pure form under lab scale and present as a by-product [1]. Brookite is found to be more active in photocatalytic activity than anatase and rutile [2-3]. For instance, Kandiel et al. [4] also stated that the brookite (1.0×10^{-3} mol l^{-1}) showed higher performance in photocatalytic hydrogen evolution activity compared to pure anatase (0.9×10^{-3} mol l^{-1}) nanoparticles. Tran et al. [2] reported that brookite (~70%) exhibits higher photocatalytic activity for the degradation of cinnamic acid (CA) under sunlight and high pollutant loading compared to anatase (~60%) and rutile (~50%). Further work is deemed necessary to explore the brookite's advantages and to better understand its potential performance.

For the brookite films synthesis, a variety of preparation methods have been applied such as dip coating [5], spin coating [6], chemical vapor deposition [7], pulsed laser deposition [8], vapor phase [9] and spray pyrolysis [10]. Among these techniques, sol–gel spin coating is one of the simple, cost-effective, fast, good homogeneity methods suitable for thin film deposition on different substrates [11-12]. Common TiO_2 formulations use precursors, solvents, catalysts, or additives in the sol–gel process. However, long term exposure to alcoholic solvents such as diethylene glycol, phenols and alcohol can be hazardous to the environment and human bodies, especially in respiratory and thyroid functioning [13]. In an effort to embark on green technology practice, this study focused on studying TiO_2 synthesis using a green so–gel route where the sol formulation is prepared without the use of any alcoholic solvent. To date, research conducted on brookite synthesis via common TiO_2 formulation has shown that the structural and optical properties of the produced brookite are affected by the heat treatment temperature within the range of 400°C to 500°C.

In reviewing the structural characteristics of brookite that were produced with the presence of alcoholic solvent, it was shown that heat treatment temperature had affected the phase orientation and crystallite size of brookite thin film formation. The spin coating method (with ethanol as a solvent) was used to produce nanobrookite thin films (211) with a crystallite size of 4.1–11.9 nm at a heat treatment temperature of 450°C [6]. While, Komaraiah et al. [14] obtained brookite thin films (110), (111) and (023) (via the spin coating method using ethanol in the sol formulation) with a crystallite size of the brookite thin films of 67 nm and 54 nm when heated at 400°C and 500°C, respectively. Also, Novotna et al. [15] reported a brookite film formation with a crystallite size of 50 ± 10 nm by the sol–gel method heated at 500°C in the presence of propanol and acetyl acetone. Thus, it can be observed that the higher the temperature of the heat treatment, the lower the crystallite size.

Heat treatment temperature has also influenced the optical properties of brookite film. Arier and Tepehan [6] reported that nanobrookite thin films possessed band gap energies in range of 3.44 eV and 3.51 eV when heated at 450°C. While, Komaraiah et al. [14] produced brookite thin films with high transparency (97%) at wavelength of 405 nm and band gap energy of 3.30 eV at 400°C and 3.48 eV at 500°C. It should be noted that when the heat treatment temperature is increased, the band gap energy increases.

Next, focusing on the hydrophilicity, Bellardita et al. [16] had obtained brookite films with water contact angle of 10° when heat treatment was conducted at 400°C indicating that the film had high hydrophilic properties. However, Novotna et al. [15] observed a similar water contact angle (~10°) of brookite thin films when heat treatment is carried out at 500°C. Bellardita et al. [16] claimed that the water contact angle in the films is influenced by many factors, such as crystalline structure, composition, surface roughness, amount of –OH. Consequently, in relation to structural and optical formation, it is important to know the effect of heat treatment temperature on the water contact angle properties of the brookite film.

In summary, heat treatment temperature has shown a significant impact on the structural, optical, and hydrophilicity properties of brookite thin films developed with a common TiO_2 sol formulation. Nevertheless, there is no report yet on the analysis of the effect of heat treatment temperature on brookite thin film's structural, optical, and hydrophilicity properties by using the green sol-gel method. Therefore, it is essential to study how the heat treatment temperature influences the structural, optical, and hydrophilicity properties of brookite thin films synthesized by the green sol–gel route spin coating process that will contribute to better photocatalytic activity.

