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Durable superhydrophobic and superoleophilic filter paper for oil–water separation prepared by a colloidal deposition method

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ABSTRACT

A method for manufacturing durable superhydrophobic and superoleophilic filter paper for oil–water separation was developed via colloidal deposition. A porous film composed of PTFE nanoparticles was formed on filter paper, which was superhydrophobic with a water contact angle of 155.5° and superoleophilic with an oil contact angle of 0°. The obtained filter paper could separate a series of oil–water mixtures effectively with high separation efficiencies over 99%. Besides, the as-prepared filter paper kept stable superhydrophobicity and high separation efficiency even after 30 cycle times and could also work well under harsh environmental conditions like strong acidic or alkaline solutions, high temperature and ultraviolet irradiation. Compared with other approaches for fabricating oil–water materials, this approach is able to fabricate full-scale durable and practical oil–water materials easily and economically. The as-prepared filter paper is a promising candidate for oil–water separation.

1. Introduction

Oil–water separation is becoming an important worldwide problem in the area of industrial production, environment protection and energy conservation [1–5]. Many industries such as crude oil production and refinery, petrochemical and metal finishing, textile and leather processing, and food processing and lubricant create large amount of oily wastewater inevitably which has become the most common pollutant [6–9]. Besides, frequent accidents of marine oil spill bring severe pollution and energy waste [10,11]. Except for ensuring safety of navigation to prevent the accidents, treatment of the spilled oil is much more challenging [12,13]. Actually, both of the treatment of oily wastewater and spilled oil involve in the problem of oil–water separation. A lot of technologies for the separation of oil and water mixtures have been developed during the past decades, such as ultrasonic separation, air flotation, electric field separation, biological treatment and membrane filtration, but the limitation of low separation efficiency, the generation of second pollutants, the strict requirements of oil–water mixtures, the membrane fouling problems or the high cost have always caused difficulty in practical applications [14].

In recent years, the development of superhydrophobic and superoleophilic materials for adsorption of oil from water and separation of oil and water has attracted much attention due to their high separation efficiency and wide applicability. The superhydrophobic property makes materials repel water completely, while the superoleophilic property lets oil permeate freely. Therefore, superhydrophobic and superoleophilic materials can separate oil-water efficiently [14]. A variety of methods have been developed to fabricate superhydrophobic and superoleophilic materials for separation of water and oil, including wet chemical process [15], electrochemical deposition [16], electrochemical etching [17], vapor phase deposition [18,19], sol–gel process [20,21], self-assembly process [22,23], electrospinning techniques [24,25], and others [26–30]. Generally, all these methods can be divided into two kinds: (1) chemical modification of a micro/nanostructured surface with low-surface-energy materials and (2) construction of micro/nanostructures on low-surface-energy materials. For example, Feng et al. [1] first reported a polytetrafluoroethylene (PTFE) film on a stainless steel mesh with both superhydrophobicity and superoleophilicity by a spray and dry method in 2004, which successfully separated the mixture of diesel oil and water. Zhu et al. [31] fabricated superhydrophobic and superoleophilic sponges that could effectively absorb oil from water with a simple solution-immerse method. Zhou et al. [32] developed a robust and durable superhydrophobic cotton fabric for oil–water separation. Wang and co-workers created a thermoplastic polyurethane mat with bead-on-string morphology by electrospinning, which can separate oil and water mixtures after further treated by hydrophobic nanosilica. Although many methods have been created for the fabrication

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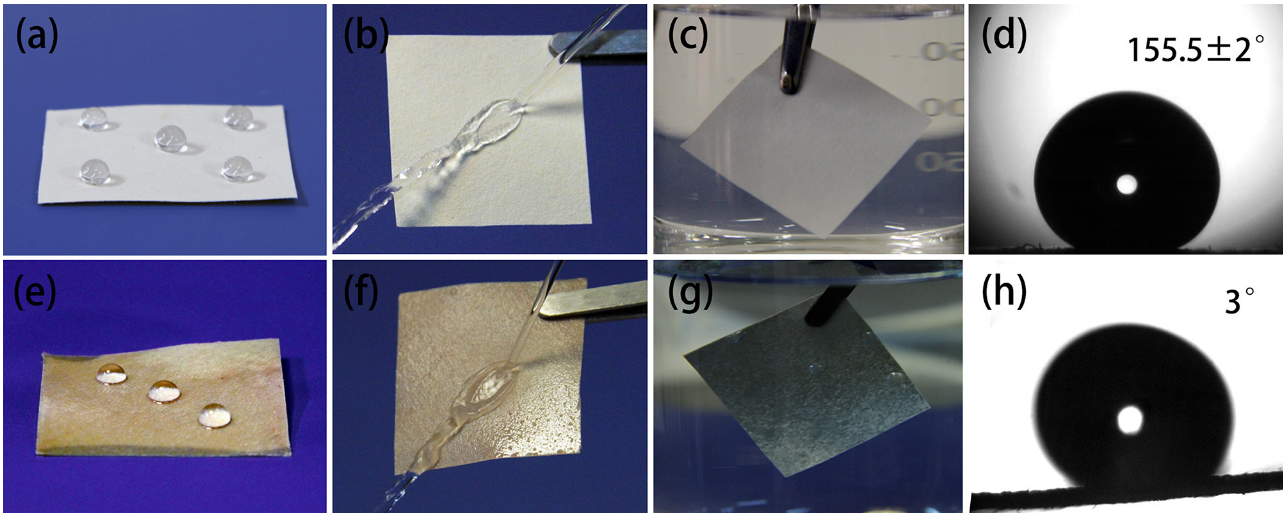

