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Effect of graphene oxide on microstructure and optical properties of TiO_2 thin film

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Abstract. GO/TiO_2 thin films have been synthesized from titanium (IV) isopropoxide (TTIP) by a sol-gel method. The films were deposited onto a glass substrate using spin coating deposition technique then were subjected to annealed process at 350 °C. The different amount of graphene oxide (GO) was added into the parent solution of sol in order to investigate the microstructure, topography, optical band gap and photocatalytic activity of the thin films. The prepared thin films were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), UV-VIS spectrophotometry and degradation of methylene blue (MB). AFM images reveal a rougher surface of GO/TiO_2 thin film than bare TiO_2 thin film due to GO particles. Moreover, the SEM images showed the formation of semispherical microstructure of bare TiO_2 changes to some larger combined molecules with GO addition. The UV–Vis spectrophotometer results show that with optical direct energy gap decreases from 3.30 to 3.18 eV after GO addition due to the effect of high surface roughness and bigger grain size. Furthermore, the optical results also indicated that GO improved the optical properties of TiO_2 in the visible range region.

1 Introduction

Titanium dioxide (TiO_2) belongs to the family of transition metal oxides and is also occurring as a mineral in the nature. TiO_2 has received a great deal of attention due to its chemical stability, non-toxicity, low cost and other advantageous properties [1]. According to, the physical properties of TiO_2 make it suitable for thin film applications.
There are three types of crystal phases of TiO_2 which are anatase, brookite and rutile [2][3]. Among the three phases of TiO_2, anatase is known to be the most active under UV irradiation. However, the photooxidation process of anatase is still restricted for wide application because

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of low activity under visible light irradiation. To overcome these issues, several experiments have been made to enhance the reactivity and improve the visible photocatalytic activity of TiO_2. Numerous efforts was done such as noble metal deposition, cationic and anionic doping, sensitization and addition of sacrificial agents [4], [5]. Though the noble metal deposition has several advantages over others, high cost and low abundance of the noble metals restrict their use in large scale applications [6]. In this study, TiO_2 thin film was modified by adding various amount of graphene oxide to improve the photocatalytic activity performance of the thin film.

2 Experimental

An amount of GO (5, 10, 15 and 20) mg powder was mixed with some amount of ethanol and sonicate in ultrasonic bath for 30 minutes. In different beaker, titanium (IV) isopropoxide (TTIP) was mixed with ethanol with a ratio 1:20 (TTIP: ethanol) by using magnetic stirrer. The solution was stirred for about 5 minutes. Then the sonicated GO solution was added to the TTIP solution and the solution was continued vigorous stirring for 1 hour. Afterward, a few drops of acetic acid (~ 0.30ml) that act as a catalyst to the hydrolysis process were slowly dropped into the solution with vigorous stirring until clear solution is formed.

When GO/TiO_2 sol-gel solution was ready, the GO/TiO_2 with and without additives sol-gel were deposited onto the clean glass substrate by spin coating technique at 800 rpm for 30 seconds by using VTC-50 desktop spin coater. The glass substrate was coated with the GO/TiO_2 solution for 3 layers to make sure that all the surface covered with the solution. Next, the coated glass substrate will be annealed in a muffle furnace at 350 °C for 1 hour soaking time with annealing rate of 10°C/minute

3 Results and Discusssion

3.1 Phase Analysis

The XRD pattern of aTiO_2, aGO_5, aGO_{10}, aGO_{15} and aGO_{20} thin films with different amount of GO, 0 mg, 5 mg, 10 mg, 15 mg and 20 mg GO respectively, were presented in Fig. 1. Based on XRD pattern of GO/TiO_2 thin films, the results indicated that all the thin film sample presented only brookite phase. According to the standard ICDD card No. 00-029-1360, characteristic diffraction peaks for brookite phase of TiO_2 are shown at $2\theta = 33.5°$ which corresponded to (121) plane. The diffraction peaks of aGO_5, aGO_{10} and aGO_{15} showed mixed phase of anatase and brookite, where 2θ values of 24.8° can be attributed to (101) plane of anatase while 2θ value of 33.5° can be attribute to (121) plane of brookite TiO_2 (ICDD Card No. 01-070-8501). It can also be seen in that there is a sharp peak at $2\theta = 21.9°$ which indicate the silicone(Si) peak resulted from the substrate XRD pattern.

