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PII:	80167-7322(20)36910-5
DOI:	https://doi.org/10.1016/j.molliq.2020.114668
Reference:	MOLLIQ 114668
To appear in:	Journal of Molecular Liquids
Received date:	15 September 2020
Revised date:	16 October 2020
Accepted date:	26 October 2020

Please cite this article as: R. Manivannan, J. Ryu and Y.-A. Son, Ultrasonic assisted fabrication of dual function surface on PET and preparation of single component ink to attain efficient self-cleaning function via digital printing, *Journal of Molecular Liquids* (2020), https://doi.org/10.1016/j.molliq.2020.114668

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# Ultrasonic Assisted Fabrication of Dual Function Surface on PET and Preparation of Single Component Ink to Attain Efficient Self-Cleaning Function via Digital Printing

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#### Abstract

The self-cleaning effects of polyethylene terephtharize fabric (**PET**) through the photocatalytic effects of TiO<sub>2</sub> (**T**), porphyrin (**P**) and silvate (**S**, have been explored ultrasonically using bath type (WUC-D22H, Daihan Scientific, Korea). The ultrasonic power and frequency were 100 W and 30 kHz, respectively. The surface nodification in fabric was achieved by the ultrasonic deposition of anatase TiO<sub>2</sub> (**T**), porphyrin (**P**), and further modification by silane (**S**) was used to achieve dual-function (photocat lytic and superhydrophobic) self-cleaning behavior. The dye-degrading abilities of the moduli fabric surface confirmed by the photo discoloration of various organic pollutants by visible light treatment. From the tested various dye, methylene blue (MB) decomposition was monitored using UV-Vis spectroscopy by measuring the changes in concentrations in the fabric at altered time breaks. The attachment of silane and its stability after washing the surface of fabric confirmed by measuring the water contact angle (WCA). The self-cleaning efficacies were in the order **PET@TP** > **PET@TPS**. The modifications are done in fabric surface characterized and confirmed by XRD, XPS, UV-Vis, and FESEM analyses. Fabric's self-cleaning effect examined with common daily life pollutants. Easy to make single-

component ink prepared using silane (S) and used as digital printing ink and printed on fabric, exclusively attained hydrophobic surface in the printed area.

**Keywords:** Ultrasonic finished coating; Porphyrin, Stain; Superhydrophobic; Self-Cleaning; Digital Printing

#### 1. Introduction

In current centuries, there is a great attention in research related to functionalizing fibrous materials to meet specific requirements, such as self-cleaning, reviewion against pollutants and microorganisms, and deodorization [1]. In particular, self-cleaning textile materials are of considerable importance in daily life due to their commental usages [2]. Self-cleaning surfaces attained by coating fibrous materials with either hvd.oph.bic or hydrophilic compounds have undergone rapid advances towards achieving t xtnes with self-cleaning properties. Apart from their fundamental properties, these , aterials should possess properties such as superhydrophobicity, which leads to encelent liquid repellency and allows various applications including antisticking, anti-icin, entifogging, antipollution, self-cleaning and water/oil separation [3-11]. A surface is superhydrophobic if it has a water contact angle greater than 150° [12-14]. A surface is we er .epellent if it has a less than  $10^\circ$ , giving it a self-cleaning effect. Sufficient roughness with a low surface energy allows dirt to be easily removed by bringing the material into contact with water, and the fabrication of these surfaces can be inspired by nature, including by the lotus leaf and water strider [2,12]. However, hydrophilic self-cleaning in fibrous materials are prepared through photocatalytic modifications involving photoactive materials, and metal oxide nanoparticles, in particular  $TiO_2$  NPs, are broadly applicable [15,16].

