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A facile one-step spray-coating process for the fabrication of superhydrophobic attapulgite coated mesh used in oil/water separation

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Abstract

Oil/water separation is a worldwide problem due to the increasing industrial oily waste water and the frequent oil spill accidents. Here, we first demonstrate superhydrophobic attapulgite coated mesh films for gravity driven oil water separation, which was fabricated by a facile one-step spray-coating process. The as-prepared attapulgite coated mesh films show both superhydrophobic and superoleophilic properties simultaneously with a high water contact angle of $155 \pm 1^\circ$ and an oil contact angle of 0° . Thus, it can be used to separate a series of oil/water mixtures like kerosene, chloroform, petroleum ether, etc. with the separation efficiency up to 97 % for the kerosene-water mixture. In addition, the as-prepared coated mesh still maintained separation efficiency above 94% and stable recyclability after 40 separation cycles with the surface morphology of the attapulgite coated mesh nearly unchanged. Besides, the separation mechanism for the oil/water mixture was elaborated by interpreting the different states of water droplet on the surface before and during separation, which has been discussed scarcely. Furthermore, the

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as-prepared attapulgite coated mesh could keep superhydrophobic property with various harsh conditions not only for pure water but for corrosive solutions under acidic, alkaline and corrosive salt solutions, which shows attractive potential for practical oil-water separation in industry and everyday life.

Keywords: Superhydrophobic; superoleophilic; attapulgite; oil/water separation; separation efficiency

1. Introduction

Oil/water separation has become an increasingly important and urgent issue in modern chemical industrial process and environmental protection due to the increasing industrial oily wastewater, as well as frequent oil spill accidents.¹ Since oil/water separation is governed by interfacial phenomenon, using special wettability to design novel materials is a facile and effective way.²⁻⁴ Recently, surfaces with superhydrophobic and superoleophilic properties have attracted extensive interest in the field of oil water separation because of their capacity to absorb only oil while repelling water completely, exhibiting high oil/water separation efficiency and selectivity.⁵⁻¹² Inspired by the superhydrophobic surface of lotus leaf, a variety of routes have been developed to fabricate superhydrophobic materials for separation of water and oil, including chemical etching, electrospinning techniques, sol-gel, hydrothermal methods and self-assembly processes, etc.¹³⁻²⁴ However, most of the methods used for preparation of such surfaces always involves in two steps processes: creating a hierarchical roughness surface and then chemically modifying the surface with low surface energy materials, and only a few works have been reported for the

fabrication of these surfaces in one single step.^{25,26} Therefore, if both surface roughness and low energy surface can be obtained just by one single step, the process of fabricating superhydrophobic surfaces would be simplified.

Up to now, numerous functional materials with various hybrid structures have been developed, aiming to realize high performance water/oil separation utilizing their special wettability properties, such as ZnO,²⁷ TiO₂,^{28,29} kapok,³⁰ hydrophobic aerogel,³¹ polyvinylidene fluoride (PVDF),³² carbon-based materials,^{33,34} magnetic materials,^{35,36} etc. However, the majority of the materials reported for the separation oil from water generally cannot be used in the corrosive environment of a strong acid or base and thus suffered from the limitation of recyclability. For instance, the traditional ZnO, TiO₂ or PVDF can be degraded by strong acid solution, and consequently, limiting their practical applications. Therefore, there is a great need to design chemically resistant inorganic films for practical applications in oil/water separation, which is not only suitable for all pH environments, but also realizing highly efficient oil/water separation. Among the as-known materials in nature, attapulgite is a kind of hydrated magnesium aluminum silicate mineral with exchangeable cations in its framework channels, reactive -OH groups on its surface, which has been applied in a wide range of fields.³⁷⁻⁴³ Compared with other materials for fabrication of superhydrophobic film, the advantages of attapulgite is its chemical inertness, extensive sources as well as cheapness, and thus potential mass industrial application. Accordingly, there are also few reports on superhydrophobic attapulgite surfaces recently, and much of the work is attempted to create self-cleaning

surfaces.^{44,45} However, to the best of our knowledge, superhydrophobic attapulgite coated mesh used for oil/water separation has not been reported. Moreover, the mechanism of oil/water separation process is still unclear, and needs to be improved.^{46,47}

In the present study, the fabrication of APT-coated mesh films with robust superhydrophobic and superoleophilic properties is reported using a facile one-step process by spraying hydrophobic attapulgite (APT) modified with low energy material Octadecyltrichlorosilane (OTCS) and waterborne polyurethane (PU) mixtures on stainless steel mesh, eliminating the complexity of two different steps involved in the conventional methods. The waterborne PU was added in order to increase the binding force between the APT powders and stainless steel mesh. The spray-coating is a fairly facile and commercially available method for the widest applications, which is not specific to a particular substrate and can be easily applied to large surface area.^{48,49} Since water remained exclusively on the APT-coated mesh surfaces and oil permeated through the mesh surfaces quickly, thus the as-prepared superhydrophobic APT-coated mesh could be used for separation oil from water successfully. Furthermore, the as-prepared APT-coated mesh maintained high separation efficiency and stable recyclability after the 40 times repeated separating experiments. Besides, the separation mechanism for the oil/water mixture was elaborated by interpreting the different states of water droplet on the surface before and during separation. More importantly, the as-prepared APT-coated mesh film possesses superhydrophobic properties not only for pure water but for corrosive water

under acidic, alkaline and corrosive salt solutions. This means that the as-prepared APT-coated mesh could be better applied in the realistic environment, even in harsh conditions.

