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Microstructure and Wettability of Graphene Oxide/TiO_2 Thin Film Prepared via Sol-gel Method

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Abstract. The microstructure of graphene oxide TiO_2 (GO/TiO_2) films on wettability and morphology properties were studied at different amount of Titanium isopropoxide with fixed amount of GO. GO/TiO_2 thin films were prepared by using sol-gel method and deposited on glass substrate by spin-coating technique. The formation of GO/TiO_2 was confirmed by using Fourier Transform Infrared Spectroscopy (FTIR) study while the morphology of GO/TiO_2 was observed by Scanning Electron Microscopy (SEM) analysis. The hydrophilic/hydrophobic interactions of these films were examined by wettability test by measuring the water contact angle of the water drop on the surface of the coating. The wettability tests display that the contact angle of GO/TiO_2 was increased from 90.0º to 118.7º after reduce the amount of titanium isopropoxide (TTIP). A small peaks of graphene and Ti were observed in the coated films and more pronounce peaks occur after the films were annealed. However, it was found that the annealing process does not improve the contact angle of the films as compared to the non-annealed films.

1. Introduction

Self-cleaning technology is among the technologies existing in today's world. Self-cleaning coatings can be classified into two major categories which are hydrophilic and hydrophobic. Both of the categories involve water to self-clean themselves. In a hydrophilic coating, the water is made to spread surface in which a liquid on a solid surface makes a film over the surfaces. This will carry the dirt and other impurities, whereas in the hydrophobic coating, the water droplets slide and roll over the surfaces in which a water drops remain spherical on the solid surface thereby cleaning them [1]. Self-cleaning action of TiO_2 over the past years that mainly discuss photocatalytic activity of TiO_2.

Titanium dioxide (TiO_2) also known as titania is a white inorganic solid substance and also a most investigated materials in photocatalysis [2]. Pure TiO_2 is obtained from ilmenite or leuxocene ore [3]. TiO_2 holds many holds many possible applications including environmental and energy applications due to its excellent properties such as nontoxic, chemically stable, cheap, and easily available material, having a bandgap of 3.2 eV in the ultraviolet (UV) region [4]. However, there are limitataion in the photocatalytic e□ciency of pure TiO_2 due to rapid recombination of photogenerated electron–hole pairs within TiO_2 particles and lack of visiblelight absorption. Nobel metal deposition is one of the technique to overcome the limitation [5]. Suitable metal oxides deposition can enhance the hydrophilic and hydrophobic porperties.

Graphene oxide is the appropriate nobel metal to overcome the limitation due to its high surface area, high electrical conductivity (106 S^{cm-1}), high carrier mobility (200,000 cm^2 V^{-1} S^{-1}) and e□cient electron (e^-) transfer from TiO_2 to graphene as its redox potential is just below the conduction band (CB) edge TiO_2 [6]. Graphene film can provide improved surface properties such as friction coefficient [7], optical transmittance [8], and thermal conductivity [9].

In this study, we have investigated the effects of doping with graphene oxide on the hydrophilic property and hydrophobic property at different concentration of TiO_2 as well as annealing process on the hydrophobicity of films. Sol-gel method is used to fabricate thin films due to its advantages such as easy, good homogeneity, ease of composition control and good optical properties. In particular, the sol-gel process is very efficient in producing thin and transparent multi-component oxide layers on various substrates such as stainless steel plates, alumina plates, glass panels and ceramic tiles. This work contributes to the comprehension of using modified TiO_2 as self-cleaning materials.

2. Methodology

2.1 Materials
All the chemicals used in the study were of analytical reagent grade available from several suppliers and were used as received without further purification. Graphene Oxide powder (4-10% edge-oxidized) and titanium tetraisopropoxide (TTIP) 97% was purchased from Sigma Aldrich, 2-propanol AR from QReC and Acetic Acid (99.5%) was from Daejung Reagent Chemicals. Hydrolysis reaction will result in precipitation by using precursors with strong reactivity towards water (eg. Titanium alkoxide). To overcome the percipitation, non-aqueous sol–gel techniques was used with titanium chloride or titanium alkoxides as a precursor. In case of the reactions using TiCl4 as a precursor, TiO2 forms under release of a large amount of HCl gas. Because HCl gas is toxic and chlorine impurities often remain in the final oxide material, titanium tetraisopropoxide are preferred as a precursor. In order to increase the stability of the solutions from titanium alkoxide precursors, it is not sufficient to switch to a non-aqueous sol–gel route. Indeed a chelating agent is still needed in a non-aqueous sol–gel route to obtain highly stable sols [10].

