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Fabrication of durable superhydrophobic coatings on cotton fabrics with photocatalytic activity by fluorine-free chemical modification for dual-functional water purification†

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Superhydrophobic/superoleophilic fabrics have been the subject of profound research for self-cleaning and oil–water separation applications. However, the practical application of these materials is still limited due to the complex preparation process using fluorinated chemicals and poor stability of the developed coatings on the surface of fabrics under harsh environmental conditions. In this study, we fabricated a dual-functional coating on cotton fabric with superhydrophobicity and visible light photocatalytic activity *via* an inexpensive dip coating method. The *in situ* synthesized poly-triethoxyvinylsilane (PTEVS) with the combination of polydimethylsiloxane (PDMS) was used to obtain a superhydrophobic coating and subsequently a AgBr coating to integrate the photocatalytic activity. The surface morphology and chemical structure of the coated fabric were characterized by field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. The coated cotton fabric exhibited self-cleaning, superhydrophobic and superoleophilic properties simultaneously with a water contact angle of ~154°, a water sliding angle of ~8° and an oil contact angle of ~0°. The modified fabric can effectively separate a series of oil–water mixtures after being used repeatedly for 10 cycles through an ordinary filtering process. The coated fabric further purifies water containing soluble dyes under visible light illumination. Moreover, the durability of the coating was evaluated under harsh environmental conditions for example exposure to acidic, alkaline, salty solutions, ultraviolet irradiation, mechanical abrasion, and using the adhesive tape test, and the results of all these tests suggested that the coating was stable.

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1. Introduction

Oil pollution with water soluble organic contaminants in the aquatic environment by some industrial activities such as oil production, oil delivery, oil refining and petrochemical operation has become one of the serious environmental problems. Millions of tons of refined oil and crude oil leak into the sea every year,[1] which is significantly responsible for pollution of the natural aquatic environment and ecological damage, as well as resulting in great losses in energy.[1–6] Oil contaminated water containing toxic chemicals (dyes) can adversely affect the coastal species and human health through food chain.[7] Therefore, it is of great significance to explore a simple, economical and effective method for the separation and collection of oil from oil–water mixtures.

In the recent past special wettable materials with water sliding angles (SA) less than 10° and static water contact angles (WCA) higher than 150° have stimulated much attention in the field of self-cleaning and oil–water separation.[8–11] To date several materials such as natural and complex materials (cross-linked resins) including inorganic mineral materials have been proposed for the removal and collection of oil from oil–water mixtures by combining the micro/nano hierarchical structures with low-surface energy of the surfaces.[12] Among the various materials cotton fabric materials bearing superhydrophobic and superoleophilic surfaces have received significant attention. This is mainly owing to their easy handling, high flexibility, environment friendly nature, biodegradability and high efficiency.[13–15] To separate oil–water mixtures superhydrophobic cotton can be utilized as a filter as well as an adsorbent.[16]

A number of methods including the chemical vapor deposition method, layer-by-layer technique, electrospinning technique and dip coating have been used for the development of superhydrophobic coatings on surfaces.[17–21] Among these methods, the dip coating method is a better method in comparison to

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other methods since it is an inexpensive, simple method, and offers an easy adjustment of chemical composition required for a surface to show superhydrophobic behavior.[15,22]

Surface chemical composition and roughness are the key factors for constructing a superhydrophobic surface. In order to fabricate a superhydrophobic surface, addition of various nanoparticles such as Fe_3O_4, SiO_2, TiO_2, ZrO_2, and SiO_2, halogenated compounds and polymers has been reported in the literature.[16] Very recently, Xu *et al.* developed polydopamine coated superhydrophobic cotton fabric using silver (Ag) nanoparticles with 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol.[23] The oil–water separation efficiency and self-cleaning properties were intensively investigated. Das and De fabricated ZrO_2 coated superhydrophobic and superoleophilic cotton fabric *via* immersion in an alcoholic solution of zirconia with 1*H*,1*H*,2*H*,2*H*-perfluorodecyl triethoxy silane followed by curing at 120° for 1 h. The resulting modified cotton fabric exhibited high durability and separated hexane/water mixtures with a high efficiency through ordinary filtering.[24] In addition, Zhou *et al.* reported the preparation of superhydrophobic and superoleophilic cotton fabric by incorporation of polyaniline with $FeCl_3·6H_2O$ and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane using the chemical vapour deposition method.[14] In their study, the modified cotton fabric prevented the passage of water, but allowed oil to pass through easily, leading to high separation efficiency.

Although these coatings on cotton fabrics offer high oil–water separation efficiency, the drawback of these coatings is the use of fluorinated compounds. Fluorinated compounds are environmentally undesirable because they are nonbiodegradable (persistent pollutants), expensive and can easily react with other materials resulting in environmental contamination *e.g.* they can suppress the nerve growth in children.[25]

In addition to fluorinated chemicals, chlorinated compounds have also been reported for preparation of superhydrophobic surfaces. For example, Shirgholami *et al.* fabricated superhydrophobic cotton textiles by a one-step solution immersion process using methyltrichlorosilane.[26] The resulting cotton textile exhibited superhydrophobicity with water contact angles higher than 150°. However, during the coating process hydrochloric acid forms, which can damage or reduce the mechanical properties of the as-prepared coated fabric.[27]

Therefore, it is necessary to obtain coated fabrics with superhydrophobic and superoleophilic properties by using fluorine and chlorine free chemical modifications. Recently, a number of studies have been reported to develop superhydrophobic surfaces by fluorine free chemical modification.[28,29] Cao *et al.* developed a superhydrophobic fabric for oil–water separation with self-cleaning ability by the application of organically modified silica aerogels and polydimethyl-siloxane.[28] Manatunga *et al.* prepared a superhydrophobic coating on cotton fabrics by applying hydrophobization agents (hexadecyltrimethoxy silane and stearic acid) with silica particles.[29] While these studies are mainly focused on treatment of water contaminated with insoluble organic pollutants (oils), they did not pay much attention to degradation of soluble organic pollutants from wastewater. However, the separation of insoluble organic pollutants and degradation of soluble organic pollutants are the key steps in the wastewater treatment process.

