Bioinspired Multifunctional Foam with Self-Cleaning and Oil/Water Separation

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Oil/water separation is a worldwide challenge. Learning from nature provides a promising approach for the construction of functional materials with oil/water separation. In this contribution, inspired by superhydrophobic self-cleaning lotus leaves and porous biomaterials, a facile method is proposed to fabricate polyurethane foam with simultaneous superhydrophobicity and superoleophilicity. Due to its low density, light weight, and superhydrophobicity, the as-prepared foam can float easily on water. Furthermore, the foam demonstrates super-repellency towards corrosive liquids, self-cleaning, and oil/water separation properties, possessing multifunction integration. We expect that this low-cost process can be readily and widely adopted for the design of multifunctional foams for large-area oil-spill cleanup.

1. Introduction

The 2010 Gulf of Mexico oil spill, the largest accidental marine oil spill in the history of the petroleum industry, is an unprecedented environmental catastrophe. The oil spill released about 4.9 million barrels of crude oil, resulting in extensive damage to marine and wildlife habitats and to the Gulf's fishing industry and public health. Generally, burning the oil, filtering offshore, and collecting for later processing are the three basic approaches for removing oil from water. It has become a worldwide challenge to solve the frequent oil spill accidents and the increasing amount of industrial oily wastewater and chemical leakage; addressing this challenge calls for the generation of new functional materials that can effectively separate oil and water.[1–4] Recently, a variety of functional materials for oil/water separation were fabricated through the rational control of surface structures and chemical compositions to possess simultaneous superhydrophobicity and superoleophilicity.[5–15]

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Self-cleaning is a desired property that would make the dream of a contamination-free surface come true.[16–22] The story of self-cleaning begins with the sacred lotus (*Nelumbo nucifera*), which has been a symbol of purity in Asia for more than 2000 years.[23] For the lotus leaf, the cooperation of surface multiscale structures and hydrophobic epicuticular wax confers a high water static contact-angle and a small sliding angle, resulting in the so-called self-cleaning – or lotus – effect. Self-cleaning surfaces have drawn a lot of interest for both fundamental research and practical applications. Nature is a school for scientists and engineers. Learning from nature should be an effective avenue for the design of functional self-cleaning materials.[24–26]

In nature, diatoms, natural sponges, and other biological materials exhibit high porosity and large surface area.[27] These biomaterials and their corresponding bioinspired materials demonstrate promising applications in the fields of sorption, filtration, and separation. The porous structure has fascinated natural philosophers for at least 300 years. For example, Hooke examined their shape, Kelvin analyzed their packing, and Darwin speculated on their origin and function.[28] Polyurethane foam is a kind of porous and hydrophilic polymer that has special characteristics of high absorption ability, light weight, high porosity, large surface area, low density, and good elasticity. Recently, superhydrophobic and superoleophilic polyurethane foam was applied to the separation of oil-and-water mixtures.[29] However, the fabrication process used was time-consuming and the stability towards corrosive liquids, including acidic and basic solutions, was not presented. The long-term durability for corrosive liquids is essential for application in oil/water separation owing to the complex oily wastewater environment. Furthermore, in the field of oil/water separation,[5–15] the presence of dirt particles in the oil/water mixture can destroy the wettability of a material surface, resulting in a negative effect on its separation efficiency and recyclability. Therefore, to avoid the problem, integrating a self-cleaning function into oil/water separation materials is desirable. This is very important to prevent the degradation by dust particles residing on the material surfaces and maintain the oil/water separation efficiency.

