

THESIS

A STUDY OF PROTECTIVE CLOTHING TO UNDERSTAND NANOPARTICLE  
EXPOSURE AND SURFACE CONTAMINATION

Submitted by

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## ABSTRACT

### A STUDY OF PROTECTIVE CLOTHING TO UNDERSTAND NANOPARTICLE EXPOSURE AND SURFACE CONTAMINATION

In this study, we investigated engineered nanoparticle (ENP) release associated with the contamination of personal protective clothing during the human activities of the worker wearing the ENP-contaminated protective clothing and evaluated the relative ENP retention to each used fabric type. The release of ENPs as airborne nanoparticles can cause inhalation exposure, which is the route of exposure of most concern to cause adverse health effects. The methods used were associated with four different fabric materials of contaminated laboratory coats (cotton, polypropylene, polyester/cotton blend, and Tyvek®) and three ENPs ( $\text{Al}_2\text{O}_3$ , carbon black and CNT). Two types of tests were performed: contamination and release experiments under two different durations (30 minutes and 6 hours of release processes). The magnitude of contamination and particle release were investigated in this study by measuring the number concentration increase and the weight change on fabric pieces. This study simulated real-life occupational exposure scenarios and was performed in cleanroom environments to investigate the effect of background aerosols on the measurements. Concentrations were measured using particle spectrometers for diameters from 10 nm to 10  $\mu\text{m}$ . Collected aerosol particles and contaminated fabric surfaces were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elemental carbon analysis. The magnitude of particle release from contaminated lab coat fabric was found to vary by the type of fabric material; cotton fabric showed the highest level

of particle release, followed by polyester cotton, Tyvek® and polypropylene. Moreover, Tyvek® fabric was determined as the best fabric for trapping  $\text{Al}_2\text{O}_3$  and carbon black ENPs indicating less resuspension of particles and highest mass change per unit mass after aerosolization and release processes. Two dominant forces responsible for ENP adhesion on the surface of the fabric were theoretically calculated to be van der Waals force and capillary force. To sum up, Tyvek® fabric is considered the most reliable fabric against ENPs, but not durable enough to wear for the long term compared with other fabrics.

## ACKNOWLEDGEMENTS

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## TABLE OF CONTENTS

|                                                                                         |           |
|-----------------------------------------------------------------------------------------|-----------|
| ABSTRACT .....                                                                          | ii        |
| ACKNOWLEDGEMENTS.....                                                                   | iv        |
| TABLE OF CONTENTS .....                                                                 | vi        |
| LIST OF TABLES .....                                                                    | vii       |
| LIST OF FIGURES .....                                                                   | viii      |
| INTRODUCTION .....                                                                      | viii      |
| <b>METHODS.....</b>                                                                     | <b>3</b>  |
| <i>2.1) Materials.....</i>                                                              | <i>3</i>  |
| <i>2.2) Facilities, Equipment and Procedure.....</i>                                    | <i>4</i>  |
| <i>2.3) Experimental process .....</i>                                                  | <i>7</i>  |
| 2.3.1) Aerosolization of protective clothing with ENPs .....                            | 7         |
| 2.3.2) Resuspension of particles from contaminated clothing .....                       | 8         |
| 2.3.3) Airborne particle sampling using filter-based gravimetric sampling methods ..... | 8         |
| 2.3.4) Statistical Analysis .....                                                       | 9         |
| 2.3.5) Fabric descriptive properties measurements .....                                 | 9         |
| <b>CHAPTER 3.....</b>                                                                   | <b>12</b> |
| <b>RESULTS AND DISCUSSION.....</b>                                                      | <b>12</b> |
| 3.1) Aerosolization of protective clothing with ENPs .....                              | 12        |
| 3.2) Resuspension of Nanoparticles from Contaminated Clothing .....                     | 14        |
| 3.3) Theoretical principle of particle-fabric adhesion.....                             | 19        |
| 3.4) Airborne particle sampling using gravimetric methods .....                         | 27        |
| 3.5) Mechanical properties (durability) of lab coat fabrics.....                        | 31        |
| <b>CHAPTER 4.....</b>                                                                   | <b>35</b> |
| <b>CONCLUSION.....</b>                                                                  | <b>35</b> |
| <b>REFERENCES.....</b>                                                                  | <b>37</b> |
| <b>APPENDIX A: TABLES AND FIGURES.....</b>                                              | <b>41</b> |

## LIST OF TABLES

|                                                                                                                            |    |
|----------------------------------------------------------------------------------------------------------------------------|----|
| Table 1. Calculated Hamaker constants for $\text{Al}_2\text{O}_3$ and carbon black interacting with different fabrics..... | 21 |
| Table 2. Contamination level and released airborne ENPs concentration for 30 minutes of various types of lab coat. ....    | 26 |
| Table 3. Contamination level and released airborne ENPs concentration for 6 hours of various types of lab coat. ....       | 29 |
| Table 4. Abrasion resistance measured by abrasion cycles before failure for four untreated fabrics. ....                   | 33 |
| Table 5. WCA for fabric samples <sup>a</sup> . ....                                                                        | 34 |

## LIST OF FIGURES

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1. Illustration of the contamination and resuspension process experimental setup. Clean air was flowed from the cleanroom toward the enclosure placed inside the fume hood. (a) Engineered nanoparticles (ENPs) aerosolization for contamination on lab coats. (b) Resuspension of ENPs through shaking and particle sampling. ....                                                                                                                                                                                                                   | 5  |
| Figure 2. The measured aerosolized particle number concentration vs. the particle size (on a log scale) for the three ENPs used in this study. (a) Measured number concentration of 10–420 nm size range ENPs through NanoScan SMPS. (b) Measured number concentration of 0.3–10 $\mu\text{m}$ size range ENPs through OPS. Data points represent $n = 12$ (or $n = 13$ ) replicate measurements for $\text{Al}_2\text{O}_3$ and CB (or CNT) ENPs, respectively. Histogram bars represent the averages of the replicate measurements for each ENP type. .... | 13 |
| Figure 3. Measured normalized particle concentrations released after the shaking of contaminated lab coats made from Tyvek®, cotton, polypropylene and polyester cotton. ....                                                                                                                                                                                                                                                                                                                                                                                | 16 |
| Figure 4. SEM images of resuspended ENPs collected on TDS samples (a) $\text{Al}_2\text{O}_3$ . (b) carbon black. (c) CNT. Arrow marks note single ENPs or agglomerates. ....                                                                                                                                                                                                                                                                                                                                                                                | 19 |
| Figure 5. TEM images of sampled ENPs on grid collected on TDS samples (a) $\text{Al}_2\text{O}_3$ at 50 nm and 20 $\mu\text{m}$ scale bars. (b) carbon black at 50 nm and 20 $\mu\text{m}$ scale bars. (c) CNT at 50 nm and 500 nm scale bars. ....                                                                                                                                                                                                                                                                                                          | 30 |
| Figure 6. SEM images of the surface of fabrics contaminated with three types of ENPs and released. ....                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 31 |

|                                                                                                                                                                          |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 7. Representative strain-stress curves of four untreated fabrics including cotton woven, polyester cotton woven, Tyvek® nonwoven, and polypropylene nonwoven..... | 32 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|

## CHAPTER 1

### INTRODUCTION

The nanotechnology market is expected to grow 17% annually up to 2024 [1], leading to the production of a variety of products using nanomaterials. This development of new applications in nanotechnology give rise to risks and uncertainties regarding the adverse effects to human health and the environment [2]. One main concern with the growth of nanotechnology is the protection of frontline researchers in laboratories and workers in production facilities from exposure to engineered nanoparticles (ENPs) through skin contact or inhalation. During their work, workers wearing contaminated clothing are at high risk of inhaling ENPs resuspended from clothing without any awareness of the potential danger. Moreover, when leaving the laboratory or production line, researchers and workers are unaware of possible ENP exposure from the contaminated clothing that they bring back to the office, home or public places. This contaminated clothing also causes significant risk to non-workers outside of the workplace settings. It is well-documented in previous studies that a mixture of monodisperse particles with the median sizes of 3, 5, and 10  $\mu\text{m}$  has the ability to resuspend from contaminated clothing surfaces during human physical activities [3], [4]. ENPs have diameters that are three orders of magnitude smaller, and volumes that are  $10^{-9}$  smaller, than microparticles. Therefore, ENPs represent many times more particles than an equivalent mass or volume of microparticles resuspended from contaminated clothing.

In a pilot study, Tsai et al. contaminated fabric swatches commonly used for personal protective clothing with nanomaterials and then measured the level of release of nanomaterials associated with each fabric type [5]. A substantial amount of particles were released from these

contaminated fabric swatches during the constant manipulation of the fabric in both regular room and cleanroom settings [5].

One of the possible pathways of exposure to ENPs is resuspension of ENPs released from the contaminated clothing. The resuspension of particles from contaminated clothing was reported to cause inhalation exposure [6]. Studies reported that a significant fraction of particles deposited onto clothing are subsequently resuspended into the air due to physical activities, and that this resuspension contributes to inhalation exposures [4], [6]. Exposure to individual and small agglomerates of ENPs can evoke higher inflammation when compared with micrometer sized agglomerates of ENPs [7], [8], [9].

To date, there are no published studies that evaluate the severity of ENP exposure associated with commonly available protective clothing fabrics or determine the affecting factors for contamination and resuspension of ENPs from the contaminated clothing. Thus, the objectives of this study were to study potential exposure contributed by human activities when wearing the ENP contaminated personal protective clothing, and quantitatively evaluate relative ENP to each fabric type. Moreover, this research aims to evaluate the primary factors responsible for ENP adhesion and release from these fabrics and identify optimal fabric characteristics for protection against toxic ENPs. With this study, workers in different fields can readily choose appropriate personal protective clothing when working with certain types of ENPs, as suggested from our results.

## CHAPTER 2

### METHODS

This study was comprised of two evaluations that include (1) ENP exposure at the breathing zone associated with shaking contaminated protective clothing and (2) qualitative evaluation regarding the main characteristics responsible for ENP adhesion, retention and release from these fabrics.

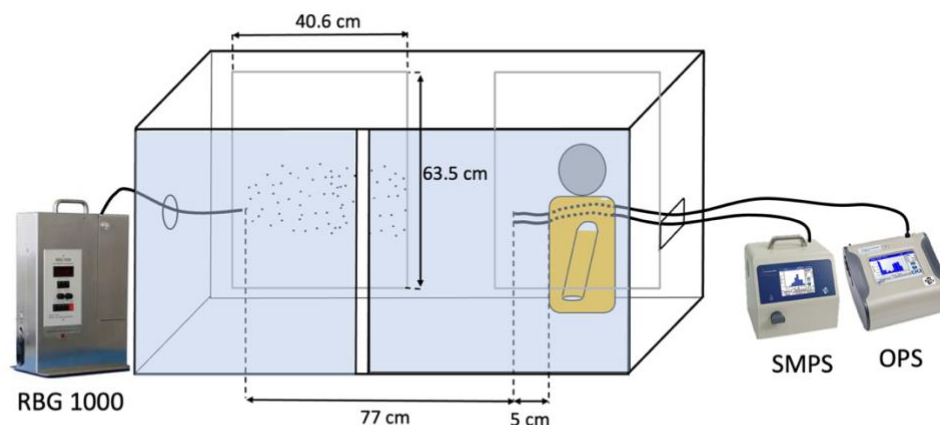
#### **2.1) Materials**

Three common types of ENPs were studied, they were aluminum oxide ( $\text{Al}_2\text{O}_3$ ), multi-walled CNTs (MWCNTs) and carbon black. Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) (Nanophase Technologies Corporation, Romeoville, IL, USA) ENPs are spherical with an average primary size of 40 nm. MWCNTs are routinely produced in industrial settings by popular chemical vapor deposition (CVD) process. The primary diameter of MWCNT (Nanolab, Waltham, MA, USA) is between 10 to 30 nm, and the lengths are in the micrometer ranges. Carbon black (Printex grade) is widely used in a dry powder form in printer toners and ink. The average primary size of carbon black (carbon black-Printex powder, Orion, Germany) is 40 nm. Four popular types of lab coat fabrics tested in this study include cotton twill woven, polyester/cotton blend (80% polyester and 20% cotton) plain woven, polypropylene spunbond nonwoven, and polyethylene spunbond nonwoven (DuPont<sup>TM</sup> Tyvek®), respectively. All lab coats were purchased in adult size S through a commercial vendor of protective clothing. Isopropyl alcohol, distilled water and cleanroom paper towels were used to carefully clean the equipment and surfaces of the enclosure in the fume hood where experiments were performed.

