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Photostable Self-Cleaning Cotton by a Copper(II) Porphyrin/TiO_2 Visible-Light Photocatalytic System

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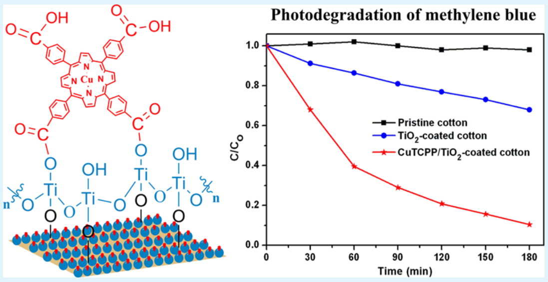
Supporting Information

ABSTRACT: Thin films of *meso*-tetra(4-carboxyphenyl)porphyrinato copper(II) (CuTCPP) in conjunction with anatase TiO_2 have been formed on cotton fabric. Their self-cleaning properties have been investigated by conducting photocatalytic degradation of methylene blue, coffee and wine stains under visible-light irradiation. CuTCPP/TiO_2-coated cotton fabrics showed superior self-cleaning performance when compared to bare TiO_2-coated cotton. Furthermore, CuTCPP/TiO_2-coated fabrics showed significant photostability under visible-light as compared to free base TCPP/TiO_2-coated fabrics. The fabrics were characterized by FESEM, XRD and UV−vis spectroscopy. An insight into the mechanistic aspects of the CuTCPP/TiO_2 photocatalysis is also discussed. Visible-light driven self-cleaning cotton based on copper(II) porphyrin/TiO_2 catalyst exhibits significant potential in terms of stability and reproducibility for self-cleaning applications.



KEYWORDS: *titania, porphyrin, visible-light, dye-sensitization, self-cleaning textiles, photocatalysis*

1. INTRODUCTION

Polycrystalline semiconductor oxides exhibiting specific physiochemical and optical properties are being employed in the field of photocatalysis. In 1972, Fujishima and Honda observed the photocatalytic properties of titanium dioxide in a UV-induced water splitting experiment using TiO_2 as a photoanode.[1] Since then, TiO_2 photocatalysis has been attractive in promising applications of solar energy conversion.[2−5] TiO_2 popularity is driven by its stability, nontoxicity, hydrophilicity, and cheap availability. Materials based on nanostructured TiO_2 have been extensively investigated in photocatalytic applications.[6] By applying TiO_2 in the form of coatings on various substrates, the concept of self-cleaning surface has been introduced in the past decade leading to the development of self-cleaning glasses, ceramics, tents, window blinds, and lamp covers.[7] TiO_2 can be immobilized on variety of substrates, such as glass, stainless steel, and activated carbon.[8] As most of these immobilization techniques required high temperature processing, application of TiO_2 to substrates of low thermal resistance, such as textiles, was limited.[9,10] However, with the development of a low-temperature sol-gol process using a nanotechnology approach, the growth of TiO_2 nanocrystals on organic fibres has been made possible in the past decade.

Anatase TiO_2-based self-cleaning textiles such as cotton, wool and polyester that show efficient photocatalytic properties under UV light have been developed.[11−13] However, the large band gap of TiO_2 (3.2 eV for anatase) requires an excitation wavelength that falls in the UV region. Since, the solar light reaching the earth consists of only 5% UV and almost 43% visible light, application of UV-based TiO_2 photocatalysis is limited. To utilize the visible region of the solar spectrum for catalysis, tailoring the optical properties of titania is therefore, indispensable. In this regard, TiO_2 can be modified by many methods; such as metal doping, nonmetal doping, ion-implantation, and surface sensitization by organic dyes.[14−18] However, very few visible-light driven self-cleaning textiles have been developed using metals and nonmetals.[19−22]

Porphyrins are considered as efficient sensitizers to harvest light on the surface of TiO_2 because they are structural analogues of chlorophyll in plant photosynthesis.[23] Because of an extensive system of delocalized π electrons, porphyrins have very strong absorption in the visible region.[24−26] In the photosensitization process, the sensitizer is excited over TiO_2 to appropriate singlet and triplet excited states. The excited state electrons are then injected to the conduction band of TiO_2. These electrons react with O_2 in the surrounding air to form superoxide radical anions ($O_2^{\bullet -}$), which can cause oxidation of organic impurities present on the surface of the catalyst.[27,28] Porphyrins have excellent photophysical properties such as; small singlet−triplet splitting, high quantum yield for intersystem crossing, and long triplet state lifetime.[29]

