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Fabrication of zirconia based durable superhydrophobic–superoleophilic fabrics using non fluorinated materials for oil–water separation and water purification†

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In the present work, simple, inexpensive (without using any sophisticated equipment), durable superhydrophobic coatings on cotton fabrics with photocatalytic properties were achieved by the application of non-fluorinated hydrophobic reagents in combination with zirconia particles and subsequently AgBr modification. A hybrid mixture of hexadecyltrimethoxy silane and stearic acid was used as a hydrophobic reagent. The as-prepared coated fabrics not only displayed superhydrophobicity (water contact angle of $\sim 153^\circ$, water sliding angle $\sim 7^\circ$) and superoleophilic properties (oil contact angle of $\sim 0^\circ$) but also showed photocatalytic degradation of methylene blue under visible light illumination. The modified fabric can effectively separate a series of oil–water mixtures with high efficiency (>99%) even after repeated use for 10 cycles through an ordinary filtering process, without any noticeable change in efficiency. More importantly, the as-prepared coated fabric retained its superhydrophobicity and superoleophilicity under harsh environmental conditions (acidic, alkaline, salty, ultraviolet irradiation, and mechanical abrasion) and repeated tear testing with an adhesive tape. Thus, the superhydrophobic material presented in this work, with dual functionality, is a promising material for degrading organic pollutants in the water phase and in the treatment of oil spills.

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1. Introduction

The deterioration of water quality by the presence of insoluble and soluble organic contaminants is of vital environmental concern. The rapid expansion of industrial activity, such as oil production, oil deliveries, oil refining and petrochemical operation, has caused increasing issues such as oil spillage, and discharge of industrial sewage and oily water containing organic pollutants.¹ Millions of tons of refined oil and crude oil leak into the sea every year, which are significantly responsible for pollution in the natural environment, ecological damage, as well as great loss in energy.^{1–6} Oil contaminated water containing aqueous organic chemicals (dyes) not only responsible for severe ecological damage but also adversely affect the coastal species and human health through food chain.⁷ Hence, in order to environmental protection, it is of great significance to explore a simple, economical and effective method for separation of oil–water mixture as well as clean-up of soluble organic contaminants (dyes) from water.^{8,9}

In the recent past special wettable materials possessing superhydrophobic and superoleophilic properties such as metallic meshes, metal foam, polyurethane sponges, silicone sponges, graphene aerogels and fabrics are becoming a good choice in separation and collection of oil from oil–water mixture because of their specific surface properties and effective separation efficiency.^{1,10–13} Among these various materials, cotton fabric material bearing superhydrophobic and superoleophilic surfaces have been received significantly attention.¹⁰ This is mainly owing to its easy handling, high flexibility, environment friendly, low cost, biodegradability, high efficiency and easily scalable fabrication.^{14–17} To separate oil–water mixtures superhydrophobic cotton can be utilized as a filter as well as an adsorbent because of its flexibility.¹⁰

In order to prepare superhydrophobic surfaces, several physical and chemical methods including spin coating, electrospinning technique¹⁸ and dip coating,¹⁹ spraying, phase separation, plasma treatments, chemical vapor deposition method,²⁰ layer-by-layer technique^{21,22} and hydrothermal treatments have been reported in literature.²³ Among these methods, the dip coating method is a better method in comparison to other methods since it is an inexpensive, simple method, and offers an easy adjustment of chemical composition required for a surface to show superhydrophobic behaviors,^{17,24} while others

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methods need special equipments, reagents, high temperature and specific substrate for coating.²⁴

The combination of surface roughness and lowering the surface free energy are the key factors for constructing superhydrophobicity on surfaces. In order to fabricate superhydrophobic surfaces, addition of various nanoparticles such as silver,²⁵ SiO₂,²⁶ TiO₂,²⁷ Fe₃O₄, ZrO₂ (ref. 28) in combination with low surface energy materials such as fluorinated compounds and polymers have been reported in literature.^{10,29}

Very recently Xu *et al.* developed polydopamine coated superhydrophobic cotton fabric using silver (Ag) nanoparticles with 1H,1H,2H,2H-perfluorodecanethiol.²⁵ The oil–water separation efficiency and self-cleaning properties were intensively investigated. Lin *et al.* developed a superhydrophobic and superoleophobic cotton fabric, which was coated by SiO₂ nanoparticles with fluoropolymer (perfluoroalkyl ethyl acrylate).³⁰ Zhu *et al.* fabricated a superhydrophobic polyester fabric by coating with Ag nanoparticles followed by surface modification with 1H,1H,2H,2H-perfluorodecanethiol.³¹ The resulting fabric exhibited mechanical stability and easy repairability by a simple method. In addition, Zhou *et al.* reported a preparation of superhydrophobic and superoleophobic cotton fabric by incorporation of polyaniline with FeCl₃·6H₂O and 1H,1H,2H,2H-perfluorooctyltriethoxysilane using chemical vapour deposition method.¹⁶ In their study, modified cotton fabric prevents water to pass, whereas oil passes easily leading to a high separation efficiency. Although these coated cotton fabrics exhibit high performance on oil–water separation efficiency, fluorinated compounds were used for the coating. Fluorinated compounds, being expensive, are environmentally undesirable as they are nonbiodegradable (persistent pollutants). In addition, these compounds can easily react with other materials resulting in environmental contamination. For example, these compounds are found to suppress the nerve growth in children.³² In addition to detrimental effect of fluorinated compounds, the fabric materials based on it as discussed above cannot degrade the soluble organic pollutants from waste water. However, the separation of insoluble and degradation of soluble organic pollutants are the key steps in the waste water treatment process.

