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Fabrication of durable super-repellent surfaces on cotton fabric with liquids of varying surface tension: Low surface energy and high roughness



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ABSTRACT

In this study, we have developed super-repellent surface on cotton fabric via a facile and eco-friendly strategy using zirconia particles with water-soluble siloxane emulsion. The coated fabric using zirconia-siloxane (ZS) coating showed super-repellency of liquids with surface tension >47.7 mN/m, like water, mixtures of isopropyl alcohol with deionized water (2% and 5%, v/v), and ethylene glycol with contact angle of 158° , 155° , 153° and 152° , respectively. Furthermore, the coated fabric displays low sliding angle, $<10^\circ$, with these liquids. The super-repellency of the coated fabric is attributed due to its lower surface energy (<1.0 mJ m $^{-2}$). The produced coating exhibited excellent durability and retained its super-repelling properties under harsh environment conditions like acidic, alkaline, salty, ultraviolet irradiation, mechanical abrasion and repeated tear test with an adhesive tape. In addition, in a mixture of water and oil (having surface tension <30 mN/m), the developed coated fabric exhibited dual nature viz., superhydrophobicity and superoleophilicity, maintaining the super-repellency with water even they are wetted with oily liquids. The materials with ability to repel water in the presence of oily pollutants are very useful in application related to sea water. Thus as-prepared coated fabric, with dual functionality, is a promising material for many applications including anti-wetting, self-cleaning, support for aquatic floating devices and as a filtration material for rapid and continuous oil-water separation.

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1. Introduction

The design and fabrication of surfaces with special wettability (i.e. superhydrophobic, superoleophobic, superamphiphobic) inspired by natural surfaces such as lotus leaf, nepenthes leaf, legs of water striders, and wings of butterfly, are of considerable focus in both scientific and industrial domains due to their versatile applications [1–4]. The wetting properties of a solid surface with respect to water or oil droplets depend on the surface roughness and surface chemistry. In order to achieve special wettability, the combination of hierarchical rough structures and materials with low surface energy are required, bestow the special wettability on the surfaces, which repel liquids with a wide range of surface tensions, with high static contact angle ($\theta > 150^\circ$) and low sliding angle ($\theta < 10^\circ$) [1,5,6]. However, the surface with simply roughness are unable to repel the oil or organic liquid that have lower surface tension than water, owing to the further decrease in contact angle [1]. Thus in order to repel low surface tension liquids, a special design

such as a re-entrant structure is highly desirable [2]. Recently it was reported that the brochosomes of leafhopper insects (diverse family of cicadellidae) having a particular type of advanced particles, i.e., which can repel water and low surface tension liquids such as diiodomethane and glycerol (surface tension >47.7 mN/m) with contact angle $>150^\circ$ but not oils (surface tension <47.0 mN/m) [7–9]. The porous honeycomb structure coating on brochosomes of leafhopper, accommodated with large amount of acids, protein and esters again emphasizes the importance of special structure in order to show antiwetting properties with low surface tension liquids [10]. However, the fabrication of such a designed special structure (re-entrant structure) is still a major challenge in surface chemistry.

In the recent past, in order to create a surface which can repel both water and oil several methods were evolved such as spraying, sol-gel, chemical vapor deposition, layer-by-layer assembly, chemical etching, photolithography and plasma treatment [5,11–14]. Among these, some of the methods are time consuming, require post-treatment by using expensive and fluorinated chemical and some are considerably destructive to the substrates. These shortcomings restricted their applications in designing surfaces with special wettability [5].

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In recent years, profound research studies have been performed to develop hydrophobic and superhydrophobic cotton fabric owing to its unique characteristics (low cost, easy handling, high flexibility and environment friendly) and promising applications like anti-sticking, anti-contamination, self-cleaning and also in oil-water separation [5,11,15]. In order to fabricate superhydrophobic surfaces, addition of various nanoparticles such as silver, SiO_2 , TiO_2 , Fe_3O_4 , ZrO_2 in combination with low surface energy materials such as fluorinated compounds and polymers have been reported in literature [15–19].

Very recently Xu et al. fabricated superhydrophobic fabric via the polymerization of dopamine in alkaline solution with Ag deposition and subsequent modification with 1H,1H,2H,2H-Perfluorodecanethiol [16]. The resulting coated fabric efficiently separated oil from oil-water mixture owing to its superhydrophobicity and superoleophilicity. Lin et al. reported superhydrophobic and superoleophobic cotton fabric, which was coated by SiO_2 nanoparticles with fluoropolymer (Perfluoroalkyl ethyl acrylate) [20]. In addition, Zhou et al. reported a fabrication of superhydrophobic and superoleophobic cotton fabric using chemical vapour deposition method by incorporation of polyaniline with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1H,1H,2H,2H-perfluorooctyltriethoxysilane [21]. In their study, modified cotton fabric exhibited water contact angles greater than 150° and water sliding angles lesser than 10° . Although these coated cotton fabrics exhibited superhydrophobicity by the application of fluorine containing reagents (low surface energy agents), the use of fluorinated compounds is expensive and environmentally undesirable as they are nonbiodegradable (persistent pollutants) [5,11]. In addition to this there are several studies that reported the fabrication of superhydrophobic coating on cotton fabric surfaces using non-fluorinated hydrophobic agents. Chatzigrigoriou et al. [22] reported water repellent coatings on various materials including cotton without using fluoro compounds. The resulting cotton obtained high water contact angle ($>160^\circ$) and low sliding angle ($<10^\circ$). Cao et al. have used organically modified silica aerogel followed by polydimethylsiloxane top coating [5]. The modified fabric repels water with contact angle $>160^\circ$ and sliding angle $<10^\circ$ but not oils [5]. Wu et al. fabricated superhydrophobic surfaces on cotton, glass and metal substrates by the application of SiO_2 and TiO_2 nanoparticles in combination with vinyltriethoxysilane modification under gravity and pressure [23]. Although, these studies are mainly focused on fabrication of superhydrophobic surfaces that can repel water from their respective surface, they did not pay much attention for super-repellency of low surface tension liquids like ethylene glycol, mixtures of isopropyl alcohol and deionized water, as reported on the surface of leafhopper brochosome. To the best of our knowledge only limited studies have focused on the modification of cotton fabric to repel both water as well as low surface tension liquids. Thus it is interesting to achieve modified cotton fabric with super-repellency to liquid having surface tension from 72.8 mN/m (water) to 47.7 mN/m (glycerol), mimicking leafhopper brochosome [7].

Beside the development of super-repellent surface on cotton fabrics as leafhopper brochosome coating, long-term durability of such coating is also an essential requirement for practical applications. Generally, coated cotton fabrics lose their superhydrophobic property easily during their applications in harsh environmental conditions, due to the weak attachment between the cotton fibers and low surface energy materials [11]. It is reported that in the presence of high acidic or alkaline liquid medium the hydrophobicity of various coated surfaces reduces with time. For example, due to dissolution of Si-O-Si bonding at strong alkaline solutions, the hydrophobicity of silica based composites decreases within certain hours [11].

