J Sol-Gel Sci Technol (2016) 78:475–481
DOI 10.1007/s10971-016-3974-7

ORIGINAL PAPER: FUNCTIONAL COATINGS, THIN FILMS AND MEMBRANES (INCLUDING DEPOSITION TECHNIQUES)

Synthesis and characterization of superhydrophobic–superoleophilic surface

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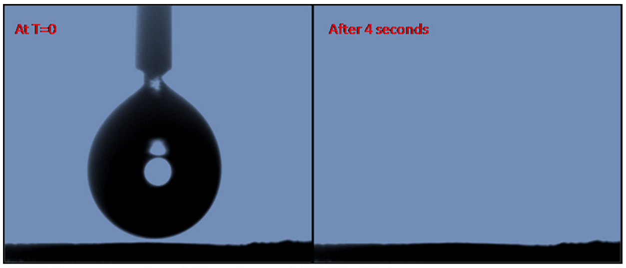
Received: 16 November 2015 / Accepted: 29 January 2016 / Published online: 1 March 2016

Abstract The binary superhydrophobic–superhydrophilic surface has been successfully achieved by a combination of nanoscale texture roughness on micro-textured cotton thread network by layer-by-layer deposition method through the single-step sol–gel route. Furthermore, microstructures with improved wettability were produced, in which silica nanotextures were grown without modifying the chemical method to form superoleophilic and superhydrophobic networks. A superoleophilic surface (oil contact angle 0°) and a superhydrophobic coated cotton fabric with surface free energy of $\gamma^{\text{total}} = 13.23 \pm 0.37$ mJ m^{-2} (water contact angle of $167 \pm 1°$ and a small sliding angle of $4 \pm 1°$) were successfully obtained. The results were exemplified here by the creation of immiscible oils separation membranes, and the innumerable applications of this technology also include self-cleaning fabrics, antistaining fabrics, water purification, and antiwetting fabrics for military applications.

Graphical Abstract



Attractive superoleophilic nature of fabric with kerosene

Keywords Layer-by-layer deposition method · Superhydrophobic–superoleophilic surface · Sol–gel processing · Contact angle

1 Introduction

Extraordinary superhydrophobic surface with a superoleophilicity has contact angle of oils below 5°, and surface water repellency and absorbtion of oil have been actively investigated in both scientific and engineering fields in the past decade [1–5]. A variety of physical and chemical approaches have been developed for the designing of superhydrophobic–superoleophilic surfaces, including sol–gel process, chemical vapor deposition, electrodeposition, templating, self-assembly, spray coating, lithography, spin coating, and dip coating [6–19]. The multifunctional superhydrophobic surfaces can be potentially applied as self-cleaning, antiadhesion, paints, textiles to low-friction surfaces for fluid flow, corrosion-resistant surfaces, oil–water separating fabric, etc. [20–23]. The superhydrophobicity is combined with superoleophilicity on the same

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surface that is useful to separate oil from water, or water from oil[24–26]. The surface tension of water is commonly larger than of oils (including diesel, petrol, and kerosene). Therefore, if the surface tension of a solid substrate lies between those of water and oils, it might show hydrophobicity and oleophilicity [27]. Combining the low-energy surface with a proper surface design, surfaces with superhydrophobicity and superoleophilicity on the same surface can be prepared. However, there are only a fewer number of reports available on surfaces involving both superhydrophobicity and superoleophilicity on cotton fabric. It is considered that such surfaces can be used for the effective separation of oil from water in a number of potential industrial and domestic applications [28]. In the past decade, a great number of methods have been developed to prepare superhydrophobic surfaces of metals, inorganic, and polymers. Currently, to produce a superhydrophobic coating on textile suffering from instability water-repellent during the washing becomes an important issue for fabrication approaches [29, 30].

In the study reported here, fabrications of cotton textile fabric with superhydrophobic–superoleophilic properties were performed by an easy and inexpensive layer-by-layer deposition method. Methyltrimethoxysilane (MTMS) is a silica precursor used for the synthesis of special wettability surface with superhydrophobicity and superoleophilicity on cotton fabric shows CA of 167 ± 3° and 0 for water and oil, respectively.

