

Fabrication of filter paper with tunable wettability and its application in oil–water separation

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Abstract Artificial materials with controllable wettability are of global interests in oil–water related applications. In the present report, a surface with superhydrophilicity/superoleophilicity and underwater superoleophobicity was constructed on filter paper via dip-coating ZnO colloids. However, the wettability of the filter paper was converted to be superhydrophobic and superoleophilic after being modified by octyltrimethoxysilane, and water contact angle on the surface is larger than 150° while oil contact angle is smaller than 5°. The filter paper can be employed to selectively adsorb oil floating on water or separate water–oil mixtures via filtration process because of its superhydrophobicity and superoleophilicity. Additionally, the filter paper has also the capacity to hold water, which is expected to be used as a material for manufacturing labwares.

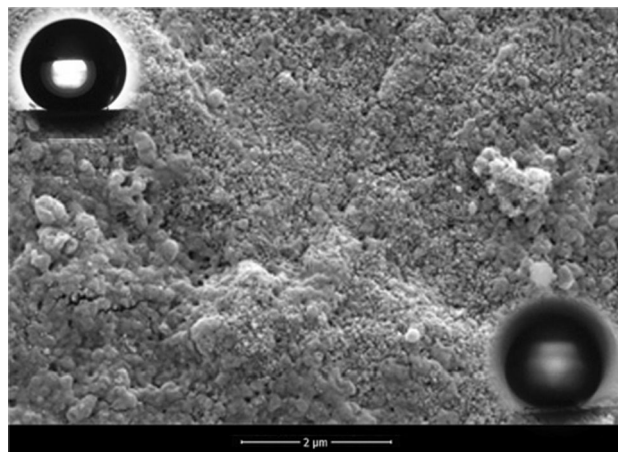
Graphical Abstract A filter paper with superhydrophobicity and superoleophilicity was fabricated by dip-coating and subsequent modification. Water contact angle and sliding angle on the filter paper are 157° and 6°, respectively. The filter paper with superhydrophobicity and superoleophilicity could be employed to separate oil–water mixture with high efficiency.

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1 Introduction

How to separate oil from oily water is attracting global attention because of the increasing pollution accident caused by oil spills. The typical example is the explosion of the “Deepwater Horizon” happened in 2010, which is one of the most catastrophic pollution accidents of the last decade, and 210 million gallons of oil was discharged into the Gulf of Mexico [1]. With the pollution accident, many toxic compounds were brought to the ocean, which may threaten people’s health or even cause a series of eco-catastrophes for species. Confronted with the serious threat of oil pollution, it is urgent and necessary to develop an effective method to collect and remove oil from oily water. Compared with the traditional technique of burning oil,

artificial materials which can selectively adsorb oil from oily water are more favorable because the as-spilled oil can be recollected, separated and reused without causing secondary pollution.

In the past decades, materials with superhydrophobicity and superoleophilicity have incited broad attention because of their distinctive advantages in the separation of oil from water [2–6]. To date, three typical materials, superhydrophobic/superoleophilic [7], superoleophobic/superhydrophilic and underwater superoleophobic materials [8, 9], have been successfully designed and employed to separate oil/water mixture based on the selective oil/water adhesion. In the published literatures, metal meshes with pore-structured semipermeability, have been frequently employed to separate oil/water mixture due to their unique properties of superhydrophobicity/superoleophilicity or superoleophobicity/superhydrophilicity [7–9]. In addition, textiles with superhydrophobicity/superoleophilicity have also been extensively used to separate oil–water mixtures because of their features of flexibility and low cost [10]. Moreover, some commercially available 3D porous materials, such as polyurethane foam sponges, which have high capacity due to the well-developed pores and high surface areas, were also employed to fabricate superhydrophobic adsorbents for oil–water separation [11]. Recently, materials with superhydrophilicity and underwater superoleophobicity are often used to separate oil–water mixtures [12]. Unlike superhydrophobic/superoleophilic materials which allow oil phase to penetrate the surface (or adsorb the oil phase) while repelling water, superhydrophilic and underwater superoleophobic materials allow water phase pass through freely but repelling oil totally. In addition to metal meshes, textile and 3D porous materials, filter paper has also been regarded as an ideal substrate to separate oil/water mixtures. Lu et al. constructed superhydrophobic/superoleophilic filter paper by treating the filter paper with a mixture of hydrophobic silica nanoparticles (silica was modified with polydimethylsiloxane) and polystyrene solution in toluene; the filter paper could effectively separate oil and ethanol from water and selectively adsorb oil floating on water surface or in aqueous emulsion [13]. Moreover, Du et al. [14] manufactured durable superhydrophobic and superoleophilic filter paper by colloidal deposition, which could effectively separate a series of oil–water mixtures with high separation efficiencies over 99 %.

