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CHARACTERIZATION OF SnO₂/TiO₂ WITH THE ADDITION OF POLYETHYLENE GLYCOL VIA SOL-GEL METHOD FOR SELF-CLEANING APPLICATION

TiO₂ is one of the most widely used metal oxide semiconductors in the field of photocatalysis for the self-cleaning purpose to withdraw pollutants. Polyethylene glycol (PEG) is recommended as a stabilizer and booster during preparation of water-soluble TiO₂. Preparation of SnO₂/TiO₂ thin film deposition on the surface of ceramic tile was carried out by the sol-gel spin coating method by adding different amount of PEG (0g, 0.2g, 0.4g, 0.6g, 0.8g) during the preparation of the sol precursor. The effects of PEG content and the annealing temperature on the phase composition, crystallite size and the hydrophilic properties of SnO₂/TiO₂ films were studied. The X-ray diffraction (XRD) spectra revealed different phases existed when the films were annealed at different annealing temperatures of 350°C, 550°C and 750°C with 0.4 g of PEG addition. The crystallite sizes of the films were measured using Scherrer equation. It shows crystallite size was dependent on crystal structure existed in the films. The films with mixed phases of brookite and rutile shows the smallest crystallite size. In order to measure the hydrophilicity properties of films, the water contact angles for each film with different content of PEG were measured. It can be observed that the water contact angle decreased with the increasing of the content of PEG. It shows the superhydrophilicity properties for the films with the 0.8 g of PEG annealed at 750°C. This demonstrates that the annealed temperature and the addition of PEG affect the phase composition and the hydrophilicity properties of the films.

Keywords: TiO₂; SnO₂; Thin Film; Polyethylene Glycol; Self-Cleaning

1. Introduction

Titanium dioxide (TiO₂) has various environmental applications. Under UV light, the oxidation of biological species and organic compounds occurred through the photocatalytic properties of TiO₂, providing a self-decontamination function. Next, TiO₂ under the exposure of UV promotes photocatalytically induced superhydrophilicity which transforms the more hydrophobic surface to have better hydrophilic properties with better uniformity water film [1-3].

TiO₂ is present in nature mainly in three crystalline forms: rutile, anatase and brookite [4]. The properties of TiO₂ depend on many parameters like crystal phase, nanoparticle size and morphology. Of many materials that have been studied for photocatalysis, TiO₂ has been extensively researched because

it possesses many merits such as high photocatalytic activity, excellent physical and chemical stability, low cost, non-corrosive, nontoxicity and high availability [5]. The photocatalytic activity of TiO₂ depends on its phase. The anatase phase is metastable and has a higher photocatalytic activity, while the rutile phase is more chemically stable but less active. Some TiO₂ with a mixture of both anatase and rutile phases exhibit higher activities compared to pure anatase and rutile phases [6]. A large number of research works have been published on TiO₂ modification to enhance its photocatalytic properties. There are numerous studies on surface modification by doping metal oxides with TiO₂ for improvement in hydrophilicity and photocatalytic activity of the TiO₂ thin films. Doping SnO₂ with TiO₂ thin films will give enhancement in charge carriers separation and reduction in oxidation rate, hence it is more effective in reactions of photocatalytic [1,7].

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Furthermore, polyethylene glycol (PEG) has been recommended as a booster of photocatalytic and hydrophilic for the TiO₂ films. Previous works has been reported by adding PEG during the synthesizing of TiO₂ via sol-gel which gives a prominent improvement in self-cleaning properties on the crystallite size, microstructure and surface adhesion of the TiO₂ thin films [8-10]. Porous films have been obtained by using PEG as a chelating agent. Some researchers used PEG in order to control the porosity of Fe³⁺ doped TiO₂ films starting with Ti(OC₂H₅)₄ as TiO₂ precursor and PEG with molecular weight of 600. The porosity increases with the PEG amount introduced in the film. Other researchers prepared TiO₂ films starting with Ti(OC₃H₇)₄ and PEG with different molecular weights and amounts [11].

Sol-gel technique is a general and powerful technique which enables high-purity materials to be synthesized at low temperatures. Sol-gel technique has become a trend amongst researchers when synthesizing TiO₂ films in the various environment due to its simplicity, speed, and reproducibility [12-16]. This research focuses on SnO₂ doped with TiO₂ thin film via synthesizing, using the sol-gel spin coating method.

