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Facile preparation and characterization of free-standing stiff carbon-based composite films with excellent performance

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ABSTRACT

Novel free-standing stiff all carbon films based on multi-walled carbon nanotube (MWNT)/glassy carbon (GC) with excellent performance were fabricated. MWNTs, as excellent reinforcing materials, were successfully dispersed in polyimide (PI) matrix by *in situ* polymerization. The resultant MWNT/PI nanocomposite films were used as precursors and underwent carbonization process. As a result, all carbon constituted MWNT/GC composite films were obtained. Mechanical results showed the maximum 3-point bending strength and modulus reached 575.5 MPa and 7.7 GPa respectively, improved by 54% and 78% compared to those of neat GC films. This method is simple, and the free-standing composite films can be prepared in large scales, which hold great potential in many applications.

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1. Introduction

Free-standing paper-like or foil-like materials play important roles in our technological society, including protective layers, chemical filters, components of electrical batteries or supercapacitors, adhesive layers, electronic or optoelectronic components, and molecular storage [1,2]. Carbon-based films, including flexible graphite foils [3], 'bucky paper' [4], graphene or graphene oxide paper [2,5,6] and diamond, etc., attract much attention in many fields, such as reinforcement materials, the storage of energy, supports for important catalytic process and so on [7–9].

Glassy carbon, as another allotrope of carbon, has glass-like appearance with low cost, high stiffness, superior thermal and chemical stability in extreme environments [10], which makes it popular in many applications, such as electrode material [11], mold material [12], carbon foams [13] and so on. It is expected that free-standing carbon-based films based on glassy carbon will arouse much attention because of their high modulus, high strength, as well as high stiffness. However, it is very difficult to fabricate free-standing glassy carbon films owing to their brittleness characteristics. In order to obtain this type of free-standing stiff carbon films, it is necessary to modify the matrix. Many types of filler, such as carbon fibers, glass fibers, carbon nanotubes (CNTs), etc., have been utilized to enhance the mechanical properties of many matrices. Therein, CNTs have become the ideal candidates as filler materials in composites for mechanical enhancement [14]. As we know, CNTs, discovered by Iijima in 1991 [15], have aroused much attention due to their high aspect ratios, remarkable mechanical [16,17], electrical properties [18], optical [19] and thermal properties [20]. CNT-based nanocomposites have a wide range of applications, including catalysis, supercapacitors, lithium batteries, biosensors, and enforcement materials [21–27]. The improvement of mechanical, electrical and thermal properties of many matrices, including polymer, ceramic and metal, have been successfully achieved through the addition of CNTs [28–32]. Through introduction of CNTs, the crack interfaces of matrices will be bridged by nanotubes, and consequently, better performance can be realized [33]. Therefore, it is worthwhile to develop CNT-reinforced GC-based free-standing nanocomposite films. With the aid of CNTs as the reinforcement materials, it is expected that the free-standing composite films would possess excellent performance in mechanical, electrical, and thermal properties.

In this work, novel free-standing stiff all carbon films based on MWNTs-reinforced GC membranes with excellent performance were fabricated. MWNTs, as excellent reinforcing materials, were successfully dispersed in polyimide (PI) matrix by *in situ* polymerization. The resultant MWNT/PI films were used as precursors through the carbonization process, and as a result, MWNT/GC composite films were obtained. The resultant free-standing MWNT/GC composite films exhibited excellent strength and modulus, low square resistance and other advantages compared with pristine carbon films.

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2. Experimental section

2.1. Materials

The MWNTs, 10–20 nm in diameter, 10–30 μm in length and with purity over 95 wt%, were purchased from Chengdu Organic Chemicals Co. Ltd. (China). For the purpose of perfect dispersion of MWNTs in the polymer matrix, we pre-treated the MWNTs under sonication with acid treatment for 8 h, followed by filtration and washing with deionized water and finally vacuum dried in the oven. As a result, the obtained MWNTs were modified with carboxylic groups. Pyromellitic dianhydride (PMDA), 4, 4′ - diaminodiphenyl ether (ODA) and N, N-dimethylacetamide (DMAc) were purchased from Shanghai Chemical Reagent Company (China).

2.2. Preparation of MWNT/polymer composite films by in situ polymerization

The pre-treated MWNTs were firstly dispersed in DMAc under sonication for 30 min. Then ODA was added into the above DMAc solution with sonication for another 30 min, and equimolar amount of PMDA was added slowly in batches. After further stirring for 4 h at room temperature, the sticky and homogenous MWNT/polyamic acid (PAA) solution was obtained as precursor solution. Afterwards, the as-prepared MWNT/PAA solution was cast onto clean glass plates and dried at 60 °C, 90 °C, 120 °C, 150 °C respectively, each for 1 h. The films were subsequently peeled off from the glass plates, followed by undergoing heat treatment at 350 °C for 1 h in vacuum for total imidization. As a result, the solvent-free MWNT/ PI composite films were obtained.

