New Approaches to Remediation of Nanoscale Contaminants in the Workplace

by

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Abstract

It is important that all workers understand the health and safety risks of their work environment. It has been demonstrated that exposure to nanoparticles can lead to potential health concerns. A 1 mL nanoparticle solution spill can contain $>10^9$ nanoparticles, with the particles invisible to the human eye. This nanoparticle spill can cause further contamination in the work environment as workers transfer the particles from one area to another if the nanoparticles are not properly remediated. Therefore, it is essential that effective methods be developed for early identification and clean-up of such spills to avoid potential hazards to those working with these particles. One goal of this research is to develop a methodology that is simple to implement on a global scale to rapidly detect the presence of nanoparticles in different workplace environments to accompany methods for the remediation of spills containing nanoparticles. X-ray fluorescence spectroscopy was identified as a portable solution to potentially identify the presence of and the extent of a spill containing nanoparticles. Many other techniques could also be utilized, but the ease of use at the point of contamination without the requirement of sample preparation makes this an attractive solution in nanoparticle remediation.

Another goal of this research is to develop an efficient, effective and inexpensive means to remediate spills containing nanoparticle contaminants. The implementation of these remediation procedures would change how nanoparticles are treated in the workplace and promote a healthy work environment when using materials that would otherwise go unnoticed due to their small size. Remediation of nanoparticles spilled in the workplace requires a method of acknowledging that these unseen particles are appropriately being removed and to avoid spreading these particles to a wider extent throughout the workplace. Analytical techniques were used to monitor the presence of nanoparticle contaminants and, in combination with techniques to encapsulate nanomaterials within a spill, were used to assess the appropriateness of these remediation techniques for cleaning up simulated spills. These studies demonstrate a series of methods to progressively remove nanoparticle contamination from countertops in the workplace.

Keywords: Nanoparticles; workplace occupational health; signage; nanoparticle remediation; nanoparticle detection; contamination

To my family,

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Dr. Sophie Lavieri,

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List of Acronyms

AES	Auger Electron Spectroscopy
BSE	Backscattered Electrons
CBED	Convergent Beam Electron Diffraction
CCD	Charge Coupled Device
CTAB	Cetyl Trimethylammonium Bromide
DLS	Dynamic Light Scattering
EDS	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
GNR	Gold Nanorod
ICP	Inductively Coupled Plasma
LIBS	Laser Induced Breakdown Spectroscopy
MS	Mass Spectrometry
MSDS	Materials Safety Data Sheet
NFPA	National Fire Protection Agency
NSLB	New Skin Liquid Bandage
PEG	Poly(ethylene glycol)
ppb	parts per billion
PPE	Personal Protective Equipment
ppm	parts per million
PSA	Pressure Sensitive Adhesive
RF	Radio Frequency
SAD	Selected Area Diffraction
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRF	X-ray Fluorescence

1. An introduction to nanoscale particles

The fast developing field of nanoscience has produced a large variety of engineered nanoscale particles. These particles are defined as those having dimensions between 2 and 100 nm, and whose shapes can vary from a simple sphere to a complex tetrahedron to a high aspect ratio nanotube or nanowire. [1], [2], [3], [4] The properties of nanoscale particles are unique from those of bulk materials. They can have unique optical, electrical, and chemical properties, which make nanoscale particles desirable for a wide range of applications. [3], [4] These include biological applications, such as the controlled release of molecular therapeutic payloads and other approaches to killing cancer cells. [5], [6], [7] In some cases, nanoparticles such as gold nanorods or gold nanoparticles (Figure 1), which exhibit surface plasmon resonance properties, are being investigated for their photothermal properties for the management of cancer. [7], [8] Some products containing nanoparticles are also available on the market, such as zinc oxide and titanium oxide nanoparticles in sunscreens, carbon nanofibers in bikes, and silver nanoparticles in clothing. [9], [10] New synthetic methods are continuing to increase the diversity of nanoscale particles that are available. [11] There is much work that has gone into the production of nanoscale particles because of the potential reward from their properties and the benefits that may be derived from the incorporation of these materials into products.
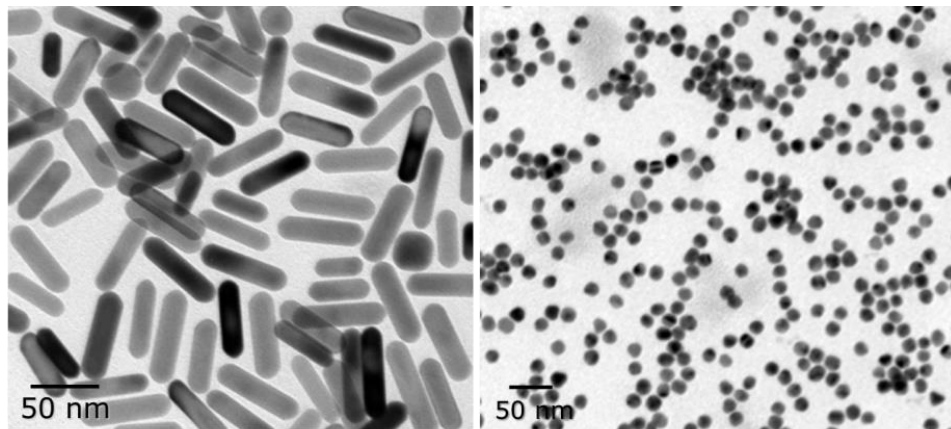
Figure 1. *Transmission electron microscopy (TEM) images of gold nanorods (left) and gold nanoparticles (right).*

1.1. Health and safety concerns of nanoparticles

Nanoscale particles, also referred to as nanoparticles, are becoming ubiquitous in the workplace as global research and development efforts are making rapid progress in identifying and utilizing the unique properties of these materials. However, the unique properties and small size of nanoscale particles could lead to unwanted physiological responses in workers and consumers alike. [12], [13], [14], [15], [16] The small size of these nanoscale particles can lead to multiple avenues for entry into the human body, which include the soft membrane of the eye, the lining of the esophagus, the pleural membrane and even through the dermis of the skin. [15], [17], [18], [19] Studies have shown that nanoscale particles can accumulate within the liver, kidneys, spleen, lymph nodes, and other organs throughout the body. [20] The digestive and lymphatic systems are very efficient at filtering the fluids that are circulating within the body. However, the body is not as efficient in breaking down and excreting foreign nanomaterials. The likelihood of clearing all of the nanoscale particles from the biological host can be very low. Accumulation of nanoscale particles in the human body may become a health hazard. [21]

As the nanoscale particles accumulate, they may potentially lead to organ failure and/or formation of cancerous tissues. [15] For example, researchers discovered that some nanoparticles widely developed in medicine can cause lung damage by triggering a type of programmed cell death in mice. [22] Studies have also shown that the

