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## ARTICLE

## Underwater Wenzel and Cassie Oleophobic behaviour

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I. E. Palamà,<sup>a</sup> S. D'Amone,<sup>a</sup> V. Arcadio,<sup>a</sup> D. Caschera,<sup>b</sup> R.G. Toro,<sup>b</sup> G. Gigli<sup>a,c,d</sup> and B. Cortese<sup>a,e</sup>

Underwater wettability and wetting transitions of non polar liquids with rough solid surfaces are herein presented. Here, we demonstrate that a hydrophobic/oleophilic surface when immersed in water can result in an oleophilic or “Cassie” state of oil-wetting. This was achieved by utilizing respectively a diamond like carbon (DLC) coating on a cotton substrate and a combination of DLC and zinc oxide (ZnO) nanorods embedded into the structure. Moreover by increasing the time of immersion the oleophilic state reverted to a Wenzel state evolving to Cassie's regime. The mechanism of the transition was identified with the diffusion of the air into the water from the trapped air pockets of the substrate interface. Finally, switchable wettability of ZnO/DLC coated substrates allows a promising oil-water separation use.

### Introduction

In the panorama of oil/water related applications, a surface that mimics an underwater “desert beetle effect” that can effectively capture and collect oil droplets in water has potential applications, such as oil-repellent coatings for ships, marine equipments, oil pipelines, antimarine biological adhesion and oil spill cleanup.<sup>1</sup> Surfaces with anisotropic oil wettability have indeed recently attracted increasing interest as functional interfacial materials for underwater oil collection.<sup>2-5</sup> However the underwater effect on the surface interface still remains a challenging topic.<sup>6</sup> Besides, underwater adhered oils can seriously affect the separation efficiency after several usages, by contamination, fouling or even blockage of pores of filters or separating materials because of their intrinsic oleophilic property. In fact the oil absorbed on oleophilic materials is difficult to remove, with a significant increase of waste of both absorbed oil and oleophilic materials.<sup>7</sup> Therefore, there is a

critical need to develop novel materials for oil/water separation with high separation capacity, oil fouling resistance which are also easily recyclable.

A key tenet of anisotropic superoleophobic systems relies on the combination of a hierarchical scale of micro and nano-features and oleophobic silanes.<sup>8-9</sup> It is increasingly recognized that surface micro/nanostructures and roughness affect oil wettability and adhesion at the oil/water/solid interface.<sup>10-13</sup> Recently our group demonstrated that diamond-like carbon (DLC) coated cotton fabrics showed superhydrophobic/oleophilic properties and could successfully perform oil/water separation.<sup>8-14</sup> Despite the challenging task of creating superoleophobic surfaces, the underwater behaviour of oil droplets on these surfaces has not received much attention.<sup>15-16</sup> Wetting is generally related to two basic regimes, i.e., Wenzel (W) and Cassie–Baxter (CB) regime usually analyzed in a triple-phase system.<sup>17-18</sup> However underwater regimes are confined to a four-phase system

(oil/water/air/solid) where the water can play the same function as air in the superhydrophobic effect solid/water/air interface. Herein, we demonstrate the preparation of organic/inorganic coating-based oil-water separation materials by introducing zinc oxide to form hierarchical micro/nano architectures of a cotton mesh with tunable wettability and underwater superoleophobicity in an oil/water/air/solid system. Zinc oxide (ZnO) was chosen to improve material functionalities and to tailor the surface properties as they represent a material widely favourably used due to their excellent stability, environmental friendliness and low cost.<sup>19-24</sup> Superhydrophobic surfaces were synthesized via DLC coating and subsequent ZnO growth to fabricate an underwater superoleophobic separation membrane with self-cleaning ability. We also investigated the effect of surface topography and chemistry on wetting transition of an underwater solid-oil water interface. We demonstrate that an immersed solid surface can drive the transition from a hydrophilic state to a Wenzel to Cassie-Baxter state, as the air layer is reduced by diffusion. Changes at the underwater solid/liquid interface and underwater oil wettability were monitored using oil CAs to establish the implicit wetting behaviour of different textured substrates, optical microscopy to visualize the form in which the Cassie to Wenzel transition occurs, and XRD measurements to chemically identify the phase composition. The main focus of this manuscript is to examine effect of micro-nanostructuring in an underwater environment on the oleophobic/oleophilic properties. This study will profit broad applications to the development of advanced oil-water separation materials for practical applications involving low-energy, underwater oil collection, and oil-repellent coatings on ship hulls and oil pipelines. It is envisioned that such unique structure is favourable to design next-generation materials for oil/water separation, which ensures attractive potential underwater applications.

## Experimental section

### Materials

The reagents used for ZnO nanorods synthesis including zinc acetate dehydrate (99.999%, Aldrich) and NaOH (96.0%), were purchased from Sigma Aldrich. The ZnO suspension was prepared by the controlled hydrolysis of zinc nitrate according to a previous reported method.<sup>10</sup> All of the chemicals were used as received without further purification. Cotton textiles (100% cotton) were obtained locally, which was further purified by ultrasonic washing with distilled water, acetone and ethanol for 5 min, respectively, and then completely dried in the oven at 80 °C.

