In-Depth Survey Report

Assessment of Nanoparticle Emissions from a Chemical Laboratory using Carbon Nanotubes

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Abstract

The National Institute for Occupational Safety and Health Engineering and Physical Hazards Branch and the University of Massachusetts Lowell (UMass Lowell) Environmental Health and Safety Team assessed nanoparticle emissions in a chemical laboratory at UMass Lowell. The laboratory conducted bench-top scale product development using 20-30 nm diameter bundles of single-walled carbon nanotubes (CNTs). The tasks evaluated in this study included weighing, mixing, sonicating, coating, drying, and cutting, which are common activities in most research and commercial production facilities. Weigh-out, mixing, and sonication were conducted on the bench-top without engineering controls, while coating, drying, and cutting were conducted inside a fume hood or a ventilated enclosure. The study results provide information on exposure potential and control for common nanomanufacturing processes.

The research teams used direct-reading instruments to monitor the tasks in real time and collected filter samples to characterize released nanomaterials by microscopy and chemical analysis. Particle emissions can be identified by comparing the aerosol concentrations at source and in the personal breathing zone (PBZ) with background data. Most of the elemental carbon (EC) concentrations obtained from filter samples in this study were estimated values due to low mass (between the lower limit of detection and the limit of quantification) collected from short sampling times. All samples were within the range of EC concentrations observed in urban environments (0.6 ± 0.72 µg/m^3), and below the NIOSH proposed recommended exposure limit (REL). At the time of publication of this report, the NIOSH proposed REL for CNTs is 7 µg/m^3.

No meaningful particle releases were identified by the direct-reading instruments or filter sampling during CNT weigh-out without control measures. However, handling nanomaterials in dry powder form has been identified as a task that commonly results in worker exposure [Brouwer 2010; Dahm et al. 2012; Methner et al. 2010]. A ducted enclosure equipped with high efficiency particulate air (HEPA) filters is recommended to protect the operator during nanomaterial handling.

Following the weigh-out, CNTs were mixed with a solution and dispersed by bath and probe sonication in an open beaker. The task of probe sonication increased EC concentrations at the source to nearly twice as high as background (0.46–0.79 µg/m^3). Transmission electron microscopy (TEM) analysis identified CNT clusters in micro size from the sample collected by the ESPnano electrostatic precipitator after probe sonication. However, only

one CNT was observed by TEM on the filter sample collected in the PBZ and none were found on the filter sample taken at the source. The inconsistent findings between the EC and TEM results could be interpreted as low mass collected on filters. It can be cautiously concluded that the task of probe sonication possibly released nanomaterials into the laboratory and posed a risk of surface contamination. Based on these results, the sonication of CNTs should be conducted inside a ventilated enclosure, such as a fume hood, to minimize the potential for worker exposure.

The tasks of spin coating and substrate cutting were performed in a conventional fume hood and a ventilated enclosure, respectively. According to the EC and TEM data, the fume hood running at a high face velocity, around 171 cm/sec (337 ft/min), prevented particle emissions from the spin coating process. The ventilated enclosure was operated at a lower face velocity, around 100 cm/sec (51 ft/min), during the cutting of the CNT-coated substrates. TEM data confirmed that carbon fibers could be generated from cutting the substrate. However, EC results for the cutting task were confusing: a high EC concentration (2.63 µg/m^3) was found in the PBZ but was not detectable near the source or at the background sampling locations.

Introduction

Background

The National Institute for Occupational Safety and Health (NIOSH) Engineering and Physical Hazards Branch (EPHB) has conducted a series of field investigations to evaluate and document effective control techniques for potential health hazards in the nanomanufacturing industry. Another purpose of these studies is to create a more general awareness of the need for or availability of effective control measures to reduce airborne nanomaterials in the workplace. This field study was conducted by NIOSH researchers from EPHB, collaborating with the University of Massachusetts Lowell (UMass Lowell).

The purpose of this study is to assess nanomaterial emissions from product development activities in a chemical laboratory. The laboratory uses microns long, 20 nm diameter bundles of single-walled carbon nanotubes (CNTs) to develop innovative coating materials. Because the studied activities are at a bench-top scale, usually involving only one operator, engineering controls are only used for certain activities (e.g., spin coating and substrate cutting). Real-time aerosol measurements and filter samples for off-line chemical analysis and microscopy inspection were collected to identify nanomaterial emissions and exposures from the activities. This report summarizes the results and findings that address the control of exposure to nanomaterials to workers in a research/laboratory facility.

Potential Health Effects

CNTs are the main nanomaterials used for predetermined research and development activities at the studied laboratory. A review report from the Institute of Occupational Medicine has identified many similarities between asbestos and high aspect ratio nanoparticles (HARN) [Tran et al. 2008]. Asbestos fibers have been classified by the International Agency for Research on Cancer as carcinogenic for humans. This suggests that HARN (e.g., CNTs) could have similar characteristics as pathogenic fibers. From animal in vivo exposure studies and cell-culture-based in vitro experiments, toxicological research on CNTs has shown that these nanomaterials at high doses can contribute to fibrotic lung response, inflammation, and granulomas, and can induce oxidative stress and cellular toxicity. Summary reports of risk assessment of CNTs are available to the public [Kobayashi et al. 2009; Nanoceo 2011; SWA 2009].

A review of published studies provides some information on the potential for health effects due to exposure to CNTs:

1) Cytotoxicity order: Asbestos, recognized as carcinogenic to humans, has less toxicological effects than single-walled CNTs (SWCNTs) but is more toxic than multi-walled CNTs (MWCNTs) [Inoue et al. 2008; Jia et al. 2005; Murr et al. 2005; Tian et al. 2006].
2) CNT purification: Purified CNTs are more toxic than their unrefined counterparts [Carrero-Sánchez et al. 2006; Wick et al. 2007]. Moreover, the cytotoxicity of purified MWCNTs can be increased to be more toxic than asbestos [Muller et al. 2005].
3) Surface area and surface chemistry of CNTs: Tian et al. [2006] has found that the material with the smallest surface area (SWCNTs in this case) is more toxic than other tested materials. Their results also give a good explanation for the effect of CNT purification: the refining process changes the aggregation state of CNTs and then modifies the surface chemistry.
4) CNT structure: Long MWCNTs exhibit asbestos-like hazards, but short and tangled MWCNTs do not show any significant toxicity [Poland et al. 2008]. The presumption of the risk associated with long CNTs is that macrophages cannot completely engulf (or phagocytose) long fibers to clear them from tissues; however, effective phagocytosis is completed for short or tangled CNTs to clear them through the lymphatic system [Kostarelos 2008].

Due to their wide market applications, the rate or incidence of adverse effects on occupational safety and health from exposure to CNTs could potentially increase. In 2008, the U.S. Environmental Protection Agency formally issued a notice to CNT manufacturers to show its intention to consider CNTs as new chemicals and therefore to regulate the manufacturing of CNTs under the Toxic Substances Control Act (TSCA). Meanwhile, NIOSH provided interim guidance about specific medical screening for workers exposed to engineered nanoparticles including SWCNTs [NIOSH 2009].

