INFLUENCE OF WATER AND PRECURSOR MOLARITY ON THE TiO_2 THIN FILMS DEPOSITED FROM SOLVENTLESS SOL-GEL

A.Y. Shuhadah[1], Z. M. Rosli[2], J. M. Juoi[1], N. D. Johari[1], F. H. Suzaim[1] and T. Moriga[3]

[1]Fakulti Kejuruteraan Pembuatan,
Universiti Teknikal Malaysia Melaka Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Faculty of Mechanical and Manufacturing Engineering Technology,
Universiti Teknikal Malaysia Melaka Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[3]Tokushima-UTeM Academic Centre,
Tokushima University, 2-1 Minami-Josanjima, 770-8506, Tokushima, Japan.

Corresponding Author's Email: [2]zmr@utem.edu.my

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ABSTRACT: Titania (TiO_2) of anatase, anatase-rutile and anatase-brookite-rutile thin films were successfully established from sol-gel dip coating technique using titanium tetraisopropoxide (TTIP) as precursors without the presence of solvent. The thin films were deposited on glass substrate and the type of TiO_2 crystalline structure produced was depending upon the molar ratio of the TTIP and water. Results shown that the TTIP molarity is more substantial in determining the TiO_2 thin films crystallinity and crystallite size as compared to the water molarity. Meanwhile, the desired phases and crystallite size can be controlled by manipulating the molar ratio of water and TTIP. Thus, the establishment of the desired phases (anatase mixed rutile), crystallinity and crystallite size (anatase: 15 nm, rutile: 30 nm) of TiO_2 thin films from solvent less sol-gel can be controlled and encouraging to explore as an effort toward producing a sustainable green photocatalytic material.

KEYWORDS: *Titanium Dioxide; Sol-Gel; Thin Film Coating; Dip Coating; Solvent Free*

1.0 INTRODUCTION

TiO_2 play an important role in solving serious environmental and pollution challenges due to its great properties such as efficient photocatalytic activity, [1-2] highest stability [3] and low in cost. There are three polymorphs of TiO_2 found in nature known as rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Sol-gel technique is one of the many examples and the most conventional and utilized methods in synthesizing TiO_2 of those three polymorphs. It offers many advantages such as low temperature processing, easy coating of large surface, provides high surface homogeneity and most importantly has a low cost [4].

Mixed phases of TiO_2 photocatalysts compositions have been reported exhibit enhanced photoactivity reaction relative to single phase TiO_2[5] depending on hydrolysis rate. Higher hydrolysis rate is good for photocatalytic due to the formation of high surface area resulted from precipitated crystalline of TiO_2 mixed phase. Furthermore, Bakardjieva et al. [6] also reported that highest photocatalytic reaction can be obtained at higher temperature such as 500°C due to the existence of mixed phases of anatase (42.9%), brookite (3.2%) and rutile (53.9%). It is believed that the existence of two phases compositions is beneficial in reducing the re-combination of photo-generated electrons and holes and enhancing the photocatalytic activity compared to single phase with the same crystallite size of anatase and rutile. Therefore, three mixtures of phases were assumed to be the best photocatalytic [6]. Besides, Liu et al. [7] claimed that mixed phases possess advantages in more efficiently utilizing solar light by combining different electronic structures compared to single phase.

Othman et al. [8] reported that using TTIP as precursors is much easier to produce TiO_2 crystalline phase than another precursor. Manjunatha et al. [9] reported that concentrations of TTIP precursor can influenced the crystallite size thus can influence the crystallinity of the TiO_2 thin films. Hanoar et al. [5] reported that excessive water led to formation of mixed anatase-brookite if the ratio between water and TTIP close to r=100. The rutile phase can be established even when the heating temperature used below 500^0C. At r=6, amorphous type structure occurred and crystalline of anatase can only be produced for temperature above 300°C and rutile transformation can

only be produced for temperature above 500°C [5]. Thus, it can be concluded that, high content of water ratio can be formed mixed phases of anatase-brookite-rutile compare to low water ratio.

