Available online at www.sciencedirect.com
ScienceDirect
J. Mater. Sci. Technol., 2010, **26**(1), 20-26.
JMST
www.JMST.org

Preparation of Large Area Double-walled Carbon Nanotube Macro-films with Self-cleaning Properties

Ziping Wu[1)], *Qianfeng Xu*[1)], *Jiannong Wang*[2)†] *and Jie Ma*[1)]

1) School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

2) Shanghai Key Laboratory for Metallic Functional Materials, Key Laboratory for Advanced Civil Engineering Materials (Ministry of Education), School of Materials Science and Engineering, Tongji University, Shanghai 200029, China

[Manuscript received June 16, 2009, in revised form September 20, 2009]

Double-walled carbon nanotube (DWCNT) macro-films with large areas, excellent flexibility and superhydrophobicity are reported. The area of the macro-film is larger than 30 cm×15 cm, and this large film can be bended, or folded without any damage, and even can be tailored freely. After a simple modification of perfluoroalkysilane, the surface of the macro-film shows excellent superhydrophobicity with a water contact angle of 165.7±2 deg. and sliding angle lower than 3 deg., the prepared superhydrophobic films showing excellent antifouling, self-cleaning and water-repellent functions. The topographic roughness and perfluoroalkysilane modification are found to contribute to the observed superhydrophobicity. Considering the outstanding electronic, chemical and mechanical properties of DWCNTs, it is expected that this multifunctional DWCNT macro-film has potential applications in many fields.

KEY WORDS: Double-walled carbon nanotubes; Large area film; Self-cleaning; Methanol

1. Introduction

Extensive studies have been performed on microscopic carbon nanotubes (CNTs) since the discovery of carbon nanotubes[1–5]. Recently, there have been growing interests in macroscopic CNTs, because such CNTs can be directly used in many applications such as solar cells, field-emission, or electroluminescence[6–10]. Some methods have been exploited to prepare CNT macro-films, such as seeded catalyst chemical vapour deposition (CVD) method[11–14], solution deposition methods[15–17] and others[18,19].

The surface state of a CNT macro-film is of scientific and technological interest. For example, if the surface of the film is treated to be superhydrophobic, it can possess some new functions such as antifouling, self-cleaning and water-repellent properties[11] that are useful for wetting environments. Generally, a surface with a water contact angle (CA) larger than 150 deg. and a dynamic sliding angle (SA) less than 10 deg. can be called superhydrophobic[12,13]. The chemical composition and hierarchical nano/microstructure of a surface are found to be the two main factors for achieving superhydrophobicity[11–13]. CNT is a kind of one-dimensional nano-materials and has obvious advantages for fabricating the special nano/micro-structure needed by superhydrophobicity. The vertically aligned CNT film with a needle-like surface structure has been proved to be very suitable for fabricating superhydrophobic surfaces by seeded catalyst CVD[20–25]. Currently, non-aligned carbon nanotube powders and films have also been fabricated for achieving superhydrophobicity[17, 26–29]. However, the fabrication of a CNT film with a large area, good mechanical stability and superhydrophobicity by applying a simple method is still a technical challenge.

† Corresponding author. Prof., Ph.D.; Tel: +86 21 65982867; Fax: +86 21 65985385; E-mail: jnwang@tongji.edu.cn (J.N. Wang).

In this study, based on an improved floating catalyst CVD method, a multifunctional non-aligned CNT macro-film is reported. The film consists of DWCNTs and has an area larger than 30 cm×15 cm. To our best knowledge, this is one of the largest CNT macro-film ever reported[14–31]. The as-prepared CNT film possesses good mechanical stability and can be bended or folded without any damage, and even can be tailored freely. After a simple modification of perfluoroalkysilane (FAS), the macro-film shows superhydrophobicity with a CA as high as 165.7 deg. and a SA lower than 3 deg. Due to the excellent water repellence of the prepared macro-film, a rolling water droplet can carry off the contaminants on the film easily, showing a self-cleaning function.

