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SELF-CLEANING TiO_2-SiO_2 CLUSTERS ON COTTON TEXTILE PREPARED BY DIP-SPIN COATING PROCESS

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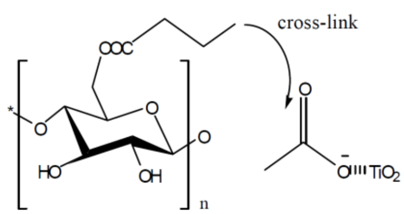
Graphical abstract



Cross-linking of cellulose with TiO_2

Abstract

Titanium-silica (TiO_2-SiO_2), a type of semiconductor metal oxide cluster compound, has been widely used as oxidative catalysts and dye agents. In this research, TiO_2-SiO_2 on cotton textile has been utilized as self-cleaning agents by cross linking with acrylic acid compound. The clusters of TiO_2-SiO_2 was modified by a series of Ti:Si molar compositions, i.e. 1:1; 2:1 and 1:2. The successful modification of the cotton textile's fiber surface was confirmed with an increase in mass. The FTIR spectra displayed an intense peak at 1700 cm^{-1}, indicating the presence of carboxyl functional groups for both the coated cottons with and without TiO_2-SiO_2 coating. SEM-EDX characterization showed that the TiO_2-SiO_2 clusters was homogeneously distributed on the cotton. The self-cleaning performance of TiO_2-SiO_2 coated cotton textile was evaluated in the degradation of methylene blue (MB) dye and examined with UV light (120 min). Results showed that TiO_2-SiO_2 coated cotton with Ti:Si molar ratio of 1:2, which was prepared by dip-spin coating in acrylic acid with 24 h of soaking time, achieved the best self-cleaning effect in the degradation of methylene blue.

Keywords: Self-cleaning, methylene blue, dip-spin coating

1.0 INTRODUCTION

Titanium dioxide (TiO_2) is the most well-known photocatalyst targeting the degradation of organic compounds under UV-Vis irradiation. The use of TiO_2 as photocatalyst has many economic benefits, such as its non-toxicity, active after the absorption of UV, biologically and chemically inert, and environmentally-friendly [1]. Among the properties of TiO_2 that affects its photocatalytic activity are the structure, size of crystal, porosity, and the surface area [2, 3]. In order to increase its photocatalytic activity, surface modification of TiO_2 by doping with silica (SiO_2) compound (TiO_2-SiO_2), chitosan and surfactant has been extensively carried out [4, 5]. Modifications have also been carried out in order to design highly crystalline, anatase-based, nano-sized, larger surface area and higher porosity TiO_2-SiO_2 [6]. The structure and properties are strongly related to the performances of the photocatalysts in electron-hole recombination, which produces radical species. These radical species can be strongly oxidative to some organic compounds, such as dyes, pesticides and microorganisms [7, 8].

This strategy has been adopted to modify the surface of cotton fiber as the self-cleaning textile by coating the photocatalytic nanoparticles, such as TiO_2, ZnO and modified TiO_2 [9]. In order to allow strong interaction between the nanoparticles and the fiber's surface, several researches carried out modifications by chemical interaction. One example is the modification of the cotton fiber by carboxylic acid, which promotes adhesion of TiO_2 nanoparticles to cotton textile's fiber [9, 10].

By coating TiO_2-SiO_2 clusters on textile fiber, the hydrophilicity of the textile fiber can be induced and multi-functionalized textile products with several properties such as: anti-microbe textile [9-12], anti-wrinkle [13], UV protection [14, 15] and self-cleaning textile [16-23] can also be obtained. Multi-functionalized textile has its benefits in terms of the economical values and practicality to the consumers [21]. It was reported that anti-bacterial textile can be designed by TiO_2 coating [24, 25]. It was demonstrated that by coating cotton and wool's surface with TiO_2-SiO_2, the textile could be used for self-cleaning purposes [26, 27]. A layer of TiO_2-SiO_2 loaded on the cotton textile showed its ability to degrade wine spot [28]. In this study, preparation of self-cleaning textile modified with TiO_2-SiO_2 clusters layer by chitosan was carried and the modified textile was used to degrade synthetic methylene blue dye. The relationship between the self-cleaning ability and the molar ratio of Ti and Si in influencing the morphology of cotton fiber was also explored. Apart from that, the advantages of using dip-spin coating on cotton textile will also be shown, as this method is not only simpler, but a more evenly distributed coating was also achieved.