Photocatalytic activity on a surface is the another form of self-cleaning property in which organic compound can decompose chemically when exposed to the light.³³ Recently various photocatalyst such as TiO₂ and ZnO are using to efficiently treat the aqueous organic pollutant from wastewater.³⁴ Xu *et al.*³³ designed and synthesized super superhydrophobic cotton fabrics with photocatalytic self-cleaning property by the combination of SiO₂ and TiO₂. The resulting cotton exhibited recovery of its superhydrophobicity after U.V. irradiation for 4 h which was contaminated with oleic acid. However, the photodegradation of organic pollutant in waste water using TiO₂ is limited because of its activeness only in U.V. radiation. Hence for this phenomenon visible light photo catalyst are urgently required, which can utilize natural solar energy.

Beside the development of superhydrophobic cotton fabrics, long-term durability of superhydrophobic coating on cotton surface is also an essential requirement for suitable application

in oil–water separation. Coated cotton fabrics lose their superhydrophobic property easily during their applications in oil–water separation, due to the weak attachment between the cotton fibers and low surface energy materials.³² 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.²⁸

Therefore, keeping in view these issues, it is highly desirable to generate durable superhydrophobic materials that can separate oil from oil contaminated water (oil-spill mixtures and industrial waste waters) with the application of inexpensive and environmentally friendly materials. Herein, we fabricated superhydrophobic ($\theta > 150^\circ$) and superoleophilic cotton fabric by treating it with non fluorinated hydrophobic reagents (hexadecyltrimethoxy silane and stearic acid) in combination with zirconia particles, and subsequently AgBr modification *via* simple sol–gel dip coating process.

The high bond dissociation energy, thermal stability, mechanical strength and strong co-valent character of zirconia are reported in literature in comparison to other ceramic materials.²⁸ Hence the application of zirconia is more appropriate in terms of durability of superhydrophobic coating. In addition, silver bromide (AgBr) is a good visible light photocatalyst for the degradation of organic compounds because it enables to absorb sunlight of wavelength up to 480 nm or even longer.³⁵ The main objectives of this study were: (1) preparation of superhydrophobic and superoleophilic cotton fabric by an inexpensive and environmentally friendly chemical modification; (2) characterization of the product with SEM and FTIR technology; (3) evaluation of self-cleaning ability, durability of superhydrophobic coating, oil separation efficiency from oil–water mixture and photodegradation ability of water soluble organic contaminant.

2. Experimental section

2.1 Materials

Zirconium(IV) *n*-propoxide (ZP) in *n*-propanol (70%), hexadecyl trimethoxysilane (HDTMS, $\geq 85\%$), acetylacetone (acac, 99%) and stearic acid (SA, $\geq 95\%$) were purchased from Sigma Aldrich. 1-Propanol and 1-butanol were purchased from Merck. Nitric acid, oxalic acid (99%) and silver nitrate (AgNO₃, $\geq 99.7\%$) were purchased from Fisher Scientific. Methylene blue from RANKEM and cetyltrimethyl ammonium bromide (CTAB, 99%) was purchased from Loba Chemie. 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 dual functionality on cotton fabrics

2.2.1 Preparation of hydrophobic zirconia solution. Initially, ZP acetylacetone solution was synthesized according to previous report.²⁸ In brief 9.4 gram 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 HNO₃ (0.002 g), 1-butanol (10 g) were added and again stirred at room temperature for 1 h.

A separate hybrid solution for hydrophobization was prepared by the addition of 3.0% (w/w) HDTMS into ethanol solution containing 3.0% (w/w) SA under vigorous stirring at room temperature followed by the adjustment of pH to 3–5 using oxalic acid. This HDTMS/SA hybrid solution was then added to the ZP acetylacetone solution and stirred for 1 h for homogeneous mixing to obtain the final hydrophobic zirconia solution (Zr–HDTMS/SA).

2.2.2 Preparation of Zr–HDTMS/SA coated cotton fabrics.

The Zr–HDTMS/SA coated cotton fabrics were fabricated according to simple dip coating method by immersing the cleaned and dried fabrics into the homogenized Zr–HDTMS/SA 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.

