

IMMOBILIZATION OF $\text{TiO}_2/\text{SiO}_2/\text{GSS}$ COMPOSITE PHOTOCATALYST ONTO SUPPORTING MATERIALS BY DIPPING METHOD AND EFFECTIVENESS ON PHOTOCATALYTIC ACTIVITY

Mia Lestari Ayuningtyas¹, Sukasem Watcharamaisakul^{1,*} and Supunnee Junpirom²

Received: April 01, 2020; Revised: May 10, 2021; Accepted: May 28, 2021

Abstract

The synthesis of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ by using the sol-gel method was done with the mass ratio of Titanium: (GSs) as 1:0.07 and calcined at 450°. The synthesized powder was immobilized onto the sponge substrate by using the dipping method with Polyvinyl alcohol as a binder prepared with the various thickness of the sponge substrate of 0.3, 0.5, 0.8, and 1 cm. The microstructure was investigated utilizing Scanning Electron Microscope (SEM) and phase composition utilizing x-ray Diffraction Spectrometer (XRD). The results of XRD pattern of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ show the presence of anatase phase and rutile (83.82%: 16.18%) and the average crystal size is 34.26 nm. The SEM photograph of synthesized powder gave a brief picture of the structure pattern of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ follow the layer pattern of GSs while the dipped samples show the tendency of powder powder-coated along the surface of fibers of the sponge. The degradation of methylene blue was analyzed under four kinds of light emission (dark, UV lamp, LED lamp, and solar light). The results show that there are no differences in photocatalytic activity under a UV lamp and solar light. The degradation of MB with the various thickness of the sponge substrate gave different results, on the first 60 min, a sample with thickness 1 cm has the highest degradation of 95% while at 3 h of experiments, all samples gave a similar result. However, the thickness of the sponge substrate in the degradation process has no significant effect occurs to the photocatalytic activity under solar light.

Keywords: TiO_2 , Substrate materials, Photocatalyst, Sol-gel method, Visible light degradation

¹ School of Materials Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand. E-mail: sukasem@sut.ac.th

² School of Chemical Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.

* Corresponding author

Introduction

Photocatalyst requires light emission to activate the catalyst function. The source of light is depended on the bandgap energy of materials. All semiconductors in nanomaterials form can be used in photocatalysis applications (Jain and Vaya, 2017). TiO₂ is the materials that have been attracted widely used due to possessing desirable physicochemical properties such as thermal and chemical stability, relative high photocatalytic activity, low toxicity, and low cost (Gupta and Tripathi, 2011; Shi and Zuo, 2011; Ola and Maroto-Valer, 2015; Bezerra *et al.*, 2017).

However, the bandgap of TiO₂ is generally a range of 3.0-3.2 eV, which gives work range as photocatalyst under UV range (100-400 nm) (Castellote and Bengtsson, 2011; Kumar and Devi, 2011; Pawar *et al.*, 2018; Kang *et al.*, 2019). It almost makes TiO₂ cannot effectively work under the radiation of solar light (no more than 4% yield of the solar spectrum) (IARC, 2012). Meanwhile, visible light adsorption can occur on semiconductors with gap energy less than or equal to 3 eV. To increase photocatalytic of TiO₂ under visible light, many methods have been introduced in much research, for example, impure doping (metal/non-metal), surface modification, hybrid composite (integration with other materials), etc (Aziz and Sopyan, 2009; Zhang *et al.*, 2010; Kumar and Devi, 2011; Chen and Liu, 2017; Liao *et al.*, 2017; Kovacic *et al.*, 2018; Negishi *et al.*, 2019).

However, non-metal doping was effective to obtain a visible light response. In recent years, the carbon in graphene form has become a more popular doping material to decrease the bandgap of semiconductors especially in photocatalyst applications (Zhang *et al.*, 2010; Lee and Park, 2013; Chen *et al.*, 2016; Najafi *et al.*, 2017; Ribao *et al.*, 2018). The graphene is considered an impurity in the TiO₂ system, as the bond between graphene and oxide on the system will produce dipole force. This force makes their band gaps overlap each other. In this case, the conduction band of graphene is lower than TiO₂ then it decreases the gap between the conduction band of graphene and valence band of TiO₂. The properties of graphene are high thermal and electrical conductivity, high specific surface area, and high charge carrier mobility at room temperature (Brownson and Banks, 2014). Therefore, the composite of graphene and semiconductors, especially TiO₂, is currently being considered as a potential photocatalyst in air and water purification applications. The graphene-based TiO₂ composite exhibits an enhanced photocatalytic activity in comparison with the ordinary TiO₂.