In general,  $TiO_2$  is one of the reliable and eco-friendly photocatalyst that possesses high stability, nontoxic, inexpensive and excellent oxidizing ability. These polycrystalline

semiconductor oxides exhibit optical properties, and these photoactive materials can spontaneously removal of absorbed contaminants through decomposition under light by photooxidation and photoreduction reactions [17-21]. However, attaching TiO<sub>2</sub> to flexible surfaces, such as paper, fabric and plastic, is challenging because of its low thermal and chemical resistance [22-24]. Based on recent reports integrating nanosized TiO<sub>2</sub> into substrates, various methods have been employed to deposit TiO<sub>2</sub> onto the fibrous materials, including by sol-gel, hydrothermal, impregnation, chemical spacer attachment, and cputtering methods [25-33]. Daoud et al. first invented self-cleaning cotton through the muchation and growth of anatase  $TiO_2$  at a low temperature and ambient pressure [3-1]. The photocatalytic self-cleaning functionalized surface has a hydrophilic self-cleaning  $co_{1}$  ing, which tends to exhibit surprising photo induced hydrophilicity after irradiation with "gr. [17,35].

Significant research has been made on the production of titanium dioxide nanocrystals on both natural and synthetic fibers [36] for the fabrication of self-cleaning materials with UVactive property. But these materials connot show self-cleaning properties under visible light because of the widespread band gap of  $TiO_2(\sim 3.2 \text{ eV})$ ; thus,  $TiO_2$  absorb approximately 385 nm [37], therefore different approaches were explored to shift its light-absorption region towards the visible region, such as doping metal and nonmetals [38,39]. Dye sensitization is another method to bring photocatalytic activity in the observable region [40]. Dye sensitization by incorporating porphyrin into  $TiO_2$  results in a solid band at 450 nm region (Soret band) and weak Q bands at approximately 500-700 nm [41]. Thus, the modified surfaces attained through this process may have outstanding self-cleaning properties and may be able to clean themselves when exposed to visible light.

Self-cleaning properties achieved by incorporating either hydrophobic and photocatalytic properties into the fabric have two advantages: 1) water-soluble impurities rolled off due to the water-repelling nature of fabric and 2) organic dyes and other common stain-causing materials can be decomposed by photocatalysis.

As a continuation, of our previous work [42], and to improve the self-cleaning effect, we developed and attached new porphyrin (Scheme 1) and silane derivative to the fabric to increase its property, in this work we used non-fluorinated silane, which condidered being less toxic when compared with fluorinated silane. The prepared porphyring contain a carboxylate-substituted phenyl group in the meso position, and the beta position a occupied by the phenyl ring of the prepared porphyrin molecule, 4,4',4",4"'-(2,3,7,8,12,1',18-octaphenylporphyrin-5,10,15,20tetrayl) tetrabenzoicacid (P) to elucidate the photo at lytic behavior. Additionally, a trimethoxy alkyl silane with 22-carbon chain, docos 'ltr' thoxysilane (S), synthesized and attached to the substrate, and determined the hydrophobicity of the modified fabric sample. After successful modification, the abilities of the mate in to degrade organic pollutants like nitrophenol (NP), rhodamine B (RB), eosin Y (E.'), indigo (IN), bromophenol blue (BB), methylene blue (MB) and common stain-causing matrials, such as coffee and soy sauce, were studied under visiblelight irradiation, and the hydrophobic properties were assessed by measuring the water contact angles. As a preliminary attempt, single component hydrophobic ink has been prepared from docosyltriethoxysilane (S), and printed on polyethylene terephthalate (PET) and examined the hydrophobic nature in the printed surface.



Scheme 1. Surface modification process for polyethylene terephthalate fabric to obtain photocatalytic, superhydrophobic, self-cleaning material.

### 2. Experimental Section

All chemicals procured from Sigma Aldrich and "C. Chemicals and used as received. 600 MHz NMR spectroscopy (AVANCE spectrom (a) to confirm the compounds. ESI mass spectra measured in 4000 Q TRAP mass spectrometer. Surface characteristics was analyzed using LYRA3 XMU system (SEM). The all sc q ion spectra were recorded using UV-Vis spectroscopy (Agilent 8453 instrument). Shir advu Solid Spec-2700 instrument were used to recorded solid-state UV-Vis spectra and Multilab 2000 spectrometer for XPS measurements. X-ray diffractometer (PHILIPS, X Pert-MPD System ( $\lambda$ =1.54056Å). Decomposition of MB was examined under visible-11ght irradiation (300 W lamp). The porphyrin (**P**) used in the present study were prepared as shown in Scheme 2.



