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Characterization and photocatalytic activity of titanium dioxide deposited on stainless steel by pulsed-pressure MOCVD

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Abstract

Titanium dioxide (TiO_2) was deposited on stainless steel 304 by pulsed-pressure metalorganic chemical vapor deposition (PP-MOCVD). Titanium tetraisopropoxide (TTIP) in toluene at the concentration of 0.5 mol% was used as the precursor. The deposition was conducted at the base pressure of 300 Pa and deposition temperatures were varied between 350°C and 400°C. At these deposition temperatures, anatase phase is expected for further photocatalysis study. The deposited TiO_2 thin films at the thickness of hundreds nanometers were analyzed using field emission scanning electron microscopy (FESEM) for surface morphology. X-ray diffraction (XRD) was applied for phase analysis. The contact angle was measured to study its relationship with surface morphology, grain size and phase. Finally, photocatalytic activity was investigated through the absorption of methylene blue using UV/Vis spectrophotometer. The deposited TiO_2 thin films were found to be rutile and anatase with various surface morphology and grain size depends on the deposition temperature. The hydrophobicity of depositedTiO_2 thin films tend to increase with the deposition temperature whereas the photocatalytic property depends on the microstructure of TiO_2 thin film.

1. Introduction

Due to increase demand and shortage of clean water sources from population growth and industrialization, wastewater treatment at low-cost and high efficiency is sought to offset the clean water sources [1]. Wastewaters are often contained suspended solids, hazardous organic compounds and biological hazardous substances [1,2]. There are lots of wastewater treatment techniques such as adsorption, sedimentation, filtration and active sludge biochemical processes. Certain processes of these involves the use of chemicals that generate secondary pollution instead [1-3]. As a result, photocatalytic activity is of interest as it can degrade organic compounds and certain biological substances completely depend on the cases without using additional chemicals [2].

Titanium dioxide (TiO_2) has been an interesting material for research for a long time for air and water purification due to its attractive properties such as highly chemical and thermal stability, non-toxic and photocatalysis capability [4,5]. The photocatalytic activity generally occurs on the surface of TiO_2. When a photon with energy equal to or greater than the band gap of TiO_2 (3.2 eV in case of anatase and 3.0 eV in case of rutile), electron-hole pairs will be generated. These electron-hole pairs can react with oxygen dissolved in wastewaters and form hydroxyl radicals. These hydroxyl radicals has strong oxidizing and deoxidizing abilities; hence reacts with organic compounds and biological substances in wastewater and polluted air and eliminates them [5].

TiO_2 is a polymeric compound that exists principally in three crystal structures, which are rutile, anatase and brookite. Nevertheless, only rutile and anatase phases are commonly synthesized due to their attractive thermodynamics characteristics and physical properties. Rutile phase has higher refractive index than the anatase, which probably due to more compact tetragonal crystal structure of rutile than anatase [1,6]. The light distribution and absorption of the rutile phase have been apply in inorganic cosmetics, sunscreens, opacifying agent for paints and high grade plastics [7]. The anatase phase is widely used in ceramics, manufacture of paper, rubber and fibers as well as photocatalytic coating for surface protection and surface treatment from various physical stresses and contaminations [8]. Considering the photocatalytic activity, anatase

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shows higher photocatalytic activity than rutile [9]. Anatase is considered to be more sensitive to ultraviolet-visible wavelength region than rutile. However, rutile has better photoabsorption property in visible wavelength region than anatase with good refractive index, high dielectric constant and excellent chemical stability [1,10,11]. A main obstacle in using TiO_2 particles in wastewater treatment is the separation of TiO_2 particles after used. This is because the TiO_2 particles are too fine to be separated by gravity settling [1,2,5]. The other obstacle is the agglomeration of TiO_2 particles, which reduced the surface area; hence photocatalytic activity decreased as well as the reusable lifespan [1]. Attempts to effectively separate TiO_2 particles are such as coagulation and membrane separation, which however caused secondary pollutants and higher treatment cost [2]. Therefore, TiO_2 thin films is an interesting solution to solve the issue of TiO_2 particles separation with numbers of methods to enhance the photocatalytic activity such as increasing the surface area, doping with noble metals and preparing composite thin films [5].