The photocatalytic activity on a surface is another form of self-cleaning property in which an organic compound can decompose chemically when exposed to light.[30] Recently various photocatalysts such as TiO_2 and ZnO have been used to efficiently treat aqueous organic pollutants from wastewater.[31] Xu *et al.* synthesized superhydrophobic cotton fabrics with photocatalytic self-cleaning properties by the combination of SiO_2 and TiO_2.[30] The resulting TiO_2–SiO_2 composite particle coated cotton fabric, which was contaminated with oleic acid, exhibited recovery of its superhydrophobicity after UV irradiation, due to the decomposition of oleic acid by the photocatalytic activity. However, the photodegradation of organic pollutants in wastewater using TiO_2 is limited because it is effective under only UV radiation. Thus for practical photodegradation of organic pollutants in wastewater, visible light photocatalysts are urgently required.

Besides the selection of the coating method and chemical composition, a third parameter, the durability of the coating under severe environmental conditions, is also an essential requirement for suitable application in oil–water separation. Therefore, considering these issues, it is highly desirable to generate durable superhydrophobic materials, using inexpensive and simple approaches that can separate oils from oil contaminated water (oil-spill mixtures and industrial wastewaters) in addition to degrading water soluble organic pollutants from water such as dyes. In this study, we have fabricated a superhydrophobic coating on cotton fabrics by treating it with *in situ* synthesized poly-triethoxyvinylsilane (PTEVS) alcosol followed by surface modification with PDMS *via* a simple sol–gel dip coating process and photocatalytic activity was integrated by overlaying a coating of AgBr on the PTEVS/PDMS coated fabric. PDMS is an inexpensive organic chemical with high flexibility and mechanical stability and can be irreversibly bound to cotton fabrics without using agglutinating agents,[21,32] whereas silver bromide (AgBr) is a good visible light photocatalyst for the degradation of organic compounds because it enables absorption of sunlight of wavelengths up to 480 nm or even longer.[33]

The main objectives of this study were (1) preparation of superhydrophobic and superoleophilic cotton fabrics with photocatalytic properties by inexpensive and fluorine free chemical modification; (2) characterization of the product with SEM, EDS and FTIR technology; and (3) evaluation of superhydrophobic performance, self-cleaning ability, durability of a superhydrophobic coating, oil separation efficiency from the oil–water mixture and synchronous photocatalytic degradation of water soluble dyes present in water under visible light.

2. Experimental section

2.1 Materials

Triethoxyvinylsilane (97%, Sigma-Aldrich Chemie, Germany), liquor ammonium (NH_3, Sp. Gr. 0.91, Qualigens Fine Chemicals, Mumbai), oxalic acid (99%, S.D. Fine Chem. Ltd, Mumbai), methanol (99%) and hexane (85%), obtained from S.D. Fine Chem. Ltd, Mumbai, polydimethylsiloxane (PDMS, Dow Corning, Sylgard 184), toluene (99.5%, Fisher Scientific), silver nitrate ($AgNO_3$, ≥99.7%, Fisher Scientific), methylene blue (RANKEM) and cetyltrimethyl ammonium bromide (CTAB, 99%, Loba Chemie) were used as received without further purification. White commercial cotton fabric was obtained from a local fabric store and rinsed with ethanol and distilled water before use followed by washing exhaustively with an excess of water and drying at 50 °C for 30 min.

2.2 Fabrication of superhydrophobic (PTEVS/PDMS) coatings on cotton fabrics

The fabrication of superhydrophobic coatings on cotton fabrics was performed using the dip coating method through the sol–gel route (as described in Fig. 1). Initially, 4 mL of triethoxyvinylsilane (TEVS) was diluted with 40 mL of methanol in a beaker with stirring for 30 min. The TEVS : methanol volume ratio was 1 : 10. 4 mL of oxalic acid solution (0.1 M) was then added dropwise into the TEVS solution with stirring and stirring was continued for 1 h for complete hydrolysis. Then, 4 mL of NH_4OH (13.36 M) was added and mixed well by constant magnetic stirring at room temperature for 1 h to allow condensation. Subsequently, a homogeneous alcosol was prepared. Finally, cleaned and dried fabrics were immersed in the above alcosol for 1 h, dried at 60 °C for 30 min, and then cured at 120 °C for 1 h. After cooling the cotton fabric obtained in the above process was immersed again in a homogeneous mixture of PDMS and toluene (1.25 gram of PDMS in 50 mL of toluene) for 1 h and then cured at 120 °C for 1 h. Thus the obtained coated fabrics are considered as PTEVS/PDMS coated cotton fabrics.

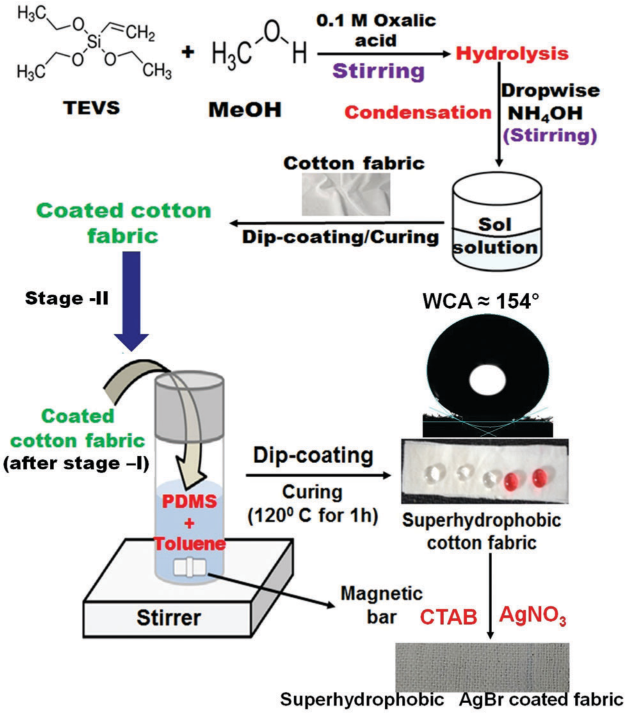

Fig. 1 Schematic representation of the fabrication of superhydrophobic fabrics *via* the sol–gel dip coating approach.