2.2.3 Preparation of AgBr coated cotton fabrics. The Zr–HDTMS/SA coated cotton fabrics were again coated with AgBr *via* a successive ionic layer adsorption and reaction method. The Zr–HDTMS/SA coated cotton fabrics were immersed into 100 mL CTAB solution (16 mg mL⁻¹) at 60 °C for 5 h and subsequently dipped in aqueous solution of AgNO₃ (10 mg mL⁻¹) for 12 h. Finally, the resulting fabrics were dried at 105 °C for 1 h in an oven.

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. In order to identify the presence of functional group on the CCF, Fourier transformed infrared (FTIR) spectra were recorded using FTIR spectrometer (KBR pellet method) in the range of 500 to 4000 cm⁻¹.

2.4 Evaluation of superhydrophobicity

The surface wetting properties such as superhydrophobicity of CCF was evaluated by measuring water contact angle (WCA) and sliding angle (SA).²⁸ The WCA and SA were measured by a goniometer (OCA 20, dataphysics, Germany) instrument using sessile water drop method with 5 µL volume of deionized water drop at the room temperature. The values of WCA and SA were measured in five different positions and the mean value of the contact angles was taken and images were captured.

2.5 Evaluation of coating durability

The stability of the coating on CCF was examined by the measurements of water contact angles 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 10 days. 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 for up to 72 hours and the contact angles of the samples were measured every 24 hours. In order to examine the coating stability, 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 1500 mesh sand paper surface along one direction (about 20 cm). The test was repeated several times and corresponding WCA and SA were recorded after each test.

2.6 Application in oil–water separation

In order to investigate the oil separation property of the CCF from oil–water mixtures, filtering experiments were conducted because CCF exhibited excellent water repellency and oils were freely permeated through the surface of CCF at atmospheric pressure condition. In this study a mixture of diesel/water, *n*-hexane/water, hexadecane/water, dichloromethane/water, dodecyl benzene/water, chloroform/water and toluene/water were taken (1 : 1 v/v). The coated cotton fabric was placed in a funnel to act as a filter membrane. After mixing properly, the mixture of oil–water (1 : 1 v/v) was poured slowly onto the CCF and oil–water separation efficiency was calculated in each case by the measurements of weight ratio of water obtained after separation with respect to weight of original water taken initially in oil–water mixture.

2.7 Evaluation of photocatalytic activity

The photocatalytic activity of the coating on CCF was evaluated by the decolorization of methylene blue (MB) dye, a heterocyclic aromatic organic compound, in aqueous solution (conc. = 1.8×10^{-5} mol L⁻¹). Initially, CCF was placed in a funnel to act as a filter membrane and a 20 mL oil–water mixture (diesel 50% v/v, water was aqueous solution of MB dye) was poured on to the CCF. After complete separation of diesel from oil–water mixture, the separated MB dyed aqueous solution was poured into a glass Petri dish. A piece of CCF (6 × 6 cm) was immersed into the separated MB dyed aqueous solution and subsequently it was kept in dark for 30 min to reach adsorption–desorption equilibrium between dye molecule and photocatalyst. Then photodegradation test was performed using two LED lamps (each 18 W, PHILIPS) as a source of visible light.³⁶ The decomposition of MB solution was monitored by measuring the absorbance, using UV-VIS-NIR spectrophotometer (Agilent), until the absorbance curve reduces to the lowest level.

3. Results and discussion

3.1 Surface morphology and chemical composition

Fig. 1 illustrate the fabrication process of the superhydrophobic and superoleophilic cotton fabric by coating the bare cotton fabric with *in situ* synthesized zirconia sol followed by surface modification with HDTMS/SA hybrid solution for hydrophobization and with CTAB/AgNO₃ for photocatalytic activity. 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.¹⁰ The surface morphologies of CCF and UCF were analyzed by FESEM (shown in Fig. 2a–d). Fig. 2a and b show the SEM image of UCF under low and high magnification, respectively. Fig. 2c and d show the SEM images of CCF under low and high magnification, respectively. It is evident from the figures, that the surfaces of CCF are rougher than uncoated original fabric. This is primarily attributed to the homogeneously deposition and distribution of coating materials within the gap between the fibers of the cotton fabric.²⁸

The EDS analysis of CCF was carried out to analyze the element content on the surface. Fig. 3a and b show the EDS



Fig. 1 Schematic representation of the fabrication of superhydrophobic fabric via dip coating approach.

