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ARTICLE TYPE

Highly efficient oil–water separators based on dual superhydrophobic and superoleophilic properties of multiwall-carbon nanotube filtration films

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A new alkyl-pyrene has been synthesized and is used to modify multiwall-carbon nanotube to form films that are both superhydrophobic and superoleophilic. The superhydrophobic property of the MWCNT films prevents water from going through and the superoleophilic property of the films attracts oil, facilitating it to pass through the MWCNT filtration films. This film can also be easily recycled to prepare brand new water-oil separation filters and can be easily scaled up for large sizes. Our results reveal that the modified MWCNT film prepared here is a promising candidate for use in removal of oils and other organic pollutants from water.

During industrial processing, oil pollution has become a worldwide problem due to the increasing oily wastewater produced by petrochemical, food, and metal industries, as well as from the frequent oil spill accidents [1]. When not attended to, oil pollution will bring about extreme harm to the environment and to public health. Conventional techniques for separation such as centrifugation, gravity separation, skimming, and flotation are useful for free oil/water mixtures, but are not applicable to oil/water emulsions [2]. The separation of emulsified oil-water mixtures is always difficult and challenging as they are prone to be present in multiple forms under different situations: surfactant-free or surfactant-stabilized emulsions by their components, oil-in-water or water-in-oil emulsions by their formulation, and micrometer and/or nanometer scale in their droplet size [3]. Therefore, advanced materials or techniques are urgently needed to effectively separate various oil-water mixtures.

Recently, superhydrophobicity and superoleophilicity films have become an attractive method to prepare oil-removing filtration materials. These materials can repel water completely and let oil flow through the filter freely, thus achieving high efficiency and selectivity [4]. Usually, meshes or fibers (metal meshes, polymer meshes, fabrics, etc.) are used to make oil-water separation films [5]. Many experimental techniques have been explored in the creation of superhydrophobic surfaces [6]. These materials all have good potential for application in oil/water separation films. However, these investigations used gravity or syringe pump to separate the oil/water mixture. The above methods are of limited commercial value.

Most recently, hydrophobic carbon nanotube (CNT) films have received considerable attention because of their usefulness in various applications, such as solar cells, flexible optical devices, electrical devices, and oil/water separation films [7]. To fabricate superhydrophobic films, the surface roughness and surface energy state of the material must be taken into account. Surface functionalization or control of CNT film surface texture can help manipulate their wettability and lead to superhydrophobicity. There are two main approaches for producing superhydrophobic CNT films: (1) adsorption or the "wrapping" of low surface energy chemicals onto the CNT surface as a result of van der Waals forces and π-π interactions and (2) covalent attachment of hydrophobic groups through reactions on the conjugated skeleton of the CNT [8]. Although these functionalized CNT films all exhibit a high water contact angle (CA), the synthesis routes to achieve such a functionalization of CNTs are quite complex. They involve either an acid oxidization of the CNTs, which damage the desirable properties of CNTs, or require multiple tedious synthesis steps to obtain the desired functionalization [9].

In our study, we propose a simple and effective method to achieve noncovalent functionalization of multiwall-carbon nanotube (MWCNT) sidewalls. A new compound (alkyl-pyrene) had been synthesized by classic aldehyde and amine coupling reactions. 1-pyrenecarboxaldehyde (0.23 g) and octadecylamine (0.27 g) were mixed in dicholormethane, and then the mixture was stirring at room temperature for 12 h to obtain alkyl-pyrene. The as-prepared alkyl-pyrene was recrystallized from ethanol to obtain a pure compound. The detailed chemical structure of alkyl-pyrene was characterized by Mass, ^{1}H NMR, and FTIR spectroscopies (Fig. S1-3). The noncovalent functionalization involves electron-rich π-stacking pyrene which can be strongly adsorbed onto the sidewalls of CNT in organic solvents [10]. Additionally, the long alkane chains of surfactants also reduce the surface energy of the CNTs, resulting in a superhydrophobic film [11]. The alkyl-pyrene was mixed with pristine MWCNTs to form the MWCNT films.

