Release characteristics of single-wall carbon nanotubes during manufacturing and handling

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Abstract. We investigated the release characteristics of single-wall carbon nanotubes (CNTs) synthesized by a pilot-scale plant. In addition to on-site aerosol measurements at the pilot-scale plant where the CNTs were synthesized, harvested, and packed, we conducted dustiness tests by vortex shaking and by transferring CNTs from one bowl to another. In the results of the on-site aerosol measurements, slight increases in the concentration were observed by aerosol monitoring instruments in the enclosure where CNTs were harvested and packed. In filter samples collected in this enclosure, micron-sized CNT clusters were observed by electron microscopy analysis. For samples collected outside the enclosure or during other processes, no CNTs were observed. The concentrations of elemental carbon at all locations were lower than the proposed occupational exposure limits of CNTs. The results of the dustiness tests revealed that submicron-sized particles were dominant in the number concentration measured by aerosol monitoring instruments, whereas micron-sized CNT clusters were mainly observed by electron microscopy analysis. The results of dustiness tests indicate that these CNTs have a low release characteristic. The lower drop impact of CNT clusters due to their lower bulk density resulted in lower CNT release from falling CNTs.

1. Introduction

Although carbon nanotubes (CNTs) have unique properties that make them potentially useful in many applications, there is growing concern regarding their potential impact on health. At present, workers (and researchers) involved in CNT manufacture and handling are potentially exposed to elevated levels of CNTs, mainly through inhalation. Recently, occupational exposure limits of airborne CNTs have been proposed [1-5]. Information on airborne CNT release, such as the magnitude, size distribution, and morphology of airborne CNTs, is required in order to evaluate and control CNT exposure.

In a previous study [6], we conducted on-site aerosol measurements at a research laboratory where a relatively small amount of single-wall CNTs were synthesized and handled. Recently, a pilot-scale plant has started the production of CNTs at a rate of 600 g/day, and the supply of CNT samples has accelerated the development of new applications. In this study, we investigated the release characteristics of single-wall CNTs synthesized by the pilot-scale plant. In addition to on-site aerosol measurements at the pilot-scale plant, we conducted dustiness (emission) tests by vortex shaking [7-8] and by transferring CNTs from one bowl to another.

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2. Methods

2.1. Materials
CNTs were synthesized using the water-assisted chemical vapor deposition (CVD) method, which resulted in the massive growth of superdense and vertically aligned nanotube forests with heights of up to a few millimeters [9]. These can be easily separated from the catalysts on the substrate, providing nanotube material with a carbon purity of 99.9%. The outer diameter of the CNTs is approximately 3 nm. The specific surface area (using the Brunauer, Emmett, and Teller (BET) N2 adsorption method) is around 1000 m²/g.

2.2. On-site aerosol measurements at the pilot-scale plant
We performed on-site aerosol measurements at the pilot-scale plant where CNTs were synthesized, harvested, and packed.

CNTs were synthesized using a continuous reactor in which a series of synthesis processes were carried out along a conveyor belt. After the synthesis of CNTs, substrates (50 × 50 cm in size) with a few grams of CNTs emerged from the reactor along the conveyor belt. Subsequently, these were placed into a case by an automatic operation. The outlet of the reactor and its surroundings (including the conveyor belt and case) were enclosed, and there were local ventilation exhaust ports to purge air from the enclosure. During the on-site aerosol measurements, the case containing the substrates with synthesized CNTs was taken out from the enclosure twice, after 27 and 7 substrates of CNTs were synthesized.

In another enclosure, the synthesized CNTs were harvested from the substrates and were placed in a plastic bag by an automatic operation. During the on-site aerosol measurements, after 27 substrates of CNTs were harvested, the enclosure was opened once and the bag was sealed and taken out from the enclosure. Subsequently, 17 substrates of CNTs were harvested.

During the synthesizing, harvesting, and packing processes, the aerosol particles inside the enclosures, outside the enclosures (at a distance of approximately 50 cm from the opening of the enclosure), and at the center of the room (at a distance of several meters from the opening of the enclosures) were measured using three sets of portable real-time aerosol monitoring instruments. These included a condensation particle counter (CPC, model 3007, TSI Inc., USA, number concentration of aerosol particles with the size range between ~10 to >1000 nm), an optical particle sizer (OPS, model 3330, TSI Inc., USA, number concentration of aerosol particles with the size range between 300 to 10000 nm in optical diameter, 16 channels), a light-scattering laser photometer (LP, DUSTTRAK II, model 8530, TSI Inc., USA, mass concentration of aerosol particles) with a cyclone for respirable dust (GS-3 Multiple-inlet Cyclone; 4 µm particles are cut by 50% at 2.75 L/min; SKC Inc., USA), and a black carbon monitor (BC, microAeth, model AE51, AethLabs, USA, mass concentration of aerosol black carbon). The sampling flow rates of the CPC, OPS, LP, and BC were 0.7, 1.0, 2.75, and 0.1 L/min, respectively. The relative responses of the LP and BC to the mass concentration of the CNTs synthesized in this plant were 1.2 and 0.23, respectively [10].