**Fabrication of ZnO seed layer:** The synthesis process involved two main steps as reported in the literature.<sup>10</sup> Details are described as follows: First, a five mM solution of inorganic precursor zinc acetate dehydrate (99.999%, Aldrich) in ethanol was made under vigorous stirring at 60 °C for 1 h. This solution (70  $\mu$ L) was spread over the entire substrate and was allowed to

evaporate for 25 s before rinsing with a copious amount of ethanol for each time to form a uniform ZnO seed layer. Between coatings the substrates were annealed at 120 °C for 15 min to ensure particle adhesion onto the substrate surface. The zinc acetate coating procedure was repeated four additional times.

**Fabrication of ZnO Nanorods:** Well-aligned ZnO nanorods can be controlled via adjusting the preparation parameters, such as precursor concentration, growth temperature and time. ZnO nanorods with an average diameter of 100 nm were chosen for this study to provide a large surface area-to-volume ratio and described as follows: growth of nanorods was carried out suspending the substrates in an aqueous solution of zinc nitrate hexahydrate (50–75 mM), HMTA (25 mM) at 100 °C for a pre-determined time from 0.5 h to 5h, depending on the desired length of nanorods. Finally the samples were thoroughly rinsed using deionized water to remove any residual salt or amino complex and allowed to dry in air at room temperature. All experiments described in hereafter were carried out under the typical conditions mentioned above.

**Surface coating deposition:** The self-assembled coatings were formed using a vapour deposition process. The samples were placed in a desiccator together with a small petri dish containing  $\approx$ 1 mL of the (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane liquid. The desiccator was pumped down to  $\approx$ 10 kPa. The pump was then shut off and the valve was closed so that the silane liquid could evaporate in the low-pressure environment of the desiccator and attach to the surfaces.

**Measurements**

**Contact Angles measurements:** The hydrophobicity of the lotus-leaf-like different systems was measured by means of the water contact angle (CA) using an OCA 20 contact angle system (Data Physics Instrument GmbH, Germany) at ambient temperature. To measure the contact angles of oil drops in aqueous media, diiodomethane (Aldrich, density = 3.325, surface energy ( $\gamma_{sv}$ ) = 50.8 mN/m ( $\gamma_d$  = 48.5,  $\gamma_p$  = 2.3)) was used. A transparent glass chamber with the attached sample to the bottom was fabricated, and deionized water poured in. After 1 h of rest, a drop of oil ( $\sim$ 3-6  $\mu$ L) was placed on the substrate, and the contact angle of the drop was measured at room temperature. An average contact angle value was obtained by measuring the CA at three different positions of the same pattern. The roll-off angles were measured by placing a specimen on a level platform and inclining the stage. Water and oil droplets (3, 50, 100, and 500  $\mu$ L) were placed onto the surface, and the angle of the stage was recorded when the drops began to roll off. The image of liquid droplets on the surface has been obtained using the digital camera of the OCA 20 contact angle system.

In the ultraviolet (UV) irradiation tests, four 15 W low-pressure mercury lamps ( $\lambda$  = 265 nm) were used as the UV irradiation source; After the UV irradiation, the films were placed in the dark for 7 days, new superhydrophobic measurements of the surfaces was obtained again for each sample.

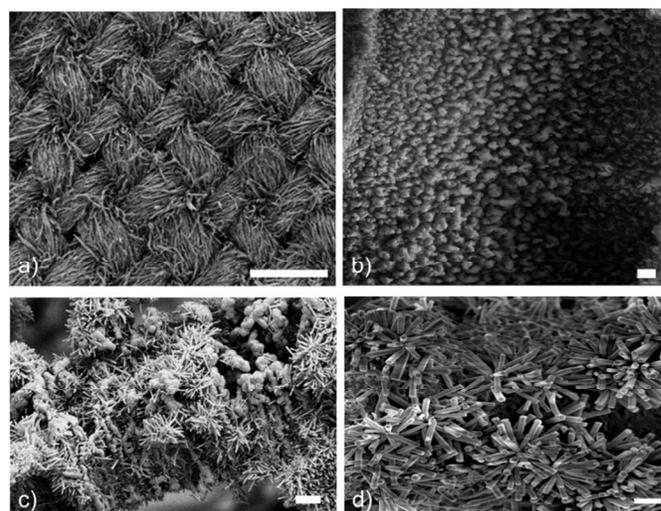
To induce hydrophilicity, the ZnO/DLC coated samples were irradiated with four 15 W low-pressure mercury lamps ( $\lambda$  = 265

nm) used as the UV irradiation source. The distance between the UV light source and the sample was approximately 12 cm. The total duration of the UV irradiation experiments was 120 min. After UV irradiation, the ZnO/DLC coated samples were subjected to different sets of storage conditions/stimulation, as follows: (i) storage in the dark under ambient environment (with relative humidity of 30–40%) for 5 days; (ii) storage under vacuum at a pressure of  $3 \times 10^{-3}$  mbar, for 40 h, following which further storage was allowed under ambient dark.