2.3. Preparation of MWNT/GC composite films

The as-synthesized MWNT/PI composite films were then put in between two carbon plates, and underwent direct carbonization with a vacuum degree of 10^{-3} Pa. The heating program of the carbonization was controlled at 2 °C/min from room temperature to 900 °C and held at 900 °C for an hour. After natural cooling, the MWNT/GC free-standing composite films were finally obtained. A series of such MWNT/GC composite films were prepared with the concentrations of MWNTs ranging from 0 wt.% to 20 wt.%.

2.4. Characterization

Transmission electron microscope (TEM) images of the acid-treated MWNTs were obtained by JEM-2100 (JEOL Ltd., Japan) at an acceleration voltage of 200 kV. Static mechanical 3-point bending tests of the composite films were evaluated by dynamic thermomechanical analysis (DMA) on TA-Q800 (TA Instruments-Waters LLC) under controlled force mode. The test specimens were cut into rectangle shapes with the dimensions of ca. 50 mm × ca. 5 mm. The specimens were mounted using 3-point bending clamps with a clamp compliance of 0.278 μm/N. The specific length and width were measured using standard calipers (Mitutoyo). The specific thickness was measured by a spiral micrometer gauge. All 3-point bending tests were conducted at room temperature in controlled-force mode with a preload of 0.01 N, and force was loaded with a force ramp rate of 0.05 N/min. Field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55) was used to observe the acid-treated MWNTs and the morphologies of MWNT/GC composite films and their failure structures after the mechanical tests. Thermal-gravimetric analyses (TGA, PerkinElmer Pyris 1) were carried out from 50 °C to 750 °C at a heating rate of 5 °C /min in air and N_2. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker (Germany) VERTEX 70 spectrometer (KBr pellets) over a range of 400–4000 cm^{-1} with DTGS or MCT as detector. Square resistance was recorded using RTS-8 4-point probes resistivity measurement system. Vickers-hardness was carried out by HXD-1000TMB/LCD micro hardness tester (Shanghai Taiming Optical Instrument Co., Ltd. in China) with 100 gf test force and 10 s duration time.

3. Results and discussion

3.1. Characterization of the acid-treated MWNTs

The FT-IR spectra of the pristine MWNTs and the acid-treated MWNTs are shown in Fig. 1. The peaks located at 3440 and 1630 cm^{-1} are corresponded to —CH stretching and C=C stretching respectively. As for the acid-treated MWNTs (Fig. 1(b)), a new peak appeared at 1715 cm^{-1}, corresponding to carboxylic groups stretching (—COOH), which confirms that the carboxylic groups were attached on the surfaces of MWNTs after the sonication with acid treatment [34]. Besides, the peaks at 3448 and 1575 cm^{-1} corresponded to —CH stretching and —COO— stretching.

Fig. 2 shows the SEM and TEM morphologies of the pristine MWNTs and the acid-treated MWNTs. It can be seen that pristine MWNTs are long, curled and twisted as ropes in Fig. 2(a). After acid treatment, the acid-treated MWNTs have been cut into short lengths and become disentangled as shown in Fig. 2(b). The majorities of acid-treated MWNTs have a length of several micrometers. TEM images in Fig. 2(c) shows that the wall surfaces become rough after the acid treatment, with some visible defects. Fig. 2(d) is an enlarged image of the individual acid-treated MWNT, which exhibits a tubular structure with an outer diameter of ∼ca. 20 nm. They still maintain their large aspect ratios, which is crucial to enhance the mechanical properties of composite films.

3.2. Thermal properties of the MWNT/PI composite films

Fig. 3 shows the digital photograph of the obtained 1 wt.% MWNT/GC composite film. It can be observed that composite film is free-standing and flat, with a diameter of 3.5 cm. Other MWNT/GC composite films loaded with different MWNT concentrations look almost the same from the appearance.

Thermal degradation can be monitored by TGA, and the behaviors of neat PI films and the MWNT/PI composite films are shown in Fig. 4(a). We can observe that neat PI films begin to decompose at 550 °C. Meanwhile, the MWNT/PI composite films have excellent thermal stability and do not decompose until 610 °C–630 °C. It is clearly known that the addition of MWNTs increases the thermal stability of the MWNT/PI composite films. In nitrogen (N_2)

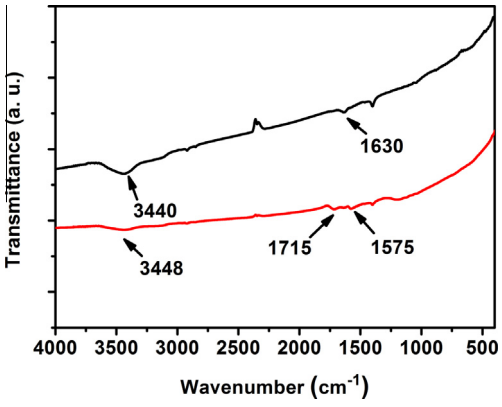

Fig. 1. The FT-IR spectra of (a) the pristine MWNTs and (b) the acid-treated MWNTs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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