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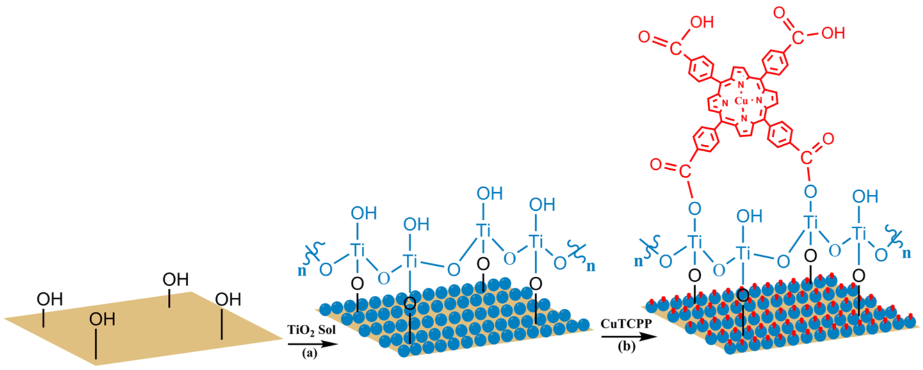
Scheme 1. Formation of Thin Films of CuTCPP on TiO_2-coated Cotton[a]



[a](a) Treatment of pristine cotton with TiO_2 colloid to form TiO_2 coating on cotton. (b) Treatment of TiO_2-coated cotton with CuTCPP solution in DMF to form CuTCPP/TiO_2-coated cotton.

The photophysical properties of porphyrins can be easily tuned by metal complexation, as they can readily coordinate with metal ions in the central cavity resulting in stronger and broader photoresponse in the visible region.[30,31] Furthermore, studies show that metal complexes of porphyrins are highly photostable, when adsorbed on the surface of TiO_2.[32] Recently, we have developed self-cleaning cotton based on *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP)-sensitized TiO_2 that showed superior self-cleaning properties under visible-light.[33] However, TCPP did not exhibit significant photostability for practical use. In view of self-cleaning applications envisaged, the stability of a photocatalyst is an important factor. Therefore, more photostable photocatalysts need to be explored.

Extending our research in this field, we have successfully prepared monolayers of *meso*-tetra(4-carboxyphenyl)porphyrinato copper(II) (CuTCPP) on TiO_2-coated cotton (Scheme 1) by a simple postadsorption method[33] that show excellent photocatalytic activity under visible-light irradiation as compared to bare TiO_2. Moreover, CuTCPP/TiO_2-coated cotton showed significant photostability under visible-light when compared to TCPP/TiO_2-coated cotton. We have particularly selected Cu in our study, as it has been reported to show efficient visible-light photocatalysis as compared to other metals, such as Zn, Fe, Ni and Co.[34−39] The self-cleaning properties of our CuTCPP/TiO_2-coated system have been investigated spectrophotometrically by the photocatalytic degradation of methylene blue (MB) under visible-light irradiation as well as in more practical situations of coffee and red wine stains.

2. EXPERIMENTAL SECTION

2.1. Synthesis of CuTCPP/TiO_2-Coated Cotton. *2.1.1. Synthesis of TiO_2-Sol.* Colloidal anatase TiO_2 was prepared by adding a solution of titanium tetraisopropoxide and acetic acid dropwise to acidified water using 1.4% HNO_3. The mixture was stirred at 60 °C for 16 h.[40]

2.1.2. Preparation of TiO_2-Coated Cotton. The TiO_2 sol was applied to scoured cotton fabric through a dip-pad-dry-cure process.[40] Cotton was scoured by a nonionic detergent (Kieralon F-OLB Conc) in order to remove impurities before application of TiO_2 sol. The scouring was carried at 80 °C for 30 min. The scoured cotton pieces were dipped in the TiO_2 sol for 1 min and then pressed in automatic horizontal press at 7.5 rpm with a nip pressure of 2.75 kg cm^{-2}. The pressed samples were then exposed to ammonia fumes until the surface pH reached 7. The neutralized samples were dried at 80 °C in a drying oven and cured at 120 °C for 3 min.

