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CHARACTERIZATION OF TiO_2 THIN FILMS DERIVED USING ACETIC ACID AND NITRIC ACID

(Pencirian Filem Nipis TiO_2 yang Dihasilkan Menggunakan Asid Asetik dan Asid Nitrik)

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Abstract

Titanium dioxide (TiO_2) thin films were prepared *via* sol gel method using different concentration of glacial acetic acid and nitric acid. The deposition of TiO_2 gel on the ITO substrate was conducted using spin coating techniques at a rate of 3,000 rpm for 30 s and was calcinated at 500 °C for 10 minutes. The study was conducted to determine the surface morphology and characteristic of the TiO_2 thin film based on the different acid precursor. The GAA – TiO_2 and HNO_3 - TiO_2 thin film were analyzed using Contact Angle Goniometer for absorption property study and Scanning Electron Microscope (SEM) for surface topography study. The result indicated that different acid and different concentration influence wettability of the synthesized TiO_2 thin film. Higher concentration of GAA results in higher contact angle of TiO_2 thin film whereas higher concentration of HNO_3 reduced the contact angle of TiO_2 thin film. However, the contact angle obtained through this study was in a range of 27.55° – 67.55° for the concentration acid of 8 – 10 mmol which represent hydrophilic characteristic of the TiO_2 thin film. For surface analysis, uneven and not uniform surface of thin film was detected for the entire sample. This might be due to the several factors such as temperature and particle size that limited the adhesion of the TiO_2 sol gel to the ITO substrate. Transform Infrared Spectroscopy (FTIR) analysis was used to validate the present of the Ti-O bond vibrations in the sample and it was observed in ranges of 515–800 cm^{-1}. On the other hand, the crystallinity structure of the synthesized TiO_2 was validated using X-ray Diffraction (XRD). The results indicated that both GAA - TiO_2 and HNO_3 - TiO_2 mixtures gave a strong anatase crystal structure. The major XRD diffraction peaks can be attributed to (101), (004), (200), (211), (204) and (116) plane of the tetragonal TiO_2-anatase phase.

Keywords: characterization, acid, thin films, titanium dioxide, titanium isopropoxide

Abstrak

Titanium dioksida (TiO_2) filem nipis telah dihasilkan melalui kaedah sol gel dengan menggunakan kepekatan asid asetik glasial dan asid nitrik yang berbeza. Pemendakan gel TiO_2 pada substrat ITO dilakukan menggunakan teknik salutan berputar pada kadar 3,000 rpm selama 30 s dan dikalsinasi pada 500 °C selama 10 minit. Kajian ini dijalankan untuk menentukan morfologi permukaan dan ciri-ciri filem TiO_2 nipis berdasarkan kepekatan asid yang berbeza. Filem nipis GAA - TiO_2 dan HNO_3 - TiO_2 dianalisis dengan menggunakan goniometer sudut sentuh untuk kajian ciri-ciri penyerapan dan mikroskop imbasan elektron (SEM) untuk kajian topografi permukaan. Hasil kajian menunjukkan bahawa asid yang berbeza dan kepekatan yang berbeza mempengaruhi kelembapan TiO_2 filem nipis yang dihasilkan. Kepekatan GAA yang tinggi menghasilkan sudut sentuh yang lebih tinggi pada TiO_2 filem nipis manakala kepekatan HNO_3 yang lebih tinggi mengurangkan sudut sentuh TiO_2 filem nipis. Walau bagaimanapun, sudut hubungan yang diperolehi melalui kajian ini adalah dalam lingkungan 27.55° - 67.55° untuk kepekatan asid 8 - 10 mmol yang mewakili ciri hidrofilik TiO_2 filem nipis. Untuk analisis permukaan, permukaan filem nipis adalah tidak rata dan tidak seragam dikesan untuk semua sampel. Hal ini mungkin disebabkan beberapa faktor seperti suhu dan saiz zarah yang menghadkan pelekatan sol gel TiO_2 kepada substrat ITO. Analisis Spektroskopi Inframerah (FTIR) digunakan untuk mengesahkan kehadiran getaran Ti-O di dalam sampel dan keputusan menunjukkan kehadiran getaran Ti-O di dalam lingkungan 515-800 cm^{-1}. Manakala struktur kristal TiO_2 yang disintesis telah disahkan dengan menggunakan pembelauan sinar-X (XRD). Keputusan menunjukkan bahawa campuran GAA - TiO_2 dan HNO_3 - TiO_2 memberikan struktur kristal anatase yang kuat. Puncak pembelauan XRD yang utama boleh dikaitkan dengan fasa TiO_2-anatase tetragonal pada (101), (004), (200), (211), (204) dan (116).

