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Water dispersed multi-walled carbon nanotubes modified by tannin acid

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ABSTRACT

In order to achieve sufficient dispersion and highly stabilized multi-walled carbon nanotubes (MWCNTs) in water, a convenient, economical and environment friendly surface modification process without any inorganic corrosive acid or elevated temperature has been developed. The MWCNTs were first treated with a mixed solution of NaOH and H_2O_2 for 12 h at room temperature. Then the MWCNTs were blended with a tannin acid aqueous solution in an ultrasonic cleaner for 2 h. The results consistently confirmed the adsorption of tannin acid onto the MWCNTs surface, while the structure of MWCNTs was not damaged. The modified MWCNTs showed much better dispersion and stability in water than those of the pristine MWCNTs.

1. Introduction

Significant attention has been paid to the application of carbon nanotubes (CNTs) since their discovery by Iijima in 1991 [1]. With unique structure and excellent strength and modulus as well as electrical and thermal conductivities along with a low density and high toughness, CNTs have attracted considerable interest in many applications [2].

In general, CNTs are extremely hydrophobic and prone to aggregation and form big bundles as they are subjected to high Van der Waals interaction forces along the long axis; thus it is difficult to disperse CNTs homogeneously in aqueous or non-aqueous solvents, which significantly limits their applications.

Surface modification of CNTs is an effectual method to disperse them in a liquid medium. The most common treatment of CNTs is to process in a mixture of concentrated sulfuric acid and nitric acid [3–9], followed by functionalization processes. However, the use of inorganic acids has a potential danger in polluting the environment during treatment due to some nitrogen oxide produced. Furthermore, the structure of CNTs may be damaged during processing [10]. Developing simple, efficient and environment friendly CNTs dispersion process is a critical issue in decreasing the air pollution [11].

In this work, water dispersed MWCNTs were obtained by a two-step process. The process involves pre-treating of MWCNTs in an aqueous solution of NaOH and H_2O_2, followed by immersion in tannin acid aqueous solution in an ultrasonic cleaner. The modified MWCNTs were analyzed by TEM, EDX, water contact angle and TGA.

2. Materials and methods

2000 mg of MWCNTs (Beijing Dk NanoTechnology Co., Ltd.) was manually blended with a solution of 15 ml 50% NaOH plus 15 ml H_2O_2 (30%), and statically immersed for 12 h at room temperature. The above MWCNTs were isolated by centrifugation at a rotation rate of 4500 rpm and washed with de-ionized water until pH 7 for the washed water prior to drying at 80 °C for 12 h. In the next step, 400 mg of dried MWCNTs was suspended in 200 mL de-ionized water containing dissolved 1000 mg tannic acid (TA), $C_{76}H_{52}O_{46}$ (Sinopharm Chemical Reagent Co., Ltd.). Mixture of MWCNTs and TA solution was processed in an ultrasonic cleaner for 2 h at room temperature. Then the MWCNTs suspensions were centrifuged for 10 min at a rotation rate of 16,000 rpm to isolate and washed by de-ionized water until pH 7 was achieved. The obtained MWCNTs were dried at 80 °C for at least 24 h.

The photographs of the pristine and modified MWCNTs dispersed in water were recorded with a digital camera after settling them for 60 d at room temperature. The water contact angles of the pristine and modified MWCNTs were measured using a JC2000D1 contact

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angle analyzer (Zhongchen Digital Technology Apparatus Co., Ltd., Shanghai, China) after the MWCNTs were dispersed in ethanol and dropped onto a PTFE plate followed by heating at 90 °C in air for 1 h. Micro-morphologies of MWCNTs were obtained by using Transmission Electron Microscopy, TEM (JEM-2100F, JEOL, Tokyo, Japan). For TEM measurements, the MWCNTs were first dispersed in de-ionized water in an ultrasonic cleaner and treated for 10 min. Then the mixture was dropped onto a copper-net micro-grid which was stored at ambient temperature for at least 24 h. Energy dispersive X-ray spectrometry, EDX (OXFORD X-Max, Oxford Instruments, Oxford, UK) was collected on a Scanning Electron Microscope, SEM (FEI INSPECT F 50, FEI, Hillsboro, OR). Thermo-gravimetric analysis (TGA) was performed using an SDT Q600 DSC–TGA instrument (V20.9 Build 20) from 15 to 1000 °C in a high-purity nitrogen flow of 100 ml/min at a heating rate of 10 °C/min. The DTG curve was calculated using a computer software.