2. Experimental

Materials

APT micro-powder supplied from Jiuchuan Clay Technology Co., Jiangsu, China, is composed of CaO (1.29%), Al₂O₃ (10.47%), Na₂O (1.52%), MgO (20.41%), SiO₂ (64.31%), K₂O (0.13%) and Fe₂O₃ (0.87%). The APT powder was firstly activated with 4 M HCl solution before use. Octadecyltrichlorosilane (OTCS) was obtained from Alfa Aesar. Waterborne polyurethane (PU) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of superhydrophobic mesh

The synthesis of hydrophobic APT powders was a key part of our strategy for the fabrication of superhydrophobic APT-coated mesh. The hydrophilic APT powders were modified with sufficient amount of OTCS. In a typical procedure, 1g of APT powders and 40 mL of toluene were placed into a Round-bottomed flask. After adding 1 mL of OTCS, they were refluxed for 3 h. The procedure imparts hydrophobicity to the APT powders by immobilizing octadecyltrichloro groups on their surface. After filtration, the obtained APT powders were dried at 353 K and ground to a fine powder using a mortar. It is important to perform multistep washing and centrifugation to ensure complete removal of the unreacted and partially functionalized APT powders. The fabrication process of superhydrophobic APT-coated mesh is shown in Fig. 1, the

amount of 0.05 g waterborne polyurethane (PU) was firstly dissolved in 20 mL acetone, and then 0.3 g APT were dispersed in the solution and stirred magnetically for at least 1 h to gain a homogeneous suspension. The suspension was then sprayed onto the stainless steel mesh substrate (200 mesh size) with 0.2 MPa compressed air gas using a spray gun. Finally, the APT-coated mesh surface was dried at ambient temperature for 1 h to allow the acetone to evaporate completely.

Oil/water separation

Five kinds of oils and organic solvents including kerosene, chloroform, petroleum ether, tetrachloroethane and toluene were used in this study. They were colored with oil red O and mixed with water that was colored with methylene blue. For oil/water separation, the superhydrophobic APT-coated mesh was fixed between two Teflon fixtures, both of which were attached with glass tubes. The device was obliquely fixed to make it easier for oil to be in good contact with the mesh film, due to the density of the tested oil in this case is lighter than water. Mixtures of oil and water (50% v/v) were poured slowly into a test tube through the APT-coated mesh. The driving force during the separation process is its own gravity. The separation efficiency was calculated according to $\eta = (m_1/m_0) \times 100$, where m_0 and m_1 were the mass of the water before and after separation process, respectively.⁵⁰

Recycling test

The kerosene/water mixture was used to test the separation efficiency of the as-prepared coated mesh versus the recycle numbers of oil/water separation. After each oil/water separation experiment, the contaminated mesh was rinsed with alcohol

to remove the absorbed oil. Subsequently, the cleaned mesh was dried in an oven at 80 °C for 30 min and the superhydrophobicity and the superoleophilicity could be recovered again.

Chemical stability test

Different water droplets with PH values ranging from 1 to 14 were used to test the chemical stability of the coated mesh. The chemical stability performance of the as-prepared APT-coated mesh was also studied by immersing the coated mesh into corrosive medium of 1 M HCl, 1 M NaCl, 1 M NaOH, acetone and toluene respectively for 24 h and then cleaning with deionized water.

Characterization

The morphological structures of the as-prepared surfaces were examined by field emission scanning electron microscopy (FE-SEM, JSM-6701F). The phase structure of the as-prepared samples was characterized by an X-ray diffractometer (XRD) (Rigaku Corp., D/max-2400) equipped with graphite monochromatized Cu K α radiation. Fourier transform infrared (FT-IR) spectroscopy was performed with a Bio-Rad FTS-165 instrument. The water and oil contact angle, sliding angle and slipping angle were measured with a SL200KB apparatus at ambient temperature. The volume of the individual water and oil droplets in all measurements was 5 μ L. The average water, oil contact and water sliding and slipping values were obtained by measuring the same sample at least in five different positions.

