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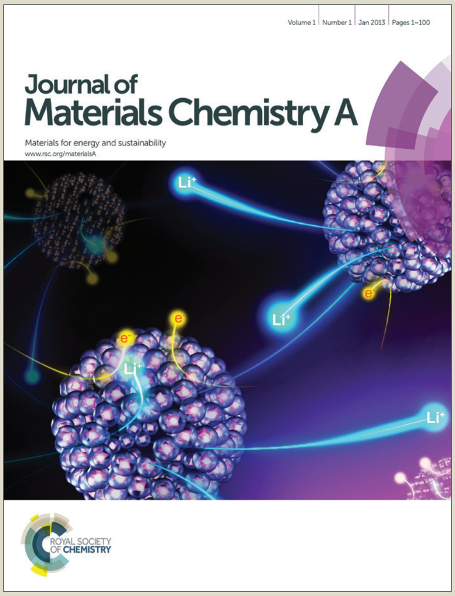

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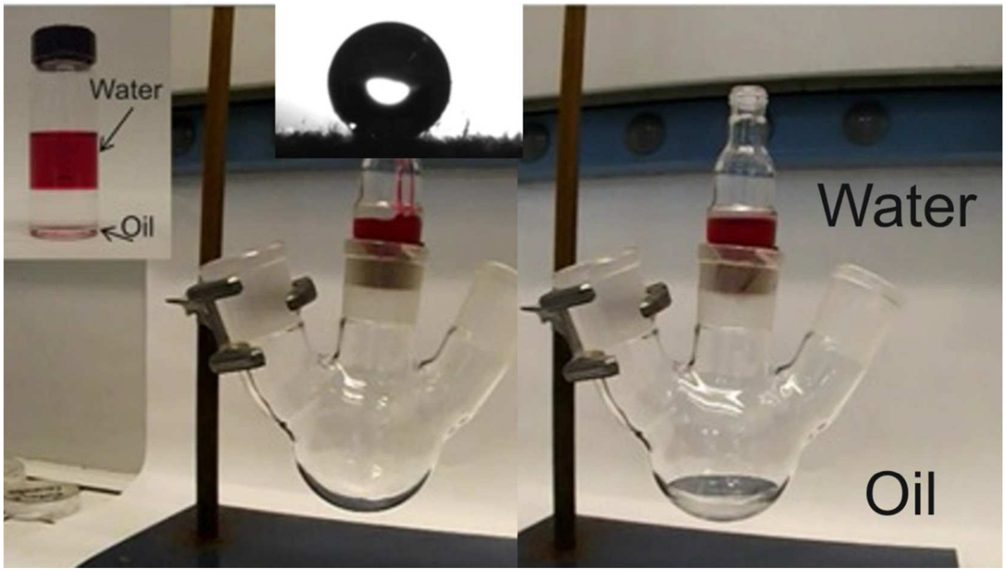

Diamond Like Carbon (DLC) coated cotton textiles showing both superhydrophobic and superoleophilic properties exhibit high controllable, energy-efficient oil/water separation.

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Superhydrophobic Fabrics For Oil/Water Separation through a diamond like carbon (DLC) Coating

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The recent oil spill in the Gulf of Mexico has already, and is continuing to have, significant global environmental issues and impacts severely on people's lives and natural resources. The ramifications of oil spill accidents highlight the difficulty to achieve effective oil-water separation and the consequences are harsh and long-term. In this work, we describe a convenient approach to fabricate cotton textiles with a hydrophilic coating, showing both superhydrophobic and superoleophilic properties. The surfaces are successfully prepared by one-step growth of diamond like carbon film onto the textile via plasma enhanced chemical vapour deposition and exhibit high controllable, energy-efficient oil/water separation with high separation efficiency. The results have important implications for oil-absorption dynamics while repelling water completely. The present work suggests encouraging uses for applications to be applied in marine spilt oil cleanup and other water/oil separating systems.

1 Introduction

Constant progressing in industrialization as well as oil production and transportation, causes every year, severe environmental and ecological problems. Massive oil leakages at sea caused by unpredicted disposal or natural disasters have a deep impact on the environment and wildlife. The intensifying of environmental awareness therefore triggers a critical need for new energy-efficient solutions that can improve and control specific wettability and absorption.[1-3] Recently, surfaces with superhydrophobic and superoleophilic properties have drawn increasing interest in the field of oil/water separation because of their capacity to absorb only oil while repelling water completely, exhibiting high oil/water separation efficiency and selectivity.[4-7] Conventional materials have often been used but with poor efficiency, low oil loading and absorption of water together with the oil and, at times, managing also to generate pollution during clean-up.[8] Filtration or absorption of oils selectively and effectively from water have been achieved using fluorochemicals,[9] chemical vapour deposition,[10,11] coating mesh,[12] carbon-based materials,[13] hydrophobic aerogels,[14] sol gel process,[15] and sponges.[16-28] Nevertheless, these materials have limitations for practical applications because of high cost or time consuming chemical preparation processes as well as showing low stability, selectivity and limited large scale fabrication and application.[19] Moreover sponges are intrinsically hydrophilic, therefore drawbacks are correlated to reduced absorption capacity as they tend to absorb water during the oil cleanup process.[20] Thus the contemporary methods are not ideal in clean-up efforts in the near future for large volumes of oil/water mixtures, such as oil leaks and spills. Textiles have in this respect attracted much interest.[10,21] Textiles exhibit a porous and hydrophilic surface with that has characteristics of high absorption ability, good elasticity, and easily scalable fabrication. However, they usually absorb both water and oils (or organic solvents), which makes them impractical for selective removal of oils from water with high efficiency. Therefore, it is essential to control of the wettability of textiles. Superhydrophobic/olephilic surfaces can be accomplished by developing a dual-scale roughness structure and tuning of surface energy.[7,12] It is well known, although not often specified, that materials with superhydrophobic properties (exhibiting water contact angles (WCA) greater than 150° and low contact angle hysteresis) are commonly superoleophilic (oil CA less than 5°).[22,23] Wenzel's and Cassie's theories are commonly used to explain the wetting behaviour on structured superhydrophobic surfaces.[24,25] Wenzel's approach takes into account that when a liquid comes in contact with a textured surface, the spaces left between the protrusions on the surface are filled by the liquid leading to a fully wetted state. This model assumes that the drop remains pinned atop the surface (sticky state). Cassie, in turn, described the hydrophobic behaviour by considering the liquid droplet to be sitting and not pinned atop the nanocomposite surface of the solid protuberances and air. The formation of the Cassie–Baxter state reduces the solid-liquid interfacial area, thereby promoting high apparent contact angles θ and low contact angle hysteresis Δθ.[26] Therefore the introduction of an appropriate microstructure would improve the hydrophobicity of the surface owing to the introduction of air pockets beneath the water droplet, whereas an oleophilic surface may become more oleophilic owing to the capillary effect.[27-29] Diamond-like carbon (DLC) films have received broad attention in different fields of research due to its excellent properties as extreme hardness, good thermal conductivity, chemical stability, and biocompatibility.[30-32]Moreover DLC has an equilibrium contact angle (CA) (on a flat surface) of 69.2° ± 1.1°, which is well below the 90° that is typically believed to be a prerequisite for superhydrophobicity .On the other hand, combining the advantages of obtaining a superhydrophobic surface from a hydrophilic coating broadens the choice for a multitude of new surface coatings with different chemical functionalities. In our previous work, we investigated the tunability in hydrophobicity of DLC coated textiles and provided a facile way to fabricate the hierarchal rough surface with controlling wettability by changing the nature of the plasma used in the pre-treatment.[33] Here we obtain an improved superhydrophobic textile which exhibits water/oil separation. By increasing the etching plasma pre-treatment, the DLC cotton textiles were endowed with promising superhydrophobicity and superoleophilicity. The effects prolonged etching on the morphology, surface wettability and porous structure of resultant coated textiles were investigated, and a convincing example showing the fast and efficient oil–water separation performance was also presented. Effective selectively (> 99%) separation of water from a broad variety of oils and organic solvents mixtures such as vegetable oil, gasoline, diesel, and even crude oil/water mixtures without any extra power are shown. No auxiliary treatments were required for the collection of oil and effective absorption capacities approaching 55 to 94 times its weight were obtained. The findings is promising for the development of low cost surfaces for the separation of oil from water being environmental friendly and recyclable.

