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Oil–water separation capability of superhydrophobic fabrics fabricated via combining polydopamine adhesion with lotus-leaf-like structure

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ABSTRACT: By the combination of dual bionic on the superhydrophobicity of lotus leaf and the bioadhesion of mussel adhesive protein, the nanoparticles were strongly immobilized onto the surface of cotton fabric to form superhydrophobic and superoleophilic coating. The as-prepared fabric can be used as effective material for separating various oil/water mixtures. The separation efficiency can reach 99.0%, 97.6%, 98.1%, 96.0%, 94.2%, and 94.5% for toluene/water, *n*-hexane/water, chloroform/water, paraffin oil/water, linseed oil/water, and crude oil/water mixtures with volume ratio of 1 : 4, respectively. In addition, the obtained fabric still kept stable superhydrophobicity and high separation efficiency for oil/water mixtures after using repeatedly for 90 cycles or ultrasonic treatment. They also exhibited excellent chemical durability in harsh conditions of strong acidic and alkaline solutions. Owning to high separation efficiency, stable recyclability, low cost, scalable fabrication, and excellent durability, the as-prepared fabric can be considered as promising material for the separation of oil/water mixtures. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42614.

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INTRODUCTION

In both industrial activity and daily life, there are many occasions such as petroleum mining, oil deliveries, oil refining, food production, and petrochemical operation, whereby waste oil is unconsciously discharged into water environment, resulting in severe impact on aquatic life and human economic actions.[1–3] In addition, unexpected oil slick can spread into many miles away to cause severe hazard to the water supplies of human. Therefore, the suitable and timely treatment for the spilled oil is very necessary to prevent the oil contamination expansion. This has attracted much attention in developing effective methods for oil contamination control and management.

Superhydrophobic surface with a contact angle higher than 150° has attracted tremendous attention due to its widespread application in various areas.[4–8] Up to now, superhydrophobic surfaces have been applied to self-cleaning, anticorrosion, oil/water separation, microfluidic, and other areas. Previous studies have demonstrated that the superhydrophobicity mainly depends on hydrophobic surface with low surface energy and hierarchical micro/nanostructures. So far, a variety of technologies such as phase separation,[9] chemical etching,[10] sol–gel method,[11] chemical vapor deposition,[12] and electrospinning,[13] and so on, have been used to construct superhydrophobic surfaces. However, many methods of preparing superhydrophobic surfaces are expensive and time-consuming. Moreover, most of superhydrophobic coatings have weak binding strength with substrate surface, which restricts their practical applications. Although a large number of superhydrophobic materials have been used for separating oils from oil/water mixture efficiently, there is still an urgent demand for superhydrophobic materials with excellent robustness and chemical stability in oil/water separation.

Recently, porous materials with superhydrophobicity have aroused broad attention because of their potential application in oil/water separation fields.[14,15] Oil can pass through the porous structures of the materials while water is completely repelled by the materials. For instance, superhydrophobic filtration fabric was prepared through decorating the surface with poly(dimethyl siloxanes) (PDMS)/silica (SiO_2) composite coating, which can effectively separate the mixture of water and oil.[9] Yang *et al.* developed a robust diamond meshes with excellent superhydrophobic and superoleophilic properties, demonstrating highly efficient water–oil separation.[16] Xue *et al.* fabricated superhydrophobic and superoleophilic textiles by a simple sol–gel coating, which can be used as a screen mesh to continuously separate oil from oil/water mixture.[17] Wang *et al.* prepared a kind of porous and superhydrophobic miniature oil containment boom by a one-step electrodepositing of Cu_2O film on Cu mesh surface, which can separate and collect oil from the surface of water in situ.[18] In these studies, oil will pass through the mesh pores while completely preventing water from penetrating. Nevertheless, the disadvantages of these materials with environmental unfriendliness in the fabrication process, high cost, nonscalable fabrication, and poor durability and recyclability limit their practical application in oil/water separation.

