

Stable superhydrophobic and superoleophilic soft porous materials for oil/water separation†

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In this paper, polyaniline nanofibers were deposited on the surface of fabrics and generated a rough structure similar to the micromorphology of a lotus leaf via the oxidative chemical polymerization of aniline. After modification with *n*-octadecyl thiol, water-repellent fabrics were obtained. Interestingly, the as-prepared fabrics showed stable and robust superhydrophobic properties towards many corrosive solutions (acidic, basic, salt liquids), hot water, and mechanical abrasion. In addition, it was proven that this method can also be applied to other porous materials with different pore diameters and chemical compositions, such as stainless steel meshes with different pore diameters and sponges. More importantly, the as-obtained diverse superhydrophobic/superoleophilic porous materials can successfully and effectively be applied to separate oil-and-water mixtures. It is expected that this general route to fabricating superhydrophobic porous materials could have many more practical applications, especially in oil/water separation.

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1. Introduction

Since the problems of oil spills and industrial oily wastewater are increasingly serious nowadays, the generation of new materials for application in the efficient separation of water/oil mixtures is necessary. Recently, a lot of porous materials for oil/water separation have been prepared by controlling the chemical composition and the surface roughness, to give possession of both superhydrophobicity (a water contact angle of more than 150°) and superoleophilicity (an oil contact angle of less than 10°).^{1–10} Feng *et al.* firstly fabricated a mesh film coating with both superhydrophobic and superoleophilic properties by a spray and dry process. This as-prepared mesh effectively achieved oil/water separation.¹ Tian *et al.* prepared a micro/nanoscale hierarchical structured superhydrophobic ZnO mesh film for the separation of water and oil.³ Choi's group prepared a sugar-templated polydimethylsiloxane (PDMS) sponge for the selective absorption of oil from water.⁶ Our team has proposed two different strategies to fabricate robust superhydrophobic fabrics and sponges, based on both transition-metal oxides and metallic nanocrystals, for application in oil/water separation.^{9,10} However, defects still exist for the above materials and methods. Firstly, the superhydrophobic porous materials normally have short stability, especially

regarding the anti-corrosion property, thermal stability to hot water, and mechanical stability, which largely restricts their practical applications and the scale-up of production. Secondly, these strategies are not fit for various porous materials, such as, fabric, sponge, mesh, *etc.* Hence, it is of interest and still a big challenge to design a versatile method suitable for the fabrication of various porous materials with stable superhydrophobicity, which can be applied in oil/water separation.

As we know, polyaniline (PANI), as a conducting polymer, has gained tremendous attention owing to its fascinating physical and chemical properties, which have been widely exploited in sensors, microelectronic devices, platinum catalyst supports, *etc.*^{11–15} Moreover, tremendous interest has been focused on its intrinsic surface properties and the integration of these properties because of its potential applications in conductive textiles, antistatic coatings, corrosion protection, *etc.*^{15–22} For instance, Jiang and co-workers fabricated a stable, superhydrophobic and conductive PANI/polystyrene film via the electrospinning method. The as-prepared surface exhibited excellent stability in many corrosive solutions, even in oxidizing solutions.²⁰ Zhang *et al.* firstly synthesized a pure PANI nanowire film for a superhydrophobic surface on a Ti/Si substrate by means of an anodic deposition method.²¹ Yan's group reported the PANI films that could be changed between the doped state and de-doped state by controlling the electrical potential, resulting in reversibly switchable superhydrophobic and superhydrophilic surfaces.²² However, so far, most reports have focused only on making a PANI film with superhydrophobicity, or tunable wettability, but not both super-

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hydrophobic and superoleophilic properties simultaneously for the separation of oil/water.

To this end, we reported herein a general route fit for producing various porous superhydrophobic materials through the oxidative chemical polymerization of aniline.^{23,24} PANI nanofibers were successfully synthesized on the surface of various porous materials, mainly fabrics, sponges and stainless steel meshes. After modification by alkyl thiol, these PANI-coated porous materials exhibited excellent superhydrophobicity and superoleophilicity. Among them, the as-prepared fabrics showed stable high hydrophobicity towards many corrosive solutions (acidic, basic, salt liquids), hot water, as well as mechanical abrasion. This means that the PANI-coated fabrics could be better applied in the realistic environment, even in harsh conditions. Importantly, the as-obtained fabrics, sponges and meshes successfully and effectively achieved the separation of an oil-and-water mixture.