2.1.3. Synthesis of CuTCPP. Copper(II) complex of *meso*-tetra(4-carboxyphenyl)porphyrin was synthesized according to literature methods.[34] CuTCPP was synthesized by refluxing 0.33 mmol of TCPP with 1.82 mmol of $CuCl_2$ in DMF for 2 h. CuTCPP was precipitated by adding water in excess. DMF and water were removed from the precipitates by repeated centrifugation. Solid dry samples of CuTCPP were obtained by freeze-drying.

2.1.4. Preparation of CuTCPP/TiO_2-Coated Cotton. TiO_2-coated cotton samples were dipped in a CuTCPP solution in DMF and heated at 100 °C for 5 h. The samples were then washed with DMF to remove unbound CuTCPP.

2.2. Characterization. The surface morphology of the cotton samples was studied using field emission electron microscopy (JEOL 7001F FEGSEM). The crystallinity of TiO_2 films on cotton was determined by low angle X-ray diffraction (XRD, Philip 1140 diffractometer). The UV−vis absorption spectra of TCPP and CuTCPP in DMF were recorded on Cary 5000 spectrophotometer. The UV−vis absorption spectra of pristine cotton and cotton samples coated with TCPP, CuTCPP and TiO_2 were recorded using 110 mm integrating sphere on Cary 5000 spectrophotometer. The cotton samples were masked allowing only 2 × 2 mm area to be exposed to illumination by the light source.

2.3. Photocatalytic Studies. For the assessment of self-cleaning properties, photocatalytic degradation of methylene blue (MB) was evaluated quantitatively. CuTCPP/TiO_2, TCPP/TiO_2, TiO_2 and pristine cotton pieces (0.5 g, 1.5 × 1.5 cm) were immersed in Petri dishes containing acidified MB (10 mL, 15.6 μM, pH 1). The Petri dishes were placed in a light-box and irradiated by visible-light for 3 h using a fluorescent lamp (30 W, 5.02 mW cm^{-2} irradiance) containing a small UV content of 0.01 mW cm^{-2} irradiance (see the Supporting Information, Figure S1). During irradiation, the Petri dishes were shaken using a benchtop shaker. Prior to irradiation, the Petri dishes were kept in the dark for 30 min in order to attain adsorption−desorption equilibrium. The change in concentration of MB was monitored by measuring UV−vis spectra at different time intervals, during the course of irradiation.

For the degradation of coffee and red wine stains, whole cotton pieces (1.5 × 1.5 cm) coated with CuTCPP/TiO_2, TCPP/TiO_2, and pristine samples were stained with coffee (0.3 g/30 mL of hot water) and red wine, followed by air drying. Each cotton piece was stained with equal volume (100 μL) of coffee and red wine. The samples, with half of the area masked, were placed in visible-light box and irradiated for 36 h using fluorescent lamp (30W, 5.02 mW cm^{-2} irradiance).

2.4. Stability of Coating. The stability of CuTCPP/TiO_2-coated cotton samples was tested against detergent, petroleum ether and water, using a modified AATCC Test Method 190−2003.[41] The samples were washed with each solvent for 45 min at room temperature at a constant stirring of 200 rpm, followed by rinsing with water and air drying. To determine the amount of porphyrin retained on the cotton samples, UV−vis spectra of the samples were recorded before and after washing. For the photostability tests, CuTCPP/TiO_2-coated samples were irradiated under visible-light for

30 h using a fluorescent lamp (30 W, 5.02 mW cm^{-2} irradiance). UV–vis spectra of the samples were recorded before and after irradiation at different time intervals.

3. RESULTS AND DISCUSSIONS

3.1. SEM Analysis. The surface morphology of pristine cotton and cotton samples coated with TiO_2 and CuTCPP were identified from the SEM images illustrated in Figure.1.