Dopamine through self-polymerization can form strong covalent and noncovalent interfacial interactions with all types of substances.[19,20] Therefore, the different types of functional materials can be immobilized onto the surface of substrate. Hydrophobic monolithic foams were fabricated via direct and robust fixation of Fe_3O_4 nanoparticles on the foam surface with the help of polydopamine layers.[21] Taking polydopamine walls as reactive templates, silver nanoparticles anchored SiO_2 particles were generated and the composite particles showed excellent water repellence.[22] Inspired by the bioadhesion of polydopamine, in this work, superhydrophobic cotton fabric for oil/water separation is prepared via robustly immobilizing SiO_2 nanoparticles on the fabric surface with the help of self-polymerization of dopamine. Although some investigations about superhydrophobic fabric for oil/water separation have been carried out, there is little information known about the combined use of SiO_2 nanoparticles and polydopamine in preparing superhydrophobic fabric with stable micro/nanostructured layer for selective separation of oil from water. The as-prepared fabric can be used for separating oil/water mixture, and the coating demonstrates excellent durability during repeated use process. More importantly, the as-prepared fabric exhibits a stable surface wettability after immersing into corrosive solutions (acidic and basic solutions). Besides, the fabrication process in here is simple without the need for expensive equipments. Therefore, the findings provide a facile route for fabricating superhydrophobic fabric that might be applied to the separation of oils and other organic pollutants from water.

EXPERIMENTAL

Materials

Cotton fabric was purchased from market, Yinchuan, China. Tetraethylorthosilicate (TEOS, chemically pure), paraffin oil, *n*-hexane, chloroform, and toluene (analytical grade) were received from Ningxia Yaoyi Chemical Reagent Co. Ltd., China. Dopamine hydrochloride (chemically pure) and Tris(hydroxymethyl)aminomethane (Tris–HCl, chemically pure) were supplied by Nanjin Aoduo Biotechnology Co. Ltd., China. Dodecyltrimethoxysilane (DTMS, chemically pure) was provided by Nanjin Chengong Organosilicon Co. Ltd, China. Ethanol (analytical grade) was supplied by Tianjin Li-An Chemical Reagent Co. Ltd., China. Linseed oil came from market, Yinchuan, China. Crude oil was supplied by PetroChina Baota Petrochemical Company, China.

Preparation of Superhydrophobic Cotton Fabric

Preparation of hydrophobic nanoparticles is simple as follows: 6 mL of TEOS and 5 mL of $NH_3 \cdot H_2O$ was added to 100 mL of ethanol and stirred for 4 h at room temperature, and then the obtained nanoparticles were collected by centrifugation and dried at 80°C for use. Before use, cotton fabric was rinsed with ethanol. In a typical experiment, 1.20 g of SiO_2 nanoparticles and 0.64 mg of dopamine hydrochloride were added into 240 mL of Tris–HCl solution to treat for 10 min under ultrasonic. Subsequently, the clean cotton fabric was immersed into the dispersion and stirred for 18 h at room temperature. Finally, the treated fabric was added into DTMS solution to modify, and then dried in an oven at 80°C to constant weight.

Oil/Water Separation Test

The as-prepared fabric was used for the determination of oil/water separation. The oils used in the separation experiments were *n*-hexane, toluene, chloroform, paraffin oil, linseed oil, and crude oil. The oil separation efficiency was determined by volume measurements. A certain amount of oil dyed with oil red O was added into distilled water (m) in a vessel and vigorously stirred for 10 min. Afterward, the as-prepared fabric was placed on top of the funnel, the oil/water mixture was poured into the surface of the fabric, and then oil will penetrate the pore of fabric into the beaker. The volume of captured water (m_1) was measured. The oil separation efficiency of the superhydrophobic fabric, was calculated by the formula $K_s = m_1/m \times 100\%$. After the oil/water separation, the fabric was washed with ethanol and dried in a vacuum at 60°C, and the resultant fabric was used for the recycled separation tests.