2. Experimental section

2.1. Synthesis

Fabrics, sponges and stainless steel meshes were obtained from a local supermarket. *n*-Octadecyl thiol (96%) was purchased from Acros Organics. All other chemicals were analytical-grade reagents and used without any further treatment. The substrates (including the fabrics, sponges, and stainless steel meshes) were sequentially cleaned with ethanol and distilled water in the ultrasonication cleaner to remove any possible impurities, and subsequently dried at 60 °C in a drying oven in air. The substrates were put into 30 ml aqueous HClO₄ (1 M) solution of aniline (0.01 M) and ammonium persulfate (APS). APS was the oxidant and HClO₄ was the dopant, and the ratio of aniline to APS was 1.5. The condition of an ice-water bath (~0 °C) was employed, and the PANI nanofibers were grown on the surface of substrates after reacting for 12 h under magnetic stirring. After that, the substrates were taken out and cleaned with distilled water many times, and then dried at 60 °C in an oven in air. Finally, the as-dried samples were immersed in 50 ml of 4 mM *n*-octadecyl thiol anhydrous ethanol for 24 h at room temperature. The samples were thoroughly cleaned with anhydrous ethanol repeatedly to remove any residual thiol and dried at 60 °C.

2.2. Characterization

The morphologies of the samples was observed by means of JSM-5600LV and JEOL JSM-6701F scanning electron microscopy (SEM) microscopes. The water contact angles were measured by a DSA100 contact angle meter (Kruss Company, Germany). The optical images and movies were obtained by a digital camera (Sony, DSC-HX 200). The chemical composition of the samples was investigated with X-ray photoelectron spectroscopy (XPS), which was conducted on a VG ESCALAB 210 electron spectrometer (Physical Electronics, USA) using Mg-K α radiation(1253.6 eV). The binding energy of C 1s (284.6 eV) was used as a reference.



Scheme 1 Schematic drawing of the synthesis procedure of the superhydrophobic PANI-coated fabric.

3. Results and discussion

Inspired by lotus leaves, combining the chemical composition with surface topography, many biomimetic superhydrophobic surfaces have been fabricated *via* chemical etching,²⁵ layer-by-layer processes,²⁶ sol-gel processes,²⁷ electrodeposition,²⁸ electrospinning,²⁹ *etc.* Based on the established theoretical and experimental results, it is believed that surface roughness plays an important role in superhydrophobic surfaces, regardless of the chemical composition.^{30–32} Herein, PANI nanofibers were grown on porous materials *via* the traditional oxidative chemical polymerization of aniline. A typical procedure of preparing the water-repellent fabrics was shown in Scheme 1. In the ice-water bath condition (0 °C), APS as the oxidant and HClO₄ as the dopant, aniline monomers polymerized into PANI nanofibers and deposited onto the fabric fibers. After modification with *n*-octadecyl thiol, superhydrophobic PANI-coated fabric was obtained.

Typical SEM images of the fabric and PANI-coated fabric were shown in Fig. 1. It can be seen that the original fabric fiber surface structure was smooth and flat (Fig. 1a–c). Therefore, the original fabric possessed superhydrophilic properties, which was confirmed by the CA measurement. However, for PANI-coated fabric, the low-magnification (Fig. 1d) and high-magnification (Fig. 1e,f) SEM images showed a large number of PANI nanofibers that were perpendicularly distributed on the microscale fabric fiber. The diameters of the PANI nanofibers ranged from 20 nm to

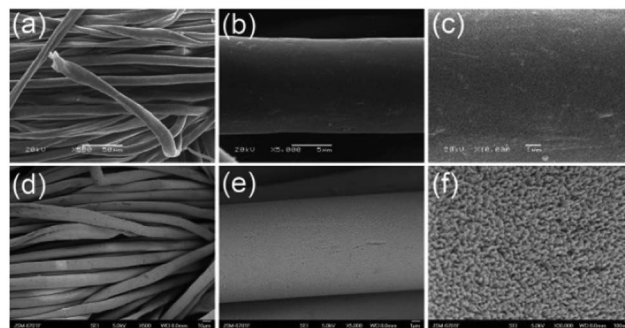


Fig. 1 SEM images of the original fabric (a) and the PANI nanofibers coated-fabric (d); (b) and (c) are the local enlarged views of (a), (e) and (f) are locally enlarged views of (d).