Scheme 2. Synthesis of the porphyrin P.

### 2.1 Procedure for the synthesis of (4,4',4'',4'''-(2,3,7,8,12,13,17,18-octaphenylporphyrin-

### 5,10,15,20- tetrayl) tetra benzo. acid) (P)

### Preparation of tetrameth' 1 4 ,4",4"'- (porphyrin-5,10,15,20- tetrayl) tetrabenzoate (1)

Methyl 4-formyl benzoate (2.5 g, 15.24 mmol) in 25 mL of propionic acid, added pyrrole (1.02 g, 15.24 mmol) slowly in drops and it was heated (150 °C) for 12 h (dark) and cooled followed by filtration to obtained purple solid which was purified by column chromatography. Yield (650 mg, 20%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz), δ (ppm): -2.88 (s, 2 H), 4.03 (s, 12 H), 8.20 (d, 8 H), 8.36 (d, 8 H), 8.73 (s, 8 H) (Fig. S1). ESI-MS: m/z calcd. 846.3, found 847.3 [M+H<sup>+</sup>] (Fig. S2).

Preparation of tetra methyl 4,4',4'',4'''-(copperporphyrin-5,10,15,20-tetrayl) tetra benzoate (2)

Tetra methyl 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl) tetra benzoate (0.3 g, 0.35 mmol) in chloroform, to that  $Cu(OAc)_2.H_2O$  (0.7 g, 3.5 mmol) in methanol was added, and it was heated (60 °C) for about 45 min. Then, it was concentrated for dryness, and it was redissolved using chloroform and further to remove the excess  $Cu(OAc)_2$  it was washed using water. Yield (300 mg, 93%). ESI-MS: m/z calcd. 907.2, found 908.3 [M+H<sup>+</sup>] (Fig. S3).

## Preparation of tetramethyl 4,4',4'',4'''-(2,3,7,8,12,13,17,18-octabromoporphyrin-5,10,15,20tetrayl)tetrabenzoate (3)

To tetra methyl 4,4',4'',4'''-(copperporphyrin-5,10,15,20-tetray<sup>1</sup>) tetra benzoate (0.3 g, 0.33 mmol) in chloroform, then bromine (0.2 g, 1.32 mmol) in chloroform is added, and was stirred for 12 h. An excess bromine quenched by adding sodium thiosultate, and then water added to the reaction mixture. The mixture then extracted with chloroform, and the organic layer was concentrated to dryness. Then, the crude reaction mixture was dissolved in chloroform and cooled to 0°C, and to the cooled solution was added conc. H<sub>2</sub>S $O_4$  (3 mL), then it was stirred for 20 min and neutralized with ammonia, the reaction mixture was extracted with chloroform and the crude product obtained was purified by column chromatography. Yield (250 mg, 51%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MH<sup>-2</sup>) c(<sup>+</sup><sub>x</sub>pm): 4.03 (s, 12 H), 8.22 (d, 8 H), 8.37 (d, 8 H) (Fig. S4). ESI-MS: m/z calcd. 1478.1, 1, 1, 1478.5 [M+H<sup>+</sup>] (Fig. S5).

## Preparation of tetramethyl-4,4',4'',4'''(2,3,7,8,12,13,17,18-octaphenylporphyrin-5,10,15,20tetrayl)tetrabenzoate (4)

A round bottom flask was charged with tetramethyl 4,4',4",4"'-(2,3,7,8,12,13,17,18octabromoporphyrin-5,10,15,20-tetrayl)tetrabenzoate (0.5 g, 0.33 mmol), phenylboronic acid (0.96 g, 7.92 mmol) and potassium carbonate (2.08 g, 15 mmol) and toluene was added (15 mL). The mixture degassed under nitrogen, and tetrakis palladium (0.078 g, 0.07 mmol) added. The

reaction mixture stirred at 100°C for 12 h, toluene removed from reaction mixture under vacuum, the residue again dissolved in chloroform and washed with water. The desired product obtained following column chromatography. Yield (230 mg, 46.7 %).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 600 MHz), δ (ppm): 3.94 (s, 12H), 6.65 (m, 40H), 7.38 (s, 8 H), 7.61 (s, 8 H) (Fig. S6). ESI-MS: m/z calcd. 1455.6, found 1456.5 [M+H<sup>+</sup>] (Fig. S7).