Published Regulations

Currently, no regulatory occupational exposure limit (OEL) for engineered nanomaterials exists, but the Occupational Safety and Health Administration (OSHA) recommends that worker exposure to respirable carbon nanotubes and carbon nanofibers not exceed 7.0 micrograms per cubic meter ($\mu g/m^3$)

as an 8-hour time-weighted average, based on the NIOSH proposed Recommended Exposure Limit (REL) [NIOSH 2010; OSHA 2013].

OSHA's 8-hour time-weighted average permissible exposure limit (PEL) and the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for carbon black is 3.5 milligram per cubic meter (mg/m^3) [ACGIH 2011; OSHA 2006]. The British Standards Institution (BSI) recommended a benchmark exposure level of 0.01 fiber per milliliter (fiber/mL) for insoluble fibrous nanomaterials (e.g., carbon nanotubes and nanowires) [BSI 2007].

In the absence of governmental or consensus guidance on exposure limits, some manufacturers have developed suggested OELs for their products. For example, Bayer has established an OEL of 0.05 mg/m^3 for Baytubes® (MWCNTs) [Bayer MaterialScience 2010]. For Nanocyl CNTs, the no-effect concentration in air was estimated to be 2.5 µg/m^3 for an 8-hr/day exposure [Luizi 2009].

Plant and Process Description

General Processes

This research laboratory is using single-walled CNTs to develop innovative coating materials. The CNTs are in the form of a nonwoven mesh of fiber bundles that are microns long and 20-30 nm in diameter. Each bundle is composed of tightly packed fibrils made of individual CNTs. The preparation of the CNT solution began with weighing CNTs, mixing them with solvents, and dispersing CNTs throughout the solution by sonication and centrifugation. The laboratory used two different methods to deposit CNTs on substrates: dip coating or spin coating. For dip coating, the substrate is dipped into the prepared CNT solution, while spin coating involves dispensing a drop of the CNT solution on top of the substrate and spreading out the solution on the surface using a spinning machine. Following coating, the CNT-coated substrates were moved to a hot plate for drying inside a fume hood. Table 1 summarizes the processes required to prepare CNT-coated substrates as well as the equipment and control measures used for each activity. Following the completion of drying, the prepared CNT-coated substrates were cut inside a ventilated enclosure.

The task of weighing CNT powders was performed in an enclosed balance (Figure 1) on a laboratory table. After weigh-out, the CNTs were transferred into a beaker where solvents in wash bottles were carefully added into the beaker for initial mixing. The CNT solution was further dispersed in a closed vial with bath sonication (Fisher Scientific, Waltham, Massachusetts, Model FS30H) for 20 minutes and later in a beaker with probe sonication (Fisher Scientific Sonic Dismembrator, Model 550) for different processing times, depending on the following coating process. To cool down the solution heated by high energy sonication, the beaker containing the CNT solution was put inside a larger beaker filled with cold water. The probe sonication process usually was paused every 20 minutes to allow the cooling water to be replaced to keep the CNT solution at an acceptable temperature. The preparation of the CNT solutions with probe sonication required 40 or 60 minutes. The last step of preparing the CNT solution was to put the solution in a closed vial and use a tabletop centrifuge for final mixing.

The laboratory used two methods to produce CNT-coated substrates. Substrates with uniform CNT coating were obtained by dipping clean substrates (5cm × 5cm) into the prepared CNT solution for a short time. Spin coating was used to generate multiple layers of CNT coating on substrates. The task of spin coating was performed inside a conventional fume hood (Figure 2). A pipette was used to dispense measureable drops of the CNT solution on top of the substrate fixed to the spin equipment. A drop of the CNT solution took 80 seconds to spread a single layer of nanomaterials on the substrate. The final step of the process was to dry the CNT-coated substrates on hot plates inside a fume hood.

Control Measures

As summarized in Table 1, the preparation of the CNT solution was conducted on the bench-top without engineering controls in place. Conventional chemical fume hoods were used for the tasks of spin coating and substrate drying during the process of preparing CNT-coated substrates. The spin coating equipment (Specialty Coating System Inc., Indianapolis, Indiana, Model P6712) was located on the right-hand side inside the fume hood (Figure 2). The fume hood was connected to the building exhaust system and had a constant exhaust flow rate. The fume hood had two movable sashes to adjust the front open space. During spin coating, the right sash was kept at the indicated design height, while the left sash, which was kept at a lower position, provided less open face area. This arrangement created an opening of 55 cm on the right front and 40 cm on the left. The total width of the fume hood was 210 cm. A similar fume hood with a single sash was used for the task of substrate drying.

The post-processing of CNT-coated substrates (i.e., substrate cutting) was performed in a ventilated enclosure (Labconco Corporation, Kansas City, Missouri, Labconco Xpert Nano Enclosure) (Figure 3). The enclosure had a constant face area—85 cm wide and 22 cm high—and exhausted contaminated air through the building exhaust system.

Methodology

Ventilation Measurement

To evaluate the fume hood (Figure 2) and the ventilated enclosure (Figure 3), hood face velocities were measured using a hotwire anemometer (TSI, Inc., Shoreview, Minnesota, TSI VelociCalc plus Model 8386). These measurements were made by placing the anemometer perpendicular to the hood or enclosure faces and recording the face velocities. For the laboratory fume hood, air velocity measurements were made at eight equally spaced locations across the middle of the hood face for each side. Overall, 16 measurements (8 on each side) were collected for evaluating containment and hood exhaust air flow rate. For the enclosure, only eight equally spaced air velocity measurements were made across the enclosure face.

Aerosol Measurements

A variety of direct-reading instruments were used to identify emission sources by monitoring airborne aerosol concentrations from the laboratory activities, and to assess the existing engineering controls by comparing particle concentrations at the source and in the personal breathing zone (PBZ). Instruments that allowed the characterization of particles across a broad size range were used to evaluate primary and agglomerated nanoparticles in the laboratory environment. The Aerodynamic Particle Sizer (APS) Spectrometer 3321 (TSI, Inc., Shoreview Minnesota) provides real-time size distributions of larger particles ranging from 0.5 to 20 µm. It is useful to detect nanoparticle agglomerates during nanomaterial handling. To monitor small airborne particles less than 0.5 µm in this field study, the Fast Mobility Particle Sizer (FMPS) Spectrometer 3091 (TSI, Inc., Shoreview, Minnesota) was chosen because of its high response rate (1 second) and high sampling flow rates (10 liters per minute) to minimize diffusion losses of ultrafine nanoparticles. The FMPS can measure size distributions of particles from 5.6 to 560 nm in real-time mode. A hand-held Condensation Particle Counter (CPC) 3007 (TSI, Inc., Shoreview, Minnesota) was used to provide instantaneous total number counts of particles from 0.01 to 1.0 µm in size. Finally, the DustTrak Aerosol Monitor 8533 (TSI, Inc., Shoreview, Minnesota) can simultaneously measure both mass and size fractions of particles in a wide size range, from 0.1 to 15 µm.

