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Effect of polyethylene glycol and sodium dodecyl sulphate on microstructure and self-cleaning properties of graphene oxide/TiO_2 thin film

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KEYWORDS

TiO_2
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Graphene

ABSTRACT

In this study, a sol gel procedure for preparation of TiO_2 thin films with graphene oxide (GO) was developed. The effect of PEG and SDS addition on the microstructure of the films as well as the photocatalytic activity of the thin film was also investigated. The morphology and surface structure of the films were studied by SEM and AFM while the photocatalytic activity of the films was analyzed by measuring the degradation of methylene blue under sunlight irradiation using UV-Vis spectrophotometer. It was found that GO/TiO_2 thin film with PEG shows a smaller and porous particle while GO/TiO_2 thin film with SDS formed a very smooth surface and very fine particles. Therefore, in AFM analysis reveals that surface roughness decreases with the addition of PEG and SDS. Finally, the photocatalytic activity showed that GO/TiO_2 thin film with SDS have the most effective self-cleaning property which degrade 64% of methylene blue that act as model of contaminants.

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1.0 INTRODUCTION

Self-cleaning is capability to clean itself where the self-cleaning materials have a potential to keep the city clean by reducing the pollutants. For the self-cleaning to occur, the surface often has hydrophilic properties where the water contact angle (WCA) of less than 5° when irradiated with UV light or sunlight. It has been reported that titanium dioxide (TiO_2) is a low cost and outstanding photocatalyst material, which has been studied for environmental purification due to its photocatalytic oxidation activity. Natural rainfall, considerably contributes to the self-cleaning efficiency of the TiO_2 surface; water penetrates the molecular level spaces between the stain and the superhydrophilic TiO_2 surface and removes the stain (Nishimoto et al., 2014). Therefore, recently, the self-cleaning technology has been growing expeditiously all over the world. Since self-cleaning coatings specifically self-cleaning glass are in very high demand. Due to that, many studies and investigations have been conducted to improve this technology.

The glass with titanium dioxide (TiO_2) films coating exhibits a great performance of self-cleaning property, antibacterial, disinfections, antifogging and a lot more advantages (Sun et al., 2008). TiO_2 owns a special properties and realistic applications in energy and environmental areas that bring studies of TiO_2 involving self-cleaning materials to the concern of researchers (Benerjee et al., 2015; Shan et al., 2010). TiO_2 thin film can be prepared by many methods such as sol gel (Schmidt et al., 2000; You et al., 2005), electrochemical deposition (Lakhonde et al., 2005), chemical vapors deposition (CVD) (Sun et al., 2008) etc. However, the sol gel method is the most widely used as a simple yet powerful way for preparing thin film. The TiO_2 thin films may be deposited on the surface of various substrates, such as glass, ceramics, metals, textiles, cement, bricks or fibers to produce layer that display self-cleaning property when it is irradiated by sunlight (Banerjee et al., 2015). Several modifications have been made to TiO_2 to enhance its outstanding properties especially in photocatalytic such as noble metal deposition, cationic and anionic doping, sensitization and addition of sacrificial agents (Rather et al., 2017). Therefore, graphene oxide (GO) has the advantages in replacing a nobel metal.

Graphene oxide has grabbed tremendous attention in this new generation of technology since it has amazing mechanical n chemical properties such as large surface area, high electrical conductivity (106 S/cm), good carrier mobility (200,000 $cm^2\ V^{-1}\ S^{-1}$) and efficient electron (e^-) transfer from TiO_2 to graphene (Sellappan et al 2013). Hence, the photocatalytic applications of TiO_2-graphene composites have been studied broadly.

To further improve the microstructure and the self-cleaning properties of the thin film, additives have been added to the thin film. Polyethylene glycol (PEG) is known as polymeric additive that will improve the GO/TiO2 thin film coating by increasing the active surface area with porous surface structure due to pore forming properties and lowering in the energy gap of TiO_2 (Nurhamizah et al., 2016). Furthermore, PEG also a hydrophilic molecule, super low fouling ability, cell adhesion and crosslinking agent that will lead to a porous TiO_2 as well where this properties will improve the microstructure and binding of GO/TiO_2 on the substrate (Segota et al 2011).

