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Fabrication of superhydrophobic cotton textiles for water–oil separation based on drop-coating route

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ABSTRACT

In the present study, we are so excited to report a simple drop-coating method for fabricating the superhydrophobic cotton textiles which can remove the water in oil (or the oil in water). It is confirmed that the superhydrophobic composite thin film containing modified-ZnO nanoparticles and polystyren (PS) has been successfully fabricated on the cotton textiles surface by a single-step procedure, and the superhydrophobic cotton textiles displays an excellent property in water–oil separation which is rarely put forward and studied. The static water contact angle on the superhydrophobic cotton sample surface arranges from 153° to 155°, and stays almost the same after exposure to ambient air or immersion in the corrosive liquids and oil, indicating the considerable range of potential applications for the superhydrophobic cotton textiles fabricated by this simple method.

1. Introduction

In the nature, many fascinating biological organisms exhibit special surface wettability, such as the self-cleaning property of lotus leaves (Wang, Li, & Xu, 2012), the superior ability to float on the water of water striders (Shi et al., 2007), the directional adhesion of butterfly wings (Zheng, Gao, & Jiang, 2007) and the antifogging functionality of mosquito eyes (Gao et al., 2007), which have attracted tremendous attention over the last decade in both academic sciences and industrial technologies (Li et al., 2005; Yao, Song, & Jiang, 2011). The biomimetic results have revealed that such special surface wettability of these biological organisms stems from their unique structural design and intrinsic material properties (Ji, Fu, & Shen, 2006; Yao et al., 2011). Taking their inspiration, the artificial surfaces with special wettability are commonly fabricated by two category methods: (1) introducing hierarchical roughness on hydrophobic substrates; and (2) coating a micro-/nanostructured surface with low surface energy molecules. In this way, many efforts including etching technique (Zheng, Feng, & Zhong, 2010), layer-by-layer self-assembly (LbL) (Han, Zheng, Cho, Xu, & Cho, 2010; Ji et al., 2006), lithographic patterning (Fü rstner, Barthlott, Neinhuius, & Walzel, 2005), electrodeposition (Badrea, Pauporte, Turminea, Dubotc, & Lincotb, 2008; Jiang, Zhao, & Zhai, 2004), polymer-phase separation (Wei, Liu, Tian, Xiao, & Wang, 2010), sol–gel methods (C.Y. Wang et al., 2011; H.X. Wang et al., 2011; Wang, Liu, et al., 2011; Wang, Shi, et al., 2011), solvothermal technique (Wu, Xia, Lei, & Wang, 2011), chemical vapor deposition (Artus et al., 2006) and others have been devoted to attain the new artificial materials or devices with special wettability.

It is well known that there are four types of fundamental wetting properties, including superhydrophobicity, superhydrophilicity, superoleophobicity and superoleophilicity, and novel surface functions can be obtained by combining any two of them (Feng & Jiang, 2006). Recently, solid surfaces possessing both superhydrophobicity and superoleophobicity or superhydrophilicity and superoleophobicity have attracted great interest for fundamental research and potential application in the field of separation films of water from oil (or oil from water) (Wu et al., 2012), such as calcium carbonate powder (Arbatana, Fang, & Shen, 2011), carbon nanotube sponge (Gui et al., 2010), metal mesh (Lee, Johnson, Drelich, & Yap, 2011; Wu et al., 2012; Yang et al., 2011), porous ceramic (Sua, Xu, Zhang, Liu, & Li, 2012), nanoporous polymers (Zhang et al., 2009; Zhang, Huang, & Han, 2006), and freestanding manganese oxide nanowire (Yuan et al., 2008). Many encouraging achievements were obtained from these studies, in spite of some limitations such as difficulty of biodegradation or recovery, low repeatability, potential toxicity, poor mechanical stability, low flexibility and high cost.