Kata kunci: pencirian, asid, filem nipis, titanium dioksida, titanium isopropoksida

Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium with chemical formula of TiO2. It is sourced from ilmenite, rutile and anatase [1]. It has been explored in a widen industrial application due to its unique physical, chemical and electro-optic characteristic such as low cost, easy handling, non-toxicity, and resistance to photochemical and chemical erosion. TiO_2 has been used as a material in solar cells, chemical sensors, for hydrogen gas evolution, as pigments, self-cleaning surfaces, and environmental purification applications [2]. Another potential of TiO_2 is in form of thin film. The research of the thin film TiO_2 has been explored by Kajitvichyanukul et al. [3] for photocatalytic reduction of chromium(VI) in photocatalysis process. The photocatalytic reactivity of the obtained thin film is at a par with the reactivity using powder TiO_2. The results indicate that the differences in photocatalytic reduction of Chromium(VI) could be correlated with the structural morphology of the thin film. As indicated by Qiu et al. [4], TiO_2 nanostructured thin films possess a large surface area and show unique chemical, physical and electronic properties that are different from those bulk materials. These characteristics make it a potential material in in constructing a novel sensing device such as electrochemical sensors and biosensors. However, the characteristic of the thin film TiO_2 might be varies based on the method used to fabricate it. Several methods have been employed to fabricate TiO_2 films, including sputtering, chemical vapor deposition, and sol-gel process [5, 6, 7]. However, the sol-gel process is one of the most appropriate technologies to prepare thin oxide coating. The interest in application of sol-gel method is due to several advantages including; good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost, and good photocatalytic properties [8].

This paper, aims to investigate effects of the preparation conditions on the surface morphology and properties of TiO_2 thin film. Titanium dioxide (TiO_2) thin film was prepared by glacial acetic acid- sol-gel method and nitric acid -sol-gel method. The phase transformation was investigated by an X-ray diffractometer (XRD) and the microstructure was characterized by a scanning electron microscope (SEM).

Materials and Methods

Preparation of sol-gel solution

The preparation of titanium dioxide solutions had been performed by sol-gel method. Fifty milliliter of absolute Ethanol (99% Merck) was mixed with 5 ml glacial acetic acid (99.5% GCC), 6.6 ml titanium tetra isopropoxide TTIP (99%, sigma-Aldrich). Then, these liquids were continuously stirred by using a magnetic stirrer on a hot plate. Acetylacetone, glacial acetic acid (GAA), distilled water and polyethylene glycol (PEG) were added and these solutions were stirred vigorously for 2 hours at temperature 50 °C and 300-500 rpm. After 2 hours, the solution was sonicated inside the ultrasonic cleaner for 30 minutes. ITO glass slides (25 mm x 25 mm x 2 mm) were used as substrate after cleaned with acetone, ethanol, and deionized water in an ultrasonic bath. Thereafter, the slides were dried with filter paper. Spin coating method was used for deposition of TiO_2 gel on the substrate at a rate of 3,000 rpm for 30 s. Then, the samples was dried at 150 °C for 5 minutes and calcined at 500 °C for 10 minutes. Reagents were used as we received from supplier without more purification. Similar procedure was repeated for nitric acid - sol-gel solution.

Characterization of TiO_2 film

The crystal structure of the TiO_2 coated on ITO was characterized by $\theta/2\theta$ X-ray diffractometer (Seifert, PTS 3000, USA) using Cu Kα radiation (λ=0.154 nm) (45 kV at 200 mA). The XRD pattern was obtained at 2θ angle range of 20–80° with a scanning step of 0.02°/step and a scanning speed of 5°/min. Scanning electron microscopy (SEM – EFI Company) was used to investigate the surface morphology of the thin films. The Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Fisher, Nicolet iG50, USA) was used to evaluate the functional group present in the synthesized TiO_2 and Contact Angle (AST, VCA 3000S, USA) analysis was used to evaluate the absorption property of the TiO_2 thin film. The method used is according to Miao et al. [9].