Another promising additive used is sodium dodecylsulphate (SDS) is the most common sulphate surfactant also known as anionic surfactant (Niraula et al., 2014). SDS is a widely used surfactant for dispersing graphene sheets in the solution (Tkalya et al., 2014). The used SDS in previous study is to improve the dispersion of nanoparticles and the transfer of electrons) Yuan et al., 2017). The TiO_2 surface was modified with sodium SDS the anionic surfactant, where the results showed better dispersion and homogeneous coating of TiO_2. SDS also important to enhance and stabilized the photocatalytic activity. Lal et al., (2017) previous study states that the addition of SDS will affect the film morphology and it was found that the films were smooth and denser as compared to the films without SDS.

In this research, sol gel method which uses organic precursors (such as titanium tetraisopropoxide (TTIP)), to prepare TiO_2 thin films deposited on a glass, utilizing polyethylene glycol (PEG) as a polymer additive and SDS as surfactant. Furthermore, effect of the additives by sol gel process on the structures of the films has been investigated. Since these parameters affect films morphology leading to variation of photocatalytic activity, decomposition of methylene blue was selected as a model reaction in order to evaluate photocatalytic activity of the films.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials

Graphene oxide powder, titanium (IV) isopropoxide (TTIP) 97%, absolute ethanol (~ 99.9%), acetic acid (glacial) 100%, polyethylene glycol 2000 (PEG) and sodium dodecyl sulphate (SDS) were used in this synthesis without further purification. Glass slide were used as a substrate to deposited the thin film. It was cut according to the dimension of 25mm (length) x 25mm (width) using diamond cutter. After that, the substrates were washed with acetone in ultrasonic bath for 20 minutes. Then, the substrates were rinsed with distilled water and put to dry at room temperature. After that, those substrates were ready to be coated.

First, 5 mg of graphene oxide powder was weighed and mixed with small amount of ethanol. Then, it was sonicated it in the 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. This TTIP:ethanol solution was stirred for about 5 minutes. Then the GO that have been sonicated mix previously, was added into the solution and continue 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 a clear solution is formed. Then, a small amount of PEG (0.10g) that was previously dissolved in small amount of ethanol was added to the parent solution during sol-gel reaction process. The mixture solution was stirred for another 15 minutes until the solution is homogenous and ready to be coated. The same procedures were repeated by replacing PEG with SDS to produce another sample. Sample without additives was also prepared as controlled sample.

When the sol-gel prepared were ready, it will be 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 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. Finally, the thin film coating will be characterized and analyzed using scanning electron microscopy (SEM), electron dispersive X-ray (EDX), atomic force microscopy (AFM) and degradation of methylene blue to study the morphology, determine the elemental composition of the thin film, examine the surface roughness and also analyzed the photocatalytic activity or also called as self-cleaning properties of the thin film.

3.0 RESULTS AND DISCUSSION

3.1 Microstructure Analysis

From SEM images, it can be seen that sol-gel process has a homogeneous TiO_2 distribution in the film samples. Figure 1(a) showed the particles of TiO_2 were coated by GO. The findings were consistent by research done by Ni et al., 2014 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 (Zhang et al., 2010).

