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The Effect of GO/TiO_2 Thin Film During Photodegradation of Methylene Blue Dye

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Abstract: Titanium (IV) isopropoxide (TTIP) was used to synthesize GO/TiO_2 thin films using a sol-gel spin-coating method onto a glass substrate, undergoing an heat tretment at 350 °C. Several amounts of graphene oxide (GO) (0-20mg) were weighed into a sol solution of TiO_2 to produce GO/TiO_2 thin films. The thin film samples were characterized by X-ray diffraction (XRD) to analyze the samples' phase and by scanning electron microscopy (SEM) to analyze the samples' microstructure. Physical testing such as water contact angle (WCA) was analyzed using an optical microscope with J-Image software. In contrast, the optical band gap and photodegradation of methylene blue under sunlight irradiation of the thin film was analyzed using UV-VIS spectrophotometry. GO_5 thin film sample showed low-intensity anatase phase formation, where the microstructure revealed a larger surface area with the addition of GO. WCA reveals that GO/TiO_2 thin film exhibits super hydrophilic properties where the angle decreases from 37.83° to 4.11°. The optical result shows that GO has improved the absorption edges by expanding into visible regions. Moreover, due to the existence of GO 3.30 eV band gap energy of TiO_2 decreases from to 3.18 eV obtained by GO_5. The improved adsorption edge allows Ti^{3+}, O_2 and interstitial states to be formed in low valence states with energy underneath than in the TiO_2 band gap. Therefore, the photodegradation of methylene blue (MB) dye increases from 48 % to 59 % in the GO/TiO_2 thin film.

Keywords: Photodegradation, methylene blue, thin-film, water contact angle, graphene oxide

1. Introduction

Titanium dioxide (TiO_2) has been shown as the most studied and successful material, including as a photocatalyst during the photodegradation of organic pollutants for the remediation of environmental pollutions [1)2)]. Furthermore, TiO_2 has also been rapidly used to convert the solar energy and dissociation of water [3)]. It has many applications because of its unique properties, including electronic devices, gas sensors, solar cells, optical applications, as well as antibacterial and catalyst material [4)5)]. Currently, TiO_2 is also used as a self-cleaning surface. Under the self-cleaning application, two separate mechanisms are involved, which are photocatalysis and hydrophobic. Under the photocatalysis process, the chemical structure of organic pollutants and other impurities on the surface is broken down by absorbing sunlight. TiO_2 usually exhibits super-hydrophilic properties under ultraviolet light [6)]. The hydrophilic property from the TiO_2 surface leads to creating the water plates on the surface by reducing the contact angle that eliminates the contamination [7)]. Instead of the many advantages of TiO_2, unfortunately, it also has disadvantages. The disadvantages are a vast band gap of 3.2 eV, which limits its versatility towards the usage of TiO_2 under the irradiation of natural sunlight [8)]. TiO_2 photocatalyst with just a little UV fraction of solar light can be excited.

Furthermore, pristine TiO_2 will face a high electron-hole recombination rate, resulting in poor efficiency of photocatalytic degradation reactions and low quantum yield 9). Besides that, a lack of utilization of sunlight that reduced the ROS (Reactive Oxygen Species) formation has to be improved. The lack of utilization of sunlight occurs since TiO_2 exhibits self-cleaning activity under light irradiation due to the oxygen vacancies and ROS formation by excitation of electron and hole 10). Evidently, various attempts for improving TiO_2 towards visible light regions has been made.