Herein, to fix these problems, the present work reports the fabrication of durable super-repellent surfaces on cotton fabric

with liquid of varying surface tension (72.8–47.7 mN/m) using zirconia particles embedded into a siloxane (Silres BS 39) material via simple sol-gel dip coating process. Recently, it was reported that the bond dissociation energy, thermal stability, mechanical strength and covalent character of zirconia are strong in comparison to other ceramic materials [11,18]. Thus the application of zirconia particles would be more favorable in terms of durability of super-repellent coating on cotton fabric surface. Silres BS 39 is a mixture of silane/siloxane/polymer content (~ 25 wt%) in water (~ 75 wt%). This is water soluble siloxane emulsion and can be used easily as a dip or spray coating solution without using of organic solvents. The synthesis of zirconia-siloxane (ZS) based superhydrophobic coating on cotton fabric followed by its super-repellency with respect to water, 2% (v/v) mixtures of isopropyl alcohol with deionized water (surface tension = 59.0 mN/m), 5% mixtures of isopropyl alcohol with deionized water (surface tension = 50.0 mN/m) and ethylene glycol (47.7 mN/m) are described. The durability of super-repellent coating under harsh environment conditions like acidic/alkaline/salty/boiling water, ultraviolet irradiation, mechanical abrasion and repeated tear test with an adhesive tape were are studied. In addition, self-cleaning property of the modified fabric was also examined for hydrophilic and hydrophobic solid particles. Moreover, the super-repellency of the coated fabrics was also evaluated with water, even the coated fabrics are wetted with oleophilic liquids.

2. Experimental section

2.1. Materials

Zirconium (IV) *n*-propoxide (ZP) in *n*-propanol (70%) and acetylacetone (acac, 99%) were purchased from Sigma Aldrich. 1-Propanol and 1-butanol were purchased from Merck. Silres BS 39 from Wacker and nitric acid was purchased from Fisher Scientific. All the chemicals were used as received without further purification. Cotton fabric was purchased from a local store and ultrasonically washed with distilled water and ethanol. Finally cotton fabric was dried at 50°C for 30 min.

2.2. Procedures for fabrication of super-repellent coating on cotton fabrics

2.2.1. Preparation of zirconia solution and water-soluble emulsion of siloxane

Initially, ZP acetylacetone solution was synthesized according to previous report [11]. In brief 9.4 g ZP was dissolved in 1-butanol (9.4 g) in a beaker and added into a mixture of acetylacetone (1.4 g) with 1-butanol (9.0 g) and then resultant mixture was magnetically stirred for 1 h at room temperature. Subsequently, distilled water (1 g), 1-propanol (10 g), 1 N HNO_3 (0.002 g), 1-butanol (10 g) were added and again stirred at room temperature for 1 h.

A separate water based emulsion (7 wt%) of silane, siloxane and organic polymer was prepared by dilution of Silres BS 39 in distilled water and stirred for 30 min to obtain homogeneous emulsion for hydrophobic coating.

2.2.2. Preparation of zirconia-Siloxane (ZS) coated cotton fabrics (CCF)

The ZS coated cotton fabrics were fabricated according to simple dip coating method by immersing the cleaned and dried fabrics into the homogenized ZP acetylacetone solution for 2 h to allow the uniform coating. Then fabrics were dried at 60°C in a drying oven for 30 min and cured at 120°C for 1 h. Subsequently the fabric samples that were treated with ZP acetylacetone solution were subjected to hydrophobization with 7% (w/w) siloxane emulsion in water. They were dipped in respective emulsion for 1 h. In addition, for comparison cleaned and dried fabrics (without treated with

ZP acetylacetone solution) were also dipped in siloxane emulsion. Finally, the resulting fabrics were dried at 40 °C for overnight and kept at room temperature for 1–2 days. In addition, a small amount of ZP acetylacetone solution was taken in another beaker and subjected to heat treatment in a drying oven similar to coated fabric. After this drying process obtained powder (modified zirconia) was used for characterization purposes.

2.3. Characterizations

The surface morphology and elemental composition of coated cotton fabric (CCF) and uncoated cotton fabric (UCF) were examined by field emission scanning electron microscopy (FESEM, Zeiss, Germany, supra-40VP) equipped with an energy-dispersive X-ray (EDS) detector. Before analysis of surface morphology, a sputtering coater was used to place the thin layer of gold film on the samples to increase the conductivity of the samples. Transmission electron microscopic (TEM) measurements were carried out with Technai G², FEI operated at 200 kV to evaluate the particle size of the powder obtained after drying ZP acetylacetone solution. A small amount of the as-obtained powder was dispersed in absolute ethanol and a small droplet of the liquid obtained after ablation was deposited on carbon coated Cu grid. In order to identify the presence of functional group on the CCF and UCF, fourier transformed infrared (FTIR) spectra were recorded using FTIR spectrometer (KBR pellet method) in the range of 500–4000 cm⁻¹. The surface roughness of the uncoated and coated cotton fabric was evaluated by optical profilometer (NanoMap 1000 WLI). X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultra-high vacuum chamber using PHI 5000 Versa Prob II, FEI Inc. spectrometer to analyse the topmost surface composition and chemical state of each sample. All of the XPS spectra were acquired using Al K α radiation (1486.6 eV) at room temperature.

2.4. Evaluation of wettability with various surface tension liquids on coated surface and surface energy measurements

The surface wetting properties such as superhydrophobicity of CCF was evaluated by measuring contact angle (CA) and sliding angle (SA) of various liquids such as water, 2% isopropyl alcohol in deionized water, 5% isopropyl alcohol in deionized water, and ethylene glycol whose surface tension ranges between 72.8–47.7 mN/m [7,24]. The CA and SA were measured by a goniometer (OCA 20, dataphysics, Germany) instrument using sessile liquid drop method with 5 μ L volume of liquid drop at the room temperature. The values of CA and SA were measured in five different positions and the mean value of the contact angles was taken and images were captured.

The value of surface energy (γ_s) of a solid is a contribution of the polar (γ_s^p) and dispersive (γ_s^d) components, which can be described by the following equation [25–27]:

$$\gamma_s = \gamma_s^p + \gamma_s^d$$

The approach of Young, Owens and Wendt allows estimation of the surface energy of a solid, and its polar and dispersion fractions by following a straight line equation in the form of $y = c + mx$: [27]

$$\frac{\gamma_l (1 + \cos\theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^d} + \sqrt{\gamma_s^p} \sqrt{\frac{\gamma_l^p}{\gamma_l^d}} \rightarrow y = c + mx$$

In the above equation, γ_l^p and γ_l^d are the polar and dispersive components of liquid surface energy and similarly, γ_s^p and γ_s^d are the unknown polar and dispersive surface energies of the solid. In order to measure these unknown components of solid surface energy, a plot between Y and X using different liquid of known γ_l^p and γ_l^d val-

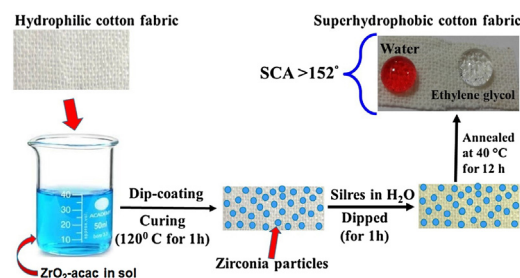


Fig. 1. Schematic representation of procedure for the fabrication of super-repellent fabric via dip coating approach.

ues (water, glycerol and ethylene glycol) gives a straight line. Thus the intercept (c) and slope (m) of the obtained linear regression equation give the value of dispersive and polar surface energies of the solid [25–27].

