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Measuring particle size-dependent physicochemical structure in airborne single walled carbon nanotube agglomerates

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Abstract

As-produced single-walled carbon nanotube (SWCNT) material is a complex matrix of carbon nanotubes, bundles of nanotubes (nanoropes), non-tubular carbon and metal catalyst nanoparticles. The pulmonary toxicity of material released during manufacture and handling will depend on the partitioning and arrangement of these components within airborne particles. To probe the physicochemical structure of airborne SWCNT aggregates, a new technique was developed and applied to aerosolized as-produced material. Differential Mobility Analysis-classified aggregates were analyzed using an Aerosol Particle Mass Monitor, and a structural parameter Γ (proportional to the square of particle mobility diameter, divided by APM voltage) derived. Using information on the constituent components of the SWCNT, modal values of Γ were estimated for specific particle compositions and structures, and compared against measured values. Measured modal values of Γ for 150 nm mobility diameter aggregates suggested they were primarily composed of non-tubular carbon from one batch of material, and thin nanoropes from a second batch of material – these findings were confirmed using Transmission Electron Microscopy. Measured modal values of Γ for 31 nm mobility diameter aggregates indicated that they were comprised predominantly of thin carbon nanoropes with associated nanometer-diameter metal catalyst particles; there was no indication that either catalyst particles or non-tubular carbon particles were being preferentially released into the air. These results indicate that the physicochemistry of aerosol particles released while handling as-produced SWCNT may vary significantly by particle size and production batch, and that evaluations of potential health hazards need to account for this.

Introduction

Single walled carbon nanotubes (SWCNT) represent a carbon-based material that shows unique physical and chemical properties. As applications of the material continue to be explored, possible

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implications to human health following exposure have been raised (Shvedova et al., 2003, 2005; Lam et al., 2004; Maynard et al., 2004; Warheit et al., 2004). The potential health hazards of single walled carbon nanotubes (SWCNT) remain poorly understood. However, it is probable that the unusual physicochemical properties underpinning their value as a new engineered nanomaterial – including high tensile strength and structure-dependent electrical conductivity – will influence their toxicity, as well as determine deposition and transportation within the body. Early studies have shown SWCNT are cytotoxic and lead to oxidative stress *in vitro* (Shvedova et al., 2003), as well as indicating pro-inflammatory and fibrogenic responses in rodent lungs (Lam et al., 2004; Warheit et al., 2004). In particular, biological response has been associated with the nanoscale structure and composition of SWCNT particles (Shvedova et al., 2003, 2005; Warheit et al., 2004). Although aerosol generation rates have been shown to be low during handling (Maynard et al., 2004), published data to date indicate that inhaled airborne material may present a pulmonary hazard.

As-produced SWCNT material is a complex matrix of carbon nanotubes, bundles of nanotubes (nanoropes), non-tubular carbon and metal catalyst nanoparticles (Bronikowski et al., 2001). The pulmonary toxicity of as-produced SWCNT released during manufacture and handling will depend on the partitioning and arrangement of these components within airborne particles. However, physicochemical characterization of airborne particles at the nanoscale presents unique challenges. Here we present a new technique for probing the nanostructure of airborne particles, and use it to show significant differences in nanostructure between 150 nm mobility diameter and 31 nm mobility diameter aerosol particles released from as-produced SWCNT.

Background

It has previously been shown that as-produced SWCNT material generated using the HiPCO™ process can release particles into the air when agitated (Maynard et al., 2004). Controlled agitation of material from a SWCNT manufacturer using the HiPCO™ process demonstrated a bimodal aerosol, with modal count median mobility diameters of approximately 400 nm, and below 10 nm (Maynard et al., 2004). Although the generation rates observed during laboratory and small-scale production conditions were very low, potential health risk following inhalation will depend on the toxicity of the airborne particles in combination with exposure.

Transmission Electron Microscopy (TEM) of the same as-produced SWCNT material confirmed that it comprised of four distinct components: carbon-coated iron-rich catalyst particles approximately 5 nm in diameter, discrete single walled carbon nanotubes, ordered bundles of single walled carbon nanotubes typically between 5 and 50 nm in diameter and non-tubular carbon material (Figure 1). The mass-fraction of iron was previously measured at 30% using inductively coupled plasma – mass spectrometry (Maynard et al., 2004). The fraction of non-tubular carbon was not quantified, although TEM analysis indicated relatively little to be present in the bulk material.