Pulsed-pressure metalorganic chemical vapor deposition (PP-MOCVD) has been reported of its capability of conformal coating over complex shapes [12-14]. It is a low cost apparatus with supplying of controlled amount of precursor through an ultrasonic nozzle in a pulsing manner to an evacuated cold-wall reactor. With ultrasonic nozzle, very small droplets of a liquid precursor is generated, which influences the liquid precursor to flash evaporate immediately. The pulsing action provides uniform coverage, relatively fast growth rates, low cooling rates of the deposition surface, and low contamination of the film [12].

In this study, characterization of PP-MOCVD coated stainless steel 304 has been carried out. The surface morphology and phase of deposited TiO_2 thin film was characterized for further deposition on complex shapes and photocatalysis capability with recyclable possibility. The contact angle and photocatalytic activity were also investigated.

2. Experimental

2.1 Materials and reagents

TiO_2 thin films were deposited on flat stainless steel 304. Stainless steel has been chosen due to its good mechanical properties and high corrosion resistance in most of the cases. In addition, nanometric chromium oxide layer is spontaneously formed on a surface of the stainless steel. This oxide layer acts perfectly as an adherent to ceramic coating TiO_2 thin film [15]. The source of liquid precursor for TiO_2 thin films deposition is titanium (IV) tetraisopropoxide (TTIP) 97% from Sigma-Aldrich dissolved in AR grade toluene to a concentration of 0.5 mol%.

For photocatalytic activity study, methylene blue trihydrate from MP Biomedicals was diluted with deionized water at a concentration of 0.5 mg/L. As standard reference, the commercial photocatalyst, Degussa P-25 nanopowder with primary particle size of 21 nm from Sigma Aldrich was used.

2.2 Preparation of TiO_2 thin films

TiO_2 thin films were deposited using a cold-wall reactor PP-MOCVD at the deposition temperatures of 350°C, 370°C and 400°C. The base pressure during the deposition was 300 Pa at the pulse time of 10 s.

2.3 Materials characterization

The phase of deposited TiO_2 thin films was analyzed using Bruker D8 Advanced X-ray diffraction (XRD). The surface morphology was characterized using JSM-7001F field emission Scanning Electron Microscope (FESEM). The wettability property of deposited TiO_2 was examined using contact angle measurement. The contact angle value was an average from four measurements on different areas of the same sample surface.

2.4 Grain size estimation

The crystallite size of deposited TiO_2 was calculated from XRD data using Scherrer equation as written in Equation 1.

$$L = \frac{K\lambda}{B(2\theta)cos\theta} \quad (1)$$

Where L is the average crystallite size; $B(2\theta)$ is the peak width; λ is the X-ray wavelength; θ is the Bragg angle and K is the Scherrer constant, which assumed to be 0.94 for the full width at half maximum (FWHM) of spherical crystals with cubic symmetry [16].

2.5 Photocatalytic experiments

The photocatalytic activity of deposited TiO_2 thin films was investigated through the decomposition of methylene blue solution. The deposited TiO_2 thin films on 1x1 cm^2 flat stainless steels were immersed into 50 ml aqueous methylene blue solution with the concentration of 0.5 mg/L in a beaker each. For Degussa P-25, 0.01 g of Degussa P-25 powder was added in a beaker with 50 ml aqueous methylene blue solution at the same concentration. A mercury tube lamp was used as an only UV source with UVA wavelength range of 320-400 nm. The immersed TiO_2 thin films were irradiated in perpendicular direction with the distance from the UV source of 10 cm. The experiment was conducted at room temperature. The decomposition of the methylene blue solution was measured through the change of concentratiton using absorption of methylene blue from PG INSTRUMENTS T92+ UV Spectrophotometer.