 Preparation
 of
 4,4',4''-(2,3,7,8,12,13,17,18-octaphenylporphyrin-5,10,15,20 

 tetrayl)tetrabenzoic acid (P)
 Image: Compared acid (P)

Tetramethyl 4,4',4'''(2,3,7,8,12,13,17,18-octa phenyl porphyrin-5,10,15,20-tetrayl) tetrabenzoate (0.2 g, 0.14 mmol) in THF (20 mL) was adourd 2 M potassium hydroxide in water (10 mL). The reaction mixture was stirred at room temper sure for 1 h and then at 80 °C for 48 h. The THF then evaporated from the reaction mixture, and 2N HCl (25 mL) added to it. The resulting green precipitate washed by distinger water. Then crystallized from methanol to get the product. Yield (120 mg, 62.5 %).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 600MHz), δ(ppn.): 5.64 (m, 40H), 7.61 (s, 8H), 8.12 (s, 8H), 12.83 (s, 4H) (Fig. S8). MALDI-TOF: m/z cal. d. 1399.5, found 1400.7 [M+H<sup>+</sup>] (Fig. S9).

### 2.2 Procedure for the cynthesis of silane (S) (Scheme S1) and TiO<sub>2</sub> (T).

### Synthesis of docosyltries oxysilane (S)

A solution of 1-docosene (0.5 g, 1.6 mmol) in THF 10 mL was reacted with triethoxysilane (1.46 g, 8.9 mmol) and a catalyst solution prepared by dissolving Karstedt's catalyst [0.1 mL, 15 mol%] in 1 mL m. xylene, and added to the reaction mixture, stirred at reflux temperature for 36 h in argon atmosphere. After completion of reaction the crude product obtained purified to get a pure liquid (colorless). Yield: 0.2 g, 26.1 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600MHz),  $\delta$  (ppm): 0.53 (m, 2 H), 0.79 (t, 3 H, J = 7.2 Hz), 1.14 (m, 47 H), 1.30 (m, 2 H), 3.72 (q, 6 H) (Fig. S10). <sup>13</sup>C NMR (CDCl<sub>3</sub>,

150MHz), δ (ppm): 9.36, 13.09, 17.27, 21.68, 21.74, 28.26, 28.35, 28.55, 28.69, 30.92, 32.19, 57.26 (Fig. S11). ESI-MS: m/z calcd. 472.4, found 473.4 [M+H<sup>+</sup>] (Fig. S12).

### Preparation and characterization of $TiO_2$ (T)

In a typical synthesis, 30 wt %, 0.5 mL of NH<sub>4</sub>OH solution and 1.0 mL of H<sub>2</sub>O were added into a combination of ethanol (150 mL) and acetonitrile (100 mL) under strong stirring. Then, 5 mL of titanium isopropoxide was quickly injected, and a milky suspension was formed within a few seconds, pH of the reaction mixture found to be in the range of around 7-8. After continuous stirring for 6 h at 200°C, the precipitate formed collected by considuration, washed with ethanol twice and dried at 60°C. The as-prepared TiO<sub>2</sub> confirme <sup>4</sup> further by XRD, and the material showed individual diffraction peaks at  $2\theta = 25.3$ , 37.9, 47.7 and 54.4° (Fig. S13).

### 2.3 Deposition process of TiO<sub>2</sub> in PET

A solution of  $TiO_2$  (**T**) was used to generate a transparent coating on the **F** by an ultrasonic assisted method (ultrasonic power and nequency were 100 W and 30 kHz). Then, the obtained sample exposed in ammonia vapor to neuralize the surface.

