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A Comparison Study of New TiO_2/PEG Immobilized Techniques Under Normal and Visible Light Irradiations

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Abstract. Novel photocatalysts of TiO_2 and TiO_2/PEG were immobilized using new technique which is double sided adhesive tape (DSAT) as a thin layer binder onto glass plate. The photocatalytic activity study of immobilized/TiO_2 and immobilized/TiO_2/PEG were carried out by irradiating of 36 mg L^{-1} MB dye in the presence of normal and visible light with rate of decolourization was estimated from aliquot concentration spectrophotometrically. The high photocatalytic activity from immobilized/TiO_2/PEG was observed with the rate constants of ca 0.06 and 0.02 min^{-1} under normal and visible light irradiation respectively. An active photocatalytic activity was observed for immobilized/TiO_2/PEG sample while no photocatalytic activity detected under immobilized/TiO_2. The high photoactivity was also detected under normal light for immobilized/TiO_2/PEG sample. This might be due to the presence of electron conjugate in PEG that acted as electron donor for TiO_2 thus increase the photocatalysis process. Moreover, this electron donor is reported to be able to become active under low energy visible light hence the immobilized/TiO_2/PEG can perfomed its photoactivity under visible light irradiation.

1 Introduction

TiO_2 is commonly known for its use in water purification since it is cheap, chemically inert and has high photo activity [1-3]. TiO_2 with a band gap of of 3.2 eV, is capable to degrade a variety of organic compounds via photo catalysis [4-5]. Nevertheless, it can only absorb UV (which constitutes 4% of the solar light) due to its wide energy band gap. Several methods have been assessed to shift its optical response to visible light region such as TiO_2 doping with metal and non-metal compound [6-8]. Even though its optical response could be shifted to Visible Light (VL) region, the preparations for samples were complicated. Currently, unsaturated polymers were applied as photosensitizer to produce the optical response of VL. For instance, Su et al. [9] had developed TiO_2/polymer by calcination process and the optical response was shifted to VL region. In addition, Zhu et al. [10] suggested that conjugated polymer such as poly (fluorene-co-bithiophene) (PFB) combined with TiO_2 to be an effective photosensitizer since 75 % of phenol was removed under visible light irradiation. For degradation of methyl orange [11], TiO_2/PVA (polyvinyl alcohol) showed a significant visible-active photodegradation. Other conjugated polymers [12] such as polypyrrole, polythiophene and polyaniline have also been reported and exhibited similar photodegradation pattern.

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In this research, a novel photocatalyst (TiO_2/PEG DSAT) was successfully prepared using brush coating method. More importantly, DSAT method was firstly reported to produce TiO_2/polymer film. The prepared composite film could effectively degrade Methylene Blue (MB) under normal and VL irradiation. Due to its cheapness and conveniences, TiO_2/PEG may contribute to application to the disposal of industrial effluents.

2 Experimental

2.1 Materials and preparation of photocatalyst

The sample solution was prepared by adding 6.5 g of titanium dioxide (TiO_2) Degussa P25 powder in 50 mL of deionised (DI) water added with polyethylene glycol (Merck, MW: 6000). The sample solution is thoroughly mixed through mechanical stirring. The compositions of the solution for obtaining immobilized/TiO_2/PEG films and molecular structure for PEG were presented in Table 1 and Figure 1 respectively. The composition presented in Table 1 has been selected based on the previous works that has established the experimental conditions to prepare pure (unmodified TiO_2) and modified TiO_2/PEG films. The sample films were prepared by using a brush-coating method applied onto glass substrates, which was cleaned and taped with Double Sided Adhesive Tape (DSAT) beforehand. The coated glass was then dried in the oven at 100 ºC for 15 minutes.

Table 1. The composition of the solution for obtaining immobilized/TiO2/PEG DSAT films.

Samples	TiO_2 (g)	DI water (mL)	PEG (8g in 100 mL of DI water)
Immobilized/TiO_2	6.5	50	-
Immibilized/TiO_2/PEG	6.5	50	1 mL

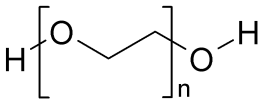

Figure 1. Molecular structure for poly ethylene glycol (PEG).