2.5. Evaluation of coating durability

The stability of the coating on CCF was examined by the measurements of water contact angle (WCA) after the treatments of CCF with various tests such as chemical stability, U.V. irradiation stability, sand paper abrasion test, and adhesive tape tear test with repetitions. In the chemical stability test the CCF was immersed into an acidic solution (pH=2) and in a basic solution (pH=12) for 24 h as well as treated in boiling water at 70 °C for 1 h. In the U.V. irradiation test an UV chamber equipped with two 8 W ultraviolet ($\lambda = 365$ nm) low-pressure quartz glass ultraviolet lamp was used for irradiation. The distance between the UV light source and the samples was approximately 5 cm. The samples were placed in the UV chamber up to 72 h and the contact angles of the samples were measured every 24 h. To study further, the CCF was pasted onto an adhesive tape and then torn by the tape. This process of tear adhesive tape test was carried out repeatedly, and the corresponding water contact angle after each test was recorded. The CCF was also subjected through an abrasion test where the fabric was dragged facing the 1200 mesh sand paper surface along one direction (about 20 cm). The test was repeated several times and corresponding WCA was recorded after each test.

2.6. Evaluation of self-cleaning properties of the CCF

In order to evaluate the self-cleaning ability of the CCF, two different types of solid particles (phenosafranin and sudan blue (III) dye) were sprinkled over a CCF specimen that was fixed on a support. Then liquid droplets were poured onto the surface in order to clean the contaminated surface, wherein liquid droplets absorb solid particles and removing them from coated CCF surface (video was recorded).

3. Results and discussion

3.1. Surface morphology and chemical composition

Fig. 1 illustrates the fabrication process of the super-repellent surface on a cotton fabric via a facile and eco-friendly strategy using zirconia particles with water-soluble siloxane emulsion. The fabrication method is inexpensive and very simple (without using any sophisticated equipment). The as-obtained coated cotton fabric (CCF) was characterized by different methods to determine their morphological and chemical properties.

The hierarchical surface structure is a very essential requirement for a surface to have superhydrophobic property [28]. The surface morphologies of CCF and UCF were analyzed by FESEM

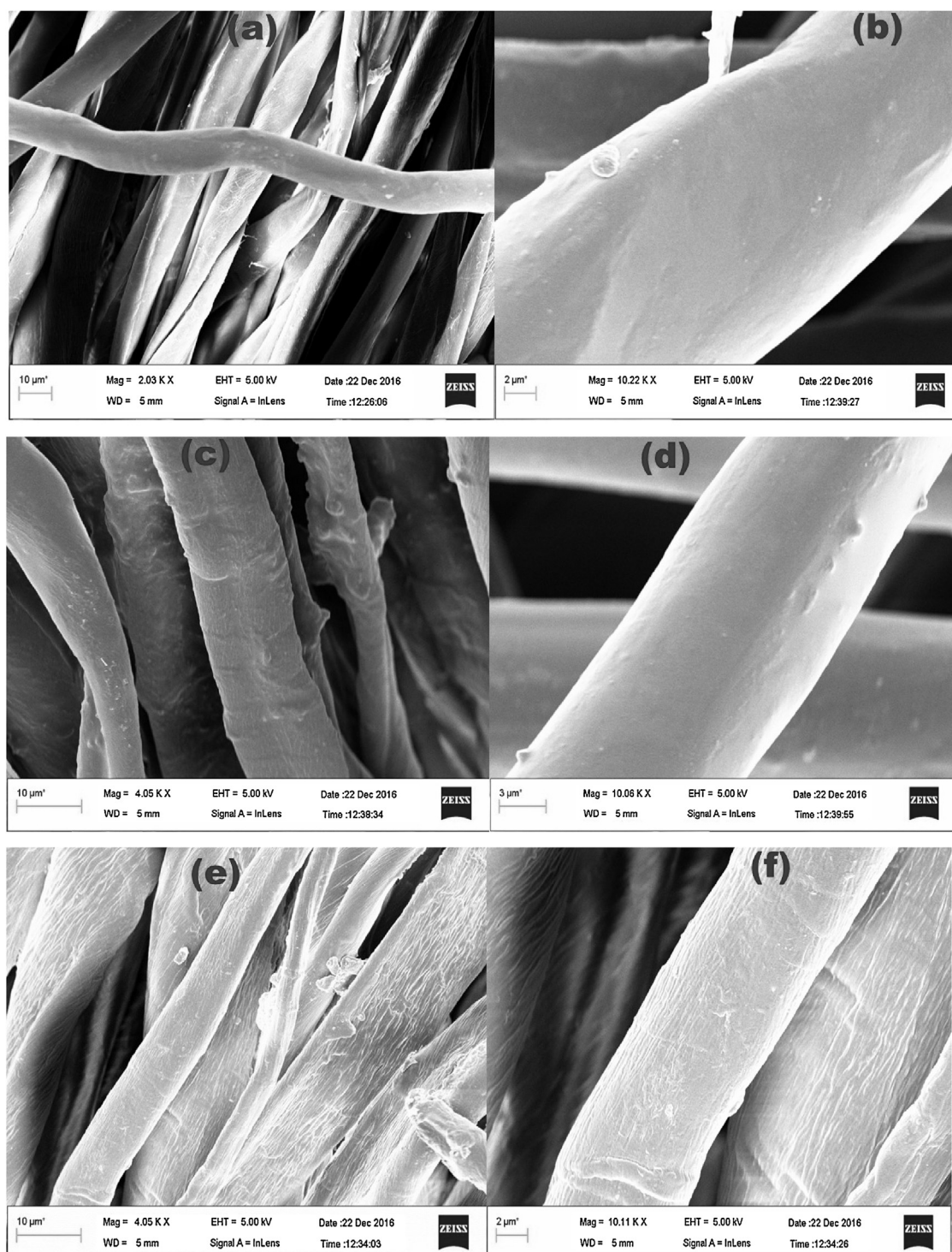


Fig. 2. SEM images of the uncoated cotton fabric in (a) low and (b) high magnification, SEM images of pure siloxane coated cotton fabric in (c) low and (d) high magnification and SEM images of zirconia-siloxane coated cotton fabric in (e) low and (f) high magnifications.

(shown in Fig. 2a–f). Fig. 2a–b show the SEM image of UCF under low and high magnification, Fig. 2c–d show the SEM image of pure siloxane (without particles) coated fabric under low and high magnification, respectively. Unlike UCF, a continuous film was deposited on the fabric coated with pure siloxane. Furthermore, the effect of zirconia particles with the siloxane on the structure of coatings is revealed by the SEM images of CCF shown in Fig. 2e–f. It is evident from the figures, that the surfaces of CCF are rougher than uncoated original fabric. This is primarily attributed

to the homogeneous deposition and distribution of coating materials within the gap between the fibers of the cotton fabric [11,18].