## **2.2) Facilities, Equipment and Procedure**

The research was conducted in a class 100 level cleanroom to eliminate background aerosols and to provide the accurate measurement of ENPs. The cleanroom was operated at slightly negative pressure, enclosed to contain particles, and exhausted to a HEPA filter with an emergency evacuation. The background particle level in this cleanroom was approximately 0 – 70 particles/cm<sup>3</sup> in the 10 nm – 10  $\mu$ m size range. A special enclosure was designed and placed inside the fume hood in the cleanroom to contain generated aerosol for experiments and provide a controlled environment for each experiment. The enclosure was made from acrylic plastic and had two front removable panels and two filter panels (40.6 cm  $\times$  63.5 cm each), which capture particles as small as 0.3  $\mu$ m, on the back sides venting the air to the hood exhaust as illustrated in Figure 1 (a). The main reason for having removeable panels was for access to the mannequin and equipment, and to enclose the mannequin for the ENP release experiments as seen in Figure 1 (b). ENPs were aerosolized by Powder Dispersion Generator RBG 1000 (Palas GmbH, Germany), dispersing particles with the primary size between 0.1  $\mu$ m and 100  $\mu$ m. When the ENP aerosol contamination onto the lab coat on the mannequin was completed, the contaminated lab coat was kept on the mannequin inside of the enclosure and isolated with a front panel in a compartment of a half-sized enclosure (Fig. 1b). At this time, the remaining aerosols outside of the compartment containing the isolated mannequin were purged away, then the panel was removed from the compartment and replaced to the front side for the particle release measurement in the enclosure. A shaker was placed underneath the mannequin and held it to simulate gentle motions of workers such as walking-related vibrations. The Roto-Shake Genie rotary shaker (Scientific Industries, Bohemia, NY) was used at 70 cycles/min with the rocking angle of 10 degrees horizontally to simulate workers' motion causing particle release from the contaminated lab coats.

(a)



(b)

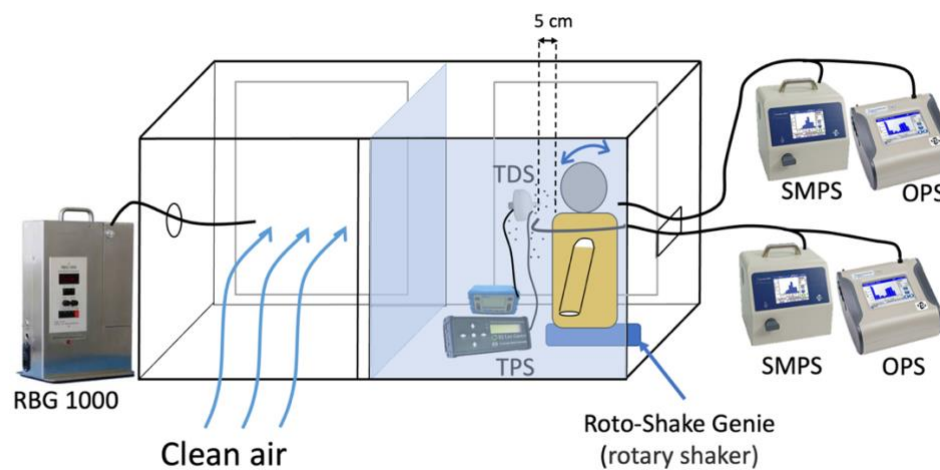


Figure 1. Illustration of the contamination and resuspension process experimental setup. Clean air was flowed from the cleanroom toward the enclosure placed inside the fume hood. (a) Engineered nanoparticles (ENPs) aerosolization for contamination on lab coats. (b) Resuspension of ENPs through shaking and particle sampling.

The right and left side of the enclosure each have a hole to allow the conductive tubing and cables of the direct reading instrument (DRIs) to go through (Fig. 1). Particle number concentrations and size distributions of resuspended ENPs during aerosolization and shaking the

contaminated lab coat were measured with DRIs, including the NanoScan SMPS Nanoparticle Sizer (TSI Model 3910, Shoreview, MN, USA, 10–420 nm, 13 channels) and the Optical Particle Sizer (OPS) (TSI Model 3330, Shoreview, MN, USA, 0.3–10  $\mu\text{m}$ , 16 channels). The sampling flow rates for NanoScan SMPS and OPS were 0.9 L/min and 1.0 L/min, respectively. Both DRIs were used to measure particle concentrations for diameters from 10 nm to 10  $\mu\text{m}$  with a 1 min response time, and the instruments were connected with conductive tubing (model 3001901, TSI, Shoreview, MN, USA) which was approximately 1 m length with inside diameter of 0.48 cm to reach the measuring locations. Mass concentrations of resuspended ENP aerosols were measured using gravimetric methods weighing the collected ENPs on the filters. We used National Institute for Occupational Safety and Health (NIOSH) analytical method (NMAM) 5040 to assess elemental carbon for MWCNT and carbon black [10], NMAM 0500 for nanoalumina and NMAM 7402 for MWCNT. NMAM 7402 is typically used for the evaluation of fiber based particles such as asbestos and CNT [11], while NMAM 0500 is used for the analysis of airborne particulate particles [12]. A thermal anemometer (VelociCalc® 9545, TSI, Shoreview, MN, USA) was used to measure the humidity, temperature and air velocity to ensure all work is done in a carefully controlled environment.

Two types of nanoaerosol samplers—a Tsai Diffusion Sampler (TDS) [5] and a thermal precipitation sampler (TPS) (RJLee, Monroeville, Pa, USA) [13], [14]—were used to collect aerosol particles during the release process. The flow rate of the TDS was 0.3 L/min; it collected nano and respirable sized particles with cut off aerodynamic diameter of 3.8  $\mu\text{m}$ . [15] A transmission electron microscope (TEM)-copper grid (SPI 200 mesh, carbon filmed) was taped onto a 25 mm diameter polycarbonate membrane filter (0.2  $\mu\text{m}$  pore) mounted in the TDS cassette and connected to a pump to collect ENPs on the grid for TEM, scanning electron microscope

(SEM), and energy-dispersive X-ray spectroscopy (EDS) experiments, to analyze morphology and elemental composition. The TPS also collects ENPs directly onto a TEM grid with the flow rate of 0.05 L/min; the grids were analyzed using TEM. Due to the ferromagnetic ability, a nickel carbon filmed TEM grid was used to sample TPS.

## **2.3) Experimental process**

### *2.3.1) Aerosolization of protective clothing with ENPs*

ENP powders were dispersed approximately 77 cm in front of the mannequin dressed in a lab coat, with swatches on the top of the protective clothing to contaminate the fabric inside of the enclosure (Fig. 1). Five fabric swatches (20 cm × 20 cm) were used for each experiment, which represent the lab coat and can be accurately weighed before and after experiments. Four fabric swatches were placed on the front side of the mannequin wearing a lab coat, and one fabric swatch was placed on the back side of the mannequin. A powder dispersion generator RBG 1000 was operated at a dispersing pressure of 2 bar, the piston velocity of 5 mm/h and a rotational brush frequency of 1194 rpm. A set of DRIs were placed in front of the mannequin wearing protective clothing to measure the total number concentrations of exposed ENPs. Background concentration measurements were taken for 10 min before the experiment to determine a clear baseline to compare the concentration increase during the contamination and resuspension processes. According to published data regarding occupational exposure concentrations of metal oxide particles, they were typically in the range of  $10^4$  to  $10^5$  particles/cm<sup>3</sup>, including background particles [5], [16]–[20]. Thus, we dispersed ENP aerosols with concentrations ranged from  $10^4$  to  $10^5$  particles/cm<sup>3</sup> for 30 min to simulate the practical contamination of a person wearing a lab coat in such a workplace.

### *2.3.2) Resuspension of particles from contaminated clothing*

After surface contamination on the lab coat, the contaminated lab coat on the mannequin was isolated with panels, as shown in Figure 2 (b). Two sets of DRIs were used to measure particle number concentrations, one set to measure at the mannequin's nose and the other set to measure at 30 cm horizontally away from the back of the head, representing the breathing zone and bystander particle exposure. TDS and TPS collect particles during the release process at the same locations as DRIs at the front of the mannequin. The contaminated fabric swatches attached on the mannequin were shaken through the shaking motion of the mannequin sitting on an automatic shaker. The mannequin was shaken automatically for 30 min to simulate worker's motion and resuspension of ENPs with no air exchange. The ENPs deposited on the fabric surface were resuspended into the air through shaking. DRIs monitored the whole process including background concentration, contamination process, post-contamination and resuspension concentrations. The weight of the fabric swatches was measured before the aerosolization of ENP and after the release process to evaluate the change of weight of fabric swatches after contamination and release processes.

At the end of each experiment, fabric swatches were stored in a sealed bag then disposed of as hazardous waste. All surfaces were cleaned using distilled water and alcohol following standard cleanroom cleaning procedures to ensure no cross-contamination and overall safety.

### *2.3.3) Airborne particle sampling using filter-based gravimetric sampling methods*

The experimental procedure of collecting resuspended ENPs using filter-based NIOSH Manual of Analytical Methods (NMAM) sampling method was similar to the process shown in Figure 1. The difference was the longer duration of the experiment (one hour contamination and six hours shaking) to provide a higher amount of ENPs deposited onto the lab coat and higher level

of resuspension sufficient for filter sampling. NMAM 5040 was used for elemental carbon analysis for MWCNT and carbon black in 37 mm cassettes with a quartz-filter by NMAM specifications at a sampling flow rate of 2 L/min [10]. NMAM 0500 was used to collect Al<sub>2</sub>O<sub>3</sub> ENPs in 37 mm closed face cassettes with a poly vinyl chloride (PVC) filter [12] and NIOSH 7402 was used to collect CNT in a 25 mm open faced cassette with mixed cellulose ester (MCE) membrane filter [11] by NMAM specifications at a sampling flow rate of 2 L/min. The particles collected through the NMAM 0500 and NMAM 7402 methods were weighed to obtain the mass change. The deposited particles on the fabric swatches were examined by SEM.

#### *2.3.4) Statistical Analysis*

Statistical analysis was conducted with the R and RStudio software package (version 1.4.1106, BCorps™, Boston, MA, USA). The aerosolized particle number concentration of different ENPs and release of ENPs for different fabrics were assessed and evaluated for correlation analysis. The mass change per unit mass were assessed and evaluated using standard ANOVA techniques followed by Tukey's honestly significant difference test. At a 95% confidence level,  $p$ -values  $< 0.05$  were considered statistically significant.

#### *2.3.5) Fabric descriptive properties measurements*

Fabric characterizations were conducted on uncontaminated fabrics according to ASTM standard testing methods for textiles. Fabric thickness was measured using a thickness tester (Custom Scientific Instruments, Easton, PA USA) according to ASTM method D1777. Five 5 cm × 5 cm square fabric swatch samples of each lab coat were used to determine fabric thickness. Water vapor transmission rate (WVTR, g/(m<sup>2</sup> × day)) of a fabric is the amount of water vapor that penetrates the fabric in a unit area in 24 hours. WVTR can be used to evaluate fabric breathability

and wearing comfort of textiles. A W3/062 water vapor transmission rate test system (LabThink International Inc., Boston, MA, USA) was used to measure the WVTR of the lab coat fabrics via ASTM D6701 method. Six circular fabric swatch samples with 6.50 cm diameter were tested for each lab coat. The circular samples were loaded into the test cells that also contained deionized water. Water loss in the test cells was measured at testing conditions of 38 °C and 10 % relative humidity. In addition, tensile testing and abrasion resistance testing were used to measure fabric durability. ASTM D3884 and ASTM D5034 methods were used for testing abrasion resistance and tensile strength, respectively. First, tensile testing was conducted using an Instron tensile tester (Instron Worldwide, Norwood, MA) in accordance with ASTM D5034 Standard Test Method for Breaking Strength and Elongation of Textile Fabrics (Grab Test). The load cell used in the testing was 500 N. Eight replicates of “dog-bone” fabric swatches were used for testing each lab coat. The fabric swatches were stretched at a rate of 10 mm/min and stress-strain curves were collected. Abrasion resistance was measured using an abrasion tester in accordance with ASTM D3884 Standard Guide for Abrasion Resistance of Textile Fabrics (Rotary Platform, Double-Head Method). Eight replicates of circular fabric swatches with a diameter of 11 cm were used for testing each lab coat. Each fabric swatch was rubbed until a visible hole on fabric surface was observed and the cycle of rubbing on the platform was recorded.