Each of these components is likely to represent a different toxicity within the lungs. The US National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limits (REL) for carbon black (assumed to be analogous to the non-tubular carbon) and iron oxide fume

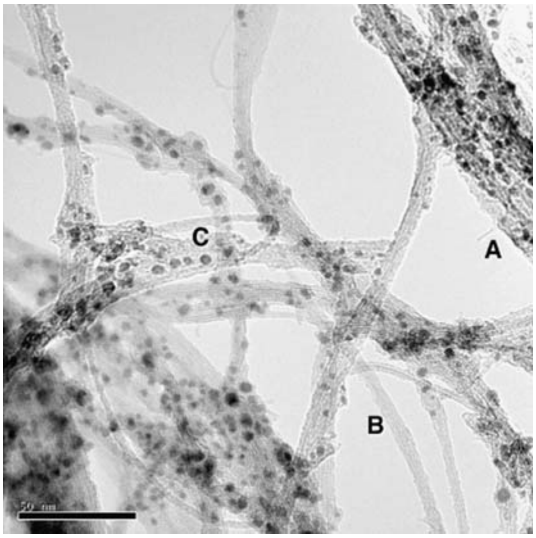

Figure 1. TEM image of as-produced SWCNT (second batch of material). Three of the four principle components are identified: A: discrete single walled carbon nanotubes; B: bundles of carbon nanotubes (nanoropes); C: iron catalyst particles. The non-tubular carbon component is not visible in this micrograph.

are 3.5 mg/m^3 and 5 mg/m^3 respectively. There have been indications that SWCNT may be as toxic as crystalline quartz in the lungs (Lam et al., 2004) – which has an REL of 0.05 mg/m^3 – and Shvedova et al. have indicated that the presence of nanometer-diameter iron particles within as-produced SWCNT lead to Fenton-type reactions and the release of reactive oxygen species (Shvedova et al., 2003). An unusual inflammatory and fibrogenic response to SWCNT aspirated into the lungs of mice has also been observed (Shvedova et al., 2005).

In addition to an inhalation hazard determinant on the composition of SWCNT-derived airborne particles, the physical structure of the generated particles will possibly contribute to their pulmonary toxicity. Shvedova et al. (2005) identified distinct responses in the proximal and distal regions of mice lungs aspirated with SWCNT, and speculated that the regional responses were associated with different agglomerate structures.

A recent review of engineered nanomaterial toxicity screening tests emphasized the importance of structure as well as chemistry in determining potential hazard, and stressed the need to fully characterize the physicochemical nature of materials under study (Oberdörster et al., 2005). In the case of particles released from as-produced SWCNT, possible variations in particle structure and composition place stringent requirements on characterization, which push the bounds of current analytical techniques. When agitated under controlled conditions, 150 nm mobility diameter particles were released from as-produced SWCNT at a sufficient rate to allow physicochemical characterization using TEM. However, given low aerosol generation rates and material availability, it is estimated that TEM analysis of particles in the sub−35 nm diameter mode would require unfeasibly long sample collection times.

Method

To explore the nature of smaller aerosol particles released from the bulk material, we have developed a new approach to probing the physical structure of airborne nanoparticles by combining differential mobility analysis (DMA) with Aerosol Particle Mass analysis (APM). These two techniques have previously been used together to explore the structural properties of aerosols (McMurry et al., 2002; Park et al., 2004b). Here, we define the structural parameter Γ, and use it to estimate the composition and structure of sampled airborne particles.

Differential mobility analysis enables airborne particles with a specific electrical mobility diameter to be differentially selected from an aerosol, and is capable of producing monodisperse aerosols with modal diameters from a few nanometers upwards (Knutson & Whitby, 1975). For open-structured and compact particles with Knudsen numbers greater than 1 (Kn, defined as the mean free path of the suspension gas divided by particle radius), electrical mobility diameter is comparable to the diameter of a sphere with the same projected area (Rogak et al., 1993; Park et al., 2004a; Ku & Maynard, 2005). Mobility diameter can therefore be used to derive particle surface area for a range of particle morphologies. In general, particles differentially classified using the DMA will have the same ‘active’ surface area – defined as the surface area associated with particle-molecule interactions that determine drag (Keller et al., 2001).

