

Researches of visible light photo-sensitized porphyrin-TiO₂ photocatalyst and its related self-cleaning effects

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ABSTRACT

A visible light sensitized hydrophilic self-cleaning PET fabric exhibiting photocatalytic dye degrading properties has been prepared by step wise deposition of anatase TiO₂, porphyrin with carboxylic acid as an anchoring group (**TCPP**), the modified PET fabric showed excellent photo degradation of Rhodamine dye, the dye degradation ability in visible light for the modified fabric also monitored at different time intervals by UV-Vis spectral technic. The degradation efficiency found to be in the order TiO₂/**TCPP** > TiO₂ > PET. The fabrics were characterized by UV-Vis, FESEM. Synthesized porphyrin and TiO₂ were confirmed by ¹H-NMR and XRD analysis respectively.

Keywords: Anatase TiO₂, porphyrin, Rhodamine, hydrophilic, Photocatalysis

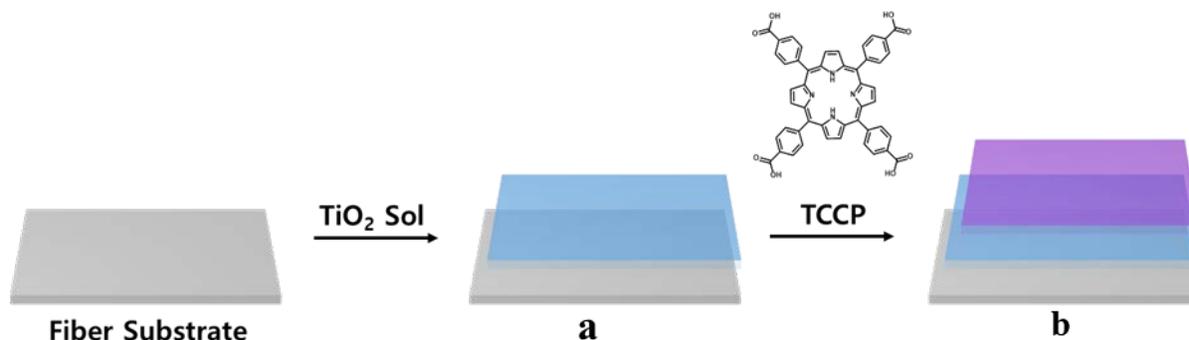
1 INTRODUCTION

In recent years there is an increasing demand for functional fibrous materials, where fibers not only have the basic properties, but also possess environmentally friendly functionalities such as self-cleaning, antimicrobial, and anti-pollution. Self-cleaning coating technologies are developing rapidly at present, particularly focusing on self-cleaning fibrous materials. Self-cleaning surfaces are classified to be hydrophobic or hydrophilic. The hydrophobic nature popularly known as the lotus effect, can be achieved by surface modification either chemically or geometrically. On the other hand, hydrophilic self-cleaning, obtained by photocatalytic effect and it is a chemical surface modification that uses photoactive material. These photo active material chemically decompose adsorbed dirt, contaminants, pollutants or microorganisms through photo oxidation and photo reduction reactions in the presence of light [1,2]. Following recent reports on incorporating nanostructured photocatalysts into flexible substrates [3,4], several studies on the deposition of titanium dioxide particles on fibrous materials have been carried out using various application methods, such as hydrothermal

treatment [3], sol-gel processing [4,5]. In 1995, Fujishima research group, in collaboration with TOTO Ltd., Japan, discovered titanium dioxide possesses a high photo-induced

hydrophilicity after light irradiation, which widened the application of the photocatalyst as surface coating [1,6]. Ever since, industrial products using photocatalytic surface functionalization treatment are marked as hydrophilic self-cleaning coating. Photocatalytic self-cleaning fibers are fibrous materials formed by imparting photocatalytic function through surface functionalization treatment, wherein the fibers are able to clean themselves when exposed to light. Due to its non-toxicity, low cost, chemical stability and high oxidizing ability, anatase TiO₂ has been regarded as the most promising environment-friendly photocatalyst [7].

Extensive research has been carried out to grow TiO₂ nanocrystals on natural and synthetic fibres [8], leading to the successful development of a number of UV-active self-cleaning textiles. In order to extend the light absorption of TiO₂ toward the visible region, various strategies have been implemented including doping TiO₂ with metals [9] and non-metals [10]. Dye-sensitization has been considered as an alternative approach to induce visible-light photocatalysis [11]. Transparent thin layers of nano crystalline anatase TiO₂ were formed on PET fabric by a dip-coating process, then the self-assembled monolayers of porphyrins with anchoring group such as carboxylic (**TCPP**) functionalities interacts with the TiO₂-coated PET, as shown in Scheme 1. Further Rhodamine(RB) dye decomposition were investigated, these dyes are widely used as a colorant in textiles and food stuffs, and also a well-known water tracer fluorescent [12]. It is harmful to human beings causes skin and eye irritation. The carcinogenicity, developmental toxicity, neurotoxicity and chronic toxicity toward living beings have been experimentally proven [13]. Thus, keeping harmful effects in view, it was considered sensible to make efforts to degrade RB and to study the PET fabric towards hydrophilic self-cleaning property, through photocatalytic effect.



