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Microwave purification of multi-wall carbon nanotubes in gas phase

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ABSTRACT

It is a known fact that Multi-Walled Carbon Nanotubes (MWNTs) is one of the best reinforcement in conventional composites. However, impurities (like amorphous carbon blacks, graphite scraps, and catalyst particles) are generated inevitably when MWNTs are prepared. These impurities could affect the excellent properties of MWNTs as a reinforcing phase. In this paper, MWNTs were purified by microwave purification method using their excellent microwave absorbing properties. The simple purification process in the gas phase was expected to remove impurities effectively. Raman spectroscopy (Raman), X-ray Diffraction (XRD), Atomic Fluorescence Spectroscopy (AFS), Specific Surface Area (SSA), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) suggest that impurities are removed efficiently after microwave heating and simple acid pickling. The optimal purification result is obtained when MWNTs are microwave heated at 500 °C for 20 min, the morphology and structure remain intact. At last, the mechanism of purification is discussed.

1. Introduction

Carbon nanotubes (CNTs) are a kind of novel carbon form between fullerene and graphene, which are tubulous carbon molecules constituted by a graphite hexagonal structure. The huge length-to-diameter ratio of CNTs leads to excellent mechanical properties and electrical properties, such as low density, good plasticity, high toughness and strain energy, high conductivity and thermal conductivity [1,2]. Besides, CNTs have extraordinary fine performances for acid-resisting and alkali-resisting [3]. The exceptional mechanical, thermal, elastic, and electrical properties observed at CNTs give motivation to the development of nanotube-based composite material. There are three types of CNTs according to the number of concentric tubes: Single-Walled Carbon Nanotubes (SWNTs), Double-Walled Carbon Nanotubes (DWNTs) and Multi-Walled Carbon Nanotubes (MWNTs). DWNTs and MWNTs are simply composed of concentric SWCNTs. MWNTs are the most popular conformation because of the easier processing method and lower preparation cost. No matter which type of the CNTs, depending on the synthesis method employed, the yield of undesirable byproducts in the soot varies and these impurities interfere with the properties of the nanotubes [4]. The excellent properties of MWNTs as reinforcement materials are limited and inhibited by the impurities like amorphous carbon blacks, graphite scraps, and catalyst particles; hence, purification is the first step to use the CNTs as reinforcements. Reyhani et al. calcined as-received MWNTs in O_2 first and then immersed MWNTs in 3 M different acid solutions, in terms of TGA, the yield of as-received and purified MWNTs in HNO_3, H_2SO_4, HCl and HF reaches 48.5%, 92.6%, 87.1%, and 51.2% respectively [5]. Ling et al. purified MWNTs with boiling concentrated HNO_3 (68%) and concentrated HCl (36–38%) firstly, and then treated with air flow at 400 °C for 4 h, the purity of MWNTs increases to 97.23% [6].

In consequence of the exceptional properties of MWNTs, it is commonly used as a reinforce phase. MWNTs can bridge particles of matrix materials well. It undertakes and transfers much stress so that properties of the composite are improved as stress is dispersed. Zhang et al. purified commercial CNTs by acid treatment in order to prevent strength degradation of sintered CNT–Al_2O_3 composite caused by impurities in CNTs such as transition metal catalyst particles, amorphous carbon, and nanocrystalline graphite [7]. Reinforcing differences are introduced by using the purified MWNTs and the raw MWNTs. Impurities in raw MWNTs will evolve into microdefect, which will lead to the stress concentration and crack propagation. Hence, a remaining challenge is the purification of the nanotube material obtained from the different processes.

Methods that aim at purification usually employ various oxidation steps, such as sonication [8], thermal treatments, and chemical acid treatments [9,10], among others. For example, Ivar Kruusenberg et al. and Voitko et al. soaked CNTs in concentrated acid to remove impurities [11,12]. MacKenzie et al. add microwave heating in acid pickling process to improve purification result [13,14]. Huang et al. purified MWNTs

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with vacuum annealed method and acid treatment method in different orders and compared the purification result of the two methods [15]. However, these methods have many disadvantages such as complicated process, difficult operations and inefficiency. Microwave heating is a superior heating style which makes the polar molecule vibrating sharply and turns electromagnetic energy into the internal energy of material. Microwave heating has the characteristics of rapid heating, bulk heating, selective heating, etc. In addition, CNT is an excellent wave-absorbing material, it absorbs the electromagnetic energy of microwave effectively and be heated rapidly. Song et al. heated 10 wt.%-MWNT/SiO_2 into 600 °C easily because of the great microwave absorbing ability [16]. Va'zquez et al. exposed CNTs to microwaves, strong absorptions were observed and it produced intense heating [17].

In this paper, microwave gas phase oxidation method is employed to purify MWCNTs using a simple operation, expect to obtain high efficiency purification results.

2. Experimental

As-received MWNT powders (OD = 8–15 nm, length = 30–50 μm, purity > 90 wt.%, SSA > 180 m^2/g) fabricated by CVD method were acquired from Chengdu Organic Chemicals Co. LTD. Chinese Academy of Sciences. There were graphite particles, amorphous carbons, metal oxide carriers, metal catalyst particles, etc. in the MWNT powders as impurities. The starting powder samples were placed in a microwave furnace (3 kW, 2.45 GHz) and quickly microwave heated to specified temperatures (350 °C–500 °C) in about 1–2 min and then held for some periods of time. The microwave heating process is conducted in dry laboratory air and the microwave chamber is open to laboratory air. The samples were cooled to room temperature and soaked in 32% sulfuric acid for 2 h. The acid pickling removes metal particles effectively and it doesn't introduce more impurities. Actually, the technique not only removes the impurities but also be likely to introduce some functional groups on the surface of CNTs, the groups can enhance the reinforcing when CNTs play as a reinforcing phase. The obtained samples were washed to neutrality with deionized water and dried under the vacuum condition.