To further examine the changes in surface roughness of cotton fabric before and after the zirconia-siloxane coating, optical profilometer was used. Fig. 3a–b presents the images of optical profilometer, which verified that the cotton fabric significantly increased its surface roughness after zirconia-siloxane coating.

The EDS analyses of UCF, pure siloxane coated and zirconia-siloxane coated cotton fabric (CCF) were carried out to analyze the

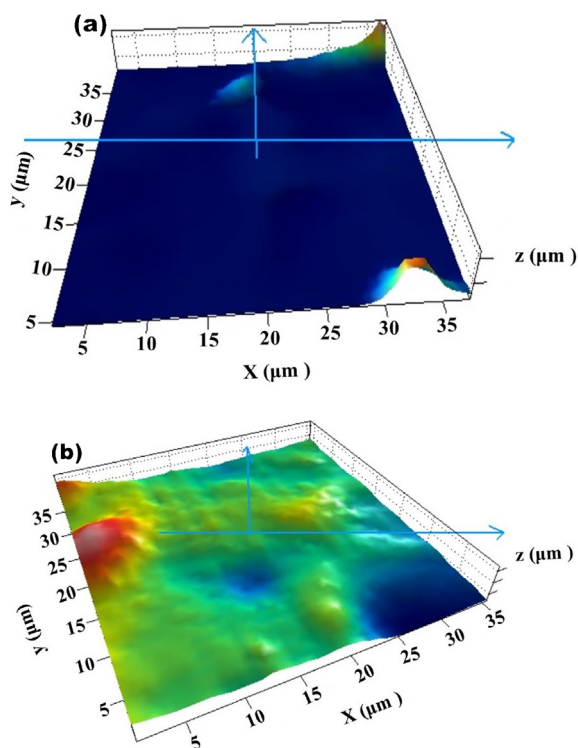


Fig. 3. Optical profiler images of the surface of (a) uncoated cotton fabric, (b) zirconia-siloxane coated cotton fabric.

element content on the surface. Fig. 4a–c show the EDS spectra of UCF, siloxane coated cotton fabric and zirconia-siloxane cotton fabrics respectively, which are acquired from different portions of the materials. The obtained spectrum displays the peak area of Si elements present in siloxane coated fabric (spectrum 4b) and Zr, Si,

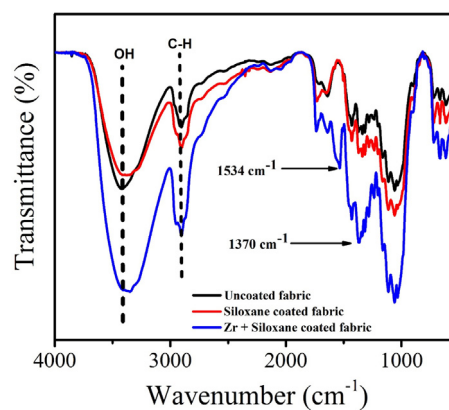


Fig. 5. FTIR spectra of the uncoated, pure siloxane coated and zirconia-siloxane coated cotton fabrics (CCF).

elements in zirconia-siloxane coated fabric (spectrum 4c), confirming the presence of these elements on the coated surfaces. The TEM image of zirconia based particles in Fig. 4(d) shows that particles are almost irregular in shape and display sizes less than 20 nm.

The FTIR spectroscopy is a powerful tool to investigate the functional groups present in the coating [11,29]. In order to understand the chemical modification underwent by the cotton fabric upon treatment, FTIR was used. Fig. 5 shows the FTIR spectra of UCF, pure siloxane coated fabric and zirconia-siloxane coated fabric (CCF) over the range 4000–500 cm^{-1} . We observed two peaks at 3400 cm^{-1} and 2917 cm^{-1} in the FTIR spectra of CCF, corresponding to the –OH and C–H stretching vibrations, respectively [5]. After coating on fabric with zirconia-siloxane, the peaks around 1370 and 1534 cm^{-1} indicate the presence of $\text{SiOCH}(\text{CH}_3)_2$ and complex of Zr with acetyl acetone, respectively [11,30]. Thus, the FTIR results indicate the successful synthesis of zirconia-siloxane coated fabric samples.

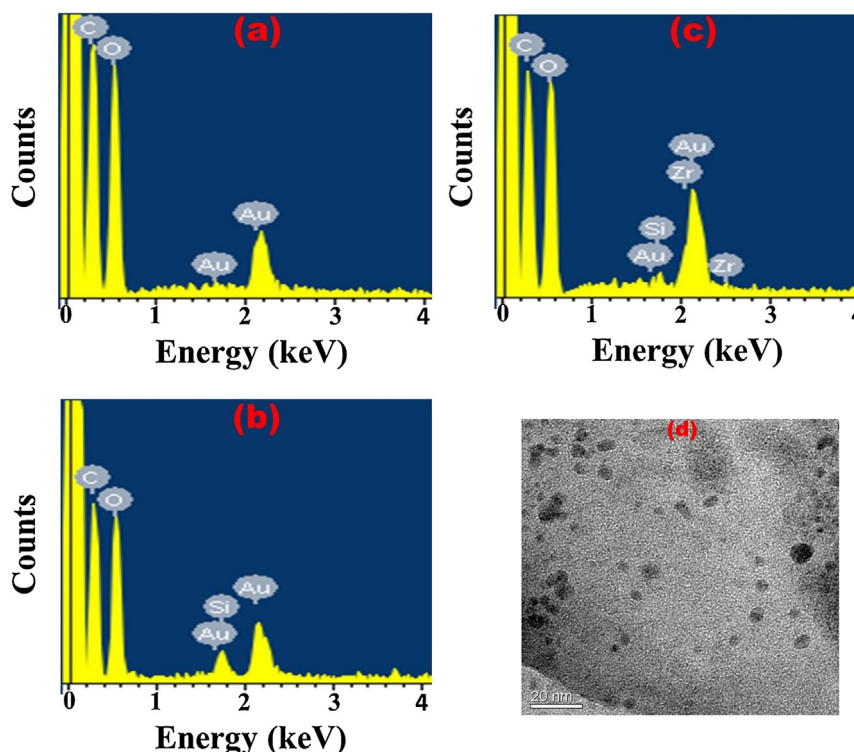


Fig. 4. Magnified EDS spectra of (a) the uncoated cotton fabric (b) of pure siloxane coated cotton fabric coated cotton fabric (c) of zirconia-siloxane coated cotton fabric and (d) TEM image of zirconia based particles.