2.0 EXPERIMENTAL

2.1 Materials

The materials used in this study were silky cotton textile (100 % cotton), hydrochloric acid (HCl), acetic acid (CH_3COOH), dietanol amine ($C_4H_{11}NO_2$), isopropanol (C_3H_8O), tetra ethyl orthosilicate ($C_8H_{20}O_4Si$), acrylic acid ($CH_2CHCOOH$), sodium lauryl sulfate surfactant (SLS, $C_{12}H_{25}OSO_3Na$), methylene blue dye ($C_{16}H_{18}ClN_3S$) (Merck), aquadest, titanium isopropoxide ($C_{12}H_{28}O_4Ti$, Aldrich 97%) and commercial chitosan ($(C_6H_{11}NO_4)_n$).

2.2 Instrumentation

Glasswares, magnetic stirrer, furnace, oven, analytical measure, spin coating machine, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (Hitachi S-3400N), Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific, Nicoleti S10).

2.3 Synthesis of TiO_2-SiO_2 Clusters with Chitosan as Template

TiO_2-SiO_2 powder with different Ti:Si molar ratios (1:1; 2:1 and 1:2) was synthesized by sol-gel method. The precursor was titanium isopropoxide as the TiO_2 source and tetra ethyl orthosilicate as the SiO_2 source. Both precursors were mixed homogeneously for 8 h to form a stable gel in isopropanol as the solvent and dietanol amine (DEA) as the sol stabilizer. Chitosan in 5% acetic acid, as the dispersion agent and porous printing template, was added to the earlier mixture. Then, incubation done at 110 °C for 15 min for gel formation. Finally, calcination at 500 °C for 3 h was carried out in order to form TiO_2-SiO_2 powder.

2.4 The Dipping of Cotton textile Fiber into Acrylic Acid Binder

Cotton textile (8x8 cm^2) was washed with detergent (2 g/L), rinsed with aquadest and then dried at 80 °C for 5 min. The cotton textile was then dipped into an acrylic acid binder and dried at 80 °C for 5 min.

2.5 TiO_2-SiO_2 Clusters Layer on the Cotton textile Fiber by Dip-Spin Coating

TiO_2-SiO_2 suspension, which consisted of 1 % (w/v) TiO_2-SiO_2 powder and 1 % (w/v) SLS surfactant, was dispersed in isopropanol (total volume of 5 mL). The cotton textile (8x8 cm) was dipped into the TiO_2-SiO_2 suspension prepared and the coating process was continued by using spin-coating machine at the speed of 2500 rpm for 90 min in order to ensure the TiO_2-SiO_2 suspension is well-distributed on the textile's surface. The resulting coated cotton textile was dried at 80 °C for 5 min. This process was repeated for 2–3 times for both of the surfaces. Non-coated cotton textile was used as the control.

2.6 The Measurement of Textile Mass to the Number of Coated TiO_2-SiO_2 Clusters

The resulting mass of the coated TiO_2-SiO_2 clusters on cotton fiber was determined by measuring the mass of the textile after drying in oven. This measurement was carried out twice.

2.7 Self-Cleaning Characterization of Cotton textile Fiber

2.7.1 Qualitative Measurement

The qualitative measurement of the self-cleaning agent was done by observing the ability of the modified cotton textile (3x3 cm^2) to degrade 75 µL of methylene blue spot (15 ppm) under UV light (536 Lux) for 0–24 h with 30 min of interval time.

