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Porous carbon nanotube/polyvinylidene fluoride composite material: Superhydrophobicity/superoleophilicity and tunability of electrical conductivity

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ABSTRACT

Porous carbon nanotube/polyvinylidene fluoride (CNT/PVDF) composite material can be fabricated via formation and freeze-drying of a gel. The field emission scanning electron microscopy, nitrogen adsorption–desorption and pore size distribution analysis reveal that the introduction of a small amount of carbon nanotubes (CNTs) can effectively increase the surface roughness and porosity of polyvinylidene fluoride (PVDF). Contact angle measurements of water and oil indicate that the as-obtained composite material is superhydrophobic and superoleophilic. Further experiments demonstrate that these composite material can be efficiently used to separate/absorb the insoluble oil from oil polluted water as membrane/absorbent. Most importantly, the electrical conductivity of such porous CNT/PVDF composite material can be tuned by adjusting the mass ratio of CNT to PVDF without obviously changing the superhydrophobicity or superoleophilicity. The unique properties of the porous CNT/PVDF composite material make it a promising candidate for oil-polluted water treatment as well as water-repellent catalyst-supporting electrode material.

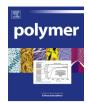© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The removal of oil from oil polluted water generated in various manufacturing industries as well as through accidental oil spills has emerged as a worldwide challenge [1–4]. Many approaches such as, oil skimmers, centrifuges, coalesces, settling tanks, depth filters, magnetic separations, flotation technologies, oil-absorbing materials and combustion [5–8], have been employed to treat oil polluted water. However, the challenge of meeting strict environmental standards whilst meeting the demands of intensifying economic demands requires materials that can effectively separate oil and water. In 2004, L. Feng et al. [9] reported a new kind of superhydrophobic and superoleophilic mesh for separating oil from oil polluted water. Such materials are attractive because they can simply and efficiently separate oil from water by filtration. Recently, several materials have been developed for this purpose including; titanium oxide coated meshes [9], cuprous oxide coated copper meshes [10], marshmallow-like microporous gels [11], polyvinylidene fluoride (PVDF) membranes [5], polytetrafluoroethylene (PTFE) coated meshes [12,13], trichloromethylsilane coated polyester textiles [14], nanoporous polydivinylbenzene material [15], cross-linked oil-absorbing polymer gels [16,17], and boron nitride nanotubes coated meshes [18]. Following these pioneering works, it is now of great importance to develop novel materials for the separation of oil from water with high efficiency, good recyclability and novel properties.

In parallel, superhydrophobic materials with good electrical conductivity have been attracting interest due to their applications as non-wetting electromagnetic interference shielding materials [19] and smart textiles [20,21] as well as in the printing of electronics [22]. Accordingly, an increasing number of conducting

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superhydrophobic films have been reported by dispersing nano-structured conductive fillers in hydrophobic polymer matrices [23,24]. However, robust conducting superhydrophobic materials that adhere strongly, are resistant to mechanical abrasion and a range of solvents and can withstand elevated temperatures are in demand and need to be further developed [25].

Previous work has demonstrated that PVDF membranes can be used as filters for the separation of oil from water [5]. More importantly, the electrical conductivity of PVDF can be tuned by adding CNTs as a minor component [26,27]. Here we report the fabrication of a new kind of porous CNT/PVDF composite material *via* a simple and inexpensive process whereby a gel is formed and freeze-dried. The hydrophobicity and oleophilicity of the CNT/PVDF composite material produced with different mass ratios of CNT to PVDF were examined by measuring the static water and oil contact angles (CAs). The selectivity and efficiency of this CNT/PVDF material for oil polluted water treatment were also investigated. Additionally, the electrical conductivity of these composites was characterized by DC current—voltage (I–V) measurements from −10 to +10 V.

2. Experimental

2.1. Samples preparation

PVDF ($Mr = 20000-30000$) was dissolved in N, N-dimethyl formamide (DMF, 10 wt%) to form a homogeneous PVDF/DMF solution. Different mass ratios of CNT to PVDF precursors (Table 1) were prepared by adding CNTs to the PVDF/DMF solution. Stable suspensions of CNT/PVDF/DMF were formed by ultrasonication. The CNT/PVDF/DMF suspensions were then kept in a closed container connected to a reservoir of methanol. The CNT/PVDF/DMF suspensions were gradually changed into gels by the adsorption of methanol vapour. Usually, gels were aged for three days to obtain a stable porous structure. In order to thoroughly remove the DMF solvent, from the gels without damaging their structure, the aged gels were further immersed into distilled water for another 4 days. Finally, the gels were freeze-dried at −40 °C (<0.2 mbar) for 20 h to produce dried porous material. In addition, pure PVDF material was prepared by the same process for comparison.