Cotton textiles, as a type of material with various excellent properties such as flexibility, biodegradability, low cost and density and high mechanical stability, have received intensive attention for practical application. However, due to the abundant hydroxyl groups on its surface, the cotton fabrics can be easily wetted by water and oil at the same time. To the best of our knowledge, many investigations about superhydrophobic

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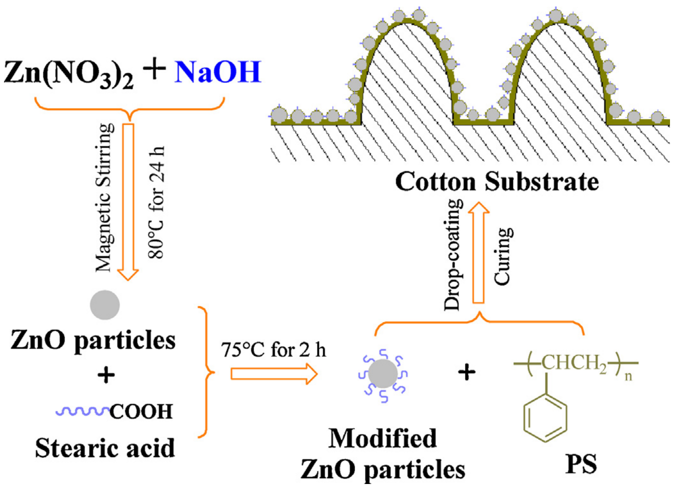

Fig. 1. Experimental strategy for the fabrication of superhydrophobic cotton taxtiles.

textiles have been performed. For instance, Zimmermann et al. reported a simple, one-step gas phase coating method for attaining the textile fabrics with long-term water resistance (Zimmermann, Reifler, Fortunato, Gerhardt, & Seeger, 2008). Deng et al. prepared a fluorinated acrylate monomer on cotton fabric which possessed a stable superhydrophobicity (Deng et al., 2010). Zhou et al. used polydimethylsiloxane, filled with fluorinated alkylsilane functionalized silica nanoparticles and fluorinated alkylsilane, as the material to produce a superhydrophobic coating on fabrics (Zhou et al., 2012). Wang et al. demonstrated that fabrics coated with hydrolyzed fluorinated alkylsilane have a remarkable self-healing super-liquid-repellent surface (C.Y. Wang et al., 2011; H.X. Wang et al., 2011; Wang, Liu, et al., 2011; Wang, Shi, et al., 2011). Gao et al. reported the cotton fabric with excellent water and oil repellency, which was coated by a series of polyhedral oligomeric silsesquioxane (Gao, He, & Qing, 2011). However, a bottom-up application of superhydrophobic cotton textile for water–oil separation has not been published yet. Uniquely, Zhang et al. prepared a type of superhydrophobic and superoleophilic textile for oil/water separation and selective oil absorption via chemical vapor deposition of trichloromethylsilane, which exhibited excellent reusability, oil/water separation efficiency, and selective oil absorption capacity (Zhang & Seeger, 2011). Regrettably, the separation of oil and water mixture by this textile had only been investigated qualitatively, while the real separation efficiency needs a detailed quantitative study.

In the experiments described in the following, the superhydrophobic modified-ZnO/polystyrene nanocomposite coating was prepared on cotton textiles surface by a simple, mild and cost-effective drop-coating procedure, and the chemical structures and the procedure used to prepare the superhydrophobic cotton textiles are presented in Fig. 1. As we all know, many tremendous practical challenges for artificial superhydrophobic surface still remain due to its unattainable robustness of hierarchical roughness and instability of surface chemistry. Therefore, in this work, the superhydrophobic stability of the prepared cotton textiles has been investigated after exposure to ambient air or immersion in corrosive liquids and oil to identify whether this type of superhydrophobic cotton textiles can be used in real applications. In addition, the superhydrophobic cotton fabric displays an excellent property in water–oil separation, and the separation of water and oil mixture by this cotton textile has been investigated qualitatively and quantitatively.

2. Materials and methods

2.1. Materials

The reagents used for ZnO particles synthesis including Zn $(NO_3)_2{\cdot}6H_2O$ (99.0%) and NaOH (96.0%), were purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. and Tianjin Kaitong Chemical Reagent Co., Ltd., respectively. Stearic acid (97.0%), employed to modify the ZnO particles, was also obtained from Tianjin Kaitong Chemical Reagent Co., Ltd. Polystyrene (PS) (Mw= 100,000) was provided by Daqing petroleum chemical industry plant. 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.