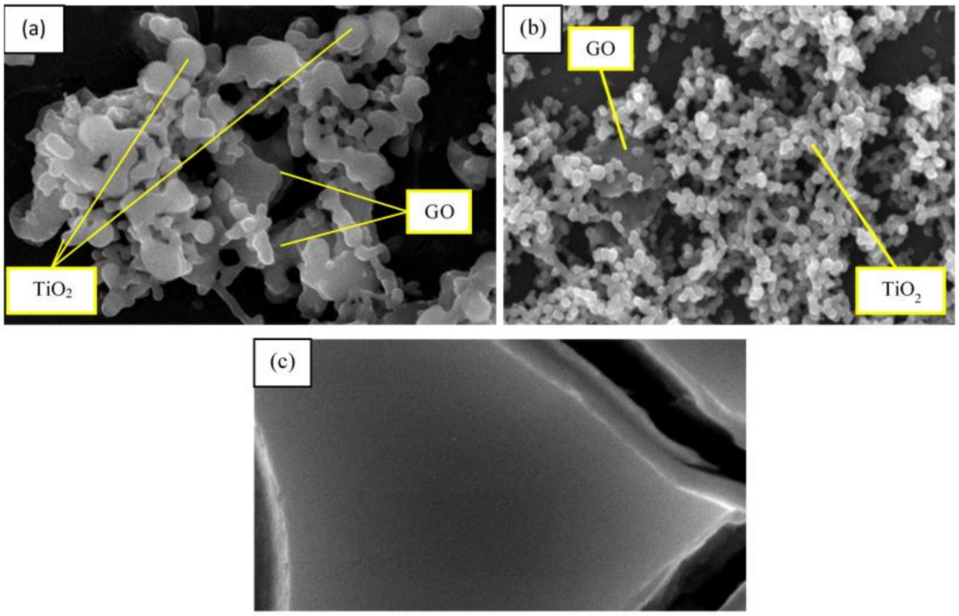

Figure 1: The particles of TiO_2 were coated by GO.

As can be seen in Figure 1(b), addition of PEG formed smaller and porous microstructure of GO/TiO_2 thin film. The use of PEG affects the particle size and its distribution range. It is worth mentioning that the smaller the particle size, increases the surface area which is favourable for adsorption This is similar to previous study by Samadi et al., where the study involve the effect of different polymers to TiO_2 thin film (Samadi et al., 2017). Meanwhile in Figure 1(c), it can be observed that the particles of TiO_2 became uniform nanosize particles which formed a very smooth surface. This is coinciding with the previous findings from Yuenyongsuwan et al., (2018) studies which explained that when surfactant is used, smaller nanoparticles of uniform size were produced with the control of the micelle space and shape. In addition, surfactant lowers the energy required to increase the interfacial area and form smaller nanoparticles (Yuenyomgsuwan et al., 2018).

The chemical composition of the thin films was conducted and proved by Energy Dispersive X-Ray (EDX). Table 1 showed that carbon and oxygen present in all the thin films are almost the same because the amount of GO addition is the same for all the samples. This proved the presence of carbon, oxygen and titanium which confirms the formation of GO/TiO_2 films where carbon must be originated from GO, titanium contributed from TiO_2 and oxygen will be from both GO and TiO_2 (Timoumi et al., 2018).

Table 1: EDX analysis of GO/TiO_2, GO/TiO_2 + PEG and GO/TiO_2 + SDS thin films.

Samples	**Elements (Atomic %)**			
	C K (Atomic %)	**O K (Atomic %)**	**Si K (Atomic %)**	**Ti K (Atomic %)**
GO/TiO_2	11.88	54.33	22.28	11.51
GO/TiO_2+PEG	11.23	53.14	25.75	9.89
GO/TiO_2+SDS	8.30	54.81	14.80	22.08

3.2 Surface Roughness and Topography Analysis

Surface roughness and topography analysis was examined by using Atomic Force Microscope (AFM) for all the produce thin films. The with 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 2 presents the average roughness (Ra) and root mean square roughness (RMS) of GO/TiO_2, GO/TiO_2 + PEG and GO/TiO_2 + SDS thin films. The RMS values of GO/TiO_2thin film decrease from 3.16×10^2 nm to 2.09×10^2 nm after adding PEG and 2.34×10^2 nm after adding SDS. This indicates that the surface become fine and smooth after adding additives as compared to GO/TiO_2 film. For addition of PEG, this is due to the oxidation and decomposition of PEG to carbon dioxide which left numerous small cracks mention as pore forming. The similar findings were obtained by Huang et al., 2010 previous research where PEG 2000 was used as a templating reagent to synthesize porous TiO_2 thin film by sol–gel process. Meanwhile, according to Lal et al., 2017, the surfactant SDS improved the quality and surface smoothness which the morphology changed drastically and the films became denser and the heat treatment also contributes in reducing the surface roughness and the films obtained were compact.

Table 2: Roughness average (Ra) and roughness root mean square (RMS) of GO/TiO_2, GO/TiO_2 + PEG and GO/TiO_2 + SDS thin films.