2 Experimental section

Materials and DLC deposition

Cotton textiles (Cod.558-795, RS components, UK) were cut into the size of 15 cm x 15 cm, cyclically cleaned in an acetone bath in Soxhlet for 3 h, thoroughly rinsed with distilled water and then dried at 50°C for 15 min. The cleaned samples were mounted on a water-cooled cathode of 12 cm diameter into plasma chamber. Plasma pre-treatments and DLC depositions were performed in a PECVD apparatus, operating at 13.56 MHz and room temperature.[33] All solvents were purchased from Sigma-Aldrich. In brief samples were initially exposed to an oxygen plasma pre-treatment (plasma conditions 50 W, 1.4-1.6 x10^{-1} mbar) with varying exposure times. The cleaned textile which did not undergo plasma pre-treatment were labeled as "cotton" and used as reference sample. Subsequent DLC deposition was performed on the pre-treated samples and on untreated cotton, avoiding air exposition. DLC coatings were deposited at 50 W RF power, and using a mixture of CH4 (40 sccm), H2 (5 sccm) and Ar (50 sccm), as reactive atmosphere at room temperature. The working pressure was maintained at 3.7 x10^{-1} mbar and the Bias Voltage was fixed at -220 V. Operating at the same conditions, the thickness of the DLC film deposited on a silicon (100) substrates was estimated by profilometer measurement to be of about 500 nm (deposition rate of 20 nm/min).

Characterization

Field Emission Scanning Electron Microscope (FE SEM/EDS) characterization was carried out by a high-brilliance LEO 1530 field emission scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS) INCA 450 and a four sectors backscattered-electron detector (BSD). SEM images were recorded both in the secondary electron image (SEI) and backscattered image (BSD) mode at an acceleration voltage ranging from 2 to 20 kV. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K 250 carbon coating attachment and a carbon cord at a pressure of 1 × 10^{-2} mbar in order to produce a carbon film with a constant thickness of about 3.0 nm. The chromium coating was deposited by using a Bal-Tech SCD 500 equipped with turbo pumping for ultra-clean preparations at a pressure of 5x10^{-3} mbar in order to produce a chromium film with a constant thickness of about 0.5 nm.

XPS analysis was carried out using an ESCALAB 250Xi spectrometer (Thermo Scientific, UK) equipped with a monochromatized Al Kα excitation source over a specific 400-μm area. The survey scan spectra were collected operating at 100 eV pass energy (CAE) and step 1.0 eV, while the core level spectra were collected operating at 100 eV pass energy (CAE) and 0.1 eV step. The C KLL Auger signal was acquired operating at 100 eV pass energy (CAE) with 0.2 eV step. Spectroscopic data were processed by the CasaXPS software, subtracting the Shirley background and using a peak-fitting routine with symmetrical product mix of Gaussian–Lorentzian functions L=30% and G=70%. The sample was positioned at the electron take-off angle normal to the surface with the hemispherical analyzer. The base pressure in the analysis chamber was typically around 6x10^{-9} mbar (6x10^{-7} Pa). The insight of XPS (or information depth) is of few nanometers. The spectra were recorded from at least three locations on each sample. The selected area of 1 mm x 1 mm was analyzed. Surface elemental concentrations and O/C ratios were calculated from the survey-scan spectra.

Wetting properties

Contact angle measurements were carried out to investigate the superhydrophobicity and superoleophilicity of the cotton fabrics using an OCA20 (Data Physics Instruments) using a droplet (3 μl) of deionised water or lubricating oil as an indicator. All the contact angles were determined by averaging values measured at 6 different points on each sample surface.

