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Letters to the Editor

Particle exposure levels during CVD growth and subsequent handling of vertically-aligned carbon nanotube films

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Carbon nanotubes (CNTs) are being researched worldwide to create countless new technologies [1,2], including transistors, solar cells, biomaterials, and hybrid advanced composites [3–7]. Concerns exist about the possibility of nanoscale particle release, notably release of CNTs and catalyst particles, during CNT growth and subsequent handling and processing steps. Limited animal toxicity data raises concerns about possible adverse health effects from CNTs, such as pulmonary inflammation, oxidative stress, onset of early interstitial fibrosis, and granulomas [8–11]. Additional concerns exist about potential exposures to other nanoscale carbonaceous particles, such as carbon black, which have been shown to cause oxidative stress in biologically relevant media such as human blood serum [12–14]. The main objective of this work is to evaluate potential exposure to nanoscale particles during CVD growth of vertically-aligned "forests" of CNTs in a university research lab, and during subsequent handling as the CNTs are removed from the furnace and detached from the growth substrate.

Forests of vertically-aligned CNTs are grown by atmospheric pressure CVD at 750 °C [7], using a horizontal quartz tube furnace at atmospheric pressure, where the tube is sealed using aluminum end caps with lip-style ring seals (SKF) [15]. Growth occurs on a silicon substrate coated with a Fe/Al_2O_3 film; typically, the CNT forest grows to approximately 1.5 mm (3 mg/cm^2) in 20 min, and the CNTs in the forest have an average outer diameter of 8 nm. The furnace is heated and stabilized under flow of 400/100 sccm H_2/He (99.999%, Airgas), and 100 sccm C_2H_4 (99.5%, Airgas) is added during growth. The exhaust from the furnace passes through a bubbler containing paraffin oil, and then into the building ventilation system. At the end of the growth period, the furnace is purged with 400 sccm He, while the tube and substrate cool to below 200 °C (approximately 20 min). Next, the end caps are removed from the quartz tube and the sample is pushed out of the tube using a stainless steel rod.

For this study, the sample was placed on a lab bench, and the forest was removed from the substrate by gentle mechanical action using a razor blade, without local exhaust ventilation. This growth and "harvesting" sequence is a typical first step in preparation of a hybrid composite including aligned CNTs [16]. Importantly for understanding exposure, the aligned CNTs are strongly held within the film by van der Waals forces, while the CNT substrate adhesion is

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relatively weak. As a result, the CNT forest is delaminated cleanly to give a self-supporting structure which is easily manipulated using tweezers. The tendency of CNTs to adhere together during growth and harvesting has been reported in another study of aerosol levels during synthesis and harvesting of CNTs using laser ablation or high pressure carbon monoxide furnaces [17]. In the same study, only low levels of micron sized clumps of CNTs were seen as product was manually shoveled out of furnaces. Nanometer sized particles could be regenerated only at high energy levels of a fluidized bed vortex generator.

The process was monitored on three different occasions over the course of six months. During each session, continuous information was collected on particle number concentration of the background air and the surrounding air during the whole cycle of the furnace operation: furnace heating, CNT growth, furnace cool-down, opening of furnace, removal of the substrate, and mechanical removal of CNTs from the silicon substrate. These measurements were accomplished using a suite of complementary instruments, described as follows:

– A real-time particle sizer (TSI FMPS, Model 3091), which measures the number concentration of aerosol particles in the range from 5.6 to 560 nm, with 32 channels. The FMPS intakes 10 L min^{-1}, and the detection limit varies