2.3 Fabrication of AgBr coatings on PTEVS/PDMS coated cotton fabrics

The PTEVS/PDMS coated cotton fabrics were again coated with AgBr *via* a successive ionic layer adsorption and reaction method. The PTEVS/PDMS coated cotton fabrics were immersed in 100 mL of CTAB solution (16 mg mL^{-1}) at 60 °C for 5 h and subsequently dipped in an aqueous solution of $AgNO_3$ (10 mg mL^{-1}) for 12 h. Finally, the resulting fabrics (dual-layer coated) were dried at 105 °C for 1 h in an oven.

2.4 Characterization

The surface morphology and elemental composition of the coated cotton fabric (CCF) and uncoated cotton fabric (UCF) were examined by field emission scanning electron microscopy (FESEM, Zeiss, Germany, supra-40VP) and energy-dispersive X-ray spectroscopy (EDS) respectively. In order to identify the presence of functional groups on the CCF and UCF, Fourier transform infrared (FTIR) spectra were recorded using a FTIR spectrometer (KBR pellet method) in the range of 500 to 4000 cm^{-1}.

2.5 Evaluation of superhydrophobicity

The superhydrophobicity of CCF was evaluated by measuring WCA and SA.[24] The WCA and SA were measured using a goniometer (OCA 20, Dataphysics, Germany) instrument using the sessile water drop method with 4 μL water drop at room temperature. The values of WCA were measured in five different positions and the mean value of the contact angles was taken.

2.6 Evaluation of durability and stability of the coating

The stability of the coating on CCF was examined by various tests such as the chemical stability test, UV irradiation stability test, sand paper abrasion test, and adhesive tape test. In the chemical stability test the CCF was immersed in an acidic solution (pH = 2) and in a basic solution (pH = 12) for 72 h. In the UV irradiation test an UV chamber equipped with two 8 W ultraviolet (λ = 365 nm) low-pressure quartz glass ultraviolet lamps 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 48 hours and the contact angles of the samples were measured every 24 hours. In addition, to evaluate the durability of the CCF against washing, the AATCC Test Method 61-2003 test No. 1A was applied. One washing cycle (45 min) of this accelerated wash procedure is equivalent to five cycles of home machine washing. The CCF samples were washed according to this standard at 40 °C in the presence of 0.38% soap powder and 10 stainless steel balls (diameter 6 mm) for various washing times to simulate 5, 10, 15 and 20 wash cycles of home machine washing. Afterwards, the samples were rinsed with abundant water and dried at 35 °C. In order to examine the coating stability, the CCF was pasted onto an adhesive tape and then torn off the tape. This process of the adhesive tape test was carried out repeatedly, and the corresponding water contact angle after each test was recorded. The CCF was also subjected to 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 the corresponding WCA was recorded after each test.

2.7 Application in oil–water separation

In order to investigate the oil separation property of the CCF from oil–water mixtures, filtering experiments were conducted. In this study *n*-hexane/water, toluene/water, chloroform/water, hexadecane/water, dichloromethane/water and dodecyl benzene/water mixtures were taken (1 : 1 v/v) in which water was colored red with phenosafranin dye. The coated cotton fabric was placed in a funnel to act as a filter membrane. After mixing properly, the oil–water (1 : 1 v/v) mixture was poured slowly onto the CCF and the oil–water separation efficiency was calculated in each case by repetition of the filtration process up to 10 cycles. In addition, the underwater oil separation property was also evaluated by dipping a piece of the CCF into the oil–water mixture.

2.8 Evaluation of the photocatalytic activity

The water purification performance of CCF was investigated, by decolorization of MB dye, a heterocyclic aromatic organic compound, in aqueous solution (conc. = 5 mg L^{-1}). Initially, CCF was placed in a funnel to act as a filter membrane and a 20 mL oil–water mixture (hexane 50% v/v) was poured onto the CCF. Water insoluble oil (hexane) easily penetrated the CCF surface whereas water (containing MB at 5 mg L^{-1}) did not permeate the CCF. After complete separation of hexane from the oil–water mixture, the separated MB dyed aqueous solution was poured into a glass Petri dish. A piece of CCF (3 × 3 cm) was totally immersed in MB aqueous solution (10 mL) and subsequently it was kept in the dark for 30 min to reach adsorption–desorption equilibrium. Then it was exposed to visible light irradiation several times using two LED lamps (each 18 W, PHILIPS) as a source of visible light. The decomposition of MB solution was monitored by measuring the absorbance, using a UV-VIS-NIR spectrophotometer (Agilent), until the absorbance curve reduced to the lowest level.

In addition, the regeneration of superhydrophobicity of the CCF after contamination with organic pollutants was also evaluated by using an acetone solution of oleic acid (5×10^{-2} mol L^{-1}) as a model contaminant. Initially, the PTEVS/PDMS and PTEVS/PDMS/AgBr coated cotton fabrics were contaminated with oleic acid, and subsequently the fabrics were irradiated by visible-light several times. Changes in WCA on the polluted surface of the CCF were measured at different time intervals.

3. Results and discussion

3.1 Surface morphology and chemical composition

Fig. 1 illustrates the fabrication process of the superhydrophobic cotton fabric with photocatalytic properties by coating the bare cotton fabric with *in situ* synthesized silica particles followed by surface modification with polydimethylsiloxane (PDMS) and subsequently overlaying the AgBr coating on the PTEVS/PDMS coated fabric. The as-obtained CCF was characterized by a variety of methods to determine its morphological and chemical properties.

A hierarchical surface structure is a very essential requirement for a surface to have superhydrophobic properties. The surface morphologies of CCF and uncoated cotton fabric (UCF) were analyzed by FESEM (shown in Fig. 2a–d). Fig. 2a and b show the SEM images of UCF at low and high magnification. Fig. 2c and d show the SEM images of CCF at low and high magnification, respectively. It is evident from the figures that the surfaces of CCF are rougher than the uncoated original fabric. This is primarily attributed to the homogeneously distributed coating materials within the gap between the fibers of the cotton fabric.