**Surface characterization:** Low-resolution SEM characterization of the substrates was performed with a RAITH 150 EBL instrument. Typically, the images were acquired at low accelerating voltages (less than 5 kV) using short exposure times.

## Results and discussion

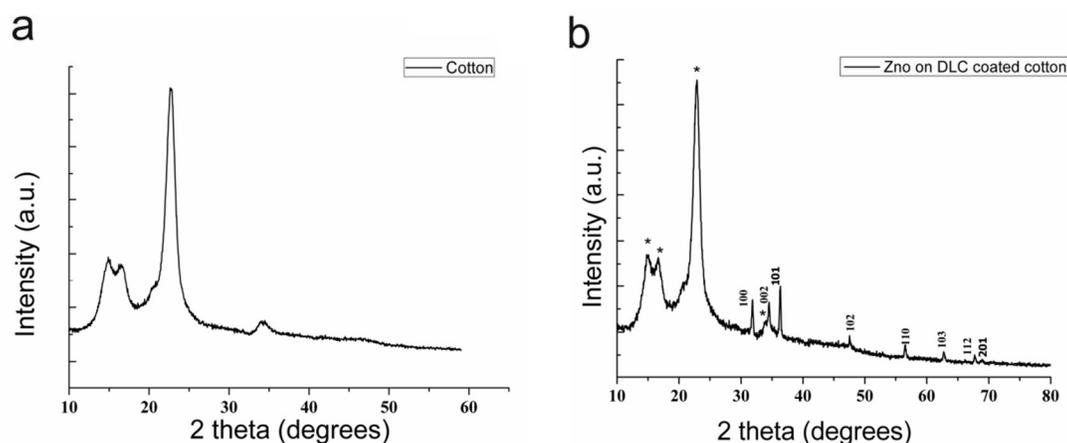
Cotton fabrics were selected as the base material due to its inherent porous structure as well as being low cost and easily available. In fact cotton fibres and their arrangement inherently act as an ideal platform presenting already a porous microstructured surface. The superhydrophobic characteristics were imparted by coating at first the cotton fabrics via DLC deposition through PECVD. This allowed to introduce a dual-scale structure on the textile surface. Zinc Oxide nanorods were subsequently grown on the DLC coated fabrics via a low-temperature hydrothermal approach, (details could be found in the Experimental Section).<sup>9–10</sup> Typically, a seed layer was deposited on the substrate followed by growth of nanorods in an aqueous solutions of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and hexamethylenetetramine (HMTA,  $(\text{CH}_2)_6\text{N}_4$ ) heated to  $100^\circ\text{C}$  for 5 h. The ZnO nanorods deposited were rinsed thoroughly with deionized water and ethanol and dried at room temperature. Figure 1 shows 1–500  $\mu\text{m}$  SEM images of the fabric, subsequent DLC deposition and of the ZnO nanorods grown on the DLC coated fibre substrate. It can be seen that for the DLC coated fabric (Figure 1b) a rough microstructured beaded-like morphology is formed on the smooth porous structure of the cotton's fibre surface. Synthesis of zinc oxide nanorods on the DLC coated cotton fabric, formed a hierarchical morphology, as clearly observed from SEM images (Figure 1c, d) where also the morphology of the DLC grown on the cotton fiber can be seen (Figure 1c).



**Fig. 1** SEM images of a) Low magnification of cotton fabrics without treatment, scale bar 500  $\mu\text{m}$ , b) plasma treated and DLC coated and c) Integrated ZnO Nanorods on the DLC coated fiber substrate, d) high magnification of the ZnO nanorods. Scale bar 1  $\mu\text{m}$

Interestingly, the zinc nanorods present a random flower-like structure that randomly interconnect with an average size of  $100 \text{ nm} \pm 10 \text{ nm}$  and length of  $1 \mu\text{m} \pm 200 \mu\text{m}$  (Figure 1 d). As shown the large quantity of nanorods self-assembled into flower structures with a closely packed mesh density and the characteristic hexagonal geometry associated with the wurtzite-type ZnO crystal. This crystal structure was also consistent with X-ray diffraction (XRD) data, reported in Figure 2.

XRD patterns of the cotton fabric without treatment showed diffraction peaks at  $2\theta$  values of 14.9, 16.5, 22.7 and  $34.3^\circ$  degree corresponding to (101), (101), (002), and (040), which present the typical structure of cellulose.<sup>25</sup> Other diffraction peaks at  $2\theta$  values of 31.85, 34.53, 36.36, 47.62, 56.65, 62.93, 67.98 and  $69.19^\circ$  degrees, were assigned to the 100, 002, 101, 102, 110, 103, 112 and 201 planes of the hexagonal wurtzite ZnO. These results indicated that ZnO has been coated on the surface of the cotton fabric. No characteristic peaks of DLC phases were observed. Excluding the cotton peaks, also, no carbon diffraction peaks except ZnO were found. This suggests that the DLC assumes a metastable form of amorphous carbon and that the cotton peaks prevail over carbon.



