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Using natural cotton fibers to synthesize carbon nanotubes and electromagnetic wave absorption properties

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ABSTRACT

In this paper, we report a new method for synthesizing carbon nanotubes (CNTs) and other carbon nanostructures such as carbon nanoparticles (CNPs) through catalytic thermolysis of natural cotton fibers. Using the new method, long CNTs (L-CNTs), which could reach to 20 μm or longer, can be readily synthesized from natural cotton fibers under hydrogen environment at a thermolysis temperature around 1200 °C. The analysis of the microstructure of synthesized L-CNTs showed that the CNT growth from the catalytic thermolysis of cotton fibers may not undergo a carbon-containing gas generation step that is different from most of other growth methods. We further studied the dielectric and electromagnetic wave (EMW) absorption properties of synthesized CNTs by embedding them in a epoxy matrix. The measurement results show that complex dielectric permittivity ε and EMW absorption ratio of the composites strongly depend on CNT loading in the frequency range from 8 to 26 GHz.

1. Introduction

The combination of the unusual electrical, thermal, mechanical, and chemical properties of carbon nanotubes (CNTs) and related carbon nanostructures (such as carbon nanoparticles (CNPs), graphene nanoplatelets (GNPs), and others) makes them very valuable for applications in many fields of nano-material science and technologies [1,2]. Especially, the one dimensional nature of the basic CNT structure drives an array of scientific and technology issues that have been studied by research groups across the globe in recent years. Nanostructured carbons such as CNTs offer advantages over traditional carbons including ultra-low resistivity ($\sim 10^{-6}\ \Omega$ cm) [3], high specific surface area (2675 m^2/g) [4], and greater chemical stability. Multi-walled carbon nanotubes (MWCNTs) have been shown to exhibit ballistic transport of charge carriers and possess exceptional electrical conductivity (1.85×10^3 S cm^{-1}) [5]. Current densities approaching 10^9 A cm^{-2} have also been reported [6]. Whereas applications in electronics and photonics may need direct growth of CNTs on patterned substrates with exquisite control on size, charity, and positioning, many other applications such as composites require CNT productions in bulk quantities to realize cost advantages. Researchers have devised different routes to synthesize CNTs from various carbon precursors. The most popular and widely used nanotube synthesis techniques include: arc discharge (AD), laser ablation (LA), and chemical vapor deposition (CVD) [7–17]. In arc discharge method, a vapor is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapor. In the laser ablation technique, the graphite target is vaporized by a pulsed laser producing a carbon based soot that is swept out of the furnace zone by the carrier gas. This soot, containing single-wall CNTs (SWCNTs), MWCNTs, fullerenes, and CNPs, is deposited on a collector. CVD is the most prominent technique to synthesize CNTs at present, owing to its relatively low cost and high yield potential. CVD involves the decomposition of carbon-rich source gases (methane, acetylene or carbon monoxide, etc.) with the aid of a catalyst at elevated temperatures of 700–1000 °C. Apart from these methods, the electrolysis [18–20], and ball milling [21,22] methods have also been used. Electrolysis method used an electrode with transition metal nanoparticles on for the collection of CNTs from a carbon containing electrolyte by using a high voltage (e.g. 1000 V). Though this method has been reported to yield good quality of carbon nanotubes, electrolysis method has not been used for large scale CNT production yet. The ball milling method, on the other hand, was mainly used to produce short CNTs.

The aim of this paper is to report the results of our recent explorations for a new method to synthesize CNTs and CNPs from natural cotton fibers, which is a renewable and sustainable agriculture product. So far, it has not been reported in literature for the synthesis of CNTs from cotton fibers and the method has not been

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well explored yet. The new CNT and CNP synthesis method is based on a catalytic thermolysis of raw cotton fibers. The new method has the potential for mass production of CNTs and CNPs with a low production cost. Unusable clothes and waste cotton fibers can also be used to synthesize CNTs and CNPs by using this method. In addition, we further studied the dielectric and electromagnetic wave (EMW) absorption properties of the synthesized CNTs by embedding them in a polymer (epoxy) matrix to form CNT-epoxy composites. The epoxy is a *good insulator and has low* EMW absorption. The measured EMW absorption properties of the composites are mainly attributed to the response of CNTs to electromagnetic wave.

The need for EMW absorbers is ever growing in various applications such as the reduction of electromagnetic interference among electronics components/circuits and reduction of the back radiation of microstrip radiators [23,24,25,26]. Other areas of applications include consumer electronics, wireless LAN devices, radar absorbers, electromagnetic shields, wireless antenna system, cellular phones, and others. Nanostructured materials have attracted attention for EMW radiation absorption purposes, due to their unique electrical properties [27,28,29]. In particular, the unique structural and outstanding electric properties of CNTs have the potentials for EMW shielding and other applications [30,31,32,33,34]. Varol and Canakci also studied Cu-based nanocomposites using CNTs, nanographite, and graphene nanosheet and assessed their effects on the microstructure, density, electrical conductivity and hardness of these nanocomposites. For the Cu-based nanocomposite groups, increasing the nano filler contents result in an decrease in hardness values and electrical conductivity [35,36,37,38].

In the following sections, we will present the synthesis experiment, experimental measurement results and discussions. A short conclusion is included in the last section.