APM analysis is a recently developed method for measuring the mass of discrete singly-charged airborne particles (Ehara et al., 1996; McMurry et al., 2002). Particles of a known mobility diameter and charge are transported axially through a narrow annular gap separating two rotating concentric cylindrical electrodes. The cylinders and particles rotate about the axis at the same angular speed. High mass particles deposit on the outer electrode, while low-mass particles deposit on the inner electrode due to electrophoresis: Only those particles where centrifugal force is precisely balanced by the inward electrostatic force traverse the device, where they are counted using a condensation particle counter. By varying the voltage between the electrodes, particles with a specific charge to mass ratio are differentially sampled. For instance, at 1000 rpm and 500 volts, particles with a modal mass of 3.95×10^{-17} kg are differentially selected, corresponding to 423 nm diameter spherical particles with a density of 1000 kg/m^3. Instrument resolution is influenced by rotational velocity, particle size and sampling flow rate (Ehara et al., 1996). McMurry et al. (2002) have shown the APM to have a relatively broad transfer function using polystyrene latex spheres, although modal values of particle number versus APM voltage enabled the

Table 1. Estimated values of Γ (Γ_{est}) as a function of particle composition and structure, for a variety of possible particle morphologies and compositions

ID[a]	Mobility Diameter (nm)	Description[b]	Γ_{est} (m^2/g)[c]
A	150	Compact non-tubular carbon particles	20
B	150	Compact non-tubular carbon particles with 30% Fe by mass	11
C	150	Compact single walled carbon nanotubes with 30% Fe by mass	12
D	150	Open agglomerate of single walled carbon nanotube with 30% Fe by mass	860
E	150	Open agglomerate of 15 nm diameter nanoropes with 30% Fe by mass	81
F	150	Open agglomerate of 5 nm diameter Fe particles	150
G	31	Compact non-tubular carbon particles	97
H	31	Compact non-tubular carbon particles with 30% Fe by mass	51
I	31	Compact single walled carbon nanotubes with 30% Fe by mass	58
J	31	Open agglomerate of single walled carbon nanotube with 30% Fe by mass	860
K	31	Open agglomerate of 5 nm diameter nanoropes with 30% Fe by mass	240
L	31	Open agglomerate of 5 nm diameter Fe particles	150

Values of Γ_{est} are based on estimates of particle mass and surface area for a given composition and structure

[a] Refer to Figures 2 and 3.

[b] Compact particles are assumed to have a minimum surface area. Open agglomerates are assumed to have a surface area determined by the dimensions of the component structures.

[c] Estimated assuming a density for carbon nanotubes and nanoropes of 1.4 g/cm^3, a density of 7.9 g/cm^3 for iron nanoparticles and a density of 2 g/cm^3 for non-tubular carbon.

mass of spherical monodisperse aerosol particles to be measured to within 5%.

In order to extend the operational range to sub-100 nm diameter particles with low densities, the APM was operated at up to 4100 rpm and 0.5 l/min sampling rate, with differential voltages between the electrodes of less than 2 volts. This revised configuration enabled differential separation of