In order to overcome the above-mentioned limitations, a new synthesis strategy for oil/water separation materials with long-term stability and self-cleaning through a simple, inexpensive, and practical approach is highly desirable. This will dramatically extend their applications and practicality for mass

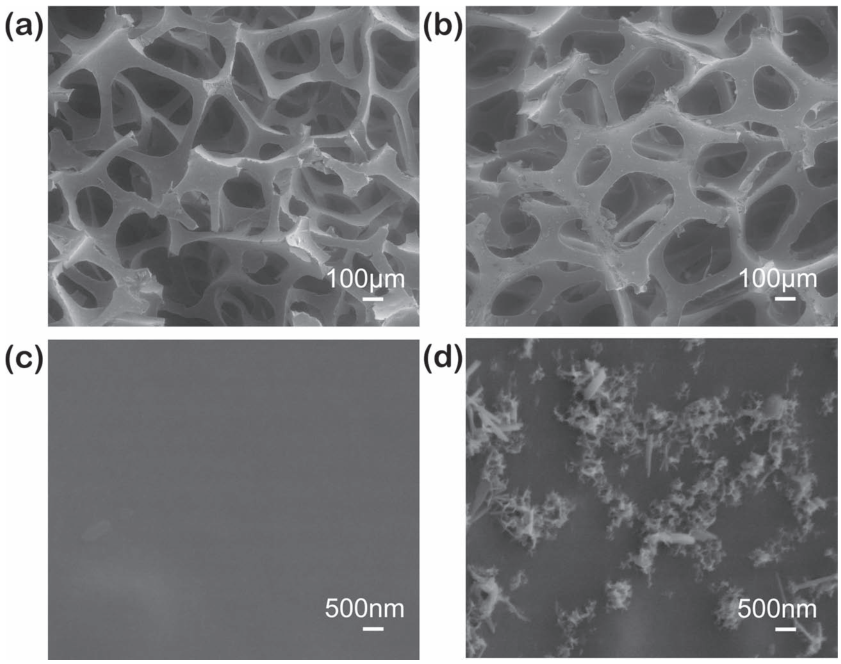


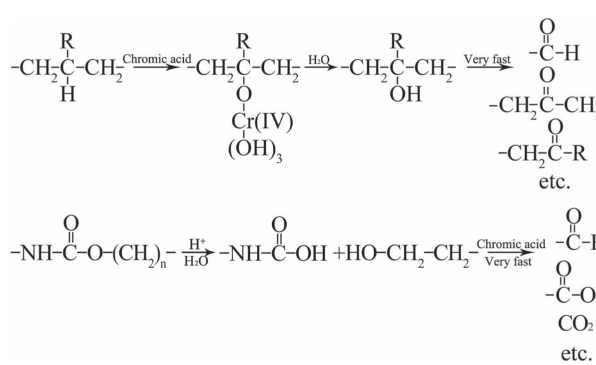
Figure 1. Representative ESEM images of polyurethane foam before (a,c) and after (b,d) chromic acid treatment at different magnifications. a,c) ESEM images of the original polyurethane foam without chromic acid treatment, exhibiting the smooth and flat nature for the pristine foam surface. b,d) ESEM images of polyurethane foam after chromic acid treatment, showing the micro- and nanoscale hierarchical structures on the resultant surface.

production. Here, inspired by the lotus leaf with self-cleaning and the biomaterials with porous structures, we report the synthesis of functional polyurethane foam possessing simultaneous superhydrophobicity with a small sliding angle and superoleophilicity, which can float easily on water owing to its low density, light weight, and special wettability. Moreover, the as-prepared foam shows stable super-repellency towards corrosive liquids, including acidic, salty, and basic solutions, self-cleaning, and oil/water separation properties, exhibiting multifunctional characteristics and potential applications in oil-spill cleanup and industrial oily wastewater treatment.