To obtain stable and homogeneous pristine MWCNT suspension, MWCNT powder was ground with N-Methyl-2-pyrrolidinone (NMP) and then stirred in a sample bottle with the surfactant. The synthesis process of superhydrophobic MWCNT film is shown in Fig. 1. MWCNT (50 mg) was suspended into NMP (20 mL) then

sonicated for 1 h to obtain a homogeneous MWCNT suspension. Alkyl-pyrene (2.5 mg) was then dissolved in the MWCNT solution and stirred for 12 h at room temperature. The MWCNT film was prepared by filtering the solution through a filter paper and washed thoroughly with NMP and acetone to get rid of the remaining alkyl-pyrene. The film was easily peeled off without displaying any visible damage. Finally, the MWCNT film was dried under vacuum conditions at 40 °C for 24 h. The MWCNT films is flexible and its thickness is about 350 μm. The detailed physical and mechanical properties of the films have be included in the Supporting Information section (Fig. S4-6).

The water CA of the resulting MWCNT film is 158±2°. This superhydrophobic property of the MWCNT film prevents water from passing through, and the superoleophilic property of the film will facilitate oil to pass through the MWCNT filter. Connection with a vacuum-assisted filtration process will accelerate the oil-water separation. In addition, the MWCNT film exhibits good recyclable performance, which is an important factor in practice.

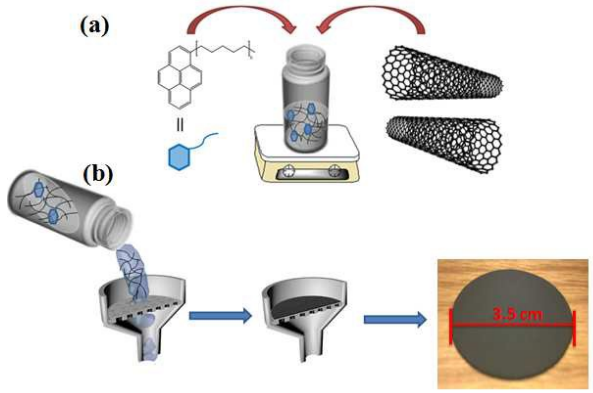

Fig. 1 Process for preparing MWCNT films: (a) the surfactant and MWCNT mix in the solvent and stir at room temperature, then (b) vacuum filtration to form a free-standing MWCNT film.

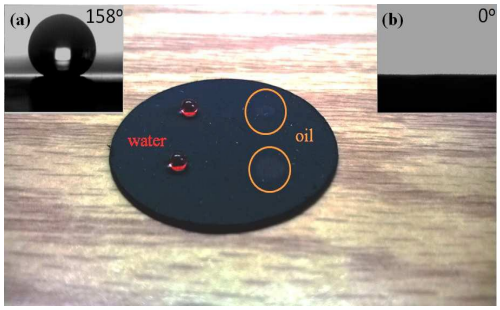

Fig. 2 The wetting behavior of superhydrophobic and superoleophilic MWCNT films. Water droplets appear as quasi-spheres while diesel oil wet entirely on the MWCNT films. The inset photographs (a) and (b) are of a water droplet and a diesel oil droplet on the MWCNT film, showing CA of 158° and nearly 0°, respectively.

The characterization of superhydrophobic MWCNT films was performed using Fourier-transform infrared attenuated total reflectance (FTIR-ATR, Fig. S7). Pristine MWCNTs displayed a featureless FTIR spectrum. The superhydrophobic MWCNT films clearly show C–H symmetric and asymmetric stretching vibrations of the aliphatic hydrocarbon groups at 2922 cm^{-1} and 2847 cm^{-1}, which give a strong indication of the attachment of the surfactant to the side walls of the nanotube [11].

Fig. 2 shows water droplets as near spherical shapes when placed on the surface of the MWCNT films. In contrast, when diesel oil was dropped on the surface of the MWCNT films, it was immediately absorbed by the MWCNT films within the marked circular area, demonstrating the film has superoleophilic property. The insets (a) and (b) in Fig. 2 are optical images of a water droplet and an oil droplet on the surface of the MWCNT film, showing CA of 158° and 0°, respectively. The superhydrophobic and superoleophilic surfaces demonstrated herein can be attributed to the combination of the hydrophobic chemical property of the alkyl-pyrene and the porous structure of the MWCNT films, respectively. The specific superwetting behavior of the MWCNT film endows its ability for oil/water separation.