2.2 Photocatalytic degradation study

The activity of the catalyst was tested by degradation of methylene blue (MB; Fluka Analytical). The experimental setup used was to flow a coated glass with 20 mL of 36 mg L-1 concentration of MB dye inside a glass cell reactor (dimension: 50 mm Length x 10 mm Width x 80 mm Height). An NS 7200 aquarium pump was used as an aeration source. Area of photo catalytic activity equals to Length X Width of DSAT applied which is 6.6 cm X 4.6 cm.The light intensity of the lamp used were 461 W m^{-2} for Visible and 6.7 wt/m^2 for UV respectively. Direct photocatalysis and adsorption reactions were also performed for the photodegradation efficiency of MB. Turning on the 55-W compact fluorescent light initiated the photocatalytic reaction and outlet absorbance was measured. A 4 mL aliquot was extracted from the glass cell reactor at pre-specified intervals. The absorbance of the aliquot was measured by an UV spectrophotometer (Varian UV-Vis detector model HACH DR 1900) set to 661 nm which corresponds to the MB absorbance. Absorbance was converted to MB concentration using a Pseudo First Order plot. With the Pseudo First Order plot, absorbance was converted to concentration and rate of degradation (k) was calculated. The experimental design was modified from previous works [13-15].

3 Results and Discussion

3.1 Photocatalytic study

Photocatalytic degration of MB dye by using immobilized/TiO_2/PEG and immobilized/TiO_2 under normal and visible light irradiations are shown in Figure 2(a) and (b) respectively. A complete MB decolorization for both immobilized photocatalysts with high photocatalytic activity was observed under immobilized/TiO_2/PEG which can be seen in Figure 2(a). It is evident that under normal light irradiation PEG gives a high photoactivity. Since PEG acts as a pore forming agent, [16-18] thus, this characteristic displays increased porosity, which resulted in high numbers of reaction sites. Therefore, a lot of photocatalytic reaction may take place onto immobilized/TiO_2/PEG surface. The degradation rate obtained at 0.06 min-1 was found to be higher than ca 0.024 of other immobilized TiO_2/polymer [19]. The lower degradation rate is subjected to less reaction sites available due to utilization of various cross-linking methods. A complete MB decolorization takes approximately 90 minutes for immobilized/TiO_2/PEG while immobilized/TiO_2 takes almost 2 hours. In Figure 2(b), decolorization of MB was observed in immobilized/TiO_2 under visible light irradiation. However, it is just observed as a result for adsorption of immobilized/TiO_2. Moreover, it is generally accepted that pristine TiO_2-has wide bandgap energy thus make visible light disable to activate electron-hole pair. Hence, no photocatalytic activity will happen under visible light as well as observed on immobilized/TiO_2 sample in Figure 2(b).

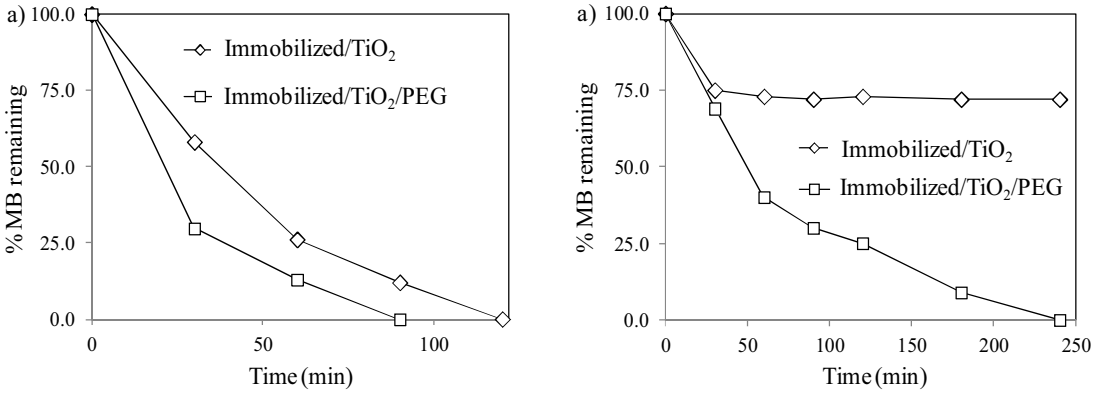

Figure 2. Decolorization of 36 mg L^{-1} MB dye using immobilized/TiO_2 and immobilized/TiO_2/PEG under a) normal and b) visible irradiations.

In contrary, an active photocatalytic activity was observed on immobilized/TiO_2/PEG sample under visible light irradiation. As can be seen in Figure 2(b), immobilized/TiO_2/PEG sample can perform a complete decolorization of 36 mg L^{-1} MB which takes around 240 minutes. An active visible light of immobilized/TiO_2/PEG might be due to the conjugated unsaturated polymer from PEG which is similar in photosensitized mechanism to the dye on TiO_2 under visible light. The sensitizer molecules adsorbed on TiO_2 are excited by visible light and electrons are subsequently injected to conduction band (CB) of TiO_2. While the CB acts as a mediator for transferring electrons from the sensitizer to substrate electron acceptors on TiO_2 surface, the valence band (VB) remains unaffected in a typical photosensitization. The excited electrons in CB of TiO_2 create a series of chain reactions and this explained visible light active for immobilized/TiO_2 sample. Subsequently, this behavior is expected as PEG is proven to enhance the transmittance value from 380-540 nm. According to Calderon et al. [20], the optical response has already shifted into VL region. For this reason, immobilized/TiO_2/PEG produced is visible-active by using PEG [21]. Nevertheless, through this

research paper, the enhancement has been made better since less power and less chemical are consumed, as compared to the previous work.

