The Effect of Growth Temperature on the Surface Properties of TiO₂ Nanostructures Grown on TiO₂ Templates

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The synthesis of TiO₂ nanostructures with uniform shape and the proper orientation is a vital task in ensuring their ability to function properly in their applications [1]. Therefore, much effort has been dedicated to discovering an effective method to synthesize TiO₂ nanostructures. In this preliminary work, TiO₂ nanostructures were successfully synthesized by a simple precipitation technique. This solution-based technique offers many advantages such as composition modifications, low cost, relatively low temperatures and implementation into large-scale production. A variety of TiO₂ nanostructures can be obtained by changing the growth temperature and time [2]. In this study, TiO₂ nanostructures were grown on a TiO₂ template at various growth temperatures ranging from 60°C to 140°C. The surface topography and morphology of TiO₂ films were investigated by atomic force microscopy (AFM). The phase of the TiO₂ nanostructures and their surface roughness properties were evaluated by Raman spectroscopy and a surface profiler (SP), respectively.

Key words: TiO₂, Nanostructure, Temperature, Immersion method, Template

1. INTRODUCTION

Research on titanium dioxide (TiO₂) nanostructures has been of much interest for many scientists and researchers due to its novel properties such as the shape and size [3] of its structure that are very useful in absorbing photon energies [4] and large surface area applications [5]. To date, TiO₂ nanostructures have been synthesized using titanium isopropoxide (TTiP) [6], titanium butoxide (TTiB) [3], titanium tetrachloride (TiCl₄), tetrabutyl titanate (Ti(OBu)₄) [7] or Ti(OC₄H₉)₄ [8] precursors. TiO₂ nanostructures have been used in many applications such as inorganic membranes [9], thin films and coatings, anti-reflection coatings (ATRs) [10], screen and mirror coatings [11], optical devices, etc., [12].

The growth of TiO₂ nanostructures on a TiO₂ glass template was investigated because it is a very important aspect of the fabrication process and must meet the requirements of different materials preparation processes [12]. The purpose of using templates is to restrict the development of the nanostructure's shape and size [13]. There are various techniques to prepare templates, such as physical vapor deposition (PVD) [14], a sol-gel technique [15], chemical vapor deposition [CVD] [16], spray pyrolysis [17], sputtering methods [18] and many others. The sol-gel spin-coating technique has been used to prepare TiO₂ nanocoatings [19] and nanostructures, [20] such as nanorods, nanospheres, nanowires and

nanotubes, because this technique allows the ability to modify the chemical solution, and addresses low cost and low temperature requirements [21]. The immersion method has been dedicated to developing an effective process of synthesizing TiO₂ nanostructures from sol-gel solutions because it is a new, promising route that can be performed simply and at a low cost.

The present work studies the effect of the growth temperature on the TiO₂ nanostructures. The temperature plays an important role in the growth of TiO₂ nanostructures and needs to be controlled based on the desired requirements and application. The temperature can change the phase structure of the material, and further increasing the temperature will cause phase transformations and nucleation processes. TiO₂ exists in three crystalline phases. The anatase phase [22] exists between 400°C to 500°C while the brookite phase [23] is formed above 700°C. The rutile phase exists when the annealing temperature increases above 800°C [24].

In this study, samples from four growth temperatures were investigated to determine the effect of growth temperature during the immersion step of the TiO₂ template in a TTiP sol-gel solution. The glass slide was used as the substrate material and template for growing TiO₂ nanostructures [25]. The substrate type affects the subsequent TiO₂ nanostructure nucleation process and growth pattern. In this paper we propose a new, simple method to prepare the TiO₂ template

and TiO₂ nanostructures (Fig. 4) at the same time with the same precursor, via a combination of the sol-gel spin coating technique and the immersion method. This method can be performed at a lower preparation temperature and is shown in Fig. 1. The TTiP sol-gel solution was deposited on the glass surface, creating the TiO₂ template, as illustrated in Fig. 1(a) and Fig. 4. Next, the TiO₂ template was immersed in the TTiP sol-gel solution, as shown in Fig. 1 (b).

Figure 1 Schematic diagram of the fabrication of TiO₂ nanostructures on a TiO₂ template:- (a) preparation of the TiO₂ template using spin coating and (b) preparation of the TiO₂ nanostructures on the TiO₂ template using the immersion method.