The chemical composition of fabric surface was analyzed by EDX spectroscopy. Fig. 3a and b show the EDS spectra of UCF and CCF, which are acquired from different portions of the materials. The presence of Si, Ag and Br elements can be clearly observed in the EDS spectra of the CCF.

The peak corresponding to the Au element in the EDS spectra arises from gold coating on the samples during the analysis. The results are shown in Fig. 3 and Table 1. The C : O : Si : Ag : Br : Au atomic ratio was 61.25 : 35.38 : 0.62 : 0.91 : 0.44 : 1.39.

FTIR spectroscopy is a powerful tool to investigate the functional groups present in the coating.[34] In order to understand the chemical modification undergone by the cotton fabric upon treatment, FTIR was used. Fig. 4 shows the FTIR absorption spectra of CCF and UCF. Several characteristic peaks related to the vibrations and deformation of functional groups are obtained within the range of 500 cm^{-1} to 4000 cm^{-1}.

In the FTIR spectra of CCF, stretching vibration modes are observed at 1057 and 801 cm^{-1} for Si–O–Si.[35] After coating, two peaks at 2968 and 2902 cm^{-1} appeared which are assigned to the C–H stretching of the CH_2 groups.[36] In addition, two characteristic peaks are observed at 1161 and 1273 cm^{-1}, which strongly indicates the presence of Si–CH_3 bonds on CCF. This indicates the presence of a least number of hydroxyl groups on the CCF surface and thereby was in favor of superhydrophobicity.

3.2 Superhydrophobicity

The wettability of coated surfaces can be theoretically understood using the Cassie equation:[21]

$$\cos\theta_C = rf\cos\theta + f - 1 \qquad (1)$$

where θ represents the local contact angle, θ_c is the measured contact angle, r is the roughness of the liquid–solid interface and f is the area fraction of the liquid–solid interface. As suggested by this equation, θ_c depends on both surface roughness and area fraction. The WCA for UCF and CCF was measured at least at five different places and the obtained mean value is reported in Table 2. These results indicate that initially the uncoated cotton fabric was hydrophilic (WCA = 0°). When the cotton fabric was treated with *in situ* synthesized silica particles using TEVS followed by PDMS modification, the WCA

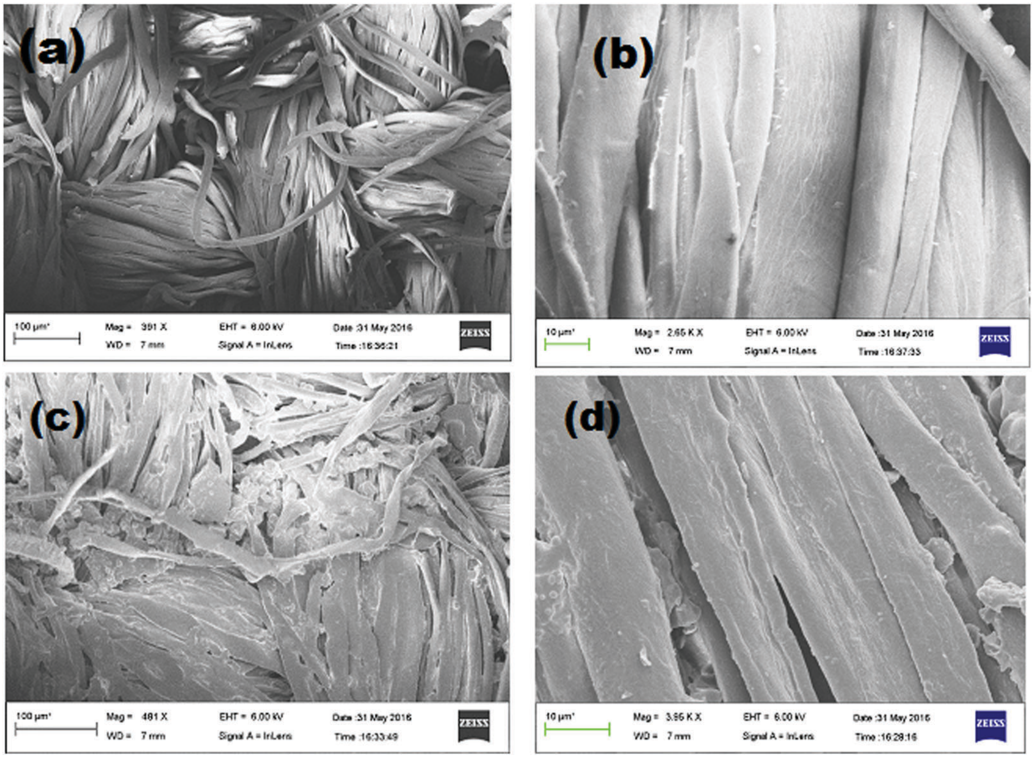

Fig. 2 SEM images of the bare cotton fabric at (a) low and (b) high magnification and SEM images of the coated cotton fabric at (c) low and (d) high magnification.

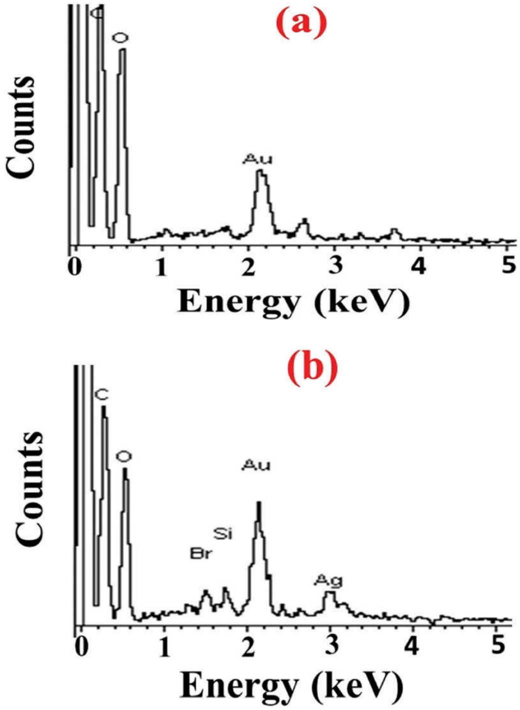

Fig. 3 Magnified EDS spectra of the (a) bare cotton fabric and (b) coated cotton fabric.