2.0 EXPERIMENTAL

2.1 Synthesis of Brookite Thin Films

In preparing the TiO_2 sol, 0.2 M of titanium (IV) isopropoxide (TTIP, 97%, Sigma Aldrich) and 64 ml of deionized water (DI) were mixed together. The TTIP was added drop by drop (1 drop / minute). Then, 0.4 ml of hydrochloric acid (HCl, 37%, Merck) was added to the solution. The solution was stirred for 3 hours. Then, the solution was kept aging for 48 hours.

For the spin coating process, 90 µℓ of sol was placed on the glass substrate. The spin speed was constant used at 1500 rpm for 30 seconds as mentioned in the previous study [17]. The spin coating process was repeated 2 times of spinning. The brookite thin films were dried in an oven at 110°C for 1 hour. Finally, the brookite thin films were heat-treated at 200°C and 300°C for 3 hours at a rate of 5°C/min.

2.2 Characterization of Brookite Thin Films

Structural properties of the brookite thin films were examined with X-ray diffractometer (XRD) PANalytical X'PERT PRO MPD Model PW 3060/60. The Scherrer's formula is applied to calculate the crystallite size [17]:

$$L = \frac{\mathrm{k}\lambda}{\beta\,(2\theta)\cos\theta} \tag{1}$$

where L is the crystallite size (nm), K represents a constant, 0.94, λ represents the wavelength of X-rays, θ represents diffraction angle and β is the full width at half maximum (FWHM). FTIR analysis was run with JASCO FT/IR-6100. For the FTIR analysis, the brookite thin film was benchmarked to commercial brookite powder, Titanium (IV) oxide, brookite nanopowder (99.99%, Sigma Aldrich). The optical absorption of brookite thin films were measured by the Lambda 35 UV-Vis spectrometer, Perkin Elmer with wavelength ranges of 200 – 1100 nm. The band gap of the brookite thin films was calculated with the Tauc plot method. The hydrophilic property of the thin films was determined by measuring the water contact angle of distilled water droplet with Image J software.

3.0 RESULTS AND DISCUSSION

3.1 Structural Analysis

Figure 1 shows the X-ray diffraction (XRD) pattern of brookite thin films heated at different temperatures. XRD patterns show that the brookite (JCPDS: 84-1750) is identified at an angle of 31.7° and 66.2° corresponding to the lattice planes (111) and (023), respectively, for the thin film heated at 200°C. At 300°C, the brookite is only detected at an angle of 31.7° which corresponds to the lattice plane (111). The crystallinity of brookite decreased with the increased heat treatment temperature due to less number of peaks observed. Brookite crystallinity may have decreased due to the thermal stability and thermodynamically metastable nature of brookite at higher temperatures (650°C) [17-18]. Li et al. [19] also observed a decrease in the amount of brookite with an increase in the amount of rutile when the heat treatment temperature increased from 200°C to 400°C; until the brookite crystal peak was not identified at a heat treatment temperature of above 400°C. Here, the presence of brookite as a transition phase was due to the fact that brookite was more thermodynamically stable than rutile at lower temperatures. The XRD patterns of this study showed a similar trend to Komaraiah et al. [14] where brookite peak intensity decreased as the temperature of heat treatment increased from 400°C to 500°C. Yet, Komaraiah et al. [14] deposited a brookite thin film via spin coating with the existing ethanol as a solvent in the TiO_2 sol formulation.

Furthermore, the decreased brookite crystallinity at higher heat treatment temperatures is also due to the TiO_2 sol formulation used being free from alcoholic solvents. During the sol-gel method, an alcoholic solvent is commonly used to reduce the hydrolysis and condensation rates. Thus, in this work where no alcoholic solvent was used, a higher rate of hydration and condensation occurred during the processing, which hence contributed to lower crystallization as observed in the diffraction pattern.