Annealing temperature can have affected the crystallite size according to Myint et al. [10]. As the annealing temperature increased, the crystallite size also improved the electron migration [10]. Besides, crystallite size growth was depended on the concentrations of TTIP precursors [11]. However, most of the work mentioned above involve the use of solvent (a non-green solution and process) either ethanol or propanol. Therefore, in this work, the influence of TTIP molarity and water molarity at selected temperatures on phases, crystallinity and crystallite size for producing green photocatalytic thin films becomes the studied subject. The sol-gel will be prepared without the attendance of solvent in establishing TiO_2 thin films of high photocatalytic green materials by manipulating the TTIP and water molarity.

2.0 METHODOLOGY

2.1 TiO_2 Sols Preparation

TiO_2 sols were using titanium (IV) isopropoxide (TTIP) (Sigma Aldrich Co.), hydrochloric acid (HCl) (Sigma Aldrich Co.) and deionized water as precursor, catalyst and hydrolysis medium respectively. TTIP was dropped into deionized water and stirred for 30 minutes at room temperature followed by dripping 0.4 ml of HCl. Then, stirred continuously for 3 hours before kept for 48 hours. Variations on the water and TTIP molarity were shown in Table 1.

Table 1: Variations on the water and TTiP molarity

Sol	H_2O (ml)	TTIP (ml)	Ratio (r)
W_{52}	52	0.2	260
W_{26}	26	0.2	130
W_{17}	17	0.2	85
T_2	52	0.2	260
T_4	48	0.4	120
T_5	46	0.5	92

2.2 Preparation of Thin Films Coating

The TiO_2 thin films were immobilized on glass substrates. The cleaned glass substrate was dipped into the TiO_2 solution with the

withdrawing rate was constant at 0.5mm/s and immersing time in 5s. After each coating TiO_2 films were dried at 110°C for 30 min. The dip-coating and drying process were repeated for 10 times to obtain desired thickness and coating uniformity. The prepare film were heated at 500°C and 600°C for 1 hour at 5°C/ min, respectively.

2.3 Characterization of TiO_2 Thin Films Coating

Phases of TiO_2 thin film were analyzed using X-ray diffraction (XRD) technique of an X'Pert Pro High Score Plus model with Cu K-Alpha of 1.54060 Å and generator settings at 30 mA and 40 kV in the range of 10-90°. The crystallite size of TiO_2 films was calculated from XRD line broadening using Debye-Scherrer's formula given by

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

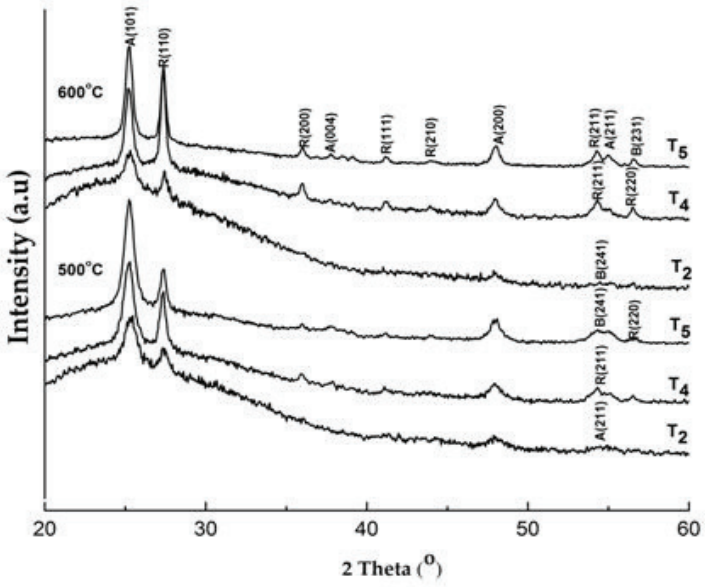
where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα and β is the line width at half-maximum height. Affirmation of the TiO_2 phases were confirm with UniRAM-3500 Raman spectroscopy with laser excitation wavelength, λ= 532 nm.

3.0 RESULTS AND DISSCUSSION

3.1 The Influence of TTIP Molarity

Figure 1(a) shows the XRD pattern of the deposited TiO_2 thin film with variation in the TTIP molarity. As seen, the films crystallinities increase as the TTIP molarity increased from T_2 to T_5, regardless of the heating temperature. The increase in the TiO_2 crystallinity can be observed through the increased in the number of peaks detected as well as its intensities. However, the influence of TTIP molarity on the TiO_2 phases is negligible and less significant. The result of Raman shown in Figure 1(b) is aligned with the XRD result obtained. Based on the Raman spectrum observed, the band at 138,192, 396, 509 and 635 cm^{-1} can be assigned to anatase [12]. The Raman band at 445 cm^{-1} is assigned to rutile and the Raman band of 240 and 318 cm^{-1} are assigned to brookite. The main reason of the undetected brookite phases with the XRD is due to the very small crystallite size produced (e.g. < 5 nm) [13].