2. Methodology

The preparation of TiO₂ and SnO₂ particle solutions were prepared separately. For TiO₂ particle solution, 0.5 mL titanium (IV) isopropoxide (Ti(OC₃H₇)₄) was added dropwise to 10 mL of absolute ethanol. For SnO₂ particle solution, 0.3g of powder tin (II) chloride 2-hydrate (Cl₂.Sn.2H₂O) is added to 5 ml of absolute ethanol. Both solutions are then mixed with 0.5 mL of acetic acid. The primary solution is prepared 5 times by varying the amount of polyethylene glycol 2000 (PEG) added. Five combination volume ratios of titanium (IV) isopropoxide (Ti(OC₃H₇)₄), tin (IV) chloride pentahydrate (SnCl₄.5H₂O), acetic acid, and polyethylene glycol 2000 (PEG) are shown in TABLE 1. Next, the mixture Sn solution is stirred via magnetic stirrer for 1 hour until it forms a clear solution. The spin coating processes are repeated 3 times at 3000 rpm for 60s to obtain a uniform and thin coating layer for samples, respectively. The films were deposited onto ceramic tiles. Lastly, the films were annealed at different temperatures which were 350°C, 550°C, and 750°C, respectively with a heating rate of 10°C/ min, for 3 hours. TABLE 2 shows the annealing temperature of samples in the Vistec tube furnace model HTF-15/20 for 3 hours.

TABLE 1

The modification of sol solution using different ratios

| Solution | Volume Ratio Combination | | | | |
|---------------------------------|--------------------------|-----|-----|-----|-----|
| | 1 | 2 | 3 | 4 | 5 |
| Titanium (IV) isopropoxide, mL | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Tin (II) chloride 2-hydrate, mL | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Acetic acid, g | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Polyethylene glycol, g | 0 | 0.2 | 0.4 | 0.6 | 0.8 |

TABLE 2

The annealing temperature used for different ratios in the tube furnace for 3 hours the modification of sol solution using different ratios

| Film | Annealing Temperature (°C) | Volume Ratio Combination | | | | |
|------|----------------------------|--------------------------|----|----|----|----|
| | | 1 | 2 | 3 | 4 | 5 |
| (a) | 350 | A1 | B1 | C1 | D1 | E1 |
| (b) | 550 | A2 | B2 | C2 | D2 | E2 |
| (c) | 750 | A3 | B3 | C3 | D3 | E3 |

2.1. Characterization of the thin films

The phase composition and crystal structure of the TiO₂ thin films were characterized by Bruker D2 Phaser which is a type of X-Ray Diffractometer with Cu K α radiation ($\lambda = 1.5406\text{\AA}$) at a scan rate of 0.1° per min ranging from 20° to 90°. On the other hand, the wettability test was conducted by measuring the contact angle of a drop of distilled water with the controlled volume on the surface of all prepared thin films. The hydrophilic property was evaluated by measuring the contact angle of the water droplet on the films under an ambient condition. A droplet was injected on the surface of the SnO₂/TiO₂ thin film using 1 μ l micro-injector. Assuming that the geometry of the water droplet was a spherical section, the contact angle could be estimated by measuring the spreading diameter of the contact circle using a reading microscope. The complexity of contact angle analysis ranges was obtained from the simple visual estimation of the contact angle using an angle measurement tool to the mathematically rigorous technique found in the Low-Bond Axisymmetric Drop Shape Analysis (LBADSA) Plugin for ImageJ.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the X-ray diffraction (XRD) diffraction pattern for the films with 0.4 g of PEG which annealed at three different annealing temperatures; 350°C, 550°C, and 750°C. The XRD pattern has only shown the pattern of 0.4 g PEG because when only small amount of PEG was added, the XRD peak existed shown a mixed phases of anatase, rutile and brookite. It can be seen the film shows rutile phase for the film annealed at 350°C. The film showed the tetragonal structure in polycrystalline with the characteristic peaks corresponding to the plane of (111), (101), (211) and (220) planes, referring to ICDD card No. 01-076-0323. Nonetheless, there is the occurrence of a mixed phase of anatase and rutile which was annealed at 550°C. The anatase phase which existed along with rutile also shows a tetragonal structure. The characteristic peaks of anatase were formed at $2\theta = 36.587^\circ$, 67.996° and 75.501° corresponding to the plane of (103), (116), and (301) (ICDD card No. 01-071-1169). The brookite phase was formed with rutile when the film was annealed at 750°C. The brookite phase with orthorhombic structure

was clearly revealed by the diffraction peaks at $2\theta = 20.388^\circ$, 68.474° and 81.307° corresponding to the plane of (110), (324), (080) (ICDD card No. 01-082-112). However, the characteristic peaks of the film which was annealed at 550°C have a greater crystallinity compared to the films annealed at 350°C and 750°C . No characteristic peaks of metal Sn or SnO₂ can be detected, because a small amount of Sn was added into the TiO₂ parent solution and the peak is below the detection limit of the XRD. Besides that, it may be due to the uniform distribution of Sn particles in the titanium matrix, or the Sn peak is covered by the TiO₂ peak owing to the high dispersion or a small amount of Sn addition. This is in a good agreement with another study reported by Xiufeng et al. [17].