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composition and size of nanomaterials can have a significant effect on cell survivability. [23] Although the ill effects of nanoscale particles on the environment and human health are still under investigation, an increasing number of studies have indicated that toxic effects can be generated through chronic exposure and prolonged contact with these materials. However, it is important to note that the biological responses to nanomaterials are sometimes inconsistent. [18] These inconsistencies could be attributed to variations in composition or impurities, size and shape of the particles being tested. [18] The conclusion from these studies is that every type of nanomaterial should be screened for its interference with the normal function of cells and tissues. [19] Samples containing identical particles, but with different impurities, would be classified as different materials, each requiring its own testing. The number of materials to test is very large. In addition, there is a dramatic increase in the use and acceptance of nanoscale particles into the workplace on a global scale. As one measure of their acceptance into the laboratory, the number of publications on nanoscale particles has steadily increased over the past 20 years (Figure 2). [24] Along with this rapid increase of reports on how to make and/or use nanoscale particles, there has been a global effort to develop best practices for handling nanoscale particles [25] and studying the potential health impacts of nanoscale particles. [26] Journals such as *Nanotoxicology*, and *Informa Healthcare*, have even been introduced that focuses on the concerns of nanoscale particles in the workplace. [27] Regardless, it would still take many decades to analyze all the materials that have been produced to date if we maintain the same rate of testing, even if we stop the design of new nanoscale materials. Nanomaterials have almost become commonplace within the workplace in recent years. Until we have a better understanding of the potential hazards presented by nanoscale materials, it is essential that we take a position of controlling and minimizing our exposure to these materials. Completely avoiding contact with these materials is the best method to ensure workplace safety, but in consideration of the possibility of exposure it is imperative to educate and inform workers on the appropriate use, storage, and handling of these particles and materials containing them.
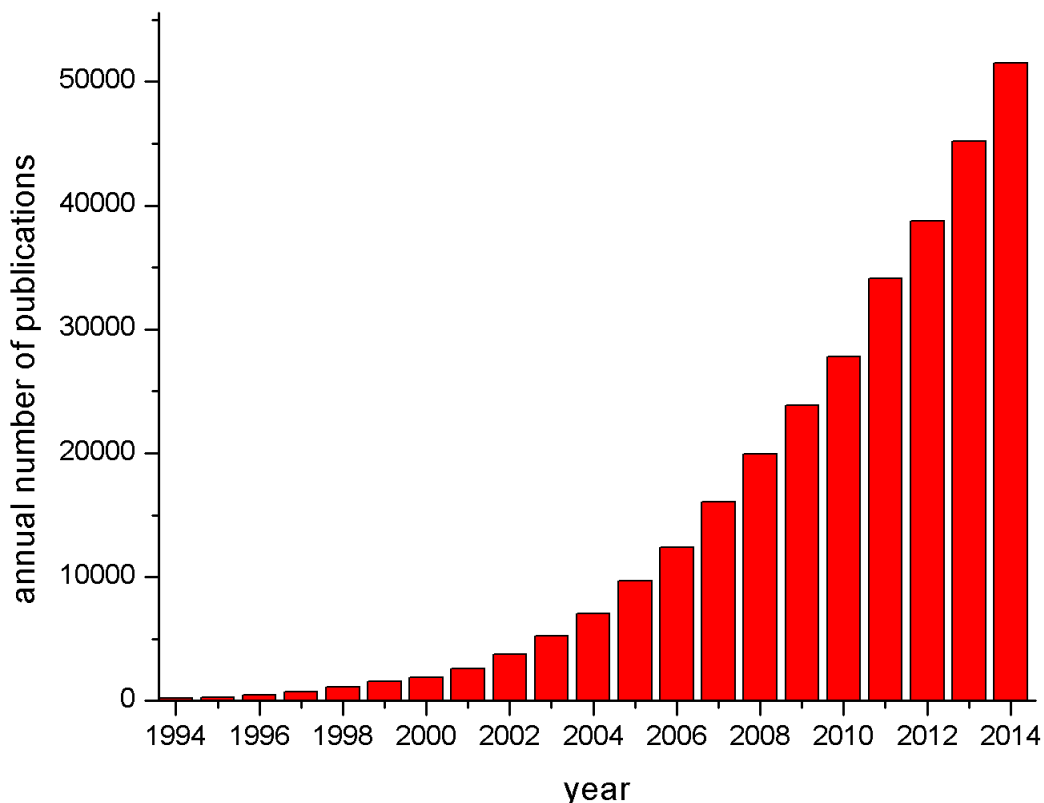
Figure 2.   *Number of annual peer reviewed publications containing the keyword search "nanoparticles" from Web of Knowledge, accessed April 2015.*

One of the best ways to inform workers on the presence of nanoscale particles is to develop a universally acceptable method for labeling chemical bottles and laboratories that contain nanoscale particles. This labeling practice could also be extended to products that incorporate these materials. The intent of these efforts is to raise awareness and to increase communication of the presence of nanoscale particles in the workplace. Communicating methods for the proper handling of and storing nanoscale particles, as well as the potential hazards associated with these particles, is essential to create a safe work environment. [28] Workers, visitors, and first responders in an emergency situation need to be informed of the risks they may encounter when entering a particular workplace. Currently there are no internationally standardized requirements for signage to indicate the use, handling or transport of nanoscale particles. We suggest that the current practice for labeling small chemical bottles or other storage and waste vessels, and laboratories containing nanoscale particles be revised for the safety of all

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workers. Standardized labelling should be developed to communicate the presence of nanoscale particles in all workplaces around the world. These labels should be simple to understand. The adopted signage should become as ubiquitous as existing hazard signs, such as those used for corrosive, explosive or toxic substances. [29] Proposals have been made for some signage to indicate the presence of nanoscale particles, [30] but these have not been widely accepted and implemented in the workplace. A search of existing signage identified a number of previous proposals for labeling of nanoscale particles. These designs either had a complex design that could be difficult to quickly identify and understand, or lacked the necessary details to communicate the potential hazards of the materials. In 2007, an estimated 30,000 people gathered at the World Social Forum in Nairobi where participants had the chance to vote for their favorite "Nano-Hazard" Symbol – a design that warns people of the presence of nanoscale particles. The competition consisted of 482 unique designs from over 24 countries. Three top designs were chosen for labelling of product packaging or on workroom walls, which were to be submitted to international standard-setting bodies responsible for hazard characterization. [30] These designs have not yet been widely implemented. There are, however, simple to read and use packaging labels available that caution against the presence of nanomaterials. [31], [32] We aim to improve upon these and the other designs previously proposed for labelling of hazards associated with nanoparticles. Like most accepted hazard signs, the proposed new design needs to be clear and specific to the potential hazards, and should be internationally accepted and ideally multilingual.

A warning system that includes proper notification of the hazards should be adopted for all shipping, storage, and waste vessels containing nanoscale particles, as well as all work environments in which these materials are manufactured, processed or otherwise used. We propose new signage to warn workers, visitors, and first responders about the presence of nanoscale materials (Figure 3a). The traditional yellow hazard triangle was chosen as a symbol people easily identify as a warning label. The incorporated phrase "nano" is widely accepted in many different cultures in association with nanoscale materials and various nanotechnologies. This label is intended to be highly visible on the outside of vessels and rooms containing nanoscale particles. In the workplace, this label would be posted on an entrance door or workroom wall to raise the

awareness of workers, visitors and first responders, and to provide information on the presence of potential hazards. This signage can be customized with the inclusion of composition of the nanoscale particles below the hazard triangle, but could be left blank or otherwise modified when nanoscale particles of different composition are present. For a workplace signage, it is recommended that more information be provided in regards to the chemical and physical properties of the nanoscale particles. One example of communicating these hazards in the workplace is that of the United States National Fire Protection Agency (NFPA) hazard diamonds for identifying chemical hazards (Figure 4). [33] These hazard diamonds provide a quickly viewed summary of information on health hazards, flammability, reactivity and other specific hazards that workers and visitors might encounter in a particular workplace environment. It also serves as a simple method to communicate hazards to first responders, in order that they also properly prepare to enter the same environment in an emergency.
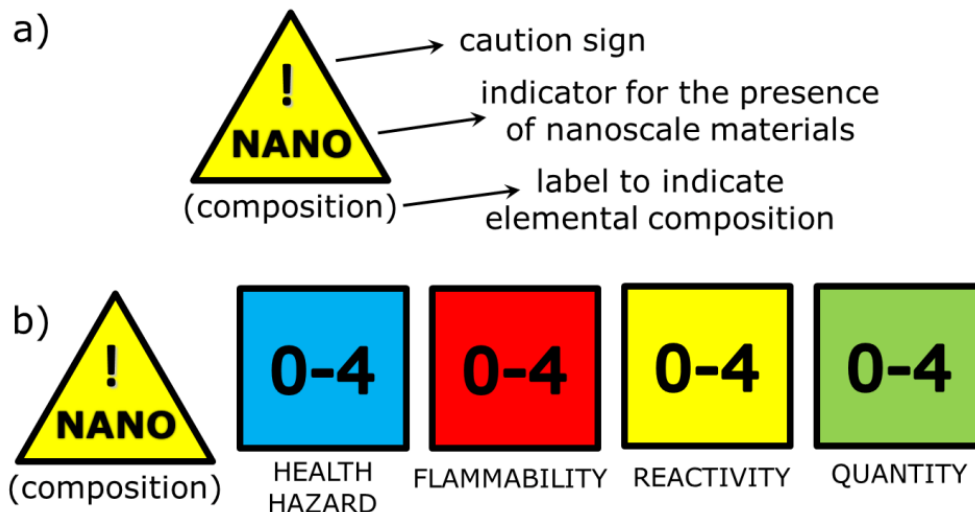
Figure 3.   *Proposed labels indicating (a) the presence of nanoparticles, and (b) the hazards associated with these nanoscale particles.*