2 Experimental

2.1 Materials

Silica precursors used to synthesize superhydrophobic coating are deposition grade methyltrimethoxysilane (MTMS) (≥98 %, Sigma-Aldrich Chemie, Germany), methanol, hexane (S.D. Fine Chem. Ltd., Mumbai), and liquor ammonia (NH_3, Sp. Gr.0.91 Qualigens Fine Chemicals, Mumbai), and a cotton textile piece (thickness $\approx$ 16 μm) was brought from a local market shop. Before the deposition of coating material, a 4×4 cm^2 square piece of cotton pieces was cleaned with fresh water and ethanol.

2.2 Preparation of superhydrophobic–superoleophilic cotton fabric

The organically modified silica (ORMSIL) superhydrophobic coatings were prepared by a three-step process: (1) alcohol preparation, (2) layer-by-layer dip coating on a cotton piece, and (3) drying. The layer-by-layer (LbL) is substrate-independent deposition method frequently used for fabricating superhydrophobic–superoleophilic coatings on cotton fabric. The layer-by-layer experiment was carried out by using a simple experimental set including beaker containing alcosol prepared at the best molar ratio. In the first step, the alcosol was prepared at the best molar ratio of MTMS (1): CH_3OH (35.22)/H_2O (2.01) with 13 M NH_4OH. Initially, methyltrimethoxysilane as precursor was diluted in methanol with vigorous stirring. Afterward, ammonium base solution was added dropwise into the sol solution. The hydrolysis and condensation were carried out at room temperature for next 24 h. A cotton piece was dipped in the sol for 2 min at room temperature and dried with the hot air dryer, and subsequently, this process was repeated 15 times. At the final step of the deposition, the cotton pieces were allowed to dry in an oven at 50 °C for overnight.

2.3 Sample characterization

A surface morphology of coatings was examined by scanning electron microscopy (SEM, JEOL JSM-6360, Japan). The characterization of the surface topography was performed using a surface imaging, analysis, and metrology software (Moutains 7, Digital Surf, France). Surface chemical composition of the coating was studied using FT-Raman spectroscopy (Bruker MultiRAM, Germany). A contact angle was measured with the goniometer (Rame hart Instrument Co., Model 501F1, USA) and sliding angle by tilting plate method with 5 μL water drop. The accounted values are taken from the average of five different measurements.

3 Results and discussion

Superhydrophobic–superoleophilic cotton fabric usually consists of cotton microscale fiber coated with silica material which instantaneously absorbs oil and repel water because of contrast surface tension. Multifunctional MTMS-based silica coating material is successively deposited on microscale cotton threads of cotton fabric with the help of layer-by-layer (LbL) deposition method without any surface modification and forms cotton template with special wettability.

3.1 Surface morphological studies

Superhydrophobic–superoleophilic cotton fabric was prepared with a layer-by-layer (LbL) deposition method through the sol–gel approach briefly described in “Experimental” section. The typical morphology of the as-deposited silica material on the cloth template at optimal deposition condition was viewed by SEM. Figure 1a shows the SEM image of the coated surface area.

A cotton template, whose pores have an average dimension of approximately $L \times H = 140 \times 200$ μm, was used as the fabric template. Uniform pore size plays an important role in wettability, which ensures trapping the air within the pore of coated cotton fabric. The enlarged view of the coating is shown in Fig. 1b, and fabric is composed of a bunch of small cotton threads with thick layer of silica material which plays an important role in stable wettability behavior against various impacts on it.

Figure 1c, d shows the high-resolution SEM image of the close view of the sides of the fabric, whose rough structures resemble that of hierarchical morphology. These results suggest that the prepared cotton fabric has a rough surface with both micro- and nanoscale structures essential for outstanding wettability, which is quite similar to the lotus leaf.

3.2 Surface topography

Surface imaging, analysis and metrology software were used to probe the surface topography, and the resulting images, root-mean-square (RMS) roughness values (Rq) and average roughness (Ra) of topographical area to the selected regions are shown in Fig. 2a–d. The cotton fabric with uniaxially stretched threads was aligned in rows perpendicular to each other (Fig. 2a–b), demonstrating the possibility of exploiting the layer-by-layer deposition method to obtain a binary texture arrangement of cotton fabric in a single-step sol–gel process. As shown in the three-dimensional topographical images and topography of Fig. 2a, b, the root-mean-square roughness values were calculated according to ISO 4287 standard. We can observe that the surface profile exhibits a micro-sized uniform thread with thickness in the range 2.5–2.5 µm. The entire cotton fabric coating is composed of a homogeneous, well-fabricated binary texture. In addition, from a surface profile of a topographical area of coating and selected thread regions clearly depicted in Fig. 2c, d, we can see binary textures consisting of a microscopic thread network (Fig. 2c) and the thread (Fig. 2d) that have a roughness of 944 and 1700 nm, respectively. As a result, the microscopic thread network of the cotton fabrics and silica nanotextures evolves into a more Cassie–Baxter stable state closer to the binary superhydrophobic texture.