2. Experimental

The large-area DWCNT macro-films were prepared directly by applying a floating catalyst CVD method. The CVD was conducted in a horizontal furnace. A solution of *n*-hexane and methanol with a volume ratio of 10:90 was used as a carbon source, ferrocene as a catalyst precursor (20 mg ml^{-1}), and thiophene as a growth promoter (3 μl ml^{-1}). Nitrogen was used as the carrier gas at a flow rate of 400 ml min^{-1}. The reactor was a quartz tube with an inner diameter of 50 mm. A piece of aluminum foil of 0.5 mm thick and 30 cm long was used as the substrate for deposition. The foil was cleaned in ethanol and futher dipped in 10% HCl to remove the oxidative surface. This foil was rolled up to form a cylinder with a diameter close to 50 mm. Such cylinder was then inserted into the quartz tube and placed in the low-temperature region (about 150–300°C) of the quartz reactor for CNT deposition. In a typical experiment, the reactor was flushed with N_2 first to eliminate oxygen. Then, the reactor was heated to 1150°C. After this temperature was reached, the mixed solution containing *n*-hexane, methanol, ferrocene and thiophene was supplied into the reactor by using an electronic squirming pump at a rate of 50 ml h^{-1}. After 10 min reaction, the cylindrical substrate was pulled out from the reactor and spread out. The deposited carbon was then peeled off from the substrate to form a macro-film with an area of about 30 cm×15 cm. Putting in a cylindrical substrate again, a second macro-film was produced in the same process.

FAS was employed to lower the surface energy of the carbon film. The FAS solution was prepared by adding FAS and water into methanol with a volume ratio of 1:3:100. First, a piece of the obtained carbon film was put on a glass substrate, and then the substrate was put into a sealed vessel containing 0.3 ml of FAS solution. The distance between the substrate and the solution was 55 mm. The sealed vessel was kept at 150°C for 3 h to cover the surface of the carbon film with FAS.

The as-prepared carbon sample was examined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM, JEOL 2010F, accelerating voltage of 200 kV). Energy dispersive X-ray spectroscopy (EDS) was used to analyze the chemical composition of the selected area. Raman spectroscopy was carried out to examine the perfection of the nanotubes using a Horiba Jobin Yvon HR 800UV with the 514.5 nm excitation wavelength laser. The purity of the sample was tested by thermogravimetric analysis (TGA) (Diamond TG/DTA6300, with the heating rate of 10°C min^{-1} from room temperature to 800°C at an air flow rate of 100 ml·min^{-1}). 4 μl of pure water (18.2 MΩ·cm in resistivity) was used to measure the static water CA and SA by a contact angle system (OCA 20, Dataphysics, Germany) at ambient atmosphere and room temperature. Water droplets were placed slowly and carefully onto the carbon film, and the CA was measured at different positions for at least five times. Field emission scanning electronic microscopy (SEM) (FEI Sirion 200) was used to examine the morphology of the superhydrophobic surface. The chemical compositions of the surface before and after the FAS modification were qualitatively analyzed by attenuated total reflection Fourier Transform Infrared technique (ATR-FTIR technique) using Bruker Equinox 55 equipped with a DTGS detector at 4 cm^{-1} resolution.

3. Results and Discussion

3.1 Preparation and characterization of large area DWCNT macro-film

The photograph of the carbon macro-film peeled off from the cylindrical substrate is shown in Fig. 1(a). The area of the macro-film can reach more than 400 cm^2 and the thickness is ∼1 μm. The macro-film could be bended, folded without any damage, and even can be tailored easily, indicating a structural uniformity and flexibility. The structure of the prepared macro-film was examined by TEM and HRTEM, and the results are shown in Fig. 1(b-c). From Fig. 1(b), nanotube bundles can be seen clearly, and each bundle contains several nanotubes and some catalyst nanoparticles. HRTEM examination reveals that the bundles consist of DWCNTs. Figure 1(c) shows the DWCNT having a large diameter[32,33]. In addition to DWCNTs, single-wall carbon nanotubes or thin walled multi-wall carbon nanotubes were also found in TEM observation. The amount of such nanotubes is estimated to be less than 15% (by volume). The selected area in Fig. 1(b) (with nanoparticles) was carried out by EDS to analyze chemical compositions. The results (Fig. 1(d)) show that the selected area is composed of C (59.24 wt pct) and Fe (35.10 wt pct) elements with minor Cu resulting from the TEM Cu grid, and S was not found.

The as-prepared DWCNT macro-film was further characterized by micro- Raman spectroscopy with a laser excitation wavelength of 514.5 nm. The Raman