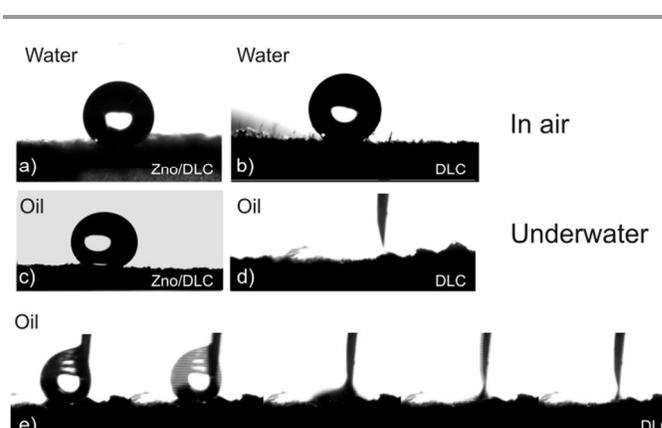
**Fig. 2** Representative XRD spectra obtained from (a) control cotton fabric without treatment and (b) the ZnO grown on the DLC coated cotton fabric after 5 h of aqueous hydrothermal growth at 100°C; the asterisk (\*) above the peaks indicate the typical diffraction peaks of cotton fibre.

It is well reiterated in literature that the wettability of surfaces is influenced by the surface free-energy as well as the surface roughness.<sup>26-27</sup> The DLC and ZnO/DLC coated surface showed properties of low free-energy and high roughness, its wettability was thereby evaluated by a contact angle system. Highly textured DLC coated cotton has been shown to exhibit superhydrophobic behavior with a contact angle of water ( $\theta_w$ ) of  $169.3 \pm 2.2^\circ$  as well as being superoleophilic in air as previously reported.<sup>8,10</sup> As for the ZnO/DLC coated surface, the rough structure formed by the 3D nanorods and microbumps still maintains the superhydrophobic/oleophilic properties of the surface (Table 1).

However underwater oil-wettability and adhesion properties of the different substrates showed opposite behaviour. The DLC coated cotton showed underwater superoleophilic properties whereas the ZnO/DLC coated surface reported underwater superoleophobic properties, as shown in Table 1.

**Table 1** The Water and Oil contact angle in air and Underwater showing the oleophilic behaviour in air and underwater oleophobicity.

Substrate	Water CA in air $\theta_w$ ( $^\circ$ )	Oil CA in air $\theta_o$ ( $^\circ$ )	Oil CA underwater $\theta_{ow}$ ( $^\circ$ )
DLC coated Cotton	$169.3 \pm 2.2$	0	0
ZnO/DLC coated Cotton	$162.7 \pm 4.4$	0	$146.2 \pm 2$



**Fig. 3** a-b: Photograph of a water droplet in air showing the superhydrophobic properties on a) the ZnO/DLC where  $\theta_w = 162.7 \pm 4.4^\circ$  and b) the DLC coated substrate where  $\theta_w = 169.3 \pm 2.2^\circ$ . c-e: Photograph of the oil droplet in contact with the surfaces under water, where c) is the contact angle of oil in water on the ZnO/DLC and d) DLC coated substrate. e) Sequence of photographs showing the contact angle of oil at the water/DLC interface, showing the quick collapse of the oil drop once in contact with the DLC surface.

If we compare the underwater superoleophobicity to the behaviour of drops in air, the key point to discuss here is the oil/water/solid three-phase interface system.<sup>10,28</sup> In a solid-water system, depending on the topography of the surface, air is likely to be trapped between the solid and water.

If we consider that the surface is composed of solid and water, theoretically Young's equation for a three phase system can be rewritten as<sup>29-30</sup>:

$$\cos\theta_{ow} = \frac{|\gamma_{oa}\cos\theta_o| - |\gamma_{wa}\cos\theta_w|}{\gamma_{ow}} \quad (1)$$

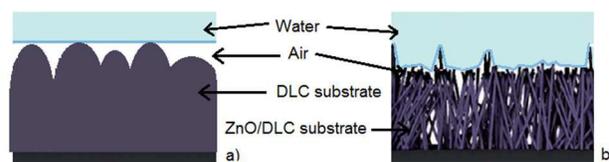
where  $\theta_{ow}$ ,  $\theta_o$  and  $\theta_w$  are the CAs of oil in water, oil in air, and water in air, respectively and  $\gamma_{oa}$ ,  $\gamma_{wa}$ ,  $\gamma_{ow}$  are surface tensions of the oil/air, water/air, and oil/water interfaces, respectively. Therefore to achieve an underwater oleophobic surface,  $\cos\theta_{ow}$  should be negative and consequently  $\gamma_{oa}\cos\theta_o$  should be lower than  $\gamma_{wa}\cos\theta_w$ .<sup>31</sup> Solving Equation 1 for both