3.3 Surface properties of cotton fabric

Whenever air pockets are present on a rough surface, the Cassie–Baxter equation can also be used to estimate the contact angle of a water drop deposited on rough surface. The Cassie–Baxter equation becomes [31]

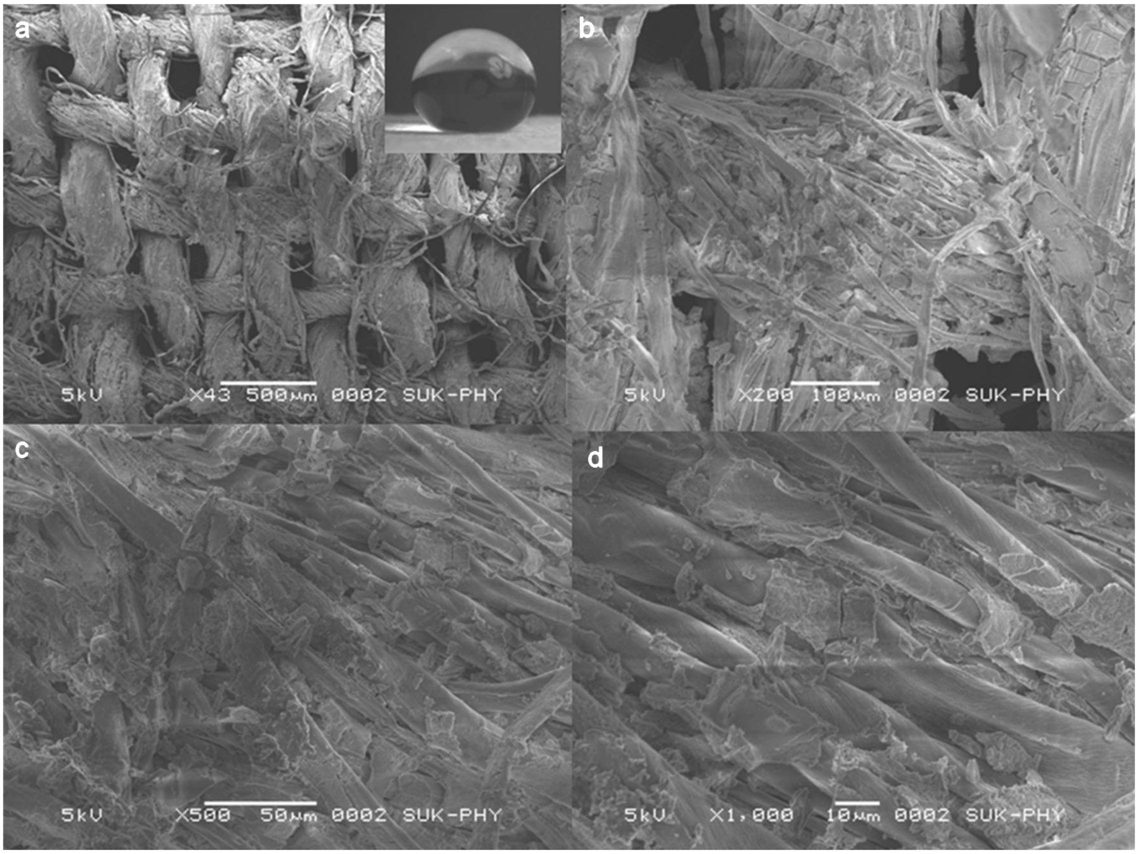

Fig. 1 Surface morphology of cotton fabric at different magnifications **a** 500, **b** 100, **c** 50, **d** ×10