TiO₂ in the powder form has difficulty to disperse in the suspension and needs another technique to separate it (Larumbe *et al.*, 2014). To avoid free nanoparticles as the colloidal in suspension water, nano-TiO₂ particles are usually immobilized on a substrate or integrated into thin-films and other materials (Doll and Frimmel, 2004). The immobilization of TiO₂ makes it easy to be installed and recycle but will be reduced photocatalytic activity because of the reduction of the effective surface area. By addition material that has high surface area into TiO₂ and/or reduced the crystal structure into nanoscale (nanostructured), gives a potential of TiO₂ to obtain high photocatalytic activity with the immobilized form. To enhance the adsorptive and surface area of TiO₂, SiO₂ will be added as the material that can improve the photocatalytic process of TiO₂ (Aziz and Sopyan, 2009). At the same time, SiO₂ act as a carrier of TiO₂ and helps to obtain a large surface area as well as to improve the surface adsorption (Zhou *et al.*, 2006).

General methods to immobilize are used various substrates materials such as glass, activated carbon, polymeric materials, and metals and dipped into a slurry of photocatalyst materials. Glass and activated carbon are the materials that usually be used as a substrate (Shan *et al.*, 2010). In this work, the sponge was used as an alternative substrate due to possessing a high surface area which is suitable for immobilization of TiO₂/SiO₂/GSs bonded with polyvinyl alcohol (PVA) as a binder. The sponge was chosen as it has more fibers to be bonded with TiO₂/SiO₂/GSs and its pores with a high surface area that will increase its area that contact with pollutants. The aim of this work will mainly be a focused study on the effect of immobilization of photocatalyst and the effect of sponge thickness on the photodegradation of methylene blue (MB) under a variety of light sources such as dark, UV lamp, LED lamp, and solar light) were investigated.

Materials and Method

Materials

Polyvinyl alcohol (PVA) was obtained from Sigma Aldrich by code P8136-250g. TiO₂/SiO₂/GSs powder was prepared with the mass ratio Ti: GSs 1:0.07 and was calcined at 450°C. The methylene blue solution was prepared by diluting 100mL of methylene blue (C₁₆H₁₈N₃SCl) 30ppm solution stock with 900mL of deionized water to become

3ppm. The sponge was prepared by size 2 cm x 3 cm x thickness.

Immobilization of TiO₂/SiO₂/GSs

A 3 g of polyvinyl alcohol was dissolved in 100 ml distilled water. The solution was stirred and boiled on the hot plate at 80°C for 24 h. 4 g of TiO₂/SiO₂/GSs was mixed with 10 ml of distilled water and 4.4 ml of polyvinyl alcohol solution. After that, TiO₂/SiO₂/GSs slurry was prepared with the ball mill for 24 h. The sponge substrate was dipped into the slurry and dried at 110°C for 22-24 h.

Characterization of TiO₂/SiO₂/GSs synthesized powder

The structure of TiO₂/SiO₂/GSs synthesized powder was characterized for identified the crystal phase of the composite that was performed using a Bruker D2 PHASER XRD. The XRD patterns indicate different peak broadening which inversely proportional to the average crystal size of TiO₂ composite according to the Scherrer equation (Najafi *et al.*, 2017; Singh and Dutta, 2018).

$$D_p = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D_p is the crystal size (nm), K is the Scherrer constant (0.94 for spherical crystal), λ is the x-ray wavelength (Cu K α 0.154178 nm), β is the full width at half maximum (FWHM), and θ is the diffraction angle. The ratio between the crystal phase of TiO₂ also can be calculated from XRD result by equation (Eshaghi *et al.*, 2011; Singh and Dutta, 2018).

$$\% \text{ of anatase phase} = \frac{100}{1 + (I_R / 0.791 I_A)} \quad (2)$$

where I_R and I_A are the strongest intensities of rutile and anatase phase respectively.

The structure of TiO₂/SiO₂/GSs was characterized by using FE-SEM JEOL JSM 7800F to analyzed surface morphology as labeled by their thickness of 0.3, 0.5, 0.8 and 1.0 cm.