In addition to real-time aerosol monitoring, the aerosol particles were collected on quartz fiber filters (37-mm diameter, 2500 QAT-UP, PALL Corporation, USA) with/without a cyclone for respirable dust (GS-3 Multiple-inlet Cyclone). The quantities of elemental carbon in respirable and total dust were measured by a carbon analysis (see section 2.6). The sampling flow rates of the respirable and total dust sampling were set at 2.75 and 3.0 L/min, respectively.

Aerosol particles were also collected on Nuclepore membrane filters (25-mm diameter, 0.080-µm pore size, Nomura Micro Science Co., Ltd., Japan) with a stainless steel filter holder at a sampling flow rate of 0.5 L/min for scanning electron microscopy (SEM) analysis.

2.3. Dustiness tests by vortex shaking
Dustiness tests were conducted by vortex shaking [7-8]. Approximately 1 cm³ of nanomaterial was placed in a test tube having an outer diameter of 25 mm and a length of 20 cm and agitated using a
laboratory vortex shaker (Cole-Parmer Instrument Co., Vortex Genie 2 Shaker), as shown in figure 1. Aerosol particles released during agitation with clean air passing through the test tube were continuously measured. Conductive silicone tubing was used to transmit the particles to the measuring instruments.

The aerosol particles were measured using the CPC, OPS, LP, a scanning mobility particle sizer (SMPS, model 3936L72, TSI Inc., USA, number concentration of aerosol particles with the size range between 14 to 400 nm in electrical mobility diameter, 64 channels/decade), and an aerodynamic particle sizer (APS, model 3321, TSI Inc., USA, number concentration of aerosol particles with the size range between 500 to 20000 nm in aerodynamic diameter, 32 channels/decade). The sampling flow rates of the CPC, OPS, LP, SMPS, and APS were 0.7, 1.0, 2.5, 1.0, and 5.0 L/min, respectively. The sheath flow rate of the SMPS was 3 L/min. The SMPS up-scan time and retrace time were 160 s and 15 s, respectively, and the SMPS data were saved at 3-min intervals by one scan. A cyclone (SKC aluminum cyclone; 4 µm particles are cut by 50% at 2.5 L/min; SKC Inc., USA) was connected to the inlet of the LP to obtain the concentration of respirable dust.

The aerosol particles were also collected on Nuclepore membrane filters at a sampling flow rate of 0.3 L/min for SEM analysis.

2.4. Dustiness tests by transferring CNTs

In an acrylic glove box with an inflow of air through a high efficiency particulate air (HEPA) filter, we repeatedly transferred approximately 100 cm³ of CNTs from one bowl to another, as shown in figure 2. The majority of the inner surface of the glove box was lined with aluminum foil for static protection.

The aerosol particles were measured using the CPC, OPS, LP, and SMPS. The sampling flow rates of the CPC, OPS, LP, and SMPS were 0.7, 1.0, 2.75, and 1.0 L/min, respectively. A cyclone (GS-3 Multiple-inlet Cyclone) was connected to the inlet of the LP to obtain the concentration of respirable dust. Conductive silicone tubing was used to transmit the particles to the measuring instruments.

Aerosol particles were also collected on Nuclepore membrane filters at a sampling flow rate of 0.3L/min for SEM analysis.

2.5. SEM analysis

The aerosol particles collected on the Nuclepore filters were observed using a field-emission scanning electron microscope (SEM, S-4300, Hitachi High-Technologies Corporation, Japan) under an accelerating voltage of 3 kV. Prior to sample collection, the filters were coated with platinum-palladium (approximately 2 nm) to avoid image charging.
2.6. Carbon analysis
The CNT mass on the quartz fiber filter was quantified as a quantity of elemental carbon using an organic and elemental carbon (OC/EC) analysis instrument (CAA-202M-D, Sunset Laboratory Inc., USA) based on the NIOSH 5040 method (however, optical pyrolysis correction was not used).

3. Results and discussion

3.1. On-site aerosol measurements at the pilot-scale plant
While ethylene gas was being used for the synthesis of CNTs, unreacted ethylene gas in the exhaust was burned in the upper portion of the reactor. During that time, increases in the number concentrations were observed by the CPCs at all locations. These increases could have been a result of the particles emitted by a combustion process, such as soot and condensation particles, as combustion processes are commonly accompanied by the emission of nanoparticles.

Slight increases in the concentration of aerosol particles in the enclosures were observed by the aerosol monitoring instruments when the first substrate with synthesized CNTs emerged from the reactor (<2 particles/cm³ with the OPS and <2 µg/m³ with the LP) and when CNTs were being harvested and packed (<30 particles/cm³ with the CPC, <2 particles/cm³ with the OPS, <10 µg/m³ with the LP, and <1 µg/m³ with the BC). No distinct increase associated with the work was observed in the concentration of aerosol particles outside the enclosures.