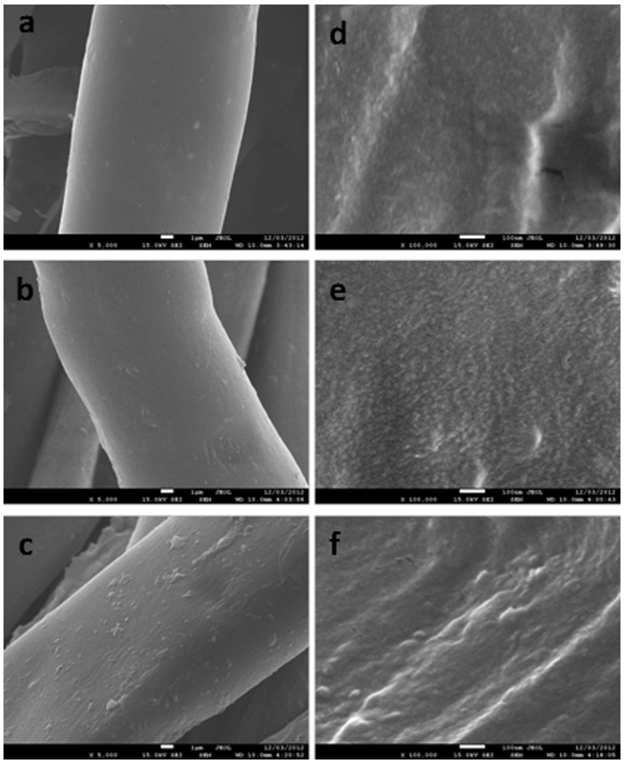


Figure 1. FESEM images of (a, d) pristine cotton, (b, e) TiO_2-coated cotton, (c, f) CuTCPP/TiO_2-coated cotton.

Low magnification images (Figure 1a, b and c) reveal no major change in surface morphology of cotton after coating with TiO_2 and CuTCPP, retaining the integrity of fibres. At higher magnification (Figure 1d–f), cotton samples coated with TiO_2 and CuTCPP appear to have rougher surface as compared to pristine cotton, presumably as a result of the coating process. Furthermore, surface aggregates can be observed in CuTCPP/TiO_2-coated sample.

3.2. XRD Analysis. To study the crystallinity of titania nanoparticles deposited on the cotton fabric, XRD analysis was performed. Anatase TiO_2 has characteristic diffraction peaks at 2θ = 25.4, 38.0, and 48.0°, all of which are observed in the TiO_2-coated and CuTCPP/TiO_2-coated samples (Figure 2b and c). As expected, the pristine sample shows the absence of these peaks (Figure 2a). The presence of anatase peaks in CuTCPP/TiO_2-coated samples indicates that the TiO_2 has retained its crystallinity (and hence reactivity) after adsorption of CuTCPP.

3.3. UV–Vis Spectroscopy. Figure 3 shows the UV–vis absorption spectra of CuTCPP and TCPP adsorbed on TiO_2-coated samples. For comparison, UV–vis spectra of pristine cotton and TiO_2-coated samples were also recorded. Visible-light absorption of porphyrins between 400 to 700 nm can be easily observed for CuTCPP/TiO_2 and TCPP/TiO_2 samples

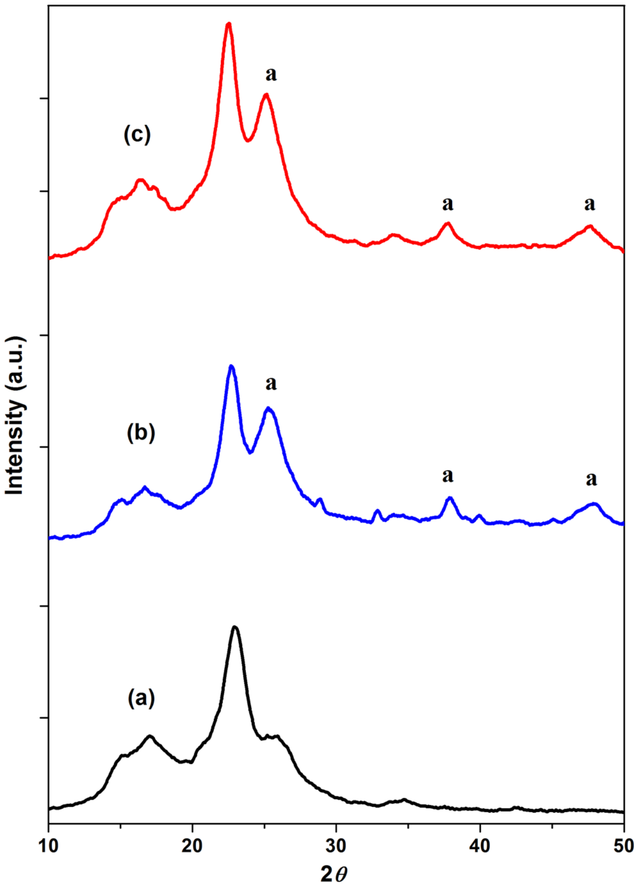


Figure 2. XRD spectra of cotton: (a) pristine, (b) TiO_2-coated, (c) CuTCPP/TiO_2-coated (a, anatase).