For this study, two sets of identical direct-reading instruments—including the APS, FMPS, CPC, and DustTrak—were used to monitor particle release from the laboratory activities: one for the potential emission sources and the other for the worker's PBZ. These instruments were mounted on mobile carts to allow their conductive plastic sampling ports to be positioned at preferred locations (i.e., sources and PBZ) during various tasks (listed in Table 1).

Filter Sampling

Filter-based air samples were collected using air sampling pumps (SKC Inc., Eighty Four, Pennsylvania, Universal XR Model PCXR4) for elemental carbon analysis and microscopy. All pumps were calibrated before and after sampling. The pumps operated at flow rates of approximately 4.0 liters per minute. In parallel to the real-time aerosol monitoring, task-based filter samples were collected at the production source and in the PBZ for the duration of the task being evaluated. To obtain background air quality, area samples were collected in the general area of the laboratory during weighing and sonication on March 20, in the general room area for spin coating on March 21, and in the general room area for substrate cutting on March 22.

To determine the airborne mass concentration of elemental carbon (EC), air samples were collected on 25-mm-diameter, open-face quartz fiber filters and analyzed according to NIOSH NMAM 5040 for Elemental Carbon (diesel particulate) using Evolved Gas Analysis by thermal-optical analyzer [NIOSH 2003]. All sample results for the 25-mm cassettes are based on an effective sampling area of 3.46 cm^2.

Alongside each mass-based air sample, an additional air sample was collected on a 25-mm-diameter, open-face mixed cellulose ester filter and analyzed for CNTs using transmission electron microscopy (TEM) with energy dispersive spectroscopy (EDS) in a manner similar to NIOSH NMAM 7402 [NIOSH 1994]. Three 3-mm copper TEM grids from each sample were examined at low magnification to determine loading and preparation quality. The counting protocol included the following rules: evaluation was stopped at 40 grid openings or 100 structures. TEM with EDS provides an indication of the relative abundance of nanostructures per volume of air, as well as other characteristics such as size, shape, chemical composition, and degree of agglomeration.

A hand-held electrostatic precipitator particle sampler (ESPnano, Spokane, Washington, ESPnano Model 100) was used to collect representative samples of airborne particles on its built-in TEM grids to be analyzed by electron microscopy. In this study, the samples from ESPnano were collected in parallel with the air filter samples for the monitored tasks.

Results

Air Flow around Fume Hood and Ventilated Enclosure

Both the fume hood and the ventilated enclosure were evaluated in the as used condition. As shown in Figure 2, the equipment and supplies were located inside the hood and blocked areas of the open face and exhaust grilles. However, no equipment was located inside the ventilated enclosure during testing. The face velocity results are summarized in Table 2 for the fume hood and in Table 3 for the ventilated enclosure.

The face velocity was highly variable across the fume hood opening due to the uneven sash heights and the blockage caused by equipment and supplies inside the hood. The overall average face velocity was 171 cm/sec (337 ft/min). The average face velocity at the right opening was ~20% higher than that at the left opening. The fume hood exhaust flow rate was estimated at 1.728 m^3/sec (3662 ft^3/min). Unlike the fume hood, the ventilated enclosure maintained a uniform face velocity of approximately 25.5 cm/sec (50 ft/min) with an estimated exhaust flow rate of 0.048 m^3/sec (101 ft^3/min).

Activity Monitoring

Direct-reading instruments did not identify major particle releases from the monitored processes that were in bench-top production scale. However, some findings from the probe sonication and spin coating processes still provided useful information for reducing potential occupational risks in scaling the processes from bench-top pilot to mass production.

Probe Sonication

As mentioned before, the probe sonication process needed to be paused every 20 minutes to replace the cooling water whose temperature was raised by high energy sonication. Two solutions were prepared for the probe sonication process in this study: Solution A for the dip coating and Solution B for the spin coating. The process times for preparing Solutions A and B were 40 and 60 minutes, which included a sequence of two and three 20-minute sonication procedures, respectively. Because the probe sonication was processed on an open bench with limited space, the instruments in use needed to be moved aside each time the operator replaced the cooling water and restarted the process.

The direct-reading instruments did not identify any major particle emissions from the probe sonication process, but the measurements indicated that the probe sonication process could generate micron-sized particles and cause work surface contamination (Figure 4). Because the sampling frequency of the CPC located at the source was accidentally set at a minute, no CPC data at source are shown in Figure 4-a and Figure 4-b for the tests done on March 20. This problem was corrected for the test of Solution B on March 21 (Figure 4-c). According to Figure 4, relocating the sampling probes to replace the cooling water during the tests could generate concentration spikes, and it was highlighted by a huge spike in Figure 4-b. Basically, all the particle concentration data presented the same pattern except those collected from the CPC at the source for the test on March 21 (Figure 4-c). The increased concentrations at the source detected by the CPC but not by the FMPS recommended that particles generated by high energy sonication were around micron sizes (>0.6 µm). Low risks of worker exposure to these micron-sized contaminants were expected, because the relatively low and stable particle concentrations were monitored at the PBZ rather than at the source.

The sampling probe of the ESPnano was located close to the top of the beaker, and contaminants were observed on the ESPnano sample probe after sonication (Figure 5). The contaminants on the ESPnano probe were collected on TEM grids by direct contact on the contaminants, and analyzed using TEM. As shown in Figure 6, micron-sized CNT clusters were identified on these samples. Using deionized water to dissolve these contaminants, CNTs were also identified as having been released from the beaker during probe sonication.

Aerosol samples were collected using ESPnano electrostatic precipitator and filter samplers. Nonfiber-structured particles were found in the aerosol samples collected by the precipitator as shown in Figure 7. Filter-based samples were collected during probe sonication on March 20 and 21. No CNTs were found on the quartz fiber filter samples for TEM analysis with the exception of 1 CNT found on the sample collected from the PBZ on March 21 (Figure 8). According to the TEM analysis, however, all the filter samples contained carbon nanoparticles.

The corresponding results of EC concentrations are summarized in Table 4. According to the tests for Solution B, higher EC concentrations were found at the production source (0.87−1.04 µg/m^3) than background (0.46−0.79 µg/m^3) and the PBZ (0−0.53 µg/m^3). The highest EC concentration (1.81 µg/m^3) was found at the PBZ for the test of Solution A on March 20, but the EC collected at the source was lower than the limit of detection (0.2 µg/sample). It was reported that the mean of observed EC concentrations from ambient air pollution over the United States is 0.60±0.72 µg/m^3 [Yu et al. 2004]. Therefore, the EC concentrations measured for the probe sonication process were all close to those observed from ambient air pollution, and below the NIOSH proposed REL of 7 µg/m^3.

The overall data collected from instruments and filter samples suggested that dissolving CNTs into the solvents with high-energy sonication equipment and no engineering controls poses a risk for worker exposure both through inhalation and dermal exposure from surface contamination. This contamination would be more significant for a similar task at the mass production scale.

Spin Coating

Spin coating of multiple layers on the substrate was evaluated to assess the potential for exposure during this task. For every layer, the operator dispensed a fixed amount of CNT solution (0.4 mL in this study) on the spinning substrate and waited 80 seconds to allow the solution to be spread on the substrate uniformly. The CNT solution for the next layer was then added after the coating process of the previous layer was finished. Ten layers of coating were applied during this process evaluation. The sampling location at the source was above the turn table of the spinning equipment inside the fume hood (Figure 2).