Table 1 Chemical composition of the CCF by EDX analysis

Element	C	O	Si	Ag	Br	Au
At%	61.25	35.38	0.62	0.91	0.44	1.39

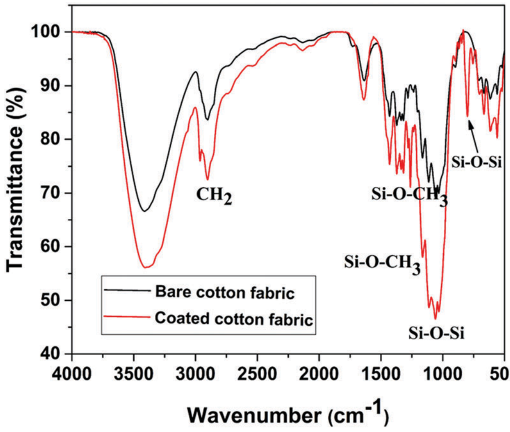

Fig. 4 FTIR spectra of the bare and coated cotton fabric (CCF).

increased significantly. It was observed that with increasing PDMS concentration in toluene from 0.5 g/50 mL (PDMS$_{0.5}$) to 1.25 g/50 mL (PDMS$_{1.25}$) the WCA on the coated surface increased. It may be due to the rougher PDMS coating on the hydrophobic silica coated fabric. The highest WCA (154 ± 1°) was obtained for cotton fabric coated with the hydrophobic silica/PDMS$_{1.25}$ (1.25 gram of PDMS in 50 mL of toluene) system. This could probably be due to the combined treatment of *in situ* synthesized

Table 2 Effect of coating on WCA, SA and OCA of coated cotton fabrics

System	WCA (°)	SA (°)	OCA (°)
Bare cotton fabric	0	—	0
Hydrophobic silica coated fabric	138 ± 1	—	0
Hydrophobic silica/PDMS$_{0.5}$ coated fabric	147 ± 1	—	0
Hydrophobic silica/PDMS$_{1.25}$ coated fabric	154 ± 1	8	0

silica particles with PDMS concentration. A similar observation has also been reported by other workers.[21]

To further test the superhydrophobicity of the material, a volume of 15 μL of dyed water (by phenosafranin dye powder) was dripped on the surface of UCF and CCF. It was observed that UCF became completely wet with colored water, whereas the dyed water floated on the surface of CCF in the form of a complete sphere drop as shown in Fig. 5a and b. After surface modification the cotton fabric exhibited superhydrophobicity (high water repellency) with a WCA of ~154 ± 1° and a low SA of ~8.0°. The higher value of the water contact angle indicates that the surface treatment method using the dip coating process, developed in this work, converts the raw cotton fabric from hydrophilic to superhydrophobic.

In addition, rolling of water droplets on the surface of CCF was captured using the high-resolution camera of the Goniometer with a fixed angle of 8° (see Video S1, ESI†). It was observed that within seconds the water droplet quickly slides on the CCF surface. Thus, the CCF surface displayed self-cleaning behavior similar to that of a lotus leaf.

To demonstrate the self-cleaning performance of the CCF, water was poured in the form of water droplets onto the phenosafranin dye powder contaminated CCF surface.[24] As shown in Fig. 6a, when water droplets were poured onto the CCF surface, the hydrophilic dye powder accumulated at the water surface and the dye powder was carried away by the water droplets because of the weaker adhesion between a hydrophobic surface and hydrophilic particles than that between water droplets and the hydrophilic dye powder. The phenosafranin dye powder was removed from the fabric surface by this "roll-to-clean" mechanism. However, we note that some dye particles penetrated the fibrous CCF, and could not participate in the roll-to-clean process. Thus, in addition, the self-cleaning quality of CCF was demonstrated by the repeated dip test in solution containing phenosafranin dye aqueous solution (red coloured) (see Video S2, ESI†). It was observed that the surface of CCF remained dry and fully cleaned after the repeated dip test. This observation indicates the good self-cleaning property of the CCF.

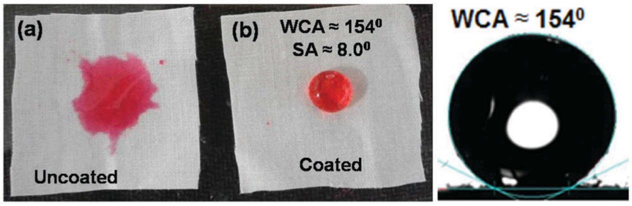

Fig. 5 Optical photographs of the dyed (phenosafranin) water drops on (a) uncoated fabrics and (b) coated fabrics, showing the superhydrophobicity of coated fabrics.

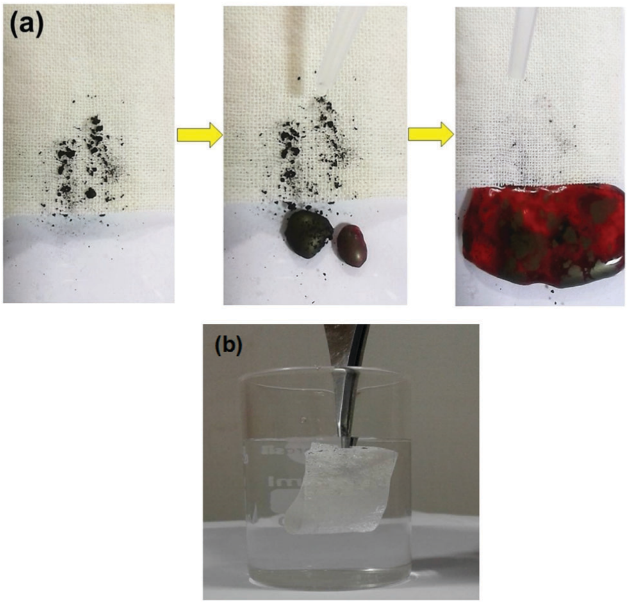

Fig. 6 Optical images (a) showing the self-cleaning process of the superhydrophobic surface and (b) formation of shiny layers (air pockets) upon forceful immersion of coated cotton fabrics into water.