2.2 Substrate Preparation
In this study, the glass slide with dimension size of 10 mm × 10 mm are used as substrate. The substrate was cleaned by using acetone and was placed in ultrasonic cleaner for 20 minutes in order to remove the contaminants on the glass surface. Then, the glass slides were rinsed with distilled water to remove the hydroxyl contaminants, and these glasses were then dried under room temperature for about 30 minutes.

2.3 Preparation of Graphene Oxide / TiO_2
Firstly, titanium tetraisopropoxide (TTIP) was mixed with 2-propanol with two different ratios (TTIP: 2-propanol) which is 1:9 and 1:20 ratio with fixed loading of 1 mg of graphene oxide was added to the solution together. This resultant titanium precursor solution was stirred vigorously for 20 minutes. Then, 0.10 mL acetic acid was added to the solution. Continue vigorous stirring for 1 hour to obtain the final solution for the preparation of graphene oxide and TiO2 thin films. After the substrate was properly cleaned, the solution was deposited dropwise on the substrate at a speed of 2000 rpm for 30s by spin coating technique. The wet films were dried at 60ºC for 10 minutes, it was then annealed at 350ºC in the muffle furnace for 1 h. The heat treated films were stored in Petri dishes with lid for further use.

2.4 Characterization of Graphene Oxide/ TiO_2 thin films
The structure analysis was determined by FTIR spectra using Jasco FTIR 4200 spectrometer (Jasco International Co. Ltd., Japan) at the room temperature in the spectral range of 600–4000 nm. The surface morphology of the layers was observed and the microstructure of the films was determined by EDX technique by Surface Electron Microscopy (SEM) JSM-6460 LA Jeol Japan in School of Material Engineering, Universiti Malaysia Perlis (UniMAP). While all contact angle measurements were conducted using self made water contact angle apparatus with image capture by optical microscope and analyze by J Image software to obtain the angle.

3. Results and Discussion

3.1 Functional Group of GO/TiO_2
The FTIR spectra of glass substrate and GO/TiO_2 are shown in Figure. 1. Figure.1(a) shows the peak of Si-Si interaction at 2300 cm^{-1} and 2123 cm^{-1}. As compared blank glass substrate with GO/TiO_2, Fig.1(b) shows that an obvious peak was observed at 1399 nm^{-1} corresponded to C=O, indicating that the existed of GO in the films. The characteristic peaks of graphene oxide can also be found at 2900 cm^{-1} and 2700 cm^{-1} confirming that successfully prepared GO-TiO_2. Moreover, Figure.1(b) shows the broad peak the broad

absorptions at low frequencies below 1000 cm^{-1} were ascribed to the stretching vibrations of Ti–O–Ti bonds in TiO_2. The peak in FTIR spectra observe similar to previous study by Martins et.al [11].

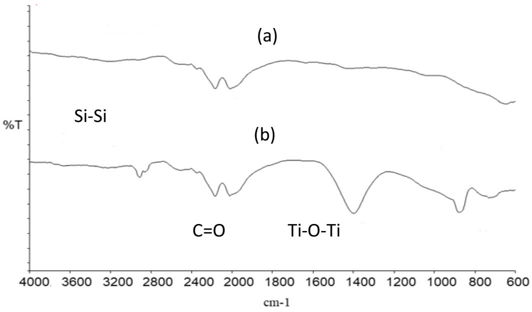


Figure. 1. FTIR spectra of (a) glass substrate and (b) GO/TiO_2 film.