Besides filter paper [15–17], other paper was also employed as substrate to fabricate superhydrophobicity, such as copy paper [18], standard printer-grade paper [19], cartridge paper [20] and high-density paper towel [21]. Filter paper, which has a strong affinity with water due to the presence of hydroxyl groups on the fibrous cellulose, is used widely in analysis chemistry to filtrate sediments from solution. If filter paper is endowed unique

properties of underwater superoleophobicity or superhydrophobicity/superoleophilicity, then the filter paper may be commonly used in separation of oil–water mixtures. In the present study, we fabricated a smart surface with controllable wettability on filter paper by combining dip-coating ZnO colloids and surface modification. As for the nanostructured ZnO materials, which have received broad attention in the past decades due to their distinguished performance in electronics, optics and photonics [22]. When the filter paper was coated by ZnO colloids, it exhibits superhydrophilic/superoleophilic and underwater superoleophobic. After modifying the ZnO coated filter paper with OTS, the wettability was converted to be superhydrophobic/superoleophilic, which can be applied to separate oil from oil–water mixtures due to its selective oil adsorption. Moreover, the filter paper with superhydrophobicity can also be used as an extremely low-cost material to design laboratory apparatus, including reservoirs for water storage and funnels for separating water from water–oil mixtures. Compared with the literatures presented above, this method is facile, low cost and environmental friendly.

2 Materials and methods

2.1 Materials

Zn(CH₃COO)₂·2H₂O and LiOH·H₂O were supplied by Shandong Laiyang chemical CO., LTD. Octyltrimethoxysilane (OTS) was purchased from Harbin Xeogia fluorine-silicon chemical company. Qualitative filter paper was obtained from Fushun civil administration filter paper factory.

2.2 Fabrication of ZnO colloids

ZnO colloids were fabricated by sol–gel according to the procedure described in published literature with further modification [23]. Briefly, 250 mL of ethanol containing 0.1 M Zn²⁺ was placed into a round-bottom flask equipped with a condenser pipe. The solution was boiled at 80 °C and stirred over a period of ~150 min. Subsequently, the solution was evaporated by rotary evaporators at 70 °C, and then, 150 mL of condensate and 100 mL of residuary reaction mixture were obtained, respectively. After that, 0.14 M LiOH·H₂O powder was added to the residuary mixture, and the suspension was placed into an ultrasonic bath for 10 min to destroy the weakly soluble powder. Finally, 2.0 mL of distilled water was added drop by drop, and the solution was stirred for 30 min at 60 °C. The addition procedure of the distilled water was repeated two additional times, and stable ZnO colloids with milky appearance were finally formed.

2.3 Dip-coating

Filter paper was dip-coated by ZnO colloids as follows. Filter paper (2 cm × 4 cm) was fixed on a slide glass by a tiny clamp and dipped in the ZnO colloids, and then, the filter paper fixed on glass was withdrawn at a speed of 14 cm/min by a homemade dipping coater. After that, filter paper was peeled off and baked in an oven at 80 °C for 5 min to ensure ZnO particle adhesion onto the substrate surface. The procedures of dip-coating and post-treatment varied from one to five times.

2.4 Chemical modification

Filter paper coated by ZnO colloids was immersed in a 5 % (v/v) ethanol solution of octyltrimethoxysilane (OTS) for 24 h at room temperature. After that, the filter paper was thoroughly rinsed with ethanol and dried at 80 °C for 30 min.

2.5 Characterization

Surface morphologies of the filter paper were characterized by a Quanta 450 FEG scanning electron microscope (SEM). The chemical composition of filter paper modified by OTS was investigated by a PHI-5702 X-ray photoelectron spectroscopy (XPS). The water contact angles (CA) and sliding angles (SA) were determined using a SL200KS (Kino, USA) equipped with a video camera and a tilting stage. The average value of five measurements using 8 μL water droplets was reported as final CA and SA.