### 2.4 Deposition of porphyrin and silane in TiO<sub>2</sub> attached PET

Porphyrin is ultrasonically deposited (ultrasonic power and frequency were 100 W and 30 kHz) on the TiO<sub>2</sub>-coated fabric by preparing a solution  $(1x10^{-5} \text{ M})$  in DMF. The process carried out by soaking the TiO<sub>2</sub>-coated fabric and ultrasonicating for 30 minutes, washing with DMF and water to take out excess unbound porphyrin and dried. Finally, silane  $(1x10^{-5} \text{ M})$  in ethanol deposited to porphyrin/TiO<sub>2</sub> coated fabric by ultrasonicated for 30 minutes, dried at 100 °C for about 1 hour and then washed the fabric in excess ethanol to remove unbounded silane.

#### 2.5 Photocatalytic self-cleaning function of organic pollutants

NP, RB, EY, IN, BB and MB in chloroform or water  $(1.5 \times 10^{-3} \text{ M})$ , and this was then drop cast on surface modified fabric (**TP** and **TPS**) and dried for an hour in the dark to reach the adsorption-desorption equilibrium. The self-cleaning abilities of the modified fabric samples were determined by measuring the change in the intensity under visible light irradiation and confirmed by recording the UV-Vis absorption spectra at altered time intervals.

### 3. Results and discussion

#### **3.1** UV-Vis spectroscopy

Attachment of TiO<sub>2</sub>, silane and porphyrin to the fabric way confirmed by recorded the UV-Visible spectra of the samples. The surface modifications resulting in the **TP**, **TPS** fabrics are shown in Fig. 1B. No peaks were observed in the visible egion of the spectra of pristine fabric, which are shown in Fig. 1B (curve a). As shown in Fig. 1B (curve b), after attaching the porphyrin **P**, strong absorption peaks were observed at 505 nm, and these can be attributed to the Soret bands of porphyrin, and they are similar to the peaks of **P** observed at approximately 486 nm in DMF solutions. Two weaker bands observed at 656 and 764 nm for **P** and these correspond to the Q-band of purphyrin (Fig. 1A). These results clearly indicate the successful decoration of **P** on the surface of the fabric. The absorbance peaks of the soret bands of **P** showed a clear redshift by 19 nm after attachment to the fabric, shift caused due to the interactions of carboxylic acid group of the porphyrin and the TiO<sub>2</sub>. In addition, in the absorption spectra of **Si**-bound fabric, no new absorption peaks were observed beyond those of porphyrin **P**, but the intensities of the peaks from **P** were lower, as shown in Fig. 1B (curve c), which is due to the silane molecules screening or shielding the surface of TiO<sub>2</sub> and porphyrin coated in fabric.



Fig. 1. UV-Vis spectra of (A) P in DMF and (B) solid-state UV-Vis spectra of (a) PET, (b) PET@TP and (c) PET@TPS.

### 3.2 XRD analysis

The crystallinities of **PET**, **PET**@**TP** and **PET**@**TPS** fabrics measured by XRD, and the patterns shown in Fig. 2. Pristine fabric showed no characteristic peaks (Fig. 2 curve a). The fabric coated with TiO<sub>2</sub> showed diffraction peaks at  $2\theta$ =25.7, 38.0 47.9, 54.5 and 62.8 (Fig. 2

curve b) correspond to the lattice planes of  $(1 \ 0 \ 1)$ ,  $(0 \ 0 \ 4)$ ,  $(2 \ 0 \ 0)$ ,  $(2 \ 1 \ 1)$  and  $(2 \ 0 \ 4)$ , respectively, which is in good agreement with (JCPDS) data [no. 04-0783]. These results, indicates anatase TiO<sub>2</sub> nanoparticles form on the fabric surface. The XRD patterns of **PET@TP** was not significantly different from that of fabric coated with TiO<sub>2</sub>, which clearly indicates that after modification with **P**, the anatase TiO<sub>2</sub> reserved its crystallinity. Finally, the samples altered with silane attachment, **PET@TPS** retained the peak intensities of the TiO<sub>2</sub> on the fabric surface.



Fig. 2. XRD spectra of (a) PET, (b) PET@T, (c) PET@TP and (d) PET@TPS.