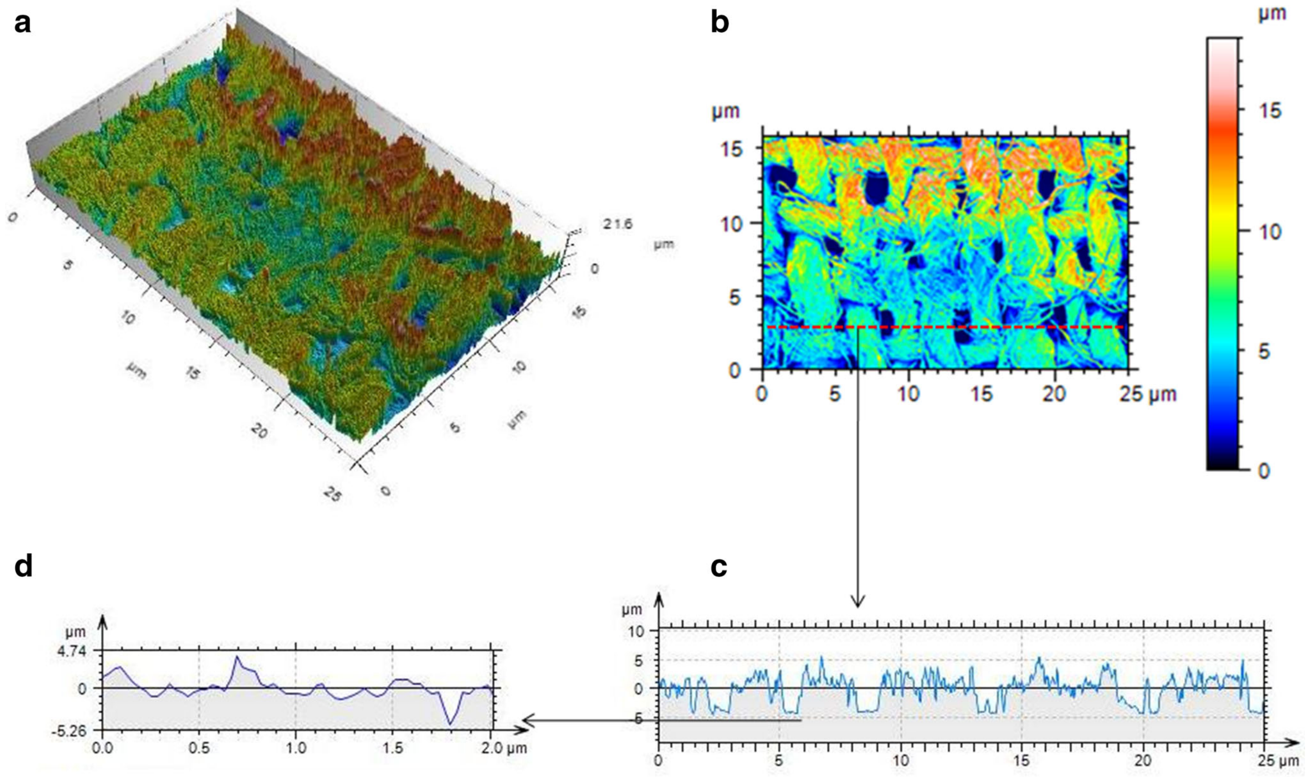

Fig. 2 Surface analysis of superhydrophobic cotton surface, **a** 3D view, **b** pseudo-color view of selected topographical area, **c** surface profile extracted *over dotted line*, **d** surface profile over a selected region of thread

$$\cos\theta_{S}^{CB} = f_{S}^{CB}(\text{geo})(1 + \cos\theta_{\text{flat}} - 1) \qquad (1)$$

where $[f_{S}^{CB}(\text{geo})]$ is the fraction of the water/solid contact surface area (the ratio of the liquid/solid contact area under the droplet to the total projected area of the drop basement) and θ_{flat} is the solid/water contact on the flat surface of the same slide. The contact angle value of the rough surface $[\theta_{S}^{CB}]$ increases with the decrease in $[f_{S}^{CB}(\text{geo})]$. The Cassie–Baxter model was found to be useful in the analysis of superhydrophobic porous cotton fabric.

The inset of Fig. 1a shows water drop on coated cotton having a contact angle equal to 167 ± 2°. We also analyzed the surface free energy of a surface by finding out contact angles of five probe fluids [including water (w), ethylene glycol (E), glycerol (G), formamide (F), and diiodomethane (D)] and quantifying the surface free energy of the solid–liquid interface using the Owens–Wendt model [32]. In Fig. 3, the surface free energy $\gamma^{\text{total}} = 13.23 \pm 0.37$ mJ m^{-2} was successfully calculated according to the two-liquid Owens-Wendt model and Owens–Wendt multiple regression method.