It can be clearly seen that all of the TiO₂ in SnO₂/TiO₂ gel has been transformed to a rutile phase when the films were annealed at 350°C . When the annealing temperature increased to 550°C , the single phase of rutile, TiO₂ started to change to dwi-phase of anatase and rutile of TiO₂. While the annealing temperature was increased to 750°C , the dwi-phase of anatase and rutile were transformed to dwi-phase of rutile and brookite of TiO₂. It can be seen that the annealing temperature had a great effect on the phase transition of TiO₂. Furthermore, the crystallite size of the TiO₂ in the films was estimated by using the Scherrer equation as follows:

$$D = \frac{k\lambda}{\beta \cos \theta} \tag{1}$$

where $k = 0.9$ is the Scherrer coefficient, $\lambda = 1.540598 \text{ \AA}$ is the Cu K α radiation wavelength, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the diffraction angle of the diffraction peak. The values of D (crystallite size of TiO₂) for each film were summarized in TABLE 3. It was observed

that crystalline size lies with a range of 5.366 nm to 13.508 nm. The crystallite size of rutile was 6.754 nm with the annealing temperature 350°C while the mixed phases of rutile and anatase formed the crystallite size of 13.508 nm when the annealing temperature increased to 550°C . With increase in the annealing temperature from 350°C to 550°C , the anatase crystallites grow bigger in size with a consequent reduction in the volume fraction of their grain boundary [18]. Then, the crystallite size of mixed phases of rutile and brookite were decreased from 13.508 nm to 5.366 nm when the temperature of annealing was increased to 750°C .

The crystallite size was not dependent on annealing temperature but it may due to the different crystal structure of TiO₂ existed in the films. TiO₂ in bulk form exists in three crystalline polymorphs [19]: Two tetragonal phases of anatase and rutile and a third orthorhombic phase, brookite. The polymorphic transformation of TiO₂ is complex. There occur in both phase conversions as well as micro-structural modification on annealing at high temperatures [18]. The smallest crystallite size was shown in the films which was annealed at high temperature (750°C). It was observed that the volume of the unit cell in the polymorph shrank slightly with the increase in the annealing temperature and it may be due to the increasing pressure developed at higher temperatures [20].

TABLE 3

Crystallite size calculated using Scherrer equation for the SnO₂/TiO₂ thin films

| Film | Annealing Temperature ($^\circ\text{C}$) | Crystallite size (nm) |
|------|--------------------------------------------|-----------------------|
| (a) | 350 | 6.754 |
| (b) | 550 | 13.508 |
| (c) | 750 | 5.366 |