Results and Discussion

Absorption properties of the TiO_2 thin films

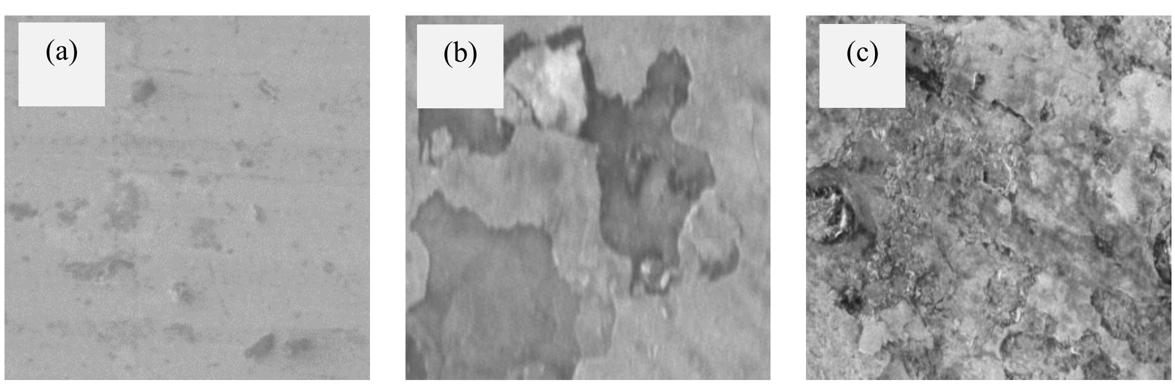
To evaluate the surface properties of the thin films, contact angle analysis was carried out in order to determine the hydrophilicity of the sample. The contact angle is the angle, conventionally measured through the liquid, where a liquid–vapor interface meets a solid surface. It quantifies the wettability of a solid surface by a liquid. Table 1 shows the result of contact angle analysis of the TiO_2 thin films. From the results, it was found that the contact angles for synthesizing TiO_2 thin films was less than 90^o which consider that the solid surface of TiO_2 thin films is hydrophilic. Two different acids were used in the preparation of TiO_2 thin film and the results indicated that nitric acid (HNO_3) gave higher contact angle value as compared to glacial acetic acid (GAA) thin film. However, increment of acid concentration reduced contact angle of the TiO_2 thin film to 34.86^o at 10 mmol HNO_3 instead of 67.6^o at 8mmol HNO_3. On the other hand, increment of GAA concentration up to 10 mmol, increased contact angle of TiO2 thin film to 39.95^o from 27.55^o at 8mmol GAA. However, all of the samples were hydrophilic film and it is suitable to be used in application of bio-liquid detection system. According to Li et al. [10], hydrophilic characteristic of thin film gave a great application potential on serving as biosensor. The finding indicated that SiN thin film surface is hydrophilic with contact angle of 45^o. Similar finding had been reported by Miao et al. [9] which indicated that the deposited porous and amorphous TiO_2 thin films enable an increase of the surface tension of the material, thereby improving absorption property of the composite structure.

Table 1. Contact angle of TiO_2 thin films with different concentration of GAA and HNO_3

Concentration GAA (mmol)	Contact Angle (°)	Concentration HNO_3 (mmol)	Contact Angle (°)
8	27.55	8	67.60
9	39.35	9	52.40
10	39.95	10	34.85

Surface morphology and surface area of the TiO_2 thin films

The surface morphology of the TiO_2 films was examined using SEM and is revealed in Figure 1. SEM images of different films derived from GAA and HNO_3 catalyst was very similar to each other. The adhesion of the TiO_2 thin film was observed for both sample but the surface was not smooth with irregularities. SEM image of GAA – TiO_2 and HNO_3 – TiO_2 at 9 mmol had shown a crack surface and not uniform structure (Figure 1b and e).