2.2. Synthesis of ZnO particles

The specific procedure was as follows: NaOH (0.04 M) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.004 M) were orderly added to 120 ml of distilled water, and vigorously stirred at 75 °C for 24 h. Then leave the mixture to cool to ambient temperature. Finally, as shown in Fig. 2, the ZnO particles with the average width and length of approximately 60 and 120 nm, respectively, were collected, purified with distilled water and ethanol, and then dried in an oven at 80 °C for 6 h.

2.3. Modification of ZnO particles

The modified ZnO particles were prepared by a hydrothermal reaction process. Typically, the as-prepared ZnO particles were dispersed in ethanol solution (10 ml) with stearic acid (0.06 g) as the surface modifying agent at 75 °C for 6 h. Then the modified ZnO particles were obtained through the repeated washing in absolute ethanol and drying at 75 °C for 2 h.

2.4. Fabrication of superhydrophobic thin films

In the typical process, PS (0.1 g) was completely dissolved in THF (5 ml), and soon afterwards, the as-prepared modified ZnO particles (0.10 g) were ultrasonically dispersed in THF solution at ambient temperature. Followed, several drops of the mixture solution were dropped on the cotton textiles which was placed on the clean glass substrate. Then the whole system was dried at 75 °C for about 20 min until the solvent was completely evaporated. Finally, the modified-ZnO/polystyrene nanocomposite coating was fabricated on the cotton textiles surface by the single-step procedure.

2.5. Characterization

The surface morphologys of ZnO particles and cotton textiles samples were characterized by using transmission electron microscopy (TEM, JEOL JEM2100) and scanning electron microscopy (SEM, FEI QUANTA200), respectively. The chemical composition of the cotton textiles before and after treatment was analyzed by using Fourier transform infrared spectroscopy (FT-IR, VARIAN FTS800), and X-ray photoelectron spectroscopy (XPS, Thermofisher Scienticfic Company, K-Alpha). The measurement of water contact angle (WCA) was carried out by using a commercial contact meter (Powreach, JC2000C) at ambient temperature, and the WCA was determined by averaging measurements taken from at least five different positions on each cotton textiles sample.

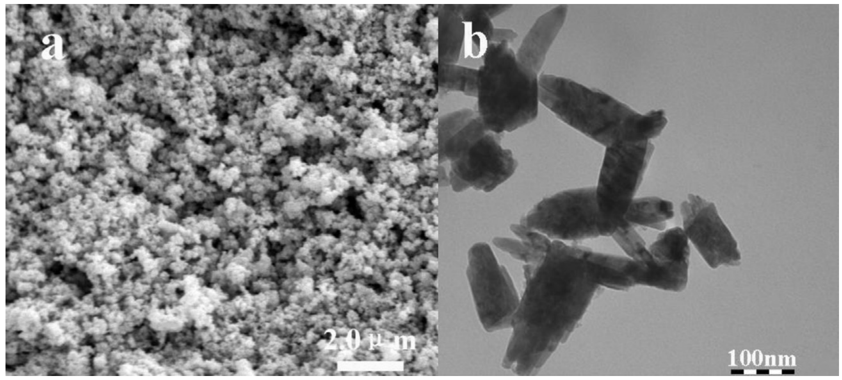

Fig. 2. SEM (a) and TEM (b) images of ZnO particles.

3. Results and discussion

3.1. Coatings on superhydrophobic cotton textiles

The surface wettability of a solid is commonly measured by the water contact angle (WCA), however, it is noteworthy that the reliable and accurate baseline of the cotton textiles for the WCA measurement is difficult to determine, which results from the macroscopic weave structure of the textile fabrics and numerous protruding fibers. Moreover, the determination of contact angle can be affected by contrast, lighting and focus as well. Thus, only the CA interval for 5 μL water droplet was reported.