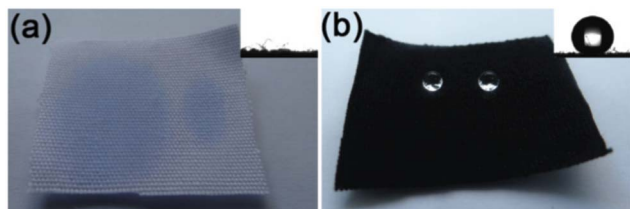


Fig. 2 Optical images of the original superhydrophilic fabric (a) and the superhydrophobic PANI-coated fabrics (b). The inset images in the upper right-hand corner of each panel are images of the static water droplets. The water droplets were dyed by methylene blue for clear observation.

30 nm. The appearance of the nanoscaled PANI nanofibers with largely enhanced surface roughness of fabric fibers, were helpful for the final formation of the superhydrophobicity due to the air trapped among the nanofibers. SEM images demonstrated that the PANI-coated fabrics have micro- and nanoscaled hierarchical structures, which resembled the multiscaled structures of lotus leaves. The PANI-coated fabric displayed superhydrophobicity after surface modification. The water droplets could easily roll on the PANI-coated fabric surface. The synergistic interplay of the surface roughness and low surface free energy contributes to the transition from the original superhydrophilic fabric (Fig. 2a) into the coated superhydrophobic fabric (Fig. 2b). XPS measurements confirmed the presence of nitrogen, carbon, oxygen, chlorine, and sulfur on the superhydrophobic fabric, as shown in Fig. 3.

It has been proven that this method can also be applied to other porous materials with different pore diameters and chemical compositions. Stainless steel meshes with different pore diameters and sponges were coated with PANI nanofibers (Fig. S1, ESI†). These PANI-coated surfaces showed water CAS higher than 150° after surface modification (Fig. S2, ESI†).

So far, many methods and materials have been used to synthesize superhydrophobic surfaces, but most of these superhydrophobic surfaces lacked excellent stability, which

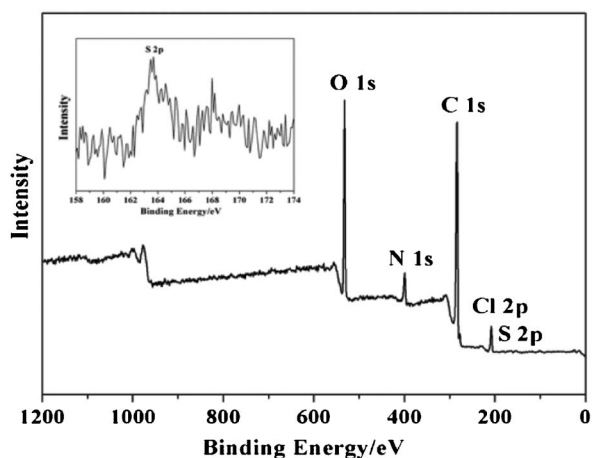


Fig. 3 XPS spectrum of the fabric coated with PANI nanofibers. Inset is a high-resolution spectra of the sulfur.

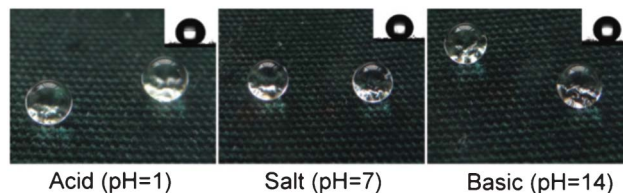


Fig. 4 Optical images of aqueous nitric acid (a), sodium chloride (b), and sodium hydroxide (c) solution droplets on the PANI-coated fabric. The inset images on the top right corner of each panel are images of the different static corrosive liquids, the corresponding contact angles are 151° (a), 157° (b), and 153° (c).

extremely restricted their actual applications. Herein, PANI-coated fabric was chosen as our research objective owing to its wide applications, and its stability was also discussed. In general, biomimetic superhydrophobic surfaces usually show high repellency towards distilled water or deionized water, while display dramatic repellency to hot water and corrosive liquids (such as acidic, basic, and salt solutions). This may be attributed to the deterioration of the topography and wettability of the superhydrophobic surfaces under the corrosive liquid. Thus, it is essential to investigate the stabilities for various liquids for the as-obtained PANI-coated fabric. The corrosion resistance of the as-prepared superhydrophobic fabric was studied *via* an investigation of a corrosive droplet at different pH values on the superhydrophobic surface. Fig. 4 showed representative photographs of acidic (Fig. 4a pH = 1), salt (Fig. 4b, pH = 7), as well as basic (Fig. 4c, pH = 14) droplets on the PANI-coated fabric surface. The shapes of these corrosive droplets on the superhydrophobic surface and the corresponding static contact angle were almost unchanged over a wide range of pH values from 1 to 14, indicating that the as-obtained PANI-coated fabric surface exhibited excellent superhydrophobicity towards many corrosive liquids.