This occured due to the annealing temperature factor where the brookite TiO_2 will form an anatase structure slowly with further annealing to 500-600°C [7]. As from the previous study by K. Fischer *et al* [8], anatase phase of TiO_2 will growth better at higher temperature. Meanwhile, D.S.C Halin *et al* have characterization of TiO_2/SiO_2 thin films formed brookite phase at higher annealing temperature (400-500°C) [3]. Interestingly, the diffraction pattern of aGO_5, aGO_{10} and aGO_{15} shows an anatase phase of TiO_2 and the intensity is slightly reduced when amount of GO increases and later at aGO_{20} thin films the phase showed brookite $TiO_2$was formed again.

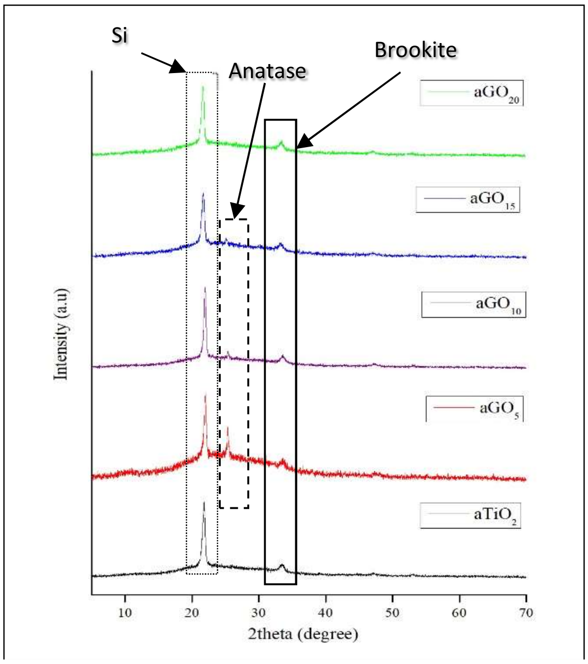

Fig. 1. XRD pattern of GO/TiO_2 thin films.

3.2 Surface Roughness and Topography Analysis

Surface roughness and topography analysis was examined by using Atomic Force Microscope (AFM) for all the produced thin films. The width the scan area was fixed at 5µm x 5µm. Ra and RMS values of thin film surfaces were calculated between microscopic peaks and valleys. Table 1 presents the roughness average (Ra) and roughness root mean square (RMS) of annealed GO/TiO_2 film samples. The aTiO_2 film having the RMS value of 2.34 x 10^2. After the addition of 5 mg GO (aGO_5) to the film, the RMS value shows a very significant increment which is 3.16 x 10^2. The RMS value was found to be the highest which indicates that by addition of 5mg GO, the surface become rougher. However, when 10mg, 15mg and 20 mg GO (aGO_{10}, aGO_{15} and aGO_{20}) added to the film, the RMS values decreases with RMS values of 1.87 x 10^2, 1.88 x 10^2 and 2.23 x 10^2 respectively.

After the addition of GO, the RMS of the surface increases which indicates the grains of regular shapes develop on the surface [9]. A significant increase in RMS value for GO/TiO_2 film with 5mg GO is observed due to the transformation process of TiO_2 to anatase phase, which involves the combination of smaller particles into bigger ones [10]. As reported by previous study by [11], high RMS indicates that GO/TiO_2 thin film exhibited high surface area, which in turn will give a greater absorption of the dye.