During process monitoring, all real-time instruments showed relatively stable particle concentrations with the exception of the FMPS in the operator PBZ. Although the overall concentrations measured by the FMPS were low, the variability of the measurements was high and increased during the spin coating process (Figure 9). The particle concentrations increased gradually at the late stage of the spin coating process around 10:39 am. The elevated particle concentrations could be generated by the frequent movements of the operator or from the room ventilation system. No EC was detected in the room and at the PBZ. The EC concentration at the source was around 1.78 µg/m^3 and close to observations from ambient air pollution (Table 5). The TEM analysis showed that no carbon nanotubes were identified.

Substrate Cutting

The task of substrate cutting by hand-operated scissors was performed in a ventilated enclosure (Table 3). According to the real-time monitoring data, this process did not generate measurable contaminants at the PBZ. The filter sample collected at the source, however, showed that carbon fibers were generated from cutting the substrate (Figure 10). Analysis of the filter samples showed that EC concentrations were not detectable at the source or background locations, but 2.63 µg/m^3 was measured at the PBZ (Table 6). As discussed before, this higher EC concentration could include a contribution from ambient air pollution.

Conclusions and Recommendations

An in-depth field survey was conducted to monitor particle emissions from processes using CNTs for product research and development. The survey used real-time monitoring with direct-reading instruments to identify particle releases and filter-based sampling to characterize airborne particles. No major particle emissions were found from the processes because of the small production scale and limited quantity of nanomaterials being handled. Most of the EC concentrations measured from the collected samples were estimated values because of the short sampling time and low concentrations below the limit of quantitation (0.67 µg/sample in this case). All the filter samples showed that EC concentrations were near levels seen in ambient air pollution (0.60±0.72 µg/m^3) and were below the NIOSH proposed REL of 7 µg/m^3.

For the probe sonication process with no engineering controls, the EC concentrations at the PBZ were either close to background or not detectable, while those at the source were nearly twice as high as background (except for the first test on March 20). TEM results confirmed that CNT release from the open beaker during sonication was possible, though only one CNT was found on the filter sample. Samples of the ESP probe also showed the potential for surface contamination in areas near the process.

The fume hood provided good control for the spin coating process: no EC or CNTs were detected at the PBZ or in the room. However, it was operated at an average face velocity of around 171 cm/sec (or 337 ft/min) which is much higher than consensus recommendations (typically 80–120 ft/min) [ACGIH 2010; AIHA 2003; SEFA 2006].

The ventilated enclosure provided good control for the manual cutting of CNT-coated substrate. This process is a low-energy, manual process and is less likely to generate large quantities of particles than a powered cutting process. TEM analysis indicated that carbon fibers can be released at the source during cutting of CNT-coated substrates, but real-time measurements for the process showed no major particle releases at the source or PBZ. Compared to undetectable EC concentrations at background and the source, a higher concentration (2.63 $\mu g/m^3$) was found at the PBZ during substrate cutting. This concentration, however, was between the limit of detection and limit of quantification for the analytical method and represents a low concentration that is near typical ambient background levels. Despite the fact that the ventilated enclosure contained emissions from this task, the low face velocity generated by the enclosure should be checked against manufacturer's specifications. Most enclosures require an inlet face velocity of at least 60-80 fpm and generally higher to ensure good containment.

The following suggestions are provided to improve particle containment during CNT weigh-out and preparation of CNT solution with probe sonication. Handling nanomaterials in dry powder form potentially releases nanoparticles to the workplace [Dahm et al. 2012; Evans et al. 2010; Tsai et al. 2009]. Because only a few micrograms of CNTs were handled in this case, no particle releases were identified by direct-reading instruments or filter sampling during CNT weigh-out without control measures. This result should not be interpreted as safe when handling small quantities of nanomaterials in an open environment. To prevent any accidental releases of nanoparticles, it is strongly recommended that fume hoods or ventilated enclosures equipped with High Efficiency Particulate Air (HEPA) filters be used for nanomaterial weighing and transferring processes. Moreover, ducted control measures that exhaust to the outside are preferred to disperse filtered air into the atmosphere. As confirmed by TEM analysis on the filter samples, probe sonication for the CNT solution in an open beaker poses a risk of nanomaterial emissions and work surface contamination. If a closed container for the CNT solution is not feasible, the task should be conducted in a ventilated enclosure (fume hood or cabinet) to limit exposure to nanomaterials.

Figures

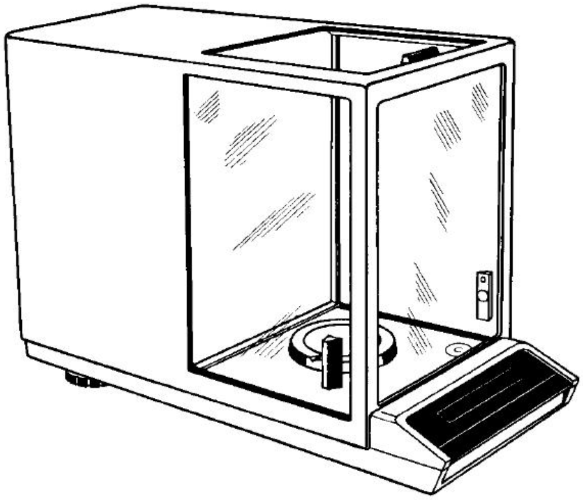
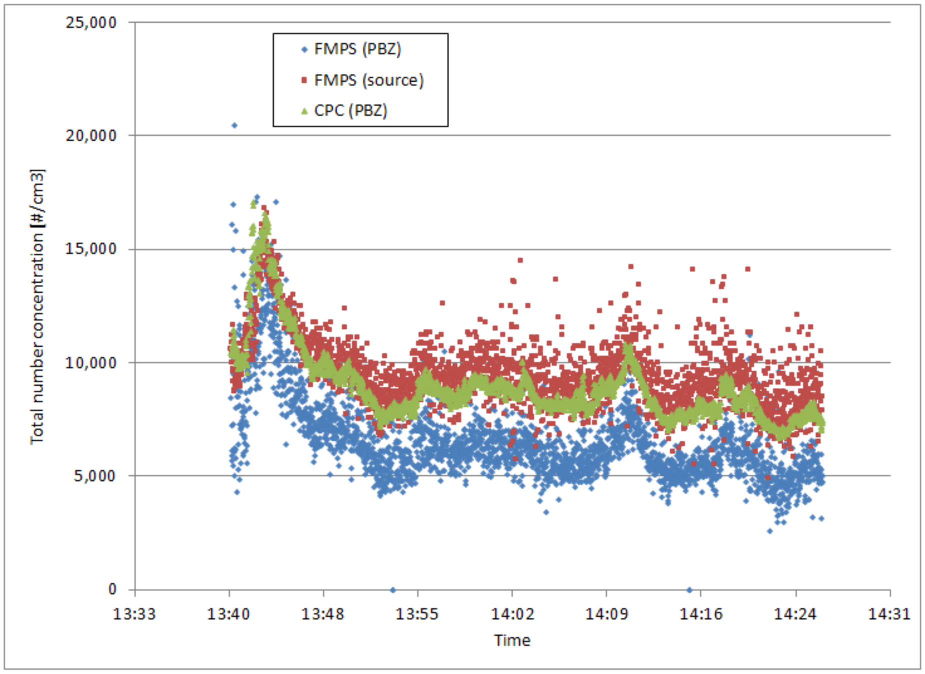


Figure 1. Electronic analytical balance used for weighing CNTs in the chemical laboratory (reprinted from Mettler AE100 operating instruction manual).