Secondly, it was reported that the hydrophobicity of the superhydrophobic surface was remarkably reduced with increasing the temperature of the water droplet due to the adverse effect of temperature on surface tension.³³ Thus, the thermal stability, as one of the most important parameters, was characterized by introducing hot water droplets to the superhydrophobic surfaces. Briefly, a drop of water (room temperature $\sim 85^\circ\text{C}$) was placed on the surface of the as-obtained PANI-coated fabric. After standing for 30 s, the profile was recorded with a digital camera and the water static contact angle was measured with the contact angle meter. As shown in Fig. 5, when the temperature of the water droplets increased from room temperature (23°C) to 85°C , the contact angles remained unchanged, indicating that the PANI-coated fabric presents excellent thermal stability and high repellency towards hot water, which would enlarge its range of applications in some harsh conditions.

In addition, mechanical stability, as an indispensable parameter of robust superhydrophobic surfaces, is a key factor in determining practical applications. It is well-known that the micro- and nanostructure of superhydrophobic coatings are

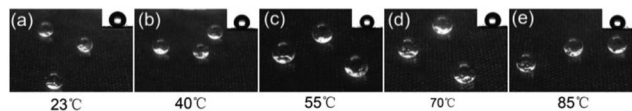


Fig. 5 (a)–(e): Optical images of water droplets at different temperatures on the PANI-coated fabric. The inset images in the top right corner of each panel are images of the static water droplets with different temperatures.

easily damaged or destroyed under mild abrasive forces, leading to the loss of water-repellency.^{34,35} Consequently, the scratch test was adopted to investigate the mechanical stability of PANI-coated fabric in order to evaluate the robustness of the as-prepared surfaces.³⁶ The detailed process of the scratch test was illustrated in Fig. 6a. Sandpaper (1500 mesh) served as an abrasive surface to test the superhydrophobic fabric. A pressure (7.5 kPa) was loaded to the fabric, the fabric was then moved slowly back and forth with a speed of 2 cm s^{-1} . As a result, the contact angle decreased from 157° to 136° after 15 cycles of abrasion, as shown in Fig. 6b, which suggested that the superhydrophobicity was partially lost after the abrasion test. However, the PANI-coated fabric still possessed a high level of hydrophobicity with a contact angle higher than 135° and a small sliding angle of less than 10° after 15 cycles of abrasion.

To sum up, the series of aforementioned experiments demonstrated that the as-prepared superhydrophobic surfaces showed excellent stability towards corrosive liquids, hot water, as well as mechanical abrasion. Therefore, the good stability of the superhydrophobic surfaces could extend to broad practical applications, even facing harsh environments.

To the best of our knowledge, a porous surface with both superhydrophobic (impermeability to water) and superoleophilic (good permeability to oil) is usually used in the devices for oil/water separation. However, it is rarely reported that the versatile strategy can be employed to various porous materials. In our experiment, a general route was presented to achieve various porous superhydrophobic materials applied to oil/water separation. Three different typical porous materials (mesh, fabric, sponge) with special wettability were used to separate oil from water.

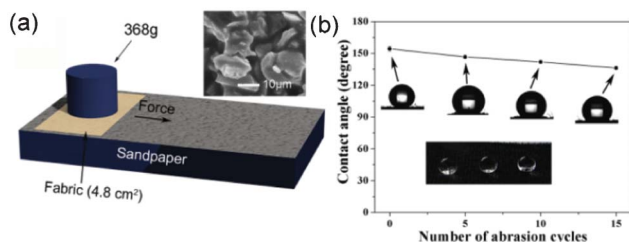


Fig. 6 (a) Schematic illustration of the scratch test used to measure the mechanical stability of the PANI-coated fabric. The inset is an SEM image of the sandpaper (1500 mesh). (b) Contact angles of PANI-coated fabric after abrasion cycles. The inset is an image of water droplet on the PANI-coated fabric after 15 abrasion cycles.