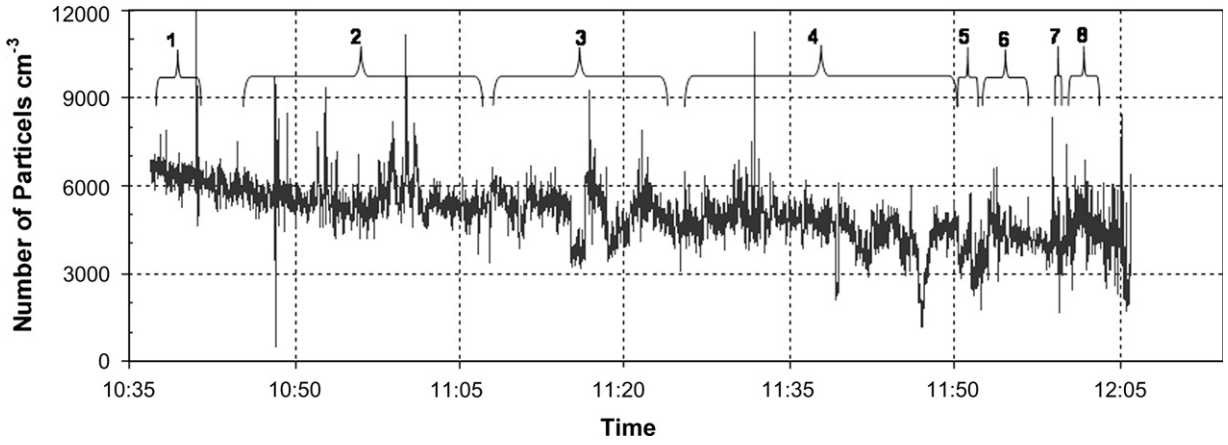

Fig. 1 – Total particle exposure levels in the 10–560 nm range during CNT growth, removal of CNT forest from substrate and subsequent CNT forest handling and harvesting. Legend: (1) Background; (2) Heating furnace; (3) CNT growth; (4) Furnace cool-down; (5) Open furnace: open both ends and push sample out; (6) Open furnace: monitor open end of furnace; (7) Delaminating CNTs from silicon substrate; (8) Transfer of CNTs to epoxy-coated substrate.

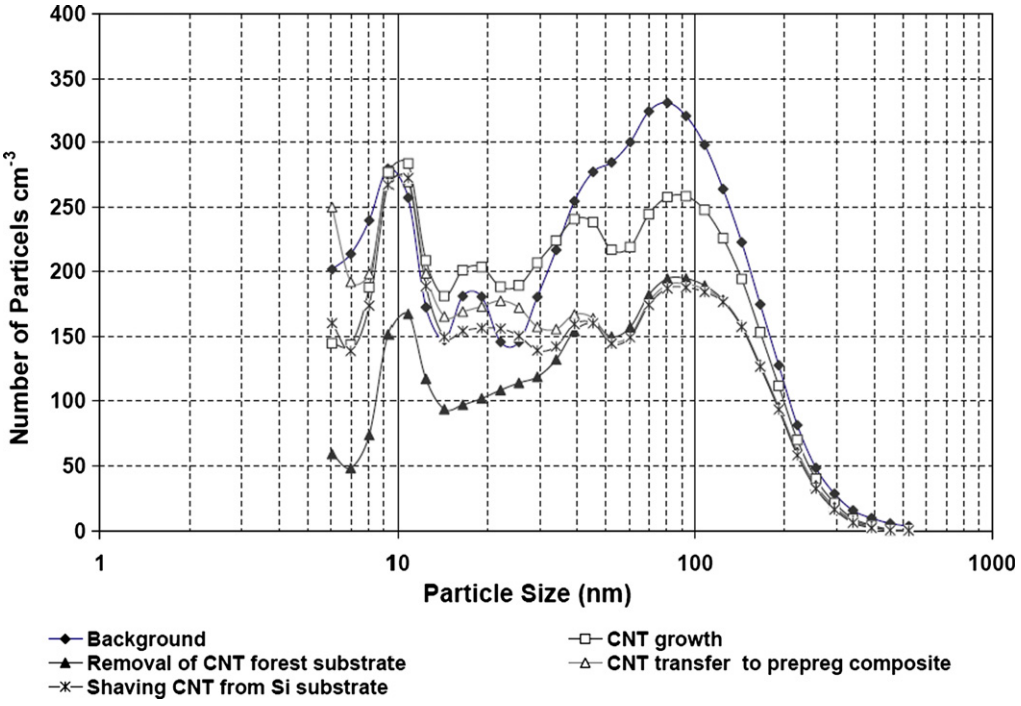

Fig. 2 – FMPS particle size distribution during listed process stages.