Durability of Superhydrophobic Cotton Fabric

To investigate the chemical durability of the as-prepared fabric in corrosive (acidic and basic) solutions, the as-prepared fabric was immersed into the solutions for different time. After being rinsed by distilled water and dried, the wettability of the as-prepared fabric was characterized by water contact angle measurements. Similarly, the durability was also performed by measuring the water contact angle after the ultrasonic treatment of as-prepared fabrics.

Characterizations

The micrographs of samples were examined using SEM (JSM–5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. The surface wettability of water on the surface of cotton fabric was observed with a digital SLR camera after the water was dripped on the surface of fabric from a syringe (1 mL). Contact angle measurements were carried out using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature, and the volumes of probing liquids in the measurements were approximately 5 μL.

RESULTS AND DISCUSSION

Formation of Superhydrophobic Cotton Fabric and Morphology Analyses

The simple preparation process of superhydrophobic cotton fabric is illustrated in Figure 1. A cotton fabric was immersed into the Tris–HCl solution containing dopamine and nanoparticles and treated for a certain time, then the treated fabric was modified in DTMS solution, and finally the nanoparticles-immobilized fabric was obtained after the rinsing and drying. In order to reveal the hydrophobic and oleophilic effect of the as-prepared fabric, the surface wettability of water and oil on the surface of pristine and modified fabrics was observed, as shown in Figure 2. The blue-colored water drop cannot stay on the surface of pristine fabric, so that no water contact angle is observed due to the presence of hydroxyl groups on the fabric surface [Figure 2(a)],

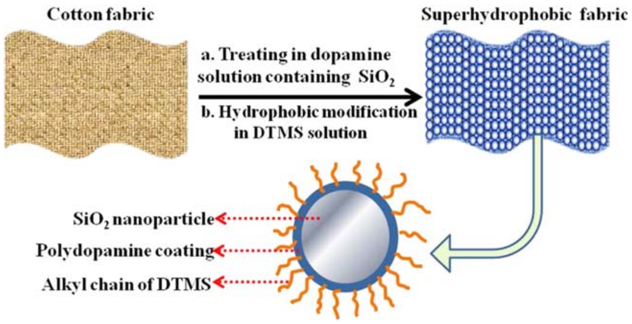

Figure 1. Schematic representation of the preparation of superhydrophobic fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

but the as-prepared fabric is demonstrated to be superhydrophobic with a water contact angle of 153° [Figure 2(a1)]. A nearly sphere-like water droplet steadily stays on the top of the rough structure fabricated by nanoparticles. Toluene dyed with oil red O and linseed oil will quickly wet the surface of pristine and as-prepared fabric to form large spreading radius [Figure 2(b, b1)], exhibiting their oleophilicity. The water drops could bounce off the fabric surface without leaving any residual water drops after spraying water jet [Figure 2(c, c1)]. These results show excellent hydrophobicity and oleophilicity of the as-prepared fabric. The superhydrophobicity of the as-prepared fabric is mainly caused by the micro/nanostructure and the low surface energy.[23–25] Thereinto, the roughness with micro/nanostructure originates from double effect of hydrophobic nanoparticles and uneven weave structure of the fabric surface. The surface appearances of pristine and as-prepared fabric are shown in Figure 3. It is evident that the surface of pristine fabric is relatively smooth with intrinsic woven fabric structure, while the fabric surface is completely covered by a large number of nanoparticles after the treatment. Such rough microstructure can be full of air, thus preventing the penetration of water droplets into the cavities or interspaces of the fabric surface to improve the hydrophobicity.[26,27] Namely, in the process of dopamine self-polymerization, a large amount of nanoparticles randomly and firmly can adhere to the fabric surface, suggesting the effectiveness of imitating bioadhesion of mytilus edulis foot protein in immobilizing nanoparticles.