Figure 2. Conventional fume hood used to reduce exposure to nanomaterials during spin coating of CNTs on substrates.

Figure 3. Ventilated enclosure used for cutting CNT-coated substrates (reprinted from the Labconco website, http://www.labconco.com/product/xpert-nano-enclosures/2202)

(a)


25,000
20,000
15,000
10,000
5,000
0
Total number concentration [#/cm3]
FMPS (PBZ)
FMPS (source)
CPC (PBZ)
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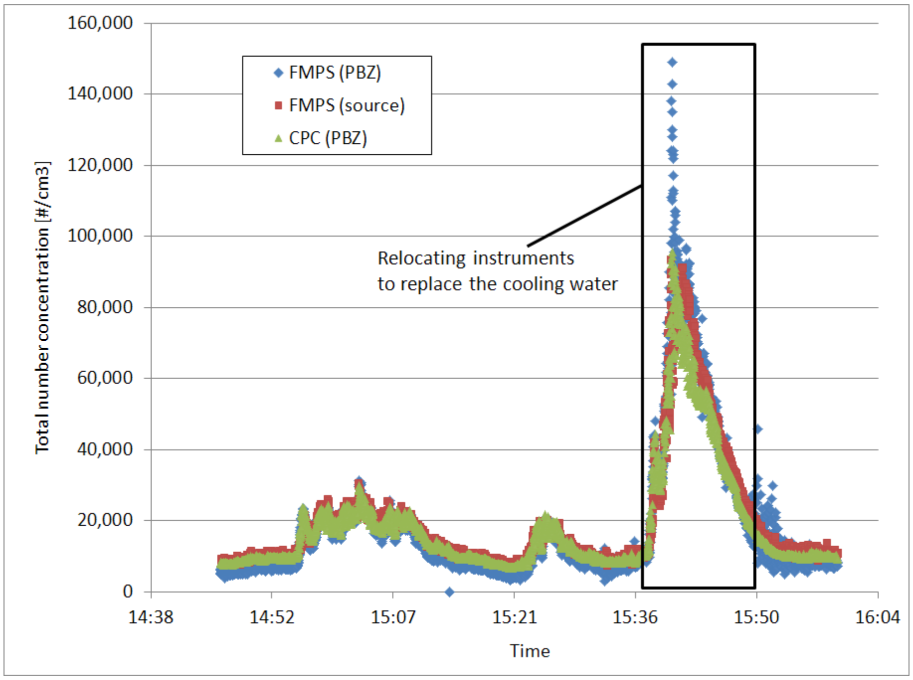
13:40
13:48
13:55
14:02
14:09
14:16
14:24
14:31
Time

(b)


160,000
140,000
120,000
100,000
80,000
60,000
40,000
20,000
0
Total number concentration [#/cm3]
FMPS (PBZ)
FMPS (source)
CPC (PBZ)
Relocating instruments
to replace the cooling water
14:38
14:52
15:07
15:21
15:36
15:50
16:04
Time

(c)

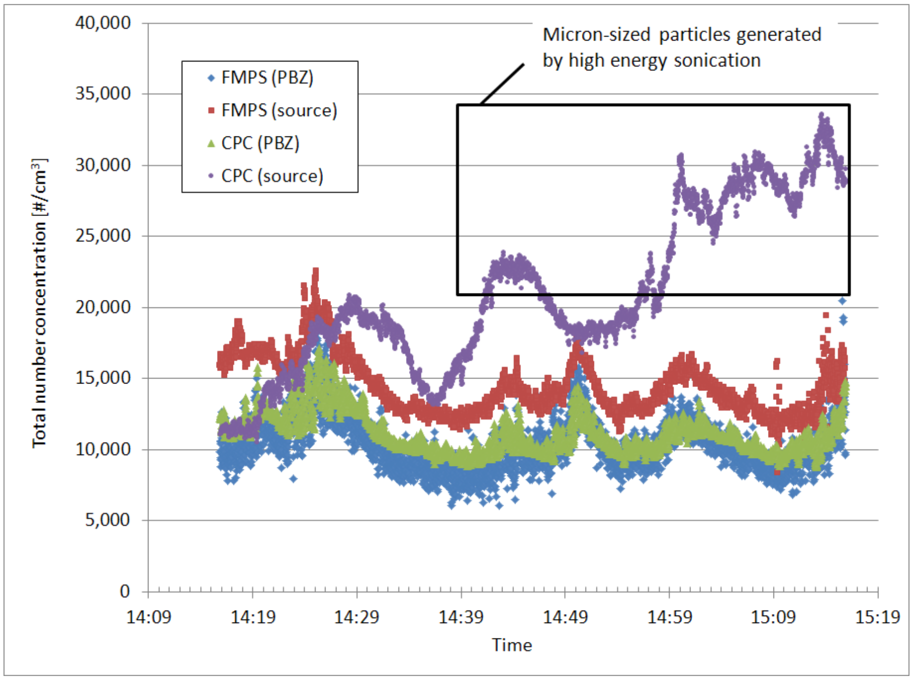
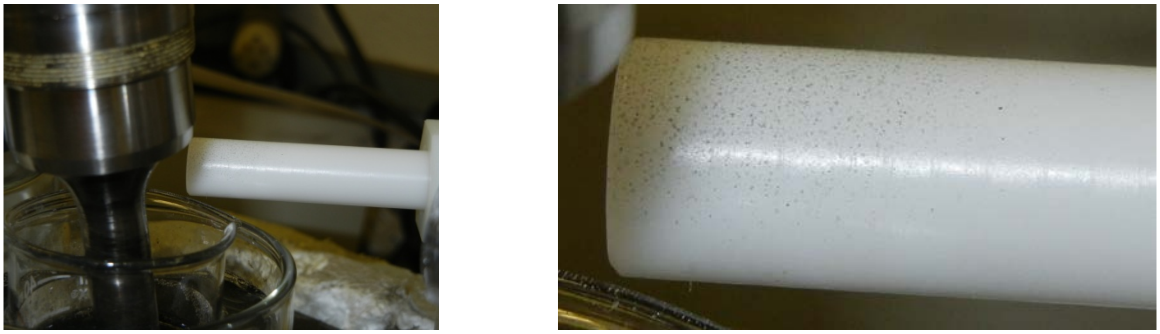
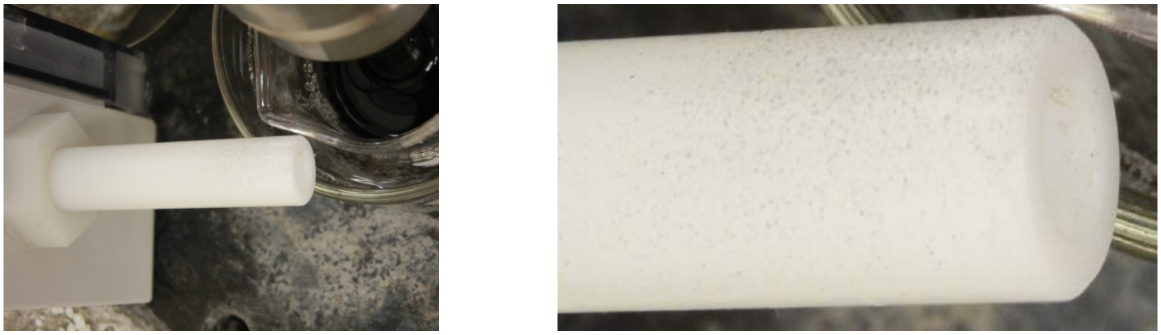


