A Facile Approach for Fabrication Superhydrophobic and UV-blocking Cotton Fabrics with Self-cleaning Properties

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Abstract: A facile method to fabricate UV blocking superhydrophobic cotton fabric based on the deposition of TiO_2 sol followed by surface modification with stearic acid is presented here. TiO_2 and STA-TiO_2 coated cotton fabrics were characterised by scanning electron microscopy, X-ray diffraction studies and X-ray photoelectron spectroscopy. The UV transmittance spectral studies showed that the STA-TiO_2 coated cotton had excellent UV blocking property in both UV-A and UV-B regions and in fact the hydrophobicity did not affect the UV blocking property of TiO_2 coated cotton. Moreover, the STA-TiO_2 coated cotton fabric had outstanding self-cleaning property which can be effectively used for oil-water separation studies. Further, the modified cotton exhibited excellent chemical durability and mechanical stability. Hence, this work can be exploited for industrial applications for the fabrication of textiles with superhydrophobic, UV blocking and self-cleaning characteristics.

Keywords: TiO_2 sol, Superhydrophobic, UV-blocking property, Self-cleaning, Oil-water separation

Introduction

Due to its high breathability, comfortness, flexibility, high moisture absorbance and softness, cotton is widely used as a textile fabric in all climatic conditions [1,2]. However, the cotton surface has high water absorbances due to presence of more number or hydroxyl groups on its surface. Because of this high absorbance nature, it get stained easily [3]. Therefore, functionalisation of cotton fabric with special properties such as superhydrophobicity [4], flame-retardancy [5], UV shielding property [6], electrical conductivity [7] and self-cleaning property [1] increases its usages in both industrial and day-to-day applications.

The domain of superhydrophobic textiles has gained more interest in recent years due to the demand for functional and comfortable textiles [8]. Many researchers and Scientists have taken efforts to fabricate textiles with super anti-wetting property [9]. It is well known that creation of micro-/ nano roughness and low energy coatings over solid surfaces are the main criteria for the creation of unique super wetting property over any kind of solid surfaces [9,10]. In superhydrophobic conditions, a water droplet placed on the solid surface, attains spherical shape and easily rolls on the solid surface even under slight vibrations. This phenomenon is observed in lotus leaf and it is literally called as Lotus Leaf effect [11,12]. By mimicking this lotus leaf effect, the super anti-wetting textiles can be prepared by covering the textile fibers with inorganic nanoparticles such as CuO, ZnO, Ag and SiO_2 [13] followed by hydrophobization. Number of traditional methods are available for the fabrication of super anti-wetting textiles which includes sol-gel process, electrospinning method, dip-coating, chemical/ physical vapour deposition, hydrothermal method, atomic layer deposition and plasma etching processing [14]. But most of the above processes are encountered with several problems such as long-time reaction, expensive equipments, tedious fabrication processes, complicated procedures and usage of highly corrosive solvents in some cases [1]. Therefore, the fabrication of super-antiwetting textiles with high stability and durability by using a simple method of preparation is the need of the hour.

Ultraviolet radiation (UV), can be subdivided into three major divisions such as UV-A (320-400 nm), UV-B (290-320 nm) and UV-C (100-290 nm). The rays of wavelengths from UV-A and UV-B may cause some acute and chronic changes in skin which includes erythema and photoaging. Continuous exposure of sunlight to skin can induce more phototoxic and photoallergic reactions which may develop into even some melanomas or carcinomas on skin [15,16]. Hence, protection from UV through clothing becomes a necessary requirement to protect us from UV rays. In general, there are two major categories in UV absorbers viz., organic absorbers and inorganic absorbers. Benzophenone and most of all-natural dyes come under the category of organic absorbers while semiconductor metal oxides such as ZnO, SiO_2 and TiO_2 etc. act as inorganic UV absorbers [15]. Among these inorganic absorbers, TiO_2 has high UV shielding capacity with high photostability, eco-friendly nature, safety and cost-effectiveness. Moreover, TiO_2 can be used as photocatalyst for the degradation of organic pollutants [17,18] and also used as photochemical biosensor [19]. They also possess good flame-retardancy, antibacterial activity and self-cleaning properties [20,21]. In addition to this, TiO_2 also imparts high dual-size roughness to the pristine cotton and the hydrophobization of TiO_2 surface is also a fairly easy task. Thus, production of cotton fabric with multifunctional properties assumes significance in view of the applications.

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In this study, we report a facile method for the fabrication of cotton textile with bifunctional property such as superhydrophobicity and UV radiation protection by coating TiO_2 sol over cotton and subsequent surface modification with long chain fatty acids.

Experimental

Materials

Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) and stearic acid ($CH_3(CH_2)_{16}COOH$) were purchased from Sigma-Aldrich. Nitric acid (HNO_3) was purchased from Nice Chemicals (P) Ltd., India. The cotton fabric used in this study was purchased from the nearby market. All chemicals used in this study were of analytical grade and used without any further purification.