2.7.2 Quantitative Measurement

The quantitative measurement of the self-cleaning function was done by checking the ability of the cotton textile to degrade 20 mL of 15 ppm methylene blue spot in the 1x1 cm^2 cotton textile. The cotton with the methylene blue spot was then put under UV light (536 Lux) for 2 h. After 30 min of incubation, the methylene blue solution was measured by UV-Vis spectrophotometer and taken down as the initial absorption (A_0). The measurement was done every 2 h of UV irradiation (A).

$$\text{Percentage of degradation} = \frac{\text{A}}{\text{Ao}} \text{ x } 100\ \%$$

2.3 Characterization

The non-coated and coated cotton textile were analyzed by Fourier transform infrared (FTIR) spectroscopy FTIR in the range of wavelength 4000-500 cm^{-1} with 4 cm^{-1} resolution at room temperature, in order to determine their functional groups. The morphology of the samples was examined by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), in order to observe the difference between the non-coated textile fiber and those after being treated by TiO_2-SiO_2 clusters.

3.0 RESULTS AND DISCUSSION

3.1 The Formation of Cross-linked TiO_2-SiO_2 Clusters on Cotton Textile Fiber

In order to strongly attach the TiO_2-SiO_2 clusters on the textile fiber, the use of a cross linking agent is needed. In this research, the cross linking agent used was acrylic acid, which consists of one carboxylic group. TiO_2-SiO_2 coating on the surface of cotton textile will occur only if there are some kind of bonding between the carboxylic group and the cotton fiber in the form of ester covalent bonding [10]. It has been evaluated that the optimum time needed to synergize cross linking agent in TiO_2-SiO_2 coating dipped into the acrylic acid was 24 h. From the weight measurement of the textile, significant mass difference was acquired after 24 h and 90 min of dipping (Figure 1). The textile mass gain can be taken as an indicator of the coating process. Different molar ration of Ti and Si will give different adhesion properties of clusters to be coated on the textile. The duration of dipping can increase the covalent interaction of the carboxylic group from the binder and the hydroxyl groups of cellulose fiber [9].

3.2 Functional Groups

FTIR spectra can be used to show the chemical interaction that occurred in the fiber of the cotton textile after being coated with TiO_2-SiO_2 clusters. Figure 2 shows that the fiber of the cellulose polymer of the cotton textile (Figure 2a) underwent changes after dipping in the cross-linking agent (Figure 2b) and followed by modification with TiO2-SiO2 clusters (Figure 2c). Through the FTIR spectra, it can be confirmed that there was some chemical interaction between the cellulose hydroxyl group and carboxylic group from the acrylic acid binder. These interaction can be shown by the increasing intensity of the C=O stretching group at 1700 cm^{-1}. The presence of C=O group in the cotton textile fiber led to the successful interaction with TiO_2-SiO_2. After the coating of TiO_2-SiO_2, the peak intensity of C=O stretching decreased, which is an indicator that the coating of TiO_2-SiO_2 has taken place. Similar observation has been reported previously [28], which stated that in order to layer the surface of cotton textile with TiO_2, the properties of the cotton's surface would need to be modified by a cross-linking agent as a binder compound, to allow electrostatic interaction. The dipping of cotton textile in acrylic acid resulted in negative charges on the surface of the cotton textile, which then promotes interaction with TiO_2 particles. The spectrum in Figure 2c shows a peak at 1400 cm^{-1}, which corresponds to the Ti-O-Ti bond [29] and this peak was not observed in the non-coated cotton.