substrates lead to  $122.5^\circ$  and  $119^\circ$  for the DLC coated cotton and the ZnO/DLC coated cotton, respectively. However for hydrophobic ( $\theta_W > 90^\circ$ ) and oleophilic ( $\theta_O < 90^\circ$ ) surfaces, equation 1 predicts that the surfaces are always oleophilic underwater in solid–water–oil interface,<sup>32</sup> which in our experiments is contradictory as the ZnO/DLC coated substrates is oleophobic immediately after immersion. To attempt to understand this conflicting phenomenon of underwater oleophobicity we considered the trapped air under water (Fig. 4). In the case of the DLC coated cotton fabric, the surface showed a micro beaded morphology on a undulated micro fibre which resulted in low roughness and voids filled with air forming a discontinuous water–air–solid three-phase contact line (TCL).<sup>7-33</sup> When the DLC coated cotton surface was just immersed into water, the rough undulation of the surface was filled with air (Fig. 5a). The air trapped on this kind of topography is continuous over a length scale that is large compared to the pitch of the texture and the thin layer of air seems to subsist over the top of micstructured undulated fibre, producing a continuous water–air interface over the large surface area. When an oil droplet is placed on the DLC film under water, oil drops will spread over the asperities because the interface that the drop contacts with the surface underwater will be a water/air interface and a four phase system (air–solid–oil–water) is formed, Figure 4.<sup>30</sup> Therefore when an oil drop contacts the DLC surface underwater, it will amend into contact with a water/air interface. Accordingly, the underwater DLC substrate is superoleophilic.

On the other hand the ZnO/DLC coated fibre presents a hierarchically structured surface, where the air is trapped at multiple length scales confined to smaller volumes and forming a discontinuous water/air interface and a semi continuous TCL. In this case, the addition of the rough nanostructure of the ZnO plays a key role in improving the oleophobicity under water triggering CB state. In fact when the ZnO coated fibres are just immersed in water, a smaller volume of air is trapped in the rough nano posts formed by the ZnO on the surface posts. The oil drop will be supported at the interface by the asperities. As immersion time increases, the layer of trapped air becomes thinner due to diffusion of air into water and the penetration of water into the pockets where the air was trapped.<sup>7</sup> In fact with increasing immersion time, the water layer thins by diffusion of air into the surrounding water due to surface tension effects, and replacing the trapped air.<sup>34</sup> Thus when the oil comes into contact with the surface, a semicontinuous contact line is formed on top of the rough surface which prevents the oil droplet from spreading out. The trapped air will further reduce with the immersing time and only remain at the bottom of pockets on the surface. In the Wenzel state, oil droplet fully penetrates the valleys of the textured surface, and the TCL is continuous and stable. Therefore, the surface generates relatively high adhesion to pin the droplet. In contrast, in the Cassie state, water molecules can be trapped in the micro/nanostructures to form a water-trapped composite

structure. Consequently the water droplet is suspended by the water molecules trapped on the surface (in composite contact mode), and TCL is discontinuous. Thus, the trapped water molecules will play a role in the decrease of the adhesive force between the oil droplet and the solid surface, and the droplet easily rolls off the surface.<sup>35-36</sup>

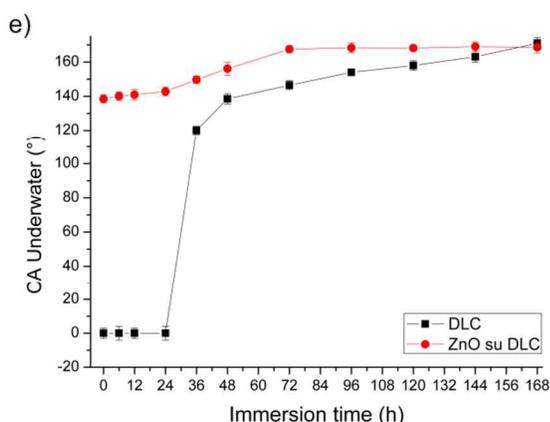
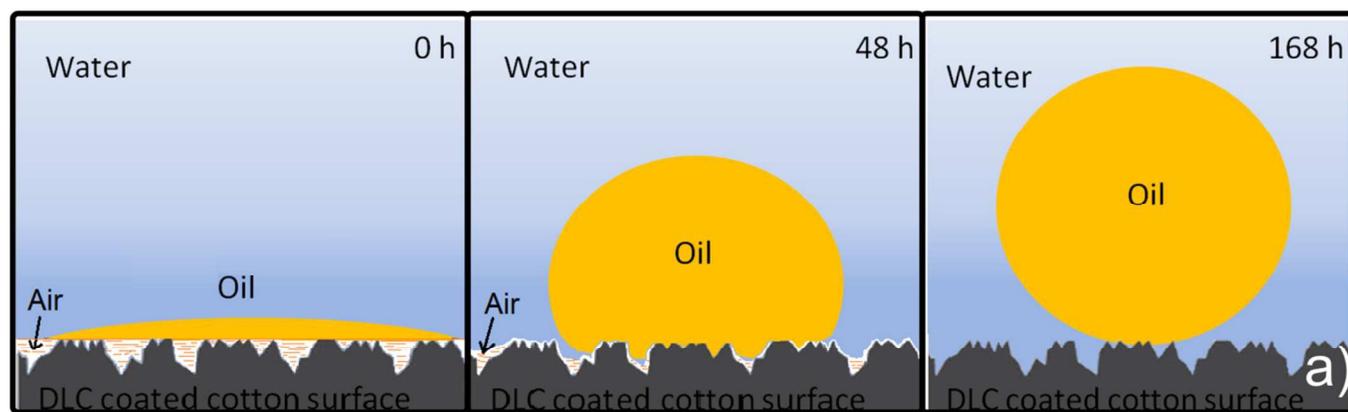
A regime change of the DLC coated substrates from the oleophilicity to oleophobicity was observed however after prolonged immersion in water. Indeed the underwater oil CA of the DLC coated cotton fabrics increased to near  $120^\circ$  after 48 hours, showing high oil-adhesion, Movie S1, Figure 5c. The oil droplet dropped on the inclined hierarchical microstructures firmly adhered clinging to the surface indicating that the underwater oil droplet was mostly in the "sticky" Wenzel state.