Samples	**Annealed**	
	Average Roughness (Ra) nm	**Root Mean Square Roughness (RMS)**
GO/TiO_2	2.57×10^2	3.16×10^2
GO/TiO_2 + PEG	1.66×10^2	2.09×10^2
GO/TiO_2 + SDS	1.91×10^2	2.34×10^2

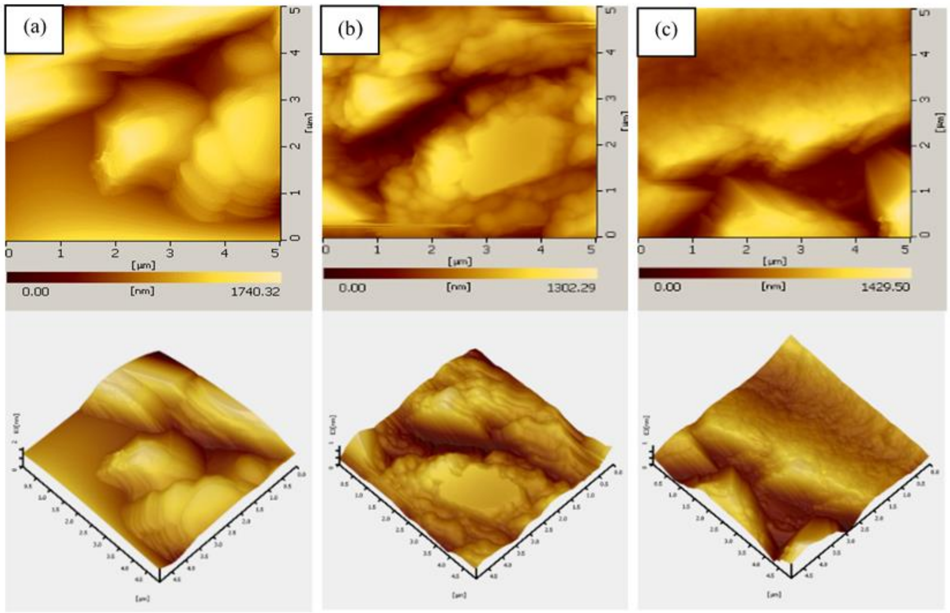

Figure 2: Topography view and also three-dimensional view of (a)GO/TiO_2, (b) GO/TiO_2 + PEG and (c) GO/TiO_2 + SDS thin films.

Figure 2 shows the topography view and also three-dimensional view of (a)GO/TiO_2, (b) GO/TiO_2 + PEG and (c) GO/TiO_2 + SDS thin films. In Figure 2 (a) resulted that 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 1740nm.It can be seen that the formation of few layers of films and the stacking of GO/TiO2 layers during formation of the thin films was also confirmed using AFM. Meanwhile, from Figure 2(b) showed that the surface is smooth with maximum height of 1302nm and Figure 2(c) exhibits that the surface appears to have clean and even distribution of GO and TiO_2 due to the addition of SDS. Addition of PEG resulted in increased roughness. This can be due to the stress induced by the PEG removal from the film at annealing temperature of 350°C proven with previous study from (Huang et al., 2010).

3.3 Self-Cleaning Property

Photocatalytic activity of GO/TiO_2 and GO/TiO_2 with additives are presented in Figure 3. Before the photocatalysis process take place, the GO/TiO_2 thin film samples were kept in the dark conditions for 60 minutes to allow the absorption of methylene blue onto the surface of the films. Photocatalytic degradation rate was also influence by the absorption where the adsorbed methylene blue molecules will act as an electron donor. Under the sunlight irradiation, the electron will be transferred to the conduction band from valence band (Thongpool et al., 2020). After 60 minutes kept in the dark, the thin films were exposed to sunlight for the photocatalytic activity to take place. As a result, after 210 minutes, The GO/TiO_2 +PEG degraded about 47% due to the porous structure obtained when the samples were introduced to heat of 350°C induced by the PEG removal from the film (Huang et al., 2010).