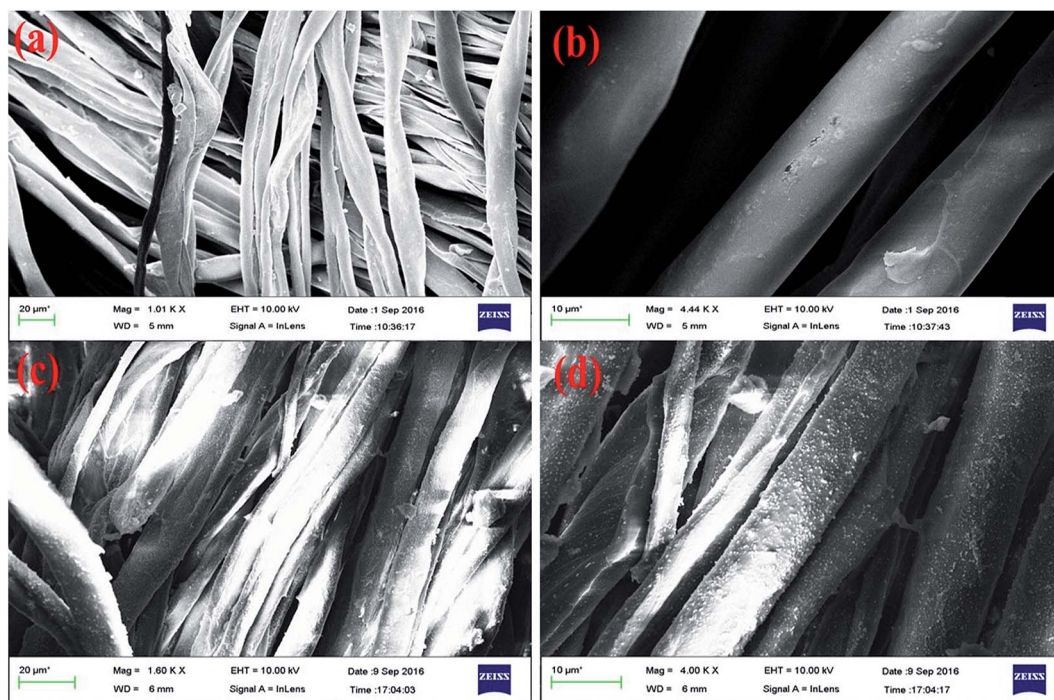


Fig. 2 SEM images of the bare cotton fabric in (a) low and (b) high magnification and SEM images of coated cotton fabric in (c) low and (d) high magnifications.

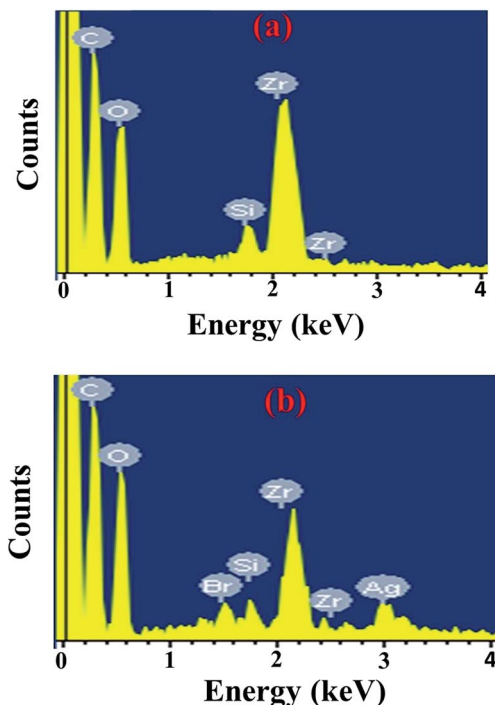


Fig. 3 Magnified EDS spectra of (a) Zr + HDTMS + SA coated cotton fabric and (b) of Zr + HDTMS + SA/AgBr coated cotton fabric.

spectra of Zr/HDTMS + SA coated cotton fabric and Zr/HDTMS + SA/AgBr coated cotton fabrics respectively, which are acquired from different portions of the materials. The obtained spectrum displays the peak area of Zr, Si elements present in Zr/HDTMS + SA coated fabric (spectrum Fig. 3a) and Zr, Si, Ag, Br elements in Zr/HDTMS + SA/AgBr coated fabric (spectrum Fig. 3b), confirming the presence of these elements on the coated surfaces.

The FTIR spectroscopy is a powerful tool to investigate the functional groups present in the coating.³⁷ In order to understand the chemical modification underwent by the cotton fabric upon treatment, FTIR was used. Fig. 4 shows the FTIR absorption spectra of CCF. Several characteristic peaks related to the vibrations and deformation of functional groups are obtained within the range 500 cm^{-1} to 4000 cm^{-1} .