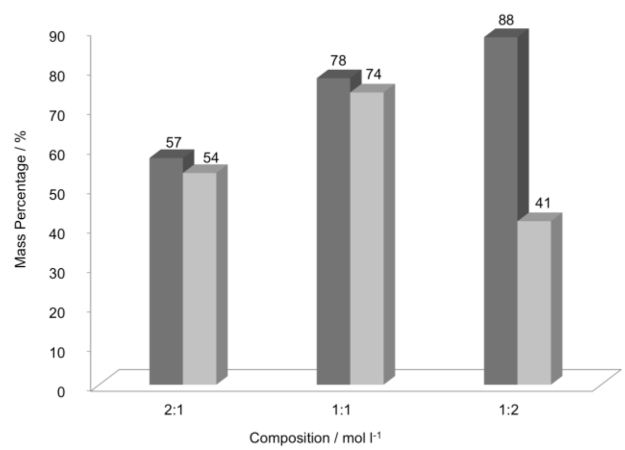


Figure 1 The mass of the cotton textile coated with TiO_2-SiO_2 with different Ti:Si molar compositions; 2:1, 1:1 and 1:2, dip-spin coating duration of: 90 minutes and 24 hours

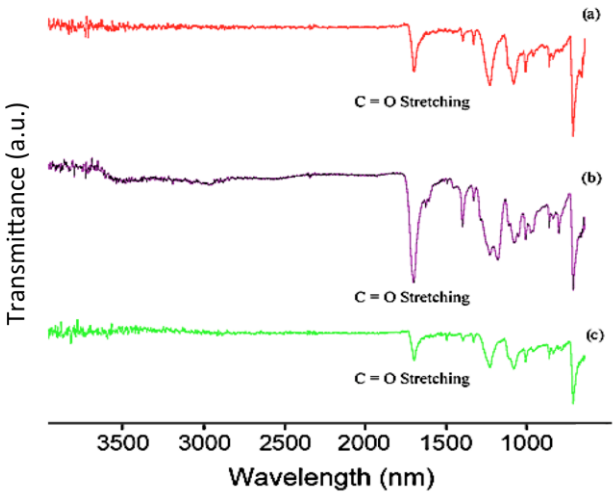


Figure 2 FTIR spectra of the cotton textile: (a) non-coated, (b) cotton dipped in acrylic acid for 24 h and (c) coated cotton dipped in acrylic acid for 24 h and after dip-spin process with TiO_2-SiO_2 for 90 min

3.3 Morphology of the Cotton Textile

SEM images can provide information on the morphology of the cotton textile which has been coated by TiO_2-SiO_2 clusters, while EDX analysis can enhance the SEM information by qualitatively showing the composition percentage of the substances. Figure 3a shows the SEM image of the cotton fiber without any treatment, which shows the fiber was wrapped by pectin and wax, the rough fiber surface. Figure 3b shows the fiber surface of cotton textile after dipping with acrylic acid for 24 h. The surface of the cotton textile was smoother because the pectin has been dissolved in acrylic acid. Figures 3c and d are the SEM images of the cotton textile coated with TiO_2-SiO_2, with 24 h of dipping time in acrylic acid, followed by TiO_2-SiO_2 coating on the cotton fiber textile. Although the particles are not well-distributed, less agglomeration can be seen, as compared Figures 3e and f, which shows the morphology of the cotton textile coated with TiO_2-SiO_2 by 90 min of dipping.

Well-distributed TiO_2-SiO_2 particles on the surface of the cotton textile is expected to enhance the self-cleaning ability of the cotton textile. A good coating process can correlated with the percentage of textile mass gain. It can be concluded that the TiO_2-SiO_2 coating in cotton fiber depends on the duration of the dipping process in acrylic acid [12]. The results show that a good coating and well-distributed particles were achieved after dipping in acrylic acid for 24 h, as compared to the dipping duration of 90 min. The influence of TiO_2-SiO_2 composition to the coating process on the surface of the cotton textile is shown in Figure 4.

EDX analysis is able to semi-quantitatively detect the substances in the cotton fiber and the results are given in Table 1 and shown in Figure 5. EDX analysis showed that it is identified that after modification, cotton fiber consists of C, H, O, Ti and Si. The amount of Ti and Si measured by EDX is found to be in correspondent with the molar composition added.