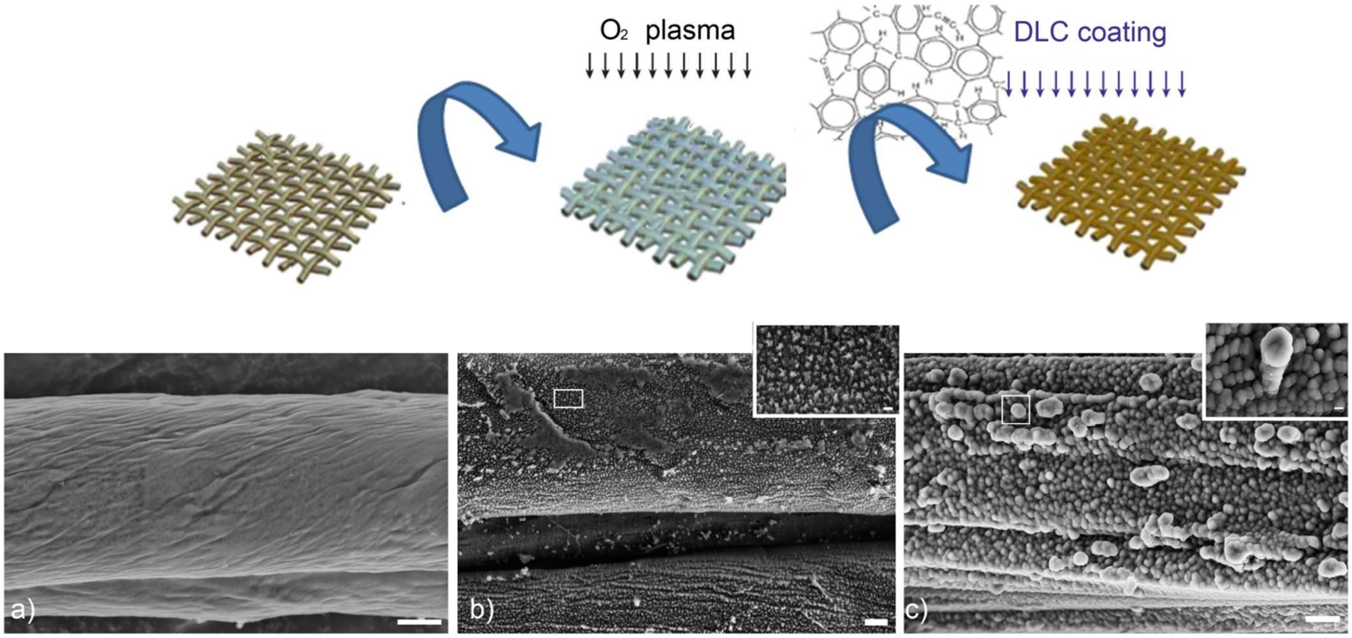

Fig. 1 SEM images of the cotton with following pre-treatment and subsequent DLC coating. Scheme showing the formation of a superhydrophobic surface on cotton based on oxygen plasma pre-treatment and DLC coating with SEM images of (a) pristine cotton fibres without plasma treatment, scale bar 2 μm; (b) Fibre after 10 min oxygen plasma pre-treatment, scale bar 2 μm. A further magnification of the surface of the fibre shows nano-rounded features which diameters range from 100 to 200 nm; (c) DLC coated fibre after the plasma pre-treatment, scale bar 2 μm. Inset shows how the morphology is characterized by a random distribution of several large columnar structures with a re-entrant texture on its surface. Scale bar 1 μm.

The absorption capacity $k =[(W_{\text{saturated absorption}} - W_{\text{initial}})/W_{\text{initial}} \times 100$ (w/w%)] was calculated from the amount of oil or organic solvent absorbed by the DLC coated cotton fabric ($W_{\text{saturated absorption}}$) and the dry weight ($W_{\text{initial}}$).

Water/Oil Separation

For oil/water separation, the DLC coated textile was used as the membrane and a mixture of 20 mL of distilled water colored with commercial Red food Dye and 20 mL of pump oil (Pfeiffer Vacuum F5 Turbo Pump Oil, PFPE Fomblin Oil, 1 Litre, PK001852T, N) was poured slowly into a test tube through the coated textile. The separated oil and water were collected with a test tube and a beaker, respectively.

Selective Oil Absorption

The demonstration oil water separation and cleaning an oil-contaminated water surface by means of the DLC coated cotton was carried out using distilled water colored by commercial Red dye food coloring, pump oil (Pfeiffer Vacuum F5 Turbo Pump Oil, PFPE Fomblin Oil, 1 Liter, PK001852T, N, density 1.88 g/ml, surface tension 22mN/m, θ_{CA}=3±1°), and motor oil (ESP Formula 151055 5W30, surface tension 24.4 mN/m, θ_{CA}=5±0.8°). Images were captured with a Fujifilm FinePix S2950 camera. For selective oil absorption, the textiles were prepared in stripes or to the form of a bag with sponge in it (textile/sponge = 1.4 by weight) owing to low absorption capacity of the textiles. The bags were immersed for the petroleum mixture in a mixture of 15 mL of motor oil (ESP Formula 151055 5W30) and a large amount of clear distilled water. For the solvent mixture in water, the stripes were immersed in a mixture of 15 mL of chloroform and distilled water colored by commercial Red dye food coloring. Efficiency of oil absorption was examined by immersion of stripes in oils or solvents till saturation.

Reusability

The DLC coated sample was immersed in 10 mL oils for 1 min to reach equilibrium, and then taken out, washed with hexane for three times and dried in an oven at 60 °C. This absorption–desorption procedure was repeated for 10 times. After each cycle, the WSA and oil absorption capacity were measured.
The high temperature and high humidity test was carried out in an alternating temperature and humidity homemade test chamber.

Laundering.

DLC-coated cotton fabrics pretreated with 60 min oxygen plasma treatment were washed together in a 100 mL flask that contained 60 mL of a 5.0 wt % aqueous detergent solution. The fabrics were stirred at 300 rpm with five balls that were made of folded aluminium foil and a Teflon blade for 15 min. After detergent treatment, the fabric pieces were flushed with running distilled water for 5 min and dried at 40 °C on a hot plate overnight. Subsequent to the washing cycles, they were used for surface property evaluation.