Interestingly, when the CCF was placed in a beaker containing water, it remained on top of the water surface. Moreover, upon forcefully immersing in water, a shiny layer (air pockets) was formed at the fabric–water interface. This was indicated by the silver mirror like appearance on the surface of the dipped sample (see Fig. 6b).[22] The underwater stability of this shiny layer is responsible for the ability of the modified cotton fabric to remain dry. A similar observation for superhydrophobic fabric in water has also been reported earlier.[22,23] The unusual behavior at the fabric–water interface is mainly attributed to the combination of the trapped air layer and treated cotton fabric, which made the material lighter than water.[12]

3.3 Durability of superhydrophobic coatings on fabrics

The stability of superhydrophobic coatings on the treated surface is an essential factor for practical applications under harsh environmental conditions.[17–24] In our daily life UV irradiation from outer sunlight is very common, and it significantly affects the stability of coatings on superhydrophobic surfaces.[37] UV irradiation tests were conducted to examine the stability of coatings, developed in this work, under the influence of UV light. In the UV-durability tests, the CCF was placed in an UV chamber, equipped with two 8 W ultraviolet (wavelength = 365 nm) low-pressure quartz glass ultraviolet lamps. The distance between the UV light source and the samples was approximately 5 cm. The samples were exposed to UV light in the UV chamber up to 72 hours and the contact angles of the samples were measured every 24 hours. After UV irradiation for 72 h, the coatings still exhibited a WCA of 154.6°, suggesting superior UV-durability. Thus the coatings showed stronger UV-resistant ability of the CCF (Fig. 7a).

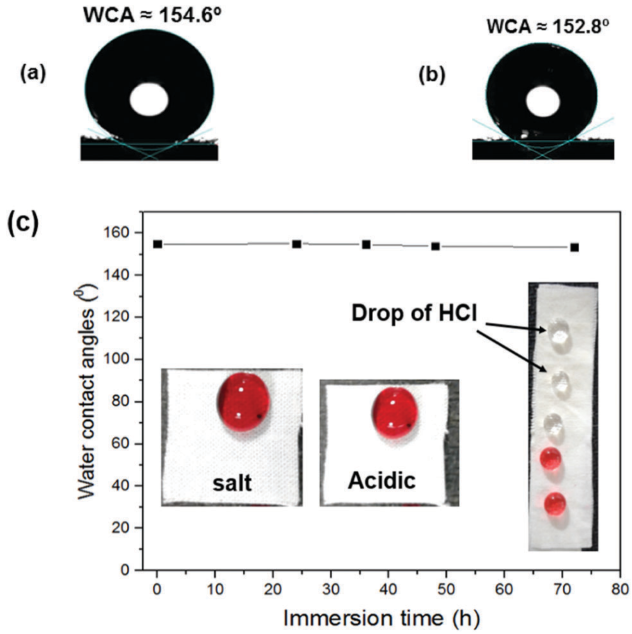

Fig. 7 Water contact angles of the superhydrophobic fabric (a) after UV irradiation for 72 h, (b) after 10 times of abrasion, and (c) after 72 h of immersion in acidic and salty solutions.

The mechanical durability of the superhydrophobic coatings was further examined by the sand paper abrasion test.[17,24,38,39] In this test the resultant coated fabric was placed face-down on sand paper (1200 mesh) under a loading of 100 g and dragged forward along one direction (about 20 cm). The test on a coated sample was repeated 10 times. After the abrasion test, the WCA of the CCF sample was found to be 152.8°, indicating the robustness of the coating (Fig. 7b).

In addition, the chemical stability of superhydrophobic coatings was also qualitatively assessed by measuring WCA after immersing them in acidic (pH = 2), salty (1 molar NaCl solution) and alkaline (pH = 12) solutions (Fig. 7c).[24,40,41] From Fig. 7c it can be seen that after 72 h immersion of CCF in acidic and salty solution the WCA almost remained constant around 154°, whereas in the case of strong alkaline solution, a slight change was observed (WCA ≈ 151.7°). In addition, when we poured 37% hydrochloric acid (HCl) drops on this coated cotton fabric, the HCl drop assumed a spherical shape without wetting the surface.

The washing durability of the fabrics is a basic requirement for practical application and its reuse. The standard method (AATCC Test Method 61-2003 test No. 1A) was used to evaluate the washing durability by measuring WCA after each repeated wash cycle.[42] It was observed that after four washing cycles, which is equal to 20 home machine washing cycles, the WCA of the CCF was >148°. Thus the prepared CCF exhibits excellent washing durability.[24]

The durability of coatings on CCF was also assessed by the repeated tear test with an adhesive tape.[16] 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 adhesive test for 20 cycles, with an almost constant WCA of ∼154°. Thus, the results of the study indicate that the as-prepared superhydrophobic fabrics are promising materials, with durable coatings, for the separation of oil–water mixtures.

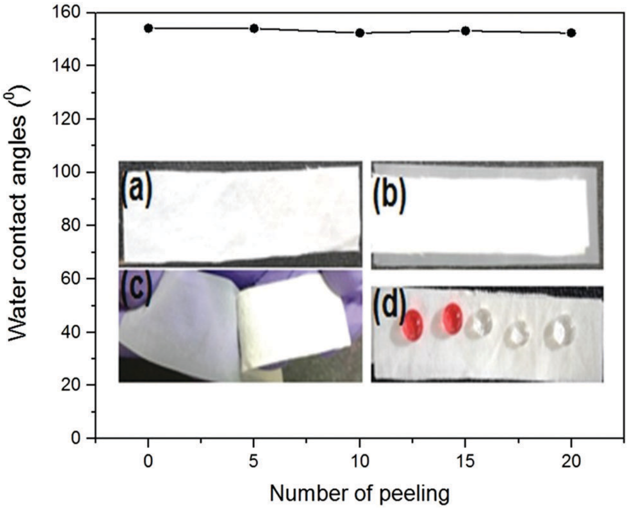

Fig. 8 Water contact angles of the superhydrophobic fabric after repeated tear tests. The inset depicts the tear process: (a) piece of fabric, (b) the fabric pasted onto an adhesive tape, (c) fabric peeled off the adhesive tape, and (d) water droplet on the fabric after peeling off the adhesive tape.