2. EXPERIMENTAL DETAILS

2.1 Preparation of 0.001 molar sol-gel solutions

A volume ratio of 0.017 of TTiP sol-gel solution to ethanol was poured into a 25 ml ethanol solution, the solvent, and then 1.25 ml glacial acetic acid (GAA) and 0.09 ml distilled water were added by a dropper into the solution. Next, one drop of triton-x, used as a stabilizer, was added, and 24.9 ml of ethanol was again added to the mixture to total 50 ml of sol-gel solution in a 100 ml beaker. The TTiP sol-gel solution was pre-heated at 60°C for 1 hour with a 3 rpm stirring speed (using a magnetic stirrer). The solution was aged under continuous stirring. The TTiP sol-gel solution was then ready for template deposition.

2.2 Preparation of 0.5 molar immersion solutions

For the immersion solution, TTiP Aldrich 99.9995% purity was used to synthesize titanium dioxide TiO₂. A volume ratio of 18.91 of TTiP sol-gel solution to ethanol was added into the 100.00 ml ethanol solvent. Then, 2.5 ml of glacial acetic acid (GAA) and 2 drops of triton-x were poured into the mixture and continuously stirred at 60°C for 1 hour. Next, 0.18 ml of distilled water was added. Afterward, the immersion solution was aged.

2.3 Preparation of titanium dioxide (TiO₂) template

A 0.001 molar concentration of sol-gel solution (refer to subsection 2.1) was deposited onto a glass surface at a spin-coating speed of 6000 rpm. Then, it was dried at 150°C for 10 minutes and further annealed at 450°C for 2 hours. The

deposited glass (TiO₂ template) was left at room temperature for 1 hour.

2.4 Immersion method

The TiO₂ template (in Fig. 4) was immersed in 20 ml of the 0.5 M immersion solution (refer to subsection 2.2), heated at 60°C and subjected to 70 mA in a Nex Immerse Heater machine for 1-1/2 hours.

These steps could be performed by hanging the 250 ml bottle containing the 0.5 M immersion solution on retort stand. After immersion, the sample was dried and annealed at 60°C. Lastly, the sample was cooled at room temperature.

This method was repeated for different growth temperatures: 80°C, 100°C and 140°C. After immersion, the sample's surface morphology, topography and roughness were characterized. Raman spectroscopy was used to analyze the phase structures in TiO₂.

3. RESULTS AND DISCUSSION

3.1 Surface morphology, 2-dimensional imaging and line profile from section analysis.

The surface morphology of TiO₂ nanostructures on the TiO₂ template was characterized by atomic force microscopy (AFM, XE-100 Park Systems), as shown in Fig. 2.

Fig. 2-(d) shows that none of the TiO₂ particles are present, but after the growth heat treatment, the number of particles slowly increased when the growth temperature increased from 60°C to 80°C. The TiO₂ particles began appearing but were blurry in the images, as shown in Fig. 2-(c). At 100°C, Fig. 2-(b) shows that TiO₂ particles can be clearly seen at the top of the template's surface and are randomly distributed. However, after the growth temperature was further increased, the TiO₂ particles disappeared from the surface of the template.

Their disappearance might be due to the presence of nanostructure particles that have a large number of disordered surface atoms that possess a surface energy greater than that of the inner layer atoms.

This behavior is influenced by the high growth temperature, which facilitates nucleation. As can be seen in the results, TiO₂ particles precipitate.

In addition, as the TiO₂ particle size decreases, its surface area increases, and the atoms are more mobile, which leads to more defects and causes the TiO₂ particles to disappear [26].

These results show that increasing the growth temperature, causes the transformation of the TiO₂ structure and affects TiO₂ template properties, such as uniformity, thickness and surface roughness [27].

Figure 2 Two-dimensional view of the tapping mode image analysis from the top of the glass template surface at different growth temperatures, -: (a) 140°C, (b) 100°C, (c) 80°C and (d) 60°C.

3.1.1 Surface roughness via AFM.

Table I shows that the surface roughness properties were analyzed using AFM (XE-100, Park System). In Table I, at a growth temperature of 100°C, the surface has an optimum roughness value of 0.316 nm as compared to 0.277 nm at a growth temperature of 140°C.

Table I Surface roughness properties of TiO₂ nanostructures on a TiO₂ template.

Growth Temperature (°C)	Root Mean Square Roughness, Rq (nm)	Surface Roughness Average, Ra (nm)
60	0.654	0.472
80	0.678	0.455
100	0.426	0.316
140	0.530	0.277

The surface roughness average is 0.277 nm at 140°C, 0.455 nm at 80°C and 0.472 nm, the highest value, at 60°C growth temperatures. From these results we can conclude that as the growth temperature increased, the surface roughness decreased. The surface roughness from AFM tapping mode analysis was related to the surface roughness profiler (SP) analysis presented in Table IV.