3 Results and discussion

As is well known, wettability is one of the most important properties of solid surfaces, which is closely related to surface topography and chemical composition [5, 24, 25]. Figure 1 shows the scanning electron microscopy (SEM) images of filter paper coated by ZnO colloids with different dip-coating times. Figure 1a–c shows the surface morphology of filter paper with one dip-coating. Low-magnification image clearly shows the netlike topography (Fig. 1a), which is consisted of cellulose fibers, having a width ranging from 10 to 20 μm. In addition, there are some apertures in filter paper, and the diameter varies from 2 to 50 μm. Figure 1b and c is the high-magnification SEM images, which reveal that numerous small ZnO nanoparticles with diameters varying from 20 to 100 nm were aggregated on cellulose fibers, and the hierarchical structures of micro/nanometer scale are evident. As the dip-coating time was increased to three, ZnO nanoparticles stack on filter paper uniformly and the globular entities aggregate more densely (as shown in Fig. 1d). When the

dip-coating time was continuously increased to five, the forest-like hierarchical structures with began to form on filter paper (as shown in Fig. 1e, f).

The pristine filter paper is composed of cellulose fibers, which can easily adsorb water and oil due to its high surface energy, and the ZnO colloids can also be easily coated on filter paper by dip-coating. After dip-coating, the filter paper exhibits superhydrophilicity and superoleophilicity with the water CA and oil CA smaller than 5° due to the high surface energy. However, the filter paper began to be superoleophobic when it was immersed in water, and the oil CA of trichloromethane on the filter paper is about $156 \pm 1^\circ$ (as shown in Fig. 2a). In addition, the underwater superoleophobicity was also observed by dripping diesel oil on it (as shown in Fig. 2b). The filter paper with superhydrophilicity and underwater superoleophobicity exhibits similar properties with fish scales, which are known to be well protected from contamination by oil pollution in sea [26]. Inspired by fish scales, membranes with superhydrophilic and underwater superoleophobic properties have aroused particular interests for their resistance to oil fouling and promising applications as water-removal materials [9, 27–29].

Unlike the superoleophobicity in air [30], the underwater superoleophobicity is achieved in oil/water/solid three-phase system by introducing the repulsive liquid phase into the micro/nanometer hierarchically structured surfaces. When the filter paper coated by ZnO colloids was immersed in water, paper will adsorb water to its balance state. Consequently, when the filter paper contacts with the oil droplets, water can be trapped in the apertures of filter paper, and the apparent contact between oil droplets and filter paper is actually a composite contact of oil/water/solid [31, 32]. The trapped water will greatly decrease the contact area between oil droplets and filter paper surface. In this composite contact mode of solid/oil/water, the triple-phase contact line is discontinuous [31], consequently, the filter paper exhibits underwater superoleophobic property, and the oil droplet can easily roll off the filter paper, which may be used to selectively separate water from oil.

Compared with superhydrophilic/superoleophobic materials, materials with superhydrophobicity/superoleophilicity are more typical oil-removing materials which have been widely used for oil–water separation during the past decades [4, 5, 33]. Properties of superhydrophobic and superoleophilic will make an oil phase spread (adsorb or penetrate) easily on the materials while the water phase will be repelled, thus separating oils from an oil–water mixture [3]. Superhydrophobic/superoleophilic materials are commonly prepared by constructing a rough structure on a hydrophobic surface or modifying a rough surface with low surface energy