3 Results and Discussion

Based on the established theoretical and experimental results, it is believed that a hierarchically dual scale structured surface roughness plays an important role in superhydrophobic surfaces.[34] This is because a hierarchical structure is commonly recognized to play a strategic role by introducing air pockets trapped between the droplet and the solid surface, minimizing the contact area. Herein cotton fibres and their arrangement inherently acted as an ideal platform for hierarchical micro/nano structured features. To introduce a dual-scale structure on the textile surface, oxygen plasma pre-treatment followed by DLC coating was carried out on the cotton fabrics, as schematically shown in Fig.1.[33] Typical scanning electron microscopy (SEM) was used to investigate the morphologies of the cotton textiles before and after a 10 min oxygen plasma pre-treatment following DLC deposition as shown in Fig. 1. As a comparison, in Fig. 1 a, the pristine cotton microfiber before treatment, showed a relatively smooth surface and evident grooves and striations along the fibre. Fig. 1 b show how after oxygen plasma treatment and DLC deposition (Fig. 1 c), the surface of the treated cotton fabric reveals a hierarchical roughness that comprises of regular fibre structures (15 to 20 μm in diameter) smeared with smaller nanometre scale asperities, which resembled the multiscaled structures of lotus leaves. The appearance of the cotton fibres after oxygen plasma with largely enhanced surface roughness of the fibres, were helpful for the final formation of the superhydrophobicity due to the air trapped among the nanoscaled structure on the fibres formed by the growth of the coating. As shown in Fig. 2 by varying the exposure of the of the oxygen plasma pre-treatment (i.e. in the range of 1–60 min), reflected a different growth behaviour in terms of density, size, and distribution of the nanoscaled asperities.

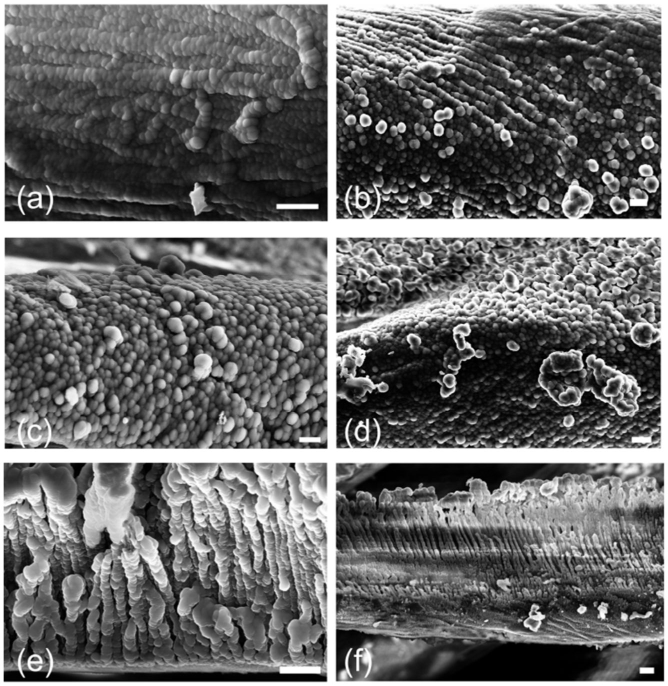

Fig. 2 SEM images of the cotton with DLC coating following different pre-treatment exposure time. SEM images of the DLC coated cotton textiles varying exposure of the oxygen pretreatment by a (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, and (f) 60 min exposure. The length and sizes of the protuberances increase as of the plasma pre-treatment time increases. A dual-scale structure is obtained on the surface of cotton fibre combining plasma treatment with DLC coating. All inset scale bars represent 1 μm.

For example, for short durations from 1 to 10 min, a round beaded morphology composed of spherical particles with diameters of about 100-200 nm was noticed on the cotton fibre.[32] More interestingly, surfaces of the films deposited after a 30 min and 60 min plasma pre-treatment, showed a highly irregular surface with threaded fibrillar structure, as shown in Fig. 2 b–f. Apparently, a restructuring process (i.e. change of surface structural characteristics) is induced during prolonged plasma treatment, as in general, polymers and cellulose containing oxygen groups are more sensitive to etching and are known to form a nanofibrillar structure by oxygen plasma.[34] Consequently, for longer duration of oxygen plasma treatment, an increased etching of the fibre is achieved on the surface of the cotton fibre which provided as a different microstructured support for DLC growth. Preliminary AFM investigations (data not shown) confirmed the surface topography observed in the SEM images.

Besides the surface structure, the effect of the surface chemistry on WCA also cannot be neglected. XPS analysis further confirmed the presence of a uniform coating on the cotton (Table 1).

Table 1 Chemical composition measured by XPS.

Sample	C 1s	O 1s	N 1s	O/C	N/C
Pristine cotton	57.9	41.2	0.9	0.711	0.015
DLC/O_2 pre-treated (10 min)	89.5	10.5	-	0.117	-
DLC/O_2 pre-treated (60 min)	92.68	7.32	-	0.079	-

XPS measurements of the coated textile revealed that the fibres were completely covered (no N 1s signal) and the coatings were mainly composed of carbon (89,5%) and a low amount of oxygen (10,5%) due to surface contamination. Prolonged oxygen plasma pre-treatment exposure (60 min) caused a negligible increase of carbon content (92,68%) and reduction of oxygen(7,32%), as reported in Table 1. Moreover the precursor stoichiometry of O/C for a 10 min oxygen plasma exposure was reduced from 0.117 to 0.079 for a 60 min exposure. Thus, longer plasma exposure yields to a minor chemical change of the DLC coating on the surface.

Wettability was determined by measuring the contact angle (CA) of a water droplet on the surface of the DLC coated cotton fibre after different oxygen plasma exposures. The water contact angle of untreated cotton was 0° as the cotton fabric readily absorbs water. Deposition of a thin DLC film onto the cotton fibres with no plasma pre-treatment provides an increase in the static contact angle to 143°± 2° (Fig. 3). The increase in CA from when DLC is coated onto unetched cotton indicates that merely coating the microfibres with DLC can impose strong water repellency on to an extent owing to the microscale roughness as well as the low-surface-tension compound covering the structure The intrinsic hydrophobicity could be improved by texturing furthermore the surface with hierarchical multiple scaled roughness to improve the substrate wettability using an oxygen plasma etch pre-treatment. Clear substantial differences were found with plasma pre-treatment exposure. Upon 1 min of oxygen plasma pre-treatment, the DLC coated surface shows a slight decrease of the water contact angle, most likely due to the preliminary etching of the fibre and the high-surface energy modification. This suggests that the beaded morphology cannot support the water droplet well enough and that the droplet 'sinks' into the pores of the structure resulting in a reduced water contact angle (Wenzel state).