Table 1. Roughness average (Ra) and roughness root mean square (RMS) of thin films at various amount of GO.

Samples	Roughness Average (Ra)	Roughness Root Mean Square (RMS)
TiO_2	1.83 x 10^2	2.34 x 10^2
GO_5	2.57 x 10^2	3.16 x 10^2
GO_{10}	1.52 x 10^2	1.87 x 10^2
GO_{15}	1.36 x 10^2	1.88 x 10^2
GO_{20}	1.81 x 10^2	2.23 x 10^2

Fig. 2 shows the topography view and also three dimensional view of (a)aTiO_2, (b)aGO_5, (c)aGO_{10}, (d)aGO_{15} and (e)aGO_{20} thin films. From the Fig. 2(a), the molecular arrangement of the crystallites can be seen in TiO_2 film. The molecule is big and rough with the maximum height of 1395 nm. After the addition of 5mg GO as shown in Fig. 2**Fig.** (b), the surface morphology does not show the round shape molecule but the molecule is attached together and arrange in layers with the maximum thickness of 1740 nm. Meanwhile in aGO_{10}, aGO_{15} and aGO_{20} shows the round shape of TiO_2 molecule are slightly arrange in layers as the amount of GO increases. The maximum heights of the film also increase when the amount of GO increases which are 1083 nm, 1192 nm and 1388 nm. It can be seen that the formation of few layers of films and the stacking of GO/TiO_2 layers during formation of the thin films was also confirmed using AFM.

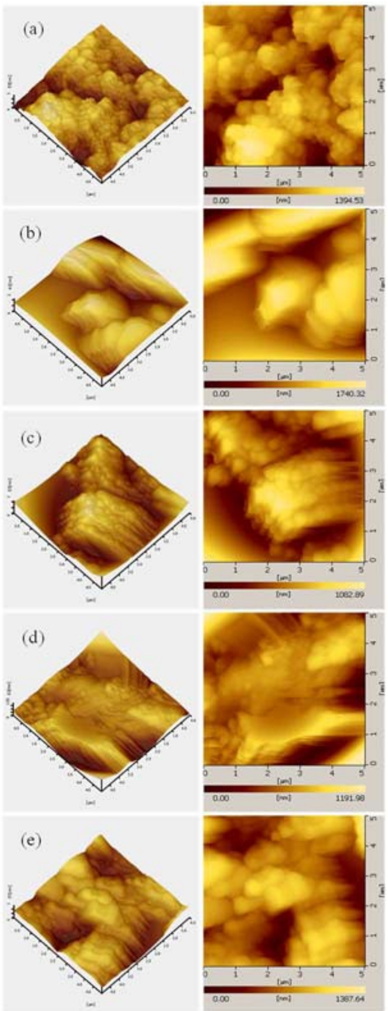

Fig. 2. AFM images of (a) aTiO_2, (b) aGO_5, (c) aGO_{10}, (d) aGO_{15} and (e) aGO_{20} thin film annealed at 350°C.

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3.3 Microstructure Analysis

Microstructure of all the GO/TiO_2 thin films prepared were analysed through scanning electron microscope (SEM) at 10000 times magnification with 20kV energy. The SEM analysis performed on annealed GO/TiO_2 films at different GO content, as can be seen in Fig. 3. From SEM images, it can be seen that sol-gel process has a homogeneous TiO_2 distribution in the film samples with the spherical TiO_2 particles. Fig. 3(a) shows a basic morphology of spherical grains presenting different sizes combined with a flower-like random formation synthesized TiO_2 photocatalyst [12] while as showed in Fig. 3(b) to (e), show that the different amount of GO in the composite obviously affect the microstructure of the films. Fig. 3(b) showed the particles of TiO_2 were coated by GO. While Fig. 3(c) and (d) the particles of TiO_2 become bigger grains size and less agglomerates were formed. It was noticed that, the molecules of the TiO_2 with coated GO shows better dispersion with even surfaces at higher loading of GO as shown in Fig. 3(d) and Fig. 3(e) respectively. Overall, the SEM shows that with addition of GO the grain size of TiO_2 becomes bigger as the amount of GO increase and aGO_5 exhibits unique microstructure. The findings were consistent by research done by [13] on microstructure of TiO_2 with GO addition shown that GO covered tightly the TiO_2 surface and the covered TiO_2 surface area increases with the GO content. Proper introduction of GO will both enhance the light absorption and the separation of photogenerated electrons and holes. In contrast, too much introduced GO will disturb the light absorption of TiO_2 and reduce the mobility of photo carriers [14].