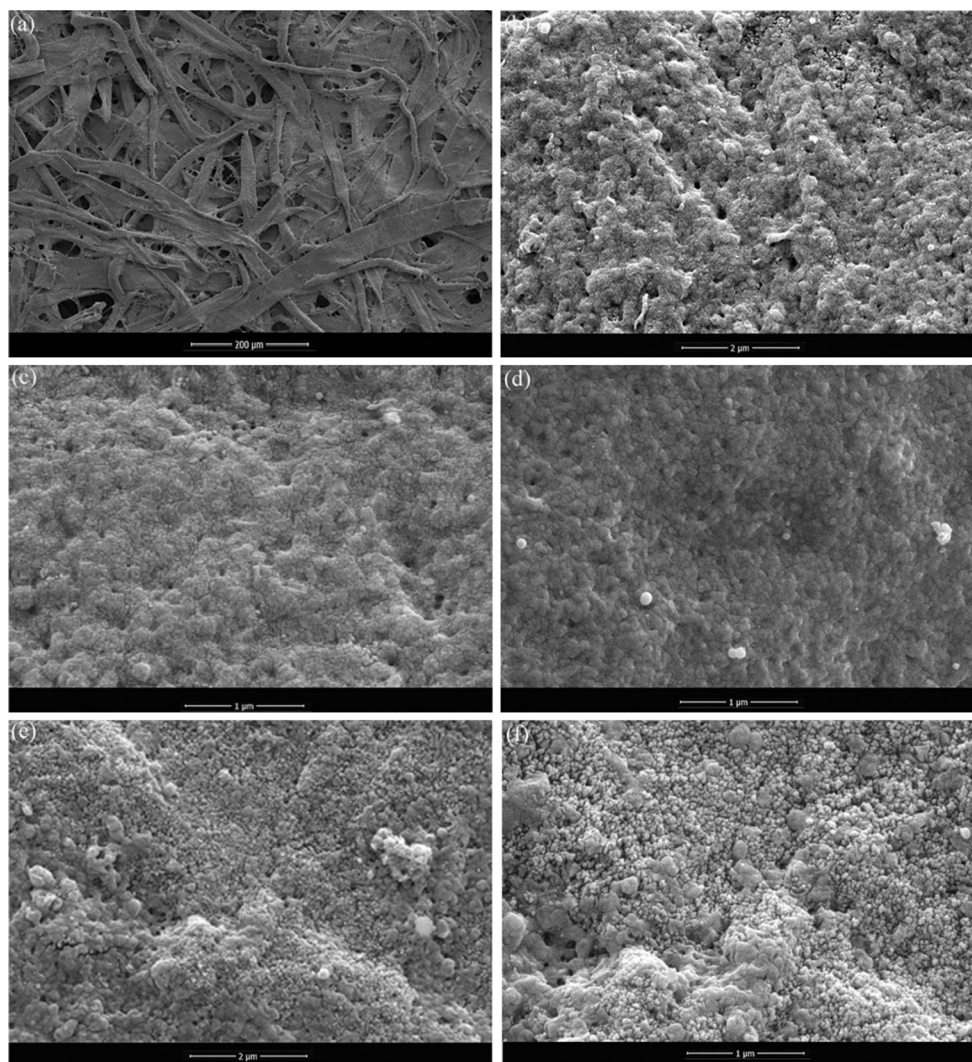


Fig. 1 SEM images of filter paper coated by ZnO colloids. The dip-coating time is one (a–c), three (d) and five (e–f), respectively

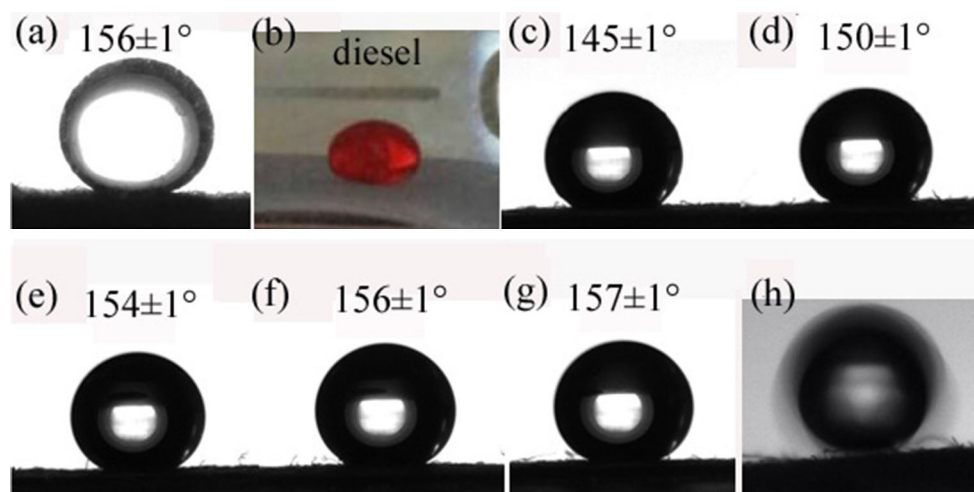


Fig. 2 a, b Images of trichloromethane and diesel oil droplet on underwater superoleophobic filter paper. c–g Optical micrographs of water droplet on superhydrophobic filter paper with different dip-

coating times (coating times varied from one to five). h Image of water droplet sliding on superhydrophobic filter