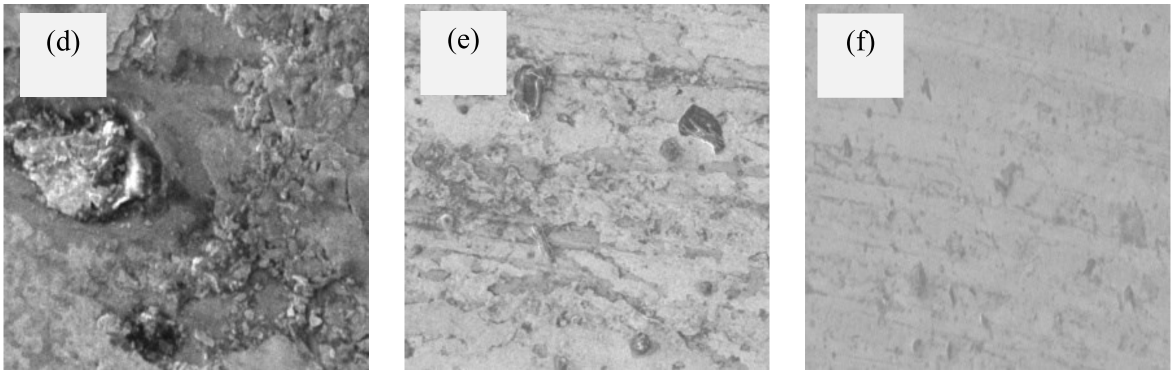


Figure 1. FE-SEM images of TiO_2 thin films (a) 8 mmol GAA (b) 9 mmol GAA and (c) 10 mmol GAA (d) 8 mmol HNO_3 (e) 9 mmol HNO_3 (f) 10 mmol HNO_3

The surface was almost plain for all sample with some agglomerations were detected at 8 mmol GAA – TiO_2 and 10 mmol HNO_3 – TiO_2 thin film (Figure 1a and f). The tendency of particle agglomeration might happen which is directly related to the increase in crystallite size. On the other hand, the temperature might influent the surface morphology of the thin film. Higher temperature during annealing may lead to non-uniform and cracked coating and reduce coating lucidity and transparency. According to Alzamani et al. [11], this is due to substrate plasticity and softening or crystalline size increase or film structure variation. In a sol-gel process of transition metal alkoxides, hydrolysis and condensation reactions occur very rapidly, so uniform and ultrafine products are difficult to obtain. With the use of bulky, branched alkoxy groups (i.e. isopropoxides), the hydrolysis and condensation rates can be reduced to favor the formation of nanometric clusters, yielding a more uniform particle size.

Fourier transform infrared spectroscopy analysis of TiO_2 powder

Figure 2 shows the FTIR pattern of TiO_2 synthesized from sol-gel method with glacial acetic acid and nitric acid in range of 515-4000 cm^{-1}. Both graph shown a similar trend and intensity of the spectrum. In all spectra measured, the bands assigned to the stretching vibrations of OH groups (at about 3400-3437 cm^{-1}) together with the bending vibrations in H_2O molecules (at about 1529 cm^{-1}) were observed, which relates to the sol-gel synthesis. The intensity of all those bands will decreases during an annealing process. While, bands connected with Ti-O bond vibrations occur in the ranges of 515-800 cm^{-1}. Similar finding was recorded by Fatma et al. [12] and Adamczyk and Dlugon [13]. Moreover, the bands at 1050, 1089, and 1138 cm^{-1} were ascribed to stretching of Ti-O-C while lower mode of amorphous TiO_2 appeared at 932 cm^{-1} [14-15]. While the peak appeared at 1249-1250 cm^{-1} and 1285 cm^{-1} was the vibration mood of C-O-O group. The doublet in 1349-1350 cm^{-1} and 1443-1445 cm^{-1} designated the symmetric and asymmetric stretching vibration of the carboxylic group coordinated to Ti as a bidentate ligand [16].

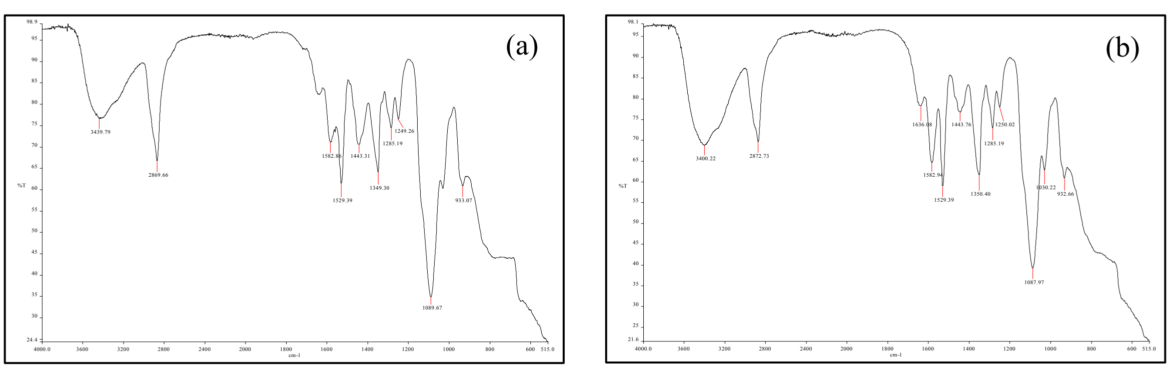


Figure 2. (a) FTIR pattern of TiO_2-GAA powder, (b) FTIR pattern of TiO_2-HNO_3 powder