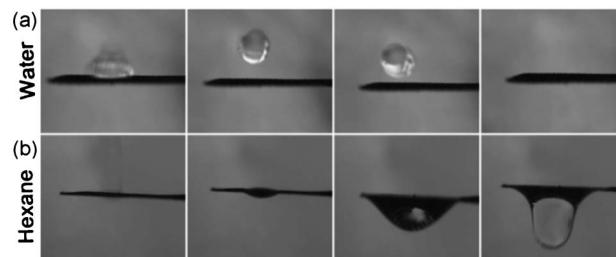


Fig. 7 The interaction of the superhydrophobic mesh with water and hexane: (a) the water droplet bounced on the mesh and then rolled off from the mesh (see the video file provided in the Supporting Information†), (b) the hexane droplet spread quickly and permeated through the mesh. As more oil was dropped, the oil droplet became larger and dropped down (see the video file provided in the Supporting Information†).

For the superhydrophobic PANI-coated stainless steel mesh, when water droplets were dropped from 20 mm onto the mesh, they bounced back up and then rolled off from the mesh surface (Fig. 7a, see Movie 1S in the Supporting Information†). Whereas for an oil droplet, it quickly spread and penetrated into the mesh surface, then dropped down when more oil was added (Fig. 7b, see Movie 2S in the Supporting Information†). This indicated that the PANI-coated mesh showed good permeability to oil and impermeability to water.

The oil/water separation experiment was performed as shown in Fig. 8 and in the Supporting Information† Movie 3S. When the mixture of water and oil (dyed with Red Dye 24 for clear observation) was poured from the separating funnel onto the mesh, the water flowed to the outside of the bottle into the beaker, while oil quickly permeated through the mesh and dropped into the bottle. The results indicated that the oil/water mixture could be effectively separated by the as-prepared superhydrophobic PANI-coated mesh. Furthermore, the mesh pore diameter was in the range of about $27 \mu\text{m}$ to $350 \mu\text{m}$, and the greater the mesh pore diameter was, the faster the oil/water separation occurred.

To our knowledge, fabrics are much softer and more flexible than stain steel meshes, and may be better candidates for oil/water separation. However, superhydrophobic fabrics have been less reported for use in oil/water separation, maybe

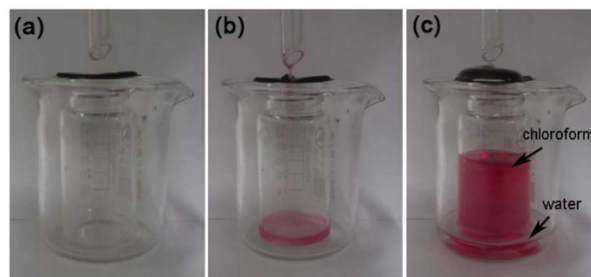


Fig. 8 Oil/water separation process of the superhydrophobic mesh coated with PANI nanofibers (see the video file provided in the Supporting Information†), the chloroform was dyed Sudan 24 for clear observation.

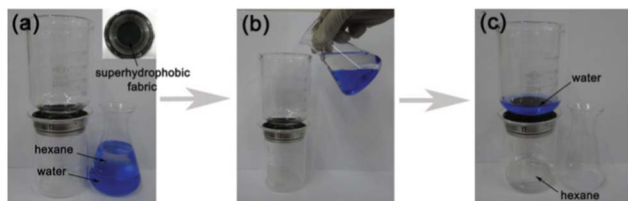


Fig. 9 (a–c) The oil/water separation process of hexane and water using the superhydrophobic PANI-based fabric (see the video file provided in the Supporting Information†). The water was dyed by methylene blue for clear observation.

owing to the weak stability of the superhydrophobic fabric. The as-prepared superhydrophobic PANI-coated fabric shows excellent stability towards corrosive liquids, hot water, as well as abrasion tests. Importantly, oil/water separation has successfully been achieved *via* the superhydrophobic/superoleophilic PANI-coated fabric, as illustrated in Fig. 9 (see Movie 4S in the Supporting Information†). When the hexane-and-water mixture was poured onto the superhydrophobic fabric, hexane quickly spread and permeated through the fabric and then rapidly dropped into the beaker underneath, whereas the water (dyed by methylene blue for clear observation) resided on the fabric.