2. Results and Discussion

Typical environmental scanning electronic microscopy (ESEM) images at different magnifications of polyurethane foam before (a,c) and after (b,d) chromic acid treatment are shown in **Figure 1**. For the pristine polyurethane foam without chromic acid treatment, it is clearly seen that the foam surface is smooth and flat (Figure 1a,c). There is no obvious micrometer- or nanometer-scale structures on the original foam surfaces. However, for polyurethane foam after chromic acid treatment, the low-magnification ESEM image showed the foam surfaces possesses randomly rough structures at the micrometer scale (Figure 1b). The high-magnification ESEM image revealed randomly distributed nanoscale structures on the polyurethane foam surfaces (Figure 1d). ESEM results demonstrated that the chromic acid treatment results in the formation of micro-nanoscale hierarchical structures on the foam surface, which is very important for the final superhydrophobicity, as observed in nature on lotus leaves, owing to their multiscale structures in the form of cilium-like nanostructures superimposed on top of the micrometer-scale papillae.[30]

In our case, the chromic acid solution is composed of $K_2Cr_2O_7$, H_2SO_4, and distilled water. Through the chromic acid etching, the surface chemical constitution of polymer surfaces can be changed, resulting in the considerable increase of the polymer surface roughness.[31,32] Therefore, a limited extent of surface etching was beneficial to the surface wettability. Usually, the etching process of polyurethane can be summarized following two principal approaches. The first is the oxidation reaction that mainly occurs in the tertiary C–H bonds of polyurethane.[33–35] The H of tertiary C–H bonds is oxidized through a chromium(IV) ester intermediate to form an alcohol.[36] The alcohol undergoes a very rapid reaction to give first an olefin and then scission products (aldehydes and ketones) which may be further oxidized to carboxylic acids.[37–39] The second is hydrolysisreaction that the urethane bonds decompose to form alcohols and carbamic acid.[36,40,41] The alcohol undergoes a very rapid reaction to give first aldehydes and then carboxylic acid, which may be further oxidized to carbon dioxide.



(1)
(2)

The difference in the geometric structures and chemical compositions is reflected in the surface wettability of the samples. The contact-angle images of polyurethane foam with and without treatment are shown in **Figure 2**. For the pristine foam (Figure 2a), the water contact-angle was about 56° (2 μL), exhibiting its intrinsic hydrophilicity. After the chromic acid treatment, the polyurethane foam surfaces possessing multiscale structures without fluoroalkylsilane (FAS) chemical modification exhibited superhydrophilicity, and the water contact-angle was about 0° (Figure 2b). The surface wettability transformation from hydrophobicity to superhydrophilicity can be attributed to the induced roughness by the acid etch. After chemical modification with FAS, the water contact-angle of polyurethane foam with