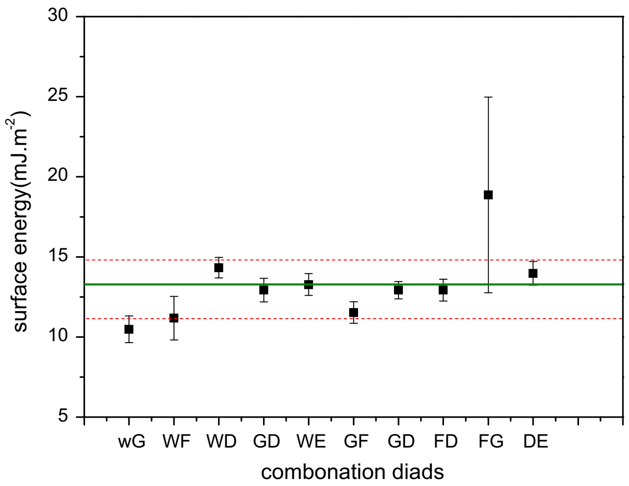

Fig. 3 Surface free energy (SFE) retrieved based on the Owens–Wendt model

The water drops easily flow in the surface without sticking and dislodges after tilting the plane cotton piece fixed on glass substrate up to 4 ± 1°. This fact is because of the presence of many non-hydroxyls –CH_3 groups on coating surface showing a Cassie–Baxter non-wetting state. In contrast, a liquid with low surface tension (28 mJ m^{-2}) like kerosene spread instantaneously on the modified coating cotton surface and permeated it thoroughly. It shows a drop of kerosene on cotton fabric before and after absorbing briefly viewed in Fig. 4a, and drop is

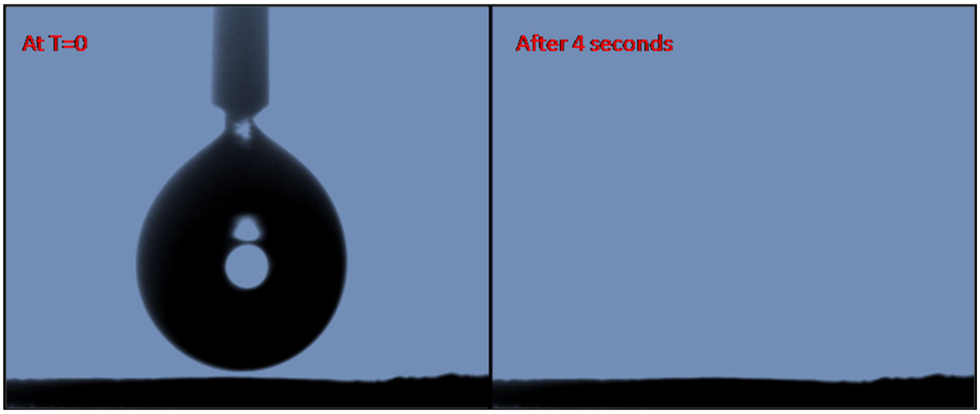

Fig. 4 Superoleophilicity of fabric with oil (kerosene)

quickly absorbed within 4 s as shown in Fig. 4b, showing highly attractive superoleophilic nature. From above, it is clear that the low surface free energy and higher contact angle of the silica network resulted in superhydrophobic–superoleophilic surface that instantly build up spherical water drop and simultaneously oil soaks over the silica network.

3.4 Superoleophilicity property of MTMS-based cotton membrane

When mixture of two immiscible solutions like petroleum oils and water was passed through superhydrophobic–superoleophilic porous surface, only the oil could bypass through it and water droplets were held on the surface without absorbing [33]. This result focused on special surface wettability enabled cotton fabric used to separate oil–water mixtures with 10-min ultrasonic treatment. The separation efficiency of the cotton fabric was further investigated. When an oil–water mixture was passed through the superhydrophobic cotton fabric surface at conical funnel, only the oil passed through the filter paper. Water drop that run off the surface were collected and simultaneously absorbed oil was collected in beaker. The separation efficiency of oil and water was calculated at constant oil/water volume ratio (1:5) as shown in Fig. 7.

In this work, we explored the separation effects of the coated cotton fabric on immiscible liquids. Generally, the nonpolar petroleum molecule is immiscible with polar water molecule because there is no difference in charge throughout the molecule. However, petroleum oils have a low surface tension quickly spread on a superoleophilic surface, which we believe a separate mixture solution [34]. When a mixture of oils and water solution was added into conical funnel with twofold of superhydrophobic cotton fabric fitted at opening, all oil passed through the filter fabric, but water remained on cotton fabric up to end after complete filtration of superoleophilic oils from the mixture. From Table 1, clear filtration efficiency of fabric is a function of the surface tension difference between two liquids. Superhydrophobic–superoleophilic fabric shows a maximum efficiency about 96 % for gasoline and a minimum of 90 % for benzene. It is clear that reported cotton fabric is effective for the separation of immiscible liquid mixture.