In the FTIR spectra of CCF two peaks at 2916 cm^{-1} and 2850 cm^{-1} appeared, which indicate the presence of long chain hydrocarbon. These are assigned to the C–H symmetric and asymmetric vibrations of the long chain stearic acid and HDTMS molecule.^{26,38} In addition, three characteristic peaks at 1020 , 1534 and 1442 cm^{-1} strongly indicate the presence of Si–O–Si, complex of Zr with acetyl acetone and Zr–O–C, respectively.^{39,40} Moreover, the molecular water band appears at around 1640 cm^{-1} . This is the water used in the synthesis of coating material in the form of acid and/or base catalysts.⁴¹ The peak at around 664 cm^{-1} is assigned to the Zr–O–Zr bond.³⁹

3.2 Wetting behavior

The wettability of coated surfaces can be theoretically understood by Cassie equation.¹⁹

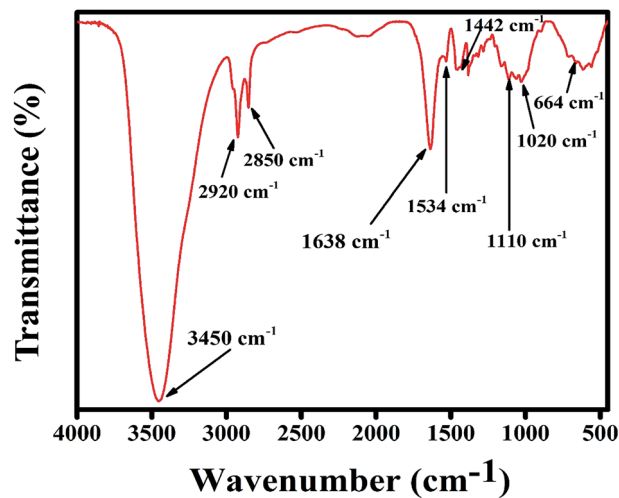


Fig. 4 FTIR spectra of the coated cotton fabrics (CCF).

$$\cos \theta^C = rf \cos \theta + f - 1 \quad (1)$$

where θ represent the local contact angle, θ^C is the measured contact angles, r is the roughness of the liquid–solid interface and f is the area fractions of the liquid–solid interface. As suggested by this equation, θ^C depends on both surface roughness and area fractions. The WCA for UCF and CCF was measured at least five different places and obtained mean value is reported as shown in Table 1. These results indicated that initially uncoated cotton fabric was hydrophilic ($\text{WCA} = 0^\circ$), when cotton fabric was treated with zirconia sol and alkyl hydrophobization agents, the WCA increased significantly. The highest WCA ($153 \pm 1^\circ$) was obtained for cotton fabric coated with Zr + HDTMS + SA system. This could be probably due to the combinational treatment of HDTMS and stearic acid with zirconia sol. A similar observation has also been reported by other workers.²⁶

To further test the superhydrophobicity of the material, a volume of $15\ \mu\text{L}$ dyed water (by phenosafranin dye powder) dripped on the surface of UCF and CCF. It was observed that UCF became completely wet with colored water, whereas dyed water float on the surface of CCF in the form of complete sphere drop as shown in Fig. 5a and b. The CCF exhibited the superhydrophobicity (high water repellency) with a high WCA of $\sim 153 \pm 1^\circ$ and low sliding angle (SA) $\sim 7.0^\circ$. Thus higher value of water contact angles signifies the conversion of raw cotton fabric from hydrophilic to superhydrophobic cotton fabric by the surface treatment using the dip coating process.

Table 1 Effect of coating on WCA, SA and OCA of coated cotton fabrics

Sample	WCA ($^\circ$)	SA ($^\circ$)	OCA ($^\circ$)
Bare cotton fabric	0	—	0
Zr + SA coated fabric	137 ± 1	—	0
Zr + HDTMS coated fabric	141 ± 1	—	0
Zr + HDTMS + SA coated cotton fabric	153 ± 1	7	0

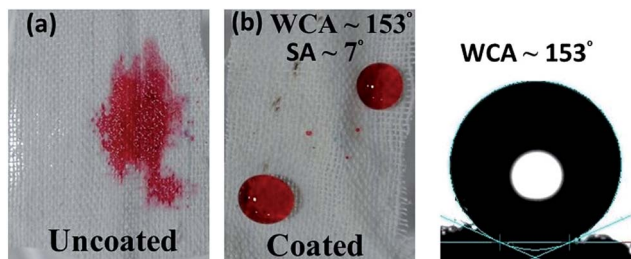


Fig. 5 Optical photographs of the dyed (phenosafranin) water drops on (a) uncoated fabrics and (b) coated fabrics: showing the superhydrophobicity of coated fabric.

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. Fig. 6a shows the formation of spherical shape droplets of these common household liquids on the surface CCF.