3.2 Surface Morphology of Graphene Oxide/TiO_2

Figure 2 shows micrographs of two different ratio of GO/TiO_2 thin films which are 1:9(GO/TiO_2) and 1:20(GO/TiO_2) microstructure of the dispersion-distribution of graphene nanosheets within the matrix TiO_2. Fig. 2(a) shows a non-annealed film at low ratio of 1:9(GO/TiO_2) while Fig. 2(b) and 2(c) were films for non- annealed and annealed at high ratio 1:20(GO/TiO_2) respectively. It can be seen that the morphology 1:9(GO/TiO_2) showed spongy morphology with most of the TiO_2 particles were combined together with each other. Interestingly, Fig. 2(b) shows the film was denser and compact at high ratio 1:20(GO/TiO_2). However, Fig. 2(c) exhibit that annealing process resulted of smaller particles with an even surface. It was clearly observed that TiO_2 particles were agglomerated at higher ratio by supported of graphene oxide sheets. The similar micrographs of GO/TiO_2 can also be observed in previous study by Abdelmajid et.al [12].

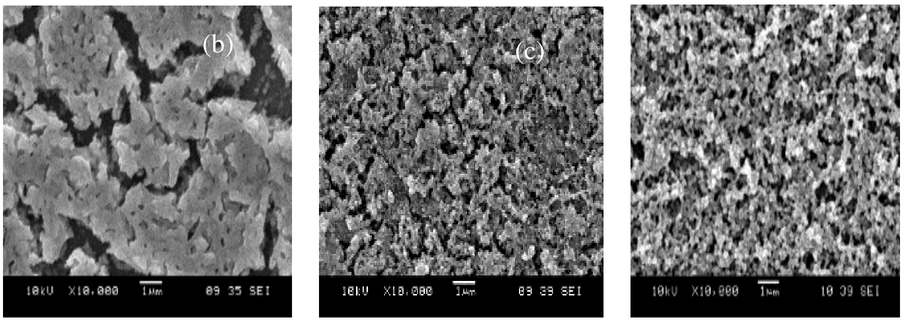


Figure 2. Scanning Electron Micrscopy micrograrphs of GO/TiO_2 films at two different ratios, (a) 1:9 without annealing) , (b) 1:20(without annealing) and (c) 1:20 (annealing at 350ºC)

3.3 Chemical Analysis

The chemical composition analysis was carried out on GO/TiO_2 thin film sample by Energy Dispersive X-ray (EDX) analysis. The representative (EDX) pattern of a ratio 1:20(GO/TiO_2) layer presented in Table 1, confirms the presence of C, O and Ti, indicating the formation of nanocomposite with high purity. The signal for C should mainly originate from the GO sheets, while those for Ti are from the TiO_2 nanoparticles. The signal of O could contribute by TiO_2 nanoparticles and a small amount of oxygen-containing groups on GO sheets.

3.4 Water Contact Angle

The water contact angle was carried out to analyze the hydrophilicity of TiO2 composite film. Fig. 4 shows the water contact angle of the prepared films with a significant decrement after addition of graphene oxide due to alteration of interaction of hydrophilic/ hydrophobic of TiO2. Figure. 4(a) shows that the photograph of water contact angle on the blank substrate. It was found that the wettability tests display that the contact angle of GO/TiO2 non-anneal was increased from 90.0º to 118.7º after reduce the amount of TTIP as shown in Figure. 4(b) and Figure. 4(c) respectively. Table 2 shows all the water contact angle of GO/TiO2 thin film at different ratio of TTIP with and without annealing process. This result shows that the films was subjected to high wettability due to addition of GO particles.