To improve the efficiency of the oil-water separation, we used a vacuum-assisted filtration system to speed up the separation of oil and water. A series of surfactant-free and surfactant-stabilized, water-in-oil emulsions were permeated through MWCNT films. Oil immediately permeated through the membrane.

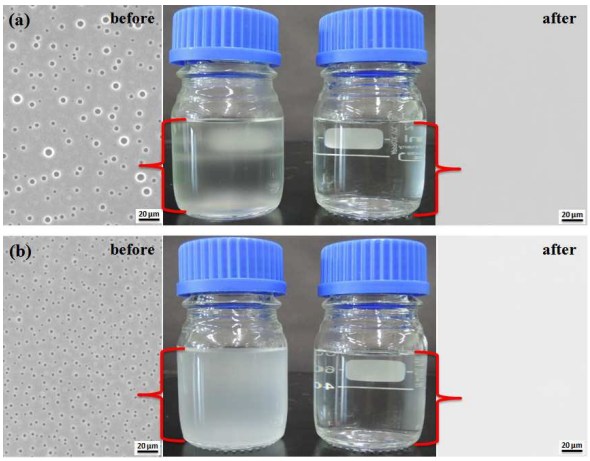

Fig. 3 Photographs and optical micrographs of (a) the surfactant-free water-in-petroleum ether emulsion and (b) surfactant-stabilized water-in-petroleum ether emulsion before and after separation.

Meanwhile, emulsion droplets de-emulsified once in contact with the MWCNT film and water was kept above the film. Surfactant-free and surfactant-stabilized water-in-oil emulsion were prepared by mixing water with an oil according to previous reports [12]. Surfactant-free water-in-oil emulsions were prepared by mixing water with an oil using petroleum ether, isooctane, cyclohexane and diesel oil (1:9 ratio between the water and solvents) and then sonicated for 1.5 h to produce white emulsion solutions. For surfactant-stabilized water-in-oil emulsions, span80 (0.2 g) was added into petroleum ether, isooctane and cyclohexane (500 mL), followed by addition of water (5 mL). The mixture was sonicated for 3 h. All the surfactant-stabilized water-in-oil emulsions were stable for more than 6 h and no de-emulsification or precipitation was observed. A series of water-in-oil emulsions including surfactant-free and surfactant-stabilized emulsions were successfully separated by just one flow-through pass.

To further examine the separation efficiency, we used an optical microscope to record images of the droplets in the original emulsions and in the corresponding collected filtrate. Fig. 3 presents optical microscopy images of the surfactant-free and surfactant-stabilized water-in-petroleum ether emulsion as

examples. No droplets are observed in the collected filtrate, confirming the effectiveness of the MWCNT film to retrieve high purity petroleum ether from the emulsions. The flux of emulsions permeating through the MWCNT film was determined by calculating the volume of permeate in unit time *via* the following equation [13]:

$$\text{Flux} = L/(A\, t\, \Delta P) \quad (1)$$

where L is the volume of the water filtered, A is the effective filtration membrane area (m^2), t is the filtration time (h), and ΔP is the suction pressure across the membrane (bar). A quantity of 25 ml of surfactant-free and surfactant-stabilized oil-water emulsions was filtered through the membrane to measure the flux with A = 5.6×10^{-5} m^2 and ΔP = 0.01 MPa. The flux of surfactant-free emulsions permeating through the MWCNT film are therefore determined to be 3.25×10^4 L m^{-2} h^{-1} bar^{-1} for petroleum ether, 2.17×10^4 L m^{-2} h^{-1} bar^{-1} for isooctane, 1.1×10^4 L m^{-2} h^{-1} bar^{-1} for cyclohexane, and 2.5×10^2 L m^{-2} h^{-1} bar^{-1} for diesel oil, as shown in Fig. 4(a). Fluxes of 1.32×10^4, 7.83×10^3, and 4.21×10^3 L m^{-2} h^{-1} bar^{-1} are obtained for surfactant-stabilized emulsions of water-in-petroleum ether, water-in-isooctane and water-in-cyclohexane, respectively. Although the flux of surfactant-stabilized emulsions are smaller than those of surfactant-free emulsions, they are still extremely high compared to those of filtration membranes reported in literature [14].