Separation of Oil/Water Mixtures

Oil/water separation properties were evaluated as displayed in Figures 4 and 5. When the six types of oil/water mixtures including *n*-hexane/water, toluene/water, chloroform/water, paraffin oil/water, linseed oil/water, and crude oil/water are poured onto the as-prepared fabric, all the tested oils can quickly spread out and then pass through the fabric and drop into the receiving vessel below (Figure 4). The water can be left on the superhydrophobic fabric surface, suggesting its excellent ability of separating oil/water mixtures. For chloroform/water mixture, when all the mixtures are poured into the fabric surface placed onto the funnel, the chloroform under the water layer will quickly penetrate through the fabric and all of water is left onto the funnel, achieving the effect of oil/water separation. The separation efficiency is calculated according to the weight of collected water, and the results are displayed in Figure 5. It can be seen that the separation efficiency is 99%, 97.6%, 98.1%, 96%, 94.2%, and 94.5% for *n*-hexane/water, toluene/water, chloroform/water, paraffin oil/water, linseed oil/water, and crude oil/water with 1 : 4 of oil/water volume ratio, respectively. For six types of oil/water mixture with different volume ratios ranging from 1 : 4 to 4 : 1, all of separation efficiencies are found to be above 90% except for separating crude oil/water mixture with volume ratio of 3 : 2 and 4 : 1. On the whole, the separation efficiency slowly decreases with increasing the ratio of oil to water. The difference in the separation efficiency for the mixtures of solvent oils (*n*-hexane, toluene, and chloroform) and water may be attributed to the experimental error, and the tiny viscosity difference among the three oils cannot significantly affect the separation efficiency. Compared with the mixtures of

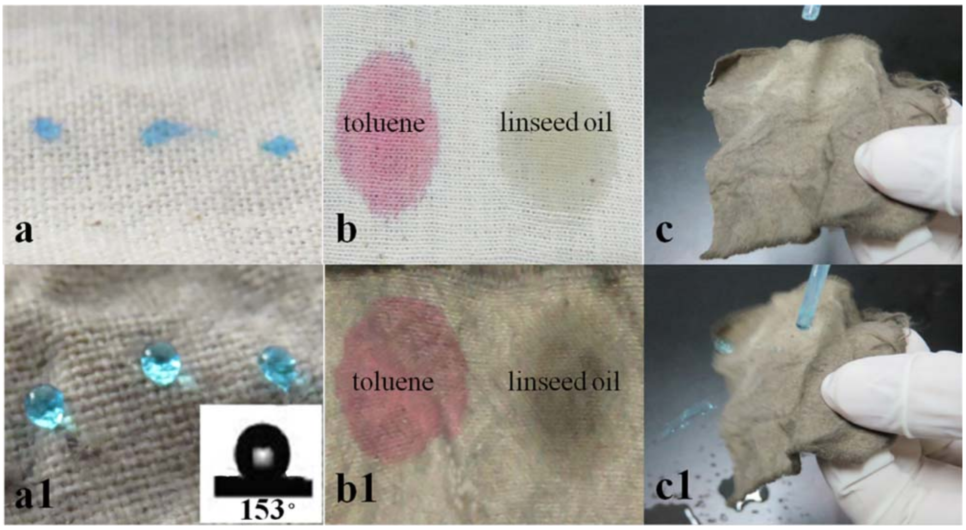

Figure 2. Water droplet dyed with methylene blue on (a) pristine and (a1) as-prepared fabric surfaces; toluene dyed with oil red O and linseed oil on (b) pristine and (b1) as-prepared fabric surfaces; (c, c1) the effect of spraying water jet on superhydrophobic fabric surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