The self-cleaning ability of CCF was established by pouring some drops of water to the phenosafranin dye (hydrophilic) powder contaminated cotton surface (Fig. 6b).²⁸ It was observed that water droplets rolled off immediately on the surface of superhydrophobic surface and making the surface free of dye without any staining (see Video S1†). The above experimental finding clearly illustrates the self-cleaning, and water repealing properties of the CCF. However, on the surface of UCF phenosafranin dye powder was not removed in a similar way. Because of the low WCA, droplets of water wet the UCF surface. In addition, rolling of water droplets on the surface of CCF was captured by the high resolution camera of goniometer with a fixed angle of 7° (see Video S2†). It was observed that CCF showed the self-cleaning behavior similar to lotus leaf, as within

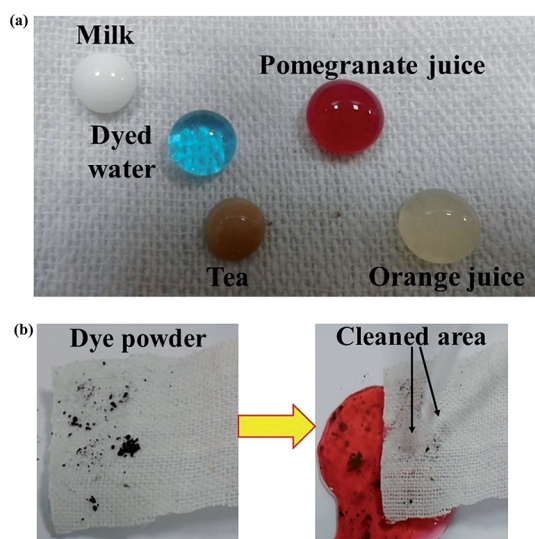


Fig. 6 (a) Droplets of the common household liquids standing on the cotton fabric: demonstrating the superhydrophobicity of the coated fabric, (b) optical images showing the self-cleaning process of superhydrophobic surface.

0.5 s water droplet quickly slides on the CCF surface.²³ Furthermore, self-cleaning quality of CCF was demonstrated by repeated dip test in aqueous solution of phenosafranin dye aqueous solution (red colored) (see Video S3†).²³ Due to self-cleaning property surface of CCF was fully cleaned after repeated dip test. Therefore, this CCF, which has good self-cleaning property, could find durable application in tackling environments during oil-water separation.

3.3 Durability of superhydrophobic coating

The stability of superhydrophobic coating on the treated surface is an essential factor for the practical applications under harsh environment condition.^{20,28} In our daily life U.V. irradiation from outer sunlight is very common, and it significantly affects the stability of coating on superhydrophobic surfaces.⁴² 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 CCF was 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 for up to 72 hours, the WCA and SA of the samples were measured every 24 hours. After U.V. irradiation for 72 h; the coatings still exhibited a WCA of 153.4° and SA of 7°, suggesting a superior UV-durability. Thus the CCF showed stronger UV-resistant ability (Fig. 7i).

The mechanical durability of superhydrophobic coating was further examined by the sand paper abrasion test.^{20,28,43,44} In this test, sand paper (1500 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 30 times for the same coated sample.

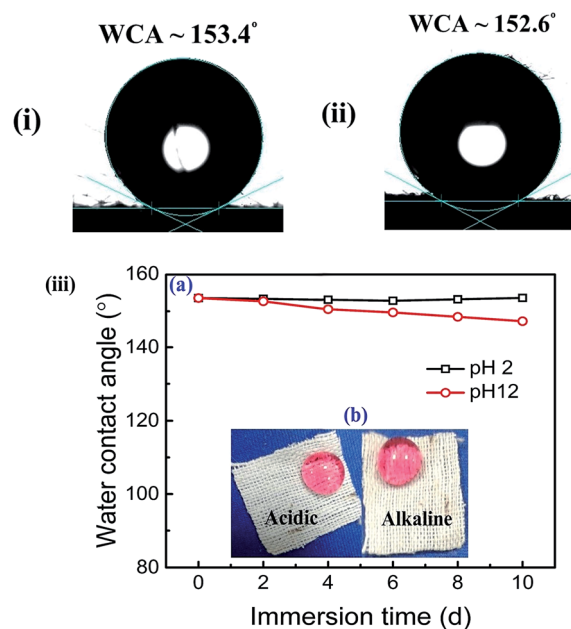


Fig. 7 Water contact angles of superhydrophobic fabric (i) after U.V. irradiation for 72 h (ii) after 30 times of abrasion. (iii) After 10 days of immersion in acidic and salty solutions.

After the abrasion test, the WCA and SA of the CCF sample were found 152.6° and 8° respectively, indicating the good mechanical robustness of the coating against abrasion (Fig. 7ii).

In addition, the chemical stability of superhydrophobic coating was also qualitatively assessed by measuring WCA and SA after immersing them into acidic (pH = 2), salty (1 molar NaCl solution) and alkaline (pH = 12) solutions (Fig. 7iii).^{14,28,45} We notice that after 10 days (d) immersion of CCF in acidic and salty solution the WCA almost remained constant around 154° (Fig. 7iii-a) and sliding angle was about 8° , whereas in case of strong alkaline solution, slight change was observed (WCA $\sim 147.7^\circ$) and sliding angle was about 12° . In addition, 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. 7iii-b). This results further demonstrating 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.¹⁰ In this test, the cotton surface was pasted onto an adhesive tape, and then it was peeled off (see Fig. 8). The developed material remained superhydrophobic and superoleophilic even after repetition of the tear test with an adhesive test for 30 cycles, with WCA greater than 150° and SA less than 10° . Thus results of the study imply that the as-prepared superhydrophobic fabrics have promising potential for the separation of oil–water mixture with durability of coating.