3.2 Strength study

Effect of strength for immobilized photocatalysts were determined by % remaining of photocatalysts after exposed under ultrasonic vibration as testing media. Figure 3 shows the % remaining of immobilized/TiO_2 and immobilized/TiO_2/PEG under sonication process. Weak adherence strength was observed on immobilized/TiO_2 sample since 56 % of photocatalyst remained on to the glass plate when applied under 20 seconds of ultrasonic vibration as opposed to TiO_2/PEG DSAT. Interestingly, coating adherence was proven to be better with PEG polymer supports with 92 % of catalyst on immobilized/TiO_2/PEG remained after 20 seconds of sonication. The strong intact on immobilized/TiO_2/PEG was due to the presence of PEG polymer to bind the TiO_2 particles. Hence, the developed immobilized/TiO_2/PEG prepared via brush coating method was proven to be strong, intact and durable. The evidence suggests that strong surface of immobilized/TiO_2/PEG is devoted to application of DSAT. It can be noticed that the photocatalyst film with PEG6000 m.wt showed a uniform, crack-free, porous and good adhesion with glass substrates [22]. In comparison to the previous work, the application of DSAT gives superior characteristic which greatly improves the durability of immobilized TiO_2 system. By far, this finding has confirmed that immobilized/TiO_2/PEG has already suppressed other immobilized TiO_2 system showing prominent strength in binding TiO_2/PEG surface.

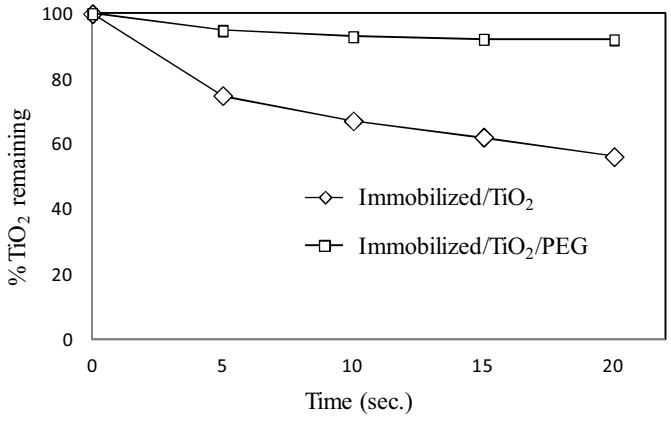

Figure 3. Percentage of immobilized/TiO_2/PEG and immobilized/TiO_2 weight remained after sonication.

4 Conclusions

The immobilized/TiO_2/PEG samples were successfully prepared by means of brush coating method. Immobilized/TiO_2/PEG exhibited higher visible light photocatalytic activity for the MB degradation in contrast to immobilized/TiO_2/DSAT. The photocatalytic activity under visible light was obviously depended on PEG dosage. The TiO_2/PEG DSAT exhibited higher activity for MB degradation which took 240 minutes to complete decolorization of MB dye under visible light irradiation. Through brush coating method, the photocatalyst surface was strong and intact in comparison to TiO_2/DSAT surface. In brief, the visible light photocatalytic activity in immobilized/TiO_2/PEG was attributed to the conjugated unsaturated polymer from PEG which is similar in photosensitized mechanism to the dye on TiO_2 under visible light.

References

[1] D. Mukherjee, Development of A Novel TiO_2-Polymeric Photocatalyst for Water Purification Both under UV and Solar Illuminations, PhD Thesis, The University of Western Ontario, Canada, (2011).

[2] N. Negishi, T. Iyoda, K. Hashimoto and A. Fujishima, Preparation of transparent TiO_2 thin film photocatalyst and its photocatalytic activity, Chem. Lett., **24**(9), 841-842, (1995).

[3] M.R. Hoffamnn, S.T. Martin, W. Choi and D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev., **95**, 69-96, (1995).

[4] K. Jatinder, dual effect of photocatalysis and adsorption in degradation of azorubine dye using nanosized TiO_2 and activated carbon immobilized with different techniques. Int. J. of ChemTech Research, **3**, 1537-1543, (2010).