Raman spectroscopy have been proved can work best for most of crystalline oxide and even amorphous oxide that have a wide range of bond angles, broadening peaks and featureless signal [14]. Therefore, the existence of the brookite phases is too small to give an effect and insignificant.



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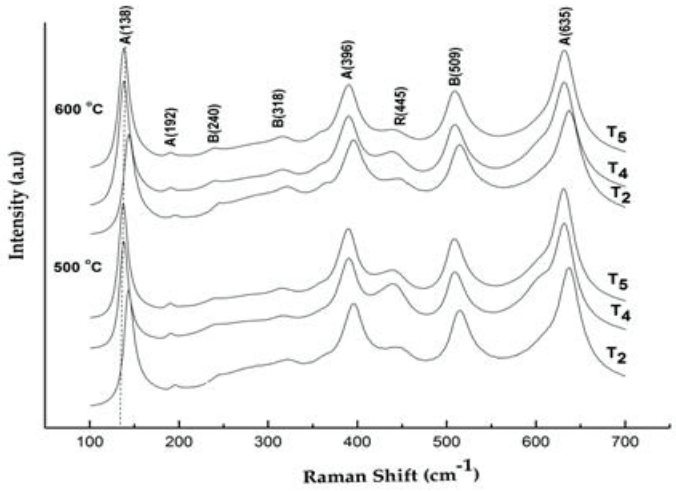
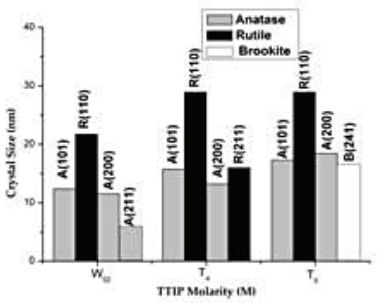


(b)

Figure 1: The XRD pattern (a) TiO_2 thin films against TTIP molarity at heating temperatures of 500°C and 600°C and (b) Raman spectrum
(A: Anatase, B: Brookite and R: Rutile)

Figure 2 shows the influence of TTIP molarity on the TiO_2 crystallite size. It is obviously seen that the TTIP molarity have a great influenced on the crystallite size. The crystallite size increased as the TTIP molarity increased regardless of the heating temperatures. The influence of precursor concentration on crystallite size was also reported in the work of Manjunatha et al. [9]. As the concentration of precursor increased, the crystallite size will also increase due to the increased in the cluster formation to form the agglomerated crystallites resulted in the formation of large crystallite size with better crystallinity [15]. In this study, a mixture of anatase-rutile TiO_2 thin films was successfully produced with an average crystallite size of 15 nm for the anatase and 30 nm for the rutile for both temperatures.



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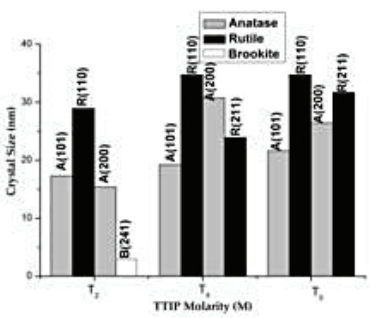


(b)

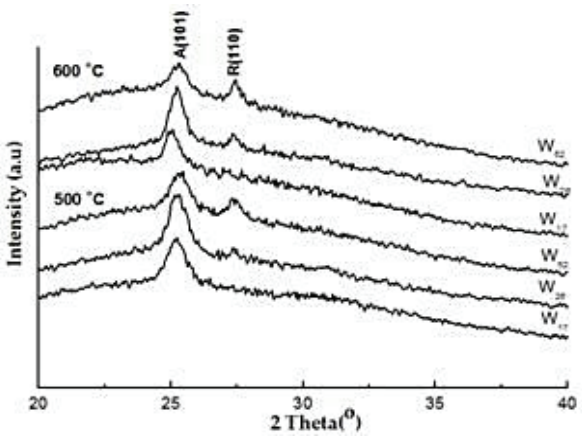
Figure 2: Crystallite size of TiO_2 thin films against TTIP molarity at different annealing temperatures: (a) 500°C and (b) 600°C