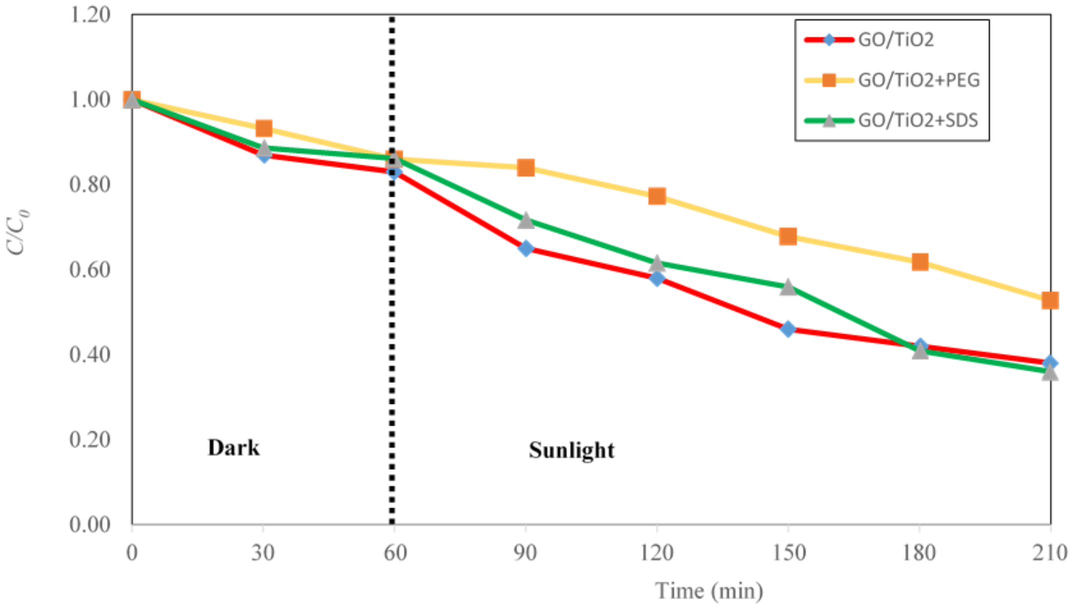

Figure 3: Photocatalytic activity of GO/TiO_2 and GO/TiO_2 with additives.

On the other hand, GO/TiO_2+SDS exhibits the most percent degradation of methylene blue after 150 minutes of sunlight irradiation which is 64% degradation. This is due to the larger surface area after adding SDS as well as lower energy gap compared to other samples which allowed more photocatalytic activity could be performed. The enhancement of photocatalytic activity also contributed by annealing factor where introduction to heat resulted in smooth and denser surface proven in surface morphology and microstructure analysis. The SDS increases the dispersion of graphene oxide and TiO_2 homogeneously as we can also observe from the SEM image (Yuan et al., 2017).

Table 3: Percentage of methylene blue absorbance and degradation for GO/TiO_2 thin films

Samples	**Percentage methylene blue absorbance in the dark (%)**	**Percentage methylene blue degradation under sunlight irradiation (%)**
GO/TiO_2	17	62
GO/TiO_2+PEG	14	47
GO/TiO_2+SDS	14	64

4.0 CONCLUSION

In this research, it was found that the GO/TiO_2 thin film with PEG and SDS as an additives affect the microstructure and the morphology of the thin films. The thin films with additives cause the surface to be uniform, dense and considerably smooth. In contrast, the film from without additives was slightly rougher surface. The film formed in the presence of PEG was porous crack-free and presence of SDS improved the quality and surface smoothness which the morphology changed drastically and the films became denser after annealing at the temperature of 350°C. Furthermore, it was also found that, the modified thin film by SDS improved the photocatalytic activity of GO/TiO_2thin films in the degradation methylene blue where it degrades 64% of methylene blue.

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REFERENCES

Banerjee, S., Dionysiou, D. D., & Pillai, S. C. (2015). Self-cleaning applications of TiO_2 by photo-induced hydrophilicity and photocatalysis. Applied Catalysis B: Environmental, 176, 396-428.

Huang, W., Lei, M., Huang, H., Chen, J., & Chen, H. (2010). Effect of polyethylene glycol on hydrophilic TiO2 films: Porosity-driven superhydrophilicity. Surface and Coatings Technology, 204(24), 3954-3961.

Lal. S, D. Gautam, and K. M. Razeeb, (2017). The Impact of Surfactant Sodium Dodecyl Sulfate on the Microstructure and Thermoelectric Properties of p-type $(Sb_{1-x}\,Bi_x)_2Te_3$ Electrodeposited Films. ECS J. of Solid State Sci. Technol., 6(3), 3017–3021

Lokhande, C. D., Park, B. O., Park, H. S., Jung, K. D., & Joo, O. S. (2005). Electrodeposition of TiO2 and RuO2 thin films for morphology-dependent applications. Ultramicroscopy, 105(1-4), 267-274.

Ni, Y., Wang, W., Huang, W., Lu, C., & Xu, Z. (2014). Graphene strongly wrapped TiO_2 for high-reactive photocatalyst: A new sight for significant application of graphene. Journal of colloid and interface science, 428, 162-169.