Scheme 1. Formation of self-assembled monolayer of anchored porphyrin molecule on TiO_2 -coated PET.

(a) Treatment of pristine PET with TiO_2 colloid (b) Treatment of TiO_2 -coated PET with porphyrin solution in DMF to form porphyrin/ TiO_2 -coated PET

2 EXPERIMENTAL SECTION

2.1. Synthesis and characterization of 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabzoic acid (TCCP).

To a solution of methyl 4-formylbenzoate (1 eqv.) in propionic acid (50 mL) was added pyrrole (1 eqv.) and the reaction mixture was refluxed 12 h in dark, then the reaction mixture was filtered and column purified to obtain the desired product. Further the product obtained was hydrolyzed by dissolving in chloroform and methanol and added sodium hydroxide in water and heated at 80°C for 48h then the reaction mixture was evaporated under vacuum and added 1N. HCl, the solid formed was filtered and washed with methanol to get the desired product. ^1H NMR (CDCl_3 , 600 MHz), δ (ppm): -2.92 (s, 2H), 8.34 (d, 8H, $J=7.8$ Hz), 8.38 (d, 8H, $J=7.8$ Hz), 8.86 (s, 8H), 13.29 (s, 4H).

2.2. Preparation and characterization of TiO_2

Anatase TiO_2 colloid preparation: A solution of titanium tetraisopropoxide and acetic acid was added dropwise to acidified water (HNO_3 , 1.4%). The mixture was vigorously stirred at 60°C for 16 h and the prepared anatase TiO_2 was confirmed by XRD which has the characteristic diffraction peaks at $2\theta = 25.5$, 38.1 , 48.0° (Fig. 1). The prepared sol was used to prepare TiO_2 thin coatings on PET fabric by a dip-coating method. After 30 min, coated samples were exposed to ammonia fumes until surface pH 7 was reached. The samples were dried at 80°C in an oven and then cured at 100°C for 10 min.

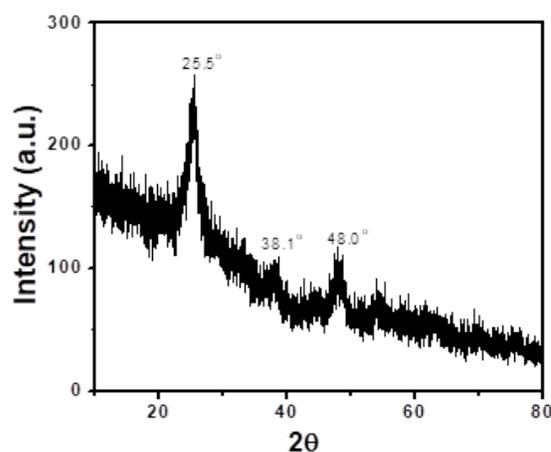


Fig. 1. XRD spectra of anatase TiO_2

2.3. Preparation of porphyrin-coated PET

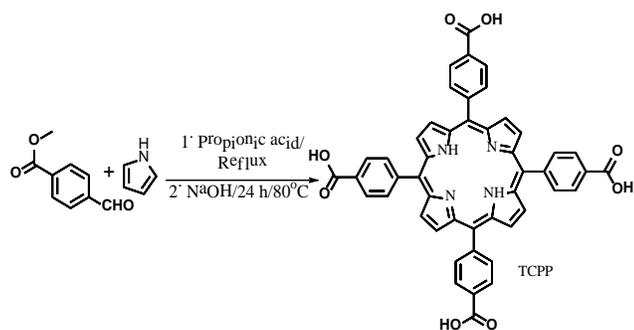
For deposition of porphyrin, TiO_2 -coated fabrics were dipped in porphyrin solution (1×10^{-5} M) in dimethyl formamide (DMF) and heated at 100°C for 5 h approximately. Samples were then washed with DMF and water in order to remove excess uncoated porphyrin.

2.4. Photocatalysis studies for experiments of photocatalytic degradation of Rhodamine (RB).

TiO_2 /porphyrin-coated PET samples were taken and RB was dissolved in chloroform (1×10^{-3} M) solution which was drop casted and dried for 1 h in dark to attain adsorption-desorption equilibrium. The change in concentration of RB was monitored by recording the UV-Vis absorption spectra at different time intervals, during the course of photocatalytic reaction.