**Fig. 4** Schematic illustrations which represents the possible trapped air underwater situation of the DLC (a) and ZnO/DLC substrate (b). Note that the DLC coated fibre presents a bumpy morphology with bigger air pockets (a) while the ZnO/DLC coated substrate (b) possesses smaller air pockets due to the different morphology of the surface.

The increase of immersion time leads to a continuous change of contact mode of the oil droplet on the substrates, and therefore to a radical change in the wetting behaviour from Wenzel, Wenzel–Cassie transitional, to the Cassie state. Figure 5 illustrates the transition from the different states.

The diffusion time will therefore depend on pinning effects and on the volume of air trapped on the surface. The oil drop therefore is initially in touch with the air pockets present on the hierarchical morphology of the DLC coated surface because the presence of air in the voids of the surface prevents full contact of the oil droplet and the substrate. As the air diffuses into the surrounding water the water–air interface moves closer to the surface. As a result, the wetting state on DLC cotton surface changes into a typical Cassie's state with an OCA higher than  $160^\circ$  (after 7 days of immersion). Moreover the oil droplet showed to spontaneously roll off the surface devoid of contact-angle hysteresis thus lowering adhesive force of oil droplets. This result is consistent with a contact mode in the Cassie state.<sup>37</sup> Therefore the water/air interface formed is discontinuous with a continuous TCL. Therefore, the reduction of air at the solid–oil–water interface can lead to the change of wetting state along with oil adhesion and no longer affects the oil droplet spreading. Furthermore, we found that these diiodomethane droplets were quite unstable on the ZnO/DLC coated fibres, and they could easily detach from the surface, suggesting a low adhesion of the surface to the oil droplets in the aqueous medium, Movie S2.



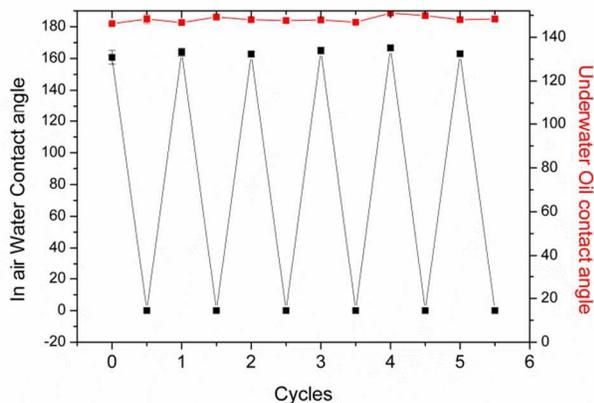
**Fig. 5** a) Schematic illustration of the different underwater oil wetting states on DLC coated cotton at different immersion times. Photograph of oil droplets in contact with the DLC coated fibre under water (b-e) showing the transition states. As soon as the substrate is immersed in water oil drops will spread out quickly indicating the surface is superoleophilic under water (b). After 48 h of immersion oil drops will collapse over the asperities in direct contact with DLC coating film resulting in high oil-adhesion, which is a typical Wenzel state (c). After 7 days of immersion more water is trapped at the interface and leads to a high ratio of water content (d). The oil wetting state turns into Cassie state with low oil adhesion. e) The wetting behaviour of the underwater oil droplet on the DLC and the ZnO/DLC coated surface at different immersion times, showing the durability and the stability of the surface.

We also tested different sizes of oil to test the dependence of oil roll-off angles on the droplet volume. As shown in Figure S2, the roll-off angle decreases as the oil droplet size increases. This was expected since, as the droplet exceeds a specific size,

its gravity would overcome the adhesion force between the substrate and the droplet. For a droplet of 3  $\mu\text{L}$  the roll off angle was about 5°. When we used a oil droplet of 100  $\mu\text{L}$  to 500  $\mu\text{L}$ , the roll-off angle on was less than 2°.