from ~100 particles/cm^3 at 10 nm to ~10 particles/cm^3 at 100 nm.
- A condensation particle counter (TSI CPC 3007), which measures the total particle number concentration (particles/cm^3), summed for sizes ranging from 10 nm to 1 μm.
- A thermophoretic precipitator (TP, Fraunhofer Institute of Toxicology, Germany) and electrostatic precipitator (ESP, courtesy of Dr. A. Miller, Spokane Laboratory, NIOSH, VW). These instruments, which were positioned side-by-side, use a thermal gradient and electrical discharge, respectively, to collect particles on a TEM Cu grid for electron microscopy characterization.
- A commercially available asbestos sampling cassette (Millipore Inc., 25 mm diameter cassette containing a 0.45 μm pore size mixed-cellulose ester filter equipped with an electrically conductive 50 mm extension cowl. This was operated at 2 L min^{-1} and used to collect a personal breathing zone air sample of the furnace operator for fiber analysis throughout the whole CVD process.

The instruments were operated simultaneously and their intakes were placed close to the output seals of the tube furnace. The asbestos cassette and the Cu grids were analyzed by SEM (JEOL JSM-7401F) and TEM (Philips EM 400T), to evaluate particle size and morphology. Elemental analysis for particles of interest was obtained with an integrated energy dispersive spectroscopy (EDS) detector (EDAX). A bulk sample of the bubbler oil was dried and characterized by FE-SEM.

No increase in the total particle number concentration (Figs. 1 and 3) and any particle size range (Fig. 2) were observed during each cycle of the furnace operation as compared to background, as measured by the FMPS and the CPC 3007 units. Within the detection limits and ranges of the instruments, and the fluctuation of background, no release of fine particles to the indoor environment was detected during all stages of furnace operation, as well as during handling of the CNT forest. Similar observations were made in the previous two monitoring sessions. Small variation seen in the total particle number concentration is normal in indoor air and in this case may be related to repositioning of the instruments inlets for point source evaluations and to thermal gradients around the furnace. The total particle number concentration in the indoor environment in the ranges measured by FMPS and CPC 3007 commonly varies between

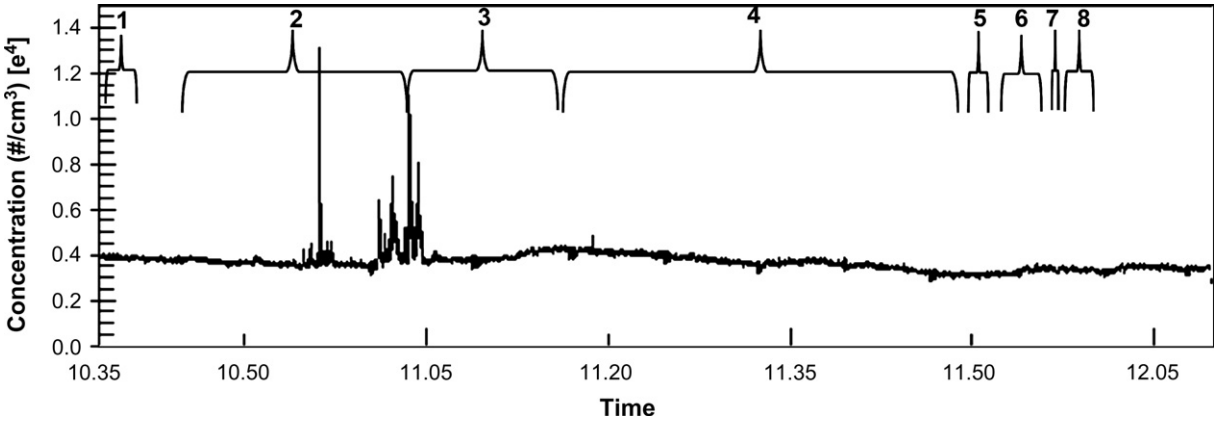

Fig. 3 – CPC 3007 monitoring data (10 nm to <1 μm). The event log corresponds to same legend as Fig. 1.