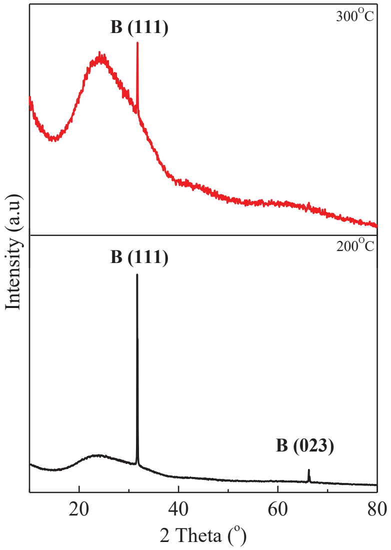


Figure 1: XRD pattern of brookite thin films heated at different temperature

Table 1 shows the structural properties of brookite thin film obtained from XRD analyses. Based on the table, increased heat treatment temperature shows decreased in the full width at half maximum (FWHM) values and increased crystallite size of brookite thin films. The crystallite size is only obtained for the dominant peak in the brookite peak (111). The crystallite size at 200°C is 47.9 ± 19.9 nm and at 300°C is 58.4 ± 12.0 nm. Chen et al. [20] described the same observation by which increased heat treatment temperatures from 250°C to 900°C had shown increased crystallite size from 6.8 to 22.7 nm due to the thermally encouraged brookite crystallite development. At higher temperatures, the rate of the deposition reaction increases and the crystallites grow faster, resulting in a larger size.

Table 1: The summary of structural properties of brookite thin film obtained from XRD analyses

Temperature (°C)	Peak position (2theta)	d-spacing (Å)	FWHM	Crystallite size (nm)
200	31.74	2.817	0.1800	47.9
300	31.73	2.819	0.1476	58.4

Figure 2 shows the FTIR spectra of a brookite thin film heated at different temperatures. The observed transmittance bands in the range of 400–800 cm^{-1} were assigned to the stretching vibration of Ti-O and/or Ti-O-Ti bonds [21–22]. The transmittance band in the range of 1532–1693 cm^{-1} was assigned to an O-H bending mode [22]. Also, the transmittance band in the range of 3356–3363 cm^{-1} indicated the stretching vibration of the surface hydroxyl group or adsorbed water on the surface of the TiO_2 sample [21-22]. The intensities of the transmittance bands 1532–1693 cm^{-1} and 3356–3363 cm^{-1} increased as the heat treatment temperature increased. Similar findings by He et al. [23] where a reduction in the absorbance intensity of these superficial hydroxyl groups (3356–3363 cm^{-1}) occurred with an increase in the heat treatment temperature. Cetin et al. [24] also observed that the intensity of the peaks related to water absorption was decreased by an increase in annealing temperature. This is due to the elimination of O-H during the heating process, possibly by hydrogen diffusion out of the crystal and oxidation of Ti^{3+} to Ti^{4+}, proceed concomitantly [25].

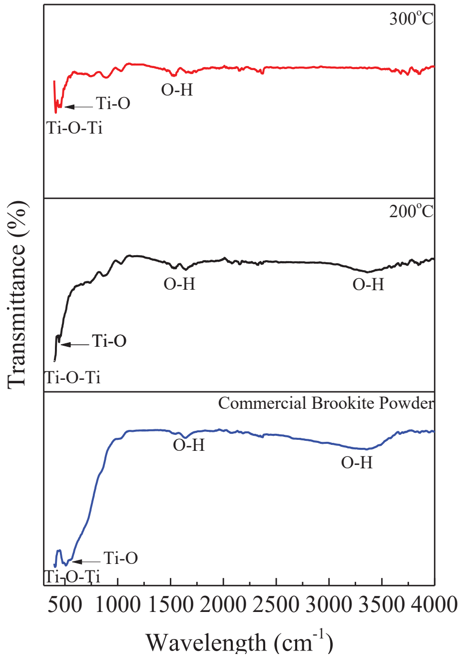
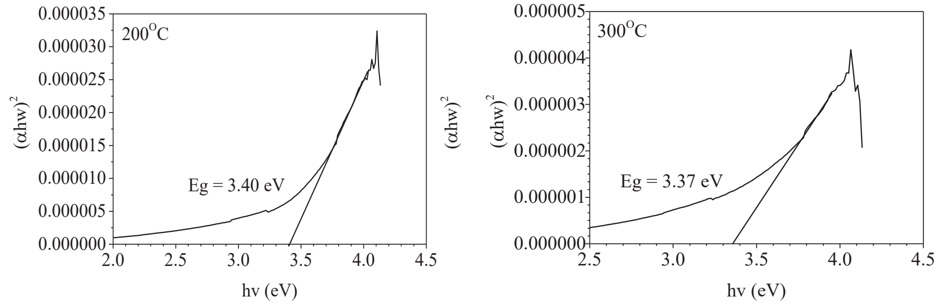


Figure 2: FTIR spectra of brookite thin films heated at different temperature

Furthermore, decreased of brookite crystallinity at higher heat treatment temperature is also due to the TiO_2 sol formulation used was free from alcoholic solvents. In common, alcoholic solvent attend to decrease the hydrolysis and condensation rate during the sol-gel method. Thus, in this work where no solvent was used, a higher rate of hydration and condensation is expected during the processing, which hence contributed to the lower crystallization as observed in the diffraction pattern.

