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Short communication

Robust superhydrophobic carbon fiber sponge used for efficient oil/corrosive solution mixtures separation

Changcheng Xu [a], Yongqian Shen [b], Jian Li [a, *], Yan Zhang [a], Zhengfang Luo [a], Houde She [a]

[a] Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

[b] State Key Laboratory of Advanced Processing and Recycling of Non-Ferrous Metals, Key Laboratory of Nonferrous Metal Alloys and Processing, Ministry of Education, School of Materials Science & Engineering, Lanzhou University of Technology, Lanzhou 730050, PR China

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ABSTRACT

Great challenges are still remained for the oil/water separation in highly acidic, alkaline, and salty environment. Low-cost, eco-friendly and being useful in harsh corrosive environment materials with special wettability are urgently desired to deal with severe environmental and ecological problems arisen from oil spills and organic leakages. Herein, we present a superhydrophobic carbon fiber (CF) sponge with excellent anti-corrosion property and without any chemical modification process was obtained, which can used for efficient oil/corrosive solution mixtures separation. Furthermore, The CF sponge not only can directly and rapidly adsorb oils from water surface, but also can being a superhydrophobic membrane to realize on-demand oil/water separation in highly acidic, alkaline, salty environment by gravity. By virtue of facile and cost-efficient and excellent adsorption/filtration performance in oils/corrosive solutions separation, the unique CF sponge holds great promise of oil spills cleanup and oil/water separation in real harsh environments.

1. Introduction

Nowadays, with increasing oily wastewater release and tighter regulations on its discharge restriction, effective separation of oils from industrial oily wastewater and floating-oil/water mixtures in extremely harsh environments has become a worldwide challenge [1–5]. Various traditional methods applied in oil/water separation have been perfected in past decades, such as oil skimmer, physical diffusion, chemical decomposition and so on [6–8]. However, the new materials with special wettability appears to be more effective and predominant for application, since oil/water separation is essentially dominated by interfacial phenomenon [9–11]. Inspired by the idea of applying special wettability surface into oil/water separation, all sorts of superwetting materials are designed to be superhydrophobic or superoleophobic, including electrospinning, chemical modification, sol-gel method and others [12–15]. Such materials are generally categorized into two types: one is "oil removing" type materials with superhydrophobicity/superoleophilicity property in air that can filter or absorb oils from water, and the other is "water-removing" type materials with superhydrophilicity in air as well as underwater superoleophobicity that can selectively retard oils in the oil/water mixtures [16–24]. In most instances, the mixtures are always existed in high acidity, alkalinity, and salt environments, which present great challenges for superwetting materials to separate oils from the mixtures. Unfortunately, most of afore-designed materials using metallic mesh, cellulose film or porous polyester as substrates, which are only serve to oil/water separation in gentle environment and become poor in extremely harsh corrosive environments [25–29]. However, carbon materials with superior anti-corrosive property and well applied in various research materials [30–36]. Although multifarious aforementioned methods have been successfully applied to the fabrication of special wettability materials, it is still great importance of exploiting novel carbon material with intrinsic superhydrophobicity to avoid complex fabrication procedures and suitable for large-scale oil/water separation in extremely harsh corrosive environments.

Herein, carbon fiber (CF) sponge with intrinsic superhydrophobicity was obtained from the factory could directly adsorb oils from the oil/water mixtures under harsh conditions. Not only so, the CF sponge can also be prepared to be a membrane for realizing on-demand oil/water separation in highly acidic, alkaline,

* Corresponding author.
E-mail address: jianli83@126.com (J. Li).

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salty environments solely by gravity. Moreover, the CF sponge presented to be superhydrophobicity towards 12 M HCl, 12 M NaOH and saturated salty solutions with contact angle (CA) up to 157°. More importantly, the sponge exhibited high adsorption efficiency (>99.97%) and separation efficiency (>99.85%) and high permeate flux more than 5525 L m^{-2} h^{-1}.

2. Experimental

The CF sponges were obtained from local factory. Prior to the experiments, the CF sponges were prepared as follow. Firstly, the CF sponge was cut into 3 × 1 × 1 cm and 5 × 5 × 0.5 cm shape. Then, the sponge was ultrasonically cleaned in ethanol and acetone for 30 min to remove impurities on the surface. Finally, the cleaned CF sponges were dried in an oven at 60 °C for 2 h. In addition, Petroleum ether, hexane, kerosene, diesel and other chemicals were purchased from the Tianjin Kaixin Chemical Industry Co. Ltd., Tianjin, China. All chemicals were analytical grade. The strong acid-base aqueous solutions were prepared using distilled water.

The morphological structures of the as-prepared surfaces were examined by field emission scanning electron microscopy (FE-SEM, JSM-6701F). Fourier transform infrared (FT-IR) spectroscopy was performed with a Bio-Rad FTS-165 instrument. The water and oil contact angles (CAs) were measured with a SL200KB apparatus at ambient temperature by injecting 5 μL of liquid droplets. The water content in the collected oil filter was measured by a micro-moisture meter (SN-WS200A). The oil in the collected water was extracted by CCl_4, and then the oil content in CCl_4 was measured by an infrared spectrometer oil content analyzer (SN-OIL480).