Raman spectroscopy data were recorded using a LabRam HR Evolution produced in France, scan ranged from 200 cm^{-1} to 2000 cm^{-1}, wavelength of the laser probe is 532 nm, and the sample is exposed to the laser for 3 s during the spectrum acquisition. XRD patterns were recorded by a D/max 2400 X-ray diffractometer. AFS was registered on a FP-6500 spectrograph made in Japan. SSA data were collected by a 3H-2000PSA2 SSA measurement. TGA was carried out using a STA 409 PC analyzer, and samples were heated from room temperature to 1000 °C at a rate of 10 °C/min in a simulated air. The surface morphology of MWCNTs was measured by a QUANTA200 SEM and the microstructure of MWCNTs was characterized using JEM-2010F-JEOL TEM at an acceleration voltage of 200 kV.

3. Results and discussions

3.1. Oxidation temperature

Starting MWNT powder samples were quickly microwave heated to 350 °C, 400 °C, 450 °C and 500 °C in about 50 s, 60 s, 80 s and 120 s respectively. Then, the microwave power source was suspended and samples were cooled down to room temperature. No heat preservation was required. The microwave heating turns the carbon impurities into carbon dioxide and carbon monoxide, etc. and they flow away. Fig. 1(a) displays the weight loss curve of samples under different temperatures. It can be observed that the weight loss percentage values are 8.87%, 13.74%, 21.59% and 23.04% respectively when temperature reaches 350 °C, 400 °C, 450 °C and 500 °C. The weight loss increases rapidly when the temperature is increased from 350 °C to 450 °C, and most of the carbon impurities are oxidized in this temperature range. The slope of the curve decreases on the weight loss-microwave heating temperature curve from 450 °C to 500 °C which indicates that the ablation of MWNTs is beginning, that is, the majority of the impurities are removed.

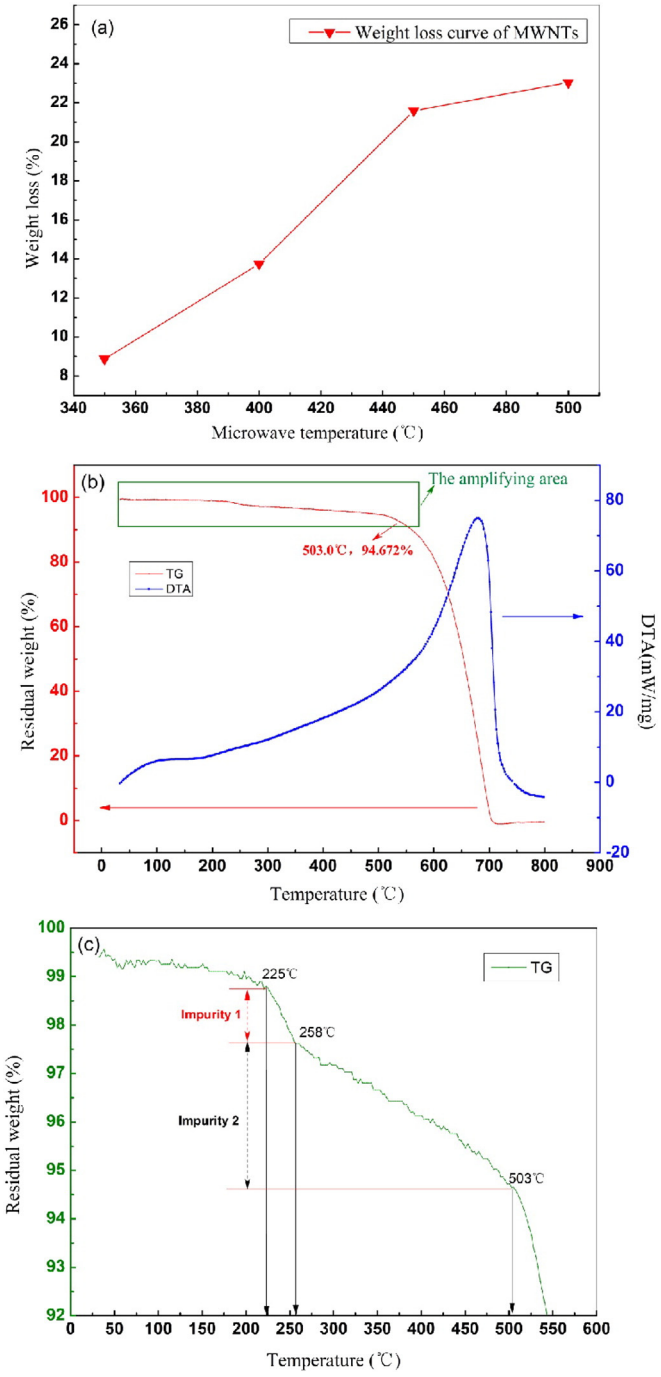

Fig. 1. (a) Weight loss curve of microwave oxidation samples under different temperatures. (b) TGA in air of 90% raw MWNTs. (c) Partially enlarged drawing of TGA.

TGA was performed to prove the accurate oxidation temperature of starting MWNT powders. The residual weight curve has a downside from room temperature to 503.0 °C because of water evaporation and carbon impurity oxidation in Fig. 1(b). Fig. 1(c) shows the enlarged drawing of the TG curve as residual weight is 100% to 92%. There are two descent stages during the temperature interval 225 °C–258 °C and 258 °C–503 °C. These results confirm that different forms of nonmetal impurities are oxidation removed. TG curve gradient increases suddenly at 503 °C, suggesting that MWNTs are beginning to be oxidized. Thus,