chemicals [34]. In this report, filter paper was firstly coated by ZnO colloids and then immersed in an OTS solution for 24 h. With the surface modification, the surface energy of filter paper was sharply decreased due to the alkyl chains of OTS assembled on filter paper. After surface modification, the wettability was changed from superhydrophilic/underwater superoleophobic to superhydrophobic/superoleophilic. As dip-coating time varied from one to five, the water CA on the modified filter paper was also increased from $145 \pm 1^\circ$ to $150 \pm 1^\circ$, $154 \pm 1^\circ$, $156 \pm 1^\circ$ and $157 \pm 1^\circ$, respectively (as shown in Fig. 2c–g). However, on the hydrophobic or superhydrophobic filter paper surfaces, oil droplets could completely spread out, which indicates the superhydrophobic filter paper surface was still superoleophilic (oil CA was $<5^\circ$). In addition, no significant water CA changes were observed as the dip-coating exceeded five times. On the modified filter paper with five dip-coating, water droplets were hard to stick and could move effortlessly due to the gravitational forces on slightly tilted surfaces, and the sliding angle (SL) was estimated to be about 6° (as shown in Fig. 2h). The larger CA and the small SL indicate the surface with five dip-coating possesses the optimum roughness for constructing perfect superhydrophobic surfaces. The microscale roughness is inherent in the netlike paper fibers, and the addition of ZnO particles provides the nanoscale roughness; the synergistic effect of the hierarchical micro/nanometer scale structures and the low surface chemical composition finally lead to the formation of superhydrophobicity on filter paper.

The larger water CA and the lower SL on filter paper indicate that the water droplets are unable to penetrate into the surface cavities, but rather are suspended on the hierarchical micro/nanometer structure surface. According to Cassie–Baxter theory [35], air could be trapped within the interstices of the micro/nanometer-scaled superhydrophobic filter surface, which considerably increases the air/water interface and effectively prevents the penetration of water droplets into the hollows and apertures. In the Cassie equation [35]:

$$\cos \theta^* = f_1 \cos \theta - f_2$$

f_1 and f_2 were defined as the area fraction of solid and air under water droplet sitting on the superhydrophobic filter paper, $f_1 + f_2 = 1$. θ^* is the apparent CA of water drop on the superhydrophobic filter paper, and θ is the intrinsic CA of water drop on an ideal flat ZnO film modified by OTS ($\theta = 106 \pm 1^\circ$, the film was roughly simulated by dip-coating ZnO colloids on a slide glass). With the measured apparent contact angle θ^* on superhydrophobic filter paper (as dip-coating times varied from two to five, θ^* was increased from $150 \pm 1^\circ$ to $154 \pm 1^\circ$, $156 \pm 1^\circ$ and $157 \pm 1^\circ$, respectively), the air fraction (f_2) under water droplets contacting with superhydrophobic filter paper

(having different dip-coating times) can be roughly estimated to be about 81.5, 86.0, 88.1 and 89.0 %, respectively (similarly, the corresponding solid fraction f_1 is calculated to be about 18.5, 14.0, 11.9 and 11.0 %, respectively). The large air fraction on the composite contacts of solid–liquid–gas indicates the water droplets on the superhydrophobic filter paper are mainly sitting on the “air pocket,” and the surface adhesion between water droplets and superhydrophobic filter paper should be extremely low, which can be evaluated by the Young–Dupre equation as follows [36–38]:

$$W_{\text{ad}} = f_s \times \gamma_L (\cos \theta_Y + 1)$$

Here, γ_L is the surface tension of water, which is 7.2×10^{-2} N/m. θ_Y is the CA in the Young model, which equals the value of θ presented above ($\theta = 106^\circ$). f_s is the solid fraction of superhydrophobic filter paper contacting with water droplets, which equals the f_1 calculated in the above Cassie equation. With the known value of f_s , γ_L and θ_Y , W_{ad} of water droplets on superhydrophobic filter paper with different dip-coating times could be roughly estimated to be about 9.7×10^{-3} , 7.3×10^{-3} , 6.2×10^{-3} and 5.7×10^{-3} N/m, respectively. The exceptionally small adhesion work is responsible for the lower sliding angle of water droplets on the superhydrophobic filter paper, and water droplets began to slide off with a slight tilt.

As for the superoleophilicity, according to an empirical definition, to be superoleophobic, the critical surface energy of the solid surface (γ_s) should be smaller than one quarter of that of the liquid [39, 40]. However, the surface tensions of trichloromethane ($\gamma = 28.9$ mN/m) are smaller than water ($\gamma = 72.8$ mN/m), which indicates extremely small surface energy is needed to achieve superoleophobicity. Compared with the formation of superhydrophobicity, the surface treatment of dip-coating and modification described above was not effective enough to prevent oil droplets penetrating into the apertures due to its relatively high surface energy. The fabrication process and wettability conversion mechanism from superhydrophilicity/superoleophilicity and underwater superoleophobicity to superhydrophobicity/superoleophilicity is schematically illustrated in Fig. 3.