The process behind the liquid/liquid interface was also confirmed by considering the equation of spreading coefficient of liquid 2 on liquid 1,  $S = \gamma_1 - \gamma_2 - \gamma_{12}$  where  $S$  is the free energy variation of liquid 2 on liquid 1, and  $\gamma_1$ ,  $\gamma_2$  and  $\gamma_{12}$  are the interfacial tension between the solution and air, substrate and air and solution and substrate, respectively.<sup>38</sup> A droplet on a fully wettable surface with  $S > 0$  will spread spontaneously. When liquid 2 is placed on liquid 1, it will bead up with a negative spreading coefficient. Considering diiodomethane with its interfacial tension with air ( $\gamma_2$ ) is 50.8 mN/m, and the water surface tension ( $\gamma_1$ ) 72.8 mN/m, the diiodomethane/water interfacial tension ( $\gamma_{12}$ ) = 35.86 mN/m.<sup>39</sup> As a result,  $S = -13.94$  mN/m  $< 0$ , indicates that the oil droplet will tend to not spread out spontaneously. The experimental results are therefore consistent with the calculation analysis. Thus presumably the air trapped under water among the features and top of the rough surface allows the oil droplet to spread out.

Photo-responsiveness of surface wettability of water and oil on the ZnO coated fibres were evaluated by exposing the coated ZnO/DLC coated sample to UV irradiation (Fig.6).



**Fig. 6** Reversible wettability changes of ZnO/DLC coatings during cyclic alternations of 120 min UV illumination and dark storage showing the stable super hydrophobicity in air and oleophobicity underwater. No significant alteration can be noted.

When the fabric was irradiated by UV light, the surface hydrophilicity was greatly improved and resulted in a contact angle of  $0^\circ$ . After placing the UV irradiated sample in the dark, the original hydrophobicity was gradually recovered as the dark storage time was prolonged. The contact angle stored in the dark for 5 days was defined to the maximum recovery contact angle. Fig. 6 showed that the process of UV irradiation/dark storage could be repeated over several cycles, which indicates that the ZnO/DLC coatings indeed exhibit excellent stably reversibility in their wettability properties. Recovery was accelerated by applying a vacuum storage process in the dark environment. Vacuum application allowed to speed up the recovery of the pre-UV hydrophobicity state (2 days), by reverting back the UV-altered polar and nonpolar components of the ZnO surface chemistry to their original conditions. Although wettability can be reversed easily even upon storage under natural ambient conditions, the overall vacuum-driven recovery process demonstrates to be more rapid and controllable. Therefore the presence of air pockets seems to extremely affect the oleophobicity/hydrophobicity of surfaces. Moreover durability was assessed by placing the surfaces repeatedly in air and water several times.

Robustness of the Cassie Baxter state was parameterized in terms of the resistance to surface penetration at high pressures. Penetration will occur above an intrusion pressure, ( $P_{int-theor}$ ), which can be estimated as following:<sup>40-41</sup>

$$P_{theor} = \frac{2\gamma_{wa}\cos\theta_w}{d} \quad (2)$$

where  $\gamma_{wa}$  is the water surface tension,  $\theta_w$  is the water contact angle on a flat surface, and  $d$  corresponds to the distance between two adjacent geometric peaks that is approximately considered here as the average diameter of the pore. Since the pore shape is irregular, we assume that the interfacial area between oil and water equals to a rectangle with length  $L$  and

width  $d$  ( $L > d$ ). The theoretical calculations are lower than the reported experimental values as  $h_{intrusion(theory)}$  is predicted to be 14.5cm using the above equation. The experimental intrusion pressure was assessed through the weight of water, therefore, the experimental intrusion pressure ( $P_{exp}$ ) values were calculated using Equation (3) :

$$P_{exp} = \rho g h_{max} \quad (3)$$

where  $\rho$  is the density of the water,  $g$  is acceleration of gravity, and  $h_{max}$  is the maximum height of water supported by the coated DLC cotton fabric. The intrusion pressure for water was above  $2.2 \pm 0.08$  kPa. No visible water leakage was observed in the collecting bottle (Figure S1).

This illustrates the stability and high advantages that the ZnO/DLC coated fibre can support.