A Krüss DSA30 goniometer was used to quantify wettability of the uncontaminated fabrics. Substrates did not require further sample preparation for WCA analysis; all data were collected under ambient laboratory conditions at  $21 \pm 1$  °C and < 25% relative humidity. The probe liquid parameters (density 0.9970 g/mL, viscosity = 0.010 P, surface tension = 72.16 mN/m) were programmed into the onboard software and employed for all WCA fitting. Static and dynamic (i.e., time-resolved) WCA data were collected depending on the nature of substrate (i.e.,

hydrophilic or hydrophobic). Static WCA measurements were collected with a 2  $\mu\text{L}$  drop of ultra-pure  $\text{H}_2\text{O}$  (Millipore,  $\geq 18 \text{ M}\Omega \text{ cm}$ ); 4  $\mu\text{L}$  drops were used in dynamic WCA measurements. Generally, the circle method was employed to fit hydrophilic surfaces and the tangent-1 algorithm was used to fit hydrophobic surfaces. Water absorption rates were determined via video analysis,  $t = 0 \text{ s}$  is defined as the time the water droplet first contacts the material surface. An adsorption rate was calculated by dividing the drop volume by the time it took for the drop to be fully adsorbed by the material.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### *3.1) Aerosolization of protective clothing with ENPs*

To characterize the contamination levels for each ENP studied, the average normalized number concentration of ENPs produced by the Powder Dispersion Generator RBG 1000 was measured in the size range between 10 and 420 nm using a NanoScan SMPS Nanoparticle Sizer. Measurements were repeated three times. The average measured normalized distribution for each of three ENPs is plotted in Figure 2. The data shows that the apparatus can produce ENPs in the range of  $10^4 - 10^5$  particles/cm<sup>3</sup>. The highest number concentration was found for Al<sub>2</sub>O<sub>3</sub>, followed by carbon black and CNTs. While the dispersed concentration of Al<sub>2</sub>O<sub>3</sub> and carbon black are found to be comparable, they are about 2 times larger than the concentration of dispersed CNTs. Within the 10 and 420 nm size range, each contaminant showed well-defined maxima with Al<sub>2</sub>O<sub>3</sub> and carbon black peaking at a size of ~90 nm while CNTs showed a peak nearer to ~115 nm.

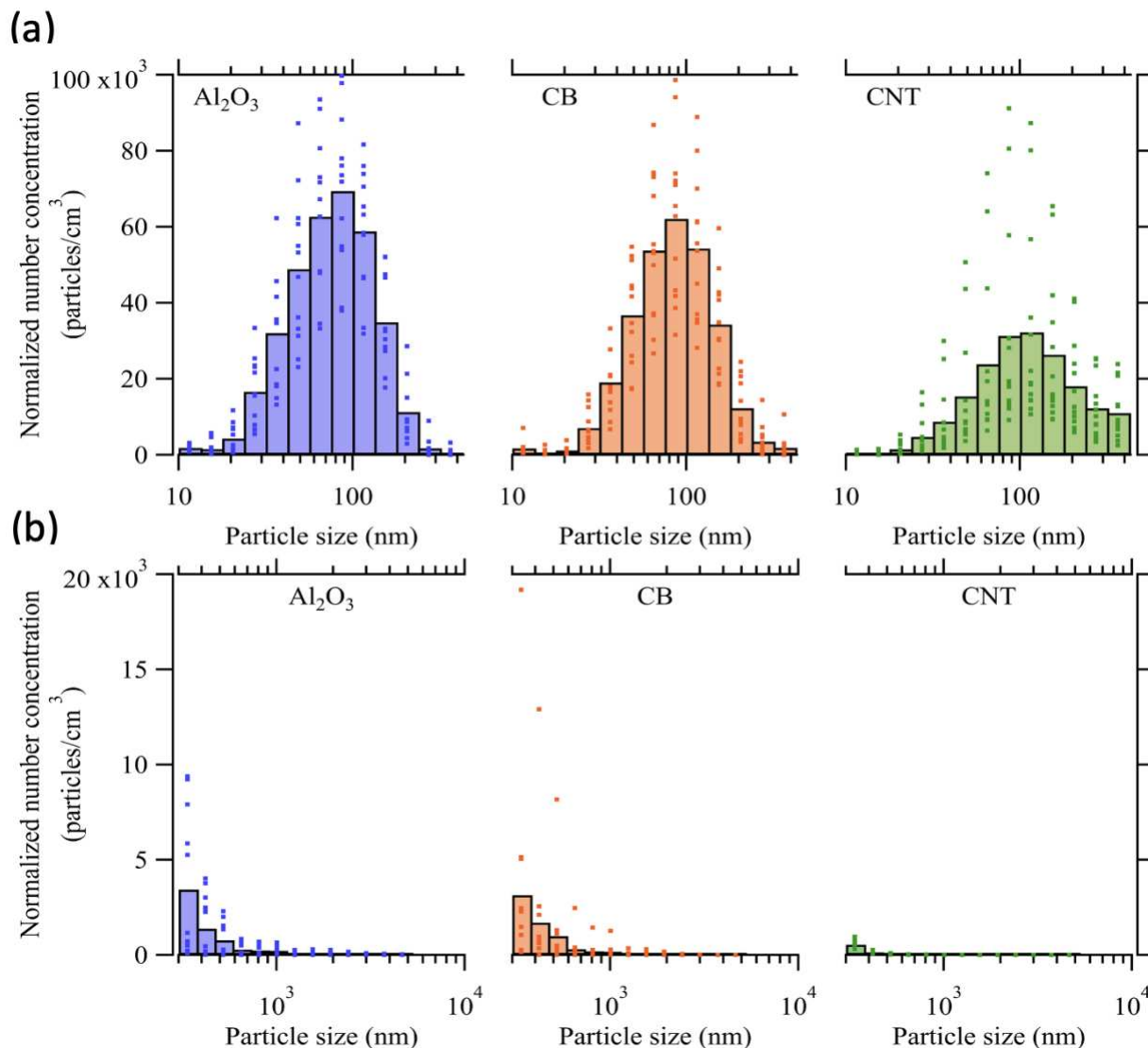


Figure 2. The measured aerosolized particle number concentration vs. the particle size (on a log scale) for the three ENPs used in this study. (a) Measured number concentration of 10–420 nm size range ENPs through NanoScan SMPS. (b) Measured number concentration of 0.3–10  $\mu\text{m}$  size range ENPs through OPS. Data points represent  $n = 12$  (or  $n = 13$ ) replicate measurements for  $\text{Al}_2\text{O}_3$  and CB (or CNT) ENPs, respectively. Histogram bars represent the averages of the replicate measurements for each ENP type.

A dominant feature in Figure 2 is the difference in magnitude of the total number concentration between the three contaminants. The average concentration of aerosolized CNT ENPs was about a factor of 2 less than the average concentrations of  $\text{Al}_2\text{O}_3$  and carbon black. This

might be explained by considering the degree of agglomeration of the three different ENPs. Most of the CNT ENPs were agglomerates, resulting in the CNT ENPs having a greater relative number of larger sized particles than the other two samples, as shown in Figure 2.

From Table S1 in supplementary material, the analysis of aerosolized particles to contaminate the protective clothing (Fig. 2) resulted in a strong correlation coefficient of 0.984 between  $\text{Al}_2\text{O}_3$  and carbon black. Moreover, the high correlation was obtained between  $\text{Al}_2\text{O}_3$  and CNT ENPs with the correlation coefficient of 0.784 and the significance of  $p$ -value were 0.001 meaning that there is a significant relationship between these ENPs. Overall, the particle size distribution from the contamination of used ENPs were highly correlated between each other.

### *3.2) Resuspension of Nanoparticles from Contaminated Clothing*

To minimize safety risks, it was important to identify those fabrics that release ENPs after contamination. Furthermore, any size-dependent adhesion of ENPs to a given fabric is revealed by comparing the normalized distribution of released ENPs to the normalized distribution of ENPs that contaminated the fabric. If the released distribution of ENPs was proportional to the contamination distribution, then the ENP size does not play a significant role in adhesion. If the size distribution of the released ENPs is significantly different than the size distribution of the generated ENPs, then the fabric preferentially traps or releases ENPs differently depending on the ENP size.

To investigate these questions further, the total normalized number concentration of airborne particles released from the contaminated protective clothing for each type of ENPs was measured by shaking the fabric after the contamination process. The results are presented separately in Figure 3. The total number concentration of released airborne particles from

contaminated protective clothing for each type of ENPs are presented separately in Figure 3. Based on Figure 3 (a), the cotton fabric showed the highest level of particle release, followed by polyester cotton and polyethylene. The highest number concentration of  $\text{Al}_2\text{O}_3$  ENPs released from cotton fabric were 134 particles/ $\text{cm}^3$ , whereas polypropylene fabric released the least number of particles, with number concentrations less than 33 particles/ $\text{cm}^3$ . The total number concentrations of airborne ENPs released from polyester cotton fabric and Tyvek® fabric were 101 and 37 particles/ $\text{cm}^3$ , respectively. According to Figure 3 (b), the number concentrations associated with carbon black ENP release from cotton and polyester cotton fabric were lower compared with  $\text{Al}_2\text{O}_3$  ENP release, whereas the release total number concentrations from polypropylene and Tyvek® are found to be comparable with 21 particles/ $\text{cm}^3$  and 23 particles/ $\text{cm}^3$  on average respectively. Figure 3 (c) shows that Tyvek®, polypropylene and polyester cotton fabric materials showed approximately similar levels of CNT ENPs release concentration during manipulation; the cotton fabric released the most, followed by the Tyvek®, polyester cotton and polypropylene fabric based on the average release concentrations.

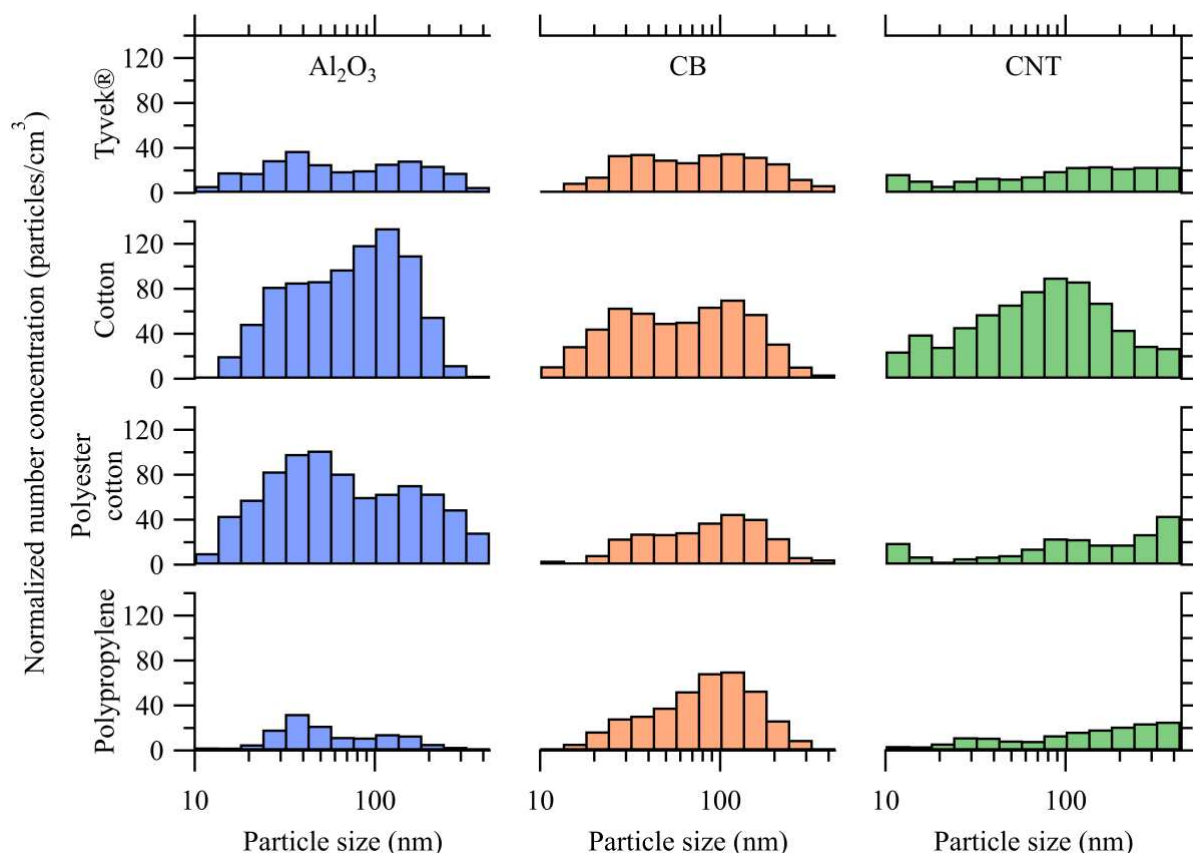


Figure 3. Measured normalized particle concentrations released after the shaking of contaminated lab coats made from Tyvek®, cotton, polypropylene and polyester cotton.