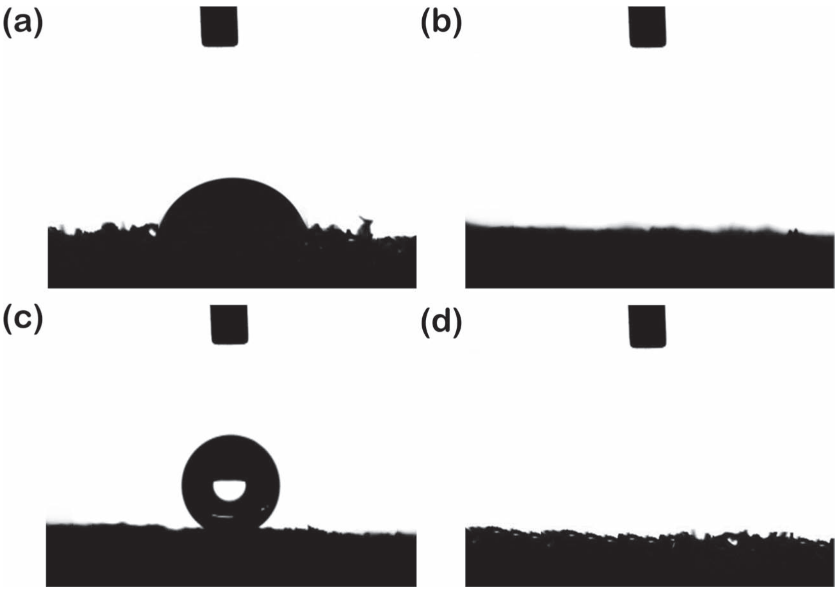


Figure 2. a) Water contact-angle image of the pristine polyurethane foam, showing intrinsic hydrophilicity (the water contact-angle is about 56°). b) Water contact-angle image of the chromic acid-treated foam without the FAS modification, exhibiting superhydrophilicity (the water contact-angle is about 0°). c,d) Contact-angle images of the chromic acid-treated foam after the FAS modification, demonstrating superhydrophobicity (c; the water contact-angle is about 155°) and superoleophilicity (d; the gasoline contact-angle is about 0°).

multiscale structures was changed from nearly 0° (Figure 2b) to about 155° (Figure 2c). Water droplets deposited on the surface form almost perfect spheres. This can be attributed to the introduction of low surface energy FAS. Therefore, the cooperation of surface chemical compositions and hierarchical structures is very important for the final formation of superhydrophobicity. The oil contact-angle of polyurethane foam with multiscale structures after the FAS modification was about 0° (Figure 2d), showing the superoleophilic property. Simultaneous superhydrophobicity and superoleophilicity is critical for the application of porous materials in oil/water separation.

Although the pristine polyurethane foam possesses low density and light weight, it will sink beneath the surface of water owing to its characteristics of hydrophilicity and high absorption ability towards water. In our case, the resultant polyurethane foam can float easily on water, which can be attributed to its superhydrophobicity and light weight (**Figure 3**a). When the superhydrophobic foam was immersed in water by application of an external force, the foam surface was surrounded by air bubbles, exhibiting a silver mirror-like surface (Figure 3b). After releasing the external force, the superhydrophobic foam could float immediately on water without the absorption of water. This implies that the superhydrophobic foam can be used to absorb organic solvents on water (the density of organic solvents is lower than that of water) and has important applications in oil/water separation. In addition to the water repellency, the resultant polyurethane foam also exhibited stable repellency towards corrosive liquids, such as acidic, basic, and salt solutions. The static contact-angle is almost unchanged over a wide range of pH values from 1 to 14. Figure 3c shows the representative digital image of acidic (left, pH = 1), salt (middle, pH = 7), and basic (right, pH = 14) droplets on the foam surface. All these aqueous solution droplets with spherical shapes were located uniformly on the foam, exhibiting stable wettability even towards many corrosive solutions.