3.4 The Self-Cleaning Performance of the Cotton Textile Fiber

The self-cleaning ability of the cotton fiber after being coated with TiO_2-SiO_2 clusters was tested out in the photodegradation of methylene blue dye irradiated under UV light. The selection of UV light was based on the measurement of TiO_2-SiO_2 clusters absorbance, which is shown in Figure 6. The maximum absorbance at 368 nm showed that the energy gap of TiO_2-SiO_2, has the same or higher energy than UV light. If UV light with λ_{max} of 365 nm was used as the irradiation source for self-cleaning purposes, the degradation percentage of methylene blue would be optimum. Self-cleaning photocatalytic performance in the degradation of methylene blue by cotton fiber coated with TiO_2-SiO_2 clusters by higher energy than the energy band (3.2 eV) will result in electron excitation from the valence band, forming an electron-hole pair (e^- h^+). This will then produce oxidative free radicals, which play an important role in the photocatalytic decomposition of organic dye [30].

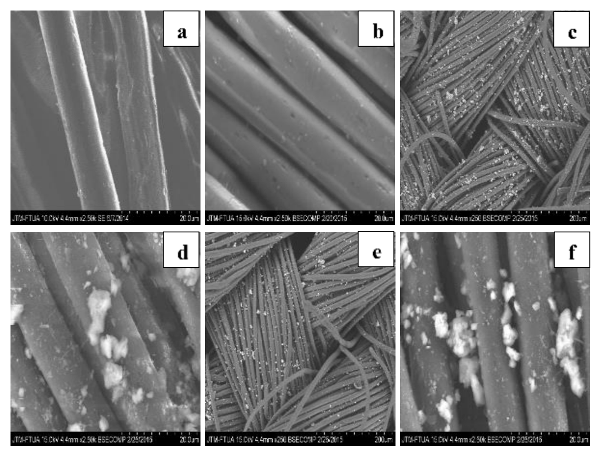


Figure 3 The SEM images of (a) cotton textile; (b) cotton textile dipped in acrylic acid for 24 h; (c) and (d) cotton textile coated by 1:2 TiO_2-SiO_2 with 24 h dipping of acrylic acid; (e) and (f) cotton textile coated with 1:2 TiO_2-SiO_2 with 90 min dipping of acrylic acid

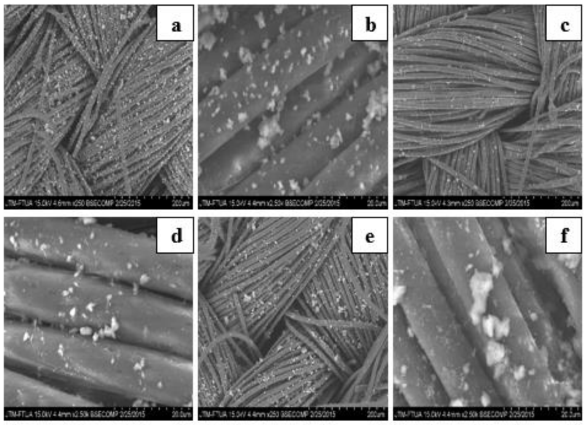


Figure 4 The SEM images of the cotton textile coated with TiO_2-SiO_2 with Ti:Si molar composition of (a) and (b) 2:1; (c) and (d) 1:1; (e) and (f) 1:2.

3.5 Qualitative Self-Cleaning Testing of Cotton Fiber

The qualitative self-cleaning test was done by observing the blue color of the dye during UV irradiation at 368 nm is shown at Figure 7. The pure cotton before being modified by TiO_2-SiO_2 clusters was more hydrophobic, due to the cellulose fiber being wrapped by pectin and wax.