#### **3.3 SEM and EDX analysis**

SEM to investigate the structures and morphologies of the pristine and surface modified fabrics. As shown in Fig. 3(a), pristine fabric possesses a braided structure and has a thin, sheet-like morphology. After decoration with  $TiO_2$  nanoparticles, we observed that  $TiO_2$  particles with an average size of 200 nm uniformly and densely dispersed on the surface of the fabric, as shown in Fig. 3(b). For the **TP** samples, the size of the  $TiO_2$  particles increased, and some layered

structures were deposited on the surface of fabric. In addition, after the installation of **Si** on the surface of **TP** fabric, the  $TiO_2$  nanoparticles aggregated, which is similar to previous reports by our research group. Mapping study for **PET@TPS** has been done to confirm the presence of C, N, O, Si and Ti (Fig. 4). Furthermore, the EDX profiles confirm the presence of Ti and Si on the modified fabrics, as shown in Fig. S14.



Fig. 3. SEM images of (A) PET, (B) PET@T, (C) PET@TP and (D) PET@TPS.





### 3.4 XPS measurement

To investigate the chemical state of surface modifications on fabric, XPS measurement done. The survey spectrum (Fig. 5) shows that the materials was composed of C, O, N, Si and Ti, which supports the successful accoration of TiO<sub>2</sub>, porphyrin and Silane on the surface of fabric. The C1s peaks in the XPS spectra of **PET@TPS** (Fig. S15A) appear as two deconvoluted peaks at 285.4 and 286.3, which indicate more sp<sub>2</sub>-hybridized (C-O-C & C=O) linkages. The deconvoluted O1s peaks at 533.3, 532.6 and 531.7 were ascribed to the existence of C=O, C-O and Si-O, respectively (Fig. S15C) [42,43], in the skeleton. Moreover, the peak at 530.1 eV was from the presence of TiO<sub>2</sub> on the fabric. The N1s peaks of **PET@TPS** (Fig. S15B) appearing at 399.2 eV corresponded to the porphyrin ring of pyrrole-like nitrogen. The additional peak at 103.5 eV was attributed to the Si2p peak from the silicate (Si-O) network. The Ti2p signals

appeared as two peaks at 458.8 (Ti2p3/2) and 464.2 eV (Ti2p1/2), and the O1s peak at 530.0 eV was characteristic of TiO<sub>2</sub>.



Fig. 5. XPS survey spectra of PET @ TVS.

### 3.5 Water repelling measurement of modified fabric surface

The superhydrophobicity of he surface modified fabric has been investigated by WCA (water contact angle) measurements. Fig. 6 shows that the pure and clean pristine polyethylene



terephthalate surface has a WCA of 134°. Generally, surface of **PET** is intrinsically hydrophobic, but the water droplet was not simply roll off when the surface was sloped. To achieve this, the surface of fabric was modified with TiO<sub>2</sub>, and the WCA increased (138°), corresponding to greater hydrophobicity. For comparison, after modification with porphyrin, the WCA of the fabric surface was 0° (surface of fabric becomes hydrophilic) but showed superior photocatalytic activity due to the porphyrin attachment to the fabric surface. On the other hand, further modification with Silane on the surface of the **PET@TP** resulted in superhydrophobic or waterrepelling properties, and the WCA values were found to be 152°, respectively, which are higher than that of the pristine polyethylene terephthalate surface, is shown in Fig. 6.

Fig. 6. Water contact angles of (A) PET, (B) PET@T, (C) PET@TP and (D) PET@TPS.

### 3.6 Photo decomposition of organic pollutan'

The discoloration of organic pollutant and dy, molecules such as EY, NP, BB, RB and IN were examined by attaching each chemical separately to fabric and surface modified fabric **PET@TP** and irradiated in visible-light about 3 hand the results are shown as Fig. 7 indicating almost most of the pollutant undergoes discolaration except IN.



Fig. 7. Photocatalytic discoloration of organic pollutant by pristine and surface modified fabric.