3.2 The Influence of Water Molarity

Figure 3(a) shows the influence of water molarity on the crystallinity and the phases of the established TiO_2 thin films. As seen, the influence of water molarity on increasing the TiO_2 thin films crystallinity is insignificant for both annealing temperatures. However, increasing water molarity from W_{17} to W_{52}, gave an effect in transforming the established TiO_2 thin film from pure anatase into a

mixture of anatase-rutile film for both heating temperatures. Raman spectroscopy of Figure 3(b) re-affirmed this observation. The by-product of brookite detected under the Raman band (as explain earlier) is small and negligible.

The crystallite size of anatase produced, for both temperatures, is in the range of 13 nm to 25 nm and the rutile size is around 20 nm to 30 nm as the water molarity decreased as shown in Figure 4. Interestingly that the crystallite size produced are not much different with the crystallite size produced under the influence of TTIP molarity. Results obtained under the influenced of water molarity signify that the green photocatalytic thin films of controlled phases and crystallinities can be produced from a solvent less sol-gel technique without sacrificing the crystallite size.



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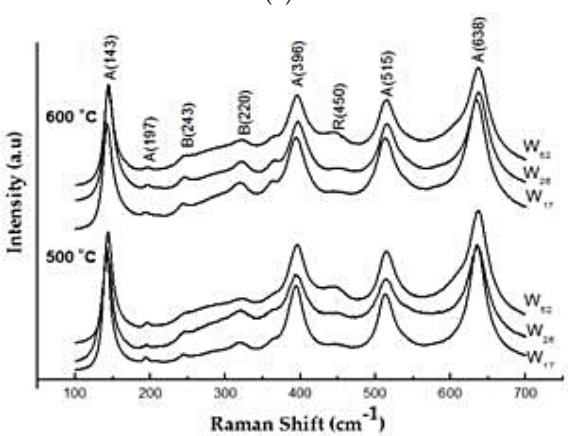

(b)

Figure 3: The XRD pattern (a) TiO_2 thin films against water molarity at heating temperatures of 500°C and 600°C and (b) Raman spectrum (A: Anatase, B: Brookite and R: Rutile)

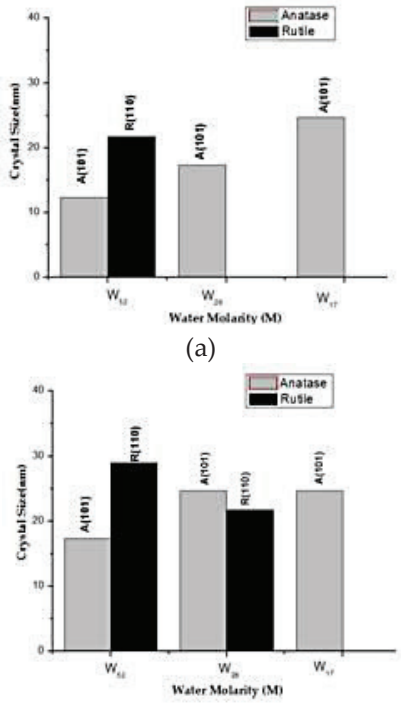

Figure 4: Crystallite size of TiO_2 thin films against water molarity at different annealing temperatures: (a) 500°C and (b) 600°C

4.0 CONCLUSION

TiO_2 thin films of controlled phases and crystallinity were successfully deposited on glass substrate from solvent less sol gel dip coating technique. The influenced of TTIP molarity is more dominant on increasing the number of crystallinity with most of the films produced comprise mixed of anatase and rutile for both temperatures of 5000C and 600^0C. Whereas the effect of water molarity is more dominant on the type of phases at both temperatures. Pure anatase films with crystallite size of about 15 nm is favorable at low water molarity and mixed anatase-rutile films is favorable at high water molarity. Interestingly, both established films either under the influence of TTIP molarity or water molarity having almost similar crystallite size of about 15 nm for the anatase and 30 nm for the rutile. The brookite phases detected with the Raman spectrum is negligible and can be considered as by-product. Thus, green and sustainable TiO2 thin films with desired phases, crystallinity and grain size can be produced by manipulating the water and precursor molarity ratio from solvent less sol-gel dip coating technique.

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