3. Results and discussion

A superhydrophobic APT-coated mesh was created by the subsequent introduction

of roughness and low energy surface via a facile one-step spray-coating deposition of hydrophobic APT powders (Fig. 1). The waterborne PU was added in order to increase the binding force between the APT powders and stainless steel mesh. The XRD pattern of APT is shown in Fig. 2a. The XRD patterns of the APT demonstrate a (110) characteristic diffraction peak at 8.4° of APT, revealing that the structure of APT is maintained very well in the preparation process.⁴¹ FT-IR spectra of APT before and after modified with OTCS were shown in Fig. 2b. In the spectrum of APT, the absorption bands at 3614 , 3551 cm^{-1} and 1636 cm^{-1} are ascribed to -OH stretching and bending vibration of APT, and the absorption bands at 1031 and 981.5 cm^{-1} are ascribed to Si-OH groups of APT.⁴⁴ After modified with OTCS, besides the -OH and Si-OH groups, the new bands at 2926 , 2855 cm^{-1} (asymmetric and symmetric stretching of CH_2) and 1465 cm^{-1} (bending CH_2) appeared in the spectra of modified APT, indicating that the APT was modified with the low energy material of OTCS successfully.^{11,51}

The surface morphologies of the pristine and the coated meshes were investigated by FE-SEM. Fig. 3a is a typical image of the porous stainless steel mesh substrate with an average diameter of approximately $75\text{ }\mu\text{m}$ (200 mesh size), and the knitting wires have a diameter of $60\text{ }\mu\text{m}$. The magnified view in the inset of Fig. 3a reveals that the original wires have smooth surface. After coated with the mixture of hydrophobic APT and PU, the macroscopic morphology of the mesh shows a little change (Fig. 3b). The low-magnification image of Fig. 3c shows that the APT is densely and randomly distributed on the surface of the wires with the microscale.

From the high magnified FE-SEM image of Fig. 3d, it is obvious that the APT was relatively aggregated with the diameter of a single fibril about 100 nm and the length of a single fibril about several hundred of nanometers, leading to the hierarchical micro- and nanoscale roughness on the APT-coated meshes. This hierarchical micro- and nanoscale roughness of the APT-coated mesh surface is essential to the superhydrophobicity.

The wettability properties of the APT-coated meshes were evaluated by water and oil contact angles measurements. The as-prepared APT-coated mesh showed superhydrophobic and superoleophilic properties simultaneously with a water contact angle as high as $158 \pm 1^\circ$ and a sliding angle as low as 8° (Fig. 4a and Fig. S1, ESI†) and an oil (kerosene) contact angle of 0° (Fig. 4b). Thus, the water droplet was repelled and stayed on the APT-coated mesh with highly spherical shape, while oil droplets permeated through the mesh quickly with few seconds (Fig. 4c).

The schematic of the separation mechanism for the oil/water mixture was shown in Fig. 5. Before separation, when a water droplet dropped onto the as-prepared APT-coated mesh surface, it was thought to be in Cassie state and could easily move away due to the low adhesive property of the as-prepared superhydrophobic APT-coated mesh (Fig. 5, left). Meanwhile, the oil droplet could quickly permeate through the superoleophilic APT-coated. However, the situation is quite different during the separation. When the oil permeated through the superhydrophobic APT-coated mesh, the mesh surface was wetted by oil. The rough structure on the mesh surface was filled with oil and it became relative flat, at this time, when a water

droplet dropped onto the surface, it preferred to keep in Wenzel state with a low water contact angle about 75° (Fig. 5, right). Meanwhile, the surface wetted by oil became easy flow for water with a water slipping angle as low as 10° , owing to the low resistance between the water and the oil wetted surface (the lower right corner of Fig. 5 and Movie S1, ESI†). After separation, the APT-coated mesh recovered its superhydrophobic and superoleophilic properties again, when the contaminated mesh was thoroughly rinsed with ethanol and deionized water to get rid of the oil residuals (Fig. S2, ESI†). Thus, the as-prepared superhydrophobic-superoleophilic APT-coated mesh could be used for the separation of oil and water mixtures successfully.

The as-prepared APT-coated mesh has great potential to separate oil/water mixtures due to the robust superhydrophobic and superoleophilic properties. A series of studies were carried out to test the oil/water separation capacities of the as-prepared APT-coated mesh. As shown in Fig. 6a and b, the coated mesh was fixed between two Teflon fixtures, both of which were attached with glass tubes. Since the density of the tested oil kerosene in this case is lighter than water, the device was obliquely fixed to make it easier for oil to be in good contact with the mesh film. As the mixture of kerosene (dyed with oil red) and water (dyed with methylene blue) was poured onto the APT-coated mesh film, kerosene passed through the mesh quickly with the driving force of gravity, while water was repelled and remained in the upper glass tube. More importantly, neither oil nor water is observed in collected water or oil respectively, indicating a high purity and effectiveness of the separation of the oil/water mixtures (see details in the Movie S2, ESI†). Mixtures of chloroform/water, petroleum

ether/water, tetrachloroethane/water, and toluene/water were also successfully separated with high efficiency. The separation efficiency of the as-prepared APT-coated mesh for the series of oil/water mixtures is shown in Fig. 6c. The separation efficiency was calculated according to $\eta = (m_1/m_0) \times 100$, where m_0 and m_1 were the mass of the water before and after separation process, respectively. The separation efficiency of the APT-coated mesh was calculated up to 97 % for the kerosene-water mixture and above 93 % for other oils. After each oil/water separation experiment, the contaminated mesh was rinsed with alcohol to remove the absorbed oil. And the APT-coated meshes still retain high separation efficiency after 40 separation cycles, which was always stayed above 94 % for the kerosene/water mixture, indicating good recyclability of the as-prepared APT-coated meshes (Fig. 6d). In addition, the surface morphology of the APT-coated mesh has not been destroyed (Fig. 6e). The inset in Fig. 6e illustrates that the surface of the mesh maintain highly hydrophobicity with a water contact angle about 142° after 40 times use, showing its stable wettability.