### 3.7 Photocatalytic activity

The detoxification of organe pollutants is of great importance in the environment and beyond. In this regard, the self-clearing function through photodiscoloration activities of fabric surface modified with **T**, **TP** and **TPS** investigated with surface-adsorbed harmful MB. Under visiblelight irradiation, MB decomposition occurred in pristine fabric and modified fabric surfaces easily monitored visually, as shown in Fig. S16. In the absence of surface modifications, the fabric surface caused no obvious color changes. On the other hand, the intense color of the MB slowly faded in the surface modified fabric. These color changes and UV-DRS spectra simultaneously monitored as a function of time (Fig. 8). The decomposition efficiency was in the order **PET**@**TP** > **TPS** > **T**. The C/C<sub>0</sub> vs time plot displayed in Figure 9. A good linear correlation between  $\ln(C/C_0)$  and the reaction time t (99.9%) was obtained (Fig. S17). The rate constant, k, of the MB discoloration was derived from the following equation [44-46]:

$$-\ln C/C0 = kt(1)$$

Where k is the rate constant and t is the reaction time.  $C_0$  and C are the initial MB concentration and the concentration at time t, respectively. In comparing, the results obtained from the above study it is noted that **PET@TP** caused a significant enhancement in the photocatalytic performance, which can be attributed to the increased photocatalytic activity decreased because the silane-modified surface masks the surface of the TrC2, porphyrin-coated in fabric, and the surface becomes superhydrophobic. Therefore, the silane molecules functionalized fabric **PET@TPS** have dual self-cleaning effect.



**Fig. 8.** Solid-state UV-Vis spectra of the decomposition of MB under visible-light irradiation by (A) **PET** (B) **PET** (C) **PET** (TP and (D) **PET** (TPS.



**Fig. 9.** Plot of C/Co Vs Time for the decomposition of MB under visible-light irradiation before and after fabric surface-modification

### 3.8 TiO<sub>2</sub>/porphyrin stabilit / s. 'dy

To check the stability and reusability of  $TiO_2$ /porphyrin-modified fabric. In this case,  $TiO_2$  has good adhesive properties, calowing to easily binding with both fabric and the porphyrin derivatives. Therefore, to evaluate the stability of  $TiO_2$  and porphyrin-modified fabric before and after irradiation with visible light (Fig. S18), exposure to water, petroleum ether and washing with detergent, the UV-Vis spectra of the samples were acquired and are shown in Fig. S19. No obvious changes in the UV-Vis spectra of the Soret and the Q-bands of the porphyrin were observed. This result indicates that the fabric surface modified with  $TiO_2$  and porphyrin retained its stability and reusability, which can be attributed to the strong interactions between the carboxylate groups of the porphyrin and  $TiO_2$ .

### 3.9 Stability of the silane coating

To assess the stability of the superhydrophobic surfaces, we measured the WCA. Previously, we determined that the stability of **PET@TP** was due to the strong affinity of TiO<sub>2</sub> towards the carboxylate groups on the porphyrin. As shown in Fig. S20, the permanence of the silane on the surface evaluated by washing samples in three different media: detergent, petroleum ether and water. Even after five washing cycles, the WCAs decreased slightly from 152° to 150° for **PET@TPS** fabric sample. Furthermore, the photostability of the surface also measured before and after 24 h of irradiation with visible-light. No drastic decrease in the WCAs observed, as shown in Fig. S20. This result indicates that the water repelling properties and photo stability retained in silane-modified fabric.

### 3.10 Photo reduction mechanism

A possible mechanism for the decomposition of MB on the surface of fabric in visible-light radiation shown in figure 10. When the fabric irradiated by visible-light, the surface modified sample can be excited to generate holes and electrons. After the absorption of light by the porphyrin, the excited electrons migrate out of the ground state (HOMO orbital) over and done



with inter system crossing. These endied level electrons (in LUMO orbital) are readily transferred to the CB of the TiO<sub>2</sub>  $_1$   $_1$   $_7$ ,  $_4$ 8]. The modified surface then reacts with oxygen to yield active superoxide radicals and subsequent protonation provides HOO• radicals, which are competing through bank viec ron transfer towards the dye+• [42]. In the meantime, the surface modified with silane retained superhydrophobic even after irradiation, which is due to the destruction of OH• on the surface of the TiO<sub>2</sub> through dye sensitization, allowing it to retain its hydrophobicity.