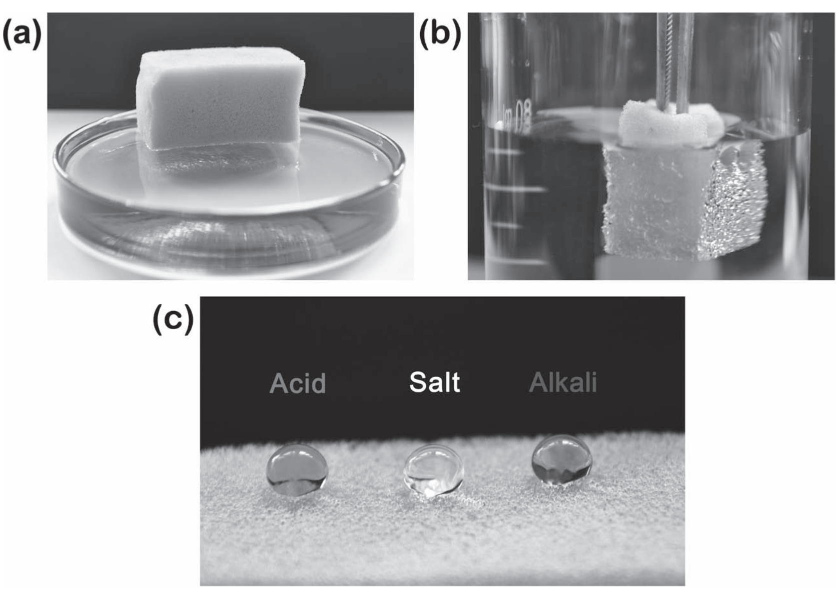


Figure 3. a) Optical image of the as-prepared polyurethane foam floated on water owing to its superhydrophobicity and light weight. b) Digital image of the superhydrophobic foam immersed in water by an external force, exhibiting a silver mirror-like surface due to the surrounded air bubbles. c) Optical image of aqueous hydrochloric acid (left, pH = 1), NaCl (middle, pH = 7), and NaOH (right, pH = 14) solution droplets with spherical shapes on the resultant polyurethane foam, demonstrating stable wettability towards different corrosive liquids.

In addition to the super-repellency, the resultant polyurethane foam showed a low adhesion to water. The water droplet is hardly able to stick to the foam surface, allowing water droplets to roll off quite easily (see Movie 1 in the Supporting Information). By contrast, gasoline or diesel oil, a liquid with a low surface tension, spread quickly on the foam and permeated it thoroughly (Movie 2 in the Supporting Information), exhibiting highly oleophilic properties. This can be directly confirmed by the evolving contact process of a water droplet on the superhydrophobic foam surface (**Figure 4**). The water droplet rolled off the surface quite quickly

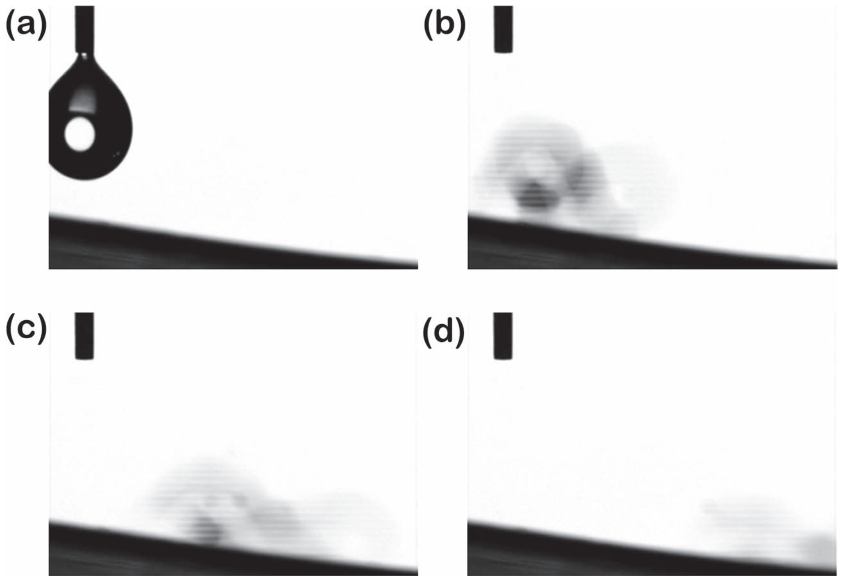


Figure 4. The representative contact process of a water droplet (8 μL) on the resultant superhydrophobic polyurethane foam surface, with a sliding angle less than 5°. Times were: a) 0.000 s, b) 0.039 s, c) 0.083, and d) 0.167 s.

within a very short time (about 0.167 s) when the foam was tilted by about 5°. The simultaneous superhydrophobicity with a small sliding angle and superoleophilicity make it possible to use the foam in the field of oil/water separation, especially when the density of organic solvents is close to that of water.