Elements of the NFPA hazard diamond have been incorporated into a new design we propose for communicating hazards associated with nanoscale particles (Figure 3b). The proposed label includes four sub-categories: (i) health hazard, (ii) flammability, (iii) reactivity and (iv) quantity. In each sub-category, a number is listed to quantify each of these risks associated with nanoscale particles in the workplace. Similar to the NFPA hazard diamonds, each hazard is numbered between 0 and 4. The higher

the assigned number the greater the specific hazard. The use of a rectangular layout of the sub-categories helps to differentiate the specific hazards of nanoscale materials from those of bulk materials. This proposed signage also provides a simplified summary of the extent of the risks in a manner that can be quickly read.
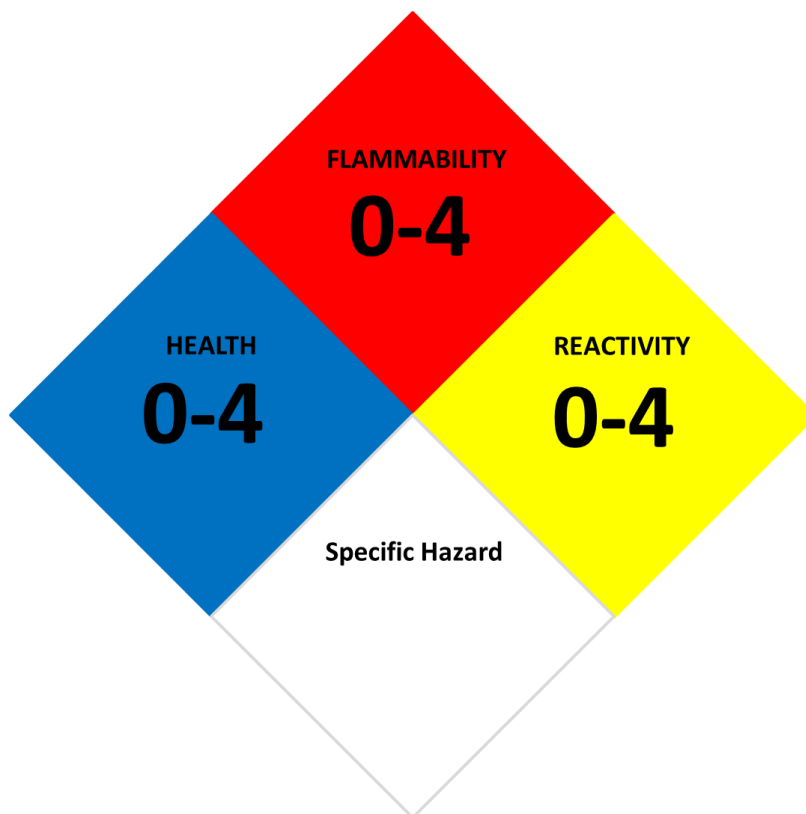
Figure 4.   *The United States National Fire Protection Agency chemical hazard sign, indicating the health, flammability, and reactivity hazards, as well as any specific hazard such as oxidizer (OX), highly reactive with water (W) and asphyxiant gas (SA) present in a workspace. Each number is on a scale from 0 (no hazard) to 4 (severe hazard).*

The newly proposed design resembling the NFPA has been further adjusted to the needs of communicating nanoparticle hazards by replacing the NFPA designation for specific hazards with the quantity of material present. We believe that the quantity of nanoparticles present in a storage vessel or work environment is a very important measure of risks associated with these materials. [34] The other hazards remain similar to the NFPA standards, but are specifically aimed at nanoscale materials. The health hazards associated with nanoparticles can include toxicity, as well as the potential to accumulate in biological organisms. Flammability is an assessment of the material's

ability to ignite and serve as a fuel source, and reactivity is a measure of its ability to easily undergo a chemical reaction. With the high surface area to volume ratio, small dimensions (e.g., relative to cells, subcellular components), and the variety of shapes and compositions possible for nanoscale particles, increases the diversity of properties for these materials. There is often no direct correlation between the properties and hazards of nanoscale materials and those of macroscale materials with an identical composition. On-going research is required to properly assess the hazards associated with each particular type of nanoscale material, specifically as these hazards pertain to the four categories discussed above. [35] This research will be necessary in order to assign an appropriate number to a given material, as well as to calibrate the interpretation of that value. Further research is also necessary to assess the stability to aging (e.g., shelf-life) of nanoscale particles, and how the hazard values for a particular nanoscale material could change over time.

Elimination of a hazardous substance is the best method for ensuring worker safety, but is rarely a feasible option. Personal protective equipment (PPE), due to its low relative cost and widespread availability, is the most common method of ensuring worker safety. The communication offered by the proposed signage (Figure 3) will prompt workers, visitors and first responders entering the laboratory to look up additional information on the hazards of the specific materials they will encounter in the laboratory. These personnel will need to choose the appropriate PPE for their circumstances to appropriately minimize exposure based on information provided from sources such as a materials safety data sheet (MSDS) and their own risk assessment of the materials present. In order to get the message out, support from local occupational and health organizations will be required and proper safety training programs will need to be implemented. The initial implementation of appropriate labelling could start with the "NANO" warning label (Figure 3a) for vessels and materials containing nanoscale particles. This warning label could also be affixed to the entrance of any workplace that produces and/or uses nanoscale particles. As further research is performed to create the more detailed label (Figure 3b), it could be incorporated primarily onto workroom doors. The label could also be extended to chemical storage bottles and shipping containers for nanoscale particles. For any newly developed synthesis of nanoscale materials it is suggested to at least have a warning label (Figure 3a) to indicate to users that they

should use appropriate precautions when handling the material. These labels also indicate to the worker that they should consult any safety documentation available for these materials, and seek further information when it's not immediately available while performing their own risk assessment.

An example of how our proposed labeling system might look for an aqueous solution of gold nanoparticles is portrayed in Figure 5. A label has been prepared for the work environment and for bottles containing the product for use in that same environment. This label indicates the presence of a particular type of metal nanoparticle and the hazards associated with these nanoscale particles when stabilized with self-assembled monolayers. [36] This particular example was prepared for a stable colloidal suspension of gold particles capped with citrate and dispersed in a phosphate buffered solution at a pH of 7.2. A rating of 2 has been chosen for the quantity of material corresponding to a 1 nM suspension of gold nanoparticles [e.g., values of 0 for <picomolar (pM) concentrations; 1 for pM; 2 for nanomolar (nM); 3 for micromolar (μM); and 4 for >μM or solids]. A value of 0 is chosen for the flammability of the colloidal solution as these gold nanoscale particles are dispersed in an aqueous solution. The monolayer capped gold colloids are susceptible to oxidative damage and can become unstable with environmental changes. [37] These particles are, therefore, assigned a value of 1 for reactivity. As for the associated health hazards, further toxicity research will be required to properly assign a value for these nanoscale gold particles, but a value of 1 has been temporarily assigned.
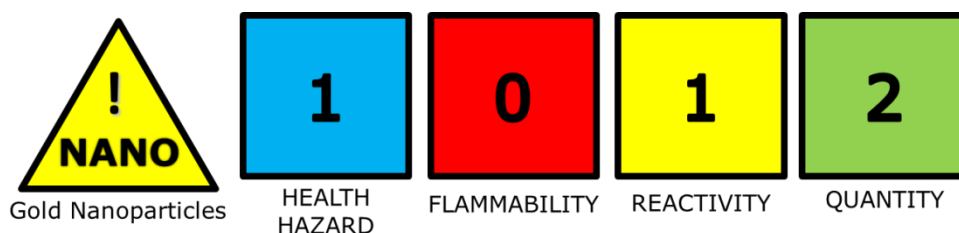
Figure 5. *Proposed signage to indicate the presence of gold nanoparticles dispersed in an aqueous solution along with their potential hazards. Proposed values for each specific hazard are included for this typical solution of nanoscale particles.*

Our proposed signage to indicate the presence of nanoscale particles is simple and should be readily identifiable in most work environments already using these

materials. This signage indicates the presence of nanoscale particles, and also communicates the amount, properties and extent of the potential hazards associated with these materials. Our intention is that through the development of a simple and detailed method for communicating the potential hazards of nanoscale particles present in the workplace, we will provide the means to help manage the safety and health risks to workers when handling nanoscale particles.