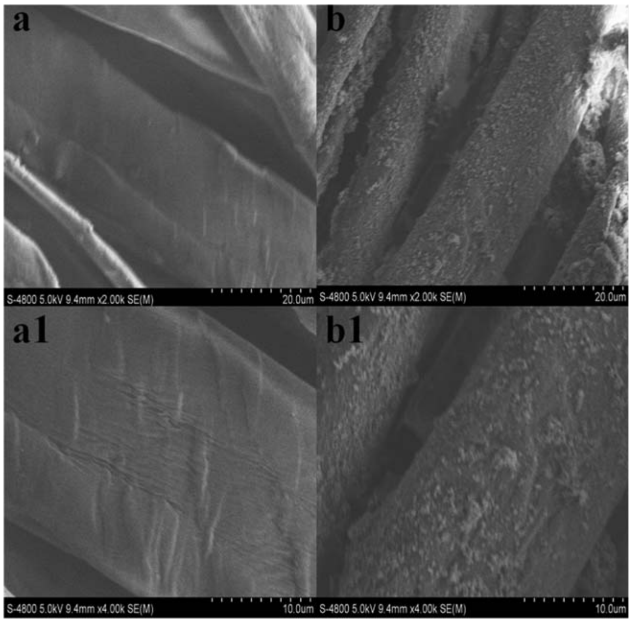

Figure 3. The morphology of (a, a1) pristine and (b, b1) superhydrophobic fabric.

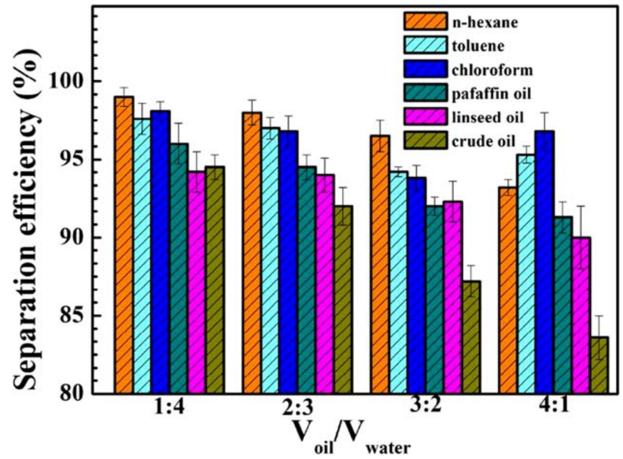

Figure 5. Separation efficiency of the superhydrophobic fabric for six kinds of oil/water mixtures with different oil/water ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvent oils and water, the separation efficiency for the paraffin oil/water, linseed oil/water, and crude oil/water mixtures decrease significantly, which is mainly caused by the high viscosity of these oils. For crude oil/water mixtures, the decrease is more evident due to its higher viscosity. Moreover, after immersing the used fabric in ethanol and then drying, the fabric can completely recover its superhydrophobicity, implying that the fabric can be used for oil/water separation again. Compared with other complicated process procedures,[28–31] the method used for fabricating superhydrophobic fabric here is simpler and more economical, which makes the as-prepared fabric easier to achieve large-scale production for practical separation of oil/water mixture.

Durability of Superhydrophobic Fabric

Durability is very important for superhydrophobic materials because the surface micro/nanostructure is easily destroyed along with the use. As oil/water separation materials, the loss of superhydrophobic property inevitably results in the decrease of oil/water separation efficiency or the failure of selective separation of oil. The use of polydopamine bioadhesion in this study will alleviate the undesirable effects mentioned above by the strong covalent bonds between the fabric surface and the nanoparticles layer, thus improving the mechanical durability of superhydrophobic surface. Durability of the as-prepared fabric is investigated for facilitating the practical application of the fabric in oil/water separation. Figure 6 displays the change of separation efficiency and water contact angle after separating toluene/water mixture (volume ratio of toluene to water ratio is 1 : 4) for 90 cycles. The as-prepared fabric shows satisfactory recyclability without obvious decrease in the separation efficiency after being used for 100 cycles [Figure 6(a)]. The stable water contact angle also proves that the rough structure on the fabric surface is not destroyed with the increase of cycle times [Figure 6(b)]. In order to further clarify the robustness of combination between the micro/nanostructure and the fabric surface, the as-prepared fabric is treated by ultrasonic to cause the stripping of the nanoparticles. As displayed in Figure 7, there is almost no any difference in water contact angle before and after treating superhydrophobic fabrics for different time (5–40 min) by ultrasonic. The fabric treated for different time exhibits high separation efficiency (>90%) in separating toluene/water mixture. These results imply that the superhydrophobic layer immobilized by the polydopamine is difficult to detach from the fabric surface.