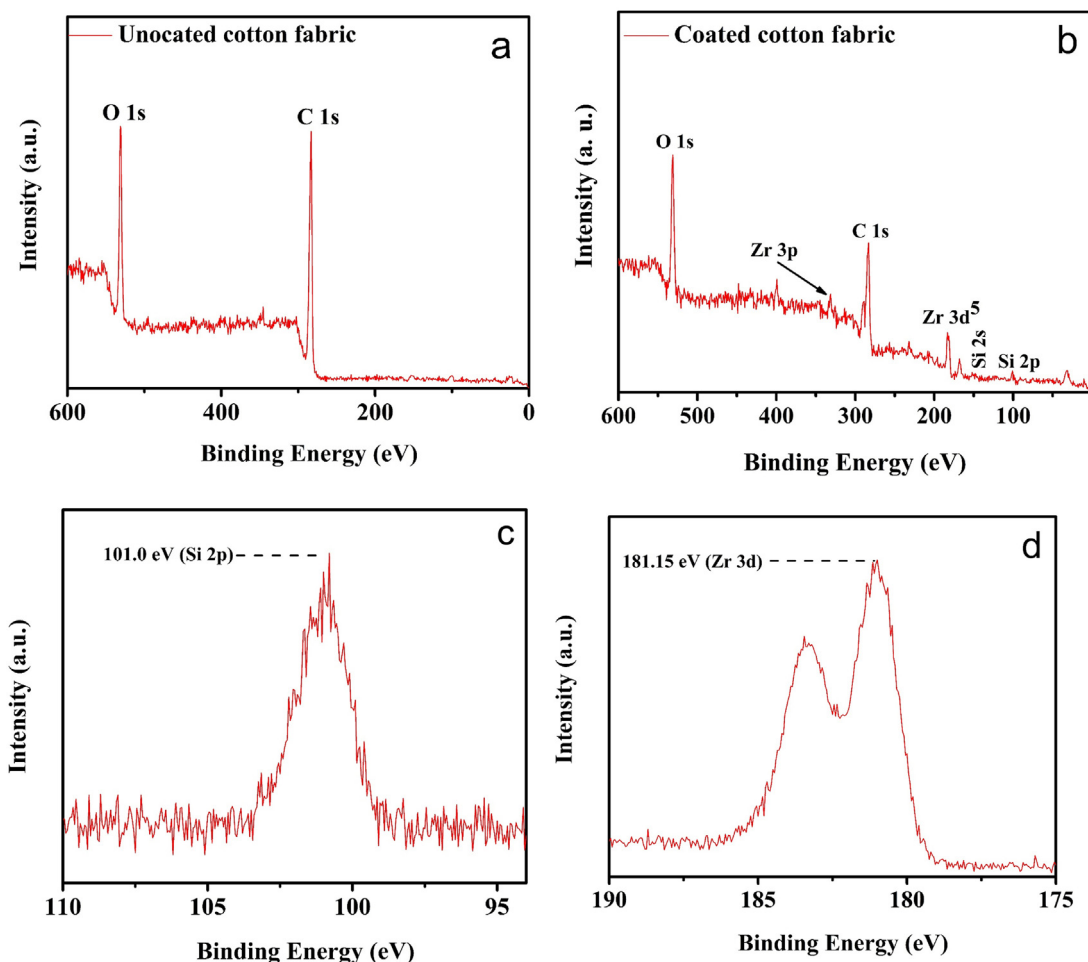


Fig. 6. XPS spectra of (a) uncoated cotton fabric, (b) zirconia-siloxane coated cotton fabrics, (c) high resolution of Si 2p peak, (d) high resolution of Zr 3d peak.

Table 1

Wettability of various surface tension liquids on cotton fabric coated with pure siloxane and Zr + Siloxane (CCF).

Liquids	Surface tension (mN/m)	Static contact angles (°)		Sliding angle (°)	
		Pure siloxane	Zr + Siloxane	Pure siloxane	Zr + Siloxane
Water	72.8	142	158 ± 1	–	8
2% isopropyl alcohol in water	59	140	155 ± 1	–	8
5% isopropyl alcohol in water	50	135	153 ± 1	–	9
Ethylene glycol	47.7	132	152 ± 1	–	9

The chemical composition of cotton fabric before and after zirconia-siloxane coating was examined by XPS (Fig. 6a–d) [5]. As displayed in Fig. 6a, the XPS survey spectra of UCF, only showed C and O signals. After zirconia-siloxane coating on cotton fabric, new peaks of the elements Zr (Zr 3d, 181.12 eV) and Si (Si 2p, 101.0 eV and Si 2s 152.0 eV) appeared (Fig. 6b) [5,31]. In addition, high resolution of Si 2p and Zr 3d peaks are shown in Fig. 6c–d. The results confirmed that cotton fabric was fully covered by zirconia-siloxane coating with strengthened intensity of the peaks. These results are consistent with that of EDS and FTIR studies [5].

3.2. Liquid repellency of the obtained coated surface

In order to evaluate the liquid-repellency, the contact angle (CA) and sliding angle (SA) were measured on the surface of pure siloxane and zirconia-siloxane coated fabric using liquids of the various surface tensions (2% v/v, isopropyl alcohol in deionized water: 59.0 mN/m, 5% v/v, isopropyl alcohol in deionized

water: 50.0 mN/m, and ethylene glycol: 47.7 mN/m) in addition to water (72.3 mN/m) [7,24]. The wettability of various surface tension liquids on cotton fabric coated with pure siloxane and zirconia-siloxane are shown in Table 1. Interestingly, the zirconia-siloxane coated fabric shows the super-repellency with CA of >151°, with all test solution of liquids. In addition, the droplets of these liquids were rolled off with a sliding angle of <9°, showing the Cassie–Baxter state. In contrast, the surface of cotton fabric coated with pure siloxane (without nanoparticles) has obtained and 142°, 140°, 135° and 132° with respect to test solutions such as water, 2% v/v, isopropyl alcohol in deionized water, 5% v/v, isopropyl alcohol in deionized water and ethylene glycol, respectively. The obtained results implying that super-repellency is achieved on zirconia-siloxane coated fabric by the significant role of zirconia particles with siloxane. The hybrid zirconia-siloxane coating enhanced the roughness feature to some extent endowing the super-repellent surface on cotton fabric [30]. Hence, the coating on CCF surface showed similarity to the leafhopper surface coating with respect

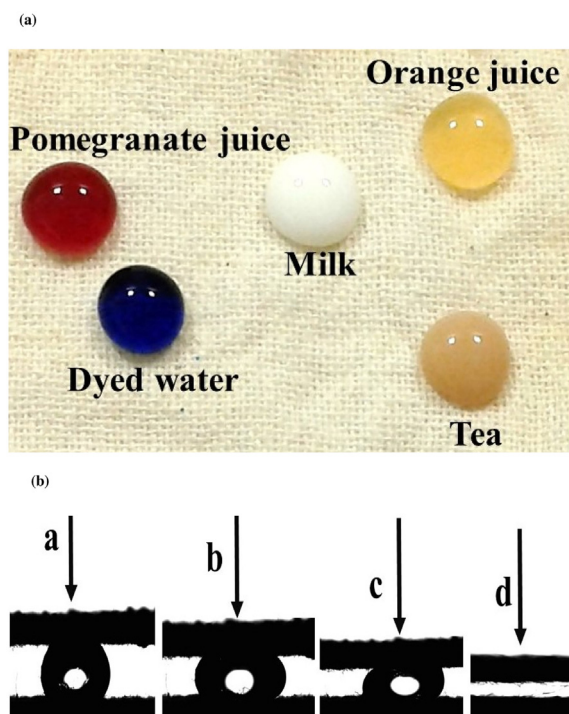


Fig. 7. (a) Droplets of the common household liquids standing on the cotton fabric: demonstrating the superhydrophobicity of the coated fabric. (b) Stability of Cassie–Baxter state. (a–d) behaviour of a 5 µL water droplet squeezed between two super-repellent fabric.