Modification of TiO_2 photocatalyst is necessary to solve the above disadvantages by coupling semiconductors, doping of nitrogen, carbon, sulphur, and noble metals 11). The doping process is one of the promising modifications to enhance the photoresponse of TiO_2. In the past decade, TiO_2 coupled with metal oxides was undergo a research studies which related to the photocatalytic activity such as SnO_2 12,13), Fe_2O_3 14,15), and some carbon nanostructure 16) were performed to enhance the photocatalytic activity of TiO_2. The outcome of doping on photocatalytic activity depends on several aspects such as type, concentration of ions, and ion doping techniques 17). Graphene oxide (GO) is an excellent replacement for noble metal that can be used as the dopants onto TiO_2. It is also well known that GO is an attractive carbon material with unique physicochemical properties. The properties include magnificent conductivity, very good mechanical strength and broad specific surface area 18). Besides that, GO consists of a huge number of functional groups that contain oxygens. This can serve as favourable anchoring centres and nucleation sites for precursors or active species. In addition, TiO_2 doped graphene has been considered a potential photocatalyst in the purification of air and water. It was also mentioned that TiO_2/graphene has a few times higher photocatalytic activity in contrast to the pure TiO_2. Self-cleaning technology can make full use of the excellent photocatalysis of the graphene semiconductor system and the transparency of graphene characteristics 19).

Thus, many researchers focus on the preparation of GO/TiO_2 instead of the composite fabrication onto the immobilized system. For example, Baig et al., (2019) prepared GO/TiO_2 films by coating the graphene layer in the first place and later deposited the TiO_2 on top of that layer 20). In another previous study by Vallejo et al., (2019), TiO_2 thin film was further improved by adding 0.15, 0.26, 0.51 and 1.1 (w/w %) graphene oxide to improve the band gap values of TiO_2 from 3.21 eV to 2.45 eV. Therefore, the thin film's photocatalytic activity performance was also improved due to the presence of GO. GO is also understood as an electron-donating material whereby the approach has improved the catalyst efficiency, which is TiO_2. This kind of donating materials reduces electron-hole pairs' recombination rate by increasing the charge-carrier mobility. The effect on the physical chemistry properties is important where the yield of photodegradation was boost due to the existance of GO 21).

Meanwhile, A.Jalaukan et al., (2019) reported that titanium dioxide was deposited first. Then, the graphene oxide layer was deposited onto TiO_2 at different concentrations to investigate the consequences of graphene oxide layer addition to the morphological, structural, antibacterial, photocatalytic activity and self-cleaning properties of TiO_2 thin films 22). For this reason, it has been published that GO/TiO_2 nanocomposites can also serve as a dye remover in aqueous solutions. Specifically, the sol-gel process shows an excellent method to produce a layer with a good property for coating applications. This includes transparent and thin under multiple component oxide layers on the numerous substrates, for example glass plates, alumina plates, stainless-steel plates, ceramic tiles, and many more. Therefore, sol-gel based fabrication has been proposed as a low-cost alternative to fabricating optical devices 23).

In this research, a modification has been made to TiO_2 thin film by adding various amounts of graphene oxide onto a glass substrate under the production of TiO_2 via sol-gel method. Then, the fresh TiO_2 sol-gel solution was doped with different concentrations of graphene oxide followed by the heat treatment of annealed process on the hydrophilicity of films. Under this system, it may prohibit the aggregation of TiO_2. It may prolong the photocatalytic time with the better photocatalytic process due to the synergistic effects between GO and TiO_2 where the performance of the thin film based on the photocatalytic activity could be enhanced. This research has contributed to the new self-cleaning materials as well as a better understanding of modified TiO_2 as self-cleaning material.

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2. Experimental

2.1 Preparation of GO/TiO_2 thin film

Analytical grade of graphene oxide powder, titanium (IV) isopropoxide (TTIP) 97 %, absolute ethanol (~ 99.9 %), and acetic acid (glacial) 100 % utilized in this synthesis were used as it is.

A glass slide with the dimension of 25 mm (length) x 25 mm (width) was used as a substrate to deposite the thin film. The glass substrates were washed for 20 minutes with acetone in an ultrasonic bath and then cleaned with distilled water and put to dry at room temperature. After that, those substrates were ready to be coated. The TiO_2 sample was synthesized from TTIP and absolute ethanol via the sol-gel process 24).