Fig. 1. Images of water wettability on the clean and entirely oil-wetted as-prepared filter paper: (a) water droplets sitting on the as-prepared filter paper, (b) a jet of water bouncing off the as-prepared filter paper, (c) the pristine filter paper immersed in water by an external force, (d) WCA measurement on the as-prepared filter paper, (e) water droplets sitting on the oil contaminated as-prepared filter paper, (f) a jet of water bouncing off the oil contaminated as-prepared filter paper, (g) the as-prepared filter paper immersed in water by an external force, and (h) the rolling state of water droplet and the measurement of SA.

of superhydrophobic and superoleophilic materials for oil–water separation, challenges still exist for easy preparation technique, full scale fabrication, recyclability and durability in mild processing environment [33].

Filter paper is widely used for adsorption of liquid and separation of solid and liquid due to its porous structure constructed by microfibers. In 2010, Wang et al. [34] created a superhydrophobic and superoleophilic filter paper with a mixture of hydrophobic silica nanoparticles (NPs) and polystyrene solution in toluene, which can successfully separate oil and water. However, the recyclability and durability in harsh processing environment were not fully tested. Herein, we report a facile preparation method for creating durable superhydrophobic and superoleophilic filter paper by colloidal deposition. The obtained filter paper has a nanoporous structure and possesses high separation efficiency (>99%) even after 30 cycle times. In addition, the as-prepared filter paper makes good performance in harsh environmental conditions such as strong acidic or alkaline solutions, high temperature and ultraviolet irradiation. All these results indicate a simple and durable way for the fabrication of oil–water separation materials.

2. Experimental

2.1. Materials

Qualitative filter paper (moderate speed, nominal pore size 15∼20 μm, thickness 340 ± 20 μm) was purchased from Hang Zhou special paper Co., Ltd., China. The monodisperse polystyrene NP colloid solution (2.5 wt%, average particle size 200 nm) was obtained from Tianjin BaseLine ChromTech Research Centre, China. The monodisperse PTFE NP colloid solution (60 wt%, average particle size 200 nm) was bought from 3F New Material Co. Ltd., Shanghai, China.

2.2. Sample preparation

The preparation of superhydrophobic filter paper was based on colloidal NP deposition. First, the PTFE colloid solution and the polystyrene colloid solution were diluted using deionized water to the mass fractions of 6 wt% and 1 wt%, respectively. Second, they were mixed with the ratio of 3:2 and ultrasonically dispersed for 15 min. After that, the filter paper was steeped in the mixed solution for approximately 30 min, removed, and dried in an oven at 70 °C for about 30 min to evaporate the solvent. Finally, the filter paper was heated at 220 °C for 20 min to make the polystyrene NPs melt and then cooled naturally. The obtained filter paper was cut into pieces of different sizes for use in different experiments.

2.3. Characterization

Water contact angles (WCAs) were measured with deionized water on a Dataphysics DCAT 21 (Dataphysics, Germany) instrument at room temperature. The volume of an individual droplet was 8 and each result was obtained from the average of five measurements of different points on each sample surface. The rolling state of water droplet and the oil penetrating process were recorded by a High Speed Imaging System (AcutEye, RockeTech Technology Corp., Ltd., China). The surface morphology of the filter paper was observed by a field-emission scanning electron microscope (SEM, FEI Quanta 200 FEG, Netherlands). The chemical composition was analyzed by the energy dispersive spectroscopy (EDS) equipped on the same SEM and an X-ray photoelectron spectroscopy (XPS, EscaLab 250XI, Thermo Scientific, USA) with Mg KR as the X-ray source operated at constant pass energy of 30 eV.

3. Results and discussion

Filter paper usually consists of wood fibers and can quickly adsorb both water and oil [34]. However, after treated by the PTFE and polystyrene NP colloidal solution, it can be seen that all droplets sitting on the as-prepared surface are ball-shaped (Fig. 1a). A jet of water from a pipet could bounce off the as-prepared filter paper without leaving anything, implying the weak interaction between water and the as-prepared filter paper (Fig. 1b). The WCA and sliding angle (SA) are shown as 155.5 ± 2° and 3° in Fig. 1d and h, definitely indicating a superhydrophobic surface. When the as-prepared filter paper was immersed into water, it showed a silver mirror-like appearance and was not wetted (Fig. 1g), while there was no such property on the pristine filter paper (Fig. 1c). This phenomenon can be attributed to the trapped air between water and the filter paper, which is consistent with the Cassie–Baxter model [35]. On the contrary, when an oil (hexane) droplet was placed onto the surface of the coated filter paper, the oil droplet was quickly absorbed within 4 ms (Fig. 2a and b),