Photocatalytic activity

The photocatalytic activity of TiO₂/SiO₂/GSs dipped sponge was investigated by using a Methylene Blue (MB) solution as organic contamination in the wastewater. The 0.1 g of synthesized composite powder was put into a 100 ml solution of 3 mg/l of MB in the black cabinet under the dark condition, UV lamp, LED lamp, and solar light. The monitoring under solar light was restricted from 11 am to 4 pm according to peak

sun-h in Thailand (5.23 h). The reaction time was in every 30 minutes for 3 h of taking data. The 5 mL of degradation solution was analyzed by using a T80+PG instrument UV-Vis spectrophotometer with absorbance at a wavelength of 665 nm. The photocatalytic activity was measured as the degradation of MB by the following equation:

$$\% \text{degradation} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)$$

where C_0 and C_t are the initial concentration and concentration at the time of MB respectively. The photocatalytic activity of optimum condition was also measured with three-time cycles.

The kinetics of photocatalytic degradation of MB was based on the most commonly Langmuir-Hinshelwood (LH) kinetics, is given by:

$$r = -\frac{dC}{dt} = \frac{k_r K C}{1 + K C} \quad (4)$$

where r is the rate reaction (mg/l min) that changes by time t (min), C is the concentration at any time during degradation (mg/l), k_r is limiting rate constants of reaction at maximum coverage, and K is an equilibrium constant for adsorption of the substrate onto catalyst.

The LH kinetics on the first order has condition $K C \ll 1$. If so, Equation (4). will become $r = k_r K C$ and be integrated into first-order kinetics and is given by:

$$\ln \left(\frac{C_0}{C} \right) + K(C_0 - C) = k_r K t \quad (5)$$

where k ($k_r K$) is the rate constant (min^{-1}) and t is the degradation time (min).

Result and Discussion

The characteristics and properties of TiO₂/SiO₂/GSs composite

The material properties such as crystal size and phase of TiO₂ affect its ability as a photocatalyst especially after dopped by GSs. The crystal phase was analyzed by XRD then the result, as shown in Figure 1. can be used to calculate its crystal size by Equation (1). and the ratio of anatase: rutile by Equation (2). and obtain the result as described in Table 1. Table 1. explains the EDS result of 0.07G TiO₂/SiO₂/GSs in % weight of its main components, such as Carbon, Titanium, Oxygen, and Silicon. Figure 2. shows the SEM

pattern of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ synthesized powder with the tendency of layers structure.

Table 1. Analysis result of 0.07G $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ powder.

EDS data (%w)	C	7.37
	Ti	43.82
	O	43.18
	Si	5.6
Crystal Size (nm)		34.26
Anatase: Rutile		83.82: 16.18

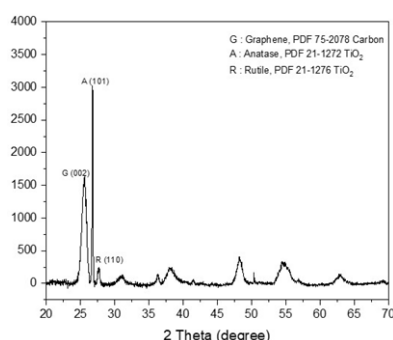


Figure 1. XRD pattern of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ photocatalyst powder.

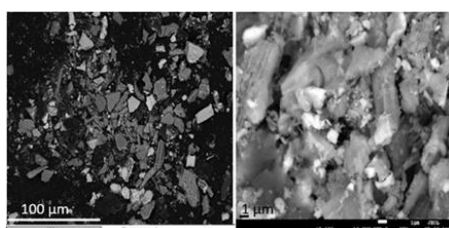


Figure 2. SEM images of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ synthesized powder.

To immobilized $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ powder into the compact one, the sponge substrates with the dimension 2 cm x 3 cm x t were dipped into the slurry of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ composition. The thickness was varied by 0.3 cm, 0.5 cm, 0.8 cm, and 1 cm (the sample was labeled by t0.3, t0.5, t0.8, and t1 respectively). To see how the photocatalyst was coated into the sponge substrate, samples as shown in SEM. Figure 3. shows the image of the fibers of the sponge and how the $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ was coated on the surface of the fiber.