Firstly, an amount of graphene oxide powder (0, 5, 10, 15, 20 mg) was weighed and mixed with a small amount of absolute ethanol. Then, it was sonicated for 30 minutes in the ultrasonic bath. By using a proportion of 1 ml of TTIP to 20 ml of absolute ethanol, TTIP was diluted with absolute ethanol under a stirring process using a magnetic stirrer for 5 minutes. After that, the previously mixed GO was poured into the TTIP:ethanol solution and proceeded with vigorous stirring for 1 hour. Afterwards, acetic acid (~ 0.30 ml) was carefully added into the solution by dropwise technique under a vigorous stirring condition until a clear solution was obtained. The acetic acid must be added to stabilize the solution and control the sol-gel precursor's hydrolysis reaction. A sample without GO was also prepared as a controlled sample.

When the sol-gel prepared was ready, the spin coating technique was used to deposit the sol-gel solution onto the clean glass substrate for 30 seconds at a speed of 800 rpm. The glass substrate was coated with three layers to ensure that the sol-gel solution will entirely cover the surface of the glass. The coated thin film was left at room temperature for a few minutes to dry before coating with the next coating layer. Then, an annealed temperature at 350 ºC will be set for the annealing process onto coated glass. The soaking time is 1 hour, while the rate of annealing is 10°C/minute. According to Dideikin et al., (2019), the typical temperature range used for thermal reduction of graphene oxide is within 400–1200°C 25). Therefore, 350°C annealing temperature was used to prepare the thin film. Finally, GO/TiO_2 thin films were obtained

2.2 Characterizations

The crystalline phase of the thin film was determined using the X-Ray Diffraction (XRD) technique with Bruker D8 Advance X-Ray Diffractometer using Cu tube, Kα (λ = 1.54056 Å) at 40.0 kV, current of 30 mA and scanning rate of 2° min^{-1} n a range of $5° < 2\theta < 70°$. The microstructure and morphology of the thin film were analyzed using the Scanning Electron Microscope (SEM) origin from Japan with model of JEOL JSM-6460LA. Before analyzing the sample in the SEM, JEOL JFC 1600 model of Auto Fine Coater was used to coat the sample with palladium (Pd). The analysis was done under high vacuum conditions with a voltage of 20kV and 20 000x magnification. The hydrophilic properties of TiO_2 and GO/TiO_2 thin films were discovered from water contact angle analysis. The contact angle of the water drop between water and the film surface was first photographed with an optical microscope and then measured using the Image-J software. Hydrophilic properties are essential to determine the self-cleaning mechanism, which will occur on the GO/TiO_2 thin film surface. The optical properties of TiO_2 and GO/TiO_2 thin films, such as the absorption rate and the amount of energy gap, were measured using a UV-Visible spectrophotometer (Perkin Elmer, Lamda 25) at 300 to 500 nm wavelength, respectively. The calculation of the optical energy gap for the thin film was also performed using the Tauc equation given in Eq. (1):

$$(\alpha hv)=A\,(hv-Eg)^{1/2} \qquad (1)$$

2.3 Photodegradation of Methylene Blue

Methylene blue dye is understood to be a non-toxic and convenient dye used to measure the photocatalytic performance of TiO_2 and GO/TiO_2 thin film samples. The photocatalytic degradation performance of the thin films were measured by the degradation or decolourization of methylene blue at the wavelength of 664 nm based on the absorbance value of methylene blue at individual irradiation time intervals. Before the photocatalysis process occurs, the thin film samples were put in the opaque container or unlighted condition for 60 minutes to allow the absorption /desorption to stablize. After 60 minutes, the thin films were exposed to sunlight for the photocatalytic activity to take place. The percent of methylene blue degradation was determined using Eq.(2) given by:

$$\%\text{ dye degradation} = \left(\frac{Co-C}{Co}\right)x100\% \qquad (2)$$

3. Results and Discussions

3.1 Phase analysis

Based on the XRD diffarctrogram of TiO_2 and GO_5 thin films in Fig. 1, the results exhibited that only a brookite phase was formed in TiO_2 thin film. Characterize diffraction peaks shown at 2θ = 33.5° indicates the presence of brookite TiO_2 brookite referred to the standard ICDD card No. 00-029-1360, which corresponded to the (121) plane. Meanwhile, GO_5 thin film diffraction peaks showed the mixed phases of brookite and anatase. Here, 2θ value of 24.8° was attributed to the anatase (101) plane, and 2θ value of 33.5° was attributed to the brookite TiO_2 (201) plane (ICDD Card No. 01-070-8501). Besides that, a single peak recorded at 2θ = 21.9° indicates the presence of silicon resulted from the substrate. According to Fig. 1, adding GO into TiO_2 somehow contributed to the development of the TiO_2 mixed phase of anatase and brookite. The diffraction pattern of GO_5 shows that the intensity of TiO_2 anatase increases and TiO2 brookite phase decreases.

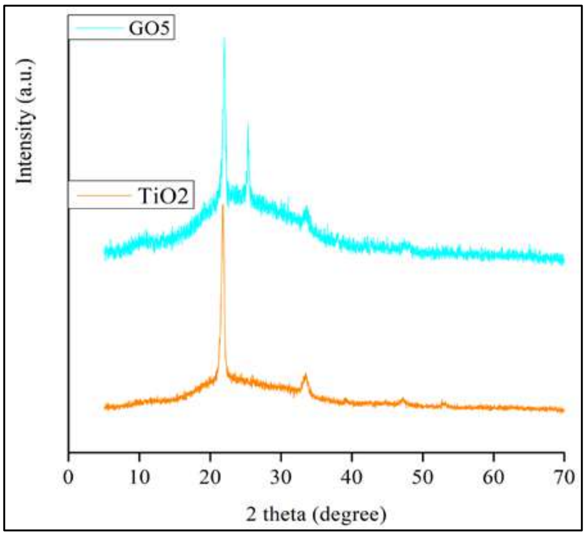

Fig. 1: XRD diffractogram of TiO_2 and GO_5 thin films.

Obviously, annealing temperature is a facctor contributed to the formation of anatase phase with poor crystallinity that occurred at 350°C annealing temperature 26). Meanwhile, further annealing up to 500-600°C will slowly transform brookite TiO_2 to anatase TiO_2 27).

Fischer et al., (2017) stated that the anatase phase of TiO_2 would grow better at higher temperatures [28]. In addition, Johari et al., (2019) previous research also stated that for brookite formation a spin-coating deposition at low temperature is preferable [29].

Meanwhile, there were no peaks identified to indicate the presence of GO. This suggests that GO exists in the form of nanoplates or lamellae that are well dispersed between TiO_2 particles [30]. Therefore, it cannot be detected by X-ray diffraction due to the small amount of GO. This can be verified in the morphology analysis. Gascho et al., (2019) also reported that the absensce of peak at $2\theta = 10°$ that represent GO in the films in X-ray diffractograms, indicating a partial reduction of the GO. This probably caused by the sheet of graphene oxide stacking again partially in the material [31].

