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# Characteristics of airborne fractal-like agglomerates of carbon nanotubes

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ABSTRACT

Airborne carbon nanotubes (CNTs) pose a health threat at workplaces and play more and more important roles in toxicity studies, yet data and model on their detailed characteristics are lacking. Thus we investigated aerosolized multiwalled CNTs (MWCNTs) by tandem measurement of the mass and mobility size in order to characterize the MWCNT agglomerates. The results revealed a fractal-like relationship between the mass and mobility size in the range 50–500 nm indicating quite compact agglomerate structure, and an effective density in the range of 0.51–0.83 g/cm$^3$. With the tube diameters and intrinsic density, the tube length in an agglomerate was determined reliably from the mass. We developed a model to compute the porosity and geometrical outer diameter of the agglomerates and derived the fractal relation between the mass and the outer diameter with a fractal dimension of 2.6, which agreed well with fractal dimensions of bulk CNT assemblies determined by other analytical methods. The effective density based on the outer diameter was in the range of 0.11–0.35 g/cm$^3$ and decreased with the increasing agglomerate size. Electron macroscopic images of the aerosolized MWCNTs provided comparable data for the outer diameter and fractal dimension.



## 1. Introduction

Carbon nanotubes (CNTs) represent a type of fascinating nanomaterial which gained numerous applications due to their special mechanical, electrical, thermal and optical properties [1]. On the other hand, CNTs are one of the most heavily studied nanomaterials for their potential impacts on human and environment [2–4].

CNTs tend to agglomerate due to their high aspect ratios and van der Walls forces. The manufacturers often provide CNTs in the powder form, which can be composed of loose agglomerates in the range of 0.1–1 mm [5]. Such large agglomerates have limited mobility, and are easier and safer to handle and transport [6]. CNT agglomerates in aqueous media have been widely encountered in toxicity studies and the agglomeration status affects the resultant toxicity [7–9]. CNT agglomerates in the airborne form are observed in many exposure studies during CNT production or handling [10–13] and CNTs are seldom present as individual straight nanofibers at workplaces [14].

The CNT diameters, length, density and agglomeration structure play significant roles in their functionality and toxic effects. For instance, improved mechanical property of CNT composite is achieved with a higher aspect ratio of single-

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walled CNTs (SWCNTs) [15]; gas adsorption properties are closely related to fractal dimension of CNT assemblies [16]. The lengths of CNTs have significant effects on agglomeration status and toxicity. Wick et al. [8] showed CNT agglomerates are more cytotoxic than well dispersed CNTs. Pauluhn [17] concluded that the toxic effects of multiwalled CNTs (MWCNTs) are determined by density of agglomerate structures, not fibrillar structures. Murphy et al. [3] examined three CNT samples of differing lengths and found only the long CNT sample caused acute neutrophilic inflammation in bronchoalveolar lavage at 1 week. The length and density of CNTs affect their mobility and transport properties. These parameters play critical roles for prediction of lung deposition due to interception, impaction and gravitational settling, therefore they are critical in inhalation dosimetry studies [18,19].

A number of studies have been dedicated to determination of the CNT characteristic parameters. The length and diameter of CNTs are usually determined by electron microscopy. Other methods and models have been developed to determine the length of individual airborne CNTs. Kim and Zachariah [20] combined electric mobility measurement and a model for cylinder shaped particles in electrical fields to compute the length of SWCNTs. Bahk et al. [21] and Chen et al. [22] used a filtration method to measure the length of MWCNTs. These methods are only applicable to cylinder-like individual CNTs.

The literature on CNT density showed substantial discrepancies, which may be related to the different types of density being considered. We use the following nomenclature: the intrinsic density refers to the density of the graphite material comprising the MWCNTs; the bulk or apparent density refers to the density of a powder with the understanding that the air in the pores of the powder contributes to both the volume and mass; the effective density refers to the density of an imaginary sphere which has the same mass and equivalent diameter with the CNT agglomerate under consideration. The equivalent diameter may be based on the particle geometric size, mobility or another physical property. Kim et al. [23] used aerosol particle mass analyzer (APM) to measure airborne MWCNTs with consideration of their cylindrical shape and reported the condensed phase density as 1.74 g/cm$^3$. Chen et al. [24] found the effective density of airborne MWCNT agglomerates with geometric mean outer diameter and length of 100 nm and 3 μm, respectively, to be 0.71–0.88 g/cm$^3$. They determined the effective density by taking the ratio between the aerodynamic diameter and the projected area diameter obtained from electron micrographs. The bulk density of Baytubes provided by the manufacturer was 0.14–0.16 g/cm$^3$ (Table 1) measured by the EN ISO 60 method, which determines the apparent density of a powder by pouring it to a cylinder with a known volume. Ma-hock et al. [19] used 0.15 g/cm$^3$ as the apparent density for their MWCNTs, but stated this value represented effects of the large pores between the more densely packed agglomerates. They considered the pores less than 1 μm as determined by the mercury porosimetry and reported the density of agglomerated MWCNTs as 0.39 g/cm$^3$. OberdÖrster [14] pointed out the CNTs usually occur as tangles of hollow tubes with different shapes, and their effective density was different from that of solid carbon.

Many studies demonstrated that a variety of distinctively different forms of CNTs can coexist, including individual CNTs that are cylinder-like or bended or coiled, CNTs bundles, and quasi-isometric shaped agglomerates [10,12,13,19,21,24,25]. Therefore characterization can hardly be achieved by using uniform parameters for all the CNT particles even in the same sample. Models have been developed for cylinder-like CNTs but are lacking for CNT agglomerates. In the present study, we performed tandem measurement of the mobility size and mass of airborne MWCNT agglomerates and demonstrated that the mass increase with size follows a power law, therefore the MWCNT agglomerates can be described as fractal-like particles. The fractal geometry has been investigated for bulk CNT assemblies [16,26,27], however, has not been applied to airborne dispersed CNT agglomerates. Based on the measured mobility size and mass, we developed a model to establish the relationship between the MWCNT properties including tube diameters, length, intrinsic density and the agglomerate properties such as the mass, porosity, effective density, surface area and characteristic diameters.

## 2. Material and experiment

### 2.1. MWCNT samples

MWCNTs with outer diameter of 15–20 nm (Baytubes) were purchased from Bayer Material Science (BMS), Germany. Another type of MWCNTs with an outer tube diameter of 10–20 nm was purchased from Timesnano (China). The properties of both types of MWCNTS provided by the manufacturer are listed in Table 1. It can be seen that the inner and outer tube diameters of them are in similar ranges. Both MWCTNs were then treated with the nitric acid refluxing method, which gave rise to the carboxyl functional group (–COOH) on the tube surfaces and reduced tube lengths, and removed the metal catalysts in the MWCNTs [28]. The surface carboxyl group increased the hydrophilicity of the MWCNTs and resulted in better dispersion in aqueous suspensions, which were then atomized to generate airborne MWCNTs. Bahk et al. [21] showed that the agglomeration status of the airborne MWCNTs could be adjusted by controlling their concentration in the suspension, with lower concentration leading to more individual airborne MWCNTs and higher concentration leading to more agglomerates. Two types of MWCNTs were used in the study to provide more comprehensive data sets and to demonstrate that the fractal-like characteristics reported here are not limited to MWCNTs of a single type.

### 2.2. MWCNT intrinsic density measurement

The intrinsic density was measured in two steps: a balance (Mettler Toledo AG, Switzerland) to measure the mass of the MWCNTs and a gas displacement pycnometry system (Micromeritics, AccuPyc II 1340) to measure the true volume occupied by the MWCNT walls. Helium was used as the