Fabrication of UV Resistant Superhydrophobic Cotton
Preparation of TiO_2 Sol

TiO_2 required for this study was synthesised by adding a solution (5 m*l*) of titanium isopropoxide into the reaction mixture containing 80 m*l* of water, 20 m*l* of ethanol, 20 m*l* of acetic acid and 1 m*l* of 2.5 % HNO_3 in a dropwise manner with vigorous stirring. This reaction mixture was heated at 60 °C for 16 h to complete the hydrolysis reaction. The obtained sol was collected and stored in an air-tight container.

Treatment of Cotton Fabric with TiO_2 Sol

Dip coating method was used for the fabrication of UV retardant super antiwetting cotton fabric. For the deposition of TiO_2 sol over cotton surface, first the cotton fabrics was thoroughly washed using copious amounts of water followed by 0.1 N NaOH in order to remove any wax over cotton fabric. The cleaned cotton fabric (2 cm×2 cm) was immersed in the TiO_2 sol for about 60 min. Then the samples were taken out and washed twice with distilled water. Finally, the TiO_2 coated cotton was dried at 120 °C in a hot air oven for further treatment processes.

Hydrophobization of Treated Fabric

For hydrophobization process, TiO_2 coated cotton was immersed in 0.1 % of ethanolic stearic acid (STA) for about 24 h in air-tight condition. Subsequently, the cotton fabric was washed with ethanol and distilled water, and the samples were allowed to dry for 12 h at room temperature and then, cured for 60 min at 80 °C.

Characterisation
Surface Characterisation Methods

The structure and surface morphology of treated samples were investigated using VEGA3-TESCAN scanning electron microscopy (SEM). The crystal phase of deposited TiO_2 films over cotton fabric was studied using XPERT-PRO X-ray diffractometer (XRD). Energy dispersive X-ray spectroscopy (EDX) (Bruker, Nano GMBH X' Flash Detector, 5010 model, Germany) was used to find the chemical elements present on the cotton surface. The chemical composition of elements present on the cotton surface was confirmed using X-ray photo electron spectroscopy (XPS) with an AES Module with Ar ions as well as C60 sputter guns (PHI 5000 Versa Probe II, FEI Inc.).

Wettability and UV Protection Characterisation

The surface wettability of the as-treated cotton samples was assessed by water contact angle measurements (WCA) [22]. Static water contact angle measurements of as-coated samples were recorded using contact angle goniometer (ramé-Hart Instrument Co., USA). Distilled water droplets with volume of approximately 10 μ*l* were carefully dispensed onto the cotton surface through syringe in room temperature. The WCA were captured after placement of droplets for about 30 sec using digital camera. To obtain the WCA, five separate measurements were taken, and the average results were considered for this study.

The UV protection ability of untreated and treated cotton samples were measured using UV-Vis-NIR Spectrometer (ocean optics, USA), and the spectra were recorded ranging from 280-700 nm.

Self-cleaning and Oil-water Separation Studies

Superhydrophobic textiles with self-cleaning property have gained considerable attention because of their unique properties. To assess the self-cleaning properties of superhydrophobic cotton fabric, the treated and untreated cotton (5 cm×2 cm) were glued with glass slide and contaminated with dirt particles. In our study, methylene blue dye was used as contaminant [1]. The water droplets were placed over the contaminated cotton fabrics to study the roll-off property of treated and untreated cotton samples. The roll-off property of water droplets and self-cleaning ability of the cotton surface were captured using digital camera.

The superhydrophobicity and superoleophilicity of as-coated cotton were very useful for oil-water separation studies [23,24]. To study the oil-water separation property of as-prepared samples, equal volume of kerosene and water mixture were taken. This agitated mixture was poured through substrate. The water separation efficiency of the superhydrophobic cotton was assessed manually by capturing using digital camera.

Durability Studies

The evaluation of the durability of superhydrophobic surface is very much essential for practical applications as the superhydrophobic surfaces lose their superhydrophobicity when exposed to harsh conditions [25].

The chemical durability, washing durability and mechanical stability of the as-coated samples were analysed as follows:

i) Chemical durability: The chemical durability of the as-prepared cotton sample was studied by free immersion of cotton samples in solutions of different pH such as 1, 5, 7, 9 and 14 for about 48 h at room temperature. Then the samples were taken out, dried and WCA angles were measured for

dried cotton samples [1].

ii) Washing durability: For assessing the washing durability of coated cotton samples, the specimens were washed with detergent and water for 60 min at room temperature with continuous stirring at a speed of 900 rpm. The WCA was measured for each washing cycle [26].

iii) Mechanical stability: The mechanical stability of superhydrophobic cotton was assessed by the abrasion test. For this test, sandpaper was used as an abrasion source and, the as-prepared cotton was rubbed with sandpaper under 100 g of weight with an abrasion length of 15 cm. The mechanical stability was evaluated by measuring the WCA after each abrasion cycles [7].