Figure 4. Photographs of (a) before and (b) after separating oil/water mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In addition, the chemical stability of as-prepared fabric is also important to practical oil/water separation in harsh environments. Thus, the chemical durability is investigated by measuring the water contact angle and the oil/water separation efficiency of the fabric after being immersed into the acidic (pH = 1) and alkaline (pH = 13) solutions (Figure 8). It can be seen that there is no obvious decrease in the water contact angle of as-prepared fabric after immersing into strongly acidic solution (pH = 1) for 8, 16, 24, 32, 40, 48, 56, and 64 h,

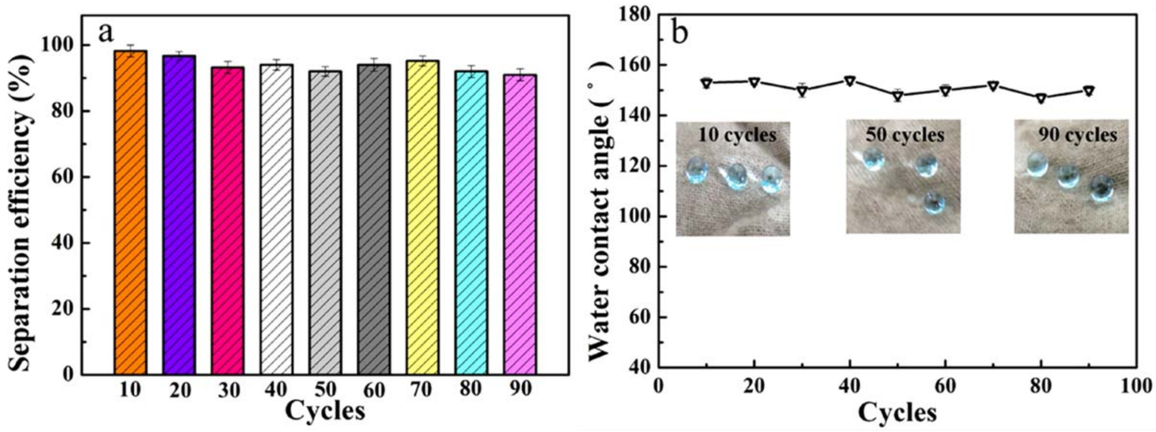

Figure 6. Change of (a) separation efficiency for toluene/water mixture and (b) water contact angle of superhydrophobic fabric versus the recycling numbers of toluene/water mixture separation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