Figure 4. Task of probe sonication process monitored with the FMPSs and CPCs for (a) Solution A on March 20, (b) Solution B on March 20, and (c) Solution B on March 21. The sampling frequency of the CPC located at the source on March 20 was accidently set at 1 minute; those data are not presented here.



Side view

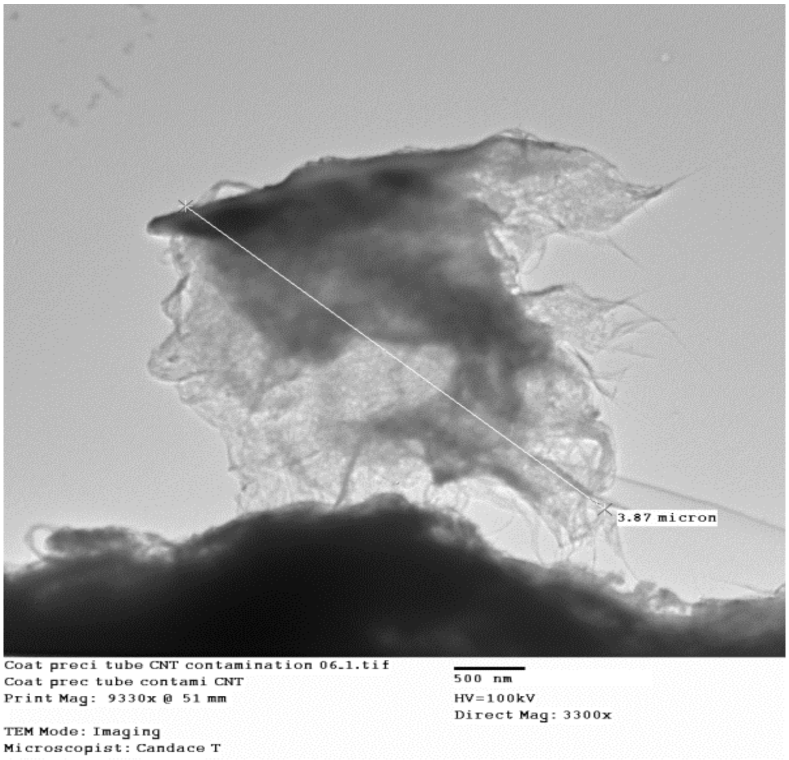
Enlarged side view



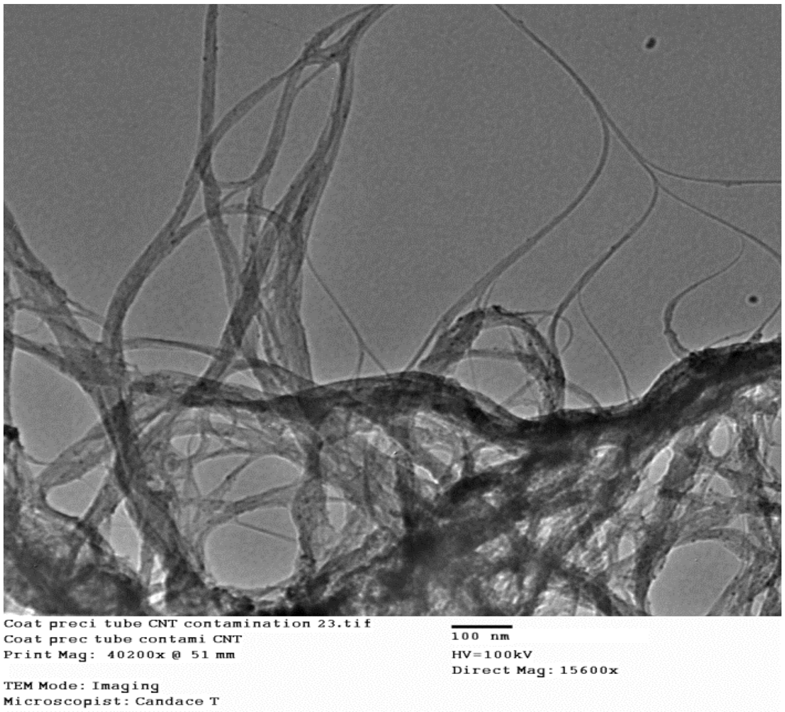
Top view

Enlarged top view

Figure 5. Photos taken during the task of probe sonication for CNT solution. The white tube is the sample tube of ESPnano.