3.2 Microstructure analysis

The SEM analysis performed on TiO_2 and GO_5 thin films were analyzed based on the microstructure formation in Fig. 2. Fig.2 (a) images reveal that the particles of TiO_2 are spherical shape showing a basic morphology of TiO_2 particles presenting a combination of various sizes particles with a flower-like formation of synthesized TiO_2 photocatalyst [3]. Besides that, it can be observed that the distribution of TiO_2 in the thin film sample are homogeneous due to the sol-gel process. On the other hand, Fig. 2(b) shows the microstructure of GO_5 thin film, revealing that GO in the thin film obviously affects the films' microstructure. The particles of TiO_2 were coated by GO. The SEM also showed that by adding GO, the particle size of TiO_2 becomes bigger and exhibits a unique microstructure where the GO layer covered the TiO_2. The findings were consistent with Ni, Wang, Huang, Lu, & Xu, (2014), who investigated the microstructure of TiO_2 with GO addition. The authors stated that GO covered the TiO_2 surface tightly, where the covered TiO_2 surface area expand with GO and its content [32]. Appropriate addition of GO enhances light absorption by having the separation of photogenerated electrons and holes and a larger specific area. In contrast, photo carriers' mobility was reduced, while the adsorption of light was also disturbed if too much GO was introduced in the samples [33]. The large particle size of TiO_2 will increase the surface area, allowing more photocatalytic activity to occur; therefore, the self-cleaning properties will be more efficient.

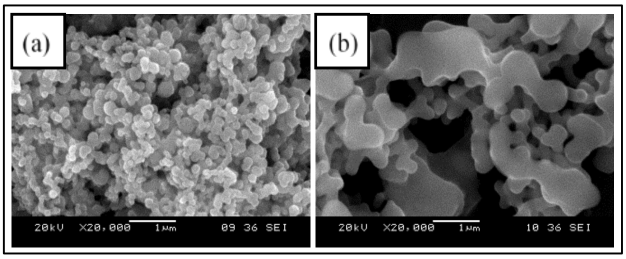

Fig. 2: SEM images of (a) TiO_2 and (b) GO_5 thin films.

3.3 Water contact angle analysis

Fig. 3 displays the water contact angles of TiO_2 and GO/TiO_2 thin films. The TiO_2 film exhibits a water contact angle of 37.83°. Interestingly, when 5 mg GO (GO_5) was added to TiO_2 film, the water contact angle drastically dropped to 4.11°. This indicated the super hydrophilicity properties of lesser than 5° water contact angle. However, a further increase in the amount of GO increased the water contact angle. Results showed that when a higher GO loading was added, such as 10mg, 15mg and 20mg (GO_{10}, GO_{15} and GO_{20}), the water contact angle also slightly increased to 9.39°, 13.15° and 56.48°, respectively. The decrement in water contact angle is due to the amount of GO added to the films. Good self-cleaning thin film is interrelated to good hydrophilic properties where the contaminants are easily removed from the surface [34].

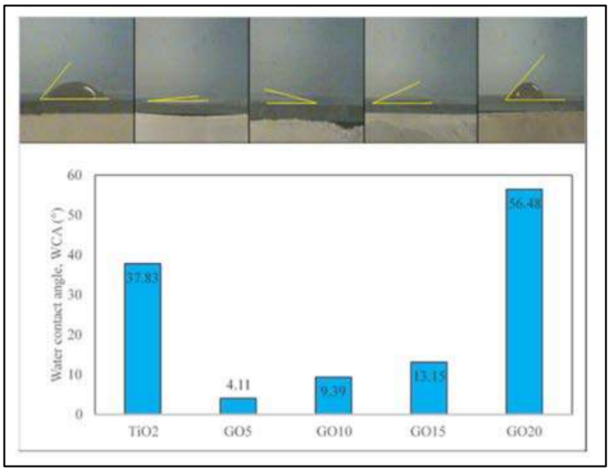

Fig. 3: Water contact angle of TiO_2 and GO/TiO_2 thin films.

3.4 Optical properties analysis

The adsorption spectra in Fig. 4 shows the absorbance of TiO_2 and GO/TiO_2 thin film samples at the wavelength ranging between 300-500 nm at a different amount of GO. For TiO_2 thin film, the adsorption is about 0.7 (arbitrary unit). In contrast, at a wavelength of 380 nm GO_5 increased the absorption to about 1.7 (arbitrary unit). The adsorption of light was significantly affected by the addition of GO [35]. The samples with the addition of GO show high adsorption in the UV range. Previous research also stated that nanoparticles incorporated in carbon nanofibers have an advantage in adsorption and fast degradation of dye. This enhances the photocatalytic activity resulting in enhanced self-cleaning properties of the thin film [36,37]. Besides that, with the increasing amount of GO used, it can be seen clearly that the adsorption edge has been shifted in the adsorption spectra. GO/TiO_2 thin film cut-off wavelength of has been extended into visible regions compared to TiO_2 thin film. The cut-off wavelength can be determined by sketching a tangent line next to the edge of the adsorption line. The intersection point to get the cut-off wavelength value and the absorption spectrum and the wavelength axis on the cut edge [38].