In filter samples collected in the enclosure during the harvesting process, elemental carbon was significantly detected (but at levels less than the quantitation limit) through carbon analysis (table 1), and micron-sized CNT clusters were observed by SEM analysis (figure 3). For samples collected outside the enclosures or during other processes, elemental carbon was not significantly detected and no CNTs were observed. The concentrations of elemental carbon at all locations were lower than the occupational exposure limits of airborne CNTs proposed by the National Institute for Occupational Safety and Health (NIOSH), US (7 µg/m³) [2] and the National Institute of Advanced Industrial Science and Technology (AIST), Japan (30 µg/m³) [3].

| Table 1. Mass concentration of elemental carbon at the pilot-scale plant (µg/m³). |
|---------------------------------------------------------------|
| Respirable dust³ | Total dust³ |
| Synthesizing CNTs (inside enclosure) | <2.3 | <2.1 |
| Synthesizing CNTs (outside enclosure) | <2.3 | <2.1 |
| Harvesting and packing CNTs (inside enclosure) | <1.2 | (2.1) |
| Harvesting and packing CNTs (outside enclosure) | <1.2 | <1.1 |
| The center of the room | <0.56 | <0.55 |

³ The values preceded by '<' are the concentrations that are below the detection limit. The values in parentheses are the concentrations that are below the quantitation limit.
3.2. Dustiness tests by vortex shaking

The number concentration of particles, with a diameter of approximately 10–1,000 nm, as measured by the CPC, was 2.1 particles/cm$^3$, whereas the mass concentration of respirable dust measured by the LP was 1.6 µg/m$^3$ (mean values from 1 min to 31 min after commencement of agitation, $n = 3$). These concentrations were considerably lower than those of most other nanomaterials [8], indicating that these CNTs have a lower release characteristic.

The number-based particle size distribution for emitted particles is shown in figure 4. Submicron-sized particles were dominant in the number concentration measured by aerosol monitoring instruments.

SEM images of emitted particles in dustiness tests are shown in figure 5. Micron-sized CNT clusters were mainly observed.
Figure 4. Number-based particle size distribution for emitted particles in dustiness tests by vortex shaking. Mean values from 1 min to 31 min after commencement of agitation (n = 3). The particle sizes are expressed in terms of electrical mobility diameter for the SMPS result, optical diameter for the OPS result, and aerodynamic diameter for the APS result.

Figure 5. SEM images of emitted particles in dustiness tests by vortex shaking.
3.3. **Dustiness tests by transferring CNTs**

Figure 6 shows the changes in the concentrations during the transfer of CNTs, as measured by the CPC, OPS, and LP. Only slight increases in the concentration of aerosol particles were observed (<10 particles/cm³ with the CPC, <1 particles/cm³ with the OPS, and <10 µg/m³ with the LP). The lower drop impact of CNT clusters due to their lower bulk density resulted in lower CNT release from falling CNTs. For the LP result, a gradual elevation of the concentration was seen. The fact that the elevated concentration was not recovered even when a HEPA filter was connected to the inlet of the LP explained that this elevation was caused by the zero-point shifting of the LD response.

![Figure 6](image-url)

**Figure 6.** Changes in the concentrations of emitted particles during the transfer of CNTs.

- **a** CNTs were dropped from one bowl at a height of approximately 30 cm to another
- **b** CNTs were poured directly from one bowl to another
The number-based particle size distribution for emitted particles during the transfer of CNTs, as measured by the OPS, together with those from harvesting and packing and vortex shaking, are shown in figure 7. The patterns of particle size distributions measured by the OPS were similar to each other. Meanwhile, the reliable particle size distribution could not be obtained from the SMPS data during the transfer of CNTs due to the low concentration.

For the filter sample collected during the transfer of CNTs, as with those collected during harvesting and packing and vortex shaking, micron-sized CNT clusters were observed by SEM analysis.

![Figure 7. Number-based particle size distributions for emitted particles in harvesting and packing, vortex shaking, and transferring of CNTs measured by OPS. The particle sizes are expressed in terms of optical diameter. For the harvesting and packing results, background concentration has been subtracted.](image)

4. Conclusions
We investigated the release characteristics of single-wall CNTs synthesized by the pilot-scale plant. In the results of on-site aerosol measurements, an obvious release of CNTs was only seen in the enclosure where CNTs were harvested and packed. For the filter sample collected in this enclosure, micron-sized CNT clusters were observed by SEM analysis. The concentrations of elemental carbon at all locations including the inside and outside of the enclosures were lower than the occupational exposure limits of airborne CNTs proposed by US NIOSH (7 µg/m³) and AIST, Japan (30 µg/m³).

The results of dustiness tests revealed that submicron-sized particles were dominant in the number concentration measured by aerosol monitoring instruments, whereas micron-sized CNT clusters were mainly observed by SEM analysis. The results of dustiness tests indicate that the CNTs have a lower release characteristic. The lower drop impact of CNT clusters due to their lower bulk density resulted in lower CNT release from falling CNTs.

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