1.2. Dealing with nanoparticle spills and potential contamination

As nanoscale particles are further developed and implanted in advanced materials and technologies, it is imperative that we focus on the health and safety risk for all employees working with nanoscale particles. According to a recent survey of nanomaterial cytotoxicity, variables in the test conditions and nanomaterial concentrations have a large influence on cell survivability. [23] The potential hazards associated with exposure to nanoparticle contamination or nanoparticle spills in the workplace is of widespread concern considering the large numbers of nanoparticles being produced and used in the world. The chance for spilling nanoparticles is no less than for any other material being handled in the workplace environment. The concern in the case of nanoparticles is that 1 mL spill of a nanoparticle solution can contain >10^9 nanoparticles and can easily go unnoticed by the unaided human eye. The potential for a prolonged exposure of a worker to a spill of nanoparticles also requires an intimate knowledge of how these nanoparticles interact with their environment and within a human being. [15], [16], [20], [38] The biotoxicity and ecotoxicity are beyond the scope of this current studies, but are included in ongoing studies throughout the world. [35], [39], [40], [41] Identifying the presence of a nanoparticle contaminant in the workplace could potentially require the assessment of a relatively large number of surfaces in order to account for primary spills and secondary transfer of material to other surfaces. Multiple areas within the workplace would require testing as it is difficult to easily identify the presence of nanoparticles. The time that is required to prepare these samples for analysis and to analyze the samples could be overwhelming. For instance, consider the case where 100 independent measurements are taken within the workplace. Some techniques require acquiring a sample, packaging or mounting the sample and labeling

the sample. While some techniques require a work-up such as acid digestion before analysis and identification. It may require approximately 30 minutes to carry out these tasks for just one sample. This translates into a period of over 2 months before a worker would be able to retrieve the final results. It would be desirable to minimize or avoid any need for sample preparation. A portable technology is ideal as it could be brought to the site of potential contamination, but the technique should provide both a quantitative and a qualitative analysis on the presence of nanoparticles.

In addition, there are currently no specific guidelines or protocols currently available for cleaning up or remediating nanomaterial spills off surfaces. Standard approaches to clean liquid or powder spills include the use of a HEPA-filtered vacuum, wiping an area with a damp cloth to remove powder and applying absorbent material or liquid traps. [4], [42] Currently, portable peristaltic pumps are used by a few organizations to transfer liquid to waste containers in order to prevent potential spills and reduce aerosolisation of nanomaterials. These pumps, because they work on positive displacement, are less prone to producing aerosols as opposed to conventional high pressure pumps. [4] However, these methods may not be sufficient enough to remediate nanomaterial spills off various types of surfaces. A method must be developed that can become widely implemented as nanoparticles are ever increasing in their acceptance as materials ready for consumption. Implementation of appropriate remediation procedures would promote a healthy work environment for a material that would otherwise go unnoticed (due to its small size) in the workplace. Having information and training of these protocols will bring awareness to the workers and employers dealing with nanoscale materials on the potential hazards of unseen nanoparticle spills.

Controlling exposure to nanoparticles requires an easy method of detecting and removing any nanoparticle spills. As mentioned before, it is best to detect a spill by directly analyzing areas of interest within the workplace, rather than gathering samples for remote analysis. Spills should be cleaned up in a timely manner to avoid any potential for any aerosol production or further spread of the contaminated area.   Quick detection at the point of contamination will aid in a quick execution of measures for remediation, reducing the contaminated area to a safe level (to be determined in the future).   Widespread implementation of control measures will, however, require adaptation of inexpensive analytical methods. Research is essential to determine the

best methods of detecting spills of nanoparticles, and being able to quantify levels of contamination. Further work is then required to establish appropriate methods for clean-up of particles while accounting for the diversity of surfaces that can be found in the workplace. Remediation of trace contaminants of nanoparticles should use techniques that directly contain or encapsulate the spill. Either approach to containment of nanoparticles aids their removal from the work environment. There are many remediation considerations (Figure 6) that should be involved when developing an ideal method for remediation. The remediation method should be safe and easy to use, require minimal labour, and effectively remediate in a timely manner, as well as widely applicable to various shapes and sizes of nanoparticle as well as remediate nanoparticle spills off different surfaces.

There are many different ideas to remediate nanoparticle spills, however, one simple method that anyone can implement is the use of adsorbant materials to assist in remediation. These materials are often inexpensive and readily available, but can leave trace amounts of nanoparticles. Simply rubbing an area with a cloth or paper absorbant can increase the area of contamination. In addition, nanoparticles can easily escape or come loose from the absorbant spreading the nanoparticles to unknown areas. An alternative method that we propose is to use an adhesive or encapsulant material. Adhesive tape, for example, is an inexpensive and readily available material that is common in many work environments. With the use of an adhesive tape, nanoparticles can transfer from the contaminated surface into the adhesive of the tape. By doing so, the nanoparticles are now contained and can be easily sent for disposal. Encapsulation would ideally provide an effective barrier between the worker and the particles, thus minimizing the potential for transfer of the contamination to other surfaces. The encapsulation would also provide a simple means to remove the particles; peeling the encapsulating layer away from the contaminated surface would ideally also remove the particles from these surfaces.
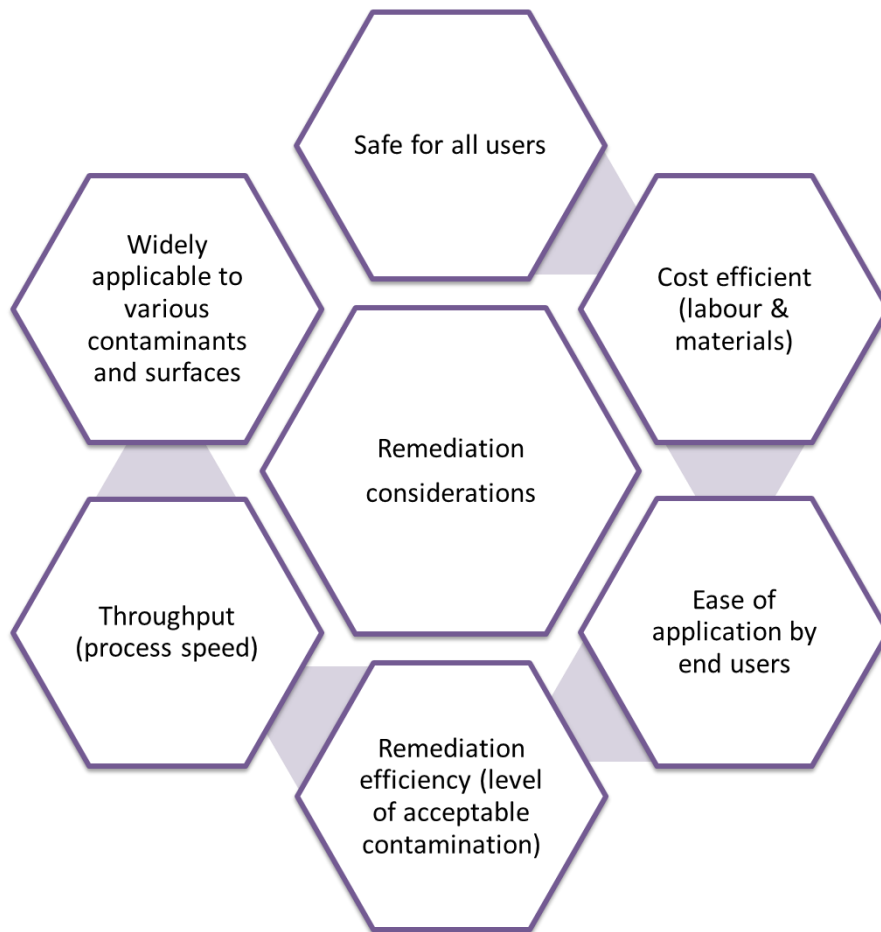
Figure 6. *Considerations for developing an optimal method to remediate nanoparticle contaminants or spills.*

2. Methods to detect nanoparticle contaminants in the workplace

Detecting nanoparticle spills and contaminants can be a challenge as the size of nanoparticles cannot be seen with the human eye. Specialized techniques are required to detect and characterize nanoparticles as various analysis techniques can provide both structural and or elemental information. On-going efforts have and will continue to be made to standardize the way nanoparticles are measured in the laboratory. To determine occupational exposure and health risks from products and environmental risk. However, there is not a single method that can be selected as the best method, but rather the method must balance restrictions of the type of sample, information required, time for sample preparation, time for sample analysis and cost of the analysis. All analyses have related costs, whether they are provided by an analysis company or if equipment is to be purchased and labor is provided by the company. These can limit the choice of techniques as some will require ongoing costs for calibration and maintenance of equipment, essential to maintaining accuracy the measurement.