Three important conclusions can be drawn from Figure 3. The plots show (1) a higher release of  $\text{Al}_2\text{O}_3$  ENPs from cotton and polyester cotton fabrics studied when compared to the release of either carbon black or CNT ENPs, (2) cotton fabric is distinctive because it shows an enhanced concentration of released  $\text{Al}_2\text{O}_3$  and CNT ENPs when compared to the other fabrics studied, and (3) the release of  $\text{Al}_2\text{O}_3$  and carbon black ENPs from all fabrics appears to have a bi-modal distribution that is not proportional to the contaminating distribution plotted in Figure 2. This result is especially pronounced for cotton fabric, indicating that  $\text{Al}_2\text{O}_3$  and carbon black ENPs contaminating cotton likely have a size-dependent adhesive character.

By comparing the normalized distributions in Figures 4 (a), (b) and (c), it is clear that the release concentration of cotton and polyester cotton in Figure 3 (a) have a higher concentration of released  $\text{Al}_2\text{O}_3$  ENPs when compared to released carbon black and CNTs found in Figures 4 (b) and (c). This result that can be understood by the higher concentration of contaminating  $\text{Al}_2\text{O}_3$  ENPs as shown in Figure 2. In addition, from Figure 3 (a), the cotton fabric released the highest level of  $\text{Al}_2\text{O}_3$  ENPs of all fabrics studied. This would suggest that when dealing with metal-oxide ENPs, a polypropylene and Tyvek® fabric would offer clear advantages in trapping the ENPs over cotton, polyester-cotton or polypropylene fabrics.

For the case of carbon black contamination, Figure 3 (b) indicates that the overall concentration associated with carbon black release from cotton and polyester cotton fabric was about a factor of 1.5 lower when compared with  $\text{Al}_2\text{O}_3$  ENP release, even though Figure 2 indicates the contaminating concentration of carbon black is comparable to that for  $\text{Al}_2\text{O}_3$ . Polypropylene and Tyvek® were found to have the lowest carbon black ENP release. The data in Figure 3 (b) further suggests a bimodal distribution of carbon black ENP release from all fabrics studied, a trend that is most clearly evident for the cotton fabric. The measured released distributions are distinctly different in shape from the contamination distribution as shown in Figure 2, indicating that 60-70 nm sized carbon black ENPs adhere more strongly to cotton fabric than carbon black ENPs with either a smaller or larger size.

For the case of CNT contamination, Figure 3 (c) shows that Tyvek®, polypropylene and polyester cotton fabric showed approximately similar levels of CNT ENP release during manipulation. The release concentration of CNT ENPs for cotton was the highest when compared to Tyvek®, polypropylene or the polyester cotton fabric.

The mean differences in particle release concentration were found to be statistically significant at the  $p = 0.05$  level. According to Table S2, the  $\text{Al}_2\text{O}_3$  release total number concentrations of the cotton and polyester cotton fabric were found to be significantly different from Tyvek® and polypropylene, while cotton is not significantly different from polyester cotton with the  $p$ -value of 0.80. Similar for carbon black release total number concentrations, cotton and polyester cotton fabrics were significantly different from Tyvek® and polypropylene, however, based on total number concentration results of CNT ENPs, cotton was turn out to be significantly different from all other fabrics at the  $p = 0.05$  level. Statistical analysis on correlation was made on release results of  $\text{Al}_2\text{O}_3$ , carbon black and CNT ENPs. Based on Table S3 and S4 from supplementary material, the strong correlation between the fabrics can be observed for particle size distributions of released of  $\text{Al}_2\text{O}_3$  and carbon black ENPs with low significance  $p$ -values, meaning that there is a strong relationship between the particle size distribution of manipulated fabrics. However, according to the Table S5, the negative correlation factor and high significance  $p$ -values can be seen which indicates that there is no significant relationship between the variables.

Additionally, the SEM images of resuspended particles collected on TDS samples are presented in Figure 4. Large agglomerates and few individual particles of  $\text{Al}_2\text{O}_3$ , all of which are smaller than  $1\text{ }\mu\text{m}$  were released from the surface of Tyvek® fabric, as shown in Figure 4 (a). Limited amount of carbon black were deposited polycarbonate filters collected by the TDS samplers, with some individual sub-micrometer-sized particles at approximately  $50\text{ nm}$  (Fig. 5b). As seen in Figure 4 (c), small CNT clusters containing single fibers were collected during the release process of Tyvek® fabric. The collected limited amount of CNT ENPs could be explained with the low release concentration observed during the shaking process, whereas the larger amount

of Al<sub>2</sub>O<sub>3</sub> ENPs and carbon black released from the surface of the fabric was due to the higher total number concentration of released particles.

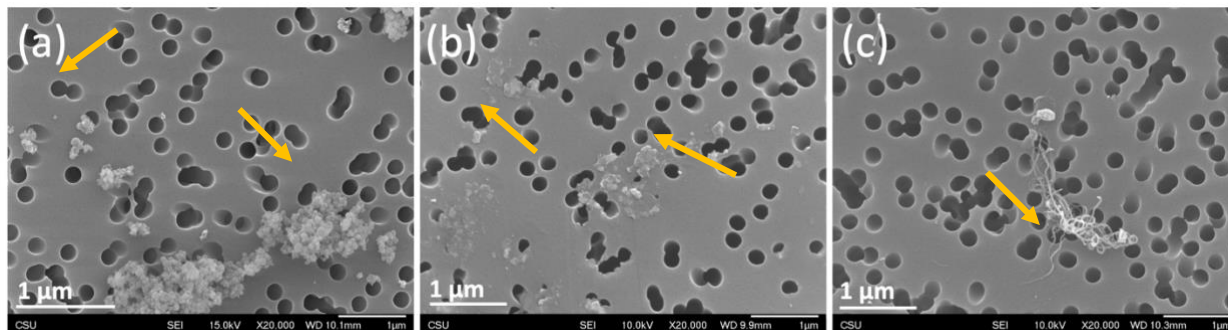


Figure 4. SEM images of resuspended ENPs collected on TDS samples (a) Al<sub>2</sub>O<sub>3</sub>. (b) carbon black. (c) CNT. Arrow marks note single ENPs or agglomerates.

### 3.3) Theoretical principle of particle-fabric adhesion

The release total number concentrations of each used nanomaterial depends on particle size and electrostatic particle charge [18]. Smaller ENPs are more readily retained on the fabrics [18]. A detailed accounting of the interaction between an ENP and a fabric surface is complicated, because it depends upon many variables, most of which are unknown and difficult to accurately determine. In the case of uncharged ENPs that do not chemically interact with a fabric surface, the dominant particle-substrate interaction is often attributed to either a surface force that arises from inter-molecular van der Waals (vdW) interactions or a capillary force due to a thin water bridge that forms between the ENP and the fabric surface. In what follows, each of these two mechanisms is considered in more detail.

The integral form of the vdW molecular interaction (often called the Hamaker force) is typically larger than electrostatic forces and thus is often invoked as the dominant force that attracts nanometer-sized particles toward a surface. Once in contact, the force that holds the two bodies

together is termed an adhesive force. If the interaction between the ENP and fabric is perfectly elastic so no energy is dissipated during their interaction, and if no chemical reaction occurs, then the adhesive force is equal in magnitude to the vdW surface force.

For the case of a perfect sphere of diameter  $D$  comprised of material 1 (the ENP) resting on a cylindrical surface of diameter  $D_c \approx 2 \mu\text{m}$  comprised of material 2 (a fiber of the fabric), the Hamaker adhesive force is complicated due to the geometry. For a relatively large cylinder such that  $D_c/D < 100$ , the interaction force between the ENP and the cylinder can be well approximated by a much simpler sphere-flat plane geometry. In this case, the adhesive force is given by the simple formula.

$$F_{ad} = \frac{H_{12}D}{12 z_0^2} \quad (1)$$

where  $H_{12}$  is the Hamaker constant describing the interaction between the ENP (1) and the planar surface (2). The parameter  $z_0$  is the separation distance between the sphere and the plane. For perfectly smooth surfaces,  $z_0$  is usually taken to equal an interatomic distance and is typically assigned a value of  $z_0 \approx 0.3 \text{ nm}$ . For a fixed ENP diameter  $D$ , it is clear from Eq. 1 that the Hamaker constant  $H_{12}$  controls the interaction strength of the adhesive force.

With the widespread use of the atomic force microscope (AFM), tabulated values for  $H_{12}$  for common materials are becoming available, but reliable values for arbitrary combinations of materials are still difficult to find. For this reason,  $H_{12}$  is often estimated using combination rules that rely on the values of the Hamaker constant inferred when identical materials interact with themselves. Thus, if  $H_{11}$  and  $H_{22}$  describe the interaction between a material 1 (or 2) with itself, then we can write

$$H_{12} \approx \sqrt{H_{11} \times H_{22}} \quad (2)$$

Using Eq. 2 and literature values for  $H_{11}$  and  $H_{22}$ , it is possible to construct estimates of  $H_{12}$  for the combination of materials relevant to this study (see Table 1 below).

Knowing  $H_{12}$ , checks can be made to determine if vdW interactions alone can qualitatively account for the trends observed for the release of ENPs presented in Figure 3. For example, if vdW interactions largely determine the adhesion of  $Al_2O_3$  ENPs to the fabrics studied, then a rank ordering of the calculated  $H_{12}$  should follow the measured trend observed in Fig. 4(a), especially for the smallest  $Al_2O_3$  ENPs (small particle size), i.e.,  $H_{12}^{polyester-cotton} \approx H_{12}^{polypropylene} \approx H_{12}^{polyethylene} > H_{12}^{cotton}$ . Table 1 lists relevant values for  $H_{12}$  calculated from Eq. 2 using literature values for  $H_{11}$  and  $H_{22}$ . The calculated values of  $H_{12}$  are rank ordered from low to high in Table 1.