3.2 Line profile from section analysis

Figure 3 Line profile of TiO₂ nanostructure grown on a TiO₂ template from sectional view analysis at different growth temperatures: (a) 140°, (b) 100°C, (c) 80°C and (d) 60°C.

AFM cross-sectional analysis showed that the TiO₂ nanostructures were uniform in size and growth pattern, giving rise to a much rougher TiO₂ template, as shown in Fig. 3-(b). This result correlated with the surface roughness properties measured by the SP. Fig. 3-(a), (c) and (d) show the nonuniform growth of existing TiO₂ nanostructures on the TiO₂ template. These can be interpreted through the height of the TiO₂ nanostructure on the y-axis (nm) of the line profile. At 100°C, the narrow peaks in Fig. 3 (b) show the uniformity of TiO₂ nanostructures on the TiO₂ template. In Fig. 3-(a) only a few TiO₂ nanostructures were consistent with the AFM topography image, shown in Fig. 7-(a).

From the line profile analysis, it can be shown that the thickness of the TiO₂ nanostructures on the TiO₂ template can be calculated based on the formula below:

$$\text{Thickness, } t = H_h - H_\gamma, \quad (\text{Equation 1})$$

where;

H_h = maximum peak height obtained from line profile, and-

H_γ = lowest valley obtained from line profile.

From Fig. 3-(b) the thickness of the TiO₂ nanostructures is 2.631 nm at 100°C while Fig. 3 (a), (c) and (d) show values of 4.340 nm, 5.420 nm and 3.691 nm, respectively. From these results it is clear that increasing the growth temperature from 60°C to 80°C, causes the TiO₂ nanostructure template to grow thicker. These results are correlated with the SP analysis presented in Table IV.

Figure 4 Schematic diagram of TiO₂ nanostructures grown on a TiO₂ template. The TiO₂ template consists of TiO₂ deposited on a glass substrate (refer to Fig. 1-(a)).

Fig. 5 shows that physically, the TiO₂ material underwent a phase transformation from a solution state (TTiP sol-gel solution) to a solid phase (TiO₂ nanostructures) once the heat was applied via an annealing temperature of 450°C (refer to section 2.3 experimental details). These states are known as transition states of the TiO₂ material. In other words, as we apply heat from the annealing step, the state of the TiO₂ material will change from a sol-gel solution state to a solid (TiO₂ nanostructures) state, and further increasing the annealing temperature will cause phase transformations (as discussed in the introduction, the last part of paragraph three). In conclusion, we propose this model (Fig. 4); the schematic diagram shows that the temperature can affect the transition states as well as the phase transformations of TiO₂ material [27].

Fig. 6 shows that further increasing the growth temperature may lead to distorted growth of the TiO₂ nanostructures and further flattening of the structure. As can be seen from the results, some did not become nanostructures, causing nonuniform growth of the TiO₂ nanostructures, shown in Fig. 7-(a) and (d). Finally, the surface of the TiO₂ template flattened, as shown in Fig. 6 and 7-(d).

Figure 5 Schematic diagram of the transitions of states for TiO₂ materials as the annealing temperature was applied.

Figure 6 The flattening mechanism of TiO₂ nanostructures on the TiO₂ template.

3.3 Surface topography from 3-dimensional AFM image analysis

Figure 7 Representative AFM 3-dimensional image surveys of TiO_2 nanostructures grown on a TiO_2 template at different growth temperatures, -: (a) 140°C, (b) 100°C, (c) 80°C and (d) 60°C.

Fig. 7-(a) to (d) show the topography images at which the TiO_2 nanostructures grow at different growth temperatures. Fig. 7-(d) shows that TiO_2 nanostructures do not grow at lower temperatures. H.G. Yang et. al., [26] found that anatase TiO_2 did not grow on the glass substrate surface at temperatures between 55°C and 80°C at constant heating time.

In conclusion, the results show that changing the growth temperature affects the uniformity and thickness of the TiO_2 nanostructures and their

subsequent effect on the template surface roughness [27].

3.4 Raman analysis

Figure 8 Raman spectra of TiO_2 nanostructures grown on a TiO_2 template at different growth temperatures.