3.4 Application of CCF in oil–water separation

Since the CCF exhibited superhydrophobicity and superoleophilicity properties, we have evaluated the oil–water separation properties using CCF as "filter cloth" as shown in optical photographs (Fig. 9a). For this experiment, a *n*-hexane and water (50%, v/v) mixture was poured onto the surface of CCF after proper mixing. Water was colored red by adding phenosafranin dye for clear visibility. It was seen that *n*-hexane (colorless) immediately passed through the cotton fabric into the collecting vessel without any external force due to the effect of gravity, whereas water (dyed with phenosafranin dye) was not permeated by the modified fabric due to the superhydrophobic nature of the fabric (see Video S3, ESI†).

Furthermore, in order to evaluate the generic separation efficiency of the coated fabric, we considered five additional mixtures, *viz.*, toluene/water, chloroform/water, hexadecane/water, dichloromethane/water and dodecyl benzene/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 the 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 the separation process. Fig. 9b clearly shows that the separation efficiency is more than 97% in all the six oil–water mixtures (50%, v/v).

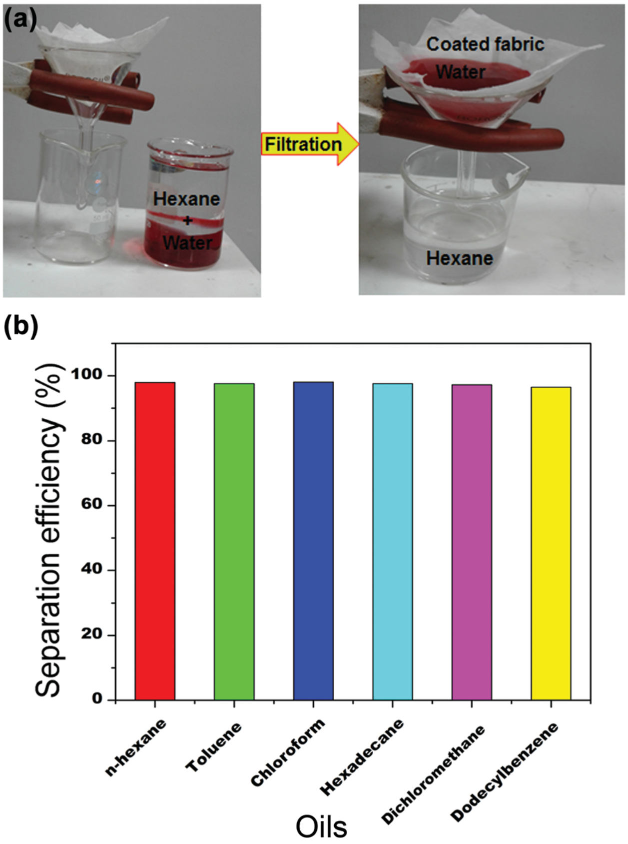

Fig. 9 (a) Optical photographs showing the separation process of the hexane–water mixture through the coated cotton fabric. (b) Separation efficiency of the superhydrophobic cotton fabric for six types of oil–water mixtures with an oil–water ratio of 1 : 1.

In addition to these experiments, separation of some other oil–water mixtures such as diesel/water and salad oils (viscous oil) *i.e.* sunflower oil/water and olive oil/water has also been evaluated with this as-prepared CCF. We notice that separation of these oil–water mixtures was successfully achieved through the ordinary filtration approach with high separation efficiency (>97%) even after repetition of the filtration process up to 10 cycles at ambient temperature. However, the CCF was unable to separate the crude oil/water mixture mainly due to the formation of emulsion. We plan to undertake a separate work to investigate emulsion separation using cotton-based fabrics.

The coated cotton fabric also exhibited stable superhydrophobic and superoleophilic properties in the separation of corrosive solution like a mixture of hexadecane (dyed with the Sudan blue II) and 1 M NaCl, after 10 separation cycles with a separation efficiency of more than 97%. The oil–water separation of this mixture can be seen in Video S4 (ESI†). The CCF was fixed in a filtration device and a hexadecane/1 M NaCl aqueous solution mixture was poured onto the CCF. After a few seconds, hexadecane permeated the CCF while the aqueous solution of NaCl was repelled beyond the CCF surface. Thus the results imply that CCF is a promising material for the separation of oil–water mixtures from the corrosive water environment.

In addition to separation of floating oils from water, the underwater oil capture efficiency of the coated fabric was also evaluated by dipping cotton fabric into oil/water mixtures with tweezers. For this experiment, some drops of dichloromethane oil (dyed with Sudan blue II) were added in a container having water (dyed with phenosafranin). It can be seen from Video S5 (ESI†) that dichloromethane was absorbed within some seconds when it came into contact with CCF. A similar behavior was observed for chloroform droplets (see Video S6, ESI†). The results revealed that the CCF has good oil affinity and significant potential for separation of specific oil–water mixtures, irrespective of lighter or heavier oil.