Table 1. Calculated Hamaker constants for  $Al_2O_3$  and carbon black interacting with different fabrics.

| ENPs                    |                  | $Al_2O_3$              | Carbon black           |
|-------------------------|------------------|------------------------|------------------------|
| $H_{11}$ (J)            |                  | $15.0 \times 10^{-20}$ | $47.0 \times 10^{-20}$ |
| $H_{22}$ (J)            | Cotton           | $5.8 \times 10^{-20}$  | $5.8 \times 10^{-20}$  |
|                         | Polypropylene    | $6.0 \times 10^{-20}$  | $6.0 \times 10^{-20}$  |
|                         | Tyvek®           | $6.3 \times 10^{-20}$  | $6.3 \times 10^{-20}$  |
|                         | Polyester cotton | $8.8 \times 10^{-20}$  | $8.8 \times 10^{-20}$  |
| $H_{12}$ from Eq. 2 (J) | Cotton           | $9.3 \times 10^{-20}$  | $1.65 \times 10^{-20}$ |
|                         | Polypropylene    | $9.5 \times 10^{-20}$  | $1.68 \times 10^{-20}$ |
|                         | Tyvek®           | $9.7 \times 10^{-20}$  | $1.72 \times 10^{-20}$ |
|                         | Polyester cotton | $11.5 \times 10^{-20}$ | $2.0 \times 10^{-20}$  |

In the same way, a similar analysis can be made to interpret the results presented in Figure 3 (b) for carbon black. If vdW interactions largely determine the adhesion of carbon black ENPs to the fabrics studied, then a rank ordering of the relevant  $H_{12}$  for the smallest carbon black ENPs (small particle size) should follow the trend observed in Fig. 4(b), i.e.,  $H_{12}^{polyester-cotton} \approx H_{12}^{polypropylene} \approx H_{12}^{polyethylene} > H_{12}^{cotton}$ . Table 1 lists relevant values for  $H_{12}$  calculated from Eq. 2 using literature values for  $H_{11}$  and  $H_{22}$ . As seen from Table 1, the Hamaker constant for carbon is  $\sim 3$  times larger than for  $Al_2O_3$ , so if vdW forces are dominant, a carbon black ENP should adhere about  $\sqrt{3} \approx 1.7$  times more strongly to a fabric fiber as an  $Al_2O_3$  ENP of the same size. The calculated values of  $H_{12}$  for carbon black are also rank ordered from low to high in Table 1.

A similar analysis for CNT ENPs is not attempted because the long tubular shape of CNTs is not well approximated by a sphere.

The observed prevailing trend evident from Table 1 does not match the results in Figures 4 (a) and (b). The calculated values of  $H_{12}$  for both  $Al_2O_3$  and carbon black ENPs predict that  $H_{12}^{polyester-cotton} > H_{12}^{polypropylene} \approx H_{12}^{polyethylene} \approx H_{12}^{cotton}$ , indicating that  $Al_2O_3$  and carbon black ENPs should adhere most strongly to polyester-cotton and that ENP release from polypropylene, polyethylene and cotton should all show similar behavior if vdW forces are dominant. In particular, the measured trend that cotton preferentially releases the highest concentration of either  $Al_2O_3$  or carbon black ENPs is not supported by considering vdW forces alone.

The second dominant interaction between an ENP and a fabric fiber is capillarity, which is related to the formation of a small bridge of moisture between the ENP and fabric. The water bridge that forms is aided by a thin equilibrated water layer that is present on all surfaces of both materials exposed to ambient conditions. The relative humidity (RH) in the lab determines the

amount of water that will spontaneously condense in the small volume between the ENP and the fabric surface. The water bridge serves to bind the ENP to the surface. In the limit of high humidity, complete immobilization of ENPs often result.

In the case of very low humidity, or if the surface chemistry of either the ENP or the substrate acts to prevent water condensation, the capillary force will be greatly reduced. Since cotton absorbs water, while polyester, polypropylene and polyethylene do not, an ENP resting on a cotton fiber should show a reduction in the capillary force when compared to the other three fabric surfaces. This is in fact what is observed in Figures 4 (a) and 4 (c), a result that strongly suggests that capillarity plays a dominant role in attaching  $\text{Al}_2\text{O}_3$  and CNTs to the fabric under study.

A similar conclusion can also be reached by examining carbon black release data that is plotted in Figure 3 (b). Once again, the cotton fabric shows a pronounced release for carbon black particle size  $< 50$  nm, consistent with the loss of capillary adhesion. At higher ENP particle size greater than  $\sim 80$  nm, the release data from the polyester cotton fabric exceeds that found in cotton. The implication is that the 20% cotton fibers present in the polyester cotton blend play a role in ENP adhesion. This suggests that for larger ENPs, the addition of only 20% cotton fibers interwoven between the 80% majority of polyester fibers might play a role in wicking away moisture, thereby reducing the effects of capillary forces between ENPs and the polyester cotton fabric surface.

In addition to DRI measurements, the total mass of fabric was measured before the contamination and after the release process. The mass increase of fabric presenting the remaining ENPs on the fabric and the mass change per unit mass of fabrics are shown in Table 2. According to Table 2, Tyvek® fabric showed the highest mass change per unit mass from the  $\text{Al}_2\text{O}_3$  ENPs

contamination (3258.7 ppm), while polypropylene, polyester cotton and cotton presented lower mass change per unit mass of 653.9, 402.2 and 50.7 ppm respectively. From the contamination and release of carbon black ENPs, Tyvek® was also found to be the fabric with the highest mass increase per unit mass with the value of 1844.5 ppm, followed by polypropylene with 760.4 ppm, polyester cotton with 334.4 ppm and polypropylene with 283.1 ppm of mass increase per unit mass. However, the mass change per unit mass of CNT ENPs was similar for all fabrics. Moreover, Table 2 provides the results of released total number concentrations, where it is clearly seen that the release concentration measured from the front side of the mannequin was higher than the release concentration measured at the back of the mannequin. Based on the total number concentrations at the front and back sides of the mannequin, the highest release concentration of Al<sub>2</sub>O<sub>3</sub> and CNT ENPs was found from manipulating cotton fabric, while polyester cotton fabric release concentration was the highest for carbon black ENPs. The total number concentration during the release of Al<sub>2</sub>O<sub>3</sub>, carbon black and CNT ENPs for Tyvek® and polypropylene fabrics were found to be the lowest.

Based on statistical analysis shown in Figure S1 (a) from supplementary material, that there is a significant difference between the mass change per unit mass of Tyvek® compared with polypropylene, cotton and polyester cotton ( $p < 0.05$ ) with 95% confidence level. However, cotton, polyester cotton and polypropylene are not significantly different from each other ( $p > 0.05$ ). Figure S1 (b) shows the significance of mass change per unit mass from the contamination and release of carbon black ENPs, where the results are quite similar to the results from Al<sub>2</sub>O<sub>3</sub> (Fig. S1 (a)). The only difference is the mass change per unit mass of Tyvek® fabric is not significantly different from the mass change per unit mass of polypropylene fabric ( $p > 0.05$ ). It is clearly seen

from Figure S1 (c), there is no significant difference between fabrics from CNT ENPs contamination and release tests.

Two major conclusions can be made from Table 2. First of all, the level of generated CNT aerosols was lower compared with  $\text{Al}_2\text{O}_3$ , which was an affecting factor showing a lower mass increase for all fabrics exposed with CNT ENPs. Since our focus was evaluating difference between fabric types with the same ENP, the variation in the generated concentrations could be neglected. Moreover, CNT ENPs are considered the lightest nanoparticles among the other used ENPs, therefore the mass increase for each type of fabric was lower compared with  $\text{Al}_2\text{O}_3$  and carbon black ENPs exposure and release. Based on these results, Tyvek® is the best fabric for trapping  $\text{Al}_2\text{O}_3$  and carbon black ENPs, resulting in less resuspension of particles from the contaminated lab coat. There is not much difference in trapping ENPs between polypropylene, polyester cotton, and cotton fabrics. Secondly, the difference in released total number concentrations between the front and back of the mannequin, as was expected the concentrations of released particles at the breezing zone are higher than particles released from the back side of the worker wearing the contaminated protective clothing.

Table 2. Contamination level and released airborne ENPs concentration for 30 minutes of various types of lab coat.

| ENPs                               | Lab coat fabric type | Plain lab coat weight | Contaminated lab coat weight after shaking | Lab coat mass change |                           | Release at front (30 min)                           | Release at back (30 min) |
|------------------------------------|----------------------|-----------------------|--------------------------------------------|----------------------|---------------------------|-----------------------------------------------------|--------------------------|
|                                    |                      | Average Mass (g)      |                                            | $\Delta m^*$ (mg)    | $\Delta m/m_0^{**}$ (ppm) | Number conc. 10-420 nm (particles/cm <sup>3</sup> ) |                          |
| <b>Al<sub>2</sub>O<sub>3</sub></b> | Cotton               | 76.33 ± 0.25          | 76.34 ± 0.25                               | 3.86                 | 50.64                     | 174 ± 64                                            | 30 ± 7                   |
|                                    | Polypropylene        | 8.29 ± 0.02           | 8.30 ± 0.03                                | 5.07                 | 611.6                     | 83 ± 41                                             | 61 ± 41                  |
|                                    | Polyester cotton     | 43.41 ± 0.13          | 43.43 ± 0.13                               | 16.77                | 386.3                     | 163 ± 46                                            | 101 ± 54                 |
|                                    | Tyvek®               | 10.63 ± 0.05          | 10.66 ± 0.04                               | 32.73                | 3078                      | 88 ± 37                                             | 45 ± 22                  |
| <b>Carbon Black</b>                | Cotton               | 64.41 ± 0.23          | 64.43 ± 0.24                               | 19.30                | 299.6                     | 96 ± 21                                             | 91 ± 22                  |
|                                    | Polypropylene        | 8.41 ± 0.02           | 8.42 ± 0.02                                | 5.40                 | 642.12                    | 74 ± 13                                             | 69 ± 16                  |
|                                    | Polyester cotton     | 40.17 ± 0.18          | 40.18 ± 0.18                               | 13.47                | 335.5                     | 102 ± 17                                            | 86 ± 19                  |
|                                    | Tyvek®               | 10.47 ± 0.04          | 10.49 ± 0.03                               | 19.08                | 1821                      | 90 ± 36                                             | 61 ± 5                   |
| <b>CNT</b>                         | Cotton               | 63.65 ± 0.21          | 63.66 ± 0.22                               | 7.24                 | 113.7                     | 126 ± 58                                            | 108 ± 47                 |
|                                    | Polypropylene        | 8.78 ± 0.03           | 8.79 ± 0.03                                | 1.24                 | 141.5                     | 52 ± 15                                             | 42 ± 12                  |
|                                    | Polyester cotton     | 39.96 ± 0.45          | 36.97 ± 0.46                               | 4.63                 | 115.9                     | 59 ± 7                                              | 37 ± 7                   |
|                                    | Tyvek®               | 10.56 ± 0.04          | 10.57 ± 0.04                               | 1.60                 | 151.6                     | 42 ± 6                                              | 32 ± 23                  |

\*:  $\Delta m$  – mass change of the contaminated lab coat after shaking from the initial lab coat weight.

\*\* :  $\Delta m/m_0$  – mass change per unit mass, where  $m_0$  – initial lab coat weight.

### *3.4) Airborne particle sampling using gravimetric methods*

Table 3 presents results of total number concentration of six hours of release process after one hour of exposure process, providing with ENPs total number resuspension concentrations during release process. It is clearly seen from Table 3 that the release concentration level after 1 hour of exposure was much higher than the 30 minutes release process concentration after 30 minutes of exposure. The total concentration during 6 hours of release from the manipulation of cotton and polyester cotton fabric were around 2 times higher than 30 minutes of release, while there was small difference between the 6 hours and 30 minutes of release of Tyvek® and polypropylene.

Additionally, we collected the resuspended ENPs during the simulated practical motions by the mannequin to understand the level of particle release using recommended methods by NIOSH. Table 3 presents the results of gravimetric analysis using NMAM 0500 for collecting Al<sub>2</sub>O<sub>3</sub> ENPs, NMAM 7402 for carbon black and CNT ENPs. It is noticeable that a high amount of carbon black and CNT ENPs were collected due to the use of the open cassette for inhalable sizes, while for the Al<sub>2</sub>O<sub>3</sub> collection was conducted using close-face NMAM 0500 cassette. According to the gravimetric results, the highest amount of released ENPs were collected from the surface of cotton and polyester cotton fabrics for all types of ENPs, while less amount of ENPs were collected from the surface of polypropylene and Tyvek® fabrics. Moreover, TEM images of the resuspended ENPs collected on the grid of TDS sample and contaminated fabric surfaces which characterized using SEM are shown in Figures 5 and 6. According to the Figure 5, individual particles and larger agglomerates of Al<sub>2</sub>O<sub>3</sub> and carbon black and the fiber of CNT collected on the grid were released from the surface of the fabric and mostly the large agglomerates were scattered on the surface of fabric as shown in Figure 6. Various morphologies of particle contaminations were seen on

polypropylene and Tyvek®; Al<sub>2</sub>O<sub>3</sub>, carbon black and CNT agglomerates were observed on both fabric fibers.

