Sensing Solution for Airborne Carbon Nanotube Exposure in Workplaces based on Surface-Enhanced Raman Spectroscopy

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ABSTRACT

Today's advances in man-made nanomaterials pose new and unprecedented health risks, arising especially from airborne, inhalable fiber-shaped nanomaterials, like carbon nanotubes (CNTs). *In vivo* studies indicate that inhalation of CNTs can cause adverse pulmonary effects including inflammation, granulomas and pulmonary fibrosis [1, 2]. As a result, the National Institute of Occupational Health and Safety (NIOSH) recommends an exposure limit of 1µg/m^3 of CNTs as a respirable mass 8-hour time-weighted average concentration [3]. However, detecting this amount is extremely challenging with the current sensing solutions. In this paper, we present a wearable compact sampler and an integrated, highly selective optical reader which enables automated monitoring of personal occupational exposure to CNTs.

Keywords: CNT, industry, occupational exposure measurement, Raman spectroscopy

1 INTRODUCTION

Carbon nanotubes (CNTs) have been in the research spotlight for decades, due to the excellent mechanical, electrical and thermal properties organized CNT architectures provide. [4] At the same time, scale up, yield increases and fabrication in several locations have significantly increased the availability of unorganized, less pure CNTs in bulk. Today, as CNTs are implemented in various products such as batteries, automotive parts, water filters and sporting goods [5], occupational exposure of personnel in the facilities that handle CNTs is becoming a significant concern.

Currently, assessment of personal occupational exposure to CNTs in workplaces is only possible through a combination of methods such as online particle counters, thermal-optical analysis, electron microscopy [6, 7, 8]; which collectively are labor intensive, time consuming and not selective. This prevents many CNT-handling facilities from monitoring CNT exposure of personnel and hinders the implementation of engineering controls in processes that generate an undesirable release of fibers.

Here, we present a wearable, cost-effective compact badge sampler with an air filtration system [9]. The badge is a personal sampling device equipped with a pump, environmental sensors and a filtration slide. Nanoporous membranes are incorporated into the filtration slide that collect aerosolized particles as air is drawn through the badge.

After sampling, the badge is inserted into a bench top-sized reader equipped with a Raman spectrometer that automatically inspects the collected samples. Our system enables detection of sub-nanogram quantities of collected CNTs and, by utilizing the advantages of Raman spectroscopy, is a solution able to uniquely distinguish carbon nanotubes from background aerosols present in air. An illustration of the badge and reader is shown on Figure 1.

Figure 1: Illustration of badge sampler (left) and reader (right).

In this paper, we present the proof of concept of the integrated system by generating CNT-containing aerosols, collecting and detecting CNTs in aerosol samples using our solution and comparatively characterizing our results with conventional particle characterization methods.

2 MATERIALS AND METHODS

2.1 CNT-Containing Aerosol Generation and Collection

In order to mimic CNT exposure in the workplace, CNT aerosol was generated by directing HEPA-filtered air into CNT powder loaded in a round bottom flask and agitated using a vortex shaker (Vortex-Genie Pulse, Scientific Industries, USA). Single-wall carbon nanotubes (SWCNT) were purchased from SouthWest Nanotechnologies (CG200, >90% carbon content). Aerosolized CNTs were collected on functionalized nanoporous silicon nitride membranes [10].

The aerosol and the filtrate were consecutively characterized using a scanning mobility particle sizer (SMPS, TSI Electrostatic Classifier Model 3082, USA) and a condensation particle counter (CPC, TSI Condensation Particle Counter Model 3775, USA) with a particle electrical mobility diameter range of 16.5nm < d_m < 697.8nm.

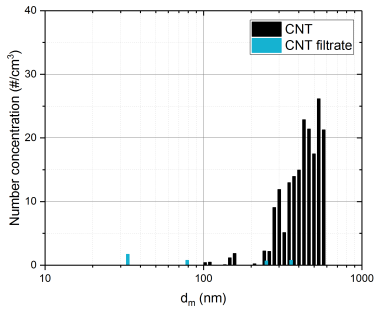

Figure 2: Number concentration of SWCNT aerosol before and after filtration through nanoporous membranes.

From Figure 2, filter capture efficiency ($N_{filtrate}/N_{all}$) was calculated as 96%. Few to no single CNT fibers were observed in the aerosol. This is consistent with the fact that commercially used CNTs are typically found in highly entangled, curved tubes that form large, complex aggregates [11].