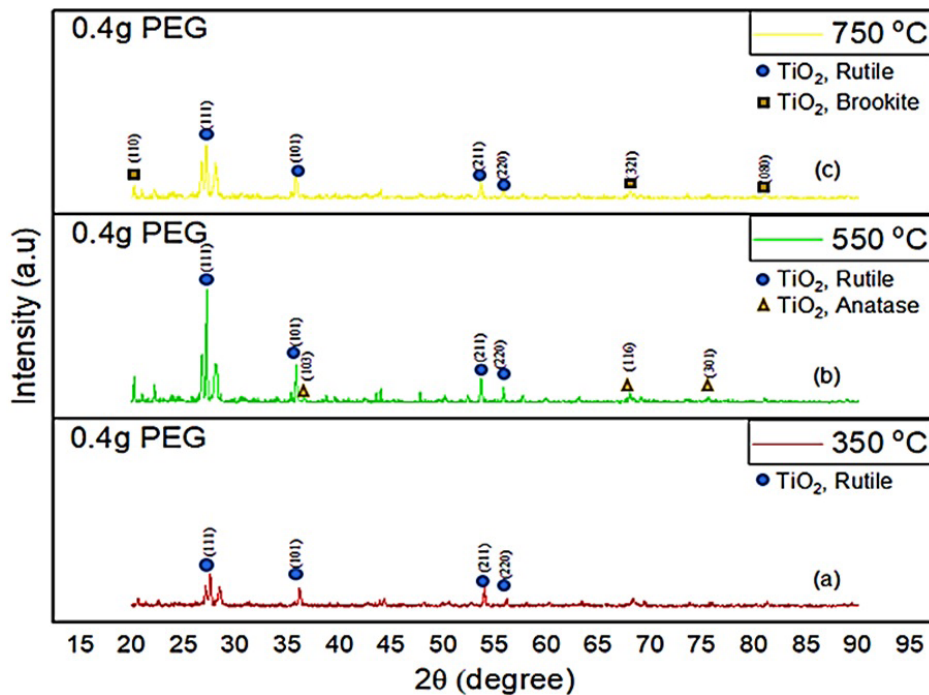


Fig. 1. XRD diffractogram for 0.4 g of PEG in SnO₂/TiO₂ thin films at different annealing temperature; (a) 350°C ; (b) 550°C ; (c) 750°C

3.2. Hydrophilicity properties

There are several self-cleaning properties and one of the most promising properties is the hydrophilic property. The hydrophilic property was based on the contact angle of the water droplet on the films between the thin film and the water droplet under an ambient condition. The hydrophilic property was reflected from a water droplet test which shows that the thin film will become hydrophilic when the contact angle is between 0° to 90° . The image of water droplet was captured by the optical microscope. The optical image obtained was input into a computer to measure its contact angle using Image J Software. Fig. 2 shows the water droplet becoming smaller as the amount of PEG increases when the thin film annealed at the temperature of 350°C , 550°C and 750°C . However, the lowest water contact angle observed was from the samples annealed at 750°C and this is known as superhydrophilicity.

The superhydrophilicity properties of films which were annealed at 750°C are in good agreement with Diebold et al. which claim that there are structural differences between the anatase, brookite and rutile surfaces, which are responsible for the different interaction of the two polymorphs with molecules and for the different photocatalytic reactivity [21-22]. Much work has been also done in recent years on the influence of sub-surface defects on the anatase surface reactivity toward water [23], so confirming that the interaction of the “clean” TiO_2 surface with water depends on the particular “form” of the considered material, including the abundance of defects present on non-stoichiometric reduced surfaces. The proportion of H_2O molecules strongly coordinated to Ti^{4+} over H_2O molecules strongly H-bonded to titanol (Ti-OH) species depends on the structural features of the “clean” surface of the different polymorphs (e.g., distances between the surface-active sites) [24].