Table 3. Contamination level and released airborne ENPs concentration for 6 hours of various types of lab coat.

| ENPs                               | Lab coat fabric type | Release at front (6 hours)                          | Released airborne ENP           | Released total carbon* |                   |
|------------------------------------|----------------------|-----------------------------------------------------|---------------------------------|------------------------|-------------------|
|                                    |                      | Number conc. 10-420 nm (particles/cm <sup>3</sup> ) | Mass conc. (µg/m <sup>3</sup> ) | µg/sample              | µg/m <sup>3</sup> |
| <b>Al<sub>2</sub>O<sub>3</sub></b> | Cotton               | 258                                                 | 29.8 <sup>a</sup> ± 0.1         | -                      | -                 |
|                                    | Polypropylene        | 73                                                  | 1.2 <sup>a</sup> ± 0.1          | -                      | -                 |
|                                    | Polyester cotton     | 210                                                 | 21.3 <sup>a</sup> ± 0.2         | -                      | -                 |
|                                    | Tyvek®               | 75                                                  | 2.2 <sup>a</sup> ± 0.4          | -                      | -                 |
| <b>Carbon Black</b>                | Cotton               | 198                                                 | 89.9 <sup>b</sup> ± 0.3         | 20 <sup>c</sup>        | 27 <sup>c</sup>   |
|                                    | Polypropylene        | 121                                                 | 10.8 <sup>b</sup> ± 0.1         | 12 <sup>c</sup>        | 16 <sup>c</sup>   |
|                                    | Polyester cotton     | 254                                                 | 79.4 <sup>b</sup> ± 0.1         | 16 <sup>c</sup>        | 22 <sup>c</sup>   |
|                                    | Tyvek®               | 114                                                 | 22.2 <sup>b</sup> ± 0.1         | 19 <sup>c</sup>        | 27 <sup>c</sup>   |
| <b>CNT</b>                         | Cotton               | 223                                                 | 12.3 <sup>b</sup> ± 2.4         | 16 <sup>c</sup>        | 23 <sup>c</sup>   |
|                                    | Polypropylene        | 72                                                  | 7.8 <sup>b</sup> ± 4.5          | 13 <sup>c</sup>        | 18 <sup>c</sup>   |
|                                    | Polyester cotton     | 105                                                 | 10.8 <sup>b</sup> ± 2.5         | 16 <sup>c</sup>        | 22 <sup>c</sup>   |
|                                    | Tyvek®               | 87                                                  | 2.9 <sup>b</sup> ± 1.3          | 12 <sup>c</sup>        | 17 <sup>c</sup>   |

a: Mass concentration calculated using NIOSH 0500 close face for collecting airborne particles for 6 hours at a flowrate of 2 L/min.

b: Mass concentration calculated using NIOSH 7402 open face for collecting airborne particles for 6 hours at a flowrate of 2 L/min.

c: Mass concentration measured using elemental carbon analysis for 6 hours at a flowrate of 2 L/min.

\*: Released total carbon is the sum of released elemental carbon and organic carbon.

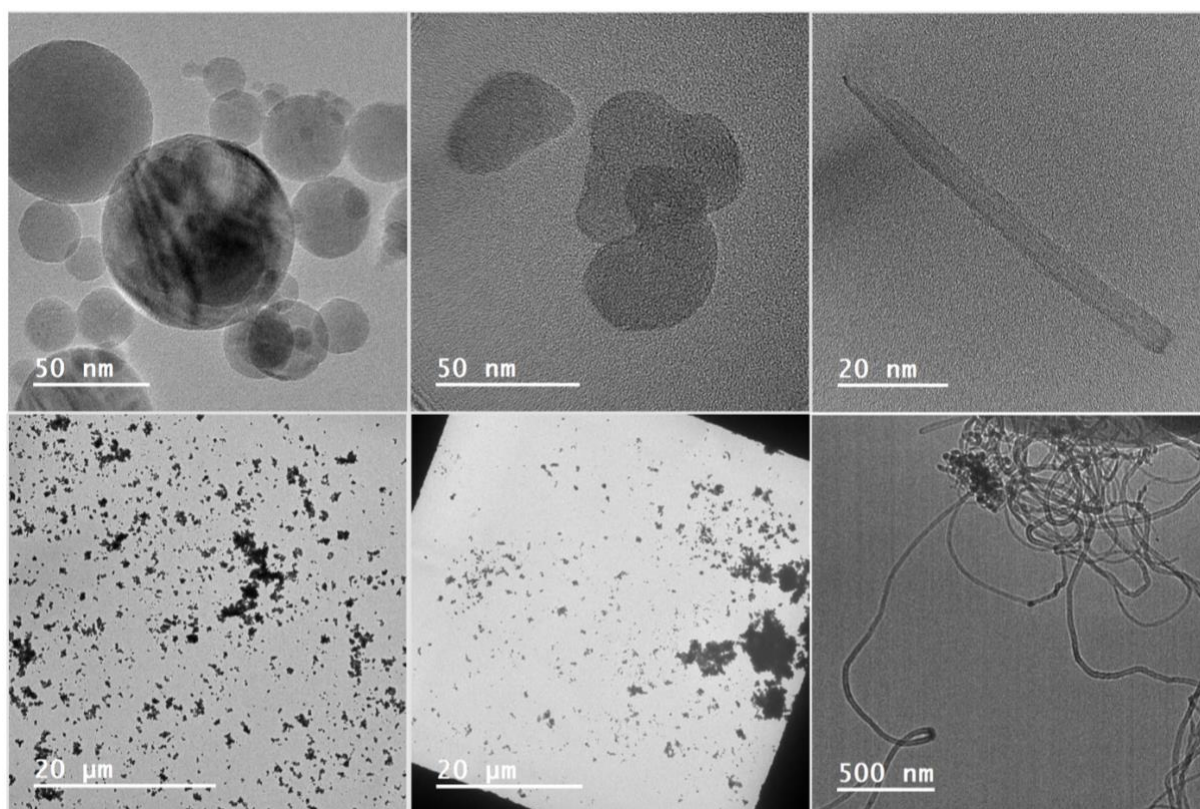


Figure 5. TEM images of sampled ENPs on grid collected on TDS samples (a)  $\text{Al}_2\text{O}_3$  at 50 nm and 20  $\mu\text{m}$  scale bars. (b) carbon black at 50 nm and 20  $\mu\text{m}$  scale bars. (c) CNT at 50 nm and 500 nm scale bars.

Besides the released airborne ENPs, the mass concentration of released total carbon for carbon black and CNT were also analyzed. According to Table 3, cotton fabric released the highest amount of carbon black ENPs based on the release mass concentration with the value of  $26 \mu\text{g}/\text{m}^3$  or  $20 \mu\text{g}/\text{sample}$ , while the least released fabric was polypropylene with the mass concentration of  $16 \mu\text{g}/\text{m}^3$ . The released mass concentration of Tyvek® and polyester cotton fabric from the exposure of carbon black were  $19 \mu\text{g}/\text{m}^3$  and  $16 \mu\text{g}/\text{m}^3$  respectively. Based on the CNT ENPs released total carbon results, cotton fabric was also found to be the most released fabric with the mass concentration of  $23 \mu\text{g}/\text{m}^3$  and Tyvek® fabric was observed with the lowest released mass concentration of  $17 \mu\text{g}/\text{m}^3$ .

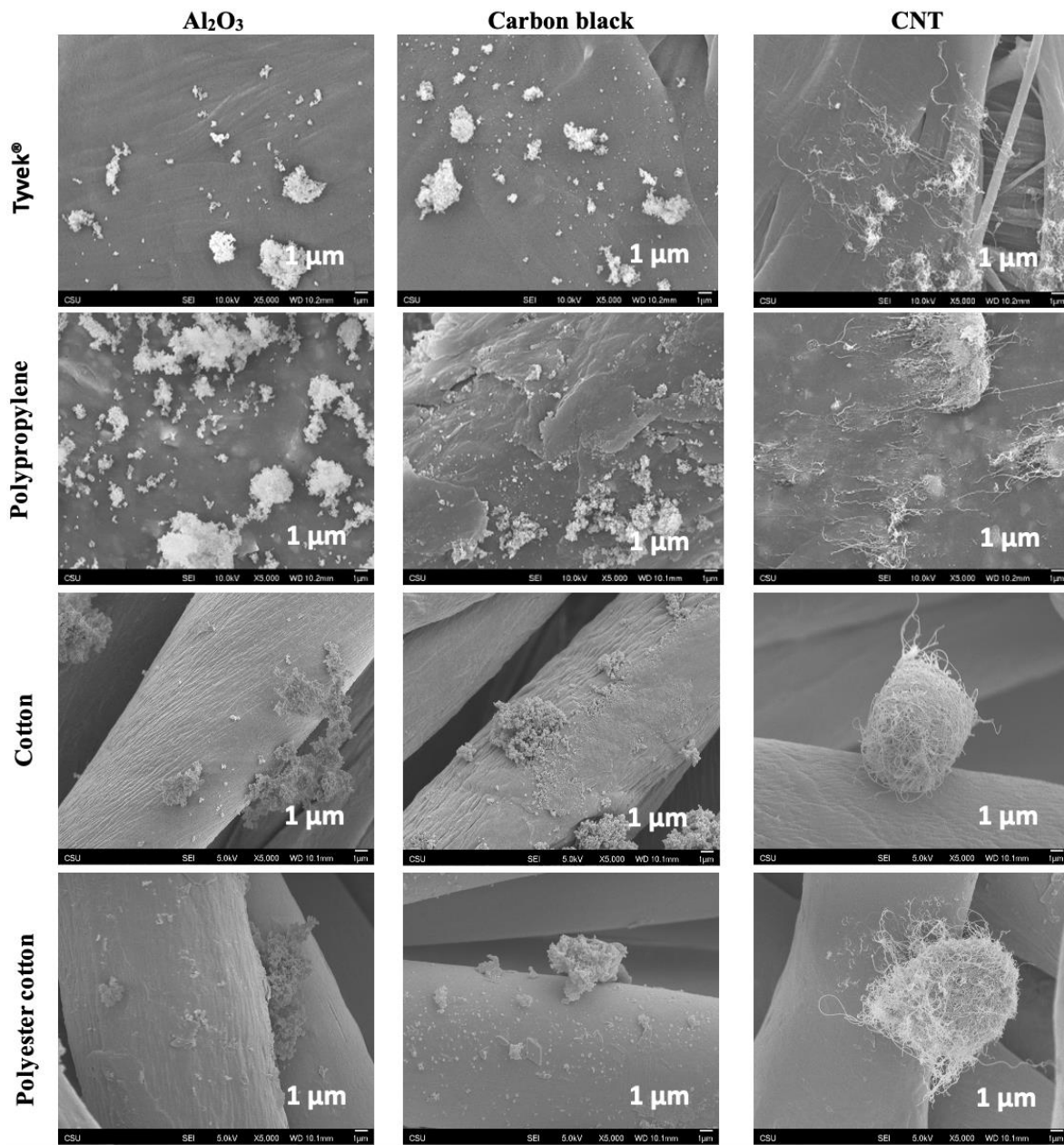


Figure 6. SEM images of the surface of fabrics contaminated with three types of ENPs and released.