2.5 Photocatalytic activity degradation rate estimation

According to Beer-Lambert's law, the concentration of methylene blue is directly proportional to the intensity of the absorption peak at 663 nm. Therefore, the decomposition efficiency of methylene blue MB can be calculated using the concentration of the methylene blue at the initial and during the irradiation as shown in Equation 2.

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\% \qquad (2)$$

Where C_0 is the initial concentration of methylene blue solution and C_t is concentration of methylene blue during irradiation [17].

3. Results and discussion

3.1 Surface morphology of deposited TiO_2

All the surface morphology of deposited TiO_2 thin films are shown in Figure 1. At the deposition temperature of 350°C, the surface morphology is petal-like with the average grain size of 5.01 nm. The surface morphology at the deposition temperature of 370°C is non- uniform. This non-uniform is likely to come from the film growth rate that causes high stress as certain cracks were observed; hence diffusion of atomic of the substrate into the film [18]. This film has both large and small microstructure with the average grain size of 3.15 nm, which is the smallest grain size among the three samples. At the highest deposition temperature studied, 400°C, the deposited TiO_2 thin films has the largest grain size with round shape crystal with the average grain size of 5.68 nm. The grain size and shape of the deposited TiO_2 thin films related to the growth rate. The higher the growth rate, the smaller the grain size as fully dense films are formed [19]. Nevertheless, this is not the case for this study. The growth rate of the deposited TiO_2 thin films is likely to be in the the mass transport of the second kind of control where the transfer of reactant in the main gas flow and the substrate surface are the slowest steps. In this regime, the mass transfer of the main gas flow and the substrate surface is through diffusion or convection. As the reaction chamber is under vacuum, the diffusion of the active gasous

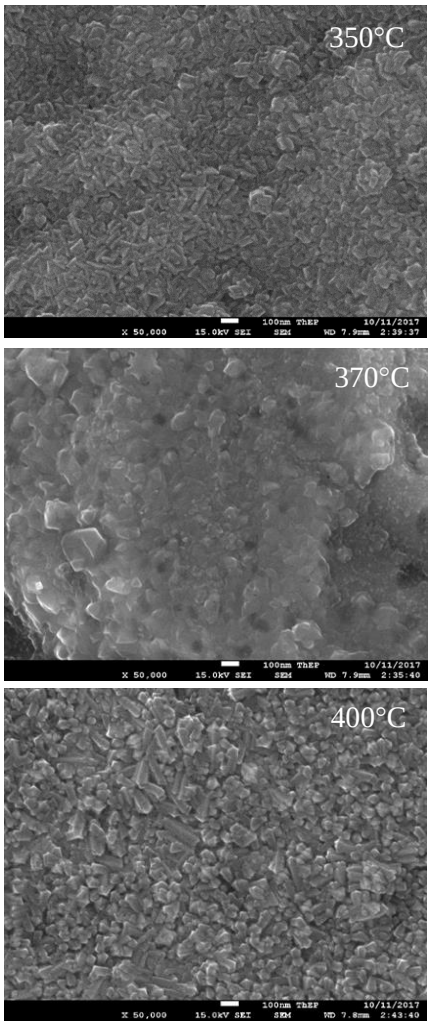

Figure 1. FESEM images of deposited TiO_2 thin films at 50 kX at the deposition temperatures of 350°C (top), 370°C (middle) and 400°C (bottom).

precursor through the boundary layer to the surface is the rate limiting step. Because the diffusion coefficients vary slightly with temperature and inversely depend on pressure. The growth rate depends weakly on the temperature, the growth rate is remarkably has smaller slope than other regimes [19,20]. As a result, the deposited TiO_2 thin films have different crystal shape and slightly different in grain size.

3.2 Phase of deposited TiO_2

The X-ray diffraction pattern of deposited TiO_2 thin films is shown in Figure 2. The difference morphology of the deposited films caused the difference in X-ray intensity. The XRD pattern shows that the deposited TiO_2 thin films have mixed phase of both rutile and anatase phases. The diffraction peaks related to the TiO_2 phase are at 2θ degrees with phases and Miller indices of anatase (101) and (200), and rutile (210). The anatase (200) was observed at the deposition temperature 370°C where the surface morphology has both large and small microstructure, which may due to the growth rate of the film [20]. The intensity of the peaks depend on the microstructure of the films. The substrate peak (S) was also detected.