[5] W. Zhao, Z. Bai, A. Ren, B. Guo and C. Wu, Sunlight photocatalytic activity of CdS modified TiO_2 loaded on activated carbon fibers, Appl. Surf. Sci., **256**(11), 3493–3498, (2010).

[6] V. Iliev, D. Tomova, R. Todorovska, D. Oliver, L. Petrov, D. Todorovsky and M. Uzunova-Bujnova, Photocatalytic properties of TiO_2 modified with gold nanoparticles in the degradation of oxalic acid in aqueous solution, Appl. Catal A: Gen., **313**(2), 115–121, (2006).

[7] J. Li, D. Shieh, D. Li, C. Ho, S. Yang and J. Lin, Photodegradation of CH3I on mesoporous TiO_2-B nanofibers with Au nanoparticles, Appl. Surf. Sci., **254**(15), 4655–4664, (2008).

[8] M. Bowker and E. Fourre, Direct interactions between metal nanoparticles and support: STM studies of Pd on TiO_2(1 1 0), Appl. Surf. Sci., **254**(14), 4225–4229 (2008).

[9] B.T. Su, X.H. Liu, X.X. Peng, T. Xiao and Z.X. Su, *Functional Nanostructures: Processing, Characterization and Applications*, Spinger, New York, (2003).

[10] J.F. Zhu, F. Chen, J.L. Zhang, H.J. Chen and M. Anpo, Visible light responsive titania-based nanostructures for photocatalytic, photovoltaic and photoelectrochemical applications, J. Photochem. Photobiol. A: Chem., **180**, 196–204, (2006).

[11] Y.Z. Wang and M.Q. Zhong, Photocatalytic activities of TiO_2 modified by poly (fluorene-co-bithiophene) under visible light, J. Applied Catalysis B: Environmental, **90**, 249–254, (2009).

[12] P.Lei, F. Wang, X. Gao, Y. Ding, S. Zhang, J. Zhao, S. Liu and M. Yang, Immobilization of TiO_2 nanoparticles in polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants, J. of Hazardous Materials, **227–228**, 185-194, (2012).

[13] C.Y Kuo, C.H. Wu and H.Y. Lin, Photocatalytic degradation of bisphenol A in a visible light/TiO_2 system, Desalination, **256**(1-3), 37-42, (2010).

[14] R. Ali and B.S Ooi, Photodegradation of New Methylene Blue in aqueous solution using zinc oxide and titanium dioxide as catalyst, J. of Technology, **45**, 31-42, (2006).

[15] W.I.N. Wan Ismail, S.K. Ain, R. Zaharudin, A.H. Jawad, M.A.M. Ishak, K. Ismail and S. Sahid, New TiO_2/DSAT immobilization system for photodegradation of anionic and cationic dyes, Int. J. of Photoenergy, **2015**, 1-6, (2015).

[16] S. Suzana, C. Lidija, D. Ljubas, V. Svetličić, I.F. Houra and N. Tomašić, Synthesis, characterization and photocatalytic properties of sol–gel TiO_2 films, Ceramics Int., **37**(4), 1153-1160, (2011).

[17] S.J Bu, Z.G Jin, X.X Liu, L. Yang and Z. Cheng, Fabrication of TiO_2 porous thin films using peg templates and chemistry of the process, Materials Chemistry and Physics, **88**(2-3), 273-279, (2004).

[18] A.A. Ramírez-Santos, P. Acevedo-Peña and E.M. Córdoba, Enhanced photocatalytic activity of TiO_2 films by modification with polyethylene glycol, Química Nova, **35**(10), 1931-1935, (2012).

[19] D. Mukherjee, S. Barghi and A.K. Ray. Preparation and characterization of the TiO_2 immobilized polymeric photocatalyst for degradation of aspirin under UV and solar light, Processes, **2**(1), 12-23, (2014).

[20] J.M. Calderon-Moreno, S. Preda, L. Predoana, M. Zaharescu, M. Anastasescu, M. Nicolescu, M. Stoica, H. Stroescu, M. Gartner, O. Buiu, M. Mihaila and B. Serban, Effect of polyethylene glycol on porous transparent TiO_2 films prepared by sol–gel method, Ceramics Int., **40**(1), 2209-2220, (2014).

[21] L.C. Chen, F.R. Tsai and C.M. Huang, Photocatalytic decolorization of methyl orange in aqueous medium of TiO_2 and Ag–TiO_2 immobilized on γ-Al_2O_3, J. Photochem. Photobiol. A: Chem., **170**(1), 7–14 (2005).
[22] N. Tasić , Z. Branković, Z. Marinković-Stanojević and G. Branković, Effect of binder molecular weight on morphology of TiO_2 films prepared by tape casting and their photovoltaic performance, Science of Sintering, **44**(3), 365-372, (2012).