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Hierarchical oil–water separation membrane using carbon fabrics decorated with carbon nanotubes

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ABSTRACT

The study adopts an efficient spin-coating method to disperse fluorinated carbon nanotubes (CNTs) onto carbon fabrics (CFs) as hierarchical oil–water separation membrane. The topography observation indicates that multi-walled CNTs with an average diameter of 30–50 nm are coated over the CF surface, forming a nano/submicron scaled roughness. The CNT–CF membrane exhibits superhydrophobic behavior (water contact angle: 165°), low wetted surface fraction (5.5%), and low work of adhesion (W_{ad}: 2.5 mJ/m^2). The oil–water separation efficiency of CNT–CF membrane can reach to 99.7%, better than the CF membrane without the CNT decoration. The robust design of CNT–CF membranes enhances not only the oil–water separation efficiency but also the permeability. The enhanced efficiency can be ascribed to the fact that the decoration of fluorinated CNTs is capable of lowering roll-off kinetic energy barrier, proved by the oil–water separation mechanism. Accordingly, the difference of W_{ad} values between oil and water droplets can be taken into account as a crucial index for evaluating the separation efficiency, favoring the development of oil–water separators and filtration units in the future.

1. Introduction

Recently, oily wastewater has become a crucial problem worldwide in a variety of fields including industrial manufacturing, environmental protection, and energy conservation [1,2]. So far, the treatment of oily wastewater is still a global challenging task because many industries such as petrochemical and metal finishing, crude oil production and refinery, textile and leather processing, and food and lubricant processing, generate a large amount of oily wastewater contaminated with oil [1,3]. This kind of wastewater has become the most common pollutant, causing damage to the natural environment. Moreover, some accidents like oil spill over sea is not just a major threat to marine ecology but also costly in terms of energy loss. It is generally recognized that the maximal oil concentration in the released water should be 10–15 mg/L, based on the environmental guidelines [4]. As a result, developing oil separation technologies is a high priority in environmental protection nowadays.

In fact, the development of superhydrophobic membranes (i.e., water contact angle (WCA) >150°) has received considerable attention due to their self-cleaning properties [5,6]. In the recent years, pioneering studies have developed various methods to assemble oil–water separation membranes, including water-permeable polylactide blend membrane [7], polyamide/polysulfone composite [8] and polysulfone/silica nanofibers [9] by electrospinning method, poly(dimethyl siloxanes) (PDMS)/silica [10] or PDMS/ZnO [11] composite coating by dipping method, magnetic polymer-based graphene foam via hydrothermal method [12], Ag nanocluster/nanofiber membranes by electroless plating [13], magnetic foams by pyrolysis of polyurethane (PU) sponge [14], iron oxide/PU/polytetrafluoroethylene foams by surface modification [15], $Cu(OH)_2$ nanoneedle arrays by self-assembled monolayer method [16], modified cotton fabric via vapor phase deposition [17], ZnO-coated stainless mesh films by hydrothermal method [18], metal oxide/fabrics by thiol modification [19], layered double hydroxide functionalized textile [20], diamond-like carbon coated cotton textiles [21], TiO_2/cotton fabrics by chemical-wet impregnation [22], and fluorinated carbon nanotube (CNT) network films by wet-chemical route [23]. Basically, the functional membranes should impart superhydrophobic or superhydrophilic performance. For example, high water repellency induces the membranes to repel water droplet penetration, whereas superoleophilic property makes the membranes oil permeate freely [1]. Therefore, the design of membranes mentioned above displays excellent efficiency toward the oil–water separation. However, there are few reports focusing on the influence of two-tier roughness on the efficiency of oil–water separation using carbon fabrics (CFs) as the support.

This study aims at the fabrication of two-tier roughened surface using CFs and CNTs for creation of micro- and nano-scaled roughness. Actually, some advanced methods have been developed to create various carbon surfaces with superhydrophobicity silica sphere–CF

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composites [24], CNT array with micro/nanoscale surface roughness [25], double-layer freestanding CNT film [26], CNT/polystyrene microsphere composition arrays [27], highly-ordered aligned CNT film [28], CNT/stainless foil [29], CNT/ceramic membrane with macro/mesopore channels [30], and Janus polymer/CNT hybrid membranes [31]. In the present work, a facile spin-coating method was adopted to decorate fluorinated CNTs onto CF membrane, forming the two-tier roughened membrane for the oil–water separation. To inspect the water–oil separation mechanism, water and oil microscopic work of adhesion (W_{ad}) on the rough surface was estimated, based on the Young–Duprè equation. Additionally, the effect of thickness on the efficiency and treatment period of oil–water separation is also investigated. The work shed some lights on the applicability of two-tier carbon membranes for high-performance oil–water separation units.