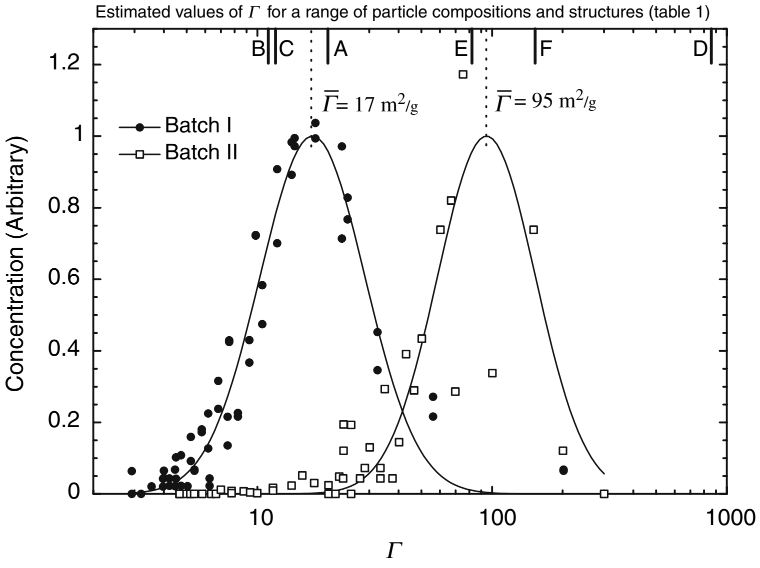

Figure 2. Measured values of Γ for 150 nm mobility diameter as-produced SWCNT-derived particles. Estimated values of Γ (Γ_{est}) for particles with specific physicochemical characteristics (Table 1) are shown for comparison along the upper x-axis. Particles from batch I have a (lognormal fit) value of $\bar{\Gamma}$ of 17 m^2/g, while the equivalent parameter for particles from batch II is 95 m^2/g. Comparing values of $\bar{\Gamma}$ with Table 1, particles from batch I are indicated as being predominantly compact particles, possibly with a significant non-tubular carbon component. Particles from batch II have a distinctly higher value of $\bar{\Gamma}$, indicative of open agglomerates of small-diameter nanoropes (Table 1).

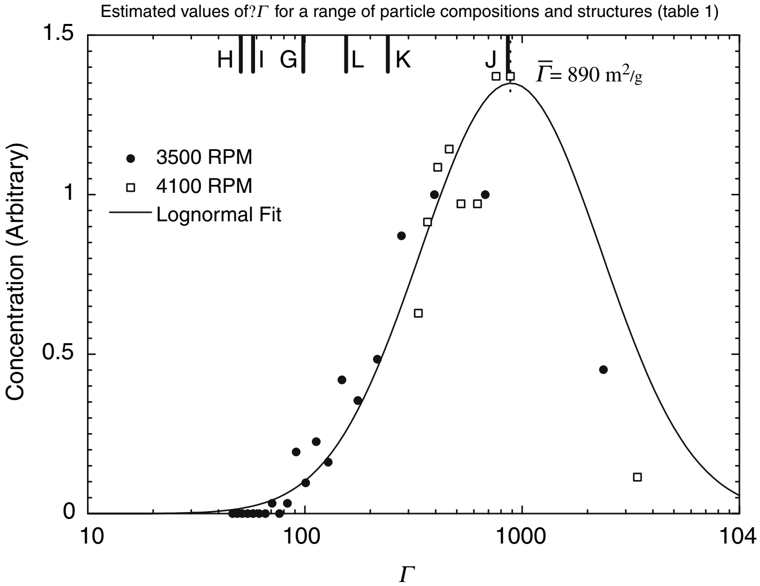

Figure 3. Measured values of Γ for 31 nm mobility diameter as-produced SWCNT-derived particles (batch I material). Estimated values of Γ (Γ_{est}) for particles with specific physicochemical characteristics (Table 1) are shown for comparison along the upper x-axis. Based on a lognormal fit, the distribution has a value of $\bar{\Gamma}$ of 890 m^2/g, although the quality of the lognormal fit at higher values is not good. The relatively high value of $\bar{\Gamma}$ suggests that the particles had an open structure dominated by discrete carbon nanotubes and nanometer-diameter nanoropes (Table 1).

particles with a mass below 2×10^{-21} kg (corresponding to a 31 nm diameter spherical particle with a density of 600 kg/m^3).

Particles with a selected mobility diameter (and therefore active surface area) were classified by mass in the APM. APM spectra for a given particle mobility diameter were used to calculate Γ, defined as

$$\Gamma = \pi \bar{d}_m^2 \frac{\omega^2 \bar{r}}{qE} \qquad (1)$$

where $\bar{d}_m$ is the modal particle mobility diameter selected by the DMA, q is the particle charge, $\bar{r}$ is the gap separating the concentric cylinders within the APM, ω is the rotational velocity of the APM electrodes and E is the electric field between the two electrodes.

Γ represents modal particle surface area (defined by the DMA), divided by modal particle mass (defined by the APM), and has units of surface area per unit mass. Plots of particle number concentration versus Γ represent a parameter closely related to particle specific surface area, convoluted by the DMA and APM transfer functions. Without de-convolution (particularly for the APM transfer function) Γ can not provide detailed structural information on aerosol particles. However, by varying E and/or ω for a given $\bar{d}_m$ and measuring particle number concentration, the modal value of Γ ($\bar{\Gamma}$) for a given mobility diameter may be estimated. Comparing $\bar{\Gamma}$ with calculated values of specific surface area for possible particle structures and compositions enables some insight to be gained into the physicochemical nature of the aerosol under study.