Fig. 3 shows that the hydrophobicity of cotton textiles is dependent on the contents of PS and modified-ZnO particles in the modified liquid, where the WCA is stable and greater than 150° when both of PS and modified-ZnO contents reach 2.22 wt% in THF. However, as shown in Fig. 3a, the wetting behavior of cotton samples covered with pure PS coatings is very bad and unstable when the content of PS in THF is lower than 2.22 wt%. Meanwhile, when the content of PS is higher than 2.67 wt%, the hydrophobicity of the cotton textiles coated by pure PS film is relatively stable, but their WCA would have a decrease. According to the optimal and economical principle, 2.22 wt% PS in THF has been employed in the following experiments. The relationship curve between modified-ZnO content and WCA of coated cotton samples, which have been treated by the modified liquid with 2.22 wt% PS and modified-ZnO particles, is quite similar to the dependence of pure PS content. In Fig. 3b, the nonwettability of treated cotton samples increased sharply at low modified-ZnO content, became superhydrophobicity when modified-ZnO content was 1.78 wt%, achieved the maximum when modified-ZnO content was 2.22 wt%, and then decreased gently at high modified-ZnO content. Consequently, 2.22 wt% PS and 2.22 wt% modified-ZnO in THF were adopted to fabricate the superhydrophobic cotton textiles.

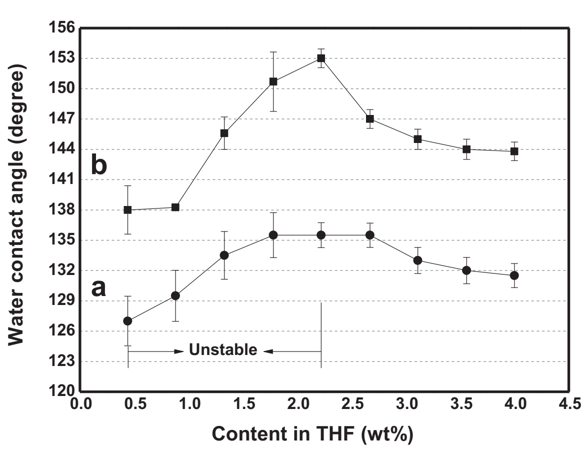

Fig. 3. The relationship between (a) WCA and PS content in THF and (b) WCA and modified ZnO content in THF.

3.2. Morphology of superhydrophobic surface

From the high-resolution scanning electron microscopy (SEM) images of pristine cotton textiles, we can clearly observe the weave structure, some protruding fibers at low magnification (Fig. 4a), and numerous longitudinal corrugations along the fiber (with the diameter of about 11 μm) at high magnification (Fig. 4b). Obviously, this microscopic structure of cotton textiles surface has provided comparative microroughness for the fabrication of superhydrophobic surface (Li, Xing, & Dai, 2008). In the SEM images of superhydrophobic cotton textiles (Fig. 4c–e), the holes between bundles and the weave structure of cotton textiles are retained to permit air passage. Therefore, we can conclude that the cotton textiles after treatment are still suitable for use as a textile (Deng et al., 2010). However, as shown in Fig. 4d, the natural texture structure on fiber has disappeared after modification, and a compact coating with a number of white nanoscale embossments caused by ZnO particals was observed. Fig. 4e clearly shows that these nanoscale granules with the diameter of approximately 150 nm have uniformly and compactly distributed on the cotton fiber surface, which created the nanoroughness on fiber surface. Combined with the micro/nano binary surface roughness and low surface energy film created by the single-step operation of drop-coating, the superhydrophobic cotton textiles with the WCA of 153–155° were successfully obtained.