3.5 FT-Raman analysis

Figure 5 shows FT-Raman spectra of coating material that can be recorded over range of 300–3600 cm^{-1}. The symmetric and asymmetric stretching mode of Si–O–Si bonds in the silica network occurs at 473 and 801 cm^{-1}, respectively [35]. The condensation of Si–CH_3 groups presented by band at 744 and 1413 cm^{-1} corresponds to the asymmetric stretching mode.

The intense vibration peaks are assigned to the C–H from –CH_3 bounds of the network, during the sol–gel transformation. Essentially, there are the symmetric and asymmetric stretching modes of the C–H corresponding to 2913 and 2974 cm^{-1}. It is cofirmed form Raman analysis that surface methyl groups play an important role in superhydrophobicity and superoleophilicity of cotton fabric.

3.6 Stability and superhydrophobicity

Fabrication of stable superhydrophobic fabrics is a very hot issue because of their tremendous potential applications in domestic and in industrial fields.

To evaluate the durability, the superhydrophobic fabric was exposing to outdoor environmental conditions. The wettability could be changed from 167 ± 1° to 151 ± 5° without any significant damage in wettability mainly caused by deposition of dust particles on hierarchical cotton fabric as shown in Fig. 6a. The superhydrophobicity remains unchanged even after the samples had been kept

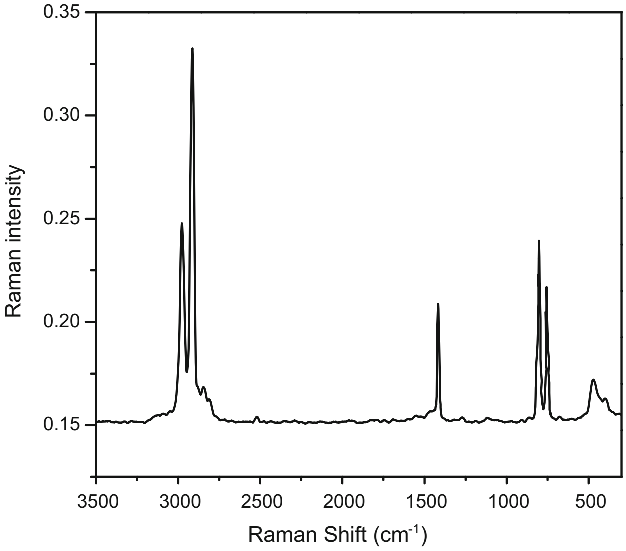

Fig. 5 Chemical analysis of functional groups of superhydrophobic–superoleophilic coating material

open outdoor environments conditions aside without special protection, at least for 60 days for reviewing their degradation behavior. In addition, the fabric was immersed in water and boiled for 5 h. The contact angle of coated fabrics was reduced by only 3°as shown in Fig. 6b, because of minor damage in fabrics texture and being difficult to observe by any visual observation. The coated cotton fabric was found to be superhydrophobic–superoleophilic even after 5-h exposure to boiled water. The superhydrophobic–superoleophilic property is diminishing under critical situations such as outdoor environmental conditions and boiling water condition. These observations suggest that the cotton fabric was coated by MTMS after deposition and that the fabric was stabled during the exposure tests.

In addition, the stability of coating in washing solution was identified by two different ways. In the short-term test, the superhydrophobic cotton fabric was placed in a beaker containing 10 % solution of caustic soda, and such assembly was placed in an ultrasonic bath at 45 °C for 10 min and afterward dried in an oven at 50 °C for 60 min. This process was repeated five times. The contact angle measurement was taken after cotton fabric purposefully treated with freshwater in an ultrasonic bath for 2 min at 45 °C in order to remove a residual layer of the ions trapped inside textures during washing process. For durability test, assembly of caustic soda and cotton fabric was extended 15 days at ambient conditions. Both tests for the superhydrophobic surfaces focused on the effect of washing solution on the wettability of cotton fabric. As shown in Fig. 7, wettability of a washed cotton surface with superhydrophobicity remains unchanged up to nine cycles of ultrasonic washing with minor variation in their wettability. However, after ten cycles of washing, coated cotton fabric lose contact angle up to 148 ± 2°. This change may be because of formation of residual $^{-}$OH charge layer on the coating surface and may affect their wettability. Specifically, residual hydroxyl $^{-}$OH ions are trapped inside a hierarchical textures, where ultrasonic cleaning treatment is not so effective. However, increasing ultrasonic treatment time can be effectively reduced the layer of residual hydroxyl $^{-}$OH ions from textures. A variation in water repellency during both tests confirms that superhydrophobic cotton fabric is relatively stable up to certain ultrasonic washing cycles.