2. Experimental section

2.1. Preparation of fluorinated CF membranes

Four types of CF supports with different thicknesses (i.e., 0.3, 0.55, 0.65, and 0.9 mm) were supplied by Taiwan Carbon Technology Company (Taiwan). Multi-layered CNTs used here were synthesized by using catalytic vapor deposition technique (CVD), in which Ni-based nanoparticles and ethylene were used as catalyst and carbon precursor, respectively. The CVD process was carried out in horizontal furnace under atmospheric pressure at 750 °C for a growth period of 1 h. The gas flow consisted of the mixture of Ar:H_2:C_2H_2 (=94:1:5 in v/v/v).

The as-grown CNTs were fluorinated by impregnating them in a fluoro-containing solution, composed of perfluoroalkyl methacrylic copolymer (Zonyl 8740, DuPont Co.) and distilled water (7/3 in v/v). This recipe of F-containing copolymer for preparing superhydrophobic carbon surfaces has been proved by our previous study [32]. The chemical-wet fluorination process was performed at ambient temperature for 2 h. After that, a spin-coating method was used to disperse the F-coated CNTs over the CFs. The F-coated CNT slurry had a concentration of 1000 mg/L, and the CF substrates were carefully cut into an area of 9 cm^2. The coating process consisted of the following steps: (i) the spinning speed of the first-stage coating process was set at 500 rpm for 8 s, and (ii) the second-stage speed was raised to 3000 rpm and maintained for 12 s. The CNT–CF composites were then dehydrated at 105 °C in an oven overnight. For comparison, one piece of CF substrate was directly fluorinated by using the spin-coating method under the same operation.

2.2. Characterization of fluorinated CF membranes

The chemical composition of the fluorine functional groups was also studied using X-ray photoelectron spectroscopy (XPS). The XP spectra were recorded with a Fison VG ESCA210 spectrometer and Mg-Kα radiation. The spectra were smoothed and a nonlinear background was subtracted. The deconvolution of the spectra was performed using a non-linear least squares fitting program with a symmetric Gaussian function. The surface composition of the samples was calculated with C 1s and F 1s peak, and the appropriate sensitivity factors. Field-emission scanning electron spectroscope (FE-SEM, JEOL JSM-5600) and high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100) were used to observe the CFs with and without the CNT decoration.

2.3. Water/oil repellencies and separation efficiencies of fluorinated CF membranes

The contact angle (CA) measurements for diary-used liquids (i.e., distilled water, bead sauce, and olive oil) were performed under ambient environment. Herein an optical CA meter (Sindatek Instruments, Model 100SL) was employed to measure the CAs of droplets on the CF surfaces. Each droplet was dropped onto the CF surfaces from a distance of 5 cm by vibrating the syringe. The volume for each droplet was held constant at around 5 μL, and the influence of gravity on shape deformation of liquid droplets could be negligible in this

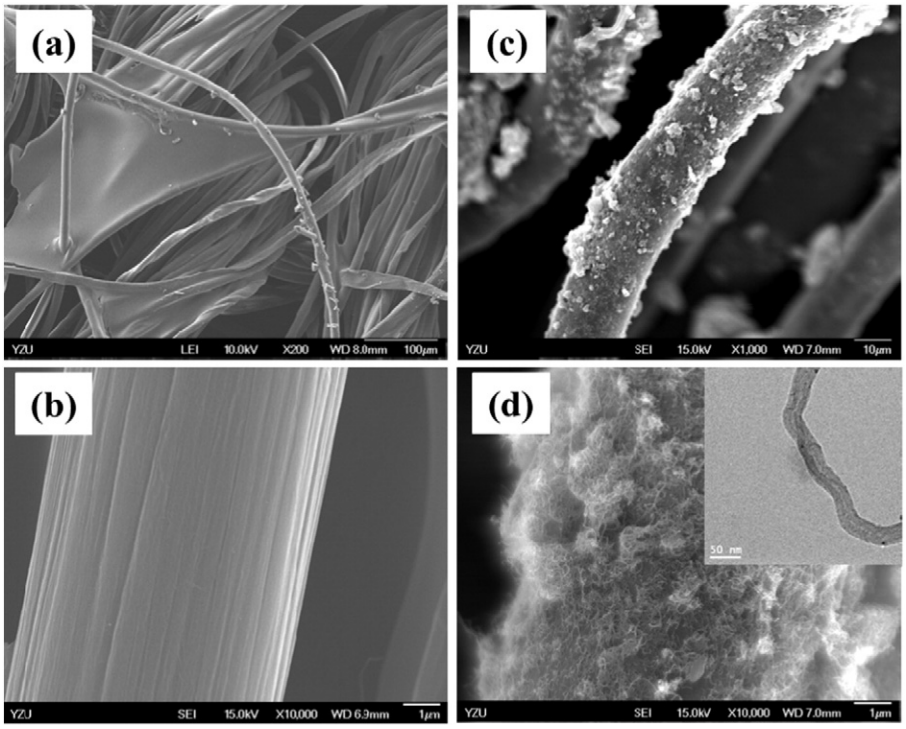

Fig. 1. FE-SEM images of fluorinated CFs with (a) low and (b) high magnification. FE-SEM images for CFs decorated with fluorinated CNTs with (c) low and (d) high magnification. The inset of panel (d) shows HR-TEM micrograph of individual CNT.