Measurement of Γ for SWCNT-derived particles with mobility diameters of 31 nm and 150 nm were made, representing particles within the two aerosol size distribution modes observed by Maynard et al. In all cases, SWCNT material was aerosolized using the method previously described (Maynard et al., 2004). Characterization of the larger diameter particles was validated using TEM. 150 nm mobility diameter particles from two batches of SWCNT produced using the same process were analyzed: A similar comparison was not possible for 31 nm diameter particles, due to excessively low generation rates from the second batch of material. Replicate measurements were made over a range of APM rotational velocities. As the aerosol generation rate varied with time, measurements made under the same conditions were combined, and then normalized for concentration within overlapping ranges of the parameter Γ. Modal values of Γ ($\bar{\Gamma}$) were estimated by fitting data using a lognormal function. Measured values of Γ were compared with estimates (Γ_{est}) associated with various particle compositions and morphologies (Table 1, Figures 2, 3).

Results and discussion

Modal values of Γ for 150 nm diameter particles differed between the two batches of material tested (Figure 2). Comparison between $\bar{\Gamma}$ for batch I and Γ_{est} (Table 1) indicated that compact particles of non-tubular carbon material were being preferentially released into the air. TEM analysis confirmed this, although sampled 100 nm mobility diameter particles had a projected area-equivalent diameter closer to 400 nm (Figure 4). Measuring projected area as a function of sample holder tilt within the TEM confirmed that these particles were planar, suggesting that particles within the DMA either aligned with the electrostatic field or tumbled, thus reducing their apparent mobility diameter.

DMA/APM analysis on batch II of SWCNT material indicated that the particles being released were dominated by a nanostructure which was relatively open (high values of Γ). Comparison of $\bar{\Gamma}$ with estimated values (Table 1) for a range of physicochemical structures, suggested that the particles being released were associated with small-diameter nanoropes or combinations of nanoropes and other nanostructured components. This was confirmed in TEM micrographs of sampled 150 nm mobility diameter particles (Figure 5). Size distribution measurements made on the batch I material confirmed previously published size distribution (Maynard et al., 2004). However, similar measurements on the batch II material

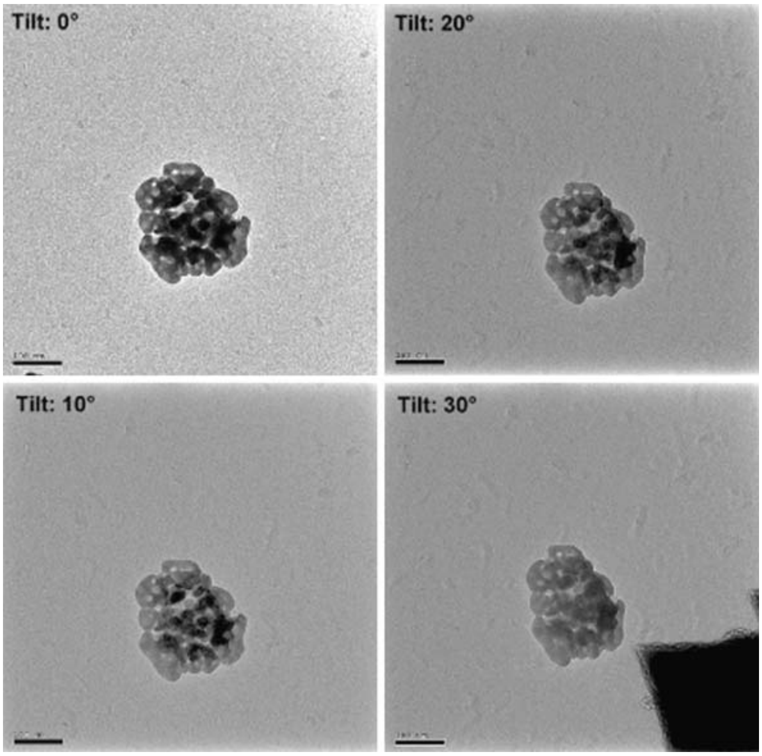

Figure 4. Micrographs of a representative 100 nm mobility diameter particle from batch I material, imaged over a number of specimen stage tilts. The particle was collected onto a lacey carbon support film using a thermophoretic sampler (Maynard, 1995). Although the projected area is indicative of particles with a mobility diameter larger than 100 nm, decreasing projected area with increasing tilt angle shows the particles to be planar. The particle is compact, and appears to be predominantly non-tubular carbon, in agreement with the physicochemical structure inferred from the modal value of Γ (Figure 2).