Generally speaking, the untreated sponge absorbed water and then sank completely in water (Fig. S3, ESI†). However, the as-prepared superhydrophobic sponge can easily float on water, which was mainly due to its superhydrophobicity and light weight (S3). The superhydrophobic PANI-coated sponge was surrounded by a continuous air layer, as a silver-mirror

surface when it was immersed in water by an external force (Fig. S3, ESI†). The PANI-coated sponge immediately floated on the water surface without the absorption of water after release of the external force, which suggested the superhydrophobic sponge can potentially be applied in oil/water separation. As illustrated in Fig. 10 (a–c), by dipping the as-obtained superhydrophobic sponge into a water-and-oil mixture, the oil was quickly absorbed in a few seconds. When the sponge was taken out of the water surface, the oil was drawn out and the water became clearer.

The absorption capacity was used to measure the weight of oils and other nonpolar organic solvents that can be captured by the as-prepared superhydrophobic PANI-coated sponge. Herein, the absorption capacity was defined as $(m_{\text{saturated}} - m_{\text{initial}})/m_{\text{initial}}$. As shown in Fig. 10d, on the one hand, the PANI-coated sponge presented an absorption capacity in the range from 30 to 60 and a maximum absorption capacity of up to about 60 times its weight. The absorption capacity varied with each sponge, and mainly depended on the density of the oil and organic solvent. On the other hand, the sponge could be retrieved after washing with ethanol and other organic solvents and drying in oven, and exhibited good recyclability for 8 cycles of absorption/desorption. After 20 cycles absorption/desorption, the sponge still maintained a high hydrophobicity (Fig. 10e). Interestingly, the 20 cycles of absorption/desorption of the sponge regained the property of superhydrophobicity after surface modification (Fig. 10f).

4. Conclusion

In summary, a general and simple route was presented for fabricating superhydrophobic/superoleophilic porous materials *via* the oxidative chemical polymerization of aniline and the modification of thiols. Based on this method, aniline monomers were polymerized into PANI nanofibers, which were deposited onto the fabric fiber. The nanoscaled PANI nanofibers largely enhanced the surface roughness of the original fabric. After modification with *n*-octadecyl thiol, water repellent fabrics were obtained. Interestingly, the as-prepared fabrics showed stable, high hydrophobicity towards many corrosive solutions (acidic, basic, salt liquids), hot water, and mechanical abrasion. Therefore, the excellent stability of the superhydrophobic fabrics strongly extended applications in realistic environments, even in harsh conditions. In addition, it was proven that this method was also applicable to other porous materials with different pore diameters and chemical compositions, for instance, stainless steel meshes with different pore diameters and sponges. More importantly, the as-obtained diverse superhydrophobic/superoleophilic porous materials were successfully and effectively applied to separate the oil-and-water mixture. Among them, the superhydrophobic PANI-coated sponge can absorb a broad variety of oils with enormous absorption capacities and excellent recyclability.

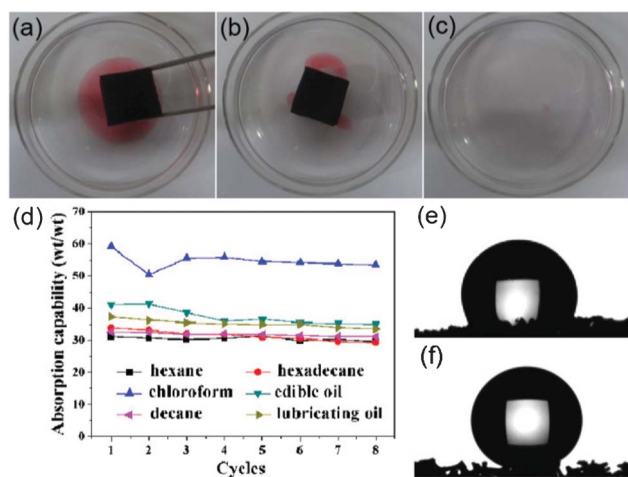


Fig. 10 (a–c) Images of the removal of hexane from the water surface by the PANI-coated sponge (see the video file provided in the Supporting Information†). Hexane was dyed by Sudan 24 for clear observation. (d) Absorption capacity of the PANI-coated sponge and its recyclability. (e) The water contact angle of the PANI-coated sponge after 20 cycles absorption/desorption (about 131°). (f) The water contact angle of the 20 cycles absorption/desorption of the PANI-coated sponge after surface modification (about 158°).

Acknowledgements

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