2.2 Comparative Characterization of Collected CNTs

SWCNT aerosol was generated as previously described and collected on membranes. CNT concentration on the membranes were characterized using a scanning electron microscope (SEM, Hitachi S-3400N, Japan).

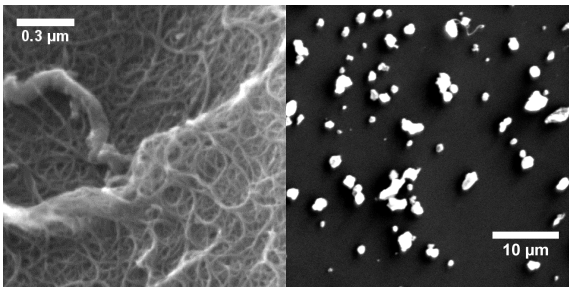

Figure 3: 44802x magnification image of a SWCNT aggregate (left, 10kV) and high contrast, low magnification image acquired for aggregate analysis (right, 30kV).

Presence of entangled CNTs were confirmed using the high magnification images (Figure 3). High contrast images were acquired in random locations throughout the membrane to be used for aggregate size analysis (n=10). Using Fiji [12], 2D surface area of the aggregates were determined. The areas were converted to a spherical equivalent diameter, which was used to estimate the weight of CNT aggregates on the membrane, using the following power law relationship from Wang et al. [13]

$$m = 1.3 \cdot 10^{-6} d_{out}^{2.6}$$

where m is mass of the individual aggregate (pg) and d_{out} is outside diameter of aggregate (nm). This correlation had only been tested for aerosolized multi-walled CNTs in the size range of 50-500 nm, so they were used to only qualitatively assess the correlation of CNT signal derived from Raman spectroscopy with the observed aggregates.

Raman spectra of the deposited CNT aggregates were collected in the form of low-resolution Raman maps. The spectra were acquired every 150 µm using a 532 nm Raman spectrometer with a 5 s acquisition time. The CNT signal was quantified by the maximum of the G-band at 1595 cm^{-1}.

Figure 4 shows an SEM image of a 4-window membrane with CNT aggregates deposited and the corresponding low-resolution Raman map. The total Raman signal from each of the membrane windows was compared with the SEM-derived aggregate mass estimate. The signals were normalized and it is evident that there is a good correlation between the two measures. It is thus shown that even these low-resolution Raman maps can be used to quantify the amount of deposited aerosol. Additionally, with a mass-calibration curve the total CNT mass deposited on the membrane can be determined using this method.

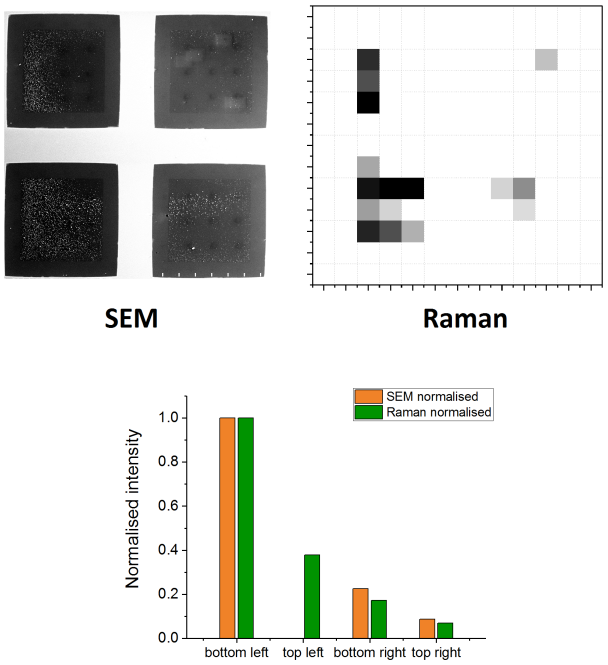

Figure 4: Correlation of SEM and Raman spectroscopy data for a 4-window membrane with CNT aggregates deposited from aerosol. Normalized intensity from top left SEM image is not available due to low quality of high magnification image for the particular window.