3.2 Optical Analysis

Figure 3 shows the band gap energy of the brookite thin film heated at 200°C and 300°C. Figure 3 (a) shows the band gap energy of brookite thin film was 3.40 eV heated at 200°C. The band gap energy of brookite thin film at 300 °C is shown in Figure 3 (b) to be 3.37 eV. This band gap value shows the characteristic of the brookite which is in range from 3.10 to 3.40 eV [26]. This result shows that an increase in heat treatment temperature has resulted in a brookite film with a decreased band gap energy. When a high heat treatment temperature is applied, the crystallite size will have reduced and will have produced a higher number of surface dangling bonds [27]. The formation of dangling bonds created some types of defects in the defects in the highly polycrystalline solids. With an increasing number of dangling bonds and defects, the concentration of localized states in the band structure also increased. Therefore, an increase in the heat treatment temperature of the films may cause an increase in the energy width of the localized state, thus decreasing the optical energy gap.



(a) (b)

Figure 3: Band gap energy of the brookite thin film heated at (a) 200°C and (b) 300°C

3.3 Hydrophilicity Analysis

Figure 4 displays the water contact angle on the surface of brookite thin films heated at different temperatures. The surface of brookite thin films at 200°C and 300°C were observed to have hydrophilic properties with a contact angle of 19.64 ± 0.34° and 13.50 ± 1.63°, respectively. These contact angles were more hydrophilic compared to anatase and rutile [3]. Mills and Crow [28] had reported similar finding where titania films become more hydrophilic with low contact angle value at higher heat treatment temperature. The contact angle was decreased from ~70° to ~35° when the temperature was increased from 300°C to 550°C. The wetting behaviour of super hydrophilic surfaces is influenced by their chemical composition and surface microstructure [29]. Eustathopoulos et al. [30] claimed that a higher content in the hydroxyl group of oxide surfaces would increase the contact angle value. The FTIR analysis revealed that the hydroxyl group intensity of the brookite thin film (3356–3363 cm^{-1}) at 200°C was greater than that of the brookite thin film at 300°C. This explains the higher water contact angle of the brookite thin films at the lower temperature.

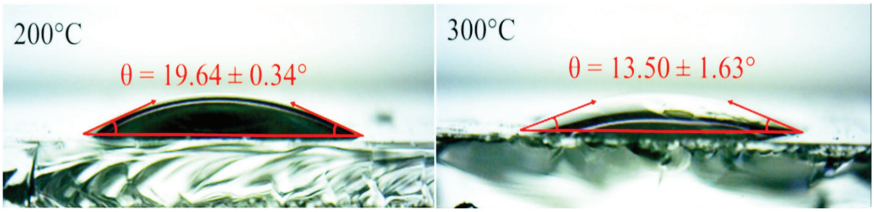


Figure 4: Water contact angle of the brookite thin films heated at different heat treatment temperature

4.0 CONCLUSION

Brookite thin film was successfully deposited using green sol-gel route spin coating at a low heat treatment temperature. In summary, the heat treatment temperature has been found to have a strong influence on the structural, optical and hydrophilicity properties of brookite thin films. The crystallinity of the brookite thin films decreased with the increased heat treatment temperature. Increasing the heat treatment temperature produced a decrease in the crystallite size of the brookite thin films (47.9 nm at 200°C and 58.4 nm at 300°C). While, the FTIR spectra shows the intensity of the hydroxyl groups of the brookite thin films decreased with increased heat treatment temperature. Meanwhile, the optical band gap energy of the brookite thin films decreased from 3.40 eV (200°C) to 3.37 eV (300°C). The water contact angle properties of the brookite thin films are 19.64° at 200°C and 13.50° at 300°C. In summary, brookite thin film at 200°C showed better crystallinity in structural properties, contributing to a preferable photocatalytic activity.

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