2. Synthesis experiment: materials and methods

Firstly, natural cottons were pre-treated in a diluted acid solution (0.5 M HNO_3 or 0.5 M H_2SO_4) at 70 °C for 6 h to remove dirt and other impurities. The pre-treated cotton was then soaked in a solution of iron acetate and cyanamide in ethanol, stirred at 60 °C until the ethanol was evaporated, followed by a heat treatment in vacuum oven at 60 °C until the cotton was completely dried. By a heat treatment at 1200 °C for 1 h in hydrogen environment, the treated cotton can be converted to Fe/carbon nanotubes/nanoparticles (Fe/CNT/CNP) composite through a catalytic thermolysis. To remove the redundant metallic iron and iron compounds, the obtained Fe/CNT/CNP composite was purified in 0.5 M HNO_3 or 0.5 M H_2SO_4 at 70 °C overnight. Finally, the sample was heat-treated again under the same conditions as used for the first heat treatment. Fig. 1 shows the schematic illustration for the preparation of CNTs by using a catalytic thermolysis of natural cotton fibers.

3. Experimental measurement results and discussions

3.1. Microstructure characterizations

The microstructure of the samples were characterized by using transmission electron microscopy (TEM) at 120 kV (JEM-1400, JEOL, Japan). For TEM studies, a drop of sonicated material suspension in ethanol was placed on a 3 mm copper grid, followed by drying under ambient conditions.

Fig. 2(a) to (e) show the TEM images (in different length scales) of the synthesized CNTs from natural cotton in hydrogen environment at an annealing temperature of 1200 °C, which is the highest

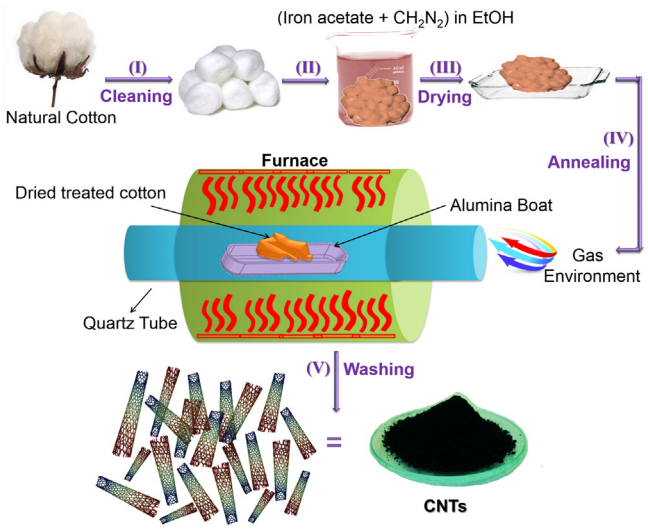

Fig. 1. Schematic illustration for the preparation of CNTs through a catalytic thermolysis of natural cotton fibers.

working temperature of our currently used furnace. Fig. 2(a) and (b) (the scale bars are 2 μm) show the overall view of the produced CNTs having relatively long length, which are much longer than other CNTs produced at relatively lower temperature or in other gas environments. In this experiment, the produced CNTs could reach to 20 μm or longer (so we name them as L-CNTs). The dark spheres shown in Fig. 2(a), (b), (d) and (e) are actually Fe catalyst nanoparticles which play a vital role for the growth of the L-CNTs. From the TEM images in Fig. 2(a) and (b), we can see that each single CNT starts from an isolated catalytic Fe nanoparticle, forming a curved L-CNT structure. Fig. 2(c) (scale bar is 50 nm) shows the TEM image of a magnified section of a L-CNT. It can be clearly seen that the wall of the L-CNT is quite smooth. The diameter of the CNT in Fig. 2(c) is about 37 nm, which are multi-walled CNTs (MWCNTs). At present, we could not grow single-wall CNT (SWCNT) from our current experiments of catalytic thermolysis of natural cotton fibers. Fig. 2(d) displays two separate L-CNTs with diameters of ~66.3 nm and ~21.2 nm, respectively; the diameters of the catalytic Fe nanoparticles from which the two L-CNTs yielded are ~222.53 nm and ~86.2 nm, respectively. Generally, the diameters of the L-CNTs grown from the catalysts depend on the sizes of the catalytic nanoparticles: larger catalytic nanoparticles produce thicker L-CNTs. The image in Fig. 2(e) shows that in the present method the catalytic nanoparticle actually possesses a core-shell structure, which mainly composes of three parts from inside to outside: a dark core, a relatively lighter intermediate layer, and a grey shell, respectively. The dark core actually is a Fe particle working as a catalytic centre for the growth of a single L-CNT; the intermediate layer of the nanoparticle, which looks lighter than the Fe core, is a mixture of Fe and C; and the major component of the outside shell of the nanoparticle is carbon. Fig. 2(e) may also shed some light on the growth mechanism of the L-CNT, which could be different from those CNTs grown from CVD method or other methods. In CVD grown CNTs, Fe catalytic nanoparticle is usually wrapped inside of CNT at one-end. The size of Fe catalyst nanoparticle strongly control the CNT diameter. A correlation between the size of the catalyst particles and the diameter of the CNTs grown from CVD method is often observed. For instance, Cheung et al. reported that Fe nanoparticles with average diameters d_{NP} of 3, 9, and 13 nm produced MWCNTs with average diameters d_{NT} of 3, 7, and 12 nm, respectively, which corresponds to a ratio of d_{NT}/d_{NP} close to 1 [39]. Schaffel et al. obtained a similar ratio d_{NT}/d_{NP} using Fe particles of 3–18 nm [40]. Chen et al. also