## Conclusions

In conclusion, underwater wetting of surfaces can be more complex than the usually predicted ones as a multiphase interface is formed when water, oil, and air contact a solid surface in an underwater environment. We have fabricated a superhydrophobic/hydrophilic and underwater superoleophobic porous substrate by synthesis of hierarchical ZnO nanorods on DLC coated cotton fabrics. The underwater oleophobicity of these substrates arises from the formation of a plastron of air on the hydrophobic surface when immersed in water. The air is initially trapped in the pockets of the surface morphology in the under aqueous environment. If the surface topography is such to form a discontinuous water-air-solid three-phase contact line (TCL) then the surface shows underwater oleophilic properties. On the other hand a morphology forming a continuous water-air-solid three-phase contact line would lead to underwater oleophobicity. However with time (2 days), the air pockets have been found to diffuse into water and eventually the surfaces become completely wetted with water and therefore develops into oleophobic. Furthermore, our approach shows that underwater oil-adhesion can be controlled by tailoring the contact mode and wetting state of oil droplets on the substrate. The trapped air layer on the micro-nano structuring of the surface plays a key role in the underwater oil wettability, which can switch from underwater superoleophilicity to underwater superoleophobicity. This is due to the correlation with the continuity of the TCL. Moreover the ZnO/DLC-coated fabric possessed excellent reversible wettability during UV irradiation and dark storage processes. Hydrophobicity was recovered more rapidly when the sample was stored under vacuum. Our study is important as cellulose materials with switchable wettability hold great potential in many fields: i.e. sensors, intelligent membranes, self cleaning surfaces. Also the development of stable underwater superoleophobic substrates, hold promising applications in bioadhesion, microfluidic technology, industrial metal cleaning and marine antifouling coating, etc.

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## Notes and references

<sup>a</sup>National Nanotechnology Laboratory-Institute Nanoscience-CNR (NNL-CNR NANO), via Arnesano, 73100 Lecce, Italy

<sup>b</sup>ISMN-CNR, Area della Ricerca di Roma Via Salaria Km 29,300, 00016 Monterotondo Scalo (Roma), Italy

<sup>c</sup>Department of Mathematics and Physics, University of Salento, Lecce, Italy

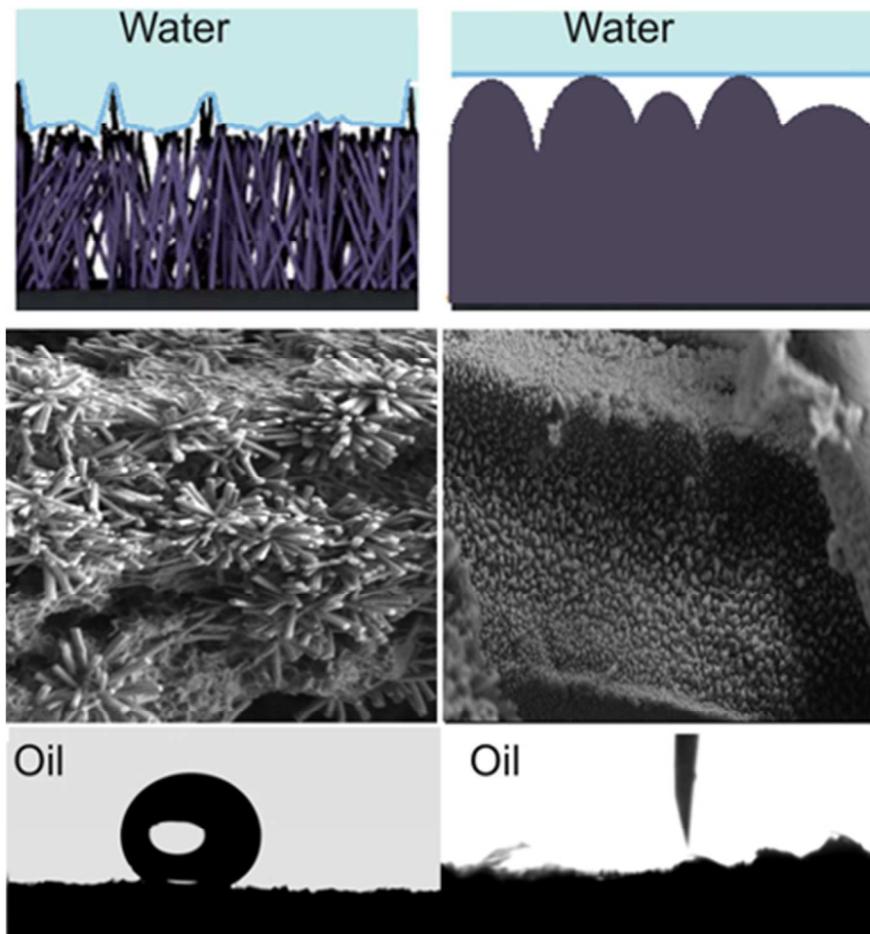
<sup>d</sup>Center for Biomolecular Nanotechnologies (CNB) of Italian Institute of Technology (IIT), Via Barsanti 73010 Arnesano (LE), ITALY

<sup>e</sup>Department of Physics, University Sapienza, P. le A. Moro 2, 00185, Rome, Italy

E-mail: barbara.cortese@nano.cnr.it

Electronic Supplementary Information (ESI) available: Movie S1 showing the high underwater oil adhesion on a DLC coated cotton surface after 48 h of immersion and Movie S2 showing the underwater oil slipping off a ZnO/DLC coated cotton surface. Figure S1 shows no visible water leakage while measuring the intrusion pressure for water, on a ZnO/DLC coated cotton fabric. See DOI: 10.1039/b000000x/

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A hydrophobic/oleophilic surface when immersed in water can result in an oleophilic or "Cassie" state of oil-wetting.

37x39mm (300 x 300 DPI)