X-Ray diffraction analysis of TiO_2 powder

Figure 3 shows the XRD images of GAA-TiO_2 and HNO_3-TiO2. The GAA-TiO_2 and HNO_3-TiO_2 diffraction peaks showing similar crystallinity properties. On diffractograms, the dominant peaks were associated with anatase (A), rutile (R) and brookite (B) phases. It can be seen that both samples showed the anatase TiO_2 crystal structure. The major XRD diffraction peaks can be attributed to (101), (004), (200), (211), (204) and (116) plane of the tetragonal TiO2-anatase phase. Theoretically, all the TiO_2 samples are polycrystalline in nature with most intense peak corresponding to (110) plane. Similar result was obtained by Tsegaa and Dejeneb [17], Yu et al. [18] and Thamaphat et al. [19]. The results show that low concentration of GAA results in higher intensity of the anatase phase at (101) plane.

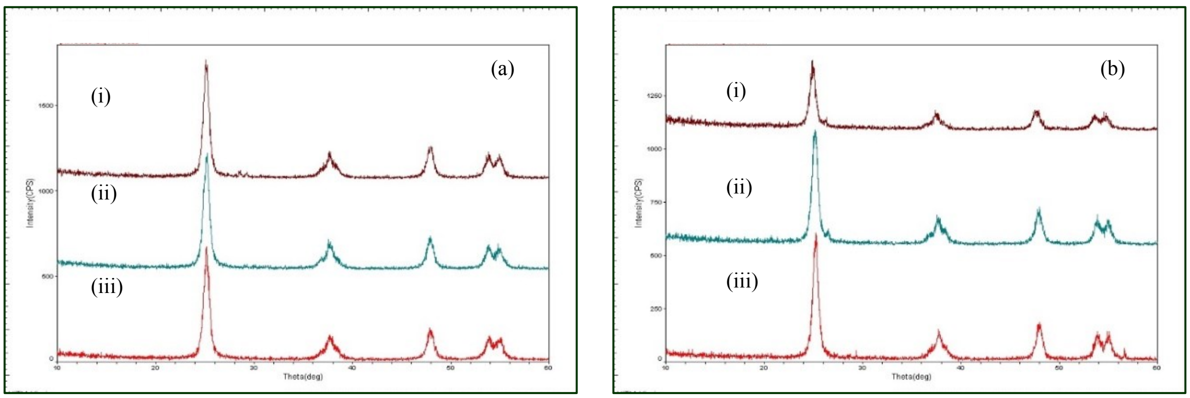


Figure 3. (a) XRD pattern of (i) 8 mmol GAA (ii) 9 mmol GAA (iii) 10 mmol GAA of TiO_2 powder, (b) XRD pattern of (i) 8 mmol HNO_3 (ii) 9 mmol HNO_3 (iii) 10 mmol HNO_3 of TiO_2 powder

On the other hand, higher concentration of HNO_3 was leaded for higher intensity of the anatase peak in HNO_3-TiO_2 sample at (101) plane. This might occurred due to the different kinds of strain such as tensile and compressive in the TiO_2 particle. In the study by Tsegaa and Dejeneb [17], the diffraction peaks of the TiO_2 were shifted slightly to the higher angle side with the increase of acid concentration. While, Serrano et al. [20] claim that nitric acids lead to the development of TiO_2 photocatalysts with convenient textural properties which produce the selective crystallization into anatase with small nanocrystals being present within the pore walls. This shown that concentration of the acid will influence the crystallinity polymorphs of the material.

Conclusion

Titanium dioxide (TiO_2) thin films was developed using 2 different acid which is GAA and HNO_3 gave different characteristic and properties of TiO_2 thin film. Both acid results in hydrophilic characteristic of thin film with contact angle value less than 90^o. However, increasing the concentration of GAA reduced hydrophilicity value of TiO_2 thin film. On the other hand, higher concentration of HNO_3 results in higher hydrophilicity value of TiO_2 thin film. On the other hand, different acid and its concentration results in similar topography image of the thin film. Deposition of TiO_2 sol gel was observed on ITO substrate but uneven and not uniform layer of TiO_2 was presented. While for FTIR and XRD analysis of the both sample, the present of Ti-O group was observed at the absorbance range of 515-800 cm^{-1} and the crystal peak observed for both sample were associated with anatase (A), rutile (R) and brookite (B) phases which represents the nature characteristic of TiO_2.

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