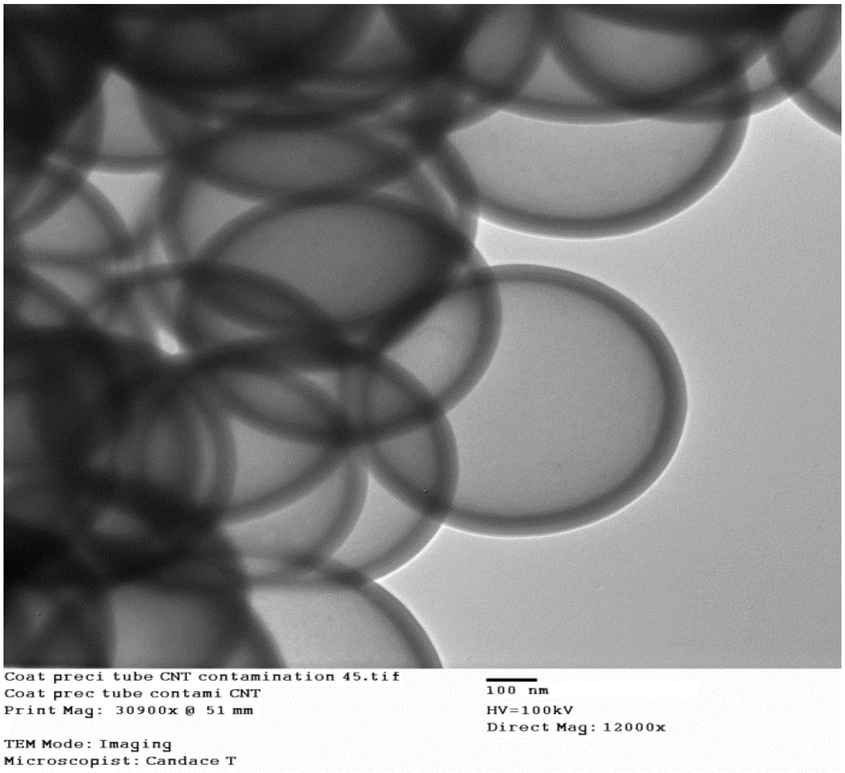
CNT contaminates



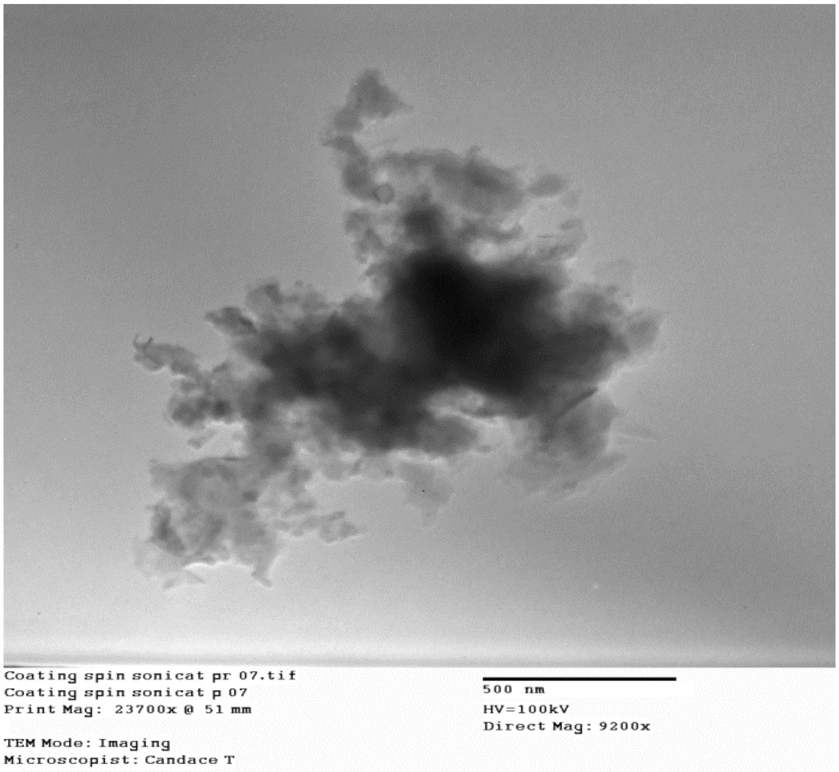
Structure of CNT

contaminants

Figure 6. CNTs on contaminated tube of the precipitator during probe sonication for the CNT solution.



Other contaminants on CNT contaminated tube



Particles collected at source during probe sonication

Figure 7. Nonfiber-structured particles found during sonication process.

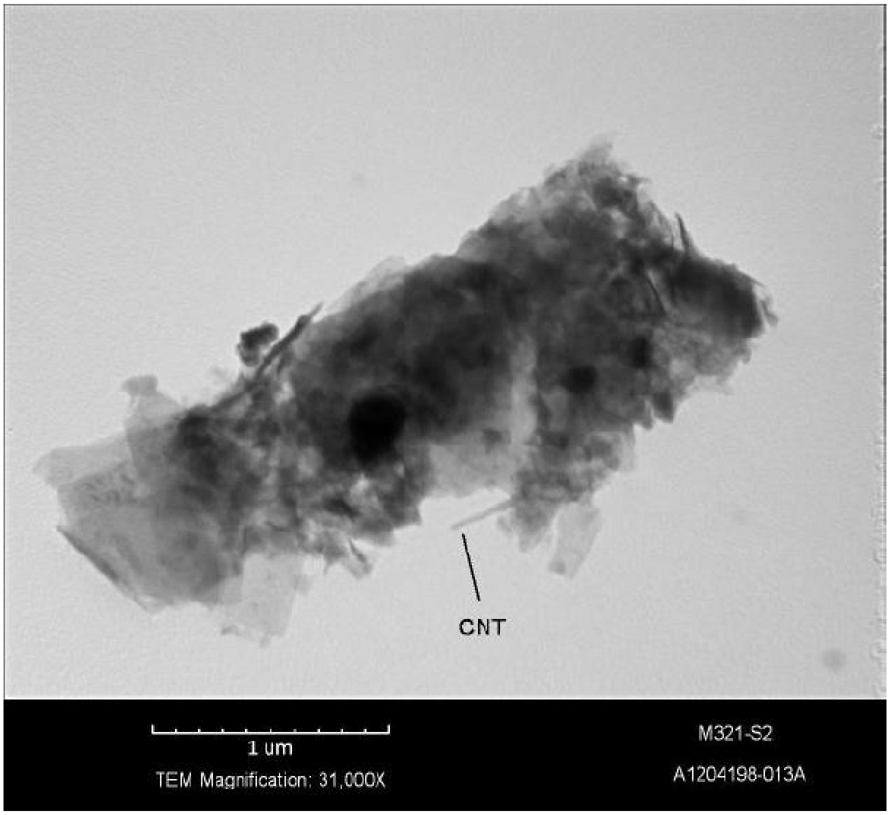


Figure 8. TEM image of a sample collected in the PBZ during the probe sonication process on March 21.