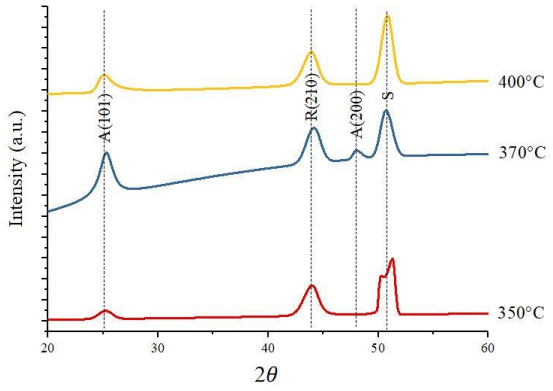

Figure 2. XRD patterns of TiO_2 thin films deposition at temperature of 350°C, 370°C and 400°C.

3.3 Wettability of deposited TiO_2

The wettability of the deposited TiO_2 thin films was studied through the contact angle measurement. The deposited TiO_2 thin films at the deposition temperature of 400°C has the highest contact angle of 95.4°. The minimum contact angle of 43.9° was at the lowest deposition temperature in this study, 350°C. Table 1 summarized the contact angle at various deposition temperatures varied in this study.

Table 1. Contact angle of deposited TiO_2 thin films at various deposition temperatures.

Deposition temperature (°C)	Contact angle (°)
350	43.9
370	75.6
400	95.4

The contact angle tends to be related to the surface morphology. It tends to increase as the grain size decreased with an increase in the deposition temperature when the deposition is in the kinetic limited regime. The deposition temperature influences the nucleation and growth of the deposited films; hence affects the properties of the deposited films. In general, the wettability depends on the chemical composition, crystal structure and surface morphology. These parameters affect the surface energy of the films [19,20]. High surface energy results in low contact angle. Therefore, it could be implied that the surface energy decreased with increased deposition temperture and reduced grain size. The grain size of the deposited TiO_2 thin film at 370°C has the smallest grain size yet not the lowest contact angle. This may due to the crystallographic orientation and roughness of the deposited thin films [20]. In addition, it could be implied that the growth rate of the deposited TiO_2 thin films are in the the mass transport of the second kind of control as mentioned in the surface morphology of deposited TiO_2 thin films section. The contact angle increases as the deposition temperature increases with larger grain size due to the decrease in growth rate when the mass transport of the second kind is the rate limiting step. The deposition temperature of 370°C has the smallest grain size, which could be implied that it has the faster growth rate in this growth regime.

3.4 Photocatalytic activity of TiO_2

The photocatalytic activity of TiO_2 thin films was investigated through the decomposition of methylene blue after UV exposure of 120 min. The absorbance measured from UV Spectrophotometer is shown in Figure 3. The absorption of methylene blue at the strongest absorption peak ≈663 nm of the full analysis wavelength of 550-700 nm is summarized in Table 2.

Table 2. Absorbance of methylene blue at various deposition tempetures compared with Degussa P25 at 663 nm.

Time (min)	Degussa P25	Deposition Temperature		
		350 °C	370 °C	400 °C
30	0.975	1.041	1.055	1.049
60	0.932	1.017	1.028	1.029
120	0.825	0.989	1.014	0.998
Degradation Efficiency (%)	15.4	5.0	3.9	4.8

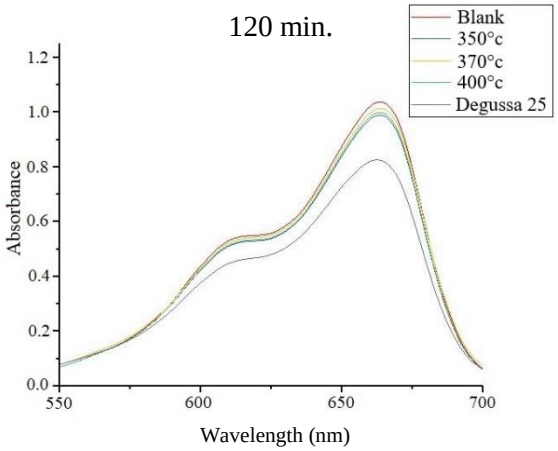

Figure 3. Absorbance of methylene blue at 120 min.