Table 2
Wettability of CCF using very low surface tension fluids.

Tested fluid	Surface tension (mN/m)	SCA (°)	SA (°)
Dodecyl benzene	30.70	Wetted	No
Ethyl benzene	29.70	Wetted	No
Toluene	28.40	Wetted	No
Dichloromethane	26.50	Wetted	No
Ethanol	22.10	Wetted	No
<i>n</i> -hexane	18.43	Wetted	No

to repellency of liquid such as water and ethylene glycol with CA >150° [7]. The observed super-repellency of the CCF towards water, 2% isopropyl alcohol in deionized water, 5% isopropyl alcohol in deionized water and ethylene glycol is attributed to the formation of continuous rough structure and very low surface energy of the CCF [7,32].

The latter can be confirmed by calculating the surface free energy of the CCF with polar and dispersion fractions from the method of Young, Owens and Wendt. The CCF possesses very low surface free energy per unit area of 0.25 mJ m⁻², with polar and dispersion components of 0.031 and 0.22 mJ m⁻², respectively. It should be noted that the surface free energy per unit area of the CCF is substantially lower than the recently reported materials for oil–water separation work of Siddiqui et al. [27], which is primarily because of lower dispersion components. This is attributed to the coating of carbon nanofiber on the surface.

In addition, the coated fabrics not only exhibited excellent superhydrophobicity with water, but also display excellent liquid repellency against common household liquids including milk, tea, orange and pomegranate juice including dyed water. Fig. 7(a) shows the formation of spherical shape droplets of these common household liquids on the surface of CCF [11].

Furthermore, the wettability of the CCF was evaluated with other liquids having surface tension <47.0 mN/m, as can be seen in Table 2. The surface was fully wetted with the contacting liquids of

lower surface tension from 30.70 to 18.43 mN/m, indicating that the three phase system (solid–air–liquid) totally collapsed. Thus the developed CCF got completely wetted during the contact with ethanol. This behavior of CCF surface is akin to that seen for the leafhopper surface [7].

The reason behind this phenomenon is that in order to show liquid repellency from a surface, the balance of three-phase system interface should be maintained until a certain impalement pressure reached [6]. The relation between this impalement pressure and surface tension of liquid can be expressed as follows:

$$P \approx \frac{2\gamma R}{r^2} \sin^2 \frac{\Theta_M}{2}$$

where p is the impalement pressure and γ is the surface tension of the liquid, r is the minimal distance between protrusions, R is the radius of the spherical aggregates and Θ_M is the advancing contact angle of the liquid on a flat surface. As suggested by this equation, in order to balance three phase (solid–air–liquid) interface a certain impalement pressure is needed and this pressure is directly proportional to the surface tension of the respective liquids which are considered in three phase interface. Thus a liquid with low surface tension such as toluene (28.40 mN/m), unlike water, could easily replace the air, which gets trapped in rough or porous structure and ultimately cause the transition from Cassie–Baxter state to the wetted Wenzel state [6].

3.3. Stability of Cassie–Baxter state

The Cassie–Baxter state describes the situation when droplet of liquid is overhung on the topside of the solid surface structure and air is trapped underneath, whereas in Wenzel state liquid completely penetrates into the structured surface [1]. However, the Cassie state may become unstable, as the air layer underneath the droplets disrupted under certain conditions such as when subjected to high pressure or when encountering liquids with impurities. In order to investigate the stability of Cassie–Baxter state on the surface of CCF, squeezing of water droplets confined between two surfaces of CCF against external pressure was performed. Fig. 7b, shows the sequence of squeezing of water droplets and demonstrate the behavior of water droplet after the treatment. It was observed that, in the presence of external pressure, although water droplets turn flat but does not wet the surface of CCF and finally water droplets slip away easily from the surface of CCF during this process, demonstrating the stability of Cassie–Baxter state [33]. This could be probably due to generation of roughness of grooves by the combinational treatment of siloxane with zirconia particles [30]. In addition, it was observed that even after this process water droplet formed complete sphere on the surface of CCF with CA >152°, exhibiting its excellent superhydrophobicity.

3.4. Durability of superhydrophobic coating in harsh environment

The stability of super-repellent coating on the treated surface is an essential factor for the practical applications under harsh environment condition [12,18]. In our daily life U.V. irradiation from outer sunlight is very common, and it significantly affects the stability of coating on superhydrophobic surfaces [11,34]. “U.V. irradiation tests were conducted to examine the stability of coating, developed in this work, under the influence of U.V. light. In the UV durability tests, the cotton fabric coated with siloxane material only (no particles) and cotton fabric coated with siloxane + particles were placed in an UV chamber, equipped with two 8 W ultraviolet ($\lambda = 365$ nm) low-pressure quartz glass ultraviolet lamp. The samples were exposed to U. V. light in the UV chamber up to 72 h and the contact angles of the samples were measured every 24 h. We notice that upon exposure of U.V. irradiation for a long time up to 72 h on