Results and Discussion

Surface Characterisation Studies

It is already known that micro-/nano roughness and low
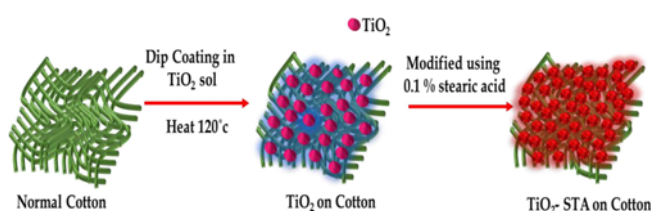
Figure 1. Schematic representation for fabrication of UV resistant and superhydrophobic cotton.

surface energy are crucial factors to fabricate superhydrophobic surfaces [27]. In this work, the micro-/nano roughness on cotton surface was created by the deposition of TiO_2 over cotton by dip coating, followed by heating. Then the surface was further modified with stearic acid to achieve low surface energy (Figure 1). Due to the ion-dipole and surface interactions, the coatings were firmly adhered over cotton fabric [28]. The surface morphological changes occurred during modification were assessed by following methods.

SEM Analysis

The successful deposition of TiO_2, stearic acid and the difference in surface between coated and uncoated cotton surface have been assessed using SEM images. Figure 2 displays the surface morphology of pristine, TiO_2 coated and superhydrophobic cotton surface. The Figure 2(a) showed the smooth longitudinal fibril surface and the woven structure of uncoated cotton. The uniform layer deposition of TiO_2 sol over cotton fabric was confirmed from low and high magnification of TiO_2 coated cotton (Figure 2(b) and 2(c)). When the surface was modified with stearic acid, the changes occurred in the surface morphology of superhydrophobic cotton which could be observed in Figure 2d and 2e. The images showed that stearic acid modified superhydrophobic cotton surface became even more rougher than TiO_2 coated cotton surface.

EDX Analysis

The chemical elements present on the cotton surface were confirmed by EDX studies. Figure 3(a) showed the EDX
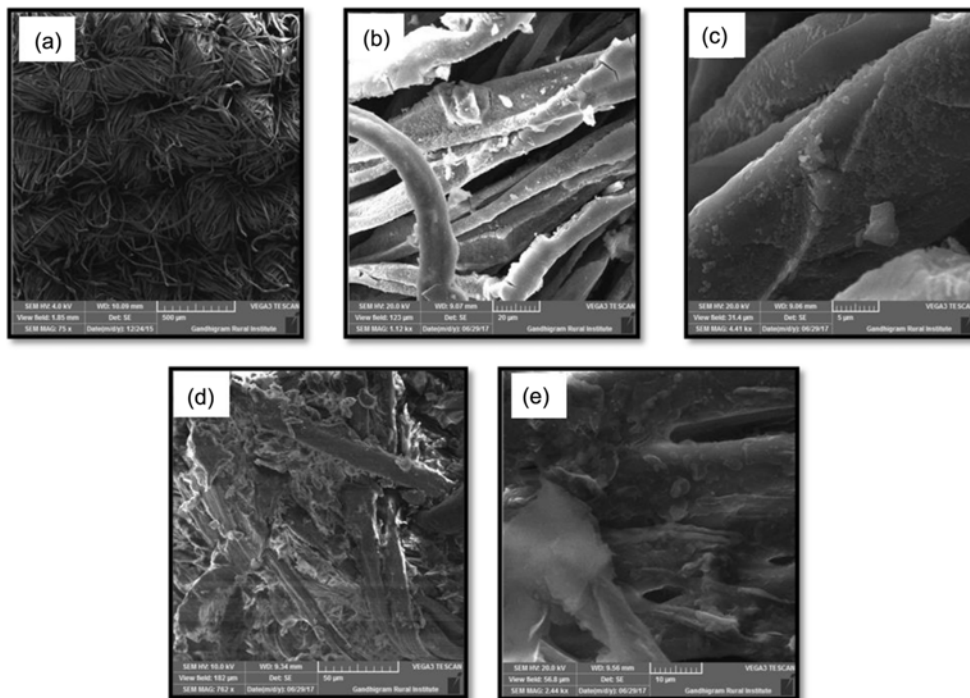