3.3. Chemical composition analysis

The FT-IR spectra of modified ZnO particles and superhydrophobic nanocomposite coatings on the cotton fiber in the range of 4000–400 cm^{-1} were presented in Fig. 5. From Fig. 5a, we can observe two strong adsorption peaks at 2916 cm^{-1} and 2847 cm^{-1}, which can be attributed to $-CH_3$ and $-CH_2$ asymmetrical stretching vibrations and symmetrical stretching vibrations, respectively, indicating the existence of a long-chain alkyl group on ZnO surface (C.Y. Wang, Piao, & Lucas, 2011; Wang et al., 2012). Additionally, the adsorption peaks at 1537 cm^{-1} and 1463 cm^{-1} should stem from the asymmetric and symmetric stretches of $-COO^-$ in $CH_3(CH_2)_{16}COO^-$ groups, further confirming the prosperous attachment of stearic acid to the ZnO surface (C.Y. Wang et al., 2011; H.X. Wang et al., 2011; Wang, Liu, et al., 2011; Wang, Shi, et al., 2011; Wang et al., 2012). As shown in Fig. 5b, a series of peaks around 3024 cm^{-1} and the two peaks at 748 cm^{-1} and 694 cm^{-1} can be detected due to the stretching vibrations and bending vibrations of C—H on the benzene ring. Furthermore, the characteristic peaks

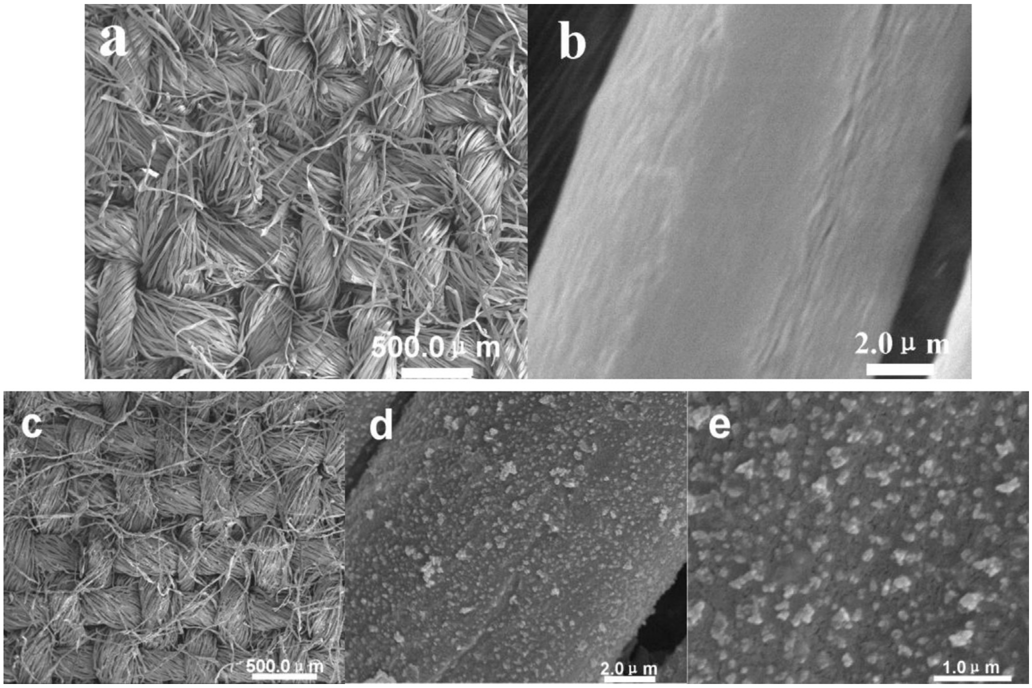

Fig. 4. SEM micrographs of pristine cotton textiles at (a) low and (b) high magnification; superhydrophobic cotton textiles at (c) low, (d) middle and (e) high magnification.