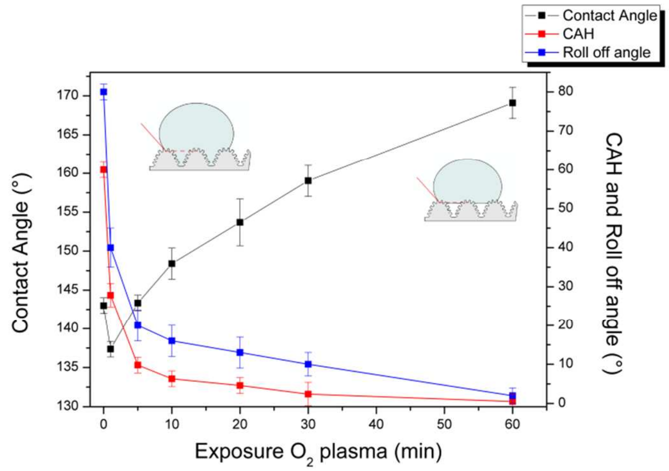

Fig. 3 Water wetting properties of the DLC coated cotton fabric. Contact angles, contact angle hysteresis(CAH) and roll off angles of water droplets on surfaces of DLC coated textile as function of plasma pre-treatment time. Insets are the schematizations of a water drop showing, on the left, a fully wetted state (Wenzel state) and on the right a drop sitting on the dual scale asperities (Cassie-Baxter state).

Increasing oxygen plasma exposure further increased the static contact angle. After 60 min of oxygen plasma pre-treatment, the contact angle of water significantly increases to 169.3 ± 2.2° through the introduction of two-tier micro/nanoscaled structure. It is evident that the superhydrophobicity of the DLC coated fibres was mainly due to the fractal-like roughness surface superhydrophobicity due to structural transformation which allowed air to be trapped between the multiscaled networks and which prevented the penetration of water into the porous network.[35,36] The high CA depends on a high percentage of liquid–solid interface replaced by liquid–gas interface. As formulated by Cassie's equation, the water contact angle increased with larger roughness of the micro/nanostructure with an increase of the fraction of the liquid–air interface area. Obviously, the dual-size-rough surface traps more air fractions than surfaces only having one level of roughness. Much like the lotus leaf, whose surface is composed of microscale bumps that are covered with nanoscale ''hairs'' of wax, the etched cotton showed, in this work, a hierarchical surface structure in the form of nanoscale structures on the fibres combined with the microscale roughness of the fibre network itself. Further significant wetting properties characterizing the contact behaviour of the surface are the contact angle hysteresis, (CAH, that is, the difference between the advancing θ_{adv}, and receding contact angles θ_{rec}, of a moving droplet) and the sliding angle (SA, that is, the surface tilt required for droplet motion). CAH highly depends upon surface heterogeneity and to the pinning of the contact line of the water droplet to the surface micro/nano roughness prior rolling off the surface, defining the self-cleaning effect.[37] As shown in Fig. 3, the CAHs decreased regularly with increasing exposure to oxygen plasma, and achieving a lowest value of 0.8° for the 60 min oxygen pre-treatment. Such a low value of hysteresis revealed that the water could not penetrate into the surface structures and it sits on the asperities of the surface with the minimum liquid solid adhesion. However, the DLC-coated cotton with no plasma treatment displays extremely high contact angle hysteresis, with advancing and receding contact angles of 150.3° ± 3.4° and ~ 60°, respectively. As a consequence, the water droplets strongly adhered to the substrate. This was confirmed by the roll off angles. Surfaces of short plasma pre-treatment required a slight agitation to dislodge the smaller droplets from the surface, while those treated with prolonged exposure rapidly rolled off the surface. This further confirms that roughness alters the wettability of solid surfaces, leading from a Wenzel state to a Cassie–Baxter regimes. The ultra low roll off angle is a direct consequence of the reduced soli-contact area due to the air trapped along the coarser scale due to the fibre. It should be noted that a possible underestimation of the contact angle may be due to the fibres sticking out from the cotton sample (Fig. 4). Furthermore, the inherent elasticity of the cotton fibres may result in a repulsive interaction between the fabric and the water/air interface, lifting the water droplet from the surface, as schematized in Fig. 4b.[38] Upon increasing the size of pores among the fibres, the DLC coated sample retained its superhydrophobic properties. In fact a DLC treated porous substrate, such as a gauze cotton dressing, clearly still repelled liquid drops which preserved a round shape, Fig. 4c. Most significantly, for a 60 min plasma treatment, spraying water on the coated textile bounced off the surface without leaving trace was shown in Fig. 4d.

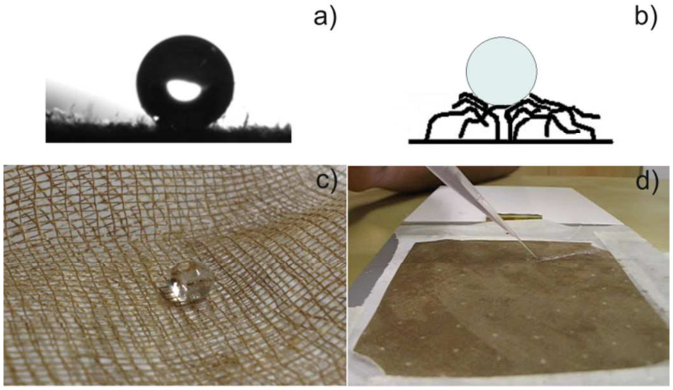

Fig. 4 Wetting behaviour of water on the as-prepared DLC coated cotton. a) An optical image of static water droplets (3 µL) at a CA of 170° on the respective DLC coated textiles modified by a 60min plasma pre-treatment. b) Schematization of the elastic deformation of the protruding cotton fibres due to forming bundles at the water/air interfaces. c) A plasma treated and DLC coated gauze showing clearly superhydrophobic properties even with bigger pore size. d) Optical image demonstrating the high superhydrophobic properties of the cotton fabrics as a jet of water cannot wet the textile but bounces off.