It is essential that effective methods be developed for early identification and clean-up of such spills to avoid hazards to those working with these particles. The chosen method of identification must be one that could become widely implemented as nanoscale materials are ever increasing in their acceptance as materials ready for use in commercial items. Implementation and training of a developed methodology for the detection of nanoscale contaminants would promote a healthy work environment for a material that would otherwise go unnoticed in the workplace.

2.1. Methods for analysis of nanoscale contaminants

Current methods to visualize or confirm the presence of nanoparticles in a qualitative or quantitative matter include techniques such as transmission electron

microscopy (TEM), scanning electron microscopy (SEM), and dynamic light scattering (DLS) and related light scattering techniques. [43] The difficulty with relying on these techniques is that within a workplace there could be many types of nanoscale materials present. Identifying the composition of nanoparticles observed is the key to determining the potential toxicity at hand. However, in order to identify composition, it would require either detailed analysis by electron diffraction or the use of complementary elemental analysis to quickly provide information on the particle's composition. Many of the nanoscale materials being pursued in these literatures are composed of transition metals, semiconductors, or lanthanides. [44] It could be possible to detect these materials by identifying either the presence of one or multiple elements within the nanoparticles. This elemental fingerprint can be used to track these particles in the workplace environment. There are multiple techniques available for both a qualitative and quantitative analysis of nanoscale materials. Few techniques can, however, be widely applied for the analysis of contamination in laboratories around the globe. One objective of our work is to develop a simple and inexpensive method for detecting and managing contamination by nanoparticles in the workplace environment. The goals are to make such a procedure widely available to workers and employers that are producing and/or using nanoparticles in the workplace in order to quickly identify the presence of a particular type of nanoparticle. Selection of the best technique to meet these goals requires evaluation of multiple analytical techniques. Various microscopy and spectroscopy techniques will be reviewed for their potential use in their identification of nanoparticle based contamination in the workplace.

2.1.1.   *Microscopy techniques*

Microscopy is a useful technique when investigating small structures, providing an image of their shape and size. However, not all types of microscopy techniques can be used when working with nanostructures due to resolution limits of the microscope. The simplest microscope one can use is an optical microscope, also known as a visible light microscope. This type of microscope uses visible light and a series of lenses to magnify samples that cannot be directly observed by eye. A significant advantage of imaging samples with an optical microscope is that it requires little pre-treatment, and can also be combined with dark field or fluorescence imaging of samples. Dark field

microscopy is a simple method for making unstained and otherwise transparent specimens clearly visible. [45] Dark field illumination requires blocking out the central light and only allowing oblique rays from every azimuth to "strike" the specimen mounted on the microscope slide. The light scattering off from the long axis of various nanoparticles can allow the end user to visualize or identify the presence of some nanostructures (e.g., nanowires and nanotubes). Prior knowledge of the material is required as this technique does not provide any quantitative or elemental information. [45] Fluorescence microscopy on the other hand, uses a much higher intensity and energy light source that induces a fluorescent species in a sample of interest. These species emits lower energy light (longer wavelengths), producing a magnified image of the fluorescent species. Florescent microscopy can be used to visually enhance 3-D features at small scales. These imaging techniques can be accomplished by selectively incorporating fluorescent molecules as stains in the samples of interest. [46] With the right calibration, quantitative analysis can be obtained. These optical imaging techniques are fast and adaptable to all kinds of samples (from biological cells to countertops). However, the main disadvantage of optical microscopy is the limited resolution. Optical microscopy can only resolve features down to a few hundreds of nanometers, typically 400-500 nm depending on 'n', the refractive index of the medium. Some microscopes can resolve features down to 250 nm to visualize individual nanowires, [47] ultimately limited by the wavelength of light. Typical optical microscopes can only magnify samples up to approximately 1000 times. In summary, optical microscopy is a relatively inexpensive and easy technique to use and can be used to quickly screen samples, but structural details for nanoparticles are limited due to the limited resolution of the technique. Instead, a more common technique to characterize nanoparticles is through the use of electron microscopy, which has a much better spatial resolution. [43]

There are two different types of electron microscopes commonly used for nanoparticle analysis: (i) a transmission electron microscope (TEM); and (ii) a scanning electron microscope (SEM). SEM provides a good overview of samples containing nanoparticles or nanowires and is relatively fast and easy to operate. SEM uses a high energy focused electron beam that is scanned over the sample surface. Secondary electrons produced by the samples are collected by a secondary electron detector or a backscatter detector. [48] The incident electrons interact with the sample producing

signals that contain information about the sample's surface topography and composition (Figure 7).
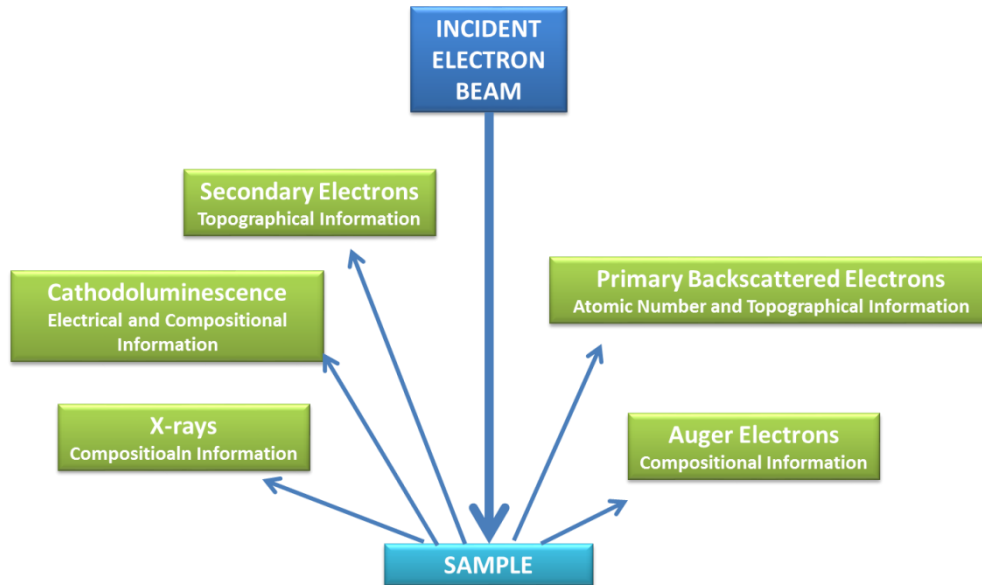
Figure 7. *Electron/specimen interactions for scanning electron microscopy techniques: when the electron beam strikes the sample both photons and electrons can be emitted. The detected signals contain information about the structure, topography, and composition of the sample.*

Although a range of different types of signals can be detected during SEM analysis, the most commonly detected signals are from secondary electrons. A secondary electron detector can produce very high resolution images of a sample surface, revealing details down to the single nanometer range. It also provides a depth of field that is useful for understanding variations in surface topography and composition of a sample. Figure 8 provides an example of the analysis of a sample's topography that also contains information on the dimensions of the selenium nanowires within the sample. A wide range of magnifications are possible, from about 10 times to more than 500,000 times, which is about 500 times the magnification limit of the best optical microscopes.

Spot | Mag | FWD | E-Beam | Tilt | Det | HFW | 10 μm
3 | 3.52 kX | 7.317 | 5.00 kV | 0.0° | SED | 43.2 μm |
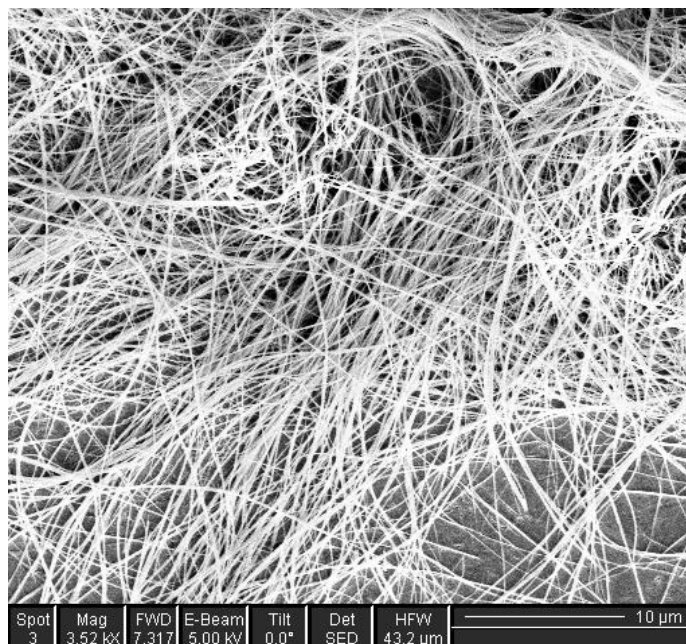
Figure 8.   ***Scanning electron microscopy (SEM) image of selenium nanowires (>100 μm in length).***

Back-scattered electrons (BSE) are reflected from the sample by elastic scattering. [49] BSE are often used in analytical SEM along with the spectra made from the characteristic x-rays. The BSE signal intensity can be correlated to the atomic number of the elements within the sample. This signal can produce images with information about the distribution of different elements in the sample.