3.4 The application of superhydrophobic surface

3.4.1 Oil–water separation. Since the CCF exhibited superhydrophobicity and superoleophilicity property, we have evaluated the oil–water separation property using CCF as “filter cloth” as shown in optical photographs (Fig. 9a). For this experiment, a mixture of diesel and water (50%, v/v) was poured onto the surface of CCF after proper mixing. Water was colored

blue by adding methylene blue dye for clear visibility. It was seen that diesel (light yellow in color) immediately passed through the cotton fabric into the collecting vessel without any external force due to effect of gravity, whereas water (dyed with dye) was not permeated by the modified fabric due to

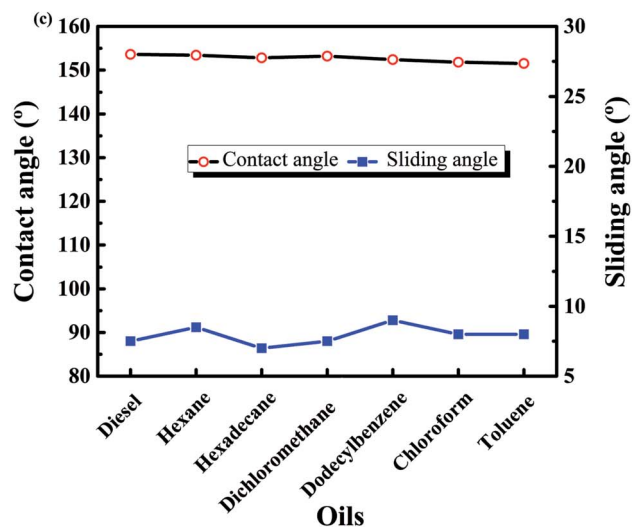
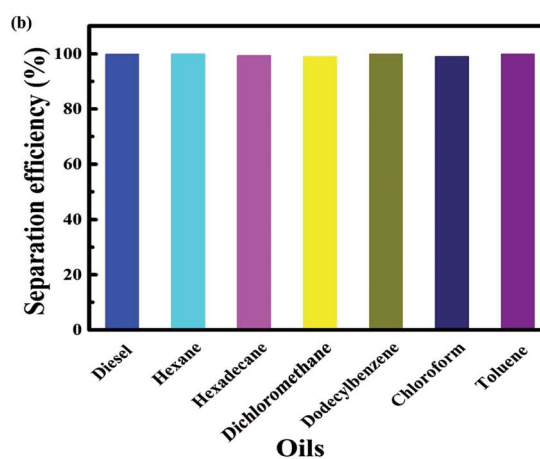
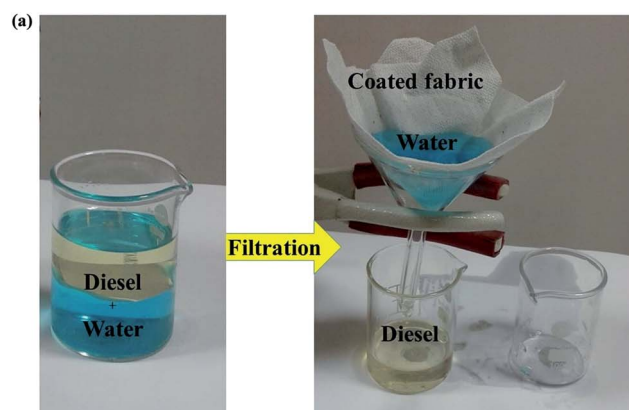


Fig. 9 (a) Optical photographs showing the separation process for diesel–water mixture through coated cotton fabric. (b) Separation efficiency of superhydrophobic cotton fabric for seven types of oil–water mixture with 1 : 1, oil–water ratio. (c) Contact angle and sliding angle of superhydrophobic cotton fabric after separation of different oil/water mixtures up to 10 cycles.