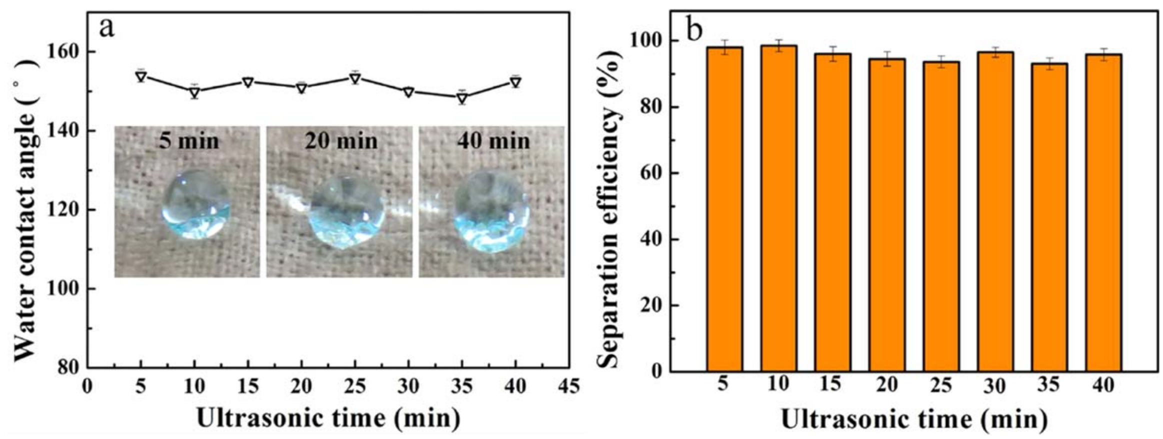

Figure 7. Change of (a) water contact angles and (b) separation efficiency (for toluene/water mixture) of superhydrophobic fabric after being ultrasonically treated for different time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. The similar results can be observed after immersing the fabric into strongly alkaline solution (pH = 13) for the same period. High separation efficiency (>90%) for toluene/water mixture also confirms the as-prepared fabric reveals excellent chemical durability and can be used for the separation of oil in the harsh water environment. These results are encouraging because superhydrophobic materials such as superhydrophobic and superoleophilic textiles,[17] superoleophilic and superhydrophobic oil containment boom,[18] candle soot-coated nickel foam,[32] SiO_2/polystyrene-coated filter paper ($V_{water} : V_{petroleum\ ether} = 1 : 4$, the separation efficiency:

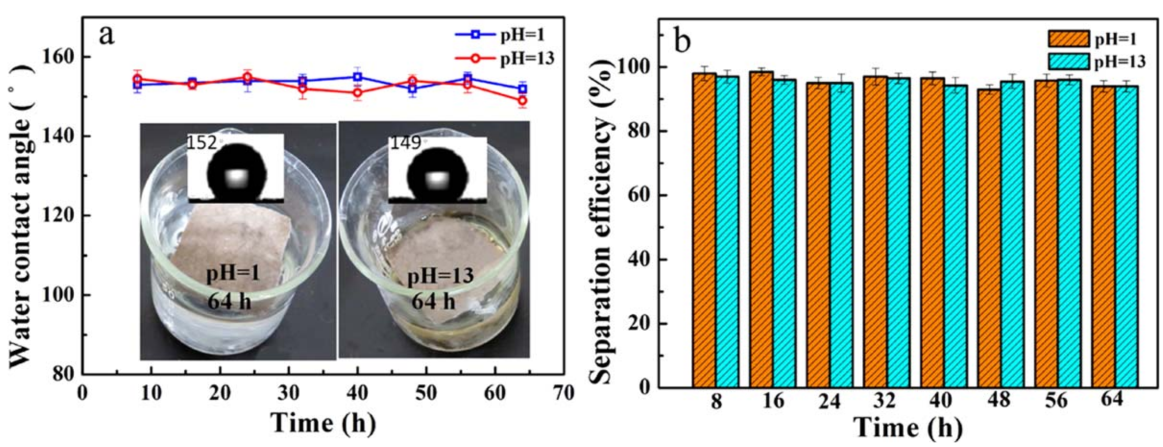

Figure 8. Change of (a) water contact angles and (b) separation efficiency (for toluene/water mixture) of superhydrophobic fabric after being exposed to acidic and alkaline solutions for different time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

96.2%),[33] and polystyrene/ZnO-coated textile[34] rarely achieve such effect of durability in separating oil/water mixture.

CONCLUSIONS

Inspired by mussel adhesion, superhydrophobic cotton fabric was fabricated through the robust immobilization of SiO_2 nanoparticles and subsequent hydrophobic modification. The strongly adhered micro/nanoscale roughness with low surface energy imparted the fabric with excellent hydrophobicity and durability. The as-prepared fabric can effectively separate a wide range of oil/water mixtures with high separation efficiency up to above 90%. More importantly, the fabric can be recycled for at least 90 times without severe loss of hydrophobicity and separation efficiency. In addition, the fabric can resist the invasion of strong acid and strong alkali solutions to be used in harsh water environments. Therefore, owing to the advantages of low cost, high separation efficiency, easily scalable fabrication, and excellent recyclability as well as durability, the as-prepared fabric is promising as a highly effective candidate for the separation of oil/water mixture.

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