**Fig. 10.** Plausible charge separation mechanism and its process for the self-cleaning function in modified fabric.

#### 3.11 Analysis of real samples

To evaluate the modified fabric surfaces for the photocatalytic self-cleaning activity and superhydrophobicity, real samples (coffee and oil stains) were tested, and the obtained results shown in Fig. 11. Coffee drops added to the surface of pristine sample and surface modified sample, and the reliability and practicality of the system verified. Under visible-light radiation, **PET@TP** surface reaches maximum decomposition at a different time than the other surfaces, which indicates that the surface has excellent photocatalytic activity, whereas the coffee droplets moved off from the silane attached fabrics **PET@TPS**, as shown in fig. 11A. On the other hand, these fabrics also tested for the decomposition of oil stains such as soy sauce. The oil present in the sauce easily adsorbed onto the surface of the fabrics, and the stains adsorbed on the modified fabrics generally degraded the stain in 6h (fig. 11B). The result obtained clearly indicates that before and after modification with silane, the fabrice surface has excellent photodecomposition ability and superhydrophobicity owing to uhe cellent self-cleaning material.



**Fig. 11.** Photocatalytic decomposition and superhydrophobicity of before and after surfacemodified fabric (A) coffee stain and (B) soy sauce.

### **3.12 Printing Application**

As a preliminary study, in the present work, we developed a single-component ink consisting of silane (0.5 g) in ethanol (10 mL) solution that is highly suitable for use as a digital printing ink, and the ink was injected into a cartridge [to facilitate visualization, dye ( $2.5 \times 10^{-3}$  M) was added to the Silane ink]. A Canon (MG2590) printer and cartridge (CL-946) used, and an image was printed on the TiO<sub>2</sub>/porphyrin-modified fabric, which is shown in fig. 12. The hydrophobicity of the printed image on the fabrics confirmed by water droplet testing, which involved placing water droplets on the image as well as on the non-printed area of the fabric. As predicted, the printed area is superhydrophobic with a WCA of 150°, and the rest of the fabric area is hydrophilic, shown in figure 12. Thus, the prepared ink can be utilized as a highly efficient printing material to make fabric surface superhydrophobic.

Solution





Water drop test



#### 4. Conclusions

A visible light active, superhydrophobic, self-cleaning fabric effectively established through surface modification by incorporating  $TiO_2$ , porphyrin and silane by ultrasonic method. The visible-light photocatalytic activity of the modified surface, the stability of the porphyrin and

silane on the surface and the overall self-cleaning efficiency discussed in detail. Self-cleaning abilities, based on the reproducible photodiscoloration of approximately 90% of MB, observed for the modified surface, a WCA of approximately 152° obtained for **PET@TPS**-coated surface, and the stability of the porphyrin and silane on TiO<sub>2</sub>-bearing fabric confirmed by washing the sample with aqueous and organic solvents and irradiating the sample under visible light. As a preliminary attempt, a single-component ink prepared using silane and used in digital printing, and the superhydrophobicity of the printed image on the fabric confirmed by water droplet testing. Thus, surface modification on fabric makes the materia. Lual-functioning self-cleaning effect.

### Acknowledgements

This work was supported by the industrial Findermental Technology Development Program (10076350) funded by the Ministry of Trade Industry and Energy (MOTIE) of Korea. This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) fundering die Ministry of Science, ICT and Future Planning (Grant No. NRF-2017R1E1A1A01074265).

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## **Credit Author Statement**

### Manuscript number: M'JL1 IQ\_2020\_5874

**Title:** Ultrasonic Assisted Fabrication of Dual Function Surface on PET and Preparation of Single Component Ink to Attain Efficient Self-Cleaning Function via Digital Printing **Journal:** Journal of Molecular Liquids

### Author contributions

**Ramalingam Manivannan:** Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing-Original Draft

Jiwon Ryu: Investigation, Formal analysis, Visualization

Young-A Son: Writing-Review & Editing, Supervision

## **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



# Highlights

• Dual function self-cleaning behavior attained in PET samples by surface modification via ultrasonic finishing method.

- Visible light responsive decomposition of different organic pollutants using TiO<sub>2</sub> and porphyrin.
- Single component ink prepared using silane and printed on surface modified fabric to attain superhydrophobic image.

Sumale