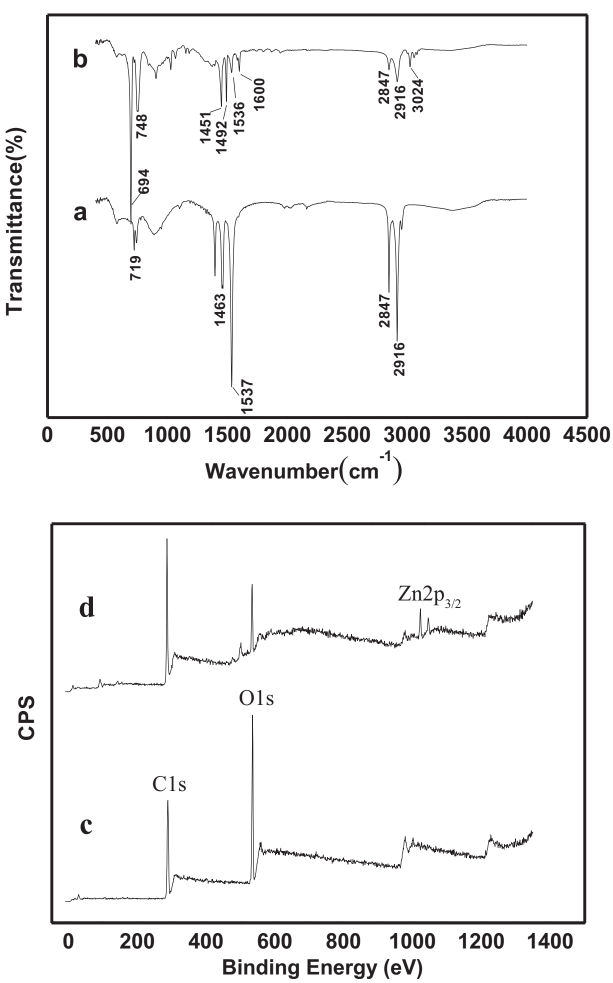

Fig. 5. FT-IR spectra of (a) modified ZnO particles and (b) superhydrophobic nanocomposite coatings; XPS spectra of (c) pristine cotton textiles and (d) superhydrophobic cotton textiles.

of benzene ring (C═C) at 1600 cm^{-1}, 1492 cm^{-1} and 1451 cm^{-1} reveal the existence of polystyrene (Wei et al., 2010). However, comparing with Fig. 5a, the presence of the peaks at 2916 cm^{-1}, 2847 cm^{-1} and 1536 cm^{-1} in Fig. 5b also indicates the existence of stearic acid. Moreover, X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition of the cotton textiles before and after superhydrophobic treatment as well. In view of the pristine cotton textiles, only peaks corresponding to C 1s and O 1s elements could be observed as provided in Fig. 5c. As a comparison, Fig. 5d presented a new characteristic peak of Zn $2p_{3/2}$ at 1024 eV, and a dramatic increase of the C 1s/O 1s ratio from 54/44 to 84/15, further confirming the successful grafting of the coatings with modified ZnO particles and PS onto the cotton fiber.

3.4. Surface wettability

The surface of cotton textiles, which was treated by the modified solution with 2.22 wt% modified-ZnO and 2.22 wt% PS, showed a very high superhydrophobicity with the water contact angle of 155° (Fig. 6b). When water (10 μL) was placed on to the superhydrophobic cotton, a nearly sphere-like water droplet was formed and steadily stayed on the fabric for extended periods of time (Fig. 6c), which is similar to that of lotus leaf (Fig. 6d). For comparison, when water was dropped on to the pristine cotton, no contact angle could be observed due to the abundant hydroxyl groups and numerous holes in the woven structure of textiles (Fig. 6a). Based on the Cassie–Baxter state (Feng & Jiang, 2006):

$$\cos \theta_c = f(\cos \theta_Y + 1) - 1$$

where θ_c and θ_Y are the CAs on the rough and smooth surfaces, respectively, f and $1-f$ are the fractions of solid contact area and air contact area with water, respectively. It can be confirmed from this equation that the smaller solid contact fraction (f) and larger air contact fraction ($1-f$) will boost the nonwettability of material surface. Here, the WCA θ_c on superhydrophobic cotton textiles is measured to be 155°, while the WCA θ_Y on glass slide covered by pure PS coatings was only 92° (Fan et al., 2011). By the use of Cassie–Baxter equation, the fraction of air in contact with water

