Size Distribution and Characteristics of Aerosol Released From Unrefined Carbon Nanotube Material

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Carbon nanotubes (CNTs) are among the most dynamic and fast-growing nanomaterials due to their novel properties. The potential of human exposure to this new type of material in the workplace, as well as in the general environment, is rising, and its impact on human health is of great concern.

In this study, we have investigated the size distributions of airborne CNT particles that were laboratory-generated by using a vortex agitator and dispersed with a very low flow of HEPA-filtered air. The number-weighted particle size distributions were monitored by a 13-stage Electrical Low Pressure Impactor (ELPI) and a 6-stage Integrating Screen Diffusion Battery (ISDB). Several industrial-grade unrefined CNT samples (raw materials) of various types have been examined, including single-walled, double-walled, and multiwalled nanotubes. The CNT samples were collected onto the aluminum substrates placed on each stage of the ELPI. For ISDB sampling, the samples were collected on an array of stainless steel screens, as well as mica discs attached on the wall between the screens. The experimental data demonstrated that all types of CNT raw materials examined can be dispersed into the air to a significant extent. The sizes of particles generated were widely distributed across all 13 stages of the ELPI, including the filter stage ranging from 7 nm to 10 μm. The ISDB results showed that the particles released from CVD-SWCNT material (HP-grade, Helix, TX) have a solo peak under 10 nm, with a mode of 2.5 nm and GSD of 1.24 in number-weighted distributions. The experimental data also showed that the size distributions varied with the type of CNTs and with the methods by which they were manufactured. The image analysis results by Atomic Force Microscopy showed that the CNTs tend to agglomerate rather than exist as single particles, physically.

These results suggest that CNTs can possibly become airborne under certain agitation conditions during manufacturing and handling processes and can expose workers via inhalation and dermal absorption. As deposition efficiency and sites of inhaled particles within the respiratory system largely depend on particle size distribution, the deposition pattern of agglomerated CNT should be similar to those larger, equivalent-sized nonagglomerated particles. Nevertheless, entrained particles depositing on/in the deep lung surfaces of the bronchioles or alveoli will contact pulmonary surfactants in the surface hypophase and the agglomerated CNT are likely to (ultimately) be de-agglomerated. Therefore, to investigate human exposure to airborne CNTs, the full-size range of inhalable particles must be taken into account.

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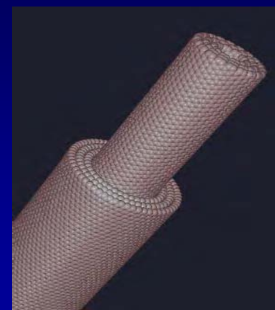
Carbon Nanotubes



Carbon nanotubes represent a new form of carbon that has closed tubular structures, consisting of nested cylindrical graphitic layers with a hollow internal cavity and capped by fullerene-like ends (Iijima 1991).

Carbon nanotubes offer a full range of electrical and thermal conductivity properties, are about a hundred times stronger than steel, and are more durable than diamonds.

Safety and Health Aspect

- Carbon nanotubes (CNTs) are among the most dynamic and fast-growing nanomaterials due to their novel properties.
- As production rate scaling up, the potential of human exposure to this new type of materials in workplace as well as in the general environments are rising.
- Their impacts on human health are of great concern by many researchers.

Inhalation Exposures

- To determine the overall risk to human and environment, not only the material toxicity but also the exposure levels need to be considered.
- For many conventional workplace contaminants, airborne route is considered the most crucial for worker protection.
- To determine the worker exposure levels to airborne nanoparticles, the particle concentration, size distribution, shape characters, as well as the agglomeration status are among the main factors.

