



# Growth mechanism and wave-absorption properties of multiwalled carbon nanotubes fabricated using a gaseous detonation method

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## ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) were fabricated via the detonation of a mixed gas consisting of ferrocene vapor, methane, and oxygen. The samples were characterized using transmission electron microscopy, X-ray diffraction, Raman spectroscopy, vibrating sample magnetometry, and a vector network analyzer. The results indicate that the samples were MWCNTs that were about 30 nm in external diameter, about 15 nm in inner diameter. The ferrocene dosage had an obvious effect on the morphology, degree of graphitization, and magnetic property of the MWCNTs. The growth mechanism of the MWCNTs in the gaseous detonation process was discussed using the detonation Zeldovich-von Neumann-Döring model and a vapor-liquid-solid growth model. The minimum reflection loss of the MWCNTs was  $-6.1$  dB at 11.2 GHz with a thickness of 2 mm, which is lower than that of the MWCNTs prepared via other methods, and the reasons for this result are analyzed in the paper.

## 1. Introduction

Carbon nanotubes (CNTs) are a very important carbon material; CNTs include both multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes. Since CNTs were discovered, researchers have studied the potential physical and chemical properties of CNTs [1–4]. It has been found that CNTs have high Young's modulus and tensile strength and display good mechanical properties when they are combined with other materials [5,6]. MWCNT walls are composed of graphite, which contribute to the high dielectric constant and thermal stability. Thus, when MWCNTs are combined with epoxy resin, silicon dioxide, or other materials, they have a high dielectric constant and good thermal stability [7–9]. The high specific surface area of MWCNTs increases the contact area with solution and provides a way to increase the catalytic activity of the catalyst particles loaded on the tubes [10–12]. Generally, MWCNTs are prepared using catalysts, such as Fe, Co, Ni, or their alloys, and thus, MWCNTs have certain magnetic properties. Because of the magnetic and dielectric properties, MWCNTs can be used as a kind of electromagnetic wave-absorption material that is lightweight and has high strength [13,14]. Therefore, preparation of MWCNTs and carbon nanotube composites still attract much attention.

MWCNTs can be prepared using a variety of methods, including arc discharge [15,16], chemical vapor deposition (CVD) [17,18], pyrolysis [19,20], laser ablation [21,22], electrolysis [23], hydrothermal

methods [24,25], and detonation methods [26]. Arc discharge is the most common method for preparing MWCNTs. MWCNTs deposit on graphite electrodes catalyzed by metal nanoparticles during the arc discharge process. Generally, methane is used as a shielding gas to obtain MWCNTs under higher energy conditions. The low-temperature reaction, low-cost, and ease of operation are why CVD is the most widely accepted method for fabricating MWCNTs. Usually, catalyst particles are used to decompose hydrocarbon gas and to prepare CNTs [17]. The structure of CNTs can be modified by changing the size or type of the catalyst and by changing reaction conditions. In the pyrolysis method, CNTs are fabricated via pyrolysis of organic matter such as ferrocene under relatively mild conditions [19,27,28]. Laser ablation is more controllable than the arc discharge method. A laser beam is used to vaporize graphite at very high temperature, and this results in high cost and requires high quality equipment [22]. The electrolysis method is not commonly used to prepare CNTs because the produced CNTs have low purity [29]. In the hydrothermal method, a heterogeneous reaction is used in the presence of aqueous solvents or metallic material. The temperature and pressure have great influence on dissolution and, in turn, affect recrystallization of insoluble materials in aqueous solution [30]. The detonation reaction is very rapid and releases a large amount of energy, and thus, CNTs can be produced and grown in a short period of time [31].

Research regarding CNT preparation is aimed at finding a method

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that can produce high quality CNTs, are low cost, and require less time. Gaseous detonation is a relatively new method that has been very well developed and has been used to fabricate nanoparticles. The products can be prepared in a very short period of time and have higher purity than samples produced via the explosion detonation method. Therefore, gaseous detonation has attracted the attention of many researchers. In 2013, Sorensen et al. [32] prepared graphite nanosheets in a stainless steel pot via the detonation of a gaseous mixture of acetylene and oxygen without a catalyst. The yield of nanosheets can be controlled by changing the molar ratio of acetylene and oxygen. In 2016, Luo et al. [33] fabricated MWCNTs via electric spark detonation of a mixed gas consisting of benzene vapor, ferrocene vapor, and oxygen, and this was a new method for preparing high purity MWCNTs. In our study, carbon-encapsulated Fe/Fe<sub>3</sub>C (Fe@C) nanoparticles were prepared via the decomposition of ferrocene under negative oxygen conditions in a gaseous detonation process [34–36]. According to our study, the carbon concentration in the products has a great influence on the structure of carbon nanomaterials. It is reported that when the carbon concentration is less than a critical value, the Fe@C structure is not present and CNTs are generated [37]. Therefore, the present paper aims to find the conditions for preparing MWCNTs using gaseous detonation to prepare Fe@C, and the growth mechanism of MWCNTs and experimental phenomena are discussed. Moreover, MWCNTs have a good electromagnetic wave-absorption property; however, there are few reports about the wave-absorption ability of MWCNTs prepared via the gaseous detonation method. Therefore, the wave-absorption ability of MWCNTs was studied in the experiment, and this will provide some useful guidance for wave-absorbing materials fabricated via the gaseous detonation method.

## 2. Experiment and characterization

### 2.1. Fabrication of MWCNTs

A certain dosage of ferrocene powders was placed uniformly in a closed titanium alloy vessel. The vessel was 110 cm long, and the volume of the vessel was 7.8 L. The vessel was then heated to sublime the ferrocene after a vacuuming process. Methane and oxygen were then filled sequentially in a volume ratio of 1:1, and the gas mixture was ignited using an electric spark. Finally, the black products were collected and marked as S1 and S2, corresponding to 1 g and 2 g doses of ferrocene.