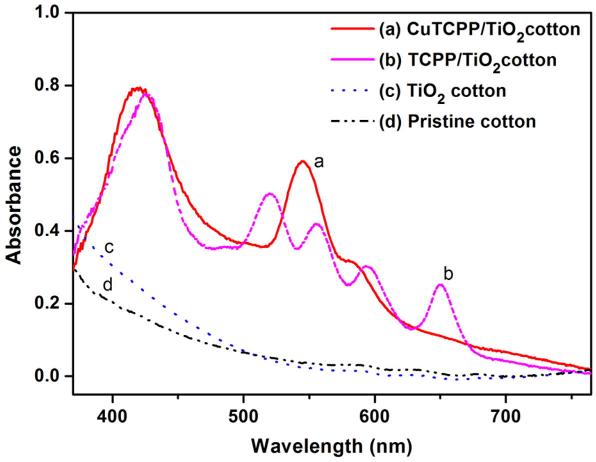


Figure 3. UV–vis spectra of (a) CuTCPP/TiO_2-coated cotton, (b) TCPP/TiO_2-coated cotton, (c) TiO_2-coated cotton, (d) pristine cotton.

(Figure 3a, b), and as expected no characteristic absorption from TiO_2-coated cotton and pristine samples was observed in this range (Figure 3c, d). The absorption spectrum of CuTCPP/TiO_2-coated cotton shows a strong peak at 419 nm identified as the porphyrin Soret band (Figure 3a). A slight red shift of 3 nm is observed for CuTCPP adsorbed on TiO_2-coated sample as compared to its absorption in DMF at 416 nm (see the Supporting Information, Figure S2). Similarly, the absorption spectrum of TCPP in DMF shows a strong peak at

418 nm for Soret band, whereas in TiO_2-coated cotton the absorption is shifted by 9 to 427 nm (see the Supporting Information, Figure S3). This red shift can be attributed to the interaction between the carboxylate groups of porphyrins and TiO_2.[34,42]

The absorption peaks in the 500−690 nm region correspond to the Q bands of porphyrin. For TCPP, four absorption peaks of Q bands can be observed at 520, 556, 594, and 650 nm. For CuTCPP, only two Q-band absorption peaks can be observed at 545 and 583 nm. However, in the presence of DMF, some of these peaks are quenched because of interaction of porphyrins with polar solvent.[43] Furthermore, a significant broadening of the Soret band peaks can also be observed in the absorption spectra of CuTCPP and TCPP adsorbed on cotton as compared to the absorption spectra in DMF. The peak broadening is a usual phenomenon observed for porphyrins incorporated on solid substrates, possibly due to dye aggregation.[44,45]

3.4. Photocatalytic Degradation of Methylene Blue (MB). Cotton samples coated with CuTCPP/TiO_2 and TCPP/TiO_2 were subjected to quantitative analysis through the photocatalytic degradation of MB under visible-light irradiation. Figure 4 shows a plot of normalized concentration of MB (C/C_0) against time. The change in concentration of MB was monitored by recording the UV−vis spectra at different time intervals. For comparison, blank MB solution and pristine cotton sample were also studied. The plateaued line obtained for pristine sample and blank MB solution indicates the absence of any photocatalytic activity by cotton itself and the stability of MB at these conditions (Figure 4a, b).

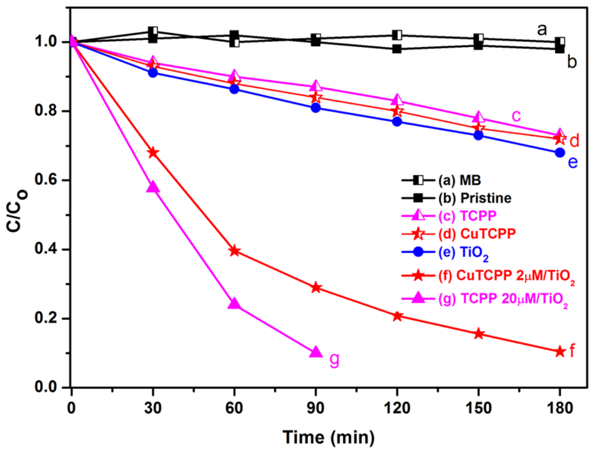


Figure 4. Degradation of MB (10 mL, 15.6 μM, pH 1) under visible-light irradiation (5.02 mW cm^{-2} irradiance) for 180 min: (a) blank MB solution, (b) pristine cotton, (c) TCPP-coated cotton, (d) CuTCPP-coated cotton, (e) TiO_2-coated cotton, (f) 2 μM CuTCPP/TiO_2-coated cotton, (g) 20 μM TCPP/TiO_2-coated cotton.