### 3.5) Mechanical properties (durability) of lab coat fabrics

Figure 7 shows representative strain-stress curves of the four untreated fabrics including cotton woven, polyester cotton woven, Tyvek® nonwoven, and polypropylene nonwoven. The

stress-strain curves of cotton and polyester cotton woven are similar while those of Tyvek® and polypropylene nonwoven are similar. The curves of two woven fabrics can be divided into two zones at the yield point: the first zone corresponds to situation when the yarns within the fabrics move due to friction, resulting in deformation of weaves; the second zone is associated with the elongation of the yarns until the yarns break at the point of breaking shown on the strain-stress curves. Higher tensile strength, was found in the polyester cotton ( $39.74 \pm 6.50$  MPa) than in the cotton ( $30.39 \pm 4.00$  MPa), suggesting that the polyester cotton fabric is stronger than the cotton fabric. The addition of polyester yarns to cotton enables reinforcement of cotton fabric. The polyester cotton Young's modulus ( $97.85 \pm 10.00$  MPa) is lower than the Young's modulus of cotton ( $152.15 \pm 10.00$  MPa).

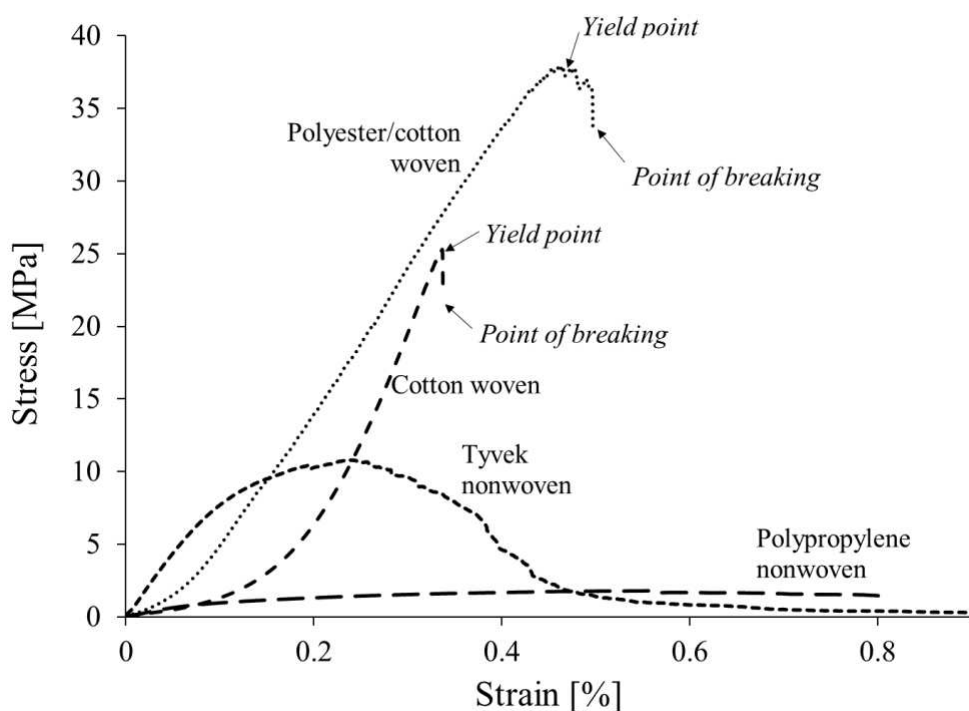


Figure 7. Representative strain-stress curves of four untreated fabrics including cotton woven, polyester cotton woven, Tyvek® nonwoven, and polypropylene nonwoven.

On the other hand, the two nonwoven fabrics (Tyvek® and polypropylene) show significantly different behaviors when they are stretched in comparison with the woven fabrics. They are stretchy without true breaking during the test. Tyvek® fabric demonstrates immediate plastic deformation and the stress flattens at approximately 0.5% strain. Polypropylene fabric shows plastic deformation during the entire test. The tensile strengths of the Tyvek® and polypropylene fabrics are  $11.64 \pm 3.35$  MPa and  $3.11 \pm 0.81$  MPa, respectively. Although they are notably lower than those of cotton and polyester cotton fabrics, the Tyvek® still shows a considerable strength against stretching compared to polypropylene. No Young's modulus was reported for the nonwoven fabrics, suggesting that both nonwoven fabrics are soft.

In a summary, the cotton and polyester cotton woven have high strength and stiffness and hence would have substantial durability in the workplace when compared to the Tyvek® and polypropylene lab coats. Comparing Tyvek® to polypropylene, Tyvek® shows appreciable durability when being used in lab coats.

Table 4. Abrasion resistance measured by abrasion cycles before failure for four untreated fabrics.

| <b>Fabric</b>    | <b>Fabric structure</b> | <b>Abrasion resistance*</b> | <b>Thickness (mm)</b> |
|------------------|-------------------------|-----------------------------|-----------------------|
| Cotton           | Twill Woven             | $605 \pm 48$                | $0.660 \pm 0.03$      |
| Polyester cotton | Plain woven             | $345 \pm 17$                | $0.406 \pm 0.003$     |
| Tyvek®           | Nonwoven                | $16 \pm 1$                  | $0.152 \pm 0.003$     |
| Polypropylene    | Nonwoven                | $41 \pm 3$                  | $0.254 \pm 0.003$     |

\* abrasion cycles before failure

Abrasion resistance is the ability of a fabric to resist surface wear caused by flat rubbing and can also be used to measure fabric durability. Table 4 shows abrasion resistance measuring average cycle before fabric failure that is defined by onsite of visible holes on fabric surface. The woven fabrics show significantly higher abrasion resistance than the nonwoven fabrics. In addition, cotton

is nearly twice as strong as polyester cotton against rubbing. First, the cotton fabric is thicker than the polyester cotton. Secondly, it is because the cotton woven has a twill structure (Fig. 8 a) that has more interlacing than a plain weave (Fig. 8 b). Therefore, twill woven hold yarns together more efficiently than plain woven. The Tyvek® and polypropylene coats both have substantially low abrasion resistance. The results are in a good agreement with the strain-stress curve results, suggesting that the cotton and polyester cotton fabrics have superior mechanical properties, while the Tyvek® and polypropylene fabrics are weak materials and would be used to make disposable lab coats.

WCA analysis of the four fabrics are shown in Table 5. These data reveal that the Tyvek® and polypropylene coats are hydrophobic (with static WCA of  $125.9 \pm 4.5$  and  $121.7 \pm 6.3^\circ$ , respectively) and the cotton polyester and cotton coats are hydrophilic (absorption rates of  $4.24 \pm 0.75$  and  $18.9 \pm 3.5 \mu\text{L/s}$ , respectively). From the known chemical structures and XPS analysis, these results are expected as polypropylene and Tyvek® (patented type of high-density polyethylene) are synthetic fibers composed of hydrocarbon polymers, while the woven materials contain some oxygen functionality.

Table 5. WCA for fabric samples<sup>a</sup>.

| <b>Fabric</b>    | <b>Static WCA (°)</b> | <b>Absorption Rate (<math>\mu\text{L s}^{-1}</math>)</b> |
|------------------|-----------------------|----------------------------------------------------------|
| Tyvek®           | $125.9 \pm 4.5$       | —                                                        |
| Polypropylene    | $121.7 \pm 6.3$       | —                                                        |
| Polyester cotton | —                     | $4.24 \pm 0.75$                                          |
| Cotton           | —                     | $18.9 \pm 3.5$                                           |

a: All analyses were performed for  $n = 9$ ; mean standard deviation are reported in parentheses.

## CHAPTER 4

### CONCLUSION

In conclusion, this study showed substantial particle release for all types of tested fabrics. The release concentration for cotton and polyester cotton fabric were determined to be the highest from the aerosolization of  $\text{Al}_2\text{O}_3$  and carbon black ENPs, while Tyvek® and polypropylene showed the lowest amount of release concentration. From the exposure of CNT ENPs, the cotton fabric showed the highest release concentration compare with either tested fabrics. The release concentration of cotton and polyester cotton were significantly different from Tyvek® and polypropylene for  $\text{Al}_2\text{O}_3$  and carbon black ENPs, while for CNT ENPs cotton fabric turned out to be significantly different from all other fabric. Moreover, for all types of tested fabrics the total number concentrations of released ENPs at the breezing zone are higher than particles released from the back side of the worker wearing the contaminated protective clothing. After comparing 30 minutes of release process after 30 minutes of ENP aerosolization and 6 hours of release process after 1 hour of ENP aerosolization, as expected, the total number concentration was higher for 1 hour contamination and 6 hour release processes which could represent the exposure of full-shift work. Based on results of mass change measured before contamination and after the release processes, Tyvek® fabric indicated the statistically highest value of mass change per unit mass from the exposure of  $\text{Al}_2\text{O}_3$  and carbon black; for CNT ENPs all fabrics showed a statistically similar level of mass change per unit mass. Some of the ENPs stay on the surface of the fabric due to the ENP adhesive forces. Two fundamental forces might be responsible for  $\text{Al}_2\text{O}_3$  and carbon black ENP adhesion are van der Waals force and capillary force but it was difficult to determine for CNT ENPs due to their non-circular shape. Overall, Tyvek® is the best fabric for trapping all three types of studied ENPs, which eliminates the resuspension to expose workers. However, this

fabric was not durable enough for workers to wear for a long term or the active motions at work might cause wear or tearing of the Tyvek fabric, reducing its barrier properties and enabling penetration of ENPs. The polypropylene fabric is the next most effective for trapping ENPs of all three types. In addition, three types of ENPs were found to cause some difference in terms of adhesion onto the fabric surface, and we found that the  $\text{Al}_2\text{O}_3$  ENPs remained on the fabric the most, especially more on the Tyvek fabric, after simulated working activities, compared to other carbon black and CNT ENPs. Cotton and polyester cotton lab coats were found to be the least effective fabric type for trapping ENPs. Although these fabrics are the most durable, comfortable and commonly used in the workplaces, they are not recommended to be used when ENPs are present in work environments.

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## APPENDIX A: TABLES AND FIGURES

Table A1. Statistical analysis results with comparisons of particle size distributions of aerosolized ENPs during contamination of ENPs.

|                                                              |                     | <b>Al<sub>2</sub>O<sub>3</sub></b> | <b>Carbon Black</b> | <b>CNT</b> |
|--------------------------------------------------------------|---------------------|------------------------------------|---------------------|------------|
| <b>Al<sub>2</sub>O<sub>3</sub></b>                           | Pearson Correlation | 1.000                              | 0.984**             | 0.785      |
|                                                              | Sig.                |                                    | 0.000               | 0.001      |
|                                                              | N                   | 13                                 | 13                  | 13         |
| <b>Carbon black</b>                                          | Pearson Correlation | 0.984**                            | 1.000               | 0.864      |
|                                                              | Sig.                | 0.000                              |                     | 0.000      |
|                                                              | N                   | 13                                 | 13                  | 13         |
| <b>CNT</b>                                                   | Pearson Correlation | 0.785                              | 0.864               | 1.000      |
|                                                              | Sig.                | 0.001                              | 0.000               |            |
|                                                              | N                   | 13                                 | 13                  | 13         |
| **. Correlation is significant at the 0.01 level (1-tailed). |                     |                                    |                     |            |

Table A2. ANOVA One way test on release total number concentration of Al<sub>2</sub>O<sub>3</sub>, carbon black and CNT ENPs.

| ENPs                                                     | Fabric                           | Mean difference | Lower Bound | Upper Bound | <i>p</i> -value |
|----------------------------------------------------------|----------------------------------|-----------------|-------------|-------------|-----------------|
| <b>Al<sub>2</sub>O<sub>3</sub></b>                       | Polyester cotton - Cotton        | -21.67          | -98.28      | 54.95       | 0.80            |
|                                                          | Polypropylene - Cotton           | -114.82         | -191.43     | -38.20      | 0.01            |
|                                                          | Tyvek - Cotton                   | -101.27         | -177.88     | -24.66      | 0.01            |
|                                                          | Polypropylene - Polyester cotton | -93.15          | -169.76     | -16.54      | 0.02            |
|                                                          | Tyvek - Polyester cotton         | -79.60          | -156.22     | -2.99       | 0.04            |
|                                                          | Tyvek - Polypropylene            | 13.55           | -63.07      | 90.16       | 0.94            |
| <b>Carbon Black</b>                                      | Polyester cotton - Cotton        | -21.31          | -58.26      | 15.63       | 0.32            |
|                                                          | Polypropylene - Cotton           | -47.96          | 84.90       | -11.01      | 0.01            |
|                                                          | Tyvek - Cotton                   | -41.99          | -78.93      | -5.04       | 0.03            |
|                                                          | Polypropylene - Polyester cotton | -26.64          | -63.59      | 10.30       | 0.17            |
|                                                          | Tyvek - Polyester cotton         | -20.67          | -57.62      | 16.27       | 0.34            |
|                                                          | Tyvek - Polypropylene            | 5.97            | -30.98      | 42.92       | 0.95            |
| <b>CNT</b>                                               | Polyester cotton - Cotton        | -79.37          | -153.82     | -4.93       | 0.04            |
|                                                          | Polypropylene - Cotton           | -79.47          | -153.92     | -5.03       | 0.04            |
|                                                          | Tyvek - Cotton                   | -81.46          | -155.91     | -7.01       | 0.03            |
|                                                          | Polypropylene - Polyester cotton | -0.10           | -74.55      | 74.35       | 0.99            |
|                                                          | Tyvek - Polyester cotton         | -2.09           | -76.53      | 72.36       | 0.99            |
|                                                          | Tyvek - Polypropylene            | -1.99           | -76.43      | 72.46       | 0.99            |
| *. The mean difference is significant at the 0.05 level. |                                  |                 |             |             |                 |

Table A3. Statistical analysis results with comparisons of particle size distributions of resuspension Al<sub>2</sub>O<sub>3</sub> ENPs.