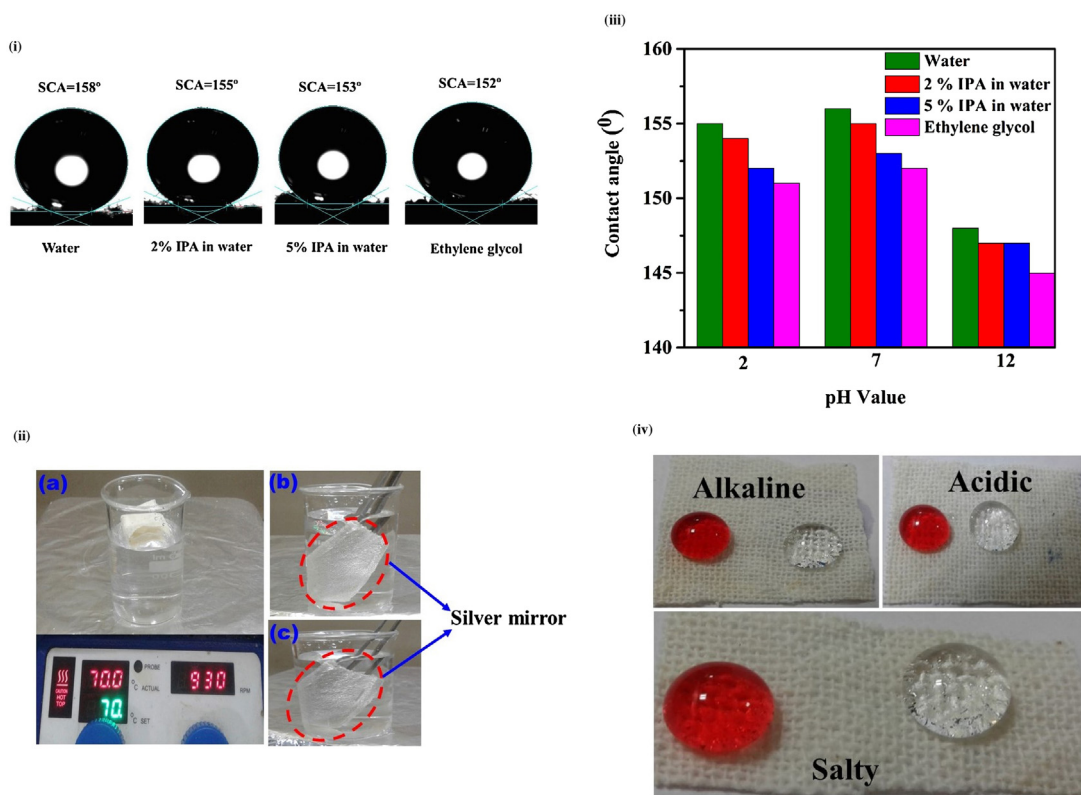


Fig. 8. (i) Contact angles of four tested liquids on coated cotton fabric after U.V. irradiation for 72 h. (ii) (a) Repellency of CCF towards water at 70 °C, presence of entrapped air (silver mirror) on CCF surface at (b) 30 °C and at (c) 70 °C. (iii) Contact angle of four tested liquids on CCF surface after 24 h of immersion in acidic, salty and alkaline solutions. (iv) Optical images of water (red color) and ethylene glycol (colorless) droplets on CCF surface after 24 h of immersion in acidic, salty and alkaline solutions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the surface of both coated fabrics, there is hardly any significant change in contact angle with respect to all four test liquids (water, 2% isopropyl alcohol in deionized water, 5% isopropyl alcohol in deionized water, and ethylene glycol), suggesting a superior UV-durability. Fig. 8(i) shows the contact angles of all four tested liquids on cotton fabric coated with siloxane + particles after U.V. irradiation for 72 h. The figures related to contact angle of liquids on the surface of fabric coated with siloxane material only (no particles) are not shown due to brevity”.

The mechanical durability of superhydrophobic coating was further examined by the sand paper abrasion test [12,35,36]. In this test, sand paper (1200 mesh) worked as abrasion surface and CCF was placed faced-down onto sand paper under loading of 100 g and dragged forward along one direction (about 20 cm). The test was repeated 20 times for the same coated sample. After the abrasion test, the WCA of the CCF sample was found >150° with respect to all four test liquids, indicating the good mechanical robustness of the coating against abrasion.

In addition to the U.V. irradiation and abrasion resistance test, the durability of CCF was further assessed by the treatment of CCF in boiling water for 1 h at 70 °C. Generally, due to the long term contact of water droplets with superhydrophobic coated surface at higher temperature, causes the replacement of entrapped air from the roughness grooves of the modified surface, resulting in loss of hydrophobicity and coated surface get wet [7]. After being treated with boiling water for 1 h (Fig. 8(ii)), the CCF was floated on water surface and no wetting was observed. Moreover, upon forcefully immersing into water, a shiny layer (air packets) was formed at the fabric-water interface. The water contact angle and sliding angle remains higher than 150° and lower than 10° respectively, demonstrating the stability of the coating on fabric [7]. In addition, we observed that the CCF maintain its color and flexibility similar

to UCF after treatment water at 70 °C. Moreover, we found light yellowish color on coated fabric on prolonged thermal treatment (>2–6 h) at higher temperature (>150 °C) due to the deterioration of cellulose components of the cotton fabric [18]. However, superhydrophobicity of the coated fabric remain unaffected.

In addition, the chemical stability of superhydrophobic coating was also qualitatively assessed by measuring CA after immersing them into acidic (pH=2), salty (1 molar NaCl solution) and alkaline (pH=12) solutions (Fig. 8(iii) [5,11]. From Fig. 8(iii), it can be seen that after 24 h, immersion of CCF in acidic and salty solutions the CA remained >150° with respect to all four test liquids, whereas in case of strong alkaline solution, slight change was observed (WCA ~ 145°). Moreover, it was observed that water droplets formed complete sphere on the surface of CCF, even after such long period of immersion into the strong acidic and alkaline solutions (Fig. 8(iv)). This results further demonstrate its excellent durability of coating against corrosive water environment.

The durability of coating on CCF was also assessed by the repeated tear test with an adhesive tape [11]. In this test, the cotton surface was pasted onto an adhesive tape, and then it was peeled off (see Fig. 9). The developed material remained super-repellent with respect to all four test liquids even after repetition of the tear test with an adhesive test for 20 cycles, with CA of >150°. Thus results of the study demonstrating the excellent stability of the coating on cotton fabric.

3.5. Self-cleaning properties of the coated fabric

The self-cleaning ability of CCF was established by pouring some drops of water to the phenosafranin dye (hydrophilic) and sudan blue (III) dye (hydrophobic) powder contaminated CCF surface (see Videos S1 and S2 in the online version at DOI: <http://dx.doi.org>).

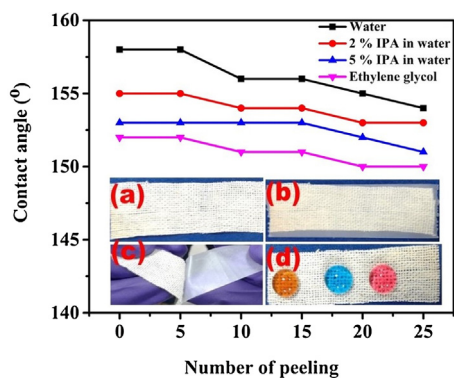


Fig. 9. Water contact angles of superhydrophobic fabric after repeated tear tests. The inset depicts the tear process (a) piece of fabric, (b) the fabric pasted onto an adhesive tape, (c) fabric peeled off the adhesive tape, (d) water droplet on the fabric after peeling off the adhesive tape.

[org/10.1016/j.apsusc.2017.04.148](http://dx.doi.org/10.1016/j.apsusc.2017.04.148) [24]. The Videos S1 and S2 in the version at DOI: <http://dx.doi.org/10.1016/j.apsusc.2017.04.148>, display the removal of phenosafranin and sudan blue (III) dye powder from the CCF surface using water droplets, respectively. Park et al. [24] reported that cleaning of hydrophobic particles from the hydrophobic surface using water droplets is difficult if the adhesion between hydrophobic particles and hydrophobic surface is higher as compared to that between hydrophobic particles and water droplets. However, in our case it was observed that water droplets rolled off immediately on the surface of superhydrophobic surface and making the surface free of dyes (phenosafranin and sudan blue) without any staining (see Videos S1 and S2 in the online version at DOI: <http://dx.doi.org/10.1016/j.apsusc.2017.04.148>). The above experimental finding clearly illustrates the self-cleaning, and water repelling properties of the CCF (Fig. 10a). However, on the surface of UCF phenosafranin dye powder adhered to the surface and was not cleaned off in a similar way.