Niraula, T. P., Bhattarai, A., Chatterjee, S. K., & Biratnagar, N. (2014). Sodium dodecylsulphate: A very useful Surfactant for Scientific Investigations. Journal of Knowledge and Innovation, 2(1), 111-113.

Nishimoto, S., Tomoishi, S., Kameshima, Y., Fujii, E., & Miyake, M. (2014). Self-cleaning efficiency of titanium dioxide surface under simultaneous UV irradiation of various intensities and water flow. Journal of the Ceramic Society of Japan, 122(1426), 513-516.

Nurhamizah, A. R., Zulkifli, M. R., & Mohd Juoi, J. (2016). Effect of Additives on the Characteristic of Ag-TiO2 Coating Deposited on Specially Made Unglazed Ceramic Tile. In Key Engineering Materials (Vol. 694, pp. 160-164). Trans Tech Publications Ltd.

Rather, R. A., Singh, S., & Pal, B. (2017). Visible and direct sunlight induced H2 production from water by plasmonic Ag-TiO2 nanorods hybrid interface. Solar Energy Materials and Solar Cells, 160, 463-469.

Samadi, S., Mirseyfifard, S. M. H., Assari, M., & Hassannejad, M. (2017). Effect of hydroxypropyl cellulose (HPC), polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) on Nd-TiO2/graphene oxide nanocomposite for removal of lead (II) and copper (II) from aquatic media. Water Science and Technology, 76(1), 15-27.

Schmidt, H., Jonschker, G., Goedicke, S., & Mennig, M. (2000). The sol-gel process as a basic technology for nanoparticle-dispersed inorganic-organic composites. Journal of Sol-Gel Science and Technology, 19(1-3), 39-51.

Šegota, S., Ćurković, L., Ljubas, D., Svetličić, V., Houra, I. F., & Tomašić, N. (2011). Synthesis, characterization and photocatalytic properties of sol–gel TiO2 films. Ceramics International, 37(4), 1153-1160.

Sellappan, R., Sun, J., Galeckas, A., Lindvall, N., Yurgens, A., Kuznetsov, A. Y., & Chakarov, D. (2013). Influence of graphene synthesizing techniques on the photocatalytic performance of graphene–TiO_2 nanocomposites. Physical Chemistry Chemical Physics, 15(37), 15528-15537.

Shan, A. Y., Ghazi, T. I. M., & Rashid, S. A. (2010). Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: a review. Applied Catalysis A: General, 389(1-2), 1-8.

Sun, H., Wang, C., Pang, S., Li, X., Tao, Y., Tang, H., & Liu, M. (2008). Photocatalytic TiO_2 films prepared by chemical vapor deposition at atmosphere pressure. Journal of Non-Crystalline Solids, 354(12-13), 1440-1443.

Thongpool, V., Phunpueok, A., Jaiyen, S., & Sornkwan, T. (2020). Synthesis and photocatalytic activity of copper and nitrogen co-doped titanium dioxide nanoparticles. Results in Physics, 16, 102948.

Timoumi, A., Alamri, S. N., & Alamri, H. (2018). The development of TiO_2-graphene oxide nano composite thin films for solar cells. Results in physics, 11, 46-51.

Tkalya, E. E., Ghislandi, M., de With, G., & Koning, C. E. (2012). The use of surfactants for dispersing carbon nanotubes and graphene to make conductive nanocomposites. Current Opinion in Colloid & Interface Science, 17(4), 225-232.

You, X., Chen, F., & Zhang, J. (2005). Effects of calcination on the physical and photocatalytic properties of TiO_2 powders prepared by sol–gel template method. Journal of sol-gel science and technology, 34(2), 181-187.

Yuan, C., Hung, C. H., Yuan, C. S., & Li, H. W. (2017). Preparation and application of immobilized surfactant-modified PANi-CNT/TiO_2 under visible-light irradiation. Materials, 10(8), 877.

Yuenyongsuwan, J., Nithiyakorn, N., Sabkird, P., Edgar, A. O., & Pongprayoon, T. (2018). Surfactant effect on phase-controlled synthesis and photocatalyst property of TiO_2 nanoparticles. Materials Chemistry and Physics, 214, 330-336.

Zhang, Y., Tang, Z. R., Fu, X., & Xu, Y. J. (2010). TiO_2− graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: is TiO_2− graphene truly different from other TiO_2− carbon composite materials. ACS nano, 4(12), 7303-7314.