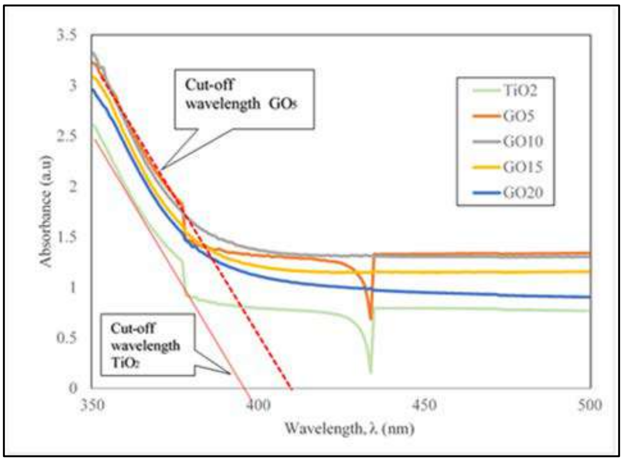

Fig. 4: Changes in adsorption by wavelength for TiO_2 thin films with different GO weights.

The cut-off wavelength of GO/TiO_2 thin film was moved further from 380 nm in TiO_2 thin film to 410 nm with an increment in the amount of GO. The shifted wavelength indicates that the absorption range of thin-film is broader than that of bare TiO_2 thin film with the addition of GO. The addition of GO improved the performance of TiO_2 by improving the light adsorption of the thin film as more GO added. The increase in adsorption is because of the low-light scattering. Therefore, this increases the particle size and reduce the size distribution of nanocrystalline [39].

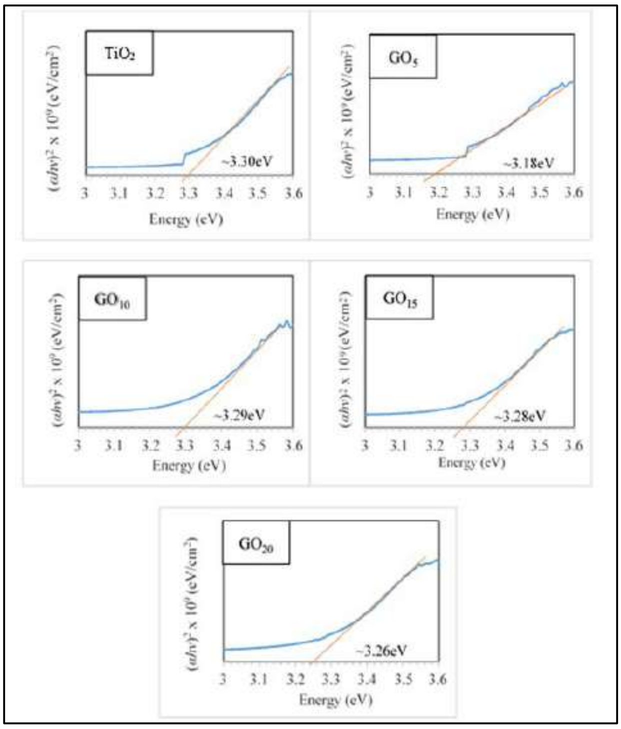

Fig. 5: The energy band gap graph of TiO_2 and GO/TiO_2 thin films.