To study further, rolling of water droplets on the surface of CCF was captured by the high resolution camera of Goniometer with a fixed angle of 8° (see Video S3 in the online version at DOI: <http://dx.doi.org/10.1016/j.apsusc.2017.04.148>). It was observed that CCF showed the self-cleaning behavior similar to lotus leaf, as within 0.5 s water droplet quickly slides on the CCF surface [11,23]. Furthermore, self-cleaning quality of CCF was demonstrated by repeated dip test in solution containing phenosafranin dye aqueous solution (red colored) and tea (see Videos S4 and S5 in the online version at DOI: <http://dx.doi.org/10.1016/j.apsusc.2017.04.148>) [23]. Due to self-cleaning property surface of CCF was remained dry and fully cleaned after repeated dip test. This observation indicates the good self-cleaning property of the CCF.

3.6. Application of coated fabric in oil-water separation

The removal and collection of oily pollutants from water is of vital environmental concern [11]. The as-prepared CCF demonstrated super-repency (with liquid which have surface tension >47.0 mN/m) and superoleophilic behavior (with organic solvent which have surface tension <47.0 mN/m). In other words, the CCF shows water repency even this is wetted with common organic solvents. Thus, the CCF can be used as membrane to separate water from mixture of water with common organic solvents. Generally, most of the superhydrophobic materials are unable to show water repency when their surfaces are blocked with other oily liquids [7].

To illustrate the oil-water separation properties, we have used the CCF as “filter” as shown in Fig. 10b. For this experiment, a mixture of dodecyl benzene and water (1:1 volume ratio) was

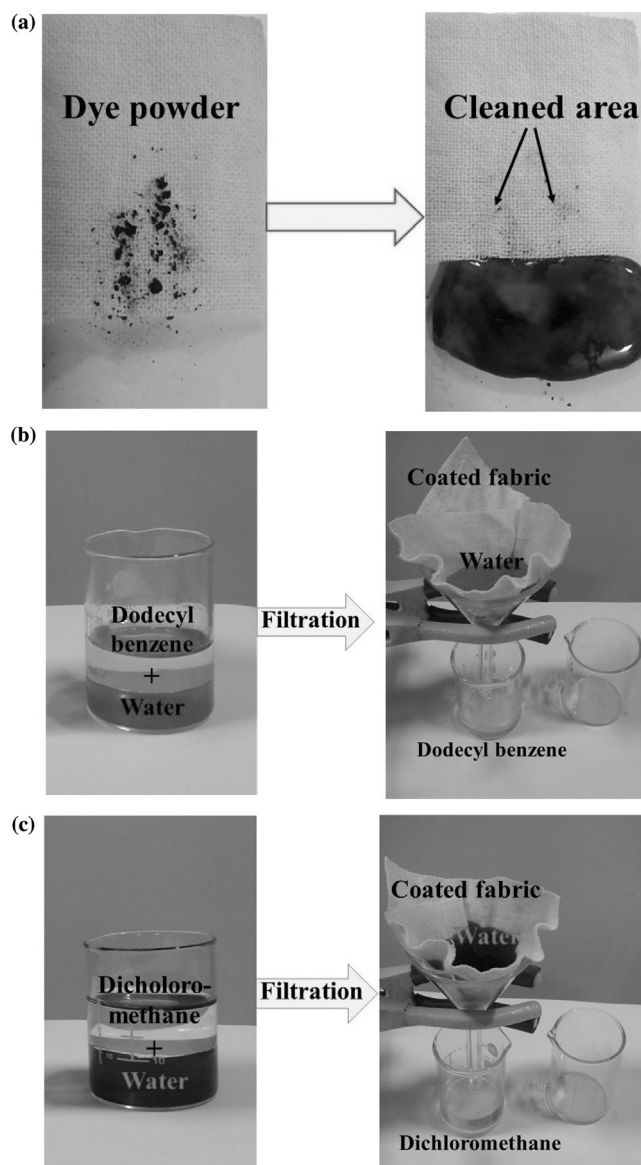


Fig. 10. (a) Images of self-cleaning effect using water on CCF surface. (b) Optical photographs showing the separation process for dodecyl benzene and water mixture through coated cotton fabric. (c) Optical photographs showing the separation process for dichloromethane and water mixture through coated cotton fabric.

poured onto the surface of CCF after proper mixing. Water was colored red by adding phenosafranin dye for clear visibility. It was seen that dodecyl benzene (colorless) immediately permeated through the CCF into the collecting vessel without any external force due to effect of gravity. On the other hand, water (dyed with dye) was not permeated by the modified fabric due to superhydrophobic nature of the fabric (see Video S6 in the online version at DOI: <http://dx.doi.org/10.1016/j.apsusc.2017.04.148>). The separation efficiency is more than 99% even after repetition of the filtration process up to 10 cycles at ambient temperature. The separation efficiency was calculated by the taking the mass ratio between water collected after separation process and water taken initially in the oil-water mixture. Similar behavior was observed for another mixture of dichloromethane and water (1:1 volume ratio) as illustrated in Fig. 10c. In this mixture water was colored blue by adding methylene blue dye for clear visibility (see Video S7 in the online version at DOI: <http://dx.doi.org/10.1016/j.apsusc.2017.04.148>). Thus as-fabricated fabrics exhibited dual nature like superhydrophobicity and superoleophilicity behavior simultaneously. Due

to this ability the CCF can be used for selective separation of oil pollutant from oil/water mixtures.

Apart from this dual nature (superhydrophobicity and superoleophilicity), it is fascinating to achieve super-repellency to liquids having surface tension >47.0 mN/m like water, mixtures of isopropyl alcohol with deionized water (2% and 5%), and ethylene glycol similar to the brochosome coating on leafhopper. Thus the results revealed that the CCF has significant potential for wide range of practical applications.

4. Conclusions

In this study, we have successfully fabricated super-repellent fabric using zirconia particles in combination with siloxane material via simple and green dip coating approach. In order to assess the wettability of the CCF, the contact angles were measured using deionized water and liquids (ethylene glycol and mixture of isopropyl alcohol and deionized water) whose surface tension was >47.0 mN/m. The CCF showed super-repellency for these liquid with high static contact angle ($>150^\circ$) and low surface energy (<1.0 mJ m $^{-2}$) similar to the original leafhopper surface. An increase in the surface roughness, reduction of surface energy and lowering of hydroxyl functional group on the surface of cotton fabric are achieved by zirconia siloxane coating. Moreover, CCF exhibited stable superhydrophobicity against U.V. irradiation, abrasion test and solution having pH range from 2 to 12, indicating its usefulness in harsh environmental conditions. The effective self-cleaning ability of the CCF has been demonstrated by using hydrophilic and hydrophobic solid particles. In addition to this, the as-prepared CCF exhibited superoleophilicity with liquids, which have low surface tension as compared to ethylene glycol. Due to this ability, the CCF was used for efficiently separation of water/oil and organic solvent mixtures. We believe that the durable super-repellent zirconia-siloxane coated fabric can be used in many applications including anti-wetting, self-cleaning, support for aquatic floating devices and as a filtration material for rapid and continuous oil-water separation, under all conditions.

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