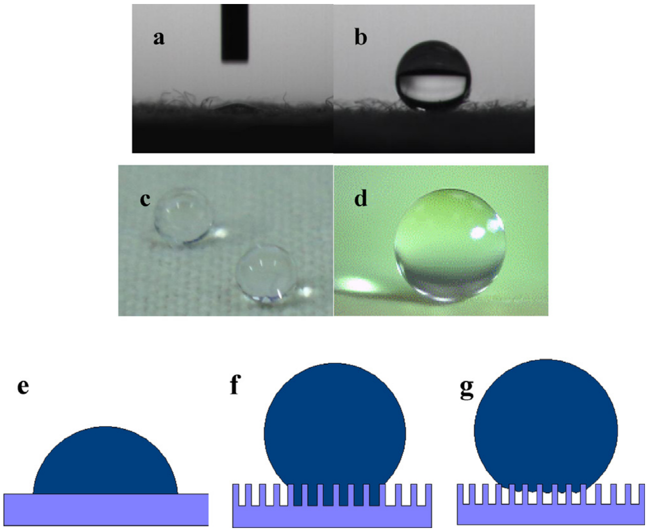

Fig. 6. Photographs of the static water droplets on (a) pristine cotton textiles, (b and c) superhydrophobic cotton textiles and (d) lotus leaf (Bhushan & Jung, 2011); Effect of surface structure on the wetting behavior of solid substrates: (e) droplet on flat substrate; (f) Wenzel model; (g) Cassie–Baxter model.

at superhydrophobic cotton textiles surface was calculated to be 0.903. It demonstrates that the water droplet could readily sit on the tops of nanostructures created by the modified-ZnO/PS composite coatings, and a large quantity of trapped air was filling in the valleys of the structures under the droplet as shown in Fig. 6g, leaving most of the superhydrophobic cotton textiles surface dry.

Moreover, it should be noted that the WCA of cotton surface coated by PS could reach 135°, while the WCA of coated glass slide was measured 92° only. This significant difference can be explained by Wenzel model (Fig. 6f), indicating that the cotton textiles itself possesses comparative microroughness, which is in favor of the fabrication of superhydrophobic surface (Feng & Jiang, 2006; Nosonovsky & Bhushan, 2008). In conclusion, the superhydrophobic cotton textiles has been successfully fabricated, which attributes to (1) double-scale roughness created by modified ZnO nanoparticles and the macroscopic weave structure of textile fabrics, and (2) low surface free energy decorated by polystyrene and stearic acid.

3.5. *Long-term stability and application*

As the importance of chemical stability for industrial applications, we have evaluated the superhydrophobic durability of coated cotton textiles after exposure to ambient air for one month, or being immersed in corrosive liquids in the entire pH range from 0 to 14 for 12 h. After the exposure and immersion tests, the superhydrophobic cotton samples had no visible change, and the WCAs were still greater than 150°, showing the excellent chemical stability of modified-ZnO/polystyrene nanocomposite coatings. Interestingly, we found that the oil droplet such as *n*-hexane, *n*-heptane, toluene, acetone, oleic acid, etc. could freely penetrate through the pores of superhydrophobic cotton textiles, but the WCAs of the cotton samples after being immersed in the oil for about 12 h were still greater than 150°. The unique wettability of the cotton textiles towards water and oil inspired us to explore its application for oil/water separation.

As a model for separating the water and oil from their mixture, Fig. 7 shows the separation process of the mixture with 30 ml oil and 30 ml water on superhydrophobic cotton textiles. When the mixture was poured onto the cotton textiles, the oil freely permeated through the textiles, and then fell into the beaker beneath it.