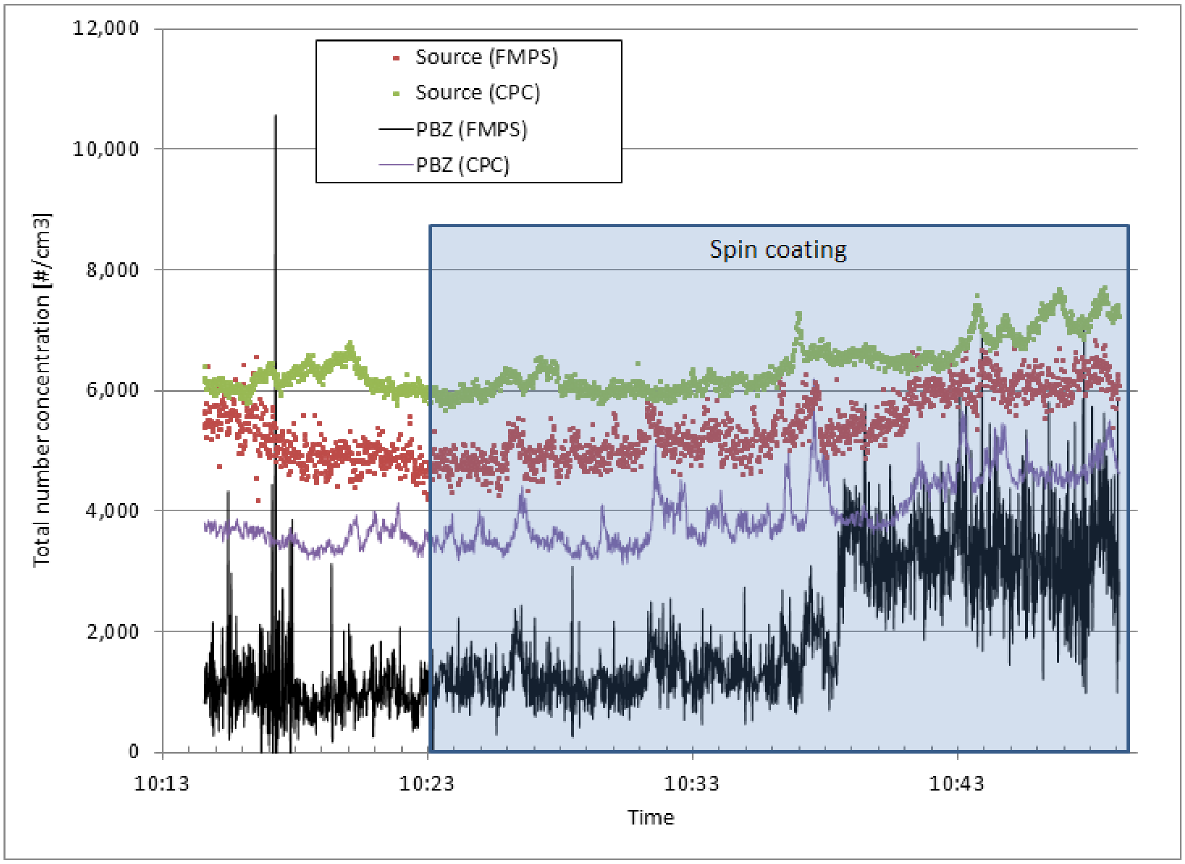


Figure 9. Real-time monitoring data for the spin coating process on March 21.

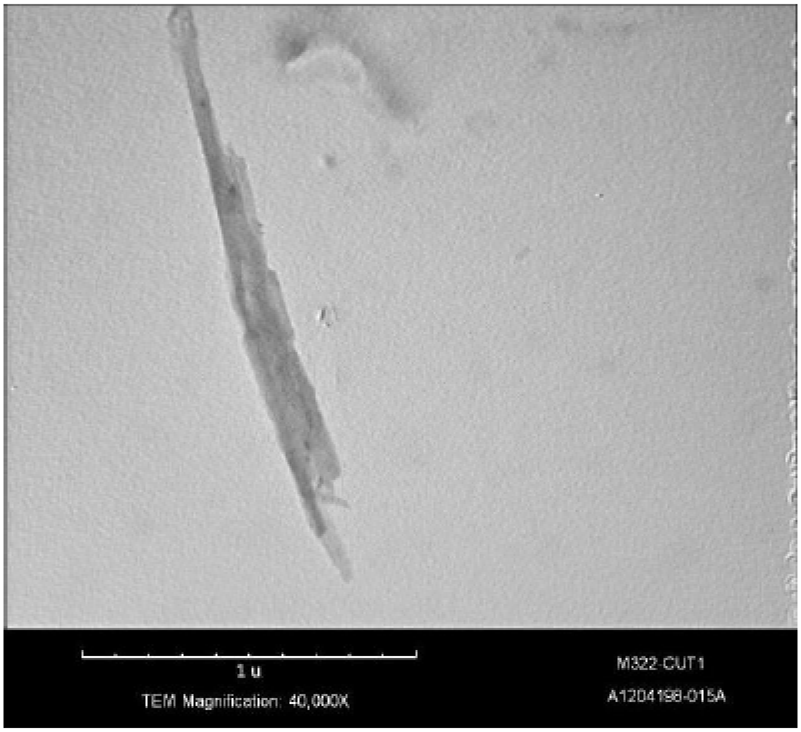


Figure 10. TEM image of the sample collected from the source during cutting CNT-coated substrates. Carbon fiber was identified by TEM.

Tables

Table 1. Processes to prepare CNT-coated substrates in the chemical laboratory.

Process	Activity	Process Equipment	Control Measure
Preparing CNT solution	Weighing	Mettler AE100 Electronic Analytical Balance	None
	Mixing	None	None
	Sonication (1) Bath (2) Probe	(1) Fisher Scientific FS30H (2) Fisher Scientific Sonic Dismembrator 550	None
	Centrifugation	Laboratory tabletop centrifuge	None
Preparing CNT-coated substrates	Coating Method A. Dip Method B. Spin	A. None B. Specialty Coating System Inc. Model P6712	A. None B. Fume hood
	Drying	Hot plate	Fume hood
Post-processing	Substrate Cutting	Scissors	Labconco XPert Nano Enclosure

Table 2. Air flow data of the fume hood for the task of spin coating.

		Left open				Right open			
Face velocity in cm/sec (*ft/min*)	Upper open	161 (*317*)	150 (*295*)	186 (*366*)	193 (*380*)	229 (*451*)	205 (*403*)	198 (*390*)	191 (*375*)
	Lower open	128 (*252*)	126 (*248*)	137 (*269*)	167 (*329*)	182 (*359*)	184 (*363*)	123 (*242*)	176 (*346*)
Overall flow rate in m^3/sec (ft^3/min)		1.728 (3662)							

Table 3. Air flow data of the ventilated enclosure for the task of substrate cutting.

Face velocity in cm/sec (*ft/min*)	Upper open	98 (*50*)	95 (*48*)	97 (*49*)	103 (*52*)
	Lower open	102 (*52*)	105 (*53*)	97 (*49*)	95 (*48*)
Overall flow rate in m^3/sec (*ft^3/min*)		0.475 (*1006*)			

Table 4. Filter sampling results for the probe sonication process.

Sampling date	Sample description		EC concentration* [µg/m^3]
March 20	Indoor background (general laboratory area)		0.46
	Solution A (13:41–14:26)	Source**	Not detectable
		PBZ	1.81
	Solution B (14:46–16:00)	Source**	0.87
		PBZ	0.53
March 21	Indoor background (in the sonication room)		0.79
	Solution B (14:16–15:16)	Source**	1.04
		PBZ	Not detectable

*All EC concentrations except the general laboratory background are estimated values, because their results were obtained from short sampling times and were between the limit of detection (0.2 µg/sample) and the limit of quantitation (0.67 µg/sample).

** The sampling for the production source was located close to the beaker containing the CNT solution (Figure 5).

Table 5. EC data for the spin coating process.

Sampling date	Sample description	EC concentration* [µg/m^3]
March 21	Indoor background (in the spin coating room)	Not detectable
	Production source (on top of the spin coating equipment)	1.78
	PBZ	Not detectable

* The EC concentration is an estimated value, because the result was between the limit of detection (0.2 µg/sample) and the limit of quantitation (0.67 µg/sample).

Table 6. EC data for the substrate cutting process.

Sampling date	Sample description	EC concentration* [µg/m^3]
March 22	Indoor background	Not detectable
	Production source (close to substrate cutting)	Not detectable
	PBZ	2.63

* The EC concentration is an estimated value, because the result was between the limit of detection (0.2 µg/sample) and the limit of quantitation (0.67 µg/sample).

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