3 RESULTS AND DISCUSSION

As depicted in Scheme 2, the photo sensitizer dye (porphyrin) was prepared by the reaction of methyl 4-formylbenzoate with pyrrole, and its structure was confirmed by ^1H NMR spectra. The photocatalytic behavior of the porphyrin (TCPP) was investigated by UV-Vis absorption spectroscopy.



Scheme 2. Synthesis of Photo sensitizer dye (Porphyrin)

3.1. SEM analysis

In order to investigate the surface morphology of coated and pristine PET samples, TCPP coated PET as a representative case recorded and illustrated in Fig. 2. The images (Fig. 2a, b and c) reveal that the PET and TiO_2 and TCPP coated samples retain the integrity of the fibers. However, PET coated with TiO_2 and TCPP observed to be having rougher surface compared to that of pristine PET, further surface aggregation can be observed in PET/ TiO_2 /TCPP coated sample.

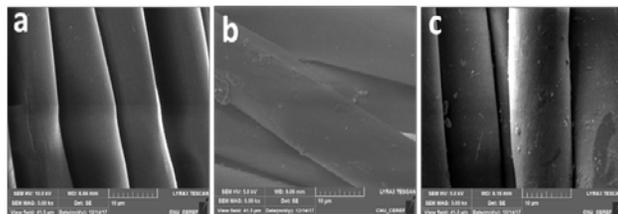


Fig. 2. FESEM images of pristine PET (a), TiO_2 -coated PET (b), TiO_2 /TCNPP-coated PET (c).

3.2. UV-Vis spectroscopy

In order to study the binding of the porphyrin dye with TiO_2 , UV-Vis spectra of TCPP in DMF (Fig. 3a) and adsorbed on PET were recorded in presence of TiO_2 (Fig. 3b). UV-Vis of pristine PET also recorded for comparison. The study shows visible-light absorption between 400 to 600 nm in all samples except for pristine PET. The absorption spectrum of TCPP in DMF shows a strong peak at 417 nm for Soret band. The absorption peaks in the 500–600 nm region correspond to the Q bands of porphyrin.

These peaks can also be observed in TCPP-coated PET samples indicating that there is a strong interaction between the anchoring groups in porphyrin with TiO_2 coated PET fabric.

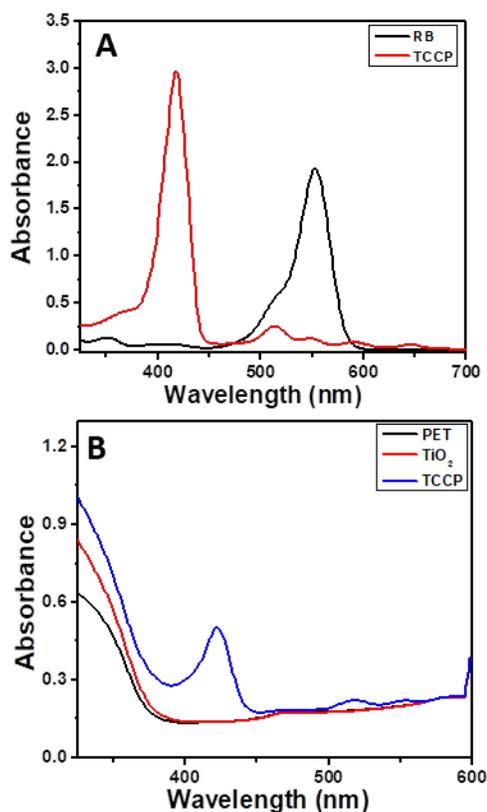


Fig. 3. UV-Vis spectra of Rhodamine(RB) and porphyrin in DMF (A) and TiO_2 , Porphyrin adsorbed on PET (B)

3.3. Photocatalytic degradation of Rhodamine

The self-cleaning properties of TiO_2 /Porphyrin coated fabrics were evaluated quantitatively by monitoring the photocatalytic degradation of Rhodamine (RB). The photocatalytic efficiency of different PET/ TiO_2 /Porphyrin coated samples compared. RB was found to be stable in PET sample. However, in presence of TiO_2 , TiO_2 /TCPP, coated samples under visible-light, RB undergoes degradation, as monitored by the UV-Vis spectra recorded at different time intervals for up to 3 h. Pristine, TiO_2 -coated, and Porphyrin-coated samples were used for comparison. The pristine sample shows no change for RB indicating no photocatalytic activity by PET itself. It is noted that the TiO_2 -coated sample, shows some photocatalytic activity towards degradation of RB. Whereas TiO_2 /Porphyrins coated samples were found to have more photoactive than TiO_2 -coated samples, the degradation experiments were carried out for 180 min irradiation under visible-light, figure 4 shows a plot of normalized

concentration (C/C_0) Vs Time (h). The result obtained confirmed that the RB dye degradation, among these samples, the photocatalytic efficiency higher for $TiO_2/TCPP$ thus the degradation efficiency in the order $TiO_2/TCPP > TiO_2 > PET$.