The phase structure of TiO_2 nanostructures on the TiO_2 template was characterized using an excitation wavelength, $\lambda = 514$ nm, on a Modu-Laser Raman Spectroscopy (Horiba Jobin Yvon). The sample immersed at a growth temperature of 60°C, (Fig. 8 (a)), shows the three Raman bands: at 570.10 cm^{-1} , assigned as anatase [28]; at 792.80 cm^{-1} , assigned as the rutile phase with multiple crystals and, peaks shifted to the left compared to previous study [29]; and at 1100.51 cm^{-1} , assigned as the rutile phase structure [30]. These peaks were compared with other reports and are presented in Table II. There is significant change in the peak positions, and the intensity of the peaks increase with an increase in the growth temperature of the heat immersion process [28]. This might be due to the annealing temperature of 450°C. Annealing and heating after immersing the TiO_2 template in the TTiP sol-gel solution can cause the growth of multiple crystals.

At growth temperatures of 100°C (Fig. 8 (c)) and 140°C (Fig. 8 (d)), the Raman bands are 803.66 cm^{-1} and 1111.37 cm^{-1} , respectively. The sample completely transformed into the rutile phase, according to the Raman bands of the rutile phase structure [30]. Raman bands at 559.31 cm^{-1} and 581.03 cm^{-1} can be attributed to the anatase phase with multiple crystals shifting to the right as compared to those from a previous study on single crystalline anatase [31]. In conclusion, narrow Raman band peaks indicate that a crystalline phase TiO_2 nanostructure has deposited on the TiO_2 template.

Table II Observed Raman shift (cm⁻¹) at 100°C and 140°C growth temperatures during heat immersion.

Present Work	S.Mandl et al. [28]	Ohsaka et al. [30]	J.Shi et al. [31]
559.31	447	513	515.0
581.03	none	519	519.0
781.94	612	639	639.0
803.66	826	none	835.0
1111.37	none	none	900.0

When the template was immersed at a growth temperature of 100°C, the full width at half maximum (FWHM) value corresponding to the peak at 1111.37 cm⁻¹ was 10.54 and was determined using the Gaussian fit to single peak software.

3.5 Surface roughness properties

The surface roughness and thickness of the TiO₂ nanostructures were analyzed using a surface profiler, (KLA-TENCOR P-6 profiler). Fig. 9 and Table III are correlated with each other wherever there is a peak with a height, measured in μm, on the template surface under the conditions of a sampling rate of 200 Hz and a scan length of 2535.000 μm. Fig. 9 (c) shows that the highest peak is 2.564 μm and has a flattened surface. At this growth condition, uniform nanostructures and distribution on the whole template surface can be seen. These results correlate with the topography image (AFM 3-dimensional image) in Fig. 7 (b), which is at 100°C.

Figure 9 Surface profiler (SP) peaks present in TiO₂ nanostructures grown on the TiO₂ template.

Fig. 9-(a), (b), and (d) show another peak that contributes to the surface roughness properties. We can conclude that a high peak and, rough surface can influence the uniformity, size, shape and number of TiO₂ nanostructures that grow on

the TiO₂ template.

Table III Roughness peak heights for TiO₂ templates subjected to a heat immersion.

Growth temperature (°C)	Peak 1	Peak 2	Peak 3
		(μm)	
60	0.415	1.114	2.006
80	none	1.6465	none
100	none	1.254	2.564
140	none	none	2.153

Table IV Roughness and thickness values of TiO₂ nanostructures on the TiO₂ template from surface profile analysis.

Growth temperature (°C)	Roughness (μm)	Thickness (nm)
60	6.0	3.60
80	5.21	5.80
100	2.10	2.60
140	5.56	4.40

The surface roughness can be calculated using the formula below:

$$Ra = \frac{A}{n} \quad (\text{Equation 2})$$

where;

Ra = surface roughness average in nm or μm,

A = total peak height in nm or μm (obtained from Fig. 9 and table III) and,

n = total number of peaks.

Table IV shows the surface roughness and thickness values of TiO₂ nanostructures grown at temperatures from 60°C to 140°C. The sample immersed at a temperature of 100°C showed lower roughness and thickness values that correlated with the AFM line profile analysis in Fig. 3 (b) and SP analyses in Table IV.

4. CONCLUSIONS

TiO₂ nanostructures were successfully fabricated on a deposited glass substrate that served as a TiO₂ template. These nanostructures were synthesized using the immersion method, which involves varying the growth temperature of the immersion solution. This method is an effective and, simple preparation technique and is low in cost. An optimum sample with uniform shape, random distribution and uniform growth of TiO₂ nanostructures was grown at 100°C. This sample has 2.10 nm and 2.6 nm of roughness and thickness, respectively.

These desirable properties are recommended for equipment that utilize coated glass and metal substrates.

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