3. Results and discussion

The pristine MWCNTs precipitated from water after settling for 60 d at room temperature (Fig. 1a), while much better dispersion

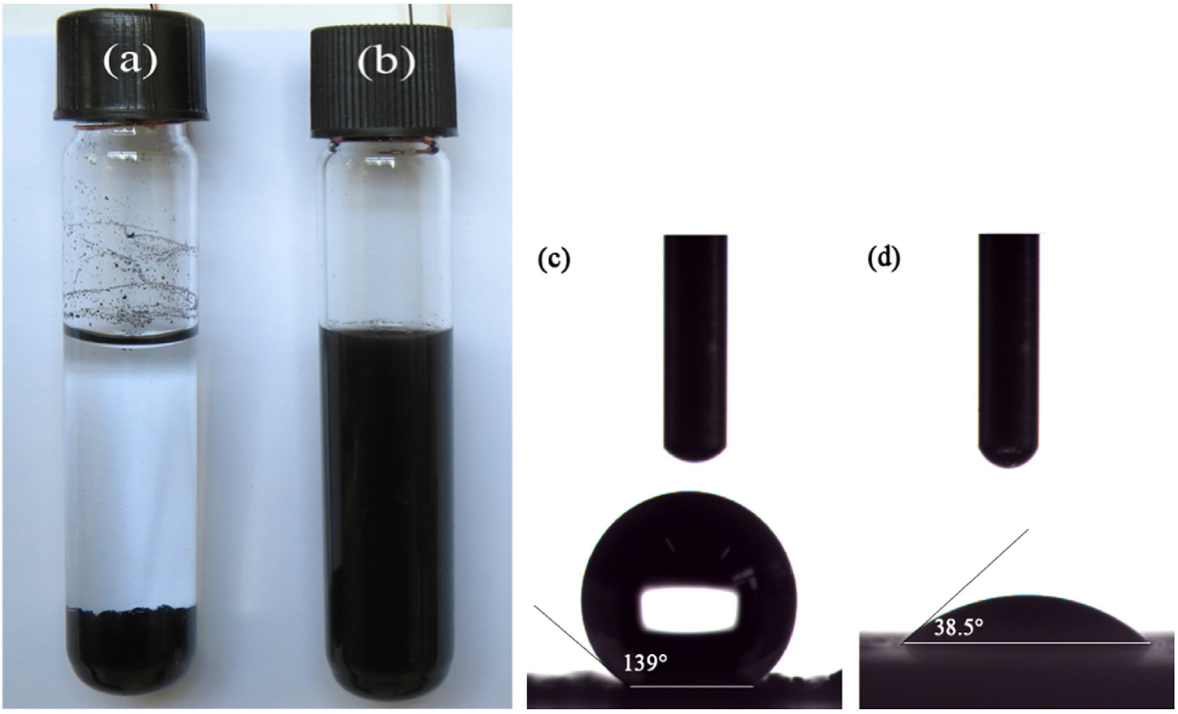

Fig. 1. Photographs of the dispersion of MWCNTs in water after settling for 60 d at room temperature: pristine (a) and TA modified (b); images of water contact angles for MWCNTs: pristine (c) and TA modified (d).

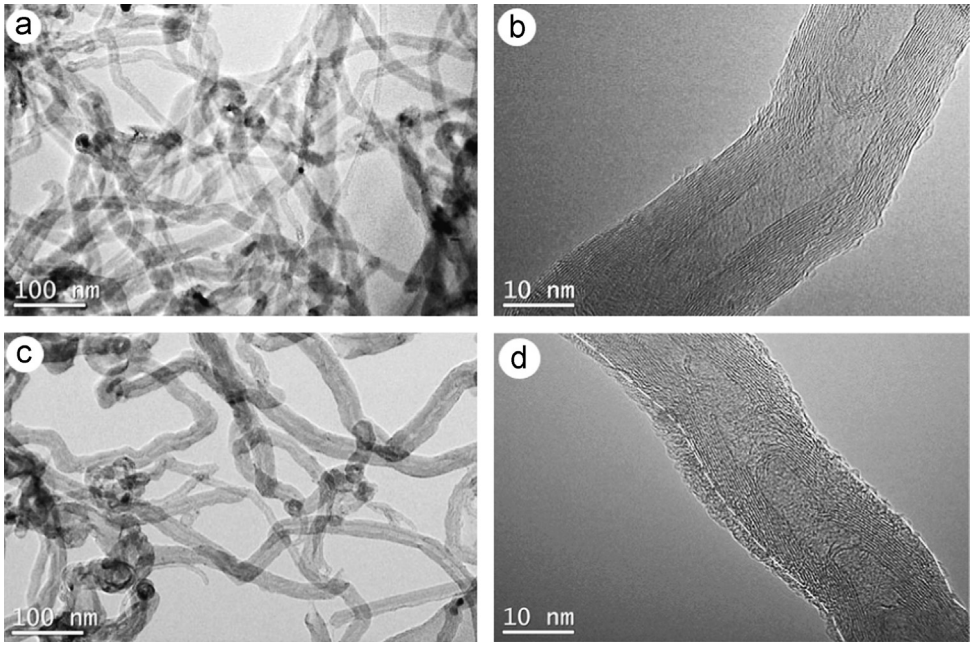

Fig. 2. TEM images of MWCNTs: (a, b) pristine and (c, d) TA modified.