The presence of a hierarchical structure is likely the reason behind the ability to attain high superhydrophobic surfaces with low hysteresis properties. Recent research has reported that even nature's most renowned superhydrophobic surface, the lotus leaf, is coated with a hydrophilic wax (CA = 74°), showing that superhydrophobicity can be attained with hydrophilic surface coatings when combined with the appropriate surface structures.[39,40] Much like the lotus leaf, whose surface is composed of microscale bumps that are covered with nanoscale ''hairs'' of wax, the DLC coated cotton also shows a similar topography with hierarchical surface structures in the form of nanoscaled structures combined with the microscale roughness of the fiber network itself. These observations do not follow Wenzel's theory. Rather, the nanometer-sized protrusions cause water to contact a composite surface of solid and air by increasing the air trapped in the accessible area, resulting in an apparent superhydrophobicity on surfaces with a CA_{flat} value of less than 90°.

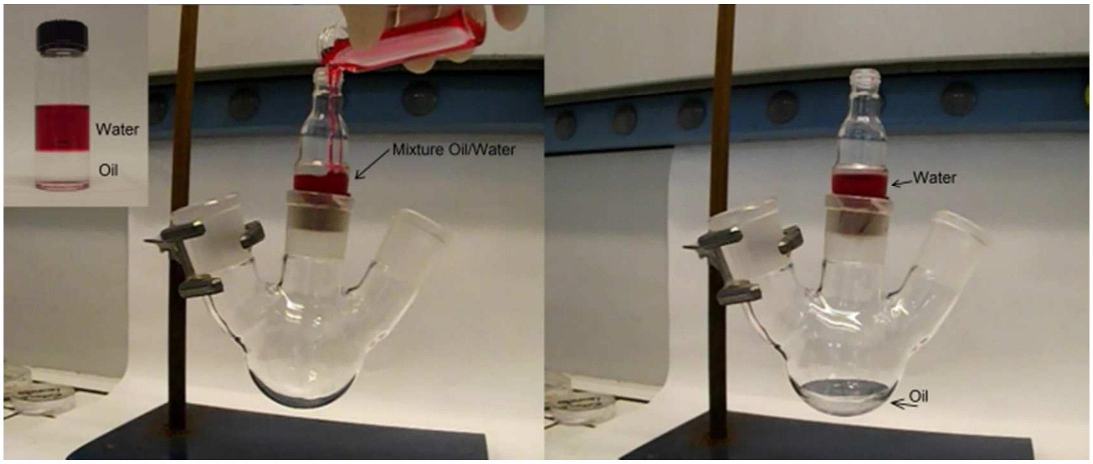

Fig. 5 Controllable oil/water separation using the DLC coated cotton textile as a membrane for filtration. The DLC cotton textile was fixed between two glass tubes as a separation membrane. A mixture of oil and red coloured water was poured into the upper glass tube. The oil selectively passed through the textile, whereas the red coloured water remained in the upper glass tube (right panel).

The combination of a hierarchical roughness of the fibers, which has the ability to support the droplet on a composite surface of air and substrate, contributes significantly to the ultrahydrophobic behaviour. Therefore, there is much to be learned from exclusively modifying the surface by varying just one of these parameters to establish certain limits such as the roughness scales needed for superhydrophobicity. Having demonstrated the superhydrophobicity of the DLC coated cotton we then evaluated the oil wettability. According to Wenzel's theory, surface oleophilicity can be enhanced by increasing the surface roughness. Oil spreads and permeates quickly into the textile indicating its super-oleophilic property.

We therefore evaluated the oil selectivity of the DLC coated cotton for discerning organic solvents or oils from water mixtures.

The ability to absorb oil from water is not enough as a solution to oil spill accidents, and it is still necessary to separate oil water mixtures toward preparing the oil skimmer and separation devices. As a proof of concept, in order to confirm the feasibility of the coated fabric as a oil/water separator, a solely gravity driven oil/water separation experiment was performed as shown in Fig. 5, see also Movie S1.†

Due to the superhydrophobic nature of the DLC coated fabric, a heavier oil was selected so that oil droplet could sink down and stand on the fabric surface. As shown (Fig. 5 and the Supplementary Movie S1†), the DLC coated textile was fixed between two glass tubes. A mixture of transparent pump oil and red coloured water (50% v/v) was poured onto the as-prepared coated textile to verify the use of the fabric with oils that had higher densities than water. Because of the superoleophilicity and superhydrophobicity of the functionalized textile, the oil quickly passed through the DLC textile, into the beaker below. Meanwhile, all of the water was retained above the membranes due to the superhydrophobicity and low water-adhesion of the DLC fabric. No external driven force was used during the fast separation process (within 3 min), only their own weight. Also no coloured water in the collected oil or oil in the collected water could be detected, which indicates a very high separation efficiency of the DLC coated cotton textile. In addition, the DLC coated cotton is easily cleaned for reuse, even high-viscosity oils can be washed away easily. Hence, our superhydrophobic fabrics showed specifically to be a good candidate as filter membranes to realize highly effective separation of oil–water mixtures and oil spill clean-up.

In order to investigate the practical application of oil spill cleanup behaviour of the DLC coated cotton fabric, we imitated the petroleumwater mixture process under natural extreme conditions. Through dispersion of petroleum and water we simulated a pre-dispersant, sludge like the oil in the Gulf of Mexico as presented in Figure 6a. A bag was fabricated and immersed in a 50:50 v:v mixture of petroleum and water.

The petroleum was gradually selectively absorbed once placed in the mixture (Movie S2†, Supplementary Material). After about 1 min, we observed that most of the petroleum had been absorbed and that the colour of the mixture had faded as demonstrated in the sequence of Fig. 6a-d. After about 2 min the water phase became clear and transparent. Subsequently, the oil was separated entirely from the water simply by taking the cotton textile out. This clearly suggests the potential use as the selective absorbent to remove oils and organic solvents from water. It is obvious that the as-prepared coated cotton textile shows an excellent and fast ability to absorb petroleum, which makes it an perfect candidate for oil-spill clean-up and oil/water separation and a possible aid for world life (i.e. the good flexibility and mechanical stability of the textile suggests a less dangerous way to remove oil for example from the plumage of the birds without harmful consequences).