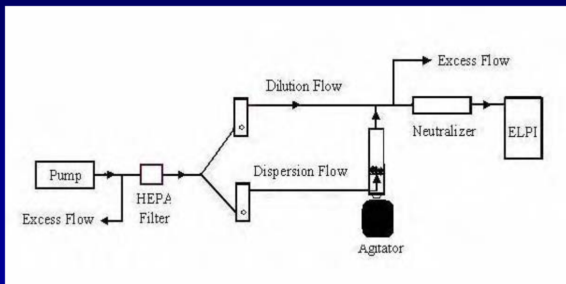
Characteristics of CNTs

- High aspect ratio (typically in a scope of 10^2 but can reach as high as 10^4).
- Highly agglomerated.
- Often coexist with non-tubular type particles, such as amorphous carbon soot, metal catalysts as well as ambient particulate matters.
- The size distributions of CNTs are hard to predict, but presumably widely spread and source dependent.

Specific Aims

- To investigate the size distribution and characteristics of aerosol particles released from various types of industrial grade CNT bulk materials due to agitation. The results will provide a foundation for developing field and personal sampling devices for CNTs.
- To develop a practical method using atomic force microscopy image analysis that is capable to classify CNTs from other co-existing nano-sized particles in general environments.
- To develop appropriate methods for monitoring the potential worker exposure levels to CNTs.

Test Aerosol Generation



Sample Material Sources

- The size dimensions of CNTs vary with the type and the methods by which they are manufactured. Therefore, size distributions of CNT aerosol particles also depend on the source of the material.
- Up-to-date 7 Industrial-grade bulk CNT samples from 3 manufacturers have been examined.
- The sample matrix includes 3 common types of CNTs, i.e., single-walled, double-walled and multi-walled, and 3 primary methods of production, i.e., arc discharge (Arc), chemical vapor deposition (CVD), and high-pressure CO conversion (HiPco).

Methods

Airborne Particle Sampling and Sizing:

- Electrical Low Pressure Impactor (ELPI)
- Integrated Screen Diffusion Battery (ISDB)

Particle Counting and Characterization:

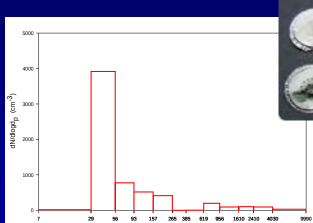
- Atomic Force Microscopy (AFM)

Calibrated Aerodynamic Cut-off Size of ELPI

Stage Number	Aerodynamic Cut-size (μm)
Filter	0.007
1	0.029
2	0.056
3	0.093
4	0.157
5	0.265
6	0.385
7	0.619
8	0.956
9	1.61
10	2.41
11	4.03
12	-
13	9.99

CVD-SWCNT Number Weighted Size Distribution

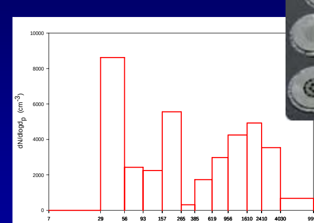
dp≤100 nm: ~80%



Sample: CVD-SWCNT
Grade: HP
Diameter: < 2 nm
Length: 0.5-40 μm
Purity: > 90%
Manufacturer: Helix, TX

Arc-SWCNT Number Weighted Size Distribution

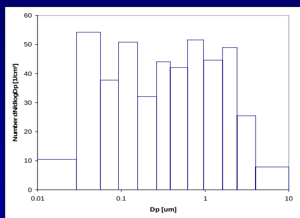
dp≤100 nm: 35%



Sample: Arc-SWCNT
Grade: AP
Diameter: 1.4 nm
Length: 2-5 μm
Purity: 50-70%
Manufacture: CarboLex, IN

CVD-SWCNT Number Weighted Size Distribution

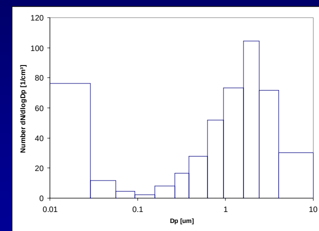
dp≤100 nm: 30%



Sample: CVD-SWCNT
Grade: LC
Diameter: 1.2-1.5 nm
Length: 0.5-3 µm
Purity: 50-70%
Manufacture: Helix, TX