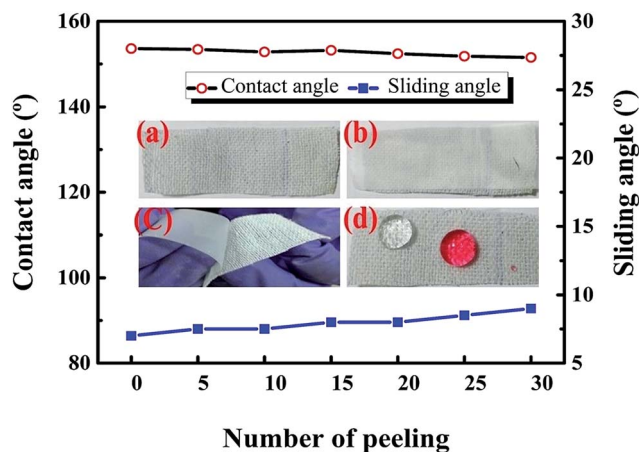


Fig. 8 Water contact angles and sliding angle of superhydrophobic fabric after repeated tear tests. The inset depicts the tear process (a) piece of fabric, (b) the fabric pasted onto an adhesive tape, (c) fabric peeled off the adhesive tape, (d) water droplet on the fabric after peeling off the adhesive tape.

superhydrophobic nature of the fabric (see Video S4†). In addition, we notice that after mixing vigorously, separation of oil–water mixture (surfactant-free) was successfully achieved through ordinary filtration approach as shown in optical photographs (Fig. 9a). However, the CCF was unable to separate surfactant-stabilized emulsions.

Furthermore, in order to evaluate generic separation efficiency of coated fabric, we considered six additional mixtures *viz.*, *n*-hexane/water, hexadecane/water, dichloromethane/water, dodecyl benzene/water, chloroform/water and toluene/water, where chloroform and dichloromethane oils have higher densities than water. The oil separation experiment was conducted using the simple filtering process, as mentioned earlier. The oil–water volume ratio was 1 : 1 in all the six types of mixtures. The separation efficiency (K_s) was calculated according to following equation:³

$$K_s = 100 \times \left(\frac{m_1}{m} \right)$$

where m is the amount of water taken initially in the oil–water mixture, and m_1 is the amount of water collected after separation process. Fig. 9b clearly shows that the separation efficiency is more than 99% in all the seven oil–water mixtures (50%, *v/v*) even after repetition of the filtration process up to 10 cycles at ambient temperature.

Moreover, after repetition of filtration process up to 10 cycles there is only slight decline in the WCA and SA, and coated fabric remain superhydrophobic with WCA greater than 150° and SA less than 10° (Fig. 9c), demonstrating its excellent superhydrophobicity.

The results revealed that the CCF has significant potential for practical separation of oil–water mixtures, irrespective of lighter or heavier oil, considering the developed material can be used repeatedly without losing its efficiency.

3.4.2 Aqueous pollutant degradation. After oil–water separation, photodegradation of MB dye in the separated water by the AgBr coated fabric was evaluated under visible light irradiation. UV-Vis spectra of MB dyed aqueous solution was

recorded before and after irradiation at a different time of interval. It can be seen from Fig. 10 that absorbance of visible light (concentration of MB aqueous solution) decrease with time and after 70 min of visible light irradiation blue color of aqueous solution was completely disappear, which indicates the full degradation of MB dye in aqueous solution. In addition, recyclability of AgBr coated fabric for photodegradation of MB aqueous solution was evaluated. After three times of successive photocatalytic experiment it was observed that aqueous solution of MB was completely degraded within 70 min of visible light irradiation. Thus results of the study inferred that developed cotton fabrics exhibit good photocatalytic activity. As reported previously, AgBr was suggested to be an excellent photocatalytic material in degradation of organic contaminants under the illumination of visible light.^{9,46} Thus results inferred that presence of AgBr coating endow the excellent photocatalytic property to the modified fabric.

4. Conclusions

We have fabricated zirconia based superhydrophobic cotton fabric with photocatalytic activity using non-fluorinated (HDTMS and SA) hydrophobic agents and subsequently AgBr modification. The as-prepared fabric not only with high separation efficiency (>99%) of a wide range of oil–water mixtures, but also showed significant photocatalytic activity in degradation of methylene blue under visible light illumination. 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. Thus as-prepared CCF has promising potential for separation of insoluble oil or organic solvents as well as photodegradation ability of soluble organic contaminants from water.

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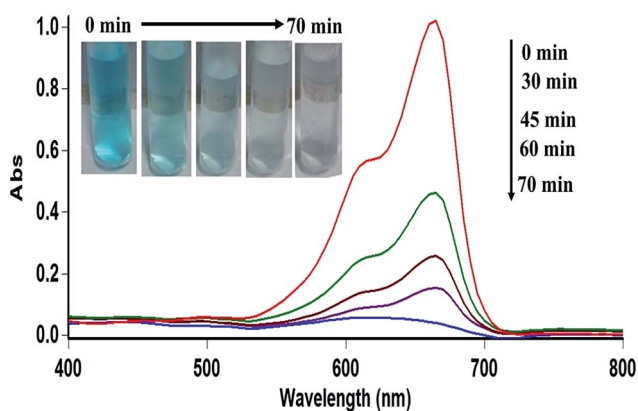


Fig. 10 The temporal absorbance curves for MB solution (10 mL, conc. = 1.8×10^{-5} mol L⁻¹) during the photodegrade process. The inset: the typical real-time images during the photodegradation of MB solution by the coated cotton fabric (6 × 6 cm).

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