The optical energy gap for the thin films was determined using the Tauc equation given in Eq. (1). Fig. 5 displays the plot $(\alpha h\nu)^2$ versus photon energy ($h\nu$) to obtain the E_g value for the GO/TiO_2 thin films. Based on the graph, the band gap energy (E_g) value is taken using the straight-line method on the *x*-axis. The lowest energy gap was obtained by GO_5, with a value of 3.18 eV. As the amount of GO increases from 0 mg to 20 mg, the value of the energy gap decreased. This is due to the existence of GO, which permitted the formation of Ti^{3+} and O_2. Therefore, intra gap states could be generated at a low valence state with energy underneath than that in the TiO_2 band gap. Therefore, at a higher wavelength, it improved the absorption of light [21]. The value of the band gap energy and the absorption spectra obtained are complementary to each other. These results suggest that the addition of GO at optimum amount can reduce the width of the gap that is not achieved by TiO_2 thin films [40].

3.5 Photodegradation Analysis

Methylene blue dye is a non-toxic and the most suitable dye used to determine TiO_2 and GO/TiO_2 thin films' photocatalytic performance. Degradation or decolourization of methylene blue at the wavelength of 664 nm was applied to measure the photocatalytic performance. This is based on the absorbance value of methylene blue at different time intervals. Thus, Fig. 6 shows a graph plot of C/C_0 against time when the thin films were irradiate under sunlight. The C_0 designate the initial concentration, while C indicates methylene blue (MB) concentration at different irradiation time intervals.

The photodegradation of the samples was carried out for 2.5 hours under sunlight irradiation. Before the photocatalysis process takes place, all the thin film samples were kept in the dark condition for 60 minutes to allow the absorption of methylene blue onto the surface of the films. In Fig. 6, thin films with GO show that it is more effective to degrade methylene blue under sunlight irradiation. After 210 minutes, the GO_{20} thin film shows a 67% degradation of methylene blue followed by GO_5, GO_{10}, GO_{15} and TiO_2 with degradation percent of 59 %, 56 %, 55 % and 48 %, respectively, as tabulated in Table 1.

Table 1. Percentage of methylene blue absorbance and degradation of TiO_2 and GO/TiO_2 thin films.

Samples	Percentage of methylene blue absorbance in the dark (%)	Percentage of methylene blue degradation under sunlight irradiation (%)
TiO_2	10	48
GO_5	10	59
GO_{10}	14	56
GO_{15}	12	55
GO_{20}	37	67

GO_{20} thin film sample shows the highest percentage of degradation of methylene blue, which is 67%, while GO_5 of 59% obtained the second-highest degradation. Based on the results, GO_5 exhibits the best photocatalytic activity, although GO_{20} shows a higher degradation efficiency. The higher degradation in the GO_{20} sample is due to the excellent absorption properties of the catalyst, which means that the photodegradation performance was not outstanding. The results obtained were compatible with the previous research, demonstrating that graphene oxide could be functioning as an adsorbent, electron acceptor, and photosensitizer. This function could also enhance photodecomposition 41). The modification made on the TiO_2 sample by adding GO improved the photocatalytic degradation of methylene blue in contrast to pure TiO_2 thin film. The photogenerated hole and electrons in the modified film were having a lower rate of recombinationand this is the factor that improve the photocatalytic activity. Firthermore, the absorption of methylene blue by GO is also helpful in photocatalytic activity 42). However, the excessive quantity of GO decreases the prepared films' photocatalytic activities as the graphene disturbs the light absorption efficiency of TiO_2 43).

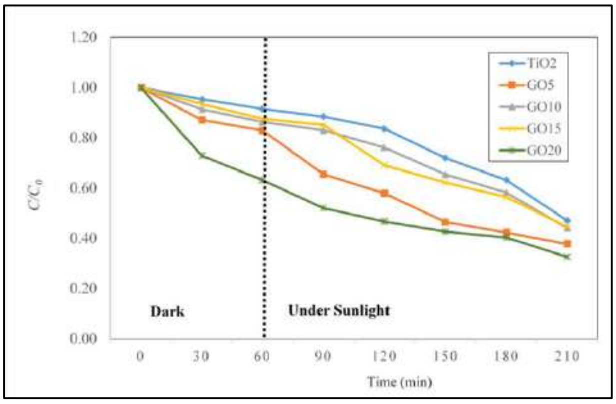

Fig. 6: Photocatalytic degradation efficiency of TiO_2 and GO/TiO_2 films.