HiPco-SWCNT Number Weighted Size Distribution

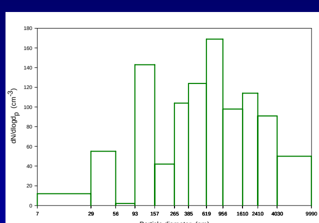
dp≤100 nm: ~3%



Sample: HiPco-SWCNT
Grade: AP
Diameter: 0.8-1.2 nm
Length: 0.1-1 µm
Purity: 65%
Manufacture: CNI, TX

CVD-DWCNT Number Weighted Size Distribution

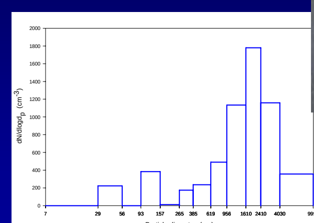
dp≤100 nm: < 20%



Sample: CVD-DWCNT
Grade: HP
Diameter: < 5 nm
Length: 0.5-40 µm
Purity: 90%
Manufacturer: Helix, TX

CVD-MWCNT Number Weighted Size Distribution

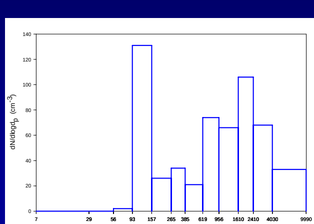
dp≤100 nm: < 5%



Sample: CVD-MWCNT
Grade: Short
Diameter: < 10 nm
Length: 1-2 µm
Purity: 95%
Manufacture: Helix, TX

CVD-MWCNT Number Weighted Size Distribution

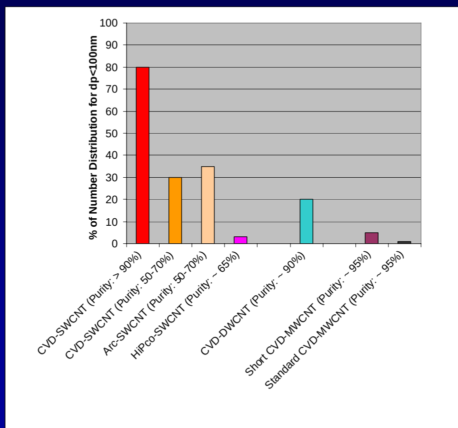
dp≤100 nm: 1%



Sample: CVD-MWCNT
Grade: Standard
Diameter: < 10 nm
Length: 0.5-40 µm
Purity: 95%
Manufacture: Helix, TX

Number Weighted 'Nano-size' Fraction of Airborne Unrefined Carbon Nanotubes

CNT Type	Grade	Manufacture Method	Manufacturer	Purity	Diameter (nm)	Length (µm)	Number Distribution for d_p < 100nm
Single-walled	HP	CVD	Helix, TX	>90%	<2	0.5-40	80%
Single-walled	AP	Arc	Carbolex, IN	50-70%	1.4	2-5	35%
Single-walled	AP	CVD	Helix, TX	50-70%	1.2-1.5	0.5-3	30%
Single-walled	AP	HiPco	CNI, TX	65%	0.8-1.2	0.1-1	3%
Double-walled	AP	CVD	Helix, TX	90%	<5	0.5-40	20%
Multi-walled	Short	CVD	Helix, TX	95%	<10	1-2	5%
Multi-walled	Standard	CVD	Helix, TX	95%	<10	0.5-40	1%

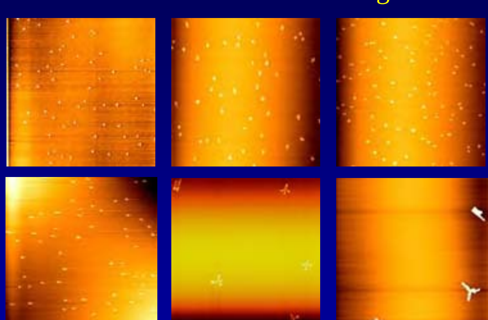


Integrated Screen Diffusion Batteries (ISDB)