From what has been described above, it is clearly shown that the superhydrophobic surface was derived from the special hierarchical structures of micro/nanometer scale and chemical composition of low surface free energy. X-ray photoelectron spectroscopy (XPS) is a classical technique for surface analysis which is often used for compositional state and chemical state analysis. Figure 4 is the XPS spectra of OTS modified filter paper with five dip-coating. The characteristic peaks at 1044.8, 1021.3, 530.2 and 284.3 eV correspond to the Zn 2p1, Zn 2p3, O1s and C1s, respectively. The stronger peaks of C1s and the

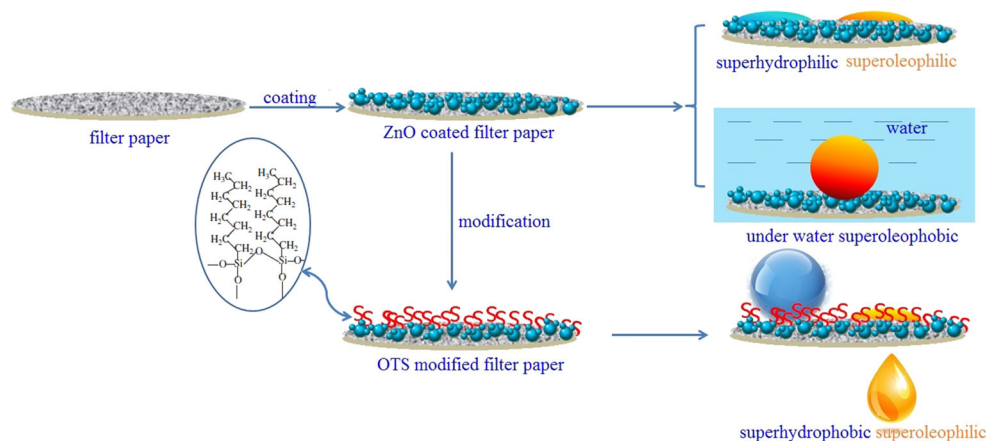


Fig. 3 Schematic illustration of fabrication and wettability conversion of filter paper from superhydrophilic/superoleophilic and underwater superoleophobic to superhydrophobic/superoleophilic