Figure 2. SEM images of (a) normal, (b, c) high and low magnification images of TiO_2 coated cotton, and (d, e) high and low magnification images of STA-TiO_2 coated cotton.
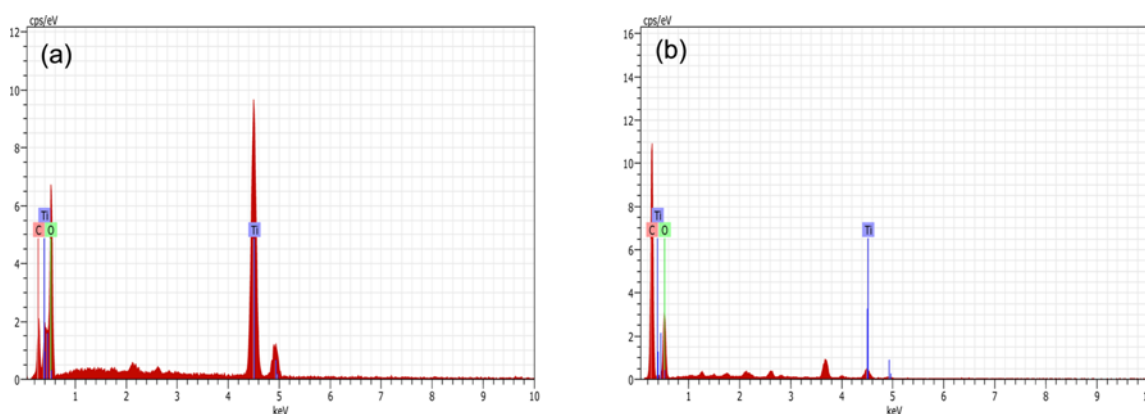
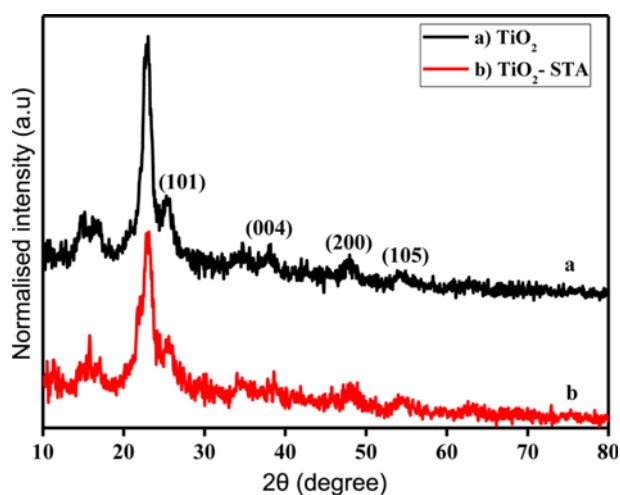**Figure 3.** EDX spectra of (a) TiO_2 coated and (b) STA-TiO_2 coated cotton.

Figure 4. XRD spectra of (a) TiO_2 coated and (b) STA-TiO_2 coated cotton.

spectrum of TiO_2 coated cotton. In this spectrum, the peaks corresponding to Ti and O confirmed the successful deposition of TiO_2 over normal cotton. The increased intensity of C in superhydrophobic cotton confirmed the hydrophobization of TiO_2 coated cotton with stearic acid (Figure 3(b)).

XRD Analysis

The crystalline nature of TiO_2 sol over coated surface was confirmed using X-ray diffraction (XRD) analysis. In Figure 4, the characteristic peak of cotton fabric could be seen at 23° in the case of both TiO_2-coated and STA-TiO_2 coated cotton surfaces [29]. The characteristic peaks at $2\theta = 25.3^\circ$, 38.1°, 48.0° and 54.1° correspond to (101), (004), (200) and (105) anatase phase of TiO_2 (Figure 4(a)) [26]. After deposition of stearic acid over TiO_2, no change was observed in the crystalline phase of anatase TiO_2 (Figure 4(b)). These results clearly confirmed the deposition of stearic acid over TiO_2 which showed that superhydrophobicity could be imparted without causing any affect to the crystalline phase of TiO_2.

XPS Analysis

To determine the chemical composition of TiO_2 over cotton surface, XPS analysis was performed. In the wide scan spectrum of TiO_2 coated cotton (Figure 5(a)), the peaks at 284.9, 532.0 and 456.4 eV correspond to C 1s, O 1s and Ti 2p which confirmed the deposition of TiO_2 over cotton. The Ti 2p spectrum showed the characteristic peaks at 459.1 eV (Ti $2p_{3/2}$) and 464.9 eV (Ti $2p_{1/2}$) with spin orbit separation of 5.8 eV which confirmed the presence of Ti^{4+} from anatase of TiO_2 (Figure 5(b)) [2]. Thus, XPS results strongly confirmed the deposition of anatase TiO_2 over cotton surface.

Wettability and UV Protection Measurement
WCA Measurements

The WCA measurements are used to assess the surface wettability of solid surfaces. Due to the presence of abundant hydroxyl groups, cotton is endowed with the moisture regain capacity [7]. The pristine cotton was quickly wetted by water with the WCA of 0° (superhydrophilic). During TiO_2 sol deposition, TiO_2 layers create rough film over cotton, which transform the superhydrophilic surface of cotton into hydrophobic surface. and the TiO_2 coated cotton showed the WCA of 89°. However, after deposition of stearic acid over TiO_2 coated cotton, the surface became much rougher and more emerged as the superhydrophobic with the WCA of 154.3°. The WCA for coated and uncoated cotton samples are shown in Figure 6.