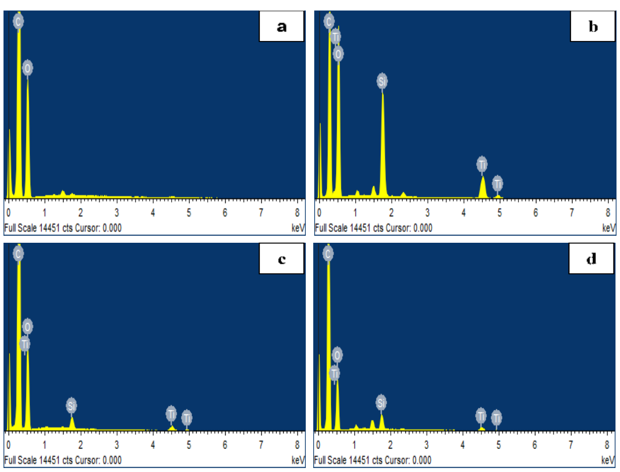


Figure 5 EDX patterns of (a) cotton textile without any coating; cotton textile coated with TiO_2-SiO_2 with Ti:Si molar ratio of (b) 1:2; (c) 1:1and (d) 1:2

Table 1 The elemental composition percentage in cotton coated by TiO_2-SiO_2 clusters

Code	Type of textile	Composition (%)			
		Ti	Si	C	O
A	Non-coated coton	-	-	63,7	36,2
B	Cotton coated by TiO_2-SiO_2 (1:1)	0.84	1.19	70.1	27.9
C	Cotton coated by TiO_2-SiO_2 (2:1)	1.17	0.73	74.6	23.5
D	Cotton coated by TiO_2-SiO_2 (1:2)	0.82	1.82	66.6	30.8
E	Cotton coated by TiO_2	3.61	-	60.1	36.3
F	Cotton coated by SiO_2	-	-	64.5	35.5

When methylene blue was dropped onto the cotton fiber, it was difficult for adsorption and liquid spreading on the surface to occur, which resulted in only a small spot (Figure 7 (a)). The coating of only TiO_2 on the textile fiber also showed hydrophobic properties, where the spot did not spread on the fiber's surface (Figure 7 (b)). However, the cotton fiber which was coated with SiO_2 showed hydrophilic properties, as the pores of SiO_2 may cause increase in the sorption capacity (Figure 7 (c)). When the cotton fiber was coated with TiO_2-SiO_2 clusters (Figure 7 (d)–(f)), the cotton's surface became hydrophilic and a wider spot was created by the drop of methylene blue [31]. The combination of TiO_2 and SiO_2 is able to raise the hydrophilic properties, mainly due to the presence of SiO_2. The sorption and self-cleaning ability of cotton fiber after being coated with TiO_2-SiO_2 was influenced by the Si molar composition over Ti [12]. The presence of SiO_2 is able to broaden the surface area of TiO_2 and increase the acidity of cotton's side surface as a medium of the optimum methylene blue sorption in the cotton fiber. If a higher amount of methylene blue is adsorbed on the surface of the cotton, the photocatalytic degradation of methylene blue by TiO_2 would also increase. SiO_2 also functions in assisting the well spot spreading of the dye, as it is easy to degrade than agglomerated spots. Based on observation (Figure 7), higher self-cleaning efficiency was achieved when the molar number of Si is higher than that of Ti (Ti:Si molar ratio of 1:2) (Figure 7f).

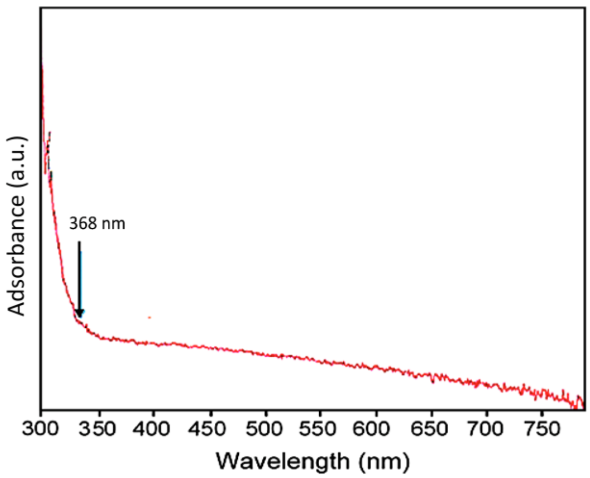


Figure 6 UV-Vis spectrum of TiO_2-SiO_2 (Ti:Si molar ratio of 2:1)