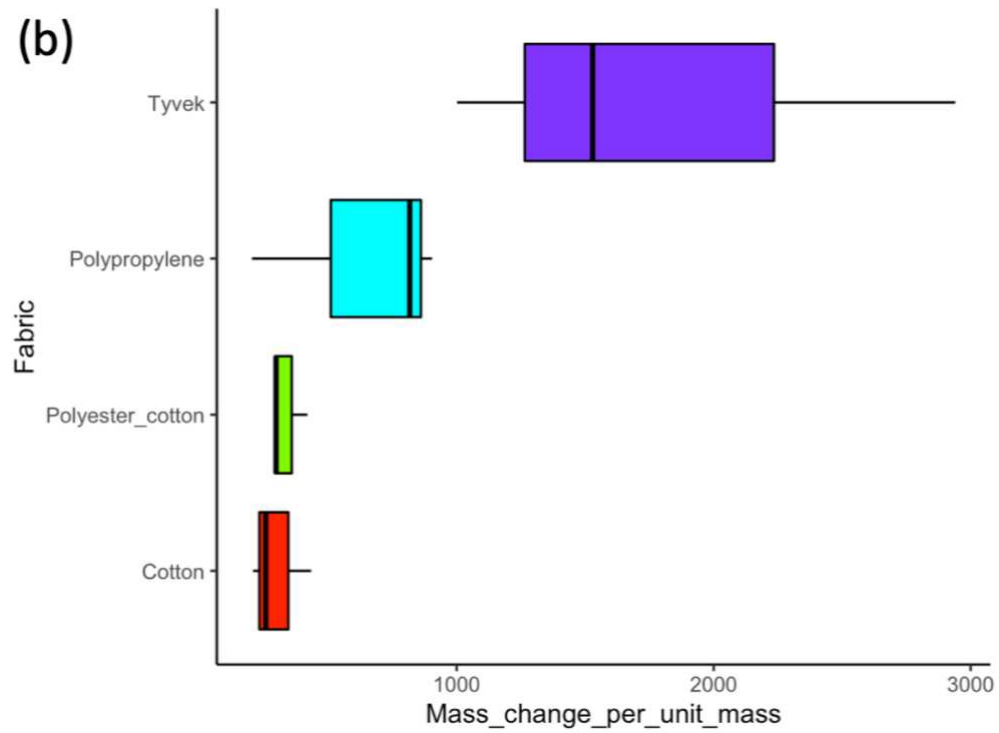
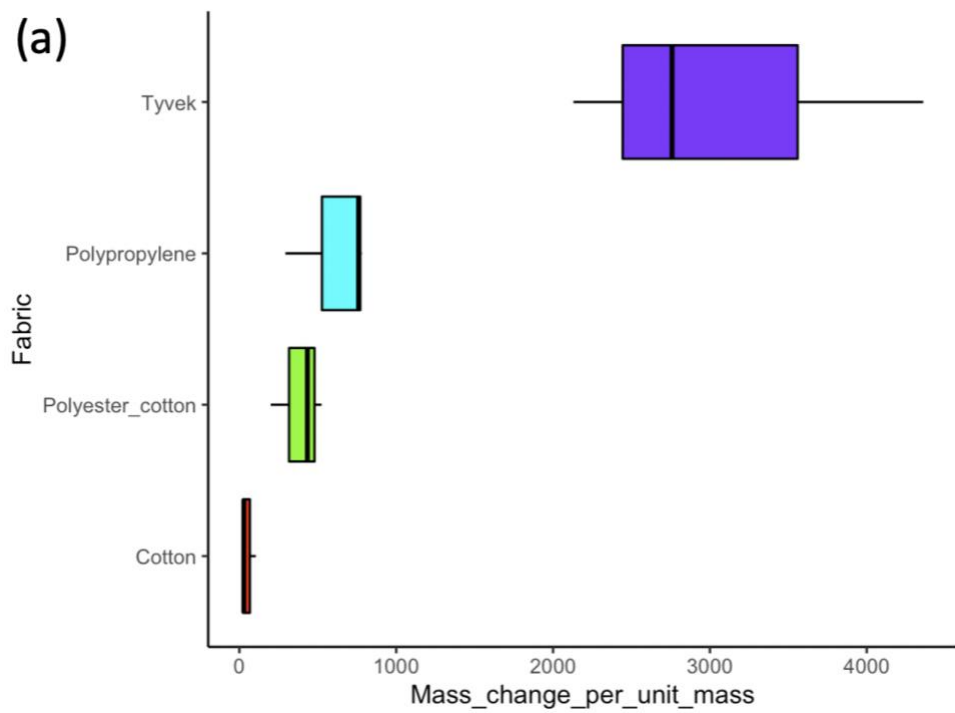
|                                                              |                     | <b>Cotton</b> | <b>Polypropylene</b> | <b>Polyester cotton</b> | <b>Tyvek®</b> |
|--------------------------------------------------------------|---------------------|---------------|----------------------|-------------------------|---------------|
| <b>Cotton</b>                                                | Pearson Correlation | 1.000         | 0.660                | 0.694                   | 0.697         |
|                                                              | Sig.                |               | 0.014                | 0.0084                  | 0.008         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Polypropylene</b>                                         | Pearson Correlation | 0.660         | 1.000                | 0.857                   | 0.845         |
|                                                              | Sig.                | 0.014         |                      | 0.000                   | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Polyester cotton</b>                                      | Pearson Correlation | 0.694         | 0.857                | 1.000                   | 0.863**       |
|                                                              | Sig.                | 0.0084        | 0.000                |                         | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Tyvek®</b>                                                | Pearson Correlation | 0.697         | 0.845                | 0.863**                 | 1.000         |
|                                                              | Sig.                | 0.008         | 0.000                | 0.000                   |               |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| **. Correlation is significant at the 0.01 level (1-tailed). |                     |               |                      |                         |               |

Table A4. Statistical analysis results with comparisons of particle size distributions of released carbon black ENPs.

|                                                              |                     | <b>Cotton</b> | <b>Polypropylene</b> | <b>Polyester cotton</b> | <b>Tyvek®</b> |
|--------------------------------------------------------------|---------------------|---------------|----------------------|-------------------------|---------------|
| <b>Cotton</b>                                                | Pearson Correlation | 1.000         | 0.846                | 0.844                   | 0.904         |
|                                                              | Sig.                |               | 0.000                | 0.000                   | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Polypropylene</b>                                         | Pearson Correlation | 0.846         | 1.000                | 0.956**                 | 0.916         |
|                                                              | Sig.                | 0.000         |                      | 0.000                   | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Polyester cotton</b>                                      | Pearson Correlation | 0.844         | 0.956**              | 1.000                   | 0.851         |
|                                                              | Sig.                | 0.000         | 0.000                |                         | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Tyvek®</b>                                                | Pearson Correlation | 0.904         | 0.916                | 0.851                   | 1.000         |
|                                                              | Sig.                | 0.000         | 0.000                | 0.000                   |               |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| **. Correlation is significant at the 0.01 level (1-tailed). |                     |               |                      |                         |               |

Table A5. Statistical analysis results with comparisons of particle size distributions of released CNT ENPs.

|                                                              |                     | <b>Cotton</b> | <b>Polypropylene</b> | <b>Polyester cotton</b> | <b>Tyvek®</b> |
|--------------------------------------------------------------|---------------------|---------------|----------------------|-------------------------|---------------|
| <b>Cotton</b>                                                | Pearson Correlation | 1.000         | -0.019               | -0.069                  | 0.188         |
|                                                              | Sig.                |               | 0.948                | 0.822                   | 0.5364        |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Polypropylene</b>                                         | Pearson Correlation | -0.019        | 1.000                | 0.742                   | 0.814         |
|                                                              | Sig.                | 0.948         |                      | 0.003                   | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Polyester cotton</b>                                      | Pearson Correlation | -0.069        | 0.742                | 1.000                   | 0.820         |
|                                                              | Sig.                | 0.822         | 0.003                |                         | 0.000         |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| <b>Tyvek®</b>                                                | Pearson Correlation | 0.188         | 0.814                | 0.820                   | 1.000         |
|                                                              | Sig.                | 0.5364        | 0.000                | 0.000                   |               |
|                                                              | N                   | 13            | 13                   | 13                      | 13            |
| **. Correlation is significant at the 0.01 level (2-tailed). |                     |               |                      |                         |               |



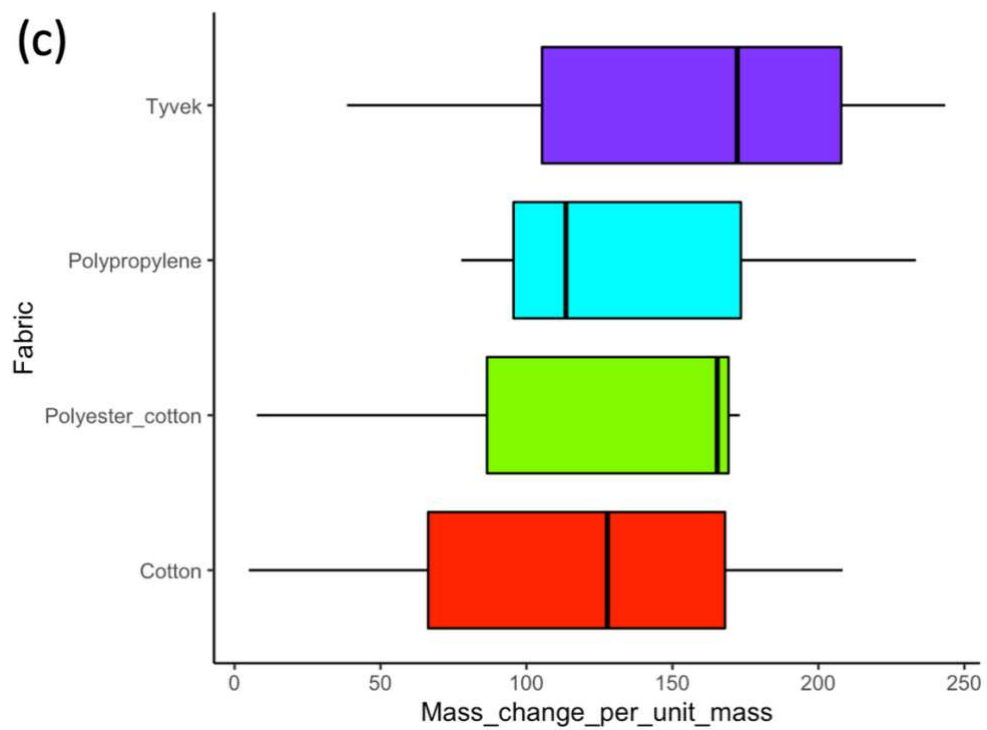


Figure B1. Statistical analysis of mass change per unit mass calculated through the measured mass before the aerosolization and release of ENPs: (a)  $\text{Al}_2\text{O}_3$ . (b) Carbon black. (c) CNT.