During the photocatalytic process, the photogenerated electrons can be transferred to the nearby methylene blue while the photocatalysts were excited. It then decomposed the methylene blue into CO_2 and H_2O when the redox reactions take place 42). The increased amount of GO in the resulting film contributes to narrowing the film energy gap and defects.

The proposed possible photocatalysis activity mechanism for the GO/TiO_2 was illustrated in Fig. 7. The photocatalytic degradation mechanism of GO/TiO_2 film occurred via four steps given by:

i. The improved surface of TiO_2 by GO was irradiated under sunlight;
ii. The e^- will excite to the conduction band (CB) from the valance band (VB) of TiO_2, leaving the h^+ in the VB;
iii. Firstlt, the e^- and h^+ will reacts with H_2O;
iv. Then, it will induced the degradation of organics.

Equations (3) to (7) explain the degradation of organic compound by GO/TiO_2 films or also know as photocatalytic process is given by:

$$GO/TiO_2 + h\nu \rightarrow e^- + h^+ \qquad (3)$$

The h^+ generated on the surface of TiO_2 reacts with water or hydroxide ions $(OH)^-$ to generate hydroxyl radicals (OH•), and the generated e^- reacts with O_2 to generate superoxide $(O_2\bullet)^-$.

$$HO_2 + h^+ \rightarrow OH^\bullet + H^+ \qquad (4)$$

$$OH^- + h^+ \rightarrow OH^\bullet \qquad (5)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \qquad (6)$$

$$OH\bullet \,/\, O_2^{\bullet -} \,/\, h^+ + \text{organics} \rightarrow \text{degraded products} \qquad (7)$$

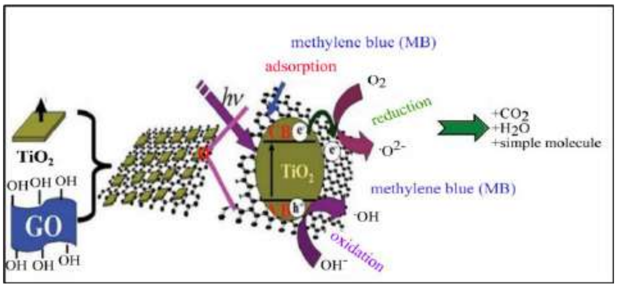

Fig. 7: Schematic diagram of proposed photocatalytic activity of and methylene blue degradation of GO/TiO_2 film under sunlight irradiation 45).

4. Conclusion

Successfully produced GO/TiO_2 thin film was synthesized via sol-gel method with spin coating deposition technique to be used as a self-cleaning coating. Characterization of the thin films exhibiting the anatase phase of TiO_2 formed with GO introduction. Meanwhile, the microstructure of the TiO_2 thin film changes when the GO is added to the thin film. The photodegradation performance of the thin film was investigated using methylene blue under sunlight irradiation. The prepared thin film coating exhibits super hydrophilic properties with a 4.11° water contact angle and lower band gap of TiO_2 from 3.30eV to 3.18eV. Therefore, this resulted in more excellent absorption, enhancing the photodegradation performance due to the synergistic effects between GO and TiO_2, which degraded about 59% of methylene blue.

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Nomenclature

GO	Graphene oxide
TiO_2	Titanium dioxide
WCA	Water contact angle
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
rpm	Rotation per minute
eV	Electrovolt
hv	Photon energy
α	alpha
Eg	Band gap energy
C_0	Initial concentration
C	Concentration

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