Moreover, the recyclability of the CCF was also evaluated after the oil–water separation experiment, which is desired for practical applications. In order to remove the adsorbed oil, the contaminated CCF was rinsed thoroughly with ethanol and dried at 60 °C. It was observed that the used fabric after rinsing with ethanol and then drying recovers its superhydrophobicity, and the clean CCF can be used in the next cycles of oil–water separation. The separation efficiency of the CCF was >97% for the dodecylbenzene–water mixture after 10 separation cycles. This finding implies that the CCF can recover its superhydrophobicity by an easier and more economical approach, without using any complicated process.[3,11]

3.5 Application of CCF in the degradation of aqueous pollutants

After oil–water separation, photodegradation of methylene blue (MB) dye in the separated water by the CCF was evaluated under visible light irradiation. The UV-vis spectra of MB dyed aqueous solution were recorded before and after irradiation at different time intervals. It can be seen from Fig. 10a that the absorbance of visible light (which indicates the concentration of MB in aqueous solution) decreases with time. After 120 min of visible light irradiation the blue colour of aqueous solution was found to completely disappear, which indicates the full degradation of MB dye in aqueous solution. In addition, recyclability of CCF for photodegradation of MB aqueous solution was evaluated. After three successive photocatalytic experiments it was observed that

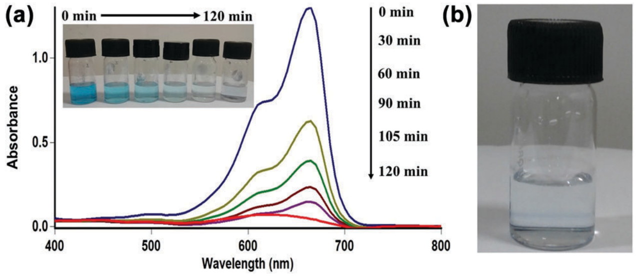

Fig. 10 (a) The temporal absorbance curves for MB solution (10 mL, conc. = 5 mg L^{-}) during the photodegradation process. Inset: The typical real-time images during the photodegradation of MB solution by the coated cotton fabric (3 × 3 cm). (b) Optical photograph of the collected sample that the CCF after one-time dual-functional water purification test was immersed in alkaline solution (pH ∼ 12) for 2 h, showing extremely transparent colour.

the aqueous solution of MB was completely degraded within 120 min of visible light irradiation. Thus the results of this study suggest that the developed CCF exhibits good photocatalytic activity and is promising for the treatment of water pollution caused by organic dyes. As reported previously, AgBr was suggested to be an excellent photocatalytic material in the degradation of organic contaminants under the illumination of visible light due to the generation of Ag^0 during the degradation process.[43]

Furthermore, in order to confirm the hypothesis of dye adsorption rather than degradation, the CCF after the dual water remediation process (removal of oil from the oil–water mixture and synchronous degradation of dyes present in water) was immersed in alkaline solution (pH $\sim$ 12) for 2 h for desorption of adsorbed dye contents on the surface of used CCF.[44] We notice that after this desorption process the collected sample exhibited an extremely transparent colour (Fig. 10b). Thus the results suggest that the presence of a AgBr coating endows excellent photocatalytic properties to the modified fabric.[45]

Moreover, the regeneration of superhydrophobicity of the CCF was examined by contamination of oleic acid (organic pollutant) and subsequently measuring the changes in WCA on CCF surfaces before and after visible light irradiation. Fig. 11 illustrates the image of water droplets on different cotton coated/polluted fabric surfaces. It is evident from Fig. 11 that after contamination of oleic acid both PTEVS/PDMS/AgBr and PTEVS/PDMS coated cotton fabrics changed from the hydrophobic to the hydrophilic state. This is observed by the change in WCA, from 154° to $\sim$0°, upon contamination. This is primarily due to the low surface tension of oleic acid which can easily allow water to wet the CCF surfaces.[30]

However, the PTEVS/PDMS/AgBr coated cotton fabric recovers its superhydrophobicity (WCA $>$ 150°) after visible light irradiation for 12 h, indicating its excellent regeneration ability after contamination with organic pollutants. The process of contamination of oleic acid on the surface of CCF and regeneration of superhydrophobicity was repeated 3 times. In contrast, PTEVS/PDMS coated fabrics retain their hydrophilicity even after visible light irradiation for $>$12 h. These results indicate that the existence of AgBr particles favors regeneration of superhydrophobicity of the coated fabrics even if they are contaminated with organic pollutants. It is believed that the regeneration of superhydrophobicity of PTEVS/PDMS/AgBr coated cotton fabrics was perhaps due to the photocatalytic decomposition of oleic acid by AgBr particles. Photocatalytic degradation of other organic compounds by AgBr particles under visible light illumination has also been reported by other researchers.[33,43]

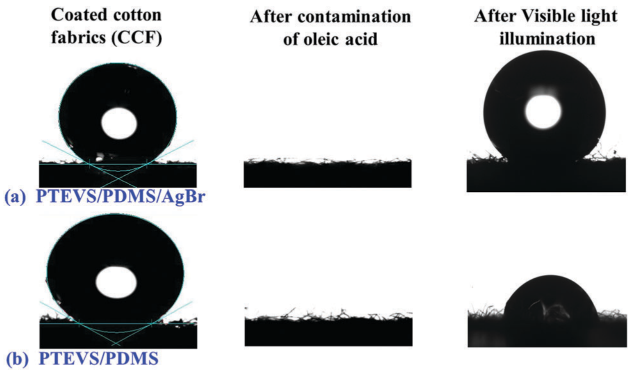

Fig. 11 Optical images of water droplets on the surface of (a) PTEVS/PDMS/AgBr coated cotton fabrics and (b) PTEVS/PDMS coated cotton fabrics before and after contamination of oleic acid and after visible light irradiation.

4. Conclusions

We have fabricated fluorine free superhydrophobic coatings on cotton fabrics by a simple, inexpensive dip coating method using environment friendly *in situ* synthesized silica particles and PDMS. The resulting CCF exhibited self-cleaning, superhydrophobicity and superoleophilicity with dual-function water purification properties. Furthermore, CCF exhibited stable superhydrophobicity against UV irradiation, abrasion test and solution having pH in the range of 2 to 12. The CCF can effectively separate oil–water mixtures such as *n*-hexane/water, toluene/water, chloroform/water, hexadecane/water, dichloromethane/water, dodecyl benzene/water, sunflower/water, olive oil/water and diesel/water with high separation efficiency ($>$97%) through an ordinary filtering process. Moreover, after the separation, the CCF can degrade water soluble dyes in the as-separated water phase by the utilization of visible light (solar energy). Thus the as-prepared CCF has promising potential for separation of oil from the water surface (floating oil) and under water (heavier oil) and also in treating water pollution created by the presence of water soluble dyes.

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