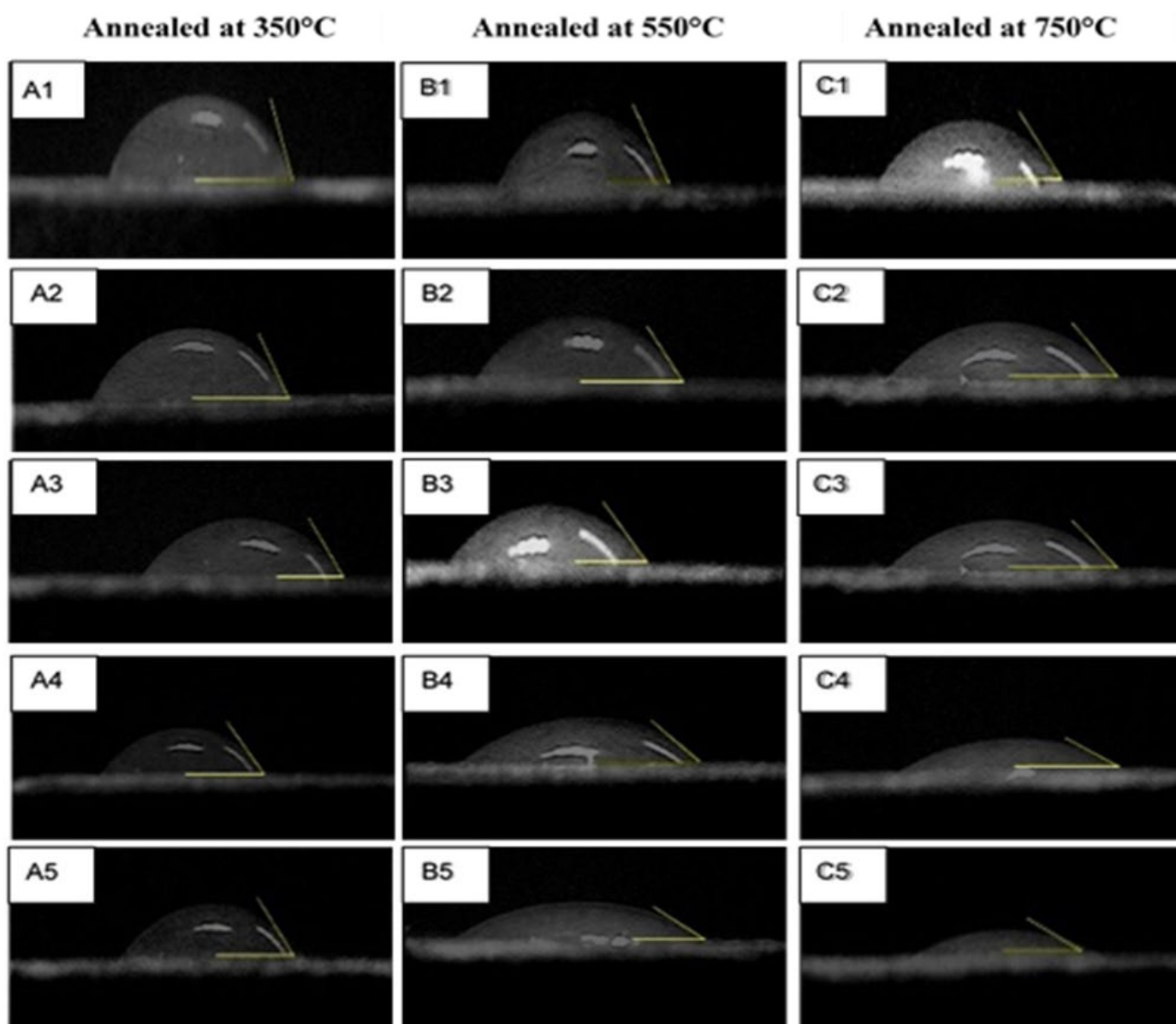


Fig. 2. Optical image of water droplet contact angle of $\text{SnO}_2/\text{TiO}_2$ thin films with different amount of PEG (0.0 g, 0.2 g, 0.4g, 0.6 g and 0.8 g) (refer Table 2)

Meanwhile, Fig. 3 shows the water contact angle versus amount of PEG added in $\text{SnO}_2/\text{TiO}_2$ thin films. The highest measured value for contact angle was 66.92° for sample A1 which was synthesized by adding 0g of PEG for the sample which was annealed at a temperature of 350°C . On the other hand, the lowest measured value for contact angle was 24.30° for sample E3 which was synthesized by adding 0.8g of PEG and the annealing temperature used was 750°C .

The results exhibit that samples A1, B1, and C1 which were synthesized using volume ratio 1, decreased due to the increasing of annealing temperature. According to Che Halin et al, at high temperature of annealing process, the formation of anatase phase will be present where the film will be oxidized and turn into oxide. This will affect the increasing of crystallite size. The formation of anatase phase and the grain growth were the result of diffusion of the titania species towards the nucleated grain. Besides that, the water contact angle also decreases when more PEG is added. PEG helps to improve the surface of the thin film by forming a porous surface. PEG also increases the active surface area with porous surface structure due to pore forming properties. It could be described that the post-annealing temperature greatly affects the hydrophilic properties that can alter the lowering of the wettability on the surface of TiO_2 by adding it from outside, to the subsequent films to strengthen the hydrophilic properties [25].

The content of PEG in samples had a clear effect on the hydrophilic properties of the film. It can be seen that the larger PEG content in the TiO_2 film, the lower the water contact angle value obtained. Generally speaking, the increase in the PEG concentration is favourable to improve wettability. This observation can be explained as follows: During the preparation, PEG was

introduced in TiO_2 solution, thin film was then coated and thermally treated at high temperature to evaporate the PEG and create pores in the film. Therefore, the presence of PEG will normally make the film highly porous and increase internal surface area, which will subsequently also enable more water molecules to be absorbed, hence increasing the number of free OH groups on the film surface. These OH groups will create hydrogen bonds with water so that the water can easily spread itself on the film surface and thus decrease water contact angle values. However, the porosity of the film can be only optimal at a certain PEG concentration. At a high content of PEG greater than the optimal concentration, the porosity of the film will be deteriorated due to phase separation of TiO_2 and PEG – they will be unevenly distributed in solution as well in film, as the aggregation of TiO_2 particles into islands will take place and the total internal surface area will decrease [26].