Fig. 4 XPS spectra of OTS modified filter paper with five dip-coating times

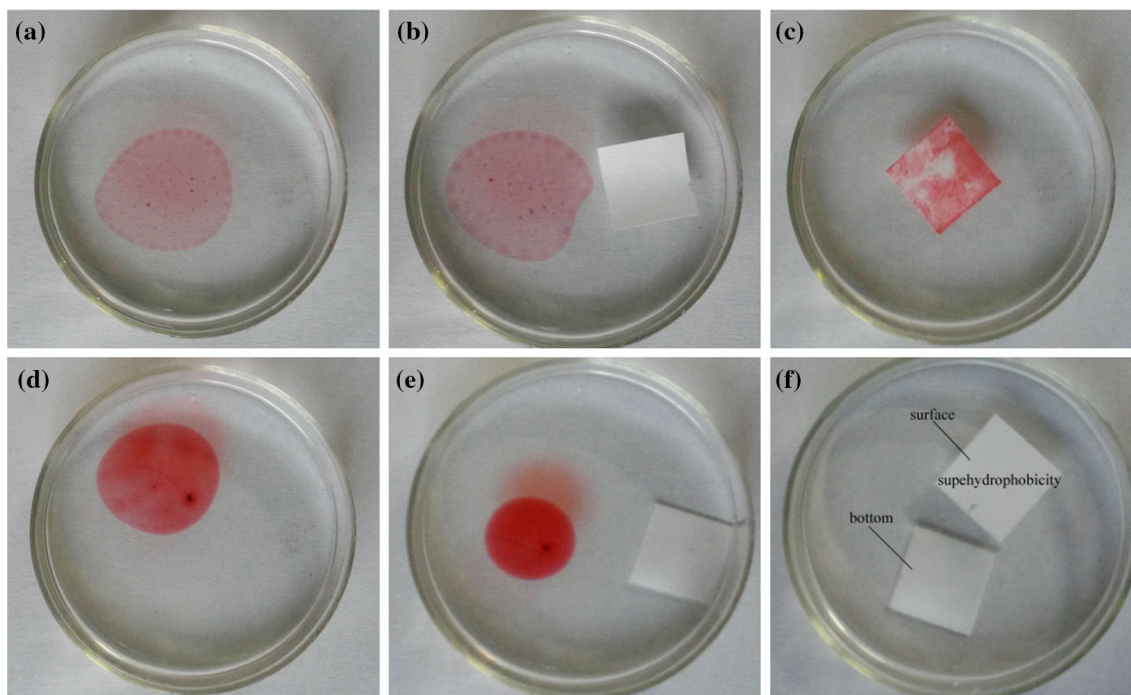
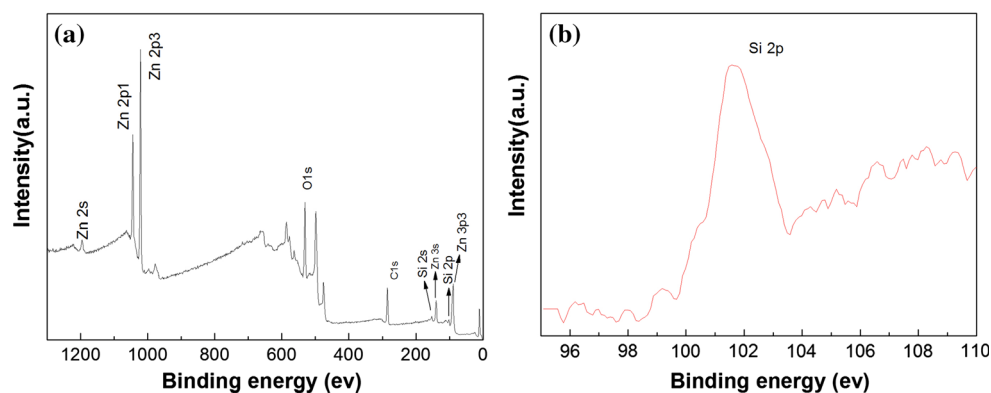
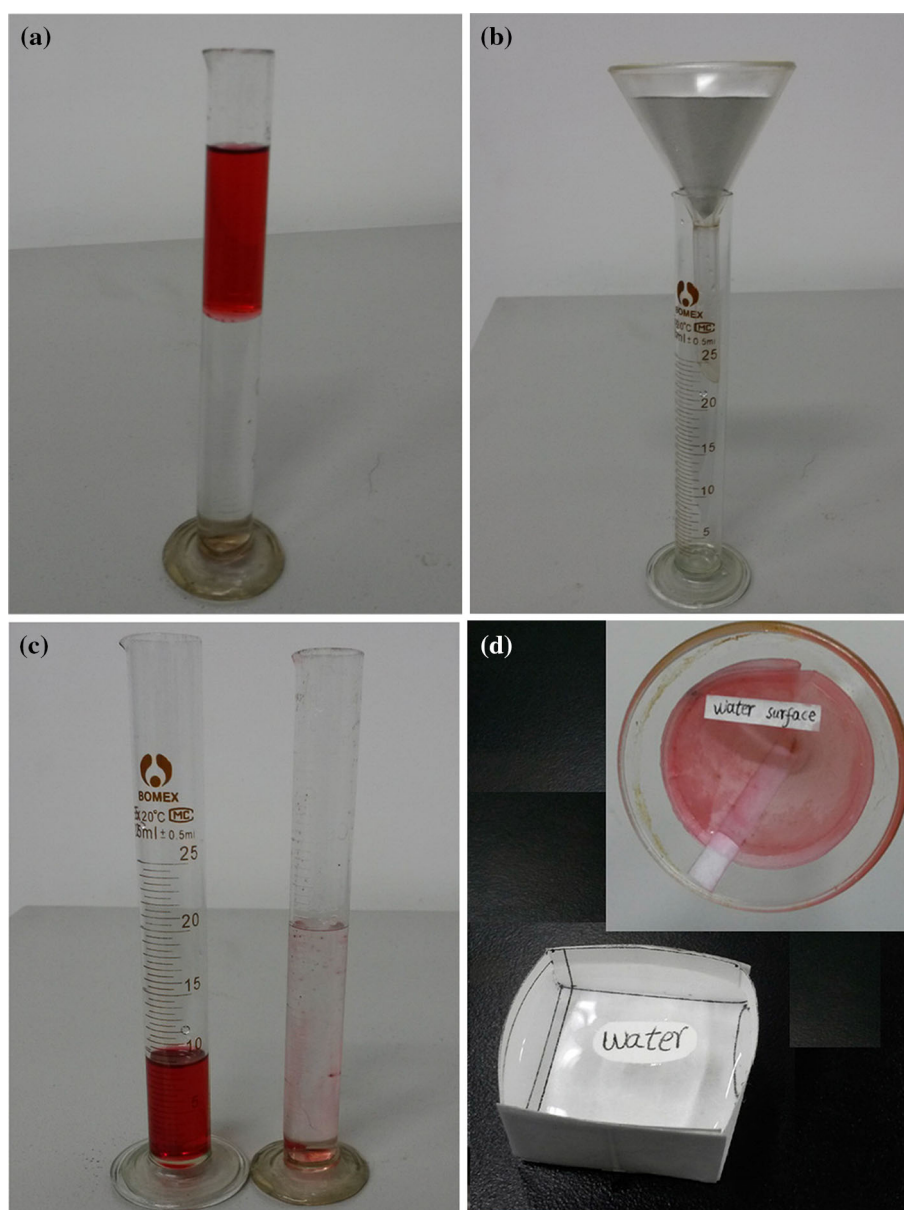