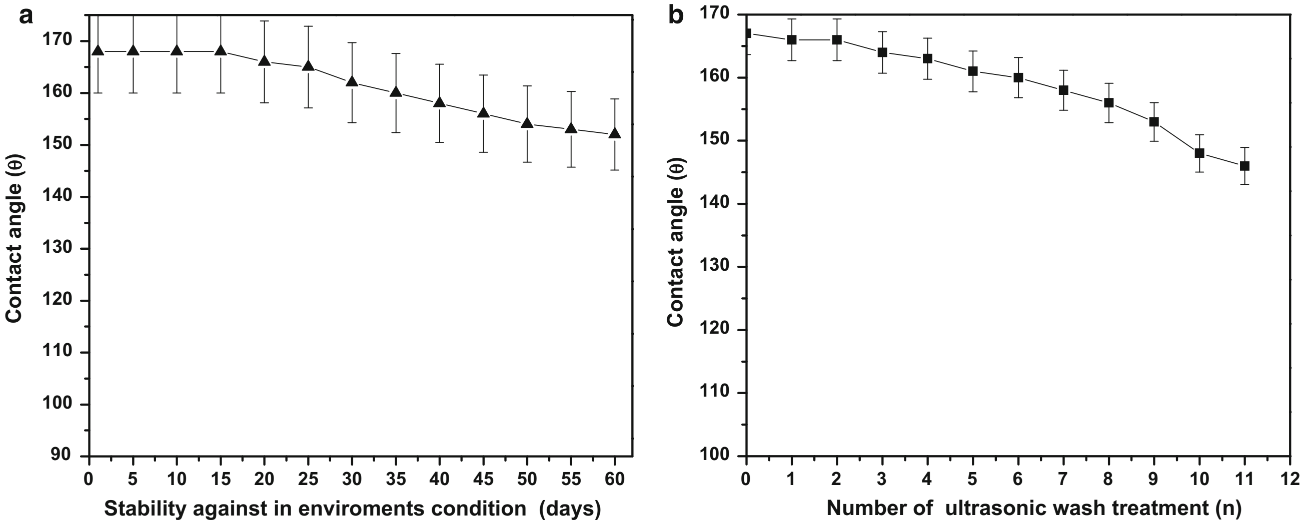

Fig. 6 Stability of coating against **a** outdoor harsh environments conditions, **b** ultrasonic washing treatment

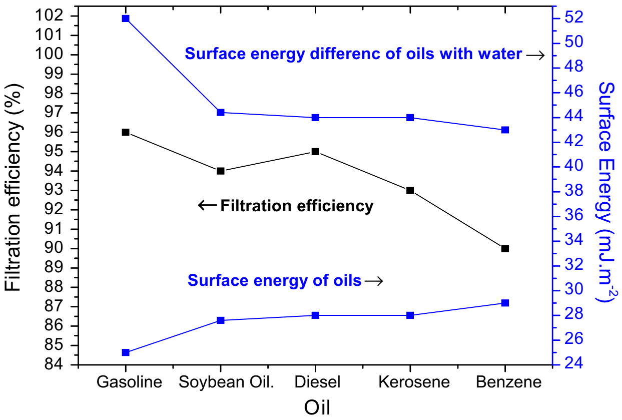

Fig. 7 Oil/water separation efficiency for coated cotton fabric at fix volume ratio 1:5

4 Conclusions

We conclude that superhydrophobic–superoleophilic coating on a cotton fabric forms hierarchical textures fabricated by integrating LbL deposition method and single-step sol–gel process. These superhydrophobic cotton fabrics can be designed for durable oil/water separation membrane, such as kerosene. Indeed, water drops impacting such fabrics are able to bounce off the surface after hydrophobic material deposition, and we expect that this approach could be extended to fabrics exposed to rain to prevent wetting. The new class of non-wetting cotton fabrics that we present here could be useful for immiscible solution separation, self-cleaning, antiwetting fabrics, and other industrial applications where holding stability under external impact is beneficial.