3. Results and discussion

In our study, the surface morphologies of CF sponges were investigated by FE-SEM. As shown in Fig. 1a, the CF sponge was made up of massive entangled carbon fibers with pore size ranging from 50 μm to 100 μm. Inset of Fig. 1a shows the transversal surface of carbon fiber. From high magnified SEM image of CF sponge, as shown in Fig. 1b and c, it reveals that micro/nano hierarchical concave and convex structures were existed on the carbon fibers surface and leading to a micro-size rough surface. This special surface structure provided carbon fiber a typical biomimetic lotus surface with superhydrophobic and low water-adhesion [37–40]. As shown in Fig. 1d, video1, when a water droplet making touch with and losing touch with the CF sponge surface, the water droplet never left the needle and kept almost spherical shape, and the size of droplet was no obviously change during the whole process. This phenomenon indicates the CF sponge surface possesses lower water-adhesion behaviors [41].

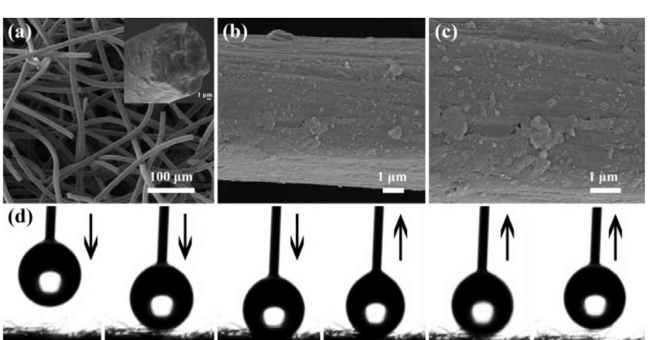

Fig. 1. (a–c) FE-SEM of CF sponges in low and high magnification. (d) A water droplet making touch with and losing touch with the CF sponge surface.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.vacuum.2017.03.022.

Furthermore, the special wettability of CF sponge can be visually observed through the wetting behavior of oil and water droplet on its surface. As shown in Fig. 2a, the water droplet (dyed with methylene blue) was repelled by CF sponge surface and thus to form a spherical shape, while the oil droplet was quickly adsorbed and permeated into the sponge due to its intrinsic superhydrophobic/supereloephilic property. Moreover, the oil and water contact angles (CAs) measurements were used to further characterize the special wetting behavior of CF sponge. The CF sponge exhibits superhydrophobic/supereloephilic in air simultaneously with high water contact angle of 157°±1° and oil contact angle of 0°, as shown in Fig. 2a and b. Furthermore, when a water droplet was beginning in contact with the CF sponge surface, a composite Cassie-Baxter state was formed, result from the droplet can only touch the solid through the top of the asperities while a spot of air was sealed in the concave and convex structure. The apparent WCA θ_{CB} can be described by the equation:

$$\mathrm{Cos}\theta_{CB} = r_f \mathrm{Cos}\theta_o + f - 1 \tag{1}$$

where, f is solid-water contact area fraction in the whole contact area, r_f is the roughness ratio of contact part of CF sponge surface, θ_o is the value of WCA on a smooth solid surface, which can be calculated by Young's equation [42]. As time go on, the air beneath the water droplet was inescapably completely occupied by the droplet with synchronously valleys of rough surface was completely filled by water and thus to form a Wenzel state. The parent WCA θ_W can be present by the equation:

$$\mathrm{Cos}\theta_W = r\mathrm{Cos}\theta_o \tag{2}$$

where, r (> 1) is the value of roughness of CF sponge surface, and also means the ratio of the real contact line to the projected contact line of the portion of solid in air [43]. Obviously, the WCA in Cassie-Baxter state was greater than Wenzel state whereas the apparent WCA on the CF sponge was still greater than 150°. In addition, the chemical heterogeneities in the CF sponge surfaces were another impact factor for forming superhydrophobic surface.

Moreover, the ultra-fast oils or organic pollutants adsorption performance of CF sponge was also studied. As shown in Fig. 3a_{1-4}, b_{1-4}, the CF sponge can rapidly adsorb oils or organic pollutants (dyed with Oil Red O) whether is floating on water surface or sinking into the water within 6s. Furthermore, after removing oil pollutants from water was finished, no oil was observed to naked eyes in clear water, as shown in Fig. 3a_4, b_4. The results demonstrated its superior effectiveness of removing oils from water. In addition, a silver mirror phenomenon appeared around the sponge surface could be clearly seen in Fig. 3b_2. The phenomenon indicated

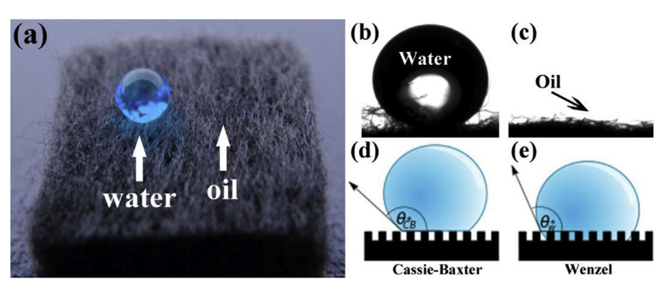

Fig. 2. (a) Photographs of oil and water (dyed with methylene blue) droplets on CF surface. (b) Photographs of water droplet on CF sponge with CA larger than 150°, (c) oil droplet on CF sponge with CA≈0°. (d) Wenzel and (e) Cassie-Baxter model of water droplet on CF sponge surface.