UV Protection Measurements

The UV transmission through coated cotton samples was measured by UV transmittance spectra measured in the ultraviolet range of 280-400 nm and the results are shown in the Figure 7. It is already known that normal cotton has poor UV-blocking property and does not absorb UV radiation. But, TiO_2 coated and STA-TiO_2 coated cotton samples exhibited excellent UV blocking property than the normal cotton. From the Figure 7, it is clearly confirmed that TiO_2 coated and STA-TiO_2 coated cotton samples have lower UV
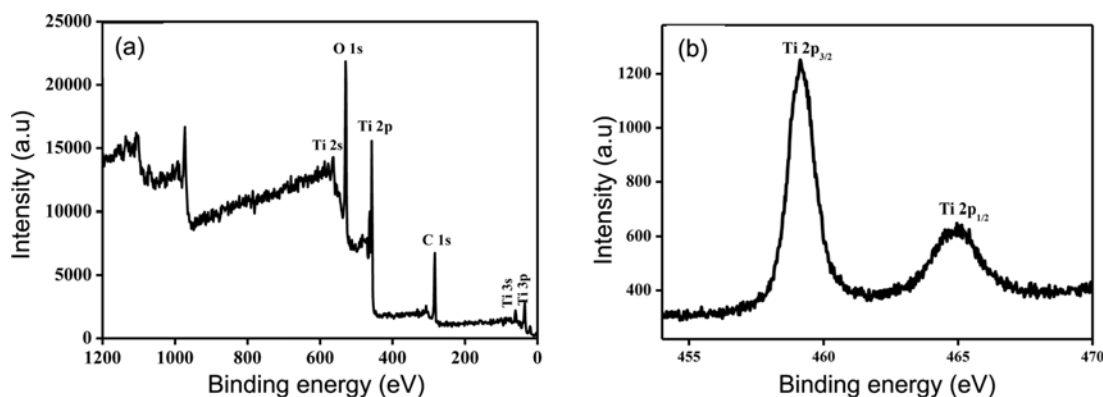
Figure 5. XPS spectra analysis; (a) survey spectrum and (b) high resolution spectra of TiO_2 coated cotton.
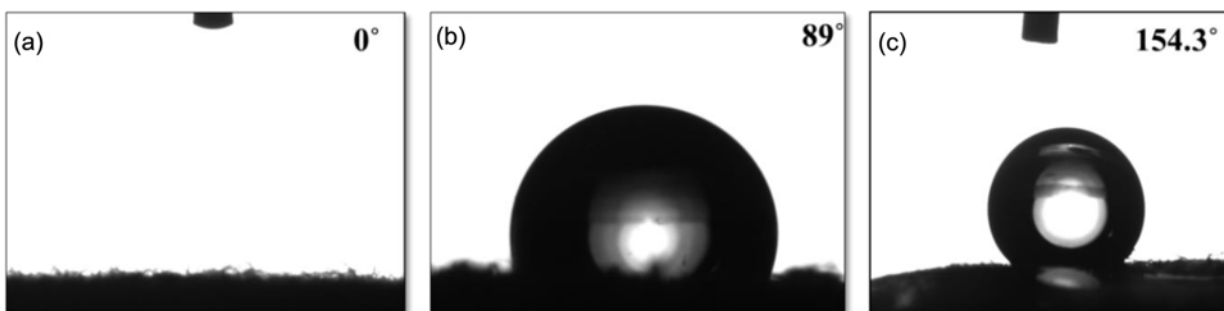

Figure 6. WCA measurements of (a) normal cotton, (b) TiO_2 coated cotton, and (c) STA-TiO_2 coated cotton.
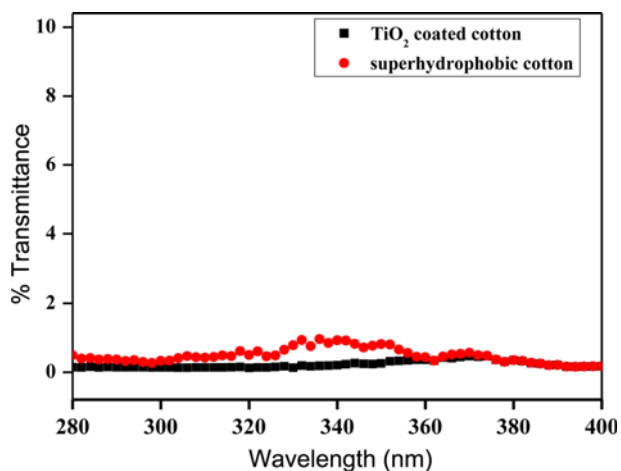

Figure 7. UV transmittance spectra of TiO_2 coated and STA-TiO_2 coated cotton samples.

transmittance values, which could be due to the higher UV absorbance and scattering property of anatase TiO_2 [9] further it also suggested that UV shielding property of TiO_2 coated cotton surface did not get affected by stearic acid deposition. These results confirmed the application of TiO_2 and STA-TiO_2 coating over cotton in shielding of UV radiation.

Self-cleaning and Oil-water Separation Studies

Self-cleaning Property of As-coated Cotton

Fabrication of superhydrophobic textiles with self-cleaning property is an important area of research due to its practical applications in daily life [30]. To study the self-cleaning property of as-prepared superhydrophobic cotton fabric, normal and superhydrophobic cotton surface was spread with sparse layer of dirt particles. Approximately three water droplets were poured on both surfaces. The water droplets with dirt particles were completely wetted on normal cotton surface. But in the case of superhydrophobic cotton, water droplets rolled into a spherical shape with dirt particles and finally, the dirt particles were completely wiped out from the surface. When tilted slightly, the dirt particles rolled out, leaving the cotton surface clean. Figure 8 showed the optical images of self-cleaning property of superhydrophobic cotton surface before and after the dust removal. These results demonstrated that the STA-TiO_2 coated cotton surface had significant self-cleaning performance.