Photocatalytic degradation of Methylene Blue (MB) solution

1) Effect of light emission

Light is one crucial thing that affects the photocatalytic process in general. Composite $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ powder is effective to work under

solar light range. But for the immobilized photocatalyst, the degradation test under different conditions was done to see what condition is the best for degradation with $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ and also if the dipping process has an aftereffect on the photocatalytic ability of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$. Figure 4. shows that $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ with 0.8 cm thick can also work under solar light with a similar final result that was done with a UV lamp (98.8%). Degradation under an LED lamp was also done to see if the degradation has occurred and it happened with the η degradation is 92.05% within 3 h.

Under dark conditions, the concentration can be decreased remarkably due to the adsorption of MB to the surface of TiO_2 that can be seen as the color-changing on photocatalyst (Tayade, Natarajan and Bajaj, 2009). It is also supported by the shape of a sponge that can expand the surface area of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ photocatalyst to adsorb MB and degrade it under suitable conditions. Figure 5. shows how the adsorption occurred in the first 1 h of the initial reaction. If compared to the thickness of photocatalyst, the adsorption was increased along. It because the thickness was followed by the amount of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ and the area that contact MB.

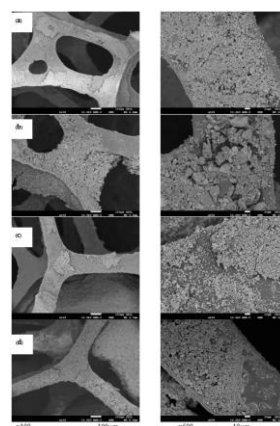


Figure 3. SEM images of sponge substrate of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ sample (a) t0.3, (b) t0.5, (c) t0.8, and (d) t1 (cm).

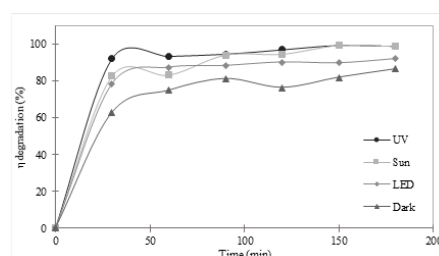


Figure 4. The effect of degradation under four conditions; dark, UV lamp (366 nm) solar light and LED lamp on t0.8 $\text{TiO}_2/\text{SiO}_2/\text{GSs}$.

2) Effect of the thickness and time

TiO₂/SiO₂/GSs was coated into sponge fibers with the help of a PVA binder. The thickness of the sponge was affected by the area of fibers in the sponge that was coated by photocatalyst. Figure 6. shows the effect of sponge thickness for TiO₂/SiO₂/GSs photocatalyst activity. The result shows how the thickness effect at the early stage of degradation but will give quite similar results after 3 h (η 94-99%).

At the early stage of degradation (30-60 mins), t1 already degraded almost 95% MB, while another sample only reached 83% of degradation. It occurred that the amount of TiO₂/SiO₂/GSs on t 0.3 was higher coated more than others. The first 60 mins of degradation can also be defined in Figure 7, while the color-changing of MB has occurred.

The result of degradation can also determine the kinetics of the reaction. By plotting time versus $\ln\left(\frac{C_0}{C}\right)$ and using Equation (5). as a linear function, the rate constant of each ratio was calculated, which is shown in Figure 8(a). The highest rate constant for the photocatalytic reaction is t 0.8 at 0.0011 min⁻¹. Later, the value of the rate constant was used to calculate the model of degradation rate for each sample. Then this model data was compared to the experiment data, as shown in Figure 8(b), when the line is representing model data and the mark represents experiment data. It shows the data from experiments were fitted with the model data.

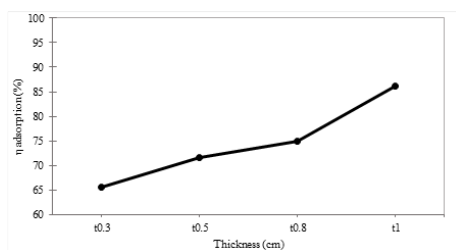


Figure 5. Adsorption of TiO₂/ SiO₂/ GSs under the dark condition for each thickness.

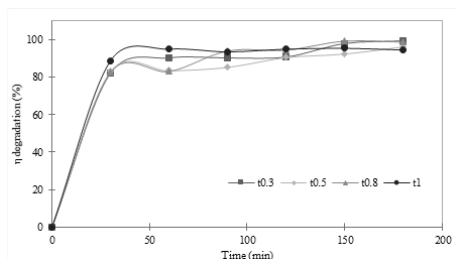


Figure 6. The effect of thickness of TiO₂/ SiO₂/ GSs compact on the sponge to η degradation (%).