To further demonstrate this, the efficiency of oil absorption was evaluated in terms of absorption capacity (k), i.e., defined as the weight of absorbed oil per unit of dry weight (Fig. 7).

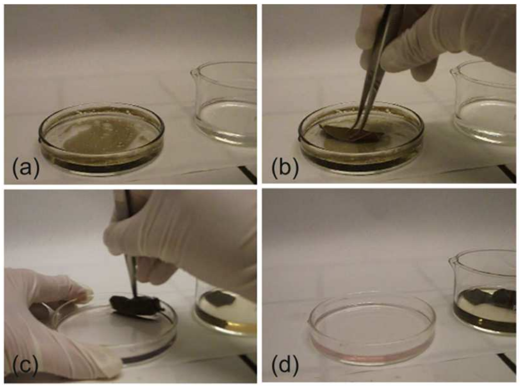

Fig. 6 The process of oil removal from an oil/water mixture. Snapshots showing the ability of the DLC coated cotton textile to remove oil mixed in water. We started with a petroleum/water mixture (a). The process of oil removal consisted in immersion of a piece of the DLC coated cotton the mixture (b), after 2 min of operation (c) clear and transparent water is clearly visible (d).

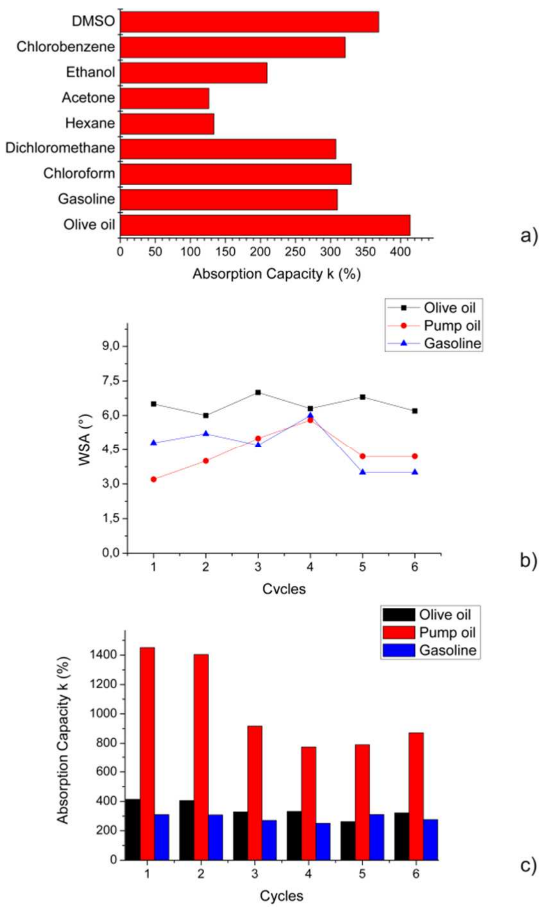

Fig. 7 Absorption capacity of the as-prepared DLC coated cotton. a) Absorption of various oils and organic solvents by the superhydrophobic DLC coated cotton fabric. b) Variation of the water sliding angle (WSA) of the superhydrophobic coated cotton with absorption cycle. c) Graph of the absorption capacities of various oils.

Various classes of organic liquids were considered in this study, e.g., common pollutants in use in daily life and industry as commercial petroleum products (gasoline and pump oil), fats (olive oil), and organic solvents, such as ethanol, hexane, chloroform dimethyl sulfoxide, alcohols, and acetone.

First contact angle measurements were performed on the on the DLC smooth silicon surface. Liquids with a markedly lower surface tension rapidly wet the surface, (see Table 2), clearly demonstrating the DLC's oleophilicity.[41,42] Next contact angles of liquids with low surface tension were measured on the 60 min plasma pre-treated DLC coated cotton fabric.

Table 2 Components of the static Contact angle (°) and Surface Tension (mN /m) of the various liquids measured on a DLC smooth surface, using Owens -Wendt equation for the surface energy calculations. [27]

	Static Contact Angle (°)	Surface Tension, γ^S (mN/m)
Water	69.2 ± 1.1	72.8
DMSO	6 ± 0.5	44
Chlorobenzene	4 ± 1.6	33.6
Ethanol	3.6 ± 0.8	22.1
Acetone	1.5 ± 1.1	25.2
Hexane	4 ± 0.6	23.3
Olive Oil	2.3 ± 1.1	32.6
Dichloromethane	3 ± 0.8	28.6
Gasoline	2 ± 1	27.5
PFPE Fomblin Oil	3 ± 0.8	22
motor oil	4 ± 0.8	24.4

On the cotton fabric, oils were quickly absorbed in a few seconds, left till saturated absorption, and weighed instantaneously to avoid evaporation. As shown in Fig. 7, the oil absorption capacities of the coated cotton for oil, gasoline and solvents like acetone, varied from 414%, 310 % to 126%, respectively. No dripping of absorbed oil was observed in the handling process indicating good absorption of oil by the coated DLC cotton. More interesting is that the absorbed oils could be recollected through a simple mechanical squeezing process. As important criteria for practical applications, recyclable use for absorption of different kinds of oil and durability was also investigated and reported in Fig. 7. After the oil/water separation experiment, the contaminated textile was rinsed thoroughly by alcohol and water to remove the absorbed oil. Subsequently, the clean textile was dried in an oven at 60 °C for half an hour, and the superhydrophobicity could be easily recovered. This separation and recovery process could be repeated for at least 30 times. As shown in Fig.7 b the water sliding angle is in the range of 3−5° with increasing absorption−desorption cycles regardless of the kind of oil. This result indicates that the DLC coated cotton still kept its superhydrophobic properties after repeated oil absorption. The oil-absorption capacities, *k*, for different kinds of oil were nearly constant even after 5 cycles of oil-water separation, exhibiting good repeatability. An initial decrease of oil absorption capacity after the first cycles was observed (especially using pump oil). This was probably caused by the residual oils in the pores of the cotton, which cannot be removed by manual squeezing. Still, the DLC cotton can be re-used for multiple times without significant loss in absorption capacity.