Oil-water Separation

Besides the self-cleaning property of superhydrophobic cotton, the as-prepared cotton can be used for oil-water separation studies also. To determine the superoleophilic property of as-coated cotton, the cotton fabrics were tested with few drops of oil. Due to superoleophilicity, the oil
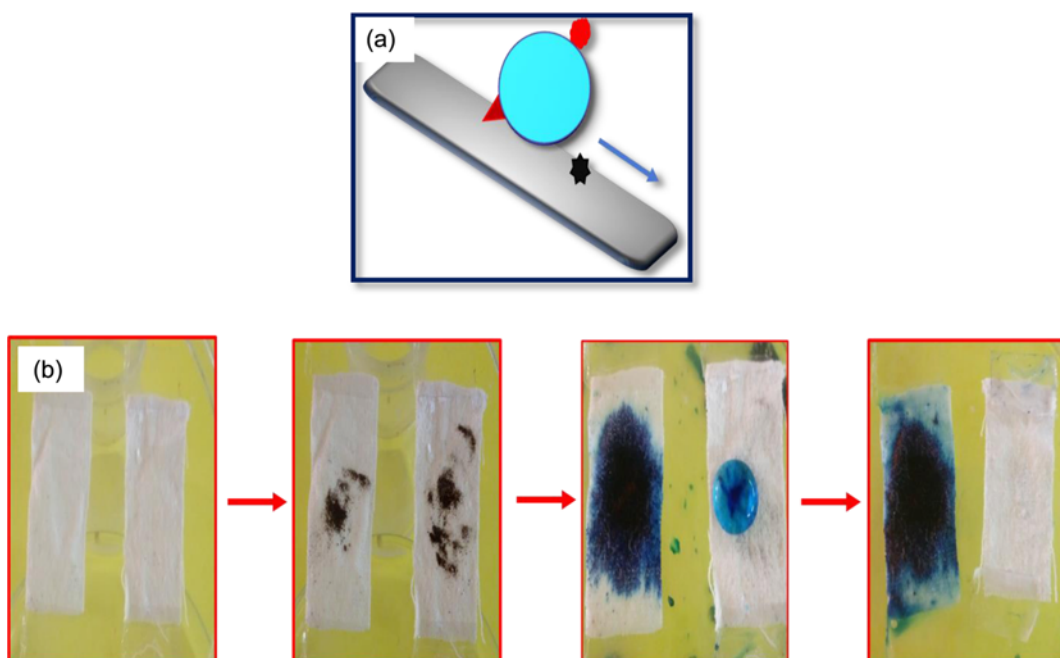
Figure 8. (a) Self-cleaning mechanism and (b) self-cleaning property of STA-TiO$_2$ coated cotton sample.

droplets were quickly absorbed. From this experiment, it could be found that the as-prepared cotton did not allow water to permeate through it, but it was found to absorb oil. Therefore, the prepared cotton can be used for oil-water separation studies. The experimental set-up used for the oil-water separation is shown in Figure 9. When water-kerosene mixture was poured through the superhydrophobic cotton, the water droplets permeated on coated cotton and kerosene was collected in the bottom container. The oil-water separation efficiency of superhydrophobic cotton was found to be 96.4 %.

Durability Studies

The durability of superhydrophobic cotton is a vital factor for the usage of as-coated cotton samples for practical applications [31]. There are many factors which affect the superhydrophobicity of coated cotton samples. In this work, the chemical durability of as-coated superhydrophobic cotton was studied by immersion in solutions of various pH. The results of the study demonstrated that all coated samples maintained their superhydrophobicity above 150° in all pH ranges even after 48 hours of immersion. The results are shown in Figure 10.

The washing durability of ultra-water repellent cotton surface was studied upto 20 cycles. The WCA values were measured after every two consecutive cycles. In the case of detergent washing, the superhydrophobic cotton surface retained its hydrophobicity for 10 cycles. On increasing the washing cycles beyond 12 cycles, the WCA was found to decrease steadily and reached 80° after 16 cycles. But in the case of water washing (without detergent), the cotton samples retained the hydrophobicity upto even 20 cycles.
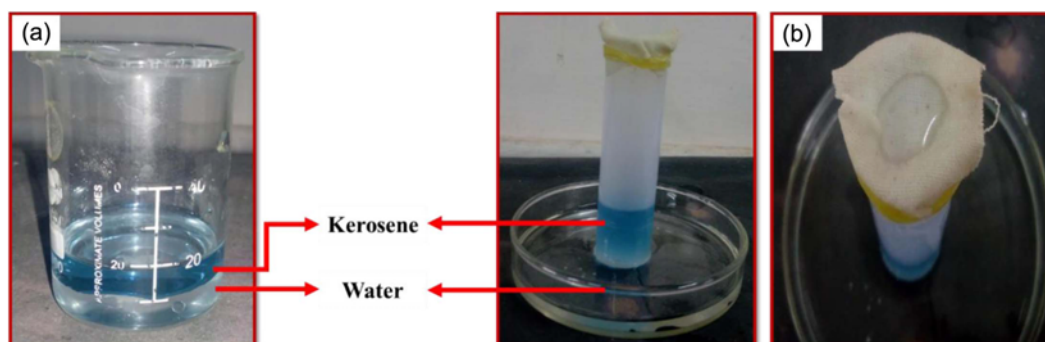

Figure 9. Oil-water separation ability of STA-TiO$_2$ coated cotton (a) kerosene-water mixture & set-up used in this study and (b) water staggered on cotton after separation (top view).