TiO_2-coated sample showed a 32% degradation of MB after 180 min, whereas, the samples coated with TCPP and CuTCPP in the absence of TiO_2 also showed some photocatalytic activity with 27% and 28% degradation of MB, respectively (Figure 4c−e). Porphyrins have been reported to exhibit photocatalytic properties on their own.[31] The samples coated with CuTCPP/TiO_2 and TCPP/TiO_2 showed a significant increase in photoactivity (Figure 4f, g). CuTCPP/TiO_2-coated samples showed almost complete degradation of MB (99%) within 180 min, whereas the TCPP/TiO_2-coated sample showed complete degradation of MB within 90 min. Thus, the degradation rate of MB for TCPP is twice as fast as that of CuTCPP.

To achieve an efficient photocatalysis, an optimum amount of the photosensitizing dye with minimum aggregation and enhanced electron injection into TiO_2 is required.[46] Therefore, cotton samples were prepared from three different concentrations of CuTCPP (1, 2, and 3 μM) and assessed for self-cleaning performance (see the Supporting Information, Figure S4). The optimized concentration showing the highest photocatalytic efficiency for CuTCPP is 2 μM. For TCPP, the optimized concentration was 20 μM, established from our previous work illustrating a compromise between amount of material and activity.[33]

3.5. Photocatalytic Degradation of Coffee and Red Wine Stains. The self-cleaning property of CuTCPP/TiO_2-coated samples was assessed qualitatively by performing the coffee and red wine stains bleaching tests. For comparison TCPP/TiO_2, TiO_2 and pristine samples were used. Figure 5 shows the degradation of coffee and wine stains on cotton samples under visible light irradiation at different time intervals. Only half the area of each cotton fabric square was irradiated,

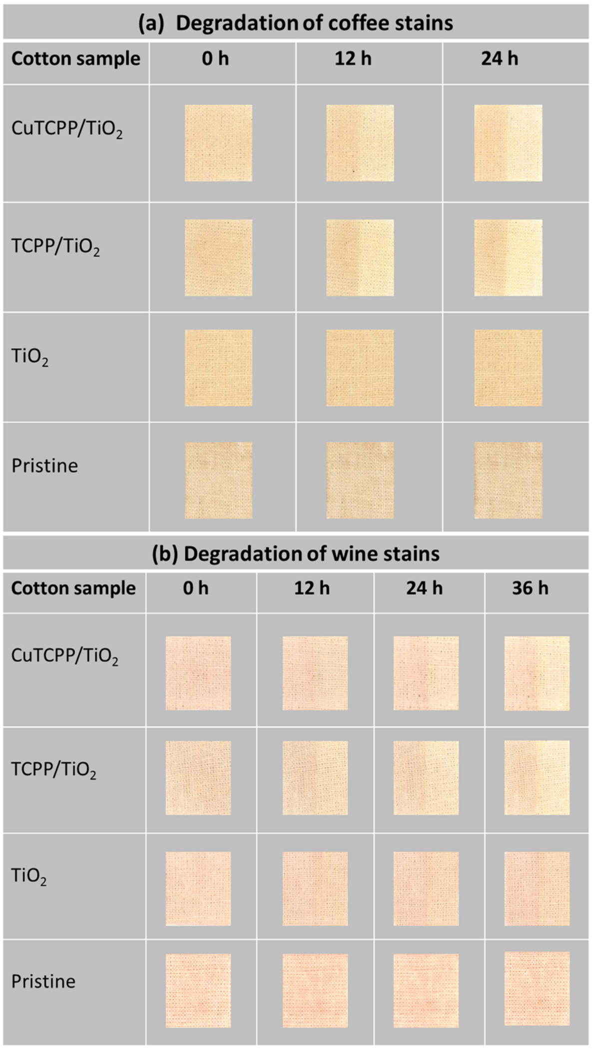


Figure 5. Photocatalytic degradation of (a) coffee stains, (b) red wine stains, by CuTCPP/TiO_2, TCPP/TiO_2, TiO_2, and pristine cotton samples at 0, 12, and 24 h of visible-light irradiation (5.02 mW cm^{-2} irradiance).

whereas the other half was masked receiving no light. Significant discolouration of coffee stains was observed for TCPP and CuTCPP samples after 24 h of irradiation (Figure 5a). However, the degradation rate of TCPP appears faster compared to that of CuTCPP. Similarly, the same trend is observed for the degradation of wine stains over 36 h of irradiation (Figure 5b).