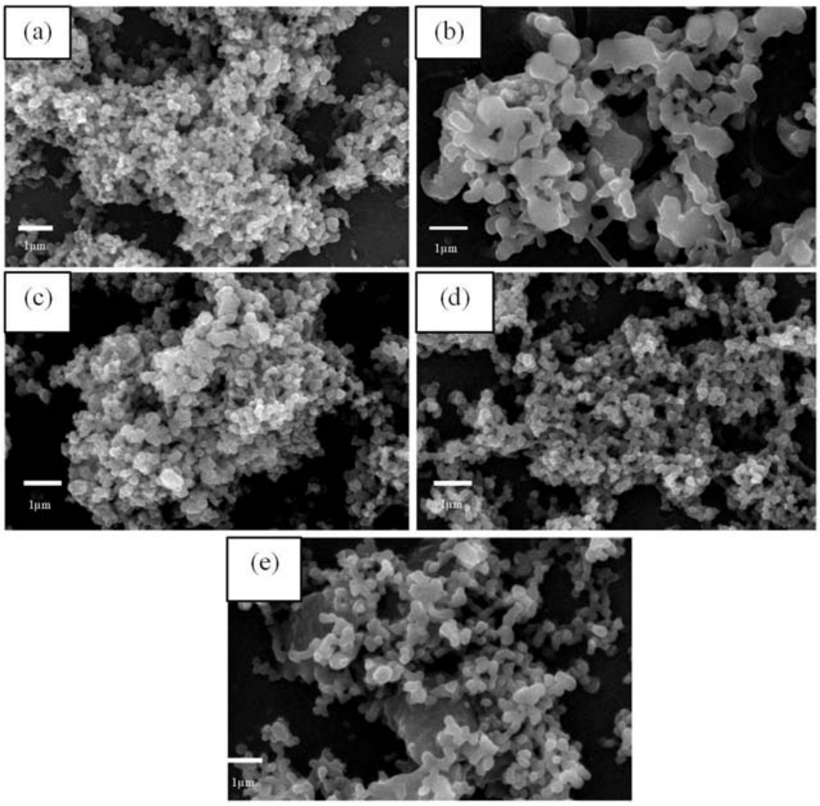

Fig. 3. SEM images for annealed thin films at 350°C (a) $aTiO_2$, (b) aGO_5, (c) aGO_{10}, (d) aGO_{15} and (e) aGO_{20}.

3.4 Optical properties

Optical analysis was conducted on to study the optical properties of the bare TiO_2 and GO/TiO_2 thin films. Optical properties of GO/TiO_2 thin films includes absorption or transmission rate, emission percentage and also energy band gap at 300 to 500 nm wavelength using visible-visible ultraviolet spectrophotometer as shown in Fig. 4. The absorption of aTiO_2 thin films is around 0.7 (arbitary unit) at a wavelength of 380 nm. With the addition of 5 mg GO (aGO_5), the absorption at a wavelength of 380 nm was about 1.7 (arbitrary unit). Highest absorption is produced by aGO_5 thin film which contain 5mg GO. The addition of GO particles has a significant effect on the absorption of light [15]. When the amount of GO increased, the absorption edge shifts in the absorption spectra. The cut-off wavelength has been expanded into visible regions with the addition GO. The cut-off wavelength can be determined by drawing a tangent along the edge of the absorption line. The intersection point with the wavelength axis on the absorption spectra and the tangent edge gives the cut-off wavelength value [16].