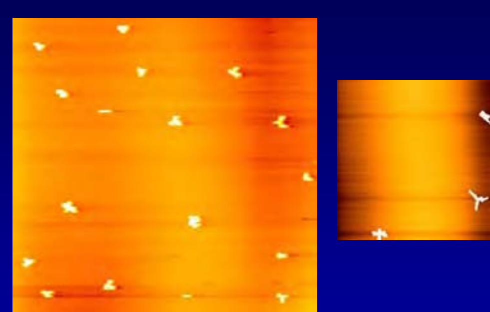
- This portable device was developed for collecting time-integrated samples of nano-sized particles, based on diffusional collection of particles on filtering elements and walls of a round tube (2 cm in diameter).
- The filtering elements used in this study are stainless steel wire screens in different mesh sizes (60 – 440).
- On the walls of the tube, between the filtering elements there are recessed slots for duplicate detectors. Mica discs were used as collectors.
- The sample collected on the mica discs can be analyzed directly by AFM.

- When particles are sampled into the tube the smallest particles, with highest diffusion coefficients, are collected first. Increasing number of bigger particles will be collected by the subsequent filtering elements.
- The collection efficiencies of the wire screens are calculated from equations presented by Cheng et al. (Cheng and Yeh 1980, Cheng et al. 1980, 1985).
- Particle size dependent deposition efficiency on the substrate is calculated with an equation developed by Ingham (1975).
- Particle size distributions are calculated using the Extreme Value Estimation deconvolution program (Paatero 1990).

AFM Images of a CVD-SWCNT Sample Collected on the Walls of a 6-stage ISDB



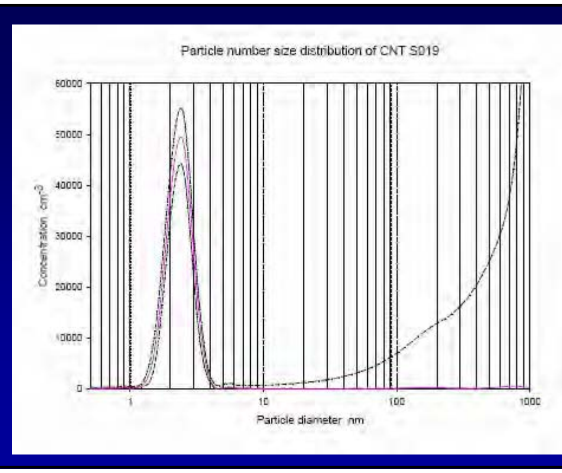
(Non-contact mode; Scan size: 25μm x 25μm,).



Non-contact mode AFM image of CVD-SWNT samples (HP grade, Helix,TX) on mica disc placed on the wall of ISDB stage 6: (a) 100μm x 100μm (b) 25μm x 25μm.

Counts of Particles Collected on the Wall of Each ISDB Stage

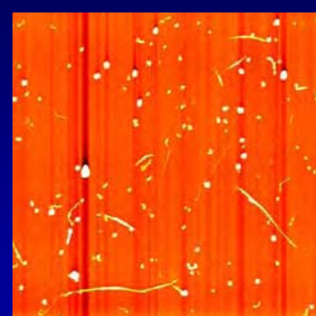
Stages	Particle Counts/10000μm2	
	mean	s.d.
1	1120	242
2	1584	156
3	1520	171
4	1000	102
5	76	7
6	46	13



Characterization of CNTs

- Sample Collection: ELPI (on Aluminum Discs placed on each stage) or ISDB (wire screens).
- Sample Analysis: Atomic Force Microscopy.
- Sample Preparation: Deagglomeration of samples by applying appropriate surfactant/solvent and sonication.

AFM Image of Deagglomerated SWCNT Samples



29 μg/ml CVD-SWCNT (HP grade, Helix, TX) deagglomerated by DMF [Scan size: 5μm x 5μm].

Summary of Experimental Results

- All common types of unrefined CNTs including single-walled, double-walled and multi-walled nanotube samples can be dispersed into air to a significant extent due to agitation.
- The sizes of particles generated from all CNT types are widely distributed across 13 stages of ELPI, ranging from 7 nm to 10 μm. The size distributions vary with the type and the nature of bulk materials.