4. Conclusion

The $\text{SnO}_2/\text{TiO}_2$ thin films were successfully synthesized by the sol-gel method via spin coating and annealed for 3 hours at 3 different temperatures; 350°C , 550°C and 750°C . The XRD pattern has only shown the pattern of 0.4 g PEG because when only small amount of PEG was added, the XRD peak show a mixed phases of anatase, rutile and brookite. It shows the annealing temperature of the film leads to crystallization in the anatase structure above 350°C . The film which was annealed at 550°C has mixed phases of anatase and rutile with tetragonal crystal structure. The mixed phase of rutile and brookite has a tetragonal and orthorhombic crystal structure which was annealed at 750°C ,

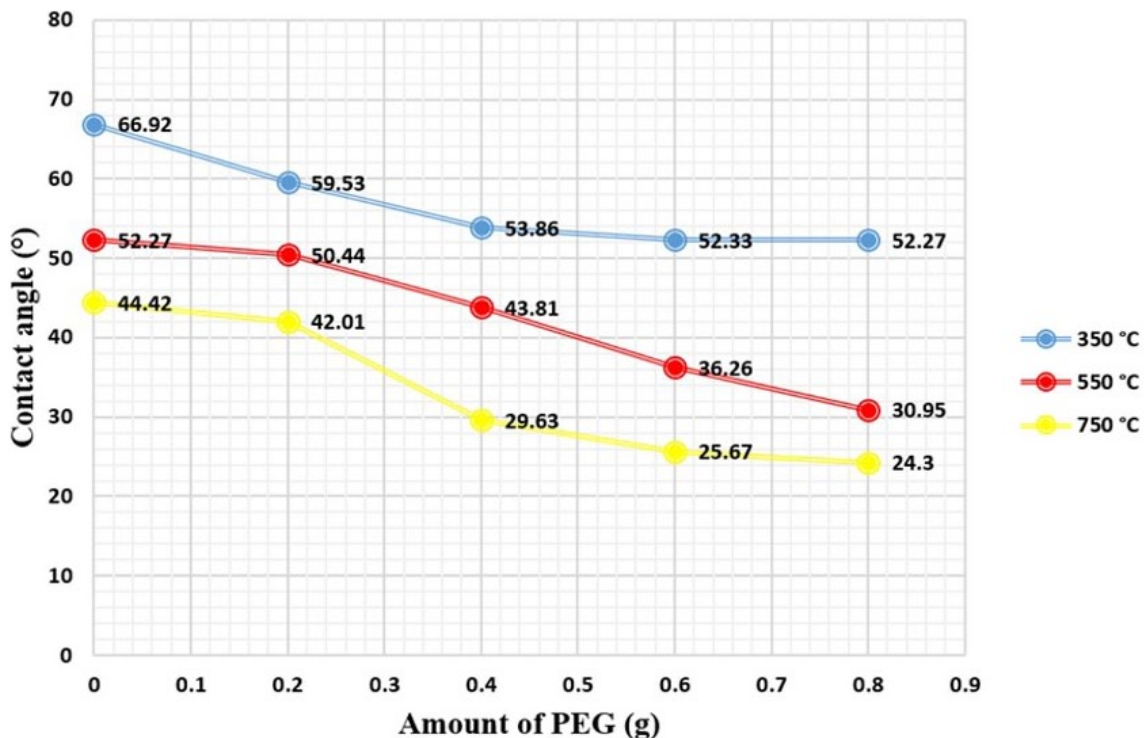


Fig. 3. Water contact angle versus amount of PEG for the $\text{SnO}_2/\text{TiO}_2$ thin film

showing the smallest crystallite size. The crystallite size and the transition phases existed in the TiO₂ was due to annealing temperature. The water contact angles for each film with different content of PEG were measured to observe the hydrophilicity properties. It can be observed that the water contact angle decreased with the increasing of the content of PEG. It shows the superhydrophilicity properties for the films with the 0.8 g of PEG annealed at 750°C. The value of water contact angle obtained for all films show a superhydrophilic property. The film with a larger amount of PEG with the annealing temperature of 750°C shows the lowest water contact angle. It shows that the annealed temperature and the addition of PEG affect the phase composition and the hydrophilicity properties of the films.

Acknowledgements

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1/2017/TK07/UNIMAP/02/6 from the Ministry of Education Malaysia and under grant number 9002-0082 from Tin Board Industry Grant. The authors wish to thank the Center of Excellence Geopolymer & Green Technology (CEGeoGTech), School of Materials, Engineering, Universiti Malaysia Perlis, UniMAP for their partial support.

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