To further study the separation ability of the as-prepared APT-coated meshes, the intrusion pressure of water was introduced. The maximum height of water that the APT-coated mesh can support determined the intrusion pressure of water (which is determined by the maximum height of water that the APT mesh can support). Therefore, the intrusion pressure (P) value was calculated by the following equation:

$$P = \rho g h_{\max}$$

where ρ is the density of water, g is acceleration of gravity, and h_{\max} is the

maximum height of water the APT-coated mesh can support. As shown in Fig. 6f, the average maximum bearable height achieved is 20.4 cm, and the intrusion pressure is about 2.0 kPa. Water cannot flow through the mesh under the pressure. Oil flux is another evaluation for the oil/water separation mesh. The oil (kerosene) flux was measured under a fixed column of oil from 5 experiments. The kerosene permeates through the APT-coated mesh with an average flux as high as $20 \text{ L m}^{-2} \text{ s}^{-1}$. Consequently, the as-prepared APT-coated mesh is capable of separating a large amount of oil/water mixtures.

The as-prepared APT-coated meshes showed stable superhydrophobicity towards many corrosive solutions, such as acidic, basic and salt solutions. Fig. 6a shows the relationship between the pH values and CAs on the obtained APT-coated meshes. The as-prepared APT-coated meshes show superhydrophobicity in PH values ranging from 1 to 14 within experimental error at all pH values, showing superhydrophobicity not just for pure water but also for corrosive liquids, such as acidic, basic and some aqueous salt solutions (Fig. 7a and Fig. S3, ESI†). Furthermore, the as-prepared APT-coated meshes also show remarkable stability of wettability to the harsh environment conditions, such as corrosive solutions (1 M HCl, NaCl and NaOH), acetone and toluene by immersing the APT-coated meshes into the corresponding solutions for 24 h. Surprisingly, the superhydrophobicity still retained with the water contact angles all larger than 150° after cleaning with deionized water, showing robust chemical resistant to the extreme environment conditions (Fig. 7b and Fig. S4, ESI†). The chemical inertness of APT-coated mesh is a very vital consideration in practical

applications, which can be attributed to the unique chemical properties of APT-coated meshes.

4. Conclusions

In summary, robust and chemical stable APT-coated meshes with superhydrophobic and superoleophilic properties have been fabricated by a facile one-step spray-coating approach. The as-prepared superhydrophobic APT-coated mesh can separate oils from water with high separation efficiency, which is up to 97 % for the kerosene-water mixture. This process can be repeated for more than 40 times with stable high hydrophobicity and nearly constant high separation efficiency. Besides, the separation mechanism for the oil/water mixture was elaborated by interpreting the different states of water droplet on the surface before and during separation. In addition, the obtained APT-coated mesh can possess superhydrophobic properties not only for pure water but for corrosive water under acidic, basic and corrosive slat conditions. Therefore, the excellent stability of the superhydrophobic APT-coated mesh strongly extended applications in realistic environments, even in harsh conditions.

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Figure Captions

Figure 1. Schematic illustration for the fabrication of superhydrophobic APT-coated mesh through a facile one-step spray-coating process.

Figure 2. (a) XRD pattern of the APT and (b) FT-IR spectra of APT and APT modified with OTCS.

Figure 3. FE-SEM images of (a) the original stainless steel mesh and (c-d) the as-prepared APT-coated mesh surface at low and high magnifications, respectively.

The inset (a) is the magnified image of the original mesh and the insets (b-c) are the shapes of water droplet and (d) is the oil.

Figure 4. The as-prepared APT-coated coating mesh shows both superhydrophobic and superoleophilic properties. (a) shape of a water droplet on the coating mesh with a contact angle of $158 \pm 1^\circ$; (b) shape of an oil droplet on the coating mesh with a contact angle nearly close to zero; (c) spreading and permeating behavior of kerosene droplets on the coating mesh. The kerosene oil spreads and penetrates through the mesh quickly (within few seconds).

Figure 5. The separation mechanism for the oil/water mixture.