These results showed that the as-coated cotton has limited washing durability in detergent washing which may be due to the weakening of the adhesion between coatings and cotton. The washing durability of superhydrophobic cotton
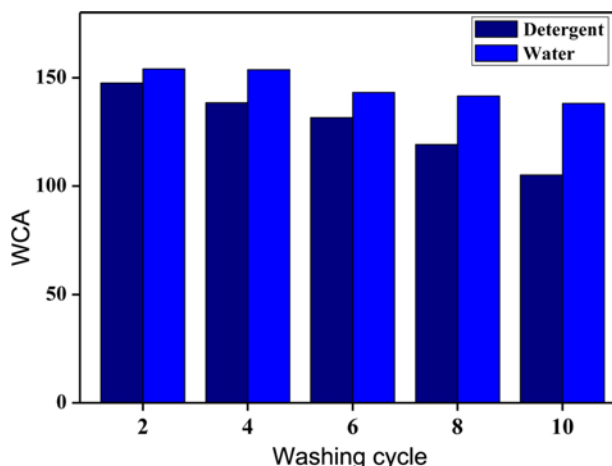

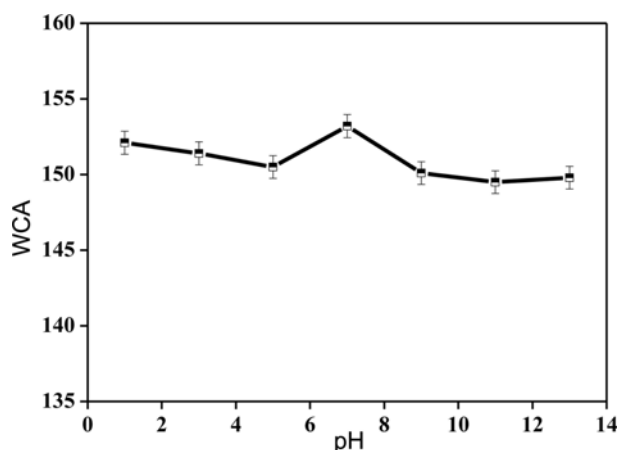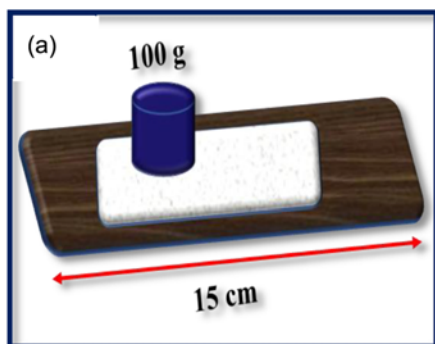**Figure 10.** Washing durability of STA-TiO$_2$ coated cotton.

Figure 11. Chemical durability of STA-TiO$_2$ coated cotton.

upto 10 washings is shown in Figure 11.

Mechanical stability is a major obstacle to scale-up operations pertaining to preparation of superhydrophobic surfaces for industrial and large scale applications [32]. In this work, scratch test [7] was used to evaluate the mechanical stability of the as-coated sample. The water repellency was tested by dropping the water droplets over damaged cotton surface upto 20 cycles. The WCA maintained its superhydrophobicity upto even 20 cycles. The water droplets could be still seen with spherical shape on the damaged surface. These results displayed that the as-prepared superhydrophobic surfaces had excellent mechanical abrasion resistance (Figure 12).

Conclusion

To conclude, cotton fabrics can be converted into a superhydrophobic ones with UV blocking and self-cleaning characteristics by this simple method. XRD and UV transmittance spectral studies showed that surface modification using stearic acid does not affect the crystalline nature and UV blocking property of TiO$_2$. Further, the STA-TiO$_2$ coated cotton showed better self-cleaning and oil-water separation property. Durability studies revealed that the cotton fabric modified with TiO$_2$ and stearic acid exhibits limited washing durability but exhibits excellent chemical durability and mechanical stability. This method has the potential to be used as the method of choice for fabrication of modified cotton textiles with special properties especially for oil-water separation.
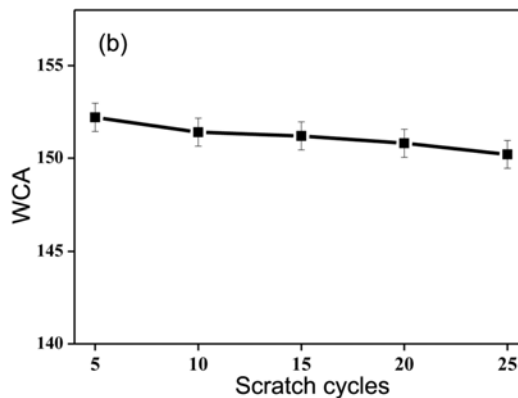
Acknowledgement

Figure 12. Schematic representation of set-up of scratch test used (a) and mechanical stability of STA-TiO$_2$ coated cotton (b).