### 2.2. Characterization

The morphologies of the samples were characterized using transmission electron microscopy (Tecnai F30, produced by FEI, with 0.2 nm point resolution and 0.1 nm line resolution). Powder X-ray diffraction (D/MAX 2400, Cu K $\alpha$  radiation, 40 KV, 30 A) was used to assess the phases for  $2\theta$  in the range of 10–80°. The degrees of graphitization of the samples were measured using laser confocal micro Raman spectroscopy (DXR Microscope, produced by Thermo Fisher). The magnetic properties of the samples were tested using a vibrating sample magnetometer (VSM) (JDM-13) at room temperature. The electromagnetic parameters were measured using an HP-8722ES vector network analyzer via the coaxial method with the frequency ranging from 1 GHz to 18 GHz. The prepared samples were homogeneously dispersed in paraffin using a sample-to-paraffin mass ratio of 20:80, and finally the mixture was pressed into a ring with an external diameter of 7 mm and an inner diameter of 3.04 mm.

## 3. Results and analysis

### 3.1. Morphology analysis

Fig. 1 shows the structure morphologies of the samples. As shown in

Fig. 1(a) and (b), there was bulk carbon structure embedded with metal nanoparticles and CNTs in S1 and S2. The CNTs grew on the edge of the bulk carbon-metal matrix under the catalysis of Fe/Fe<sub>3</sub>C nanoparticles. As seen in Fig. 1(c) and (e), curved tubular structures appeared in the samples, and according to a study about preparing Fe@C nanoparticles via gaseous detonation (deflagration), these structures are MWCNTs [34,35]. There were only four elements in the reactants that contributed to Fe@C nanoparticles and CNT preparation under negative oxygen conditions. There was a spherical or ellipsoidal catalyst particle at the end of the CNTs, and this should be a Fe/Fe<sub>3</sub>C nanoparticle generated via pyrolysis of ferrocene in the detonation reaction. A magnified view of the red rectangle in Fig. 1(c) is shown in Fig. 1(d). The outer diameter of the CNTs was about 33 nm, and the inner diameter was about 16 nm. Also, there was a carbon cap in the middle of the CNTs. In the rectangular section shown in Fig. 1(d), a cylindrical particle can be seen clearly at the end of the CNTs, and this is probably the Fe/Fe<sub>3</sub>C catalyst. As seen in Fig. 1(e), many CNTs were wound together, and the number of CNTs increased compared to that shown in Fig. 1(a). However, some core-shell particles were agglomerated, as seen in the section of Fig. 1(e) marked with an ellipse. Fig. 1(f) is a magnified view of the region that is marked with a red rectangle in Fig. 1(e); the outer diameter of the CNTs was about 27 nm, and the inner diameter was about 15 nm. The growth direction of the CNTs changed at the cap, which is marked with a red circle. With an increase in the ferrocene dosage (from 1 g to 2 g), there were slightly more CNTs in S2 compared with the number of CNTs in S1; however, the catalyst particle size decreased, which resulted in CNTs with a smaller diameter.

The micro structure of the MWCNTs was analyzed using HR-TEM, and the results are shown in Fig. 2, which indicates that the CNTs fabricated via the gaseous detonation method were MWCNTs. The lattice spacing of the carbon walls in S1 was about 0.39 nm, and this is a little larger than that of S2 (0.35 nm), which was closed to the lattice space of the (002) crystal face of graphite. The crystallinity of the catalyst in S1 was not good, and thus it is difficult to observe the lattice fringes. The lattice space of the catalyst in S2 was 0.22 nm, which was close to the lattice space of Fe<sub>3</sub>C and Fe. Fig. 2 indicates that S2, which had 2 g of ferrocene, had better crystallinity and more obvious MWCNT structures than S1.

### 3.2. Phase analysis

The sample phases were characterized using XRD, and the results are shown in Fig. 3. The diffraction peak (002) for graphite (JCPDS file no. 75-1621) appeared at  $2\theta = 26.2^\circ$  and had weak peak intensity. This phenomenon was caused by two factors. First, amorphous carbon did not have sufficient time to transform to graphite during the rapid detonation reaction, although a high temperature condition was generated via the gas detonation process. Second, the high metal content and strong peak intensity for the peak corresponding to metal made it difficult to clearly identify the diffraction of graphite. The peaks at  $2\theta = 44.7^\circ$  and  $65.2^\circ$  corresponded to the (110), (200) crystal face of the body-centered cubic structure of iron. Under the same conditions, the peak intensity of iron increased when the dosage of ferrocene was increased (S1  $\rightarrow$  S2), and this illustrates the improved iron content in the products. The peaks at  $35.2^\circ$ ,  $37.6^\circ$ ,  $39.8^\circ$ ,  $40.6^\circ$ ,  $42.8^\circ$ ,  $43.7^\circ$ ,  $45.8^\circ$ ,  $48.6^\circ$ ,  $49.1^\circ$  and so on (marked in black triangles) were the diffraction peaks of Fe<sub>3</sub>C. The peak intensity of Fe<sub>3</sub>C in S2 was a little higher than that in S1. This was probably related to the concentrations of iron and carbon in the reaction. The temperature of the detonation reaction was higher than 3000 K, and the Fe<sub>3</sub>C phase was generated according to the iron-carbon phase diagram [36]. However, the rapid energy release caused the high temperature duration to be short, and thus, some iron was left in the sample. According to the XRD analysis, the catalyst particles in Fig. 2 were Fe/Fe<sub>3</sub>C particles.

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