Degussa P-25 was used to compared the photocatalytic activity of the deposited TiO_2 thin films at various temperatures. The Degussa P-25 is the most widly used as a standard reference for comparisons of the photocatalytic activity under various treatment conditions [1]. It is in powder form consisting of both rutile and anatase crystallites [21]. It should be noted that due to the limitation of the scale, the surface area of the Degussa P-25 used was 10 times higher than the surface area of the TiO_2 coated on flat stainless steel substrates. In addition, the Degussa P-25 was applied in a slurry form and was not fixed on any substrate because the slurry form is ususally preferred. The slurry form has more surface active sites; hence is not limited by mass tranfer to the surface active sites [1].

The photocatalytic activity of the applied Degussa P-25 was the most effective after 30 min UV exposure and until 120 min UV exposure as well as its degradation efficiency. This is as expcected because the calculated surface area of the applied Degussa P-25 was 10 times higher than the surface area of the deposited TiO_2 thin films coated on flat substrate. In addition, it has been report that the mixture of the phase of the Degussa P-25 of rutile and anatase cause synergistic effects and increasing of photocatalytic activity compared to a single phase [24].

The photocatalytic activity after 120 min UV exposure of TiO_2 deposited at 370°C is the least effective. As the deposited films at all deposition temperatures are both rutile and anatase, the decreased of the photocatalytic activity is due to surface morphology of the deposited film and the diffusion of cationic impurities from the stainless steel substrate [21,25]. The surface morphology affects the adsorption of methylene blue, which generally occurs at the surface and in the near-surface region of the deposited TiO_2 film [25]. The diffusion of the cationic impurities increased the recombination process of photo-electronic carriers, which normally decreased the photocatalytic activity when the deposition temperature increased [21]. However, in this study, the photocatalytic activity did not decreased when the deposition temperature increased. This is because the nature of the PP-MOCVD that the increase of temperature does not increase the growth rate, which higher growth rate results in denser microstructure [26]. The growth rate of the deposited TiO2 films at various deposition temperatures is decreased with increased temperature; hence the photocatalytic activity tends to decrease with increased temperature. In addition, as the growth rate of the deposited TiO_2 thin films are in the mass transport of the second kind of control as discussed above, the degradation efficiency of the deposited TiO_2 thin films were not drastically different. The deposited TiO_2 thin films at the deposition temperature of 370°C has the smallest grain size; hence the degradation efficiency should be the highest. The photocatalytic activity of smaller grain size is more effective due to the increasing of specific surface active sites. Nevertheless, the internal stress is increased and can cause a crystal lattice distortion, which changed the energy band gap [5]. As a result, the influence the photocatalytic activity was not more effective when grain size is smaller. The surface morphology of the deposited TiO_2 thin films

also affect the band gap due to different surfaces; hence the photocatalytic activity as the adsorption of molecules and subsequent charge transfer to the molecules varied [27-29].

4. Conclusions

TiO_2 thin films on flat stainless steel 304 were deposited using PP-MOCVD at the deposition temperatures of 350°C, 370°C and 400°C to study the surface morphology, phase and wettability of the deposited TiO_2 thin films on the photocatalytic activity. At these deposition temperatures, different surface morphology of the deposited TiO_2 thin films was observed from FESEM at 50kX. Petal-like microstructure was found at the lowest deposition temperature, 350°C. Round shape microstructure was observed at the highest deposition temperature. The phase of the TiO_2 thin films according to the XRD is rutile and anatase with various orientations. The wettability or hydrophobicity tends to increase with the deposition temperature whereas the photocatalytic activity was maximum at the lowest deposition temperature in this studied of 350°C.

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