3.6. Photostability of CuTCPP/TiO$_2$ Catalyst. Photostability of the catalyst under excitation is an important requirement of reusability and practical application. Therefore, a photostability study of CuTCPP/TiO$_2$-coated samples was conducted against the well-performing TCPP. CuTCPP/TiO$_2$-coated sample was irradiated in visible-light for 30 h. The change in concentration of CuTCPP was measured by recording the UV−vis spectra of cotton samples before and after irradiation (Figure 6a). A slight degradation of 5% was observed for CuTCPP within the first 12 h (see the Supporting Information, Figure S5). In the following 18 h, there was no further degradation of CuTCPP, shown in the UV−vis data. The absorption peak at 419 nm (Soret band) was used as a reference to monitor the change in concentration of CuTCPP. Figure 6b shows the concentration of CuTCPP and TCPP retained on the fabric after 30 h of irradiation. Thus, CuTCPP showed significant photostability with only 5% degradation as compared to the TCPP with 78% degradation under visible-light irradiation, established from previous results.[33] Furthermore, the irradiated CuTCPP/TiO$_2$-coated sample was assessed for self-cleaning performance. A reproducible degradation (99%) of MB was observed for the sample with 95% CuTCPP retention.

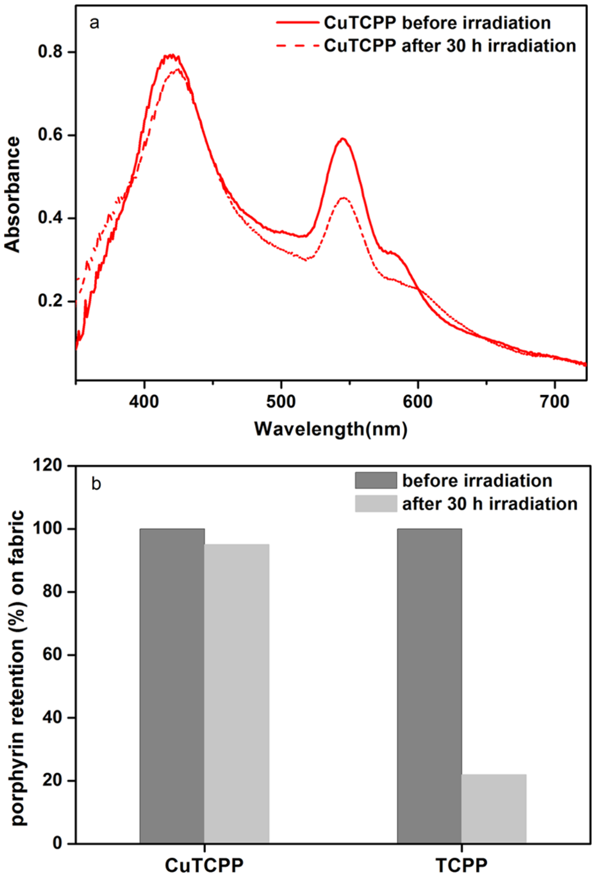


Figure 6. (a) UV−vis spectra of CuTCPP/TiO$_2$-coated cotton fabrics before and after 30 h irradiation. (b) Percentage retention of CuTCPP and TCPP on TiO$_2$-coated cotton fabrics after irradiation under visible light for 30 h.

3.7. Stability of CuTCPP/TiO$_2$-Coating. TiO$_2$ has already been reported in literature to show strong affinity toward cotton.[40] The stability of CuTCPP adsorbed on TiO$_2$-coated sample was tested by washing the samples in three different media; detergent, petroleum ether and water (Figure 7). The change in CuTCPP concentration was observed by recording the UV−vis spectra before and after washing (Supporting Information, Figure S6). All the samples washed in different solvents showed over 90% CuTCPP retention on the fabric. However, the highest dye leaching was observed for CuTCPP washed with petroleum ether, which could be due the weak interactions between carboxylate groups of dye and TiO$_2$, affected by the change in the polarity of medium.