Stability of the DLC coated cotton was evaluated by measuring the contact angle after 6 months of storage to investigate the effects of aging in air. The superhydrophobic property of the DLC fabrics were unaffected by aging in air. Long time immersion in oils affected slightly the superhydrophobicity of the samples. The WCA varied in the range of 3-7° after kept in diesel, motor oil and crude olive oil even for 30 days. This shows an inherent stability towards oils. The DLC coated fabric showed excellent stability even towards environments under various rigorous conditions. The chemical durability of DLC coated textile was examined using strong acid and base solutions. As shown in Fig. 8 a, water contact angles were in the range 166-172° when the fabric was immersed into the strong acidic (pH = 2) or alkaline (pH = 12) solutions for 72 h. Even after attack by strong acid or alkali, our fabric was still capable of effectively separating the oil–water mixture.

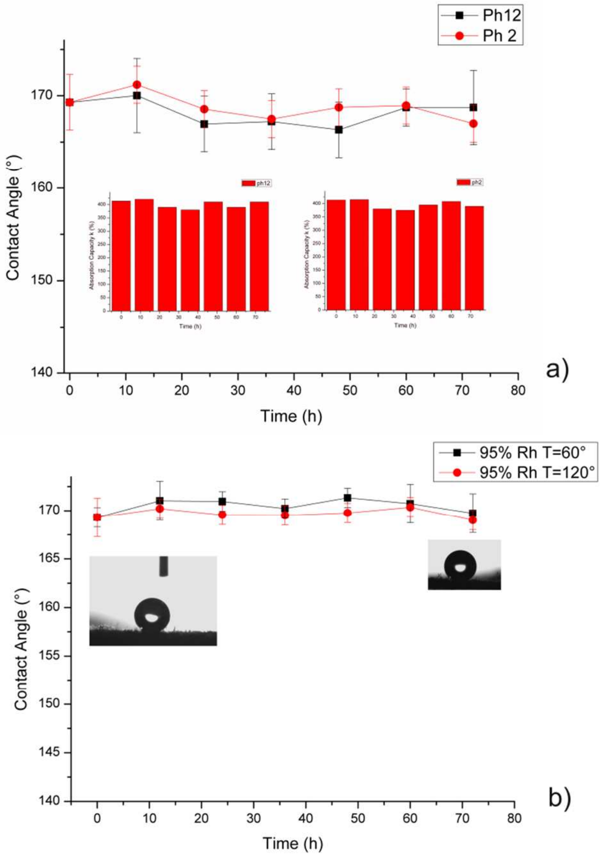

Fig. 8 Variation of water contact angles on the coated fabric (a) exposed to acidic and alkaline solutions and (b) under 95% RH at 60 °C, and at 120 °C. Insets in (a) are the corresponding separation efficiencies for the oil–water mixture.

When the coated fabric was placed in an environment with a temperature of 60 °C and a relative humidity (RH) of 95% for 72 h, the water contact angle remained unaltered within experimental error, likewise, after exposure to an extremely hot environment at 120 °C for 72 h (Fig. 8b). These results demonstrate a rather stable superhydrophobicity toward high environment temperature and high humidity and an efficient tolerance to acidic and alkaline conditions.

Durability of the superhydrophobic cotton fabrics surface is another important factor to determine its practical application.

Laundering tests were carried out on the treated DLC coated fabrics. Water contact angles on the treated DLC coated cotton fabrics after up to 20 simulated washing cycles were measured, (Fig. 9). Water-repellent abilities of the washed samples maintained a high contact angle with a minor alteration up to 20 washing cycles. The observed reduced hydrophobicity was attributed to the damage of the DLC film on the fiber due to swelling of the same. Thus, the data presented here validates the superiority of this one-step plasma treatment procedure to produce highly hydrophobic cotton fabrics.

This long-term stability will be essential when the superhydrophobic materials are introduced into practical applications.

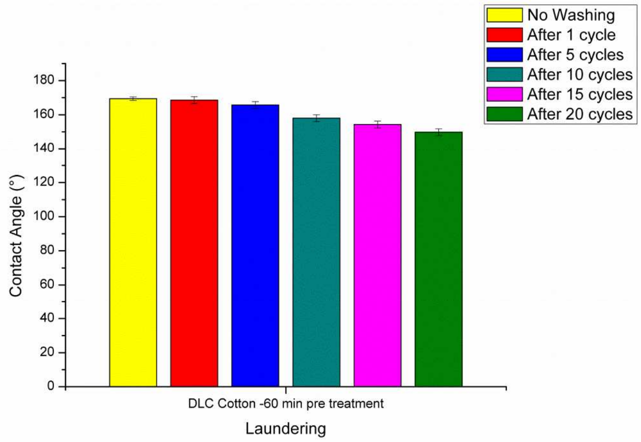

Fig. 9 Plot of the WCAs of the DLC coated cotton fabrics with 60 min plasma pre-treatment compared after a variety of laundering cycles. The washed cotton fabrics show a slightly reduced WCA attributed to the poor quality and swelling of the cotton used.

Conclusions

In summary, we have developed a superhydrophobic/oleophilic DLC coated cotton textiles that allow effective separation of oil/water mixtures using gravity. Varying the time of exposure of the gas was not only responsible for different morphology on the fibres, influenced by the etching of the fibre, but also affected cotton wettability properties. Water drops on the surface were shown to have a high contact angle up to 169° while oil drops where completely absorbed by the textile. The as-prepared cotton can selectively separate water from oil/water mixtures with high separation efficiency and selective oil absorption capacity, exhibiting reusability.

This improved method is important for engineering materials with controlled or variable wetting properties for highly developed oil/water separation. To our best knowledge, fabrics are much more malleable and flexible than stain steel meshes, and are better candidates for oil/water separation. Finally this new attempt to use special wettability to design next-generation materials for oil/water separation, suggests attractive potential applications in industrial oily waste water treatments and oil spill clean-up.

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