The change of flux with number of cycle is shown in Fig. 4(b). In one cycle, 25 mL of surfactant-free and surfactant-stabilized petroleum ether-water emulsion was permeated through the film and the film was then washed by passing through 20 mL of ethanol and dried in vacuum oven. It can be seen that the flux of petroleum ether emulsions do not decrease with increasing cycle number even up to 10 cycles. This indicates a good re-usability of the MWCNT film, which is an important consideration for practical applications.

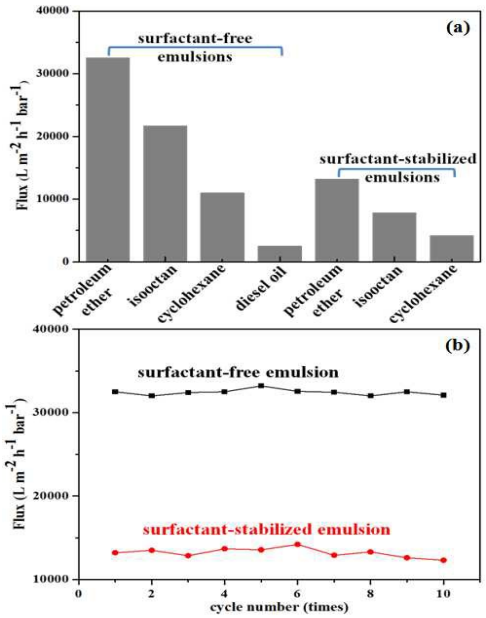

Fig. 4 (a) Permeate flux for different types of oils. (b) Change of flux with cycle times when separating petroleum ether emulsions by MWCNT film.

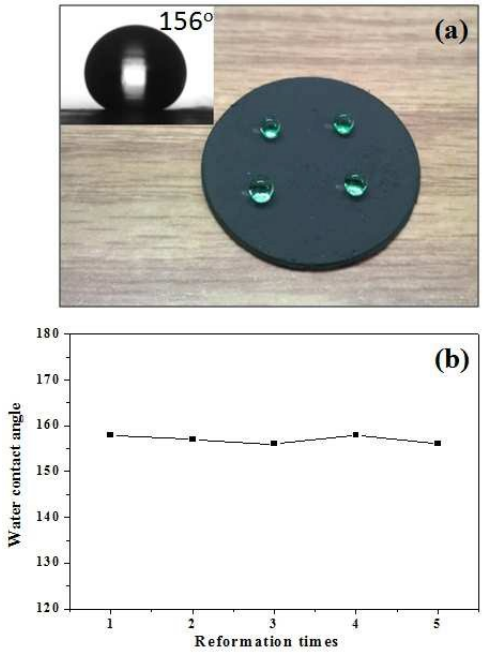

Fig. 5 (a) Photograph after the fifth recycling of the MWCNT film. The inset shows the CA=156° for water droplets on the corresponding sample. (b) Variation of the CA of the reformation MWCNT film.

To further study the re-usability property of the MWCNT film, the as-prepared superhydrophobic MWCNT film was redispersed in the solvent and stirred for 5 h; then, the precipitate was collected again by vacuum filtration to form a free-standing MWCNT film. The recycling process was repeated several times. Fig. 5(a) is a photograph of the MWCNT film after the fifth recycling. The CA of the MWCNT film is still higher than 156°. The line in Fig. 5(b) shows the surface wettability of the recycled MWCNT films. No decrease in water contact angle was observed, indicating the alkyl-pyrene is still attached to the MWCNTs and the film has kept its superhydrophobic and superoleophilic property. For practical applications, it is essential to scale up the production. In Fig. S8, we show a larger scale version of the MWCNT film. As we mention before, the MWCNT film is easy to fabricate by a vacuum filtration process. As a proof of concept, two samples with diameters of 3.5 cm and 7 cm were prepared. We believe that a large-scale, inexpensive production process is possible to make this new MWCNT-based water-oil separation filter film commercially attractive. In summary, we have demonstrated a new alkyl-pyrene synthesized by classic aldehyde and amine coupling reactions. Alkyl-pyrene can be adsorbed onto the sidewalls of MWCNT to form films that are both superhydrophobic and superoleophilic. This film can also be easily recycled to prepare brand new water-oil separation filters and can be easily scaled up for large sizes. Our results reveal that the modified MWCNT film prepared here is a promising candidate for use in the large-scale removal of oil spill containment and other organic pollutants from water.

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Notes and references

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