2.2. Separation tests of porous CNT/PVDF composite material used as a filter membrane

The porous CNT/PVDF composite material with a thickness of about 3 mm was used as a filtration membrane. The oil/water mixture was prepared by mixing water (dyed blue with methylene blue) and dichloromethane (DCM) in a volume ratio of 1:1. In the filtration process, the porous CNT/PVDF composite membrane was placed between two glass tubes (the end of the upper tube was sealed with PTFE tape). For every separation, 100 mL of oil/water mixture was slowly poured into the upper glass tube.

Table 1
The mass ratio of CNTs to PVDF.

Sample	Material		
	CNT (mg)	PVDF (g)	CNT/PVDF
1	5	1	1/200
2	16.7	1	1/60
3	25	1	1/40
4	50	1	1/20

2.3. Separation tests of porous CNT/PVDF composite material used as an absorbent

In the absorption test, hexane and DCM were used as the oil phase. For every absorption process, sufficient oil was absorbed by a certain quantity of porous CNT/PVDF composite material. The oil on the surface of the sample was removed with a paper towel before being weighed. In order to investigate the stability of the porous CNT/PVDF composite material, the absorption process was repeated 20 times. After weighing, the composite material was dried at 60 °C in air. The absorbance of the oil was calculated using the following equation:

$$R = W_{\text{adsorption}} \Big/ W_{\text{CNT/PVDF}}$$

R: ratio of weight (times);
$W_{adsorption}$: the weight of the oil absorbed by porous CNT/PVDF composite material;
$W_{CNT/PVDF}$: the weight of dry porous CNT/PVDF composite material.

2.4. Characterization

The morphologies of the PVDF and porous CNT/PVDF composite materials were observed by a field emission scanning electron microscope (FESEM, Zeiss UltraPlus). The nitrogen adsorption—desorption and pore size distribution (BET, Brunauer Emmett Teller) analysis of the PVDF and porous CNT/PVDF composite materials was performed on a Micromertics TristarII 3020 at 77.350 K. The surface wettability was examined using a KSV CAM200 contact angle goniometer. The electrical conductivity was measured with a Keithley 6517 LCR analyzer. The voltage applied in the measuring process was in the range of −10 to +10 V and the corresponding I−V data were recorded at 1 V intervals. Conductive tape was used to fix the samples to the electrodes in order to minimize the contact resistance.

3. Results and discussion

Fig. 1 shows FESEM images of pure PVDF and porous CNT/PVDF composite material with a mass ratio of CNT to PVDF of 1/200. A porous structure and rough surface are obtained for both materials. As shown in Fig. 1a, the pure PVDF is composed of spherical microparticles with a diameter in the range of 3—5 μm (Fig. 1b). Noticeably, the surface of these microparticles is not smooth, but constituted of densely distributed micro- and nano-scale microprotrusions (Fig. 1c) on the surface. Similarly, the structure of the porous CNT/PVDF composite material is also constituted of spherical microparticles (Fig. 1d). However, the diameter of these microparticles is about 1—3 μm (Fig. 1e) and thus considerably smaller than that of the pure PVDF material. Furthermore, their surfaces is characterized by nanofibrous protrusions formed by a composite CNTs and PVDF structure (Fig. 1f). Note that all the spherical microparticles for both the PVDF and CNT/PVDF composite materials are not isolated but linked together to form a network of fibres. In the gelling process, the PVDF/DMF and CNT/PVDF/DMF suspensions were kept in a closed container in which there was a reservoir of methanol. Methanol vapour slowly diffused into the PVDF/DMF or CNT/PVDF/DMF suspensions and gradually replaced the DMF solvent. Due to the immiscibility of PVDF and methanol this results in the precipitation of PVDF and the formation of a gel. Usually, this process requires three days for a stable porous structure to form. It is known that the formation of physical gels is typically dominated by the cooperative effect of liquid—liquid demixing and