One way to determine elemental information of a sample, characteristic x-rays are analyzed. Characteristic x-rays can be emitted when the electron beam removes an inner shell electron from atoms within the sample. [50] This empty space in the inner shell causes higher energy electron to fill the shell and release an x-ray with an energy equivalent to the difference in energy of these shells. These characteristic x-rays are used to identify the composition and measure the abundance of elements in the sample. This technique is known as energy dispersive x-ray spectroscopy (EDS). [50] An image of a nanostructure is obtained by SEM and a corresponding compositional analysis is acquired by EDS.

Imaging a sample by SEM is a relatively simple process, but sample preparation for SEM requires a bit of work. The sample must be maintained under a vacuum during

analysis, and the sample must be at least electrically conductive at the surface and electronically grounded to prevent accumulation of charge that will otherwise obscure the image. Therefore, samples containing metal require relatively little preparation. Some nonconductive samples on the other hand tend to accumulate a charge when imaged with a focused electron beam, which results in inaccurate imaging of the sample. [51] The latter type of samples are usually sputter coated with a <5 nm thick coating of electrically-conducting material, typically gold. Depending on sample size, multiple samples can be mounted onto a specimen holder and loaded into the vacuum chamber to reduce wait time, however this may introduce cross contamination between samples.

Transmission electron microscopy (TEM), on the other hand, provides detailed information on the atomic structure of individual nanoparticles or nanowires, but is more time-consuming and rather difficult to operate in comparison. [52] In TEM, electrons are generated from an electron gun and are transmitted through the sample. The transmitted electrons are focused using electromagnetic lenses to form an image. The imaging modes can be controlled by the use of apertures. If most of the electrons are transmitted, we obtain a bright field image. If specific diffracted electrons are collected, the image is known as a dark field image. In addition, a TEM can also be used for compositional analysis. A resolution of <1 nm and magnifications >100,000x can easily be achieved. Analytical TEM can provide elemental analysis. These techniques include Energy Dispersive X-ray spectroscopy (EDS) and Electron Energy Loss Spectroscopy (EELS). Selected Area Diffraction (SAD) and Convergent Beam Electron Diffraction (CBED), and are used to characterize the crystalline nature of samples from areas as small as microns (SAD) or tens of nanometers (CBED) via electron diffraction patterns. By determining composition of a sample as well as its crystallinity or phase, the analyst can determine the presence of nanomaterial contaminants.

For imaging applications, SEM can provide high quality images very quickly with significantly less sample preparation. However, TEM has a significantly higher image resolution in comparison to SEM. TEM is also widely used for crystallographic characterization and observation of defects in crystalline materials. No metallic coating is needed for TEM analysis, but a sample may still suffer from electron beam damage. Samples must be <100 nm thick and supported on a grid. The sample preparation process can be time consuming and this, along with the cost of analysis, are the main

criticisms of TEM for the use of detecting and analyzing nanoscale materials. Both SEM and TEM have limitations to the types of samples that can be characterized. Samples must typically be dry and free of volatile solvents or other materials, as it must be placed under a vacuum for analysis. In addition, there is a limitation on the size of the sample being analyzed. A spill of nanoparticles over a particular surface can vary up to a few square centimeters, but imaging with an electron microscope will only give you information over an area of hundreds of micrometers at most. As one of the goals of this research is to develop a method for detecting contamination of nanoparticles in the workplace environment, a more efficient and simpler form of elemental analysis is required. A contaminated surface may not be uniform on a surface as a nanoparticle spill may not produce a film or layer of nanoparticles covering any particular area. Therefore, it is important that the results be representative of and accurate to the original sample.

2.1.2.   Spectroscopy techniques

As mentioned above, electron microscopy can identify the shape and size of nanoparticles, but provides limited compositional information unless coupled with other techniques. One such technique is EDS, which is an analytical technique used for elemental analysis of samples. X-rays are emitted from a sample as a result of the interaction of electrons with this material. Each element has a unique atomic structure allowing emission of x-rays that are characteristic of the element's atomic structure. Material compositions can, therefore, be distinguished from each other. [53]

In the ground state, all electrons in an atom occupy discrete energy levels or electron shells bound to the nucleus. An incident electron beam can interact with inner shell electrons and can eject specific electrons from the inner shell. The resulting electron hole is filled with an electron from an outer shell of higher-energy, as depicted in Figure 9. The difference in energy between the higher-energy shell and the lower-energy shell may be released as an x-ray with a characteristic energy. The number and energy of the x-rays emitted from the sample can be measured by an energy dispersive spectrometer. The measured energy of the x-rays is characteristic of the difference in energy between the inner and outer shell and, therefore the atomic structure of the element, or elemental composition of the sample. As seen in Figure 10, running an EDS sample of selenium nanowires drop cast onto a copper grid coated with a thin film of

carbon, produces a peak at 1.38 keV. This 1.38 keV corresponds to the energy released from an M orbital electron to fill a hole in the L orbital. This electron transition is known as the Lα transition and is characteristic of selenium. Selenium also has a Kα transition, but due to its higher energy, 11.21 keV, these x-rays are a less probable transition. The lower probability is due to a number of factors that includes reabsorption into the bulk material and a lower relative rate of production by the incident electron beam.
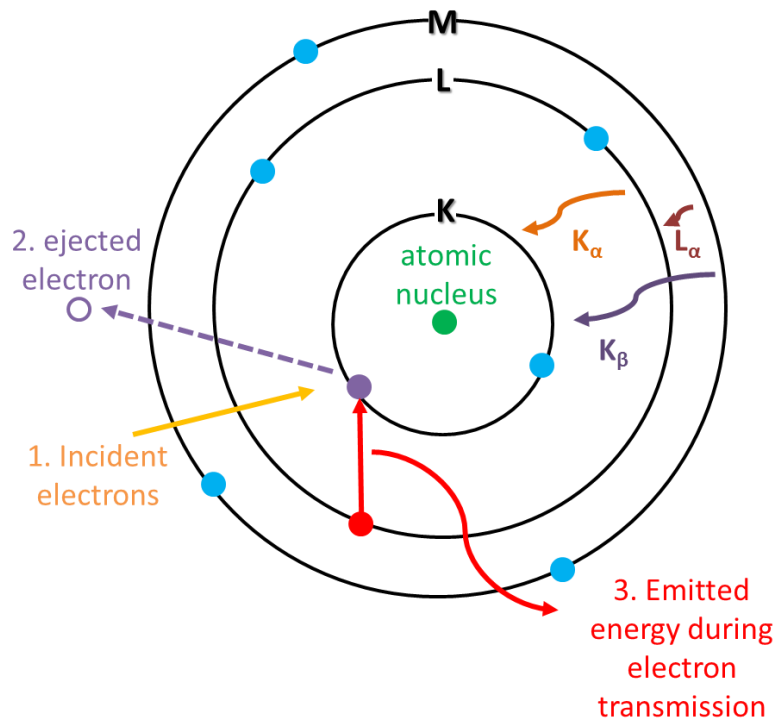
Figure 9. **An electronic orbital shell diagram depicting the process of energy dispersive x-ray spectroscopy.**