The wettability of solid surfaces is governed by both the surface roughness and the chemical composition. In our case, the acid etch resulted in the formation of multiscale structures on the foam surface, which dramatically increased the surface roughness. Moreover, the introduction of low surface free energy FAS strongly decreased the surface energy of the polyurethane foam. The cooperation of surface multiscale structures and low surface energy FAS resulted in the final formation of the stable superhydrophobicity with a small sliding angle. Therefore, the hydrophobicity mode in our case is governed by Cassie's mode,[42] possessing a discontinuous and unstable three-phase (solid–liquid–air) contact line.[43]

Similar to the lotus leaf, functional surfaces simultaneously possessing a very high static water contact-angle and a very low sliding angle have an important application in the field of self-cleaning.[16] To investigate the self-cleaning ability, the superhydrophobic foam was contaminated with carbon-black particles. As shown in **Figure 5**, the water droplet adsorbed carbon particles as it moved over the foam surface from left to right. It can be clearly observed that the droplet is covered with carbon particles. Contaminants were efficiently removed from the foam surface, demonstrating a lotus leaf-like self-cleaning effect, as found in nature. Self-cleaning is very important to remove dust particles residing on the foam surfaces and maintain the oil/water separation efficiency.

Porous materials with simultaneous superhydrophobicity and superoleophilicity have important applications in oil/water separation. In our case, a practical oil/water separation experiment of the resultant polyurethane foam was carried out in a simple setup (**Figure 6**). To test the oil/water separation capability, the foam was fixed in the glass tube. When a mixture of crude oil and water was poured onto the polyurethane foam, the crude oil penetrated through the foam and dropped into the beaker below owing to its superoleophilicity. Meanwhile, more and more water was retained on the top of the mixture due to the superhydrophobicity of the foam. The crude oil could successively penetrate through the foam because the density of crude oil is larger than that of water.

During the oil/water separation process, no external force was employed. The absorbed crude oil in the foam can be readily collected by a simple squeezing process (**Figure 7**a). No water in the collected crude oil can be found, which shows a very high separation efficiency of the polyurethane foam. The separation efficiency was calculated by the ratio (R (%)) of oil before and after separation according to the following equation.

$$R\,(\%) = (V_p + V_s) / V_o \times 100$$

Where V_o and V_p are the oil volume of the original oil/water mixture and the collected oil after one separation, respectively, and V_s is the absorbed oil in the sponges as collected by a simple squeezing process. It was found that the as-prepared multifunctional foam demonstrated effective separation for a variety of organic solvent/water mixtures, including gasoline, crude oil, hexane, and petroleum ether, demonstrating it to be a good candidate for industrial oil-polluted water treatment and oil-spill cleanup. The separation efficiency of the foam for these oil/water mixtures is above 95% (Figure 7b). Furthermore, the polyurethane foam can maintain its superhydrophobicity and is easily cleaned using water or ethanol for reuse owing to its self-cleaning effect; after 10 separations, the as-prepared foam

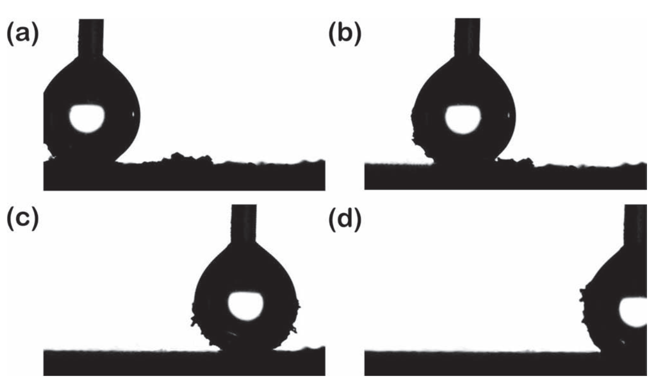


Figure 5. Demonstration of the self-cleaning ability of the resultant superhydrophobic polyurethane foam through the removal of carbon black particles from the surface using a moving water droplet (5 μL).