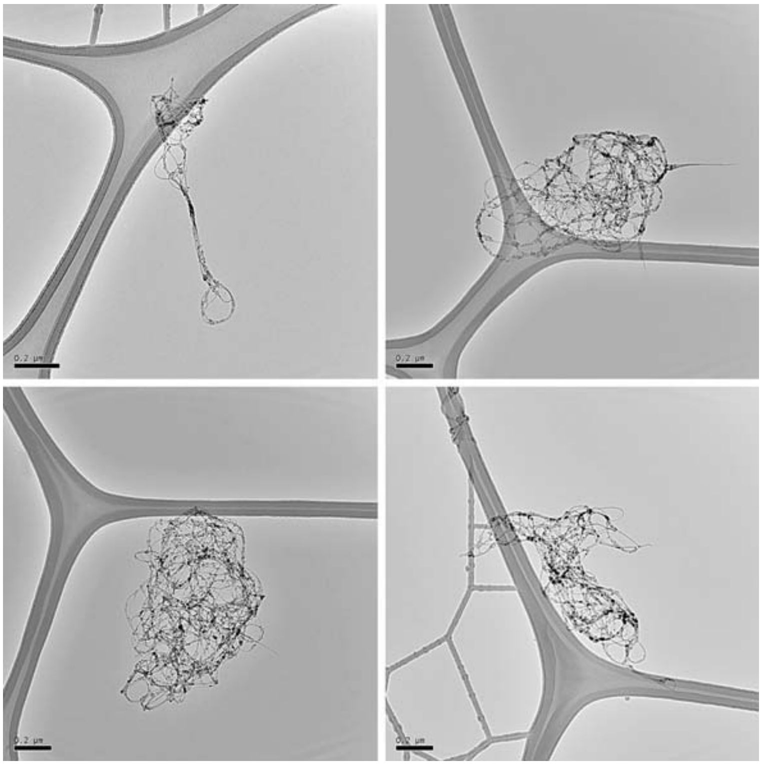

Figure 5. Micrographs of representative 150 nm mobility diameter particles from batch II material. Particles were collected onto a carbon support grid using a thermpohoretic aerosol sampler (Maynard 1995). The particles have an open structure comprising predominantly of nanometer-diameter nanoropes and Fe catalyst particles, in agreement with the physicochemical structure inferred from the data in Figure 2.

were very different: The lower-diameter mode was not well developed, and the upper-diameter mode occurred well above the upper size limit of the DMA (approximately 400 nm in this case). Although the SWCNT material for both batches was produced by the same manufacturer under similar conditions, our results indicate that subtle changes in physicochemical properties may have profound effects on hazard potential.

The estimated value of $\bar{\Gamma}$ for 31 nm mobility diameter particles from batch I material indicated a strong dependence on nanostructure (Figure 3). The analysis method was operating at its limits above approximately 800 m^2/g, and data within this region need to be treated with care. The lognormal fit used to estimate $\bar{\Gamma}$ clearly deviates systematically from the data above $\Gamma = 500\ \mathrm{m}^2/\mathrm{g}$, although the quality of the data are not sufficient to indicate whether the deviation is significant or not. However, comparison with estimated value of $\bar{\Gamma}$ clearly indicates particles with an open structure dominated by nanometer-diameter nanotubes. There is little evidence that compact carbonaceous particles were released.

Summary

Associations between structure and the properties of engineered nanomaterials challenge current approaches to evaluating hazard potential, and in many cases indicate new methods and approaches will be needed for characterizing materials. Using a new aerosol analysis technique, the size and source material-dependent physical and chemical complexity of single walled carbon nanotube aerosols has been demonstrated. Our results suggest that the physicochemistry of aerosol particles released while handling as-produced SWCNT may vary significantly by particle size and production batch, and that evaluation of potential health hazard needs to account for this.

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