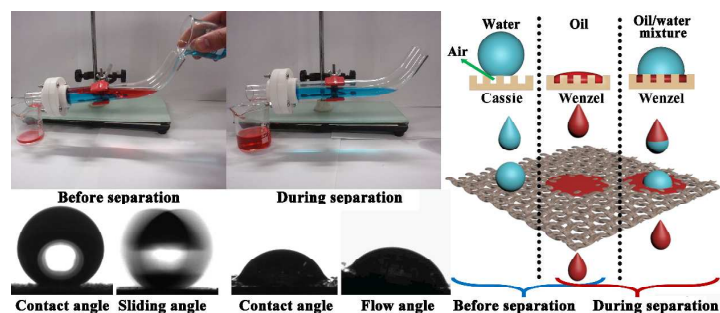
Figure 6. Oil/water separation studies of the as-prepared APT-coated mesh (water is dyed with methylene blue and oil is dyed with Oil Red O to enhance the visual effect): (a) during separation; (b) after separation; (c) The separation efficiency of APT-coated mesh for a selection of oil and water; d) Separation efficiency remains high after 40 times use by taking kerosene/water mixture as an example; e) Surface morphology has no change after 40 times use. The inset illustrates the shape of a water droplet on

the mesh after 40 times use; f) The intrusion pressure of water.

Figure 7. (a) Variation of water CAs on the as-prepared superhydrophobic APT-coated mesh as a function of pH value. (b) Water CAs on the treated superhydrophobic APT-coated mesh after being immersed into 1 M HCl, 1 M NaCl, 1 M NaOH, acetone and toluene respectively for 24 h.

The TOC graphic

Robust superhydrophobic attapulgite coated mesh fabricated by a facile one-step process could be used to separate oil from water with high efficiency. Besides, the separation mechanism for the oil/water mixture was elaborated by interpreting the different states of water droplet on the surface before and during separation.



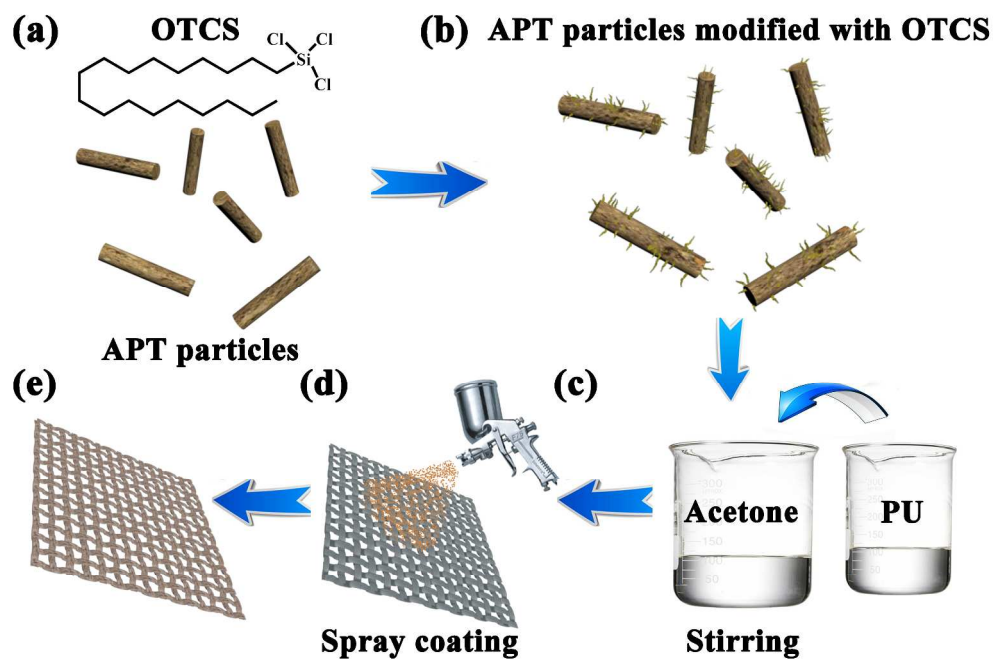


Figure 1. Schematic illustration for the fabrication of superhydrophobic APT-coated mesh through a facile one-step spray-coating process.

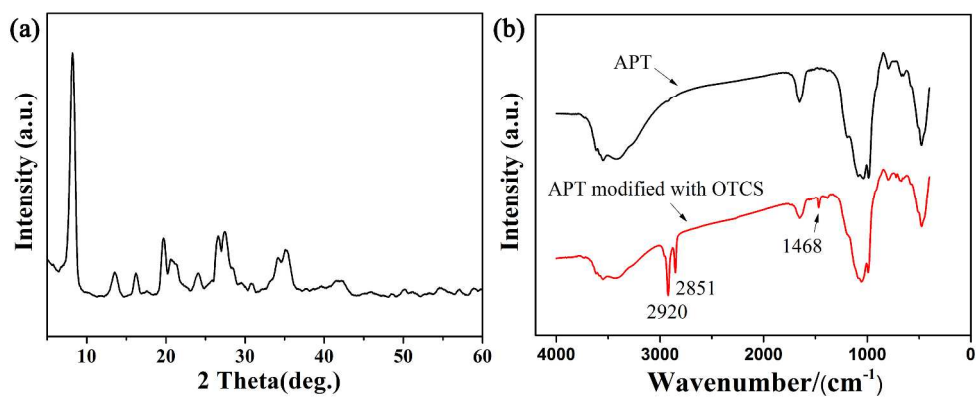


Figure 2. (a) XRD pattern of the APT and (b) FT-IR spectra of APT and APT modified with OTCS.