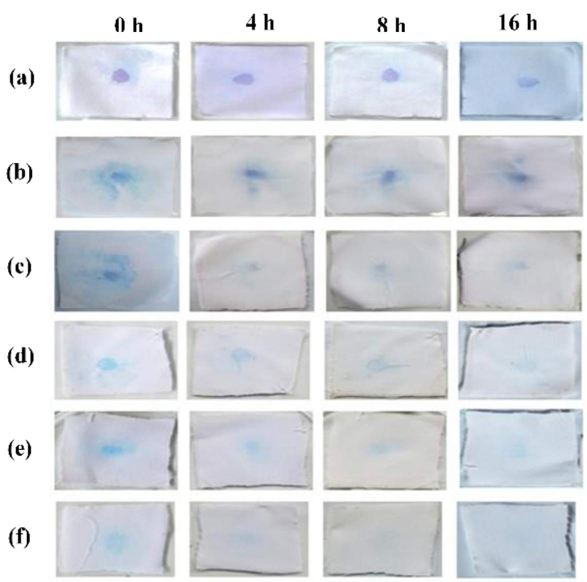


Figure 7 The degradation of methylene blue spot in cotton textile by dipping in acrylic acid for 24 h on (a) non-coated cotton; (b) cotton coated with TiO_2; (c) cotton coated with SiO_2; (d) cotton coated with TiO_2-SiO_2 (1:1); (e) cotton coated with TiO_2-SiO_2 (2:1) and (f) cotton coated with TiO_2-SiO_2 (1:2)

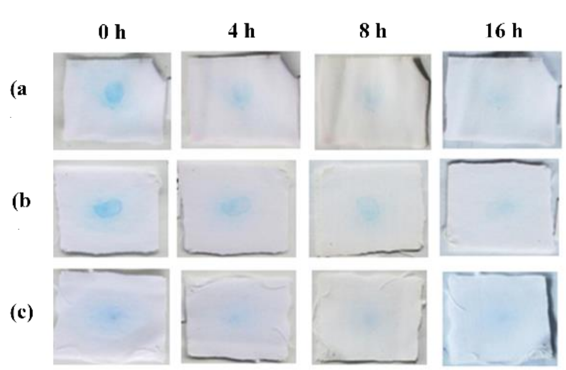


Figure 8 The degradation pattern of methylene blue spot on cotton textile coated by TiO_2-SiO_2 after being dipped in acrylic acid for 90 min: (a) Ti:Si molar ratio of 1:1; (b) Ti:Si molar ratio of 2:1 and (c) Ti:Si molar ratio of 1:2.

The self-cleaning ability of cotton textile is also influenced by the dipping duration in acrylic acid, as shown in Fig. 8. The dipping duration in acrylic acid of 24 h was chosen as the optimum time to create interactions between the carboxyl group and TiO_2-SiO_2 clusters, so as to increase the amount of TiO_2-SiO_2 that can be deposited on the textile fiber. Sample which was coated with TiO_2-SiO_2 with Ti:Si molar ratio of 1:1 different dipping duration showed different results. Cotton textile which was prepared by soaking in acrylic acid for 24 h (Fig. 7) gave a faster degradation of methylene blue to cotton textile that was soaked for a shorter time (Figure 8).

3.6 Quantitative Self-Cleaning Testing of Cotton Fiber

Quantitative self-cleaning testing of the cotton coated with TiO_2-SiO_2 was observed based on the decrease of methylene blue absorption, which can be seen from the UV-Vis spectra at 661 nm. The methylene blue degradation was calculated from the A/A_0 ratio.