3) Effect of reusable/stability

The photocatalyst is stable and can be used several times until its structure is damaged. In this step, all thickness of compact photocatalyst was reused after completed the degradation on the first batch under solar light. The photocatalyst was washed by ethanol then following by water to neutralize the pH then heated at 100°C to remove the water before using it for the next batch. This later was used to degrade a new MB solution at a fixed initial concentration of 3 mg/L for 3 h under solar light. This activity was observed for 3 cycles. Figure 9. Shows the degradation efficiency for each thickness in each cycle. For 0.3 cm and 0.8 cm thick, the degradation was dropped. Though there was a sudden drop at the second cycle on 0.8 cm thick then increase for the third cycle with a value slightly near the first one. It could have done with the mistake of the washing method, assuming that photocatalyst was unwashed properly, so the photocatalytic ability is not maximized. Meanwhile, for 0.5 cm and 1 cm thick, the efficiency of degradation seems to increase along the reusable of

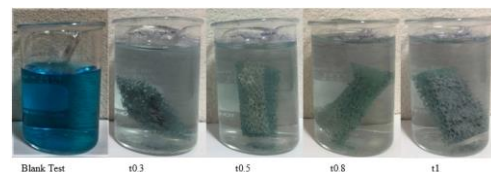
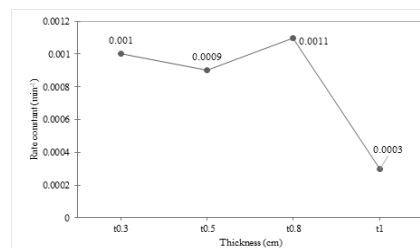
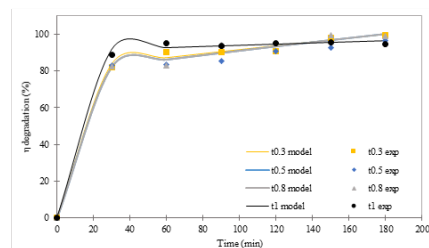


Figure 7. Comparison of color degradation of MB for each thickness under solar light for 1 h.



(a)



(b)

Figure 8. (a) Rate constant of TiO₂/ SiO₂/ GSs for each thickness and (b) validity between experiment data and model data.

$\text{TiO}_2/\text{SiO}_2/\text{GSs}$ photocatalyst, with the maximum number reached 99.8% at the third cycle. It defines that $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ compact on the sponge has photostability under solar light after three experiments with a slight change of degradation efficiency. Thus, $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ with a thickness of 0.5 cm could be stable as a photocatalyst for environmental application.

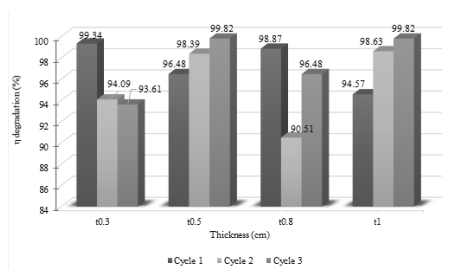


Figure 9. Effect of recycled $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ compact on the sponge to η degradation for each thickness.

Conclusion

$\text{TiO}_2/\text{SiO}_2/\text{GSs}$ samples were prepared by the dipping method on the sponge substrate followed by a drying process. The morphology was investigated for $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ powder to shows the layer pattern, that was affected by the presence of GSs while the EDS spectrum confirms the existence of Ti and C on the surface of the composite. The SEM result of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ compact shows how the photocatalyst coated the fibers of the sponge. The result of the degradation of MB showed a good result of photocatalytic activity under solar light emission. The maximum efficiency was shown by t1 in the first 60 mins with 95.04%. All samples then reached their saturated points at 98-99% within 3 h. It shows how the thickness affects the degradation proportionally with the amount of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ that was coated and also the surface area of the compact that enhances the adsorption and photocatalytic reaction of $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ composite under a dark condition with 86% adsorption. The recycled of each thickness of TiO_2 compact shows the efficiency of degradation within 90% until three times reused. Moreover, the degradation of the $\text{TiO}_2/\text{SiO}_2/\text{GSs}$ compact on the sponge under solar light depends on the thickness.

Acknowledgments

All these works are financially supported by a SUT-Ph. D Scholarship Program for ASEAN from Suranaree University of Technology.

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