Acknowledgements The author acknowledges the Department of Physics, Shivaji University, Kolhapur, India, for providing experimental facility.

References

1. Zhang W, Lu X, Xin Z (2015) Nanoscale 7:19476–19483
2. Liu F, Ma M, Zang D, Gao Z, Wang C (2014) Carbohyd Polym 103:480–487
3. Du C, Wang J, Chen Z, Chen D (2014) Appl Surf Sci 313:304–310
4. Xu L, Xiao G, Chen C, Li R, Mai Y, Sun G, Yan D (2015) J Mater Chem A 3:7498–7504
5. Wang C, Lin S (2013) ACS Appl Mater Interfaces 5:8861–8864
6. Mahadik SA, Kavale MS, Mukherjee SK, Rao AV (2010) Appl Surf Sci 257:333–339
7. Mahadik SA, Vhatkar RS, Mahadik DB, Kavale MS, Wagh PB, Gupta S (2010) Appl Surf Sci 277:67–72
8. Mahadik DB, Lee YK, Chavan NK, Mahadik SA, Park HH (2016) J Supercrit Fluid 107:84–91
9. Crick CR, Bear JC, Kafizas A, Parkin IP (2012) Adv Mater 24:3505–3508
10. Pedraza FD, Mahadik SA, Bouchaud B (2015) Phys Chem Chem Phys 17:31750–31757
11. Li Y, Jia W, Song Y, Xia X (2007) Chem Mater 19:5758–5764
12. Chen Q, Bae SC, Granick S (2011) Nature 469:381–384
13. Mahadik SA, Mahadik DB, Kavale MS, Parale VG, Wagh PB, Barshilia HC (2012) J Sol-Gel Sci Techn 63:580–586
14. Ogihara H, Xie J, Okagaki J, Saji T (2012) Langmuir 28:4605–4608
15. Li Y, Zhang J, Zhu S, Dong H, Jia F, Wang Z, Tang Y, Zhang L, Zhang S, Yang B (2010) Langmuir 26:9842–9847
16. Kavale MS, Mahadik SA, Mahadik DB, Parale VG, Rao AV, Vhatkar RS (2012) J Sol-Gel Sci Techn 64:9–16
17. Nguyen DD, Tai N, Lee S, Kuo W (2012) Energy Environ Sci 5:7908–7912
18. Parale VG, Mahadik DB, Mahadik SA, Kavale MS, Wagh PB, Gupta SC (2013) Ceram Int 39:835–840
19. Parale VG, Mahadik DB, Kavale MS, Mahadik SA, Rao AV, Mullens S (2013) J Porous Mater 20:733–739
20. Ganbavle VV, Bangi UKH, Latthe SS, Mahadik SA, Rao AV (2011) Surf Coat Tech 205:5338–5344
21. Nimittrakoolchai O, Supothina S (2008) J Euro Ceram Soc 28:947–952
22. Mahadik SA, Pedraza FD, Vathkar RS (2016) J Alloys Compd 663:487–493
23. Rao AV, Mahadik SA, Kappenstein C (2011) Appl Surf Sci 257:5772–5776
24. Ju J, Wang T, Wang Q (2015) J Appl Polym Sci 132(1–7):42077
25. Yanlong S, Wu Y, Xiaojuan F (2015) Chem J Chin U 36:1724–1729
26. Feng L, Jiang Angew L (2004) Chem Int Ed 43:2012–2014
27. Zhang X, Zhang P, Appl ACS (2012) Mater Inter 4:1742–1746
28. Pernites RB, Advincula RC (2011) Adv Mater 23:3207–3213
29. Xue X, Li Y, Ma J, Appl ACS (2014) Mater Inter 6:10153–10161
30. Zimmermann J, Seeger S (2008) Adv Funct Mater 18:1–8
31. Cassie ABD, Baxter S (1944) Trans Faraday Soc 40:546–561
32. Owens D, Wendt R (1969) J Appl Polym Sci 13:1741–1747
33. Wang D, Liu X, Zhou F (2010) J Phys Chem 114:9938–9944
34. Cheng Z, Wang J, Lai H (2015) Langmuir 31:1393–1399
35. Mahadik SA, Hegade ND, Gupta SC, Wagh PB (2013) J Colloid Interface Sci 405:262–268