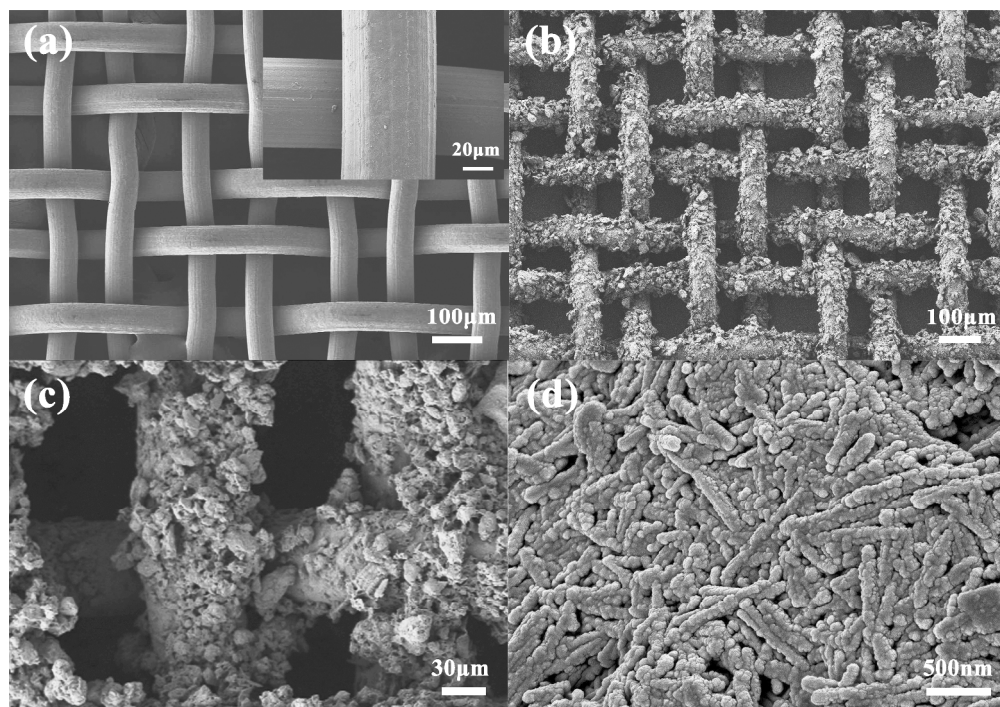


Figure 3. FE-SEM images of (a) the original stainless steel mesh and (c-d) the as-prepared APT-coated mesh surface at low and high magnifications, respectively.

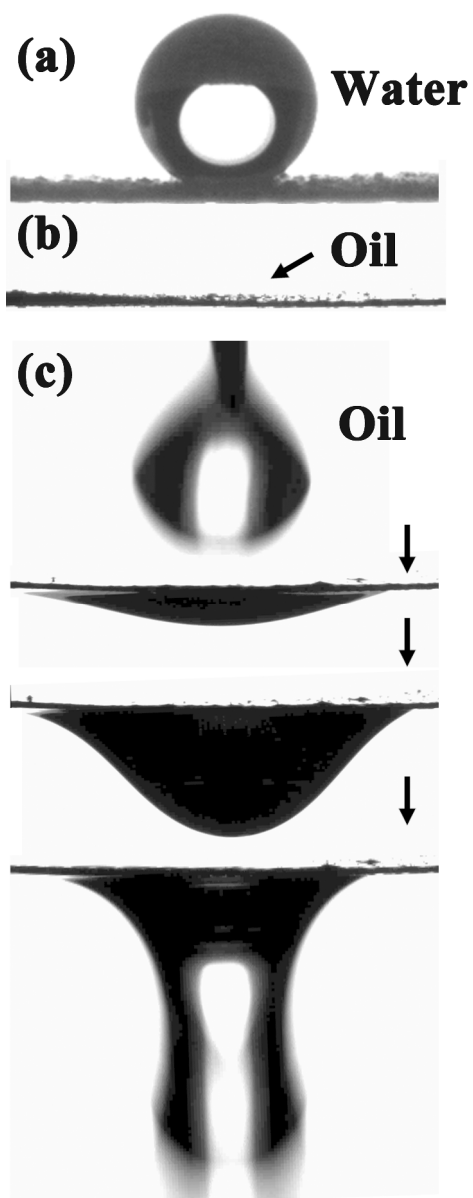


Figure 4. The as-prepared APT-coated coating mesh shows both superhydrophobic and superoleophilic properties. (a) shape of a water droplet on the coating mesh with a contact angle of $158 \pm 1^\circ$; (b) shape of an oil droplet on the coating mesh with a contact angle nearly close to zero; (c) spreading and permeating behavior of kerosene droplets on the coating mesh. The kerosene oil spreads and penetrates through the mesh quickly (within few seconds).