Fig. 5 a–c Images of the diesel oil adsorbed by superhydrophobic/superoleophilic filter paper. d–f Images of the pristine filter paper under water and superhydrophobic paper on water surface (diesel oil was labeled with oil red O) (Color figure online)

Fig. 6 a–c Separation of diesel oil–water mixture through filtration technique, **d** water on superhydrophobic filter paper after oil–water separation and a paper “boat” holding water



appearance of characteristic peak of Si 2p at 101.6 eV are an evidence of self-assembled layer of OTS on ZnO nanoparticles (as shown in Fig. 4a, b).

3.1 Selective adsorption of oil from water

In order to investigate the oil adsorption of superhydrophobic/superoleophilic filter paper in water, we put a piece of filter paper in water and found the filter paper kept dry and floating on water surface (as shown in Fig. 5a, b). However, when the filter paper contacted with the diesel oil (which was dyed with oil red O), diesel oil was quickly selectively adsorbed by paper. After the adsorption, no obvious residue of diesel oil could be observed on water surface (as shown in Fig. 5c). In order to make a

comparison of oil adsorption efficiency between pristine and superhydrophobic filter paper, we put a piece of pristine filter paper in water surface and found the pristine filter paper adsorbed water easily and finally sank down to the water (as shown in Fig. 5d–f). As for the water adsorption of pristine filter paper, Quéré deduced that liquid with an intermediate contact angle lesser than 90° could invade textured substrate, and the driving force of the so-called hemi-wicking phenomenon came from the decrease in surface energy as a result of the displacement of a solid/vapor interface to a liquid/vapor interface [41]. The results indicate that the filter paper with superhydrophobicity/superoleophilicity could be used as ideal adsorbent materials for the selective adsorption of oil from water surface.

3.2 Filtration separation of water–oil mixture

As described above, filter paper with superhydrophobicity/superoleophilicity could be applied to selectively adsorb diesel oil on water with high efficiency. In addition, the filter paper treated by dip-coating and surface modification could also be used to separate water from water–oil mixtures by filtration process. As shown in Fig. 6a–d, when the mixtures of diesel oil and water were poured onto the filter paper, diesel oil could be passed through the filter paper due to the driving force of gravity and dropped into the cylinder beneath the funnel, while water was retained on the filter paper surface and collected into another cylinder. After the separation, no obviously visible water residue was left in the collected oil, and no evident oil residue was observed in the collected water.

The separation efficiency was investigated by the ratio of the volume of collected oil (9.01 mL) to that initially added to the mixture (10.02 mL), and the corresponding separation efficiency was estimated to be about 90 %. However, the value is relatively lower than the factual separation efficiency because the filter paper will inevitably adsorb a part of oil. Therefore, it is more accurate to estimate the separation efficiency by the ratio of the volume of collected water (14.7 mL) to that initially added (15.0 mL), and the separation efficiency is about 98%. In addition, it was observed that the filter paper has the capacity to hold water because of its perfect and durable superhydrophobicity (Fig. 6d), which is expected to be applied in making labware in experiment.

Besides the diesel, the filter paper is also effective to separate mixture of gasoline–water, dodecane–water and hexadecane–water, which indicate that the filter paper with superhydrophobicity/superoleophilicity may be widely applied in the separation of oil–water mixture.

4 Conclusions

In summary, filter paper with tunable wettability was fabricated by facile dip-coating and subsequent surface modification. Before modification, the filter paper coated by ZnO colloids is superhydrophilic/superoleophilic in air and superoleophobic under water with an oil CA larger than 150°. However, the wettability was converted to be superhydrophobic and superoleophilic after surface modification with a water CA larger than 150° and an oil CA smaller than 5°. The filter paper with superhydrophobic and superoleophilic properties can be used to separate oil form oil–water mixture through selective adsorption or filtration process, and the separation efficiency was estimated to be above 90 %. In addition, the filter paper has the capacity to hold water due to the durable superhydrophobicity, which

is expected to make labwares for holding water in experiment.

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