By measuring full Raman spectra of the collected CNTs, a selectivity not achieved with standard aerosol characterization methods is gained. Carbon nanotubes and graphene can be distinguished from dust or other particulates commonly found in occupational settings, such as carbon black. Additionally, spectral data allows the user to determine from which product or process the contamination originates. This becomes of great value for facilities handling or manufacturing more than a single type of carbon nanomaterial.

Figure 5 shows the selective detection capability of the Raman system. Whereas online particle counters such as SMPS detect many particles that are not the CNTs of interest, Raman spectra can easily distinguish CNTs from a background of dust and carbon black.

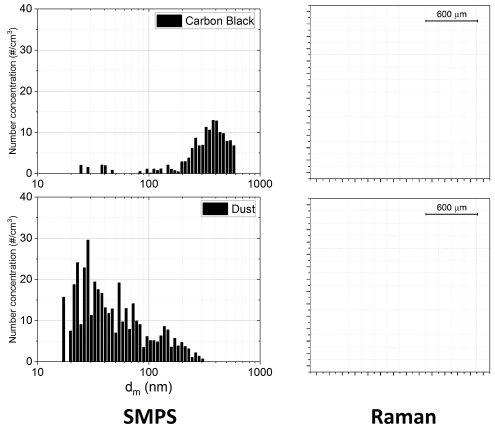

Figure 5: SMPS measurement of dust and carbon black particles deposited on the membranes and their Raman intensity map.

2.3 Modeling Size Separation of Aggregates During CNT-Containing Aerosol Collection

Certain particle sizes can translocate to specific regions of the respiratory tract when inhaled and can potentially cause adverse effects. These are defined as inhalable, thoracic and respirable fractions, with an aerodynamic cut size of 100µm, 10µm and 4µm respectively with 50% penetration. The respirable fraction of particles can penetrate to unciliated airways and is a key measure that is correlated with diseases that affect the gas exchange region of the lung. [14] Sampling particles of these defined sizes during aerosol collection facilitates the interpretation of the collected particle data into potential health risks. Thus, inlets of the air filtration slide were designed as microchannels which use a combination of particle speed and inertia to separate the particles into three different size ranges, collecting respective particle sizes on separate membranes.

Optimization of the channel structure and air flow speeds was performed using COMSOL Multiphysics (COMSOL, Sweden) laminar flow and particle tracing modules. Channel structure, the air drawn from micropump and pressure drop that originates from nanoporous membranes were modeled. 100 particles were released from density dependent positions, their trajectories were visualized and the percentage of particles that are collected at each membrane positions were counted. This was repeated for particle sizes between 0.1 – 20 µm. CNT aggregates have a wide range of densities and morphological differences, so in the model they were simplified into spherical particles with a density of 1g/cm^3. Percentage of particles collected in each membrane is shown in Figure 6.

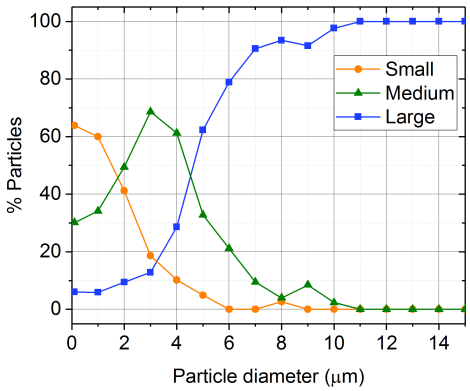

Figure 6: Percentage of particles collected on small, medium and large particle collection membranes depending on their inertia.

Figure 6 shows that at 50% collection thresholds are approximately 1 µm and 4 µm respectively for the small and medium sized particle collection membranes. In the large particle collection membrane, larger non-respirable particles are collected.

3 SUMMARY AND CONCLUSIONS

We presented proof of concept of an easy-to-use, integrated solution to monitor occupational CNT exposure. We aerosolized commercially available SWCNTs, collected them using functionalized nanoporous membranes and compared Raman spectroscopy characterization with conventional techniques such as SMPS online particle measurement and SEM. Finally, we presented an inertia-based size separation mechanism which facilitates the correlation of the acquired CNT exposure monitoring data with potential adverse health outcomes.

The type, morphology and purity of CNTs can have a significant influence on the Raman bands that are used to detect and quantify the CNTs. Thus, calibrating the detection tool for different types of CNTs will ensure their accurate detection and quantification.

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