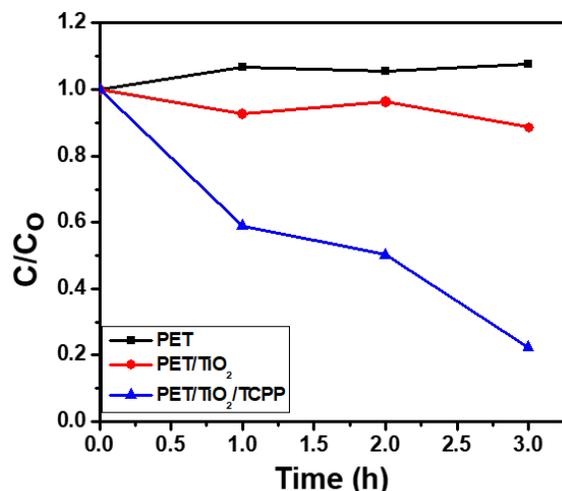


Fig. 4. Degradation of Rhodamine(RB) under visible-light irradiation (5.02 mW cm² irradiance): Pristine PET, TiO₂-coated PET, TiO₂/TCPP-coated PET samples.

3.4. Degradation mechanism

The mechanism of TiO₂ sensitization by dyes in visible-light, involves the transition of electron from the ground state of porphyrin dye [Pp] to the excited singlet state ¹[Pp]* [14]. Relaxation of the singlet excited state generates the triplet excited state ³[Pp]* through a process of intersystem crossing. Electrons from ¹[Pp]* and ³[Pp]* excited states can be transferred to conduction band of TiO₂, which can be trapped further by the adsorbed O₂, resulting in formation of O₂⁻ causing degradation of RB present on the surface of TiO₂. porphyrins with no unpaired electrons manifest long lifetime of excited state and are strongly fluorescent [15], resulting in efficient electron injection in conduction band of TiO₂.this is attributed for the degradation of RB.

4 CONCLUSIONS

Visible-light active hydrophilic self-cleaning PET has been successfully developed using a dye-sensitization approach. Self-assembled monolayers by anchor group of porphyrin have been formed on TiO₂-coated PET by a simple adsorption method, choice of anchor group can provide custom-tailored performance parameters for the photocatalytic activity, stability of the dye in PET and overall photodegradation efficiency. The surface morphology of TCPP attachment on TiO₂ coated PET has been confirmed by SEM analysis and also the TiO₂/TCPP-coated PET has shown significant photocatalytic activity in

the degradation of Rhodamine when compared to that of TiO₂-coated PET.

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REFERENCES

- [1] K. Hashimoto, H. Irie and A. Fujishima, *Jpn. J. Appl. Phys.*, 12, 8269, 2005.
- [2] A. Fujishima and X. Zhang, *C. R. Chim.*, 9, 750, 2006.
- [3] W. A. Daoud and J. H. Xin, *Chem. Commun.*, 16, 2110, 2005.
- [4] A. Bozzi, T. Yuranova and J. Kiwi, *J. Photochem. Photobiol. A*, 172, 27, 2005.
- [5] K. H. Qi, W. A. Daoud, J. H. Xin, C. L. Mak, W. S. Tang and W. P. Cheung, *J. Mater. Chem.*, 16, 4567, 2006.
- [6] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, 388, 431, 1997.
- [7] M. Peplow, *Nature*, 429, 620, 2004.
- [8] W. S. Tung and W. A. Daoud, *J. Mater. Chem.*, 21, 7858, 2011.
- [9] M. Miyauchi, A. Nakajima, T. Watanabe and K. Hashimoto, *Chem. Mater.*, 14, 2812, 2002.
- [10] L. Zhao, X. Chen, X. Wang, Y. Zhang, W. Wei, Y. Sun, M. Antonietti and M. M. Titirici, *Adv. Mater.*, 22, 3317, 2010.
- [11] S. Rehman, R. Ullah, A. M. Butt and N. D. Gohar, *J. Hazard. Mater.*, 170, 560, 2009.
- [12] S. D. Richardson, C. S. Wilson and K. A. Rusch, *Ground Water*, 42, 678, 2004.
- [13] D. Kornbrust and T. Barfknecht, *Environ. Mutagenesis*, 7, 101, 1985.
- [14] C. Wang, J. Li, G. Mele, G. M. Yang, F. X. Zhang, L. Palmisano and G. Vasapollo, *Appl. Catal. B: Environ.*, 76, 218, 2007.
- [15] G. Szintay and A. Horvath, *Inorg. Chim. Acta*, 324, 278, 2001.