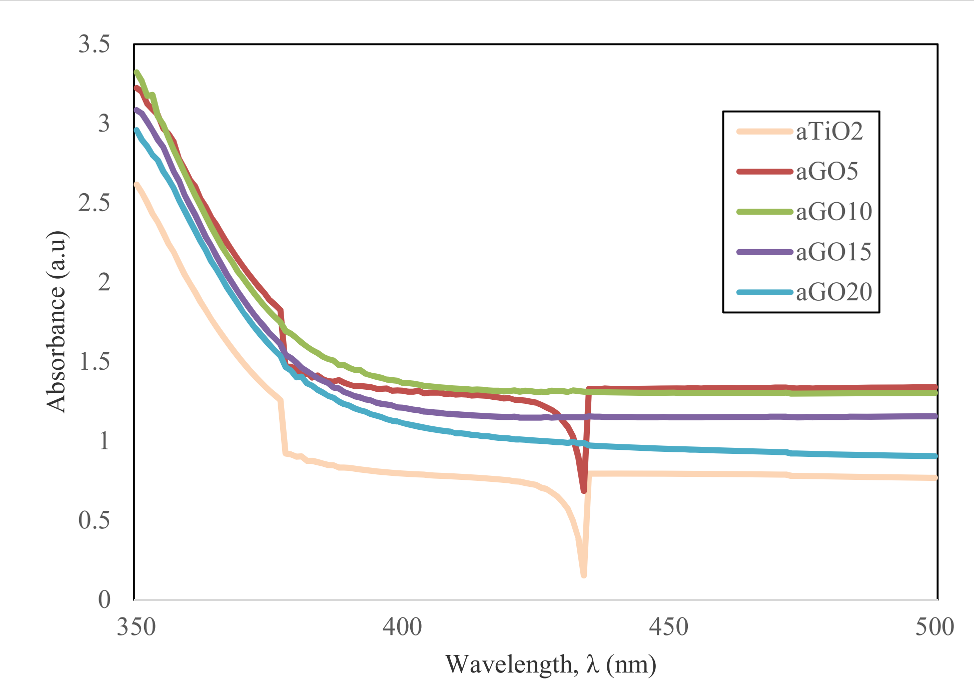

Fig. 4. Absorbance versus wavelength of GO/TiO_2 thin films.

The cut-off wavelength of annealed GO/TiO_2 thin film shifted from 380nm to 400 nm with increasing amount of GO. This indicates that the absorption range of thin film with the addition of GO is wider than that of aTiO_2 thin film. Wider cut-off wavelength in aGO_5 indicates aGO_5 is the optimum amount of GO addition to improve the performance of TiO_2 because it became narrower as more GO added. High absorption is due to low light scattering. Low light scattering is due to the increment of particle size and the decrease of nanocrystalline size distribution [17].

4 Conclusion

This work observes the effect of various GO amounts on morphological and optical properties of GO/TiO_2 thin films. The addition of various amount of GO have improved the formation of anatase phase of the thin films. It was revealed that, with small amount of GO addition, anatase phase of TiO_2 was formed in GO thin film and as the amount of GO increases the anatase TiO_2 decrease slightly and formed brookite TiO_2 again which means that the optimum amount of GO addition is 5mg. SEM image of aGO_5 was observed to have a large and unique surface area. Meanwhile, the optical properties of GO/TiO_2 thin film shows that the highest absorbance and most expended wavelength was found at aGO_5 with absorbance of 1.7(a.u) and cut-off wavelength at 400nm. Besides that, the energy gap of aGO_5 was also found to be the lowest which is 3.18eV.

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