- For HP grade CVD-SWCNT, majority of particles are in the nano-size region (< 100nm) based on the ELPI data. There is also a significant portion of particles found in the single-nanometer range based on the data collected by ISDB.
- Airborne CNT particles are highly agglomerated; no single tubes or simple ropes were observed by AFM in the original samples collected by ELPI or ISDB before treatment with surfactants.

Implications

- Carbon nanotubes can become airborne and expose workers through inhalation or dermal contact during the processes of manufacturing and handling.
- The size distributions of CNTs are wide and source dependent.
- As deposition efficiency and sites of inhaled particles within the respiratory system largely depends on particle size, the deposition pattern of agglomerated nanoparticles should be similar to those larger equivalent sized non-agglomerated particles.

- Particles depositing on/in the deep lung surfaces of the bronchioles or alveoli will contact pulmonary surfactants in the surface hypophase and the agglomerated CNTs are likely to (ultimately) be de-agglomerated.
- Investigations that define CNTs should take into account the full size range of particles to which humans are likely to be exposed.
- Adequate monitoring methods need to be established for quantification and characterization of these new types of materials in order to evaluate the worker's exposure levels and hence the potential health risks.

On-going Studies

- Developing a quantitative sample treatment method for AFM analysis that can effectively deagglomerate samples by applying appropriate surfactants, solvent, and sonication.
- Exploring other advanced AFM technologies that may be better suited for CNT characterization, such as, Conductive-AFM and Phase Imaging.
- Developing a validated field sampling method for airborne CNT particles in workplaces.

Acknowledgements

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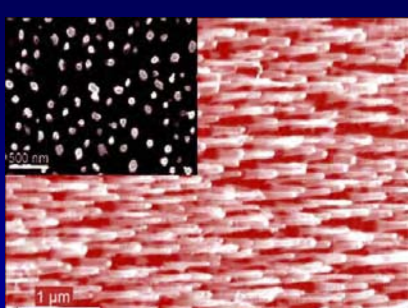

This image from NASA-Ames shows an American flag made from carbon nanotubes using a plasma carbon vapor deposition technique.

The stripes are side views of the tubes which measure one micron in length. The "stars" against the blue field are the nanotubes viewed from the top.

Thank You!

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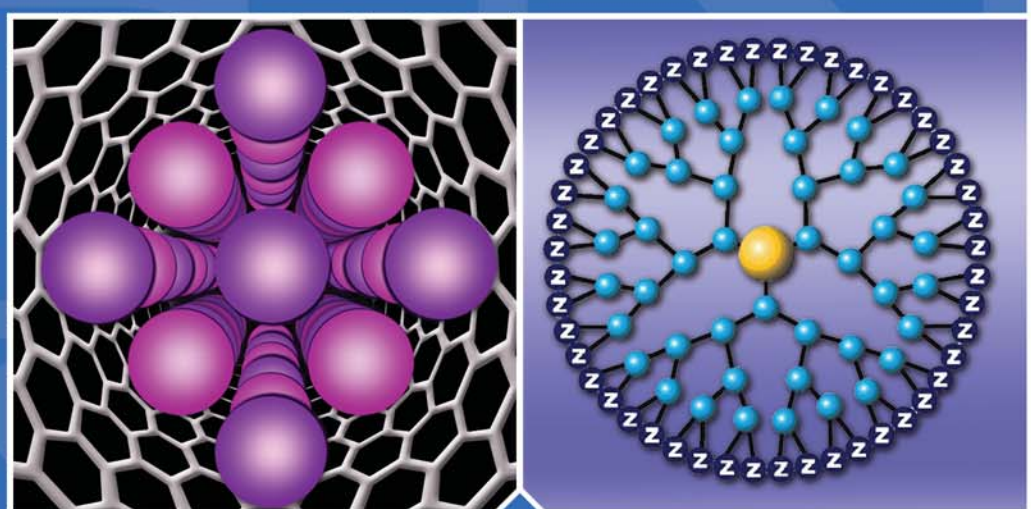

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