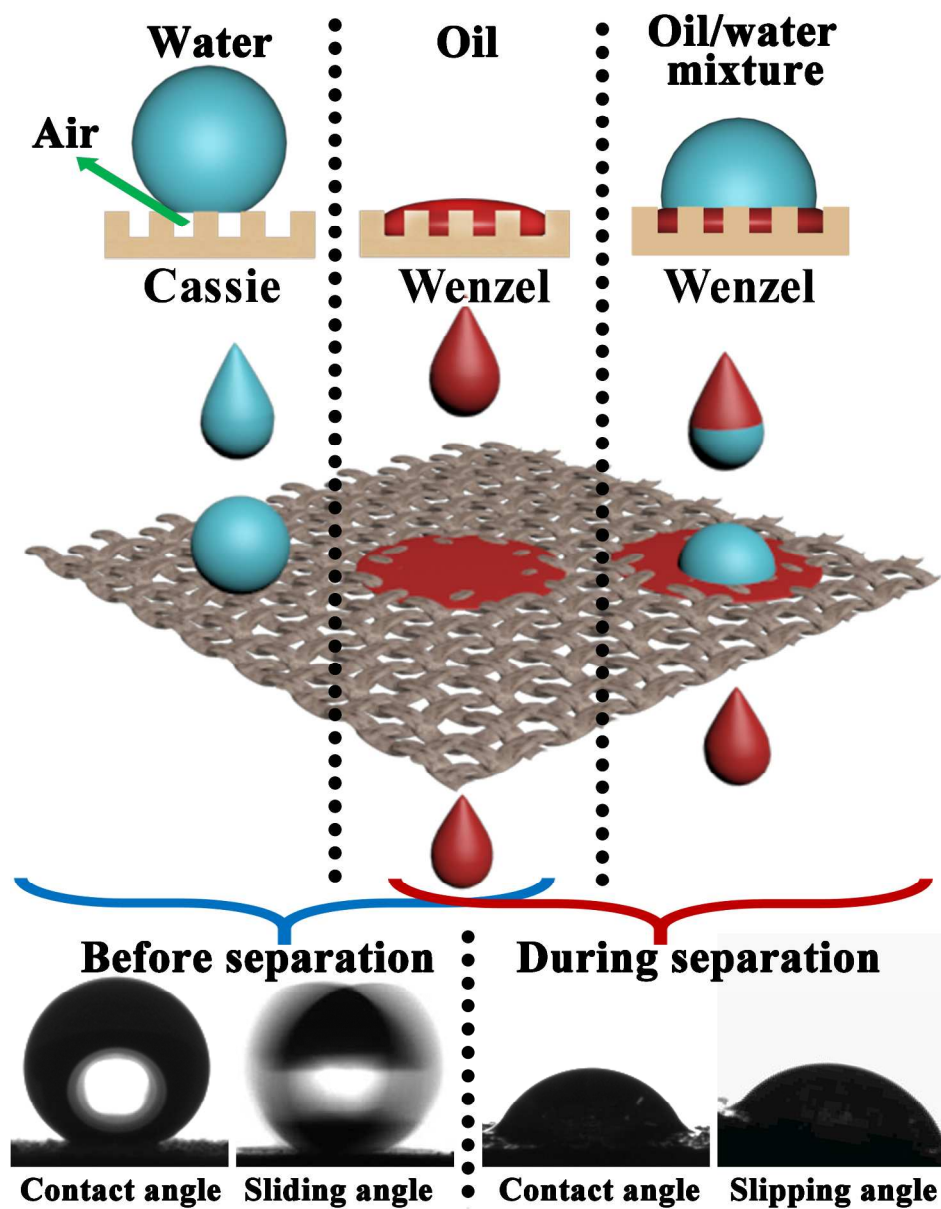


Figure 5. The separation mechanism for the oil/water mixture.