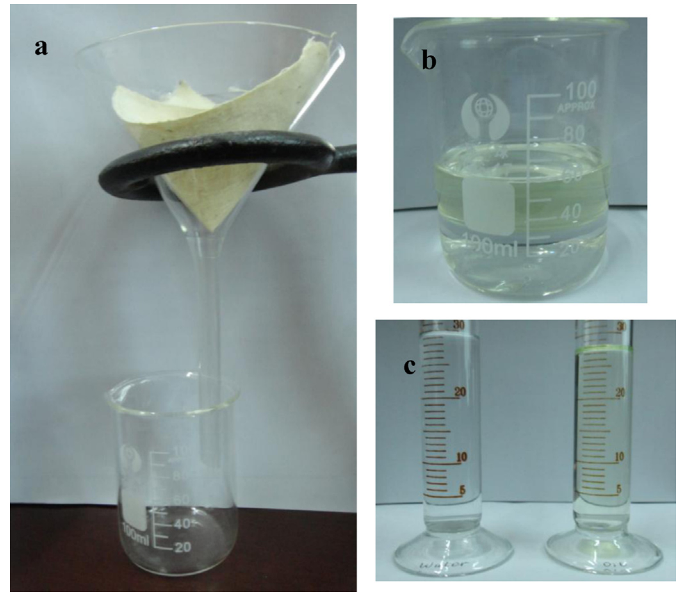

Fig. 7. Images of (a) separation device with superhydrophobic cotton textiles; oil–water mixture (b) before and (c) after filtration.

Meanwhile, more and more water was accumulated on the cotton surface, and then decanted into the measuring cylinder. From Fig. 7c, it can be clearly observed that nearly 100% of the water was collected in the measuring cylinder, and approximately 92% of the oil was decanted into another one from the beaker, showing a very high separation efficiency of the superhydrophobic cotton textiles. Additionally, we also investigated the reusability of the cotton by measuring the WCA of the textiles after repeatedly wetting–drying–wetting cycles by oil such as *n*-hexane. The WCA varied from 155° to 151° along with the increasing cycle times only (Fig. 8), exhibiting the extraordinary superhydrophobicity, chemical stability and reusability of the coated cotton textiles. Moreover, many other types of organics which are insoluble in water, such as *n*-hexane, *n*-heptane, toluene, oleic acid, acetone and so on, can be separated from their mixtures with water via the superhydrophobic cotton as well. It indicates that this low-cost, effective, accessible and environmentally friendly superhydrophobic cotton textile possesses a very extensive application prospect in water–oil separation, and can separate water and oil effectively and continuously without using any other complex means, such as rectification, making a potential candidate for oil purification.

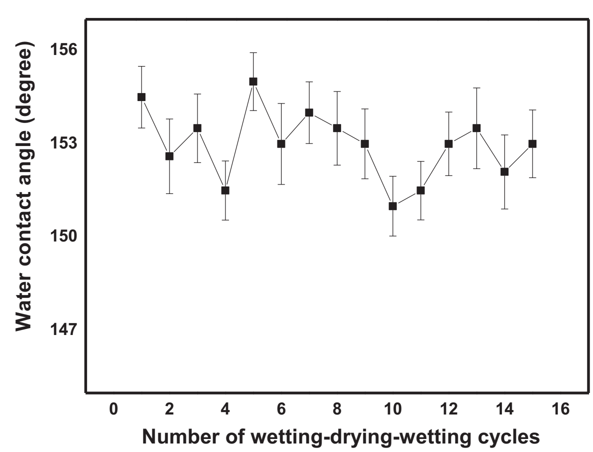

Fig. 8. Variation of WCA on the superhydrophobic cotton textiles with repeatedly wetting–drying–wetting cycles by *n*-hexane.

4. Conclusion

As summary of this study, we have reported a simple, facile, inexpensive and novel method for fabricating the cotton textiles with the important functions of superhydrophobicity, waterproofing and water–oil separation, which offers an opportunity to accelerate the large-scale production of superhydrophobic textiles materials for new industrial applications. After drop-coating the modified-ZnO/polystyrene nanocomposite films onto the cotton textiles, the wetting behavior of cotton sample could be transformed from superhydrophilicity to superhydrophobicity with the WCA of 153–155°, and stays almost the same after exposure to ambient air or immersion in the corrosive liquids and oil, exhibiting the excellent stability and outstanding superhydrophobicity of coated cotton textiles. Furthermore, the superhydrophobic cotton textiles possess a very excellent property in water–oil separation, which demonstrates that the superhydrophobic cotton textiles fabricated via this simple and cost-effective method will have a considerable range of potential applications.

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