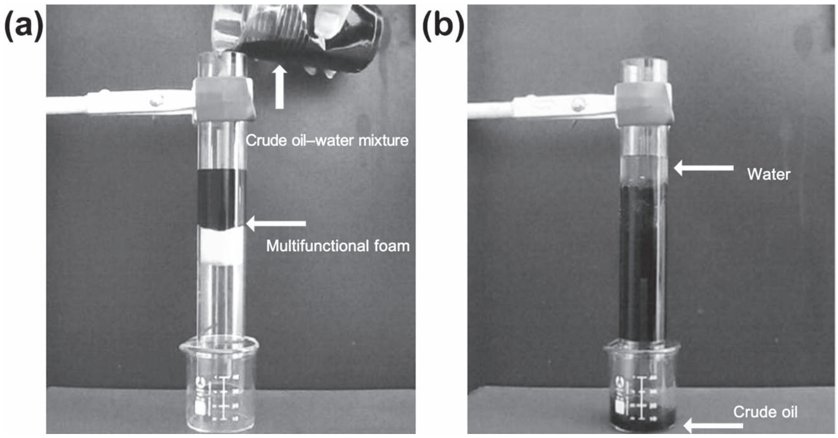


Figure 6. Optical images of the oil/water separation process designed using the polyurethane foam with superhydrophobicity and superoleophilicity: a) the polyurethane foam was fixed in the glass tube and the crude oil/water mixture was put into the glass tube; and b) the crude oil successively penetrated through the foam dependent on its own weight, water was repelled and retained on the top due to the superhydrophobicity of the foam. The polyurethane foam can be reused owing to its self-cleaning effect.

maintained high hydrophobicity and could not absorb any water (Figure 7c), therefore still possessing considerable separation efficiency.

3. Conclusions

In conclusion, a facile bioinspired synthesis strategy was proposed for the construction of polyurethane foam possessing simultaneous superhydrophobicity with a very low water sliding angle and superoleophilicity. The resultant foam exhibited super-repellency towards corrosive liquids, self-cleaning, and oil/water separation properties, demonstrating multifunctional characteristics, which strongly extend the practical applications of polyurethane foam. Learning from nature will give us more important inspiration and novel design principles for the rational design and the reproducible construction of artificial multiscale structures for functional integration. We also expect this method can be widely adopted for the fabrication of other foam materials with multifunction integration.

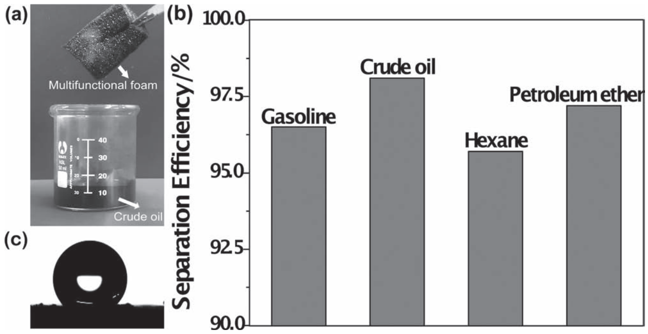


Figure 7. a) Collection of crude oils from the multifunctional foam by a simple squeezing process. b) The separation efficiency of the multifunctional foam. c) The water contact-angle of the foam after 10 separations (about 141°).

4. Experimental Section

Bioinspired multifunctional polyurethane foam with oil/water separation and self-cleaning was fabricated through the following procedure. First, the polyurethane foam was ultrasonically washed in deionized water and ethanol for 30 min to remove surface stains and oils, respectively. After the cleaning, the foam was dried in an oven. The cleaned foam was etched with chromic acid solution for 1–3 min at room temperature. After etching, the foam was rinsed sufficiently with deionized water, and then dried in an oven. The obtained polyurethane foam was modified with a 1.0% ethanol solution of fluoroalkylsilane (FAS) at room temperature for 24 h. For comparison, an equivalent polyurethane foam after the chromic acid etching was fabricated similar to the described approach, however without the FAS modification.

Surface morphologies of the obtained samples were characterized by environmental scanning electronic microscopy (ESEM; FEI Quanta 250, USA). Water contact-angles were measured on a Dataphysics OCA 20 contact-angle system at room temperature.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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