Instead of x-ray emission, the excess energy can also be transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an Auger electron, and the method for its analysis is known as Auger Electron Spectroscopy (AES). X-ray Photoelectron Spectroscopy (XPS) is also similar to EDS. It utilizes the ejected electrons in a manner similar to that of AES. Information on kinetic energy of ejected electrons is used to determine their binding energy, which is element-specific and allows chemical characterization of a sample. [54] Although all these

electron spectroscopy techniques provide elemental analysis of the samples, the sample under examination must all be placed in a vacuum chamber. It is difficult or impossible to always place materials of interest, such as the surfaces of a countertop, under vacuum for analysis. A potential solution to this issue is to use an x-ray fluorescence system, which can be portable and does not require placement of the sample under vacuum. [55]
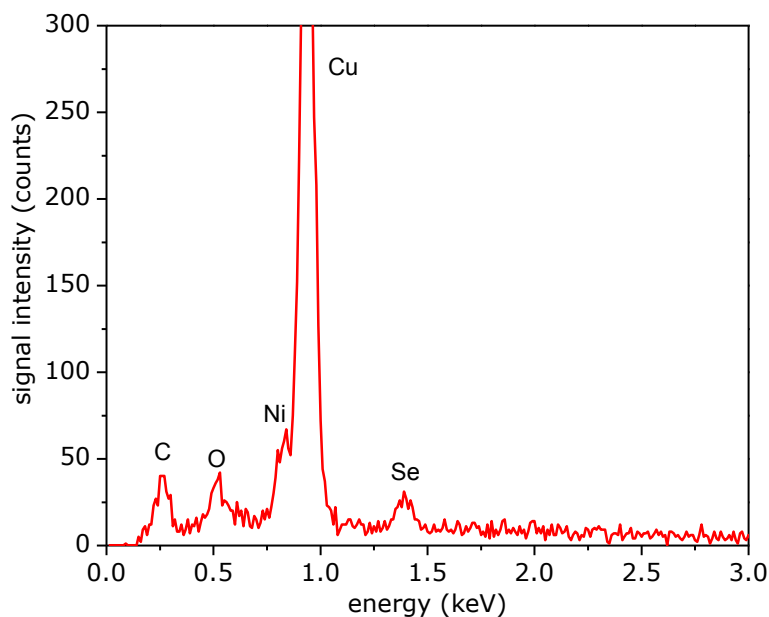
Figure 10. **An energy dispersive spectroscopy (EDS) profile of selenium nanowires on a copper substrate.**

X-ray fluorescence (XRF) is a technique that can be used to detect and quantify the elements in a sample. In visible-light based fluorescence, fluorescence emission results from incident ultraviolet light that excites low energy electrons to higher states and as these electrons relax, the electrons drop back down to a lower energy state. However, in XRF, x-ray radiations are used in place of ultraviolet light. This higher source incident energy allows for the ejection of the innermost-electron shells of an atom, resulting in a vacancy. These vacancies are filled by electrons from the outer shells and x-rays are emitted with a corresponding specific amount of energy. The energy of the emitted x-rays are characteristic of the energy levels of the electron shells in the element. In other words, the energy of the emitted x-rays are different for each element creating a specific elemental fingerprint. The distance between each shell is

different for each element as well. The energy of an electron varies inversely with distance from the nucleus. Electrons in the inner shell (K) are bound tighter to the nucleus than any subsequent shells (L,M,N,O…). Each shell contains various numbers of electrons dependent on the specific element. Each element has a unique set of electrons orbiting in shells of different energies. In a typical XRF analysis, a sample is bombarded with x-rays, creating an emission of electrons, Bremsstrahlung x-rays and characteristic x-rays. Some of the incident x-rays collide with and ionize the K and L shell electrons. Leaving vacancies in the K or L shells, which are filled by electrons from the outer L, M, or N shells. Each electron transition from an outer shell to the vacancy emits a characteristic x-ray (fluorescence emission) with energy equal to the energy difference between two shells for the specific element. Since the electron shells in all atoms of the same element have the same fixed energy levels, each similar electron transition emits an x-ray of the same discreet energy. The quantity of x-rays measured will be proportional to the number of atoms of the particular element or elements present in the sample. Figure 11 contains typical XRF spectra plotted with intensity versus energy of the detected x-rays. This example is for a gold film on a silicon wafer substrate detected at three difference particular x-ray beam energies, each with distinct accelerating potential. Different XRF systems have their own unique configuration for the source, detector, and filters that help to optimize the detection of specific elements. As seen in Figure 11, the Bremsstrahlung x-ray radiation is superimposed onto the characteristic x-ray lines from the 15 keV source, whereas for higher energy sources the lines are well separated from the Bremsstrahlung radiation.
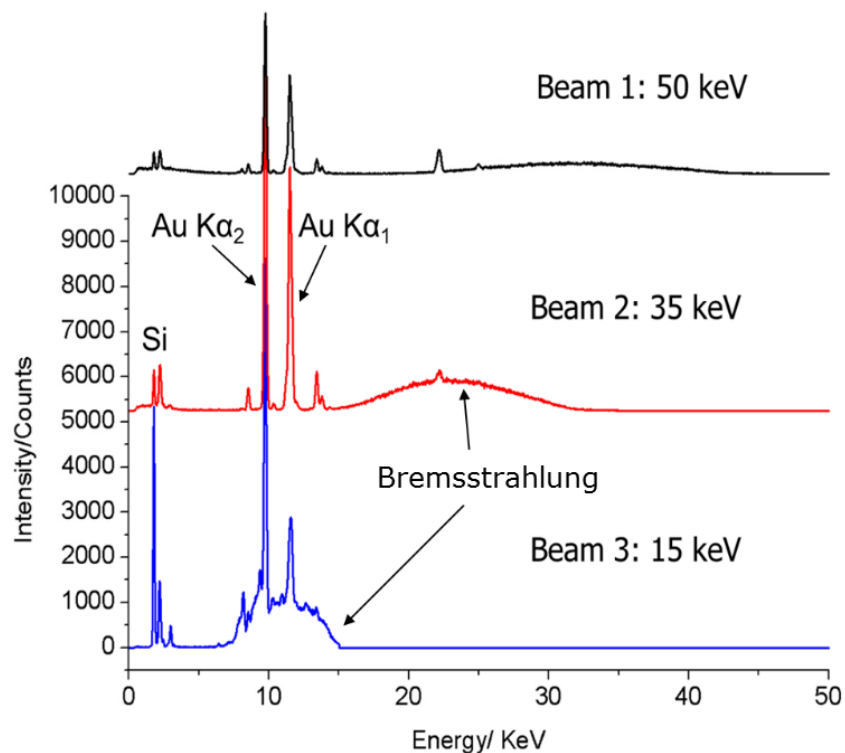
Figure 11. *X-ray fluorescence measurements of a gold film on a silicon wafer at 3 different incident energies commonly used in soil analysis.*

Analysing the energies of the x-rays emitted from a sample give details on the elemental composition and their relative concentrations in the sample. In order to determine the absolute concentrations, one must calibrate the system and the x-ray intensities associated with each element. In the case of a spill containing nanoparticles, there could be a layer of contaminants formed on a particular surface. A series of thin films each with a defined amount or thickness of particles, prepared by physical vapour deposition, is used to create an XRF calibration curve. As seen in Figure 12, five different thicknesses of gold nanoparticles on separate silicon wafer samples were prepared and analysed by XRF. From these measurements a calibration curve was prepared for gold nanoparticles on silicon and a linear correlation was observed in the data. XRF is also capable of penetrating and detecting through centimeters of material for lighter atomic elements (e.g., first row transition metals). However, radiation from the x-ray tube cannot penetrate deep into heavier elements such as lead.