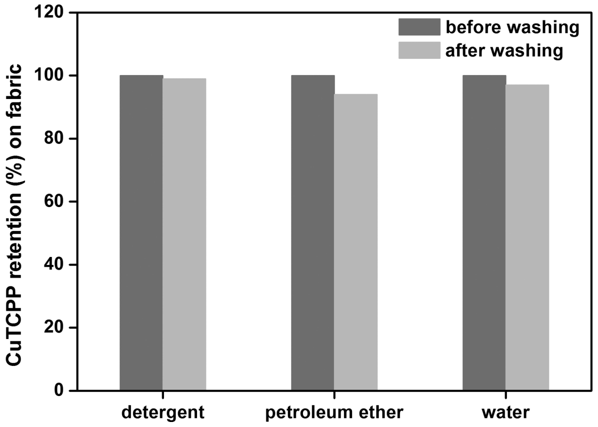


Figure 7. Percentage retention of CuTCPP on cotton fabrics after washing with detergent, petroleum ether, and water.

CuTCPP samples washed with different solvents were also analyzed for self-cleaning performance. All the washed samples showed reproducible degradation (99%) of MB in 180 min under visible-light irradiation. Thus, no change in photocatalytic activity was observed even after washing. In spite of the slight dye leaching in petroleum ether, the dye concentration retained on the fabric was sufficient enough to allow photocatalysis at the same rate as that of prewashed original CuTCPP samples.

3.8. Mechanistic Aspects. The mechanism of TiO$_2$ sensitization by dyes in visible-light, generally involves the transition of electron from the ground state of porphyrin dye [Pp] to the excited singlet state ^{1}[Pp]*.[47] 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 TiO$_2$, which can be trapped further by the adsorbed O$_2$, resulting in formation of O$_2^{\bullet -}$ causing degradation of MB present on the surface of TiO$_2$ (Figure 8).

Free-base porphyrins such as TCPP with no unpaired electrons manifest long lifetime of excited state and are strongly fluorescent,[48] resulting in efficient electron injection in conduction band of TiO$_2$, confirmed by our previous findings.[33] In contrast, metal porphyrins with unpaired electrons in *d* orbital such as Cu(II)TCPP exhibit short lifetime of excited state, as no fluorescence emission has been detected for copper porphyrins in solution,[45] resulting in poor electron injection into TiO$_2$. This can be accounted for the slower degradation

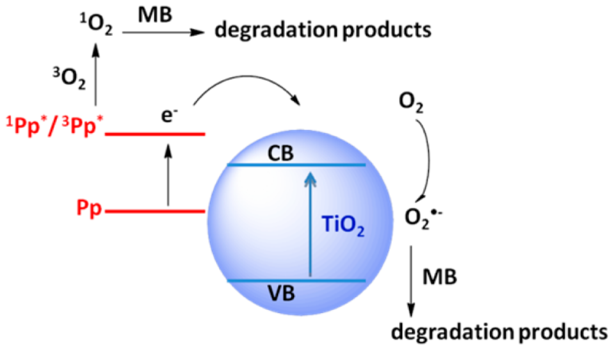


Figure 8. Proposed photocatalytic mechanism.

rate of MB in CuTCPP as compared to TCPP. Furthermore, formation of singlet oxygen ($^1O_2$) from ^{3}[Pp]* excited state of the sensitizer dye is also reported, which can cause oxidation of MB as well.[49] This is confirmed by our findings, as some photocatalytic activity is also observed for CuTCPP and TCPP cotton samples in the absence of TiO_2. Thus, overall, a co-operative mechanism is proposed for the degradation of MB involving both components of photocatalytic system.

The enhanced photostability of Cu(II)TCPP as compared to TCPP might be related to the paramagnetic nature of Cu in Cu(II)TCPP, which favors deactivation of its excited state, resulting in more recombination with no fluorescence emission and thus making Cu(II)TCPP less susceptible to photobleach.[50]

4. CONCLUSIONS

Visible-light active self-cleaning cotton has successfully been developed using copper(II) porphyrin and anatase titania. CuTCPP/TiO_2-coated cotton has shown considerable photoactivity in the degradation of methylene blue, coffee and red wine stains. In addition, CuTCPP exhibits significant photostability as compared to TCPP. The enhanced photostability of CuTCPP shows potential in view of reproducibility and practical application of self-cleaning textiles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Results of UV−vis spectroscopy for analysis of effect of concentration of dye on photocatalysis, analysis of photostability of catalyst and stability of coating. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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