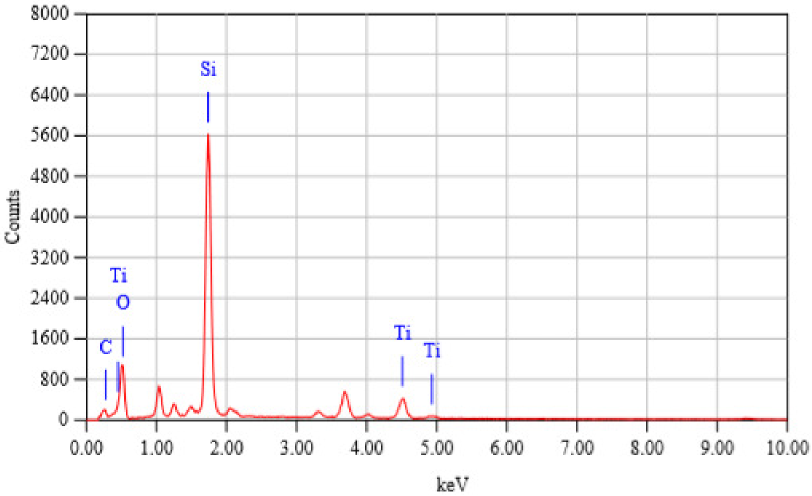
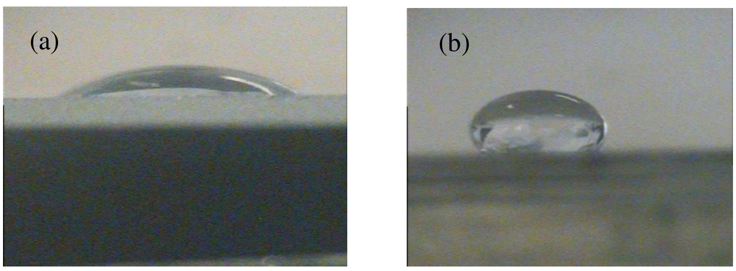


Figure 3. EDX diagram of ratio 1:20(GO/TiO2) film without annealing.

Table 1. Table of EDX element of ratio 1:20(GO/TiO_2) film without annealing

Element	Mass %	Atomic %
C K	8.62	14.94
O K	37.28	48.50
Si K	42.58	31.55
Ti K	11.51	39.39
Total	100.00	100.00

This can be confirmed in previous study by Narayanam et.al [13]. Furthermore, this finding was correlated to the amount of C, Ti and O_2 as reported in the EDX result. Nevertheless, it was found that annealing process does not improve the water contact angle of the film as observed in Figure 4(d).



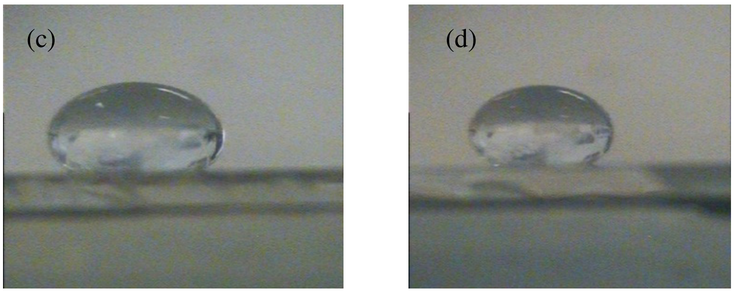


Figure. 4. Photograph of water contact angle of GO/TiO_2 at different ratio of TTIP.

Table 2. Water contact angle of GO/TiO_2 at different ratio of TTIP

Thin Film	Water Contact Angle (°)
Glass substrate without thin film	60.17
1:9 (GO/TiO_2) - without annealing	90.00
1:20 (GO/TiO_2) – annealing at 350°	114.44
1:20 (GO/TiO_2) - without annealing	118.70

4. Conclusions

From the research, GO/TiO_2 thin film were prepared in two different ratios of titanium isopropoxide with fixed amount of GO. The thin film was successfully prepared by sol-gel method using spin-coating deposition technique. Functional group analysis were obtained from FTIR spectra which indicated the presence of GO and TiO_2. While for morphology analysis by SEM analysis shows that at lower ratio (1:9) showed spongy morphology with most of the TiO_2 particles were combined together whereas at higher ratio (1:20) shows that TiO_2 particles was denser and compact. The hydrophilic and hydrophobic properties are reflected from wettability test which shows that the thin film will become hydrophobic at the higher ration of TiO_2 from 90.0° to 118.7°. From the wettability test also it was found that annealing process does not improve the contact angle of the film from hydrophilic to hydrophobic.

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