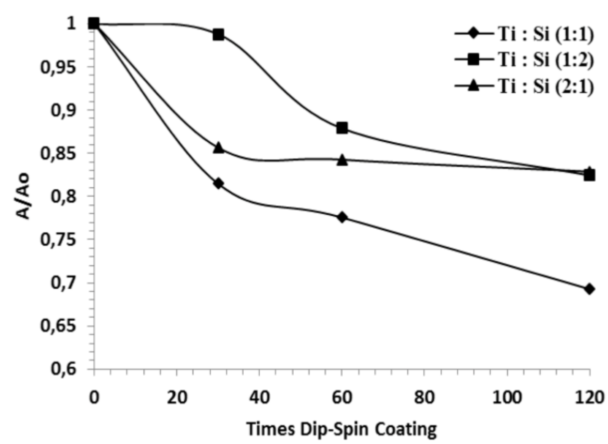


Figure 9 The degradation pattern of methylene blue on cotton fibers coated with different Ti:Si molar ratio under UV irradiation at λ_{max}= 661 nm

The self-cleaning ability of TiO_2-SiO_2 coated on the cotton textile was observed by comparing the absorption after the homogenization of methylene blue in the dark for 30 min, followed by the absorption of methylene blue under UV irradiation for 0–120 min, as shown in Figure 10. Curve a shows the absorption pattern of methylene blue (15 ppm), which was used as the control.

The absorption pattern of methylene blue on cotton textile which was coated with TiO_2-SiO_2 (different Ti:Si molar ratios) after UV irradiation for 120 min is also shown in Figure 10. It is shown that the crease in absorbance was the most obvious when cotton textile coated with TiO_2-SiO_2 with the Ti:Si molar ratio of 1:2 was used. This shows that in order to achieve good self-cleaning abilities under UV irradiation, the role of SiO_2 was greater as compared to TiO_2. The absorption area on the surface of the cotton textile promoted by SiO_2 plays a more important role as it allows easier absorption and spreading of methylene blue, before being photocatalytically degraded by TiO_2.

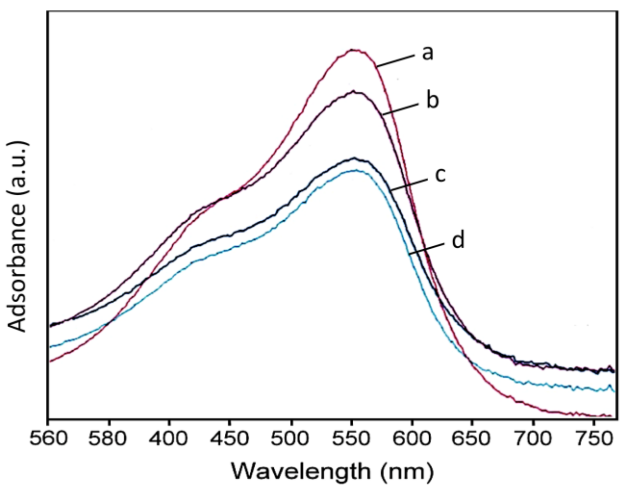


Figure 10 Absorbance pattern of methylene blue: (a) after homogenization in the dark (blank); after photodegradation on cotton coated with TiO_2-SiO_2 with Ti:Si molar ratio of (b) 2:1; (c) 1:1 and (d)1:2

4.0 CONCLUSION

Self-cleaning cotton textile has been successfully prepared by interaction with acrylic acid binder as cross link agent for 24 h, followed by spin-dip coating with TiO_2-SiO_2 clusters. The successful coating of TiO_2-SiO_2 was shown by the mass gain of the textile and further proven by the FTIR spectra and SEM-EDX analysis. From the results of the methylene blue degradation under UV irradiation, it was shown that the best self-cleaning effect was shown by the cotton textile coated with TiO_2-SiO_2 with Ti:Si molar ratio of 1:2.

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