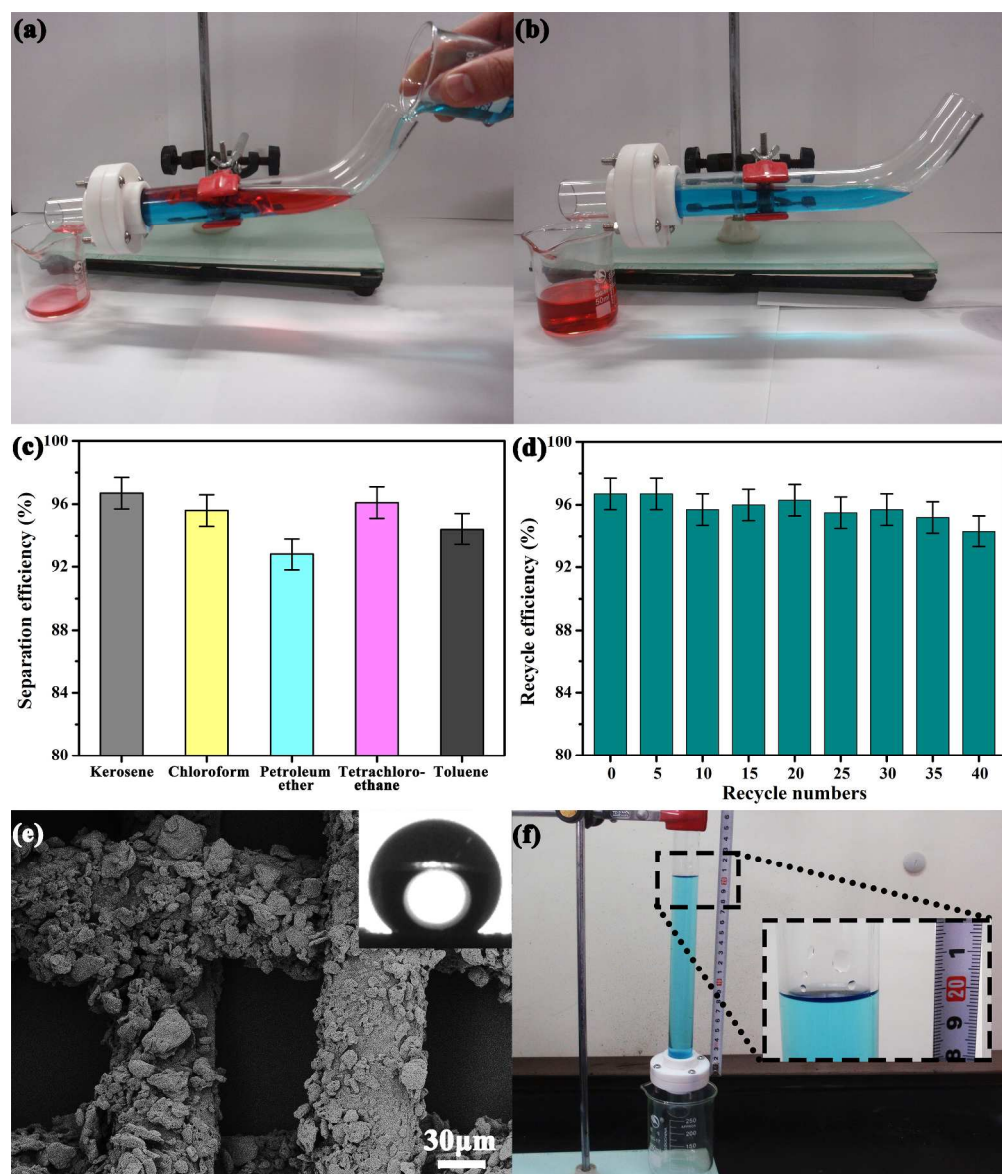


Figure 6. Oil/water separation studies of the as-prepared APT-coated mesh (water is dyed with methylene blue and oil is dyed with Oil Red O to enhance the visual effect): (a) during separation; (b) after separation; (c) The separation efficiency of APT-coated mesh for a selection of oil and water; (d) Separation efficiency remains high after 40 times use by taking kerosene/water mixture as an example; (e) Surface morphology has no change after 40 times use. The inset illustrates the shape of a water droplet on the mesh after 40 times use; (f) The intrusion pressure of water.

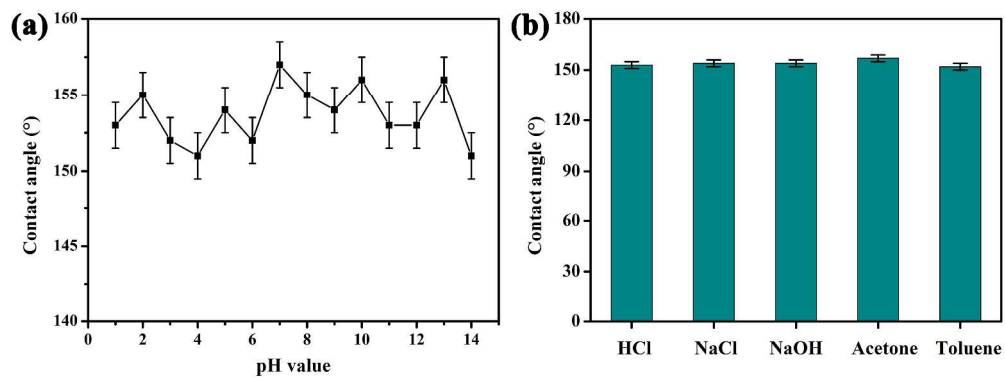


Figure 7. (a) Variation of water CAs on the as-prepared superhydrophobic APT-coated mesh as a function of pH value. (b) Water CAs on the treated superhydrophobic APT-coated mesh after being immersed into 1 M HCl, 1 M NaCl, 1 M NaOH, acetone and toluene respectively for 24 h.