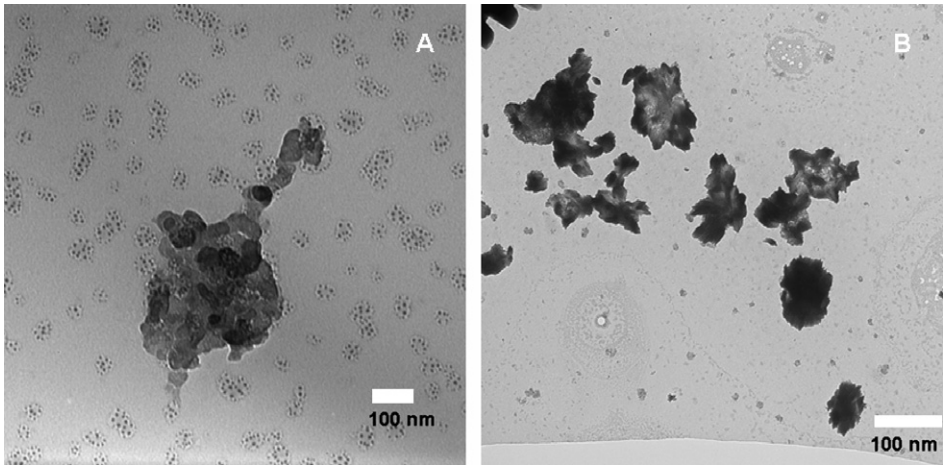

Fig. 4 – Selected TEM images of samples collected (A) from exhaust gas during CVD growth and (B) from ambient during harvesting stage.

2000 and 10,000 particles/cm^3 and the levels measured in this study (4000–7000 particles/cm^3) are normal.

Electron microscopy of multiple Cu grids collected with TP and ESP did not reveal the presence of CNTs. Nanoscale particles of ~10 and ~100 nm, prominent in the FMPS size distribution output (Fig. 2), can be clearly seen in the TEM images (Fig. 4). These nanoscale particles are commonly seen in outdoor and indoor background samples and may originate from multiple sources, especially combustion engines. Larger carbonaceous particles (confirmed by EDS, no images shown) up to 1 μm were also seen, especially during the opening of the furnace. Particle agglomerates of similar morphology and made primarily of C (EDS) were found on the backup bubbler oil. No evidence of individual or bundles of CNTs was found. The personal filter (evaluated with FE-SEM) contained particulate matter of various typical sizes but no apparent nanoscale fibers or fibrous bundles.

The results of this investigation support a conclusion that no detectable quantity of CNTs, bundles or similar-sized carbonaceous particles are released to the occupational environment during CVD growth of a vertically-aligned CNT forest on a substrates in a tube furnace, or during subsequent handling and delamination of the forest. This is an important finding as many academic and industrial laboratories utilize similar systems and processes. Although only one system was studied, we expect these findings are generally applicable to substrate-bound growth of CNTs and similar-size structures, as the placement of CNTs is directed by the location of the catalyst on the substrate, and van der Waals interactions hold CNTs to one another and/or to the substrate. Vapor-phase ("floating catalyst") processes, where CNTs and/or catalyst instead float continuously or recirculate through the furnace, would require independent investigation. The prudent approach towards handling nanomaterials currently used in many laboratories (including MIT and the US DOE) is to use exhaust ventilation such as fume hoods or gloves bags connected to HEPA vacuums to prevent release during harvesting and processing [18,19]. Any modification of a process such as functionalization or high energy processing steps that may contribute to release of nanoparticles should be performed with exhaust ventilation until aerosol monitoring indicates that no release is occurring.

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