References

1. T. Suryaprabha and M. G. Sethuraman, *Cellulose*, **24**, 395 (2017).
2. D. Cheng, M. He, J. Ran, G. Cai, J. Wu, and X. Wang, *Cellulose,* **25**, 1413 (2018).
3. Y. Zhao, Z. Xu, X. Wang, and T. Lin, *Appl. Surf. Sci.,* **286**, 364 (2013).
4. M. E. Yazdanshenas and M. Shateri-Khalilabad, *Ind. Eng. Chem. Res.,* **52**, 12846 (2013).
5. T. Suryaprabha and M. G. Sethuraman, *Cellulose,* **25**, 3151 (2018).
6. L. Wang, X. Zhang, B. Li, P. Sun, J. Yang, H. Xu, and Y. Liu, *ACS Appl. Mater. Interfaces,* **3**, 1277 (2011).
7. T. Suryaprabha and M. G. Sethuraman, *J. Alloys Compd.,* **724**, 240 (2017).
8. N. A. Ivanova and A. B. Philipchenko, *Appl. Surf. Sci.,* **263**, 783 (2012).
9. J. Y. Huang, S. H. Li, M. Z. Ge, L. N. Wang, T. L. Xing, G. Q. Chen, X. F. Liu, S. S. Al-Deya, K. Q. Zhang, T. Chen, and Y. K. Lai, *J. Mater. Chem. A,* **3**, 2825 (2015).
10. H. Zhang, X. Zeng, Y. Gao, F. Shi, P. Zhang, and J. F. Chen, *Ind. Eng. Chem. Res.,* **50**, 3089 (2011).
11. T. Zhu, S. Li, J. Huang, M. Mihailiasa, and Y. Lai, *Mater. Des.,* **134**, 342 (2017).
12. W. Duan, A. Xie, Y. Shen, X. Wang, F. Wang, Y. Zhang, and J. Li, *Ind. Eng. Chem. Res.,* **50**, 4441 (2011).
13. A. Panda, P. Varshney, S. S. Mohapatra, and A. Kumar, *Carbohydr. Polym.,* **181**, 1052 (2018).
14. C. Zeng, H. Wang, H. Zhou, and T. Lin, *RSC Adv.,* **5**, 61044 (2015).
15. M. D. Teli and B. N. Annaldewar, *J. Text. Inst*., **108**, 460 (2017).
16. S. Mondal and J. L. Hu, *J. Appl. Polym. Sci.,* **103**, 3370 (2007).
17. R. Atchudan, T. N. J. I. Edison, S. Perumal, R. Vinodh, and Y. R. Lee, *J. Alloys Compd.,* **766**, 12 (2018).
18. R. Atchudan, T. N. J. I. Edison, S. Perumal, D. Karthikeyan, and Y. R. Lee, *J. Photochem. Photobiol. A Chem*., **333**, 92 (2017).
19. R. Atchudan, N. Muthuchamy, T. N. J. I. Edison, S. Perumal, R. Vinodh, K. H. Park, and Y. R. Lee, *Biosens. Bioelectron.,* **126**, 160 (2019).
20. M. E. El-Naggar, T. I. Shaheen, S. Zaghloul, M. H. El-Rafie, and A. Hebeish, *Ind. Eng. Chem. Res.,* **55**, 2661 (2016).
21. Y. Zhang, S. Li, F. Huang, F. Wang, W. Duan, J. Li, Y. Shen, and A. Xie, *Russ. J. Phys. Chem. A*, **86**, 413 (2012).
22. A. K. Singh and J. K. Singh, *RSC Adv.,* **6**, 103632 (2016).
23. Q. Zhou, G. Chen, and T. Xing, *Cellulose,* **25**, 1513 (2018).
24. S. Li, J. Huang, M. Ge, C. Cao, S. Deng, S. Zhang, G. Chen, K. Zhang, S. S. Al-Deya, and Y. Lai, *Adv. Mater. Interfaces*, **2**, 1500200 (2015).
25. J. Wu, J. Li, B. Deng, H. Jiang, Z. Wang, M. Yu, L. Li, C. Xing, and Y. Li, *Sci. Rep*., **3**, 1 (2013).
26. S. Afzal, W. A. Daoud, and S. J. Langford, *J. Mater. Chem. A*, **2**, 18005 (2014).
27. A. K. Singh and J. K. Singh, *Appl. Surf. Sci.,* **416**, 639 (2017).
28. R. J. B. Pinto, M. C. Neves, C. P. Neto, and T. Trindade, "Nanocomposites - New Trends and Development", pp.73-96, doi: 10.5772/50553 (2012).
29. A. E. Shafei and A. Abou-Okeil, *Carbohydr. Polym.,* **83**, 920 (2011).
30. C. Xue, S. Jia, J. Zhang, and J. Ma, *Sci. Technol. Adv. Mater.,* **11**, 033002 (2010).
31. S. Qiang, K. Chen, Y. Yin, and C. Wang, *JMADE,* **116**, 395 (2017).
32. M. Zhang, C. Wang, S. Wang, and J. Li, *Carbohydr. Polym.,* **97**, 59 (2013).