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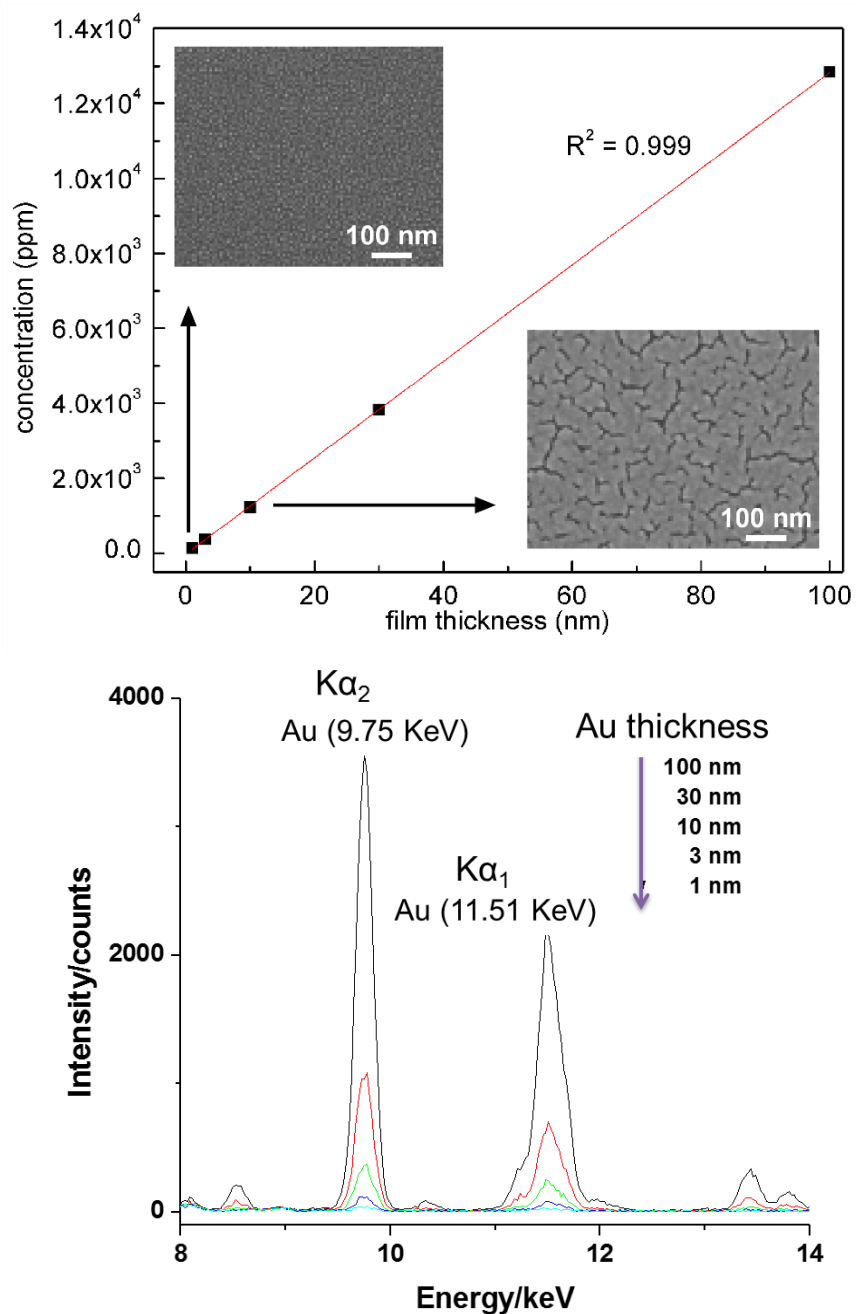
Figure 12. **X-ray fluorescence analysis for five samples (top) and its corresponding x-ray fluorescence spectra (bottom) of silicon wafer coated with the specified thicknesses of gold nanoparticles as prepared by physical vapor deposition. Inset figures are scanning electron microscope images of silicon wafers coated with a gold nanoparticles to a thickness of 1 and 10 nm.**

X-ray fluorescence systems are available as either portable benchtop systems or portable handheld systems. The analysis of samples is convenient when using a portable XRF system, because the system can be easily transported to particular job sites. XRF requires little to no sample preparation, providing relatively fast results. It can also deliver both qualitative and quantitative multi-element analyses. It is a non-destructive technique and can be used for a wide range of applications. Although XRF cannot distinguish between the presence of an element in the form of nanoparticles or as a bulk material, the tool can be used to identify the presence of a material for a spill of nanoparticles that are known to be used in the workplace. In treating a nanoparticle spill, after remediation the use of XRF can assess the presence of any remaining nanomaterial. The use of XRF will permit a quick analysis to determine if the surface is still contaminated, but without requiring the surface to be placed under a vacuum or otherwise altered for analysis. The disadvantages of XRF are that it is a surface or near surface sensitive technique, which only measures a portion of the sample directly in front of the analyzing window. In addition, XRF will only analyze a surface for contamination within a small area of typically one square centimeter. XRF also has difficulty to detect elements lighter than $Z = 14$ and in general may not have the best limit of detection of available analytical techniques, but it can quickly provide general information about a contaminated surface. Similarly, laser-induced breakdown spectroscopy (LIBS) is also an instrument that can provide quick, general information about a contaminated surface. It is also a type of atomic emission spectroscopy, but uses a high energy pulsed or continuous laser as the excitation source. If ultratrace analysis is required, an alternative method such as inductively coupled plasma mass spectrometry (ICM-MS) can be used to better assess the presence of any trace contamination from a spill containing nanoparticles.

The ICP-MS instrument comprises of a few basic components. First, an aerosol of the sample of interest is generated and ionized by the inductively coupled plasma (ICP) source. Argon gas flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off of the argon atoms, forming argon ions. These

ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma. [56]

The detection capabilities of ICP techniques can vary with the sample introduction technique used, as different techniques will introduce variations in the amount of sample that can reach the ICP plasma. Detection capabilities can vary with the sample matrix, which may affect the degree of ionization that occurs in the plasma or that can form species that may interfere with the analyte determination. Once the elements in the sample are converted into ions, they are introduced into the mass spectrometer via the interface cones. The interface region in the ICP-MS transmits the ions traveling in the argon sample stream at reduced pressure (1-2 Torr) into a lower pressure region of the mass spectrometer (<1 x 10^{-5} Torr). This is achieved through the intermediate vacuum region created by the two interface cones, the sampler and the skimmer as shown in Figure 13 below.
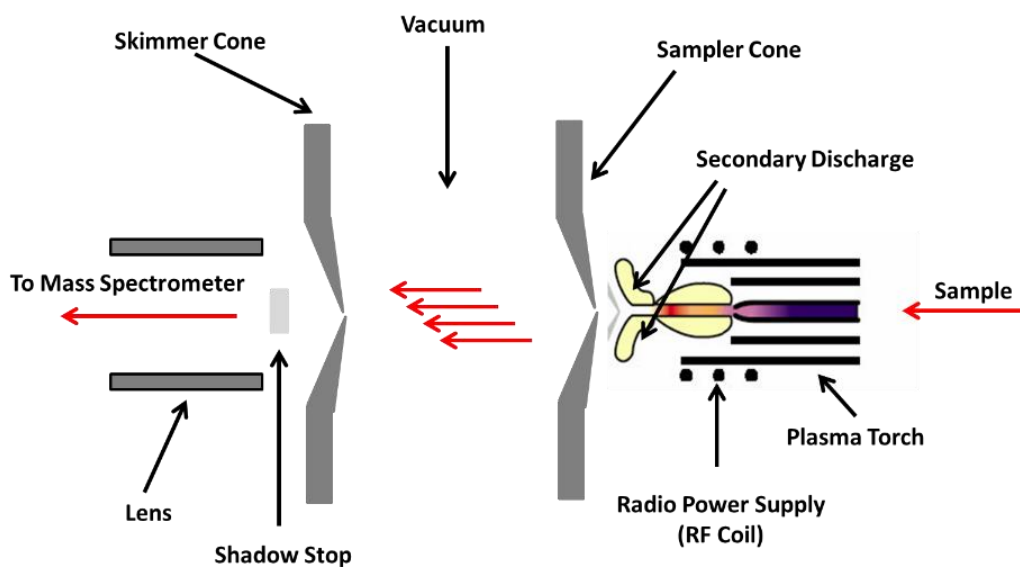
Figure 13. *Schematic of an inductively coupled plasma mass spectrometry system showing the interface region.*

The sampler and skimmer cones are metal disks with a small hole (~1 mm) in their center (Figure 13). The purpose of these cones is to obtain a sample from the center portion of the ion beam coming from the ICP torch. A shadow stop or similar

device blocks the photons coming from the ICP torch, which is also an intense light source. The ions from the ICP source are then focused by electrostatic lenses in the system. Since the ions coming from the system are positively charged, the electrostatic lens, which also has a positive charge, serves to collimate the ion beam and focuses it into the entrance aperture or slit of the mass spectrometer. Once the ions enter the mass spectrometer, they are separated by their mass-to-charge ratio. The most commonly used type of mass spectrometer is the quadrupole mass filter, composed of 4 rods (approximately 1 cm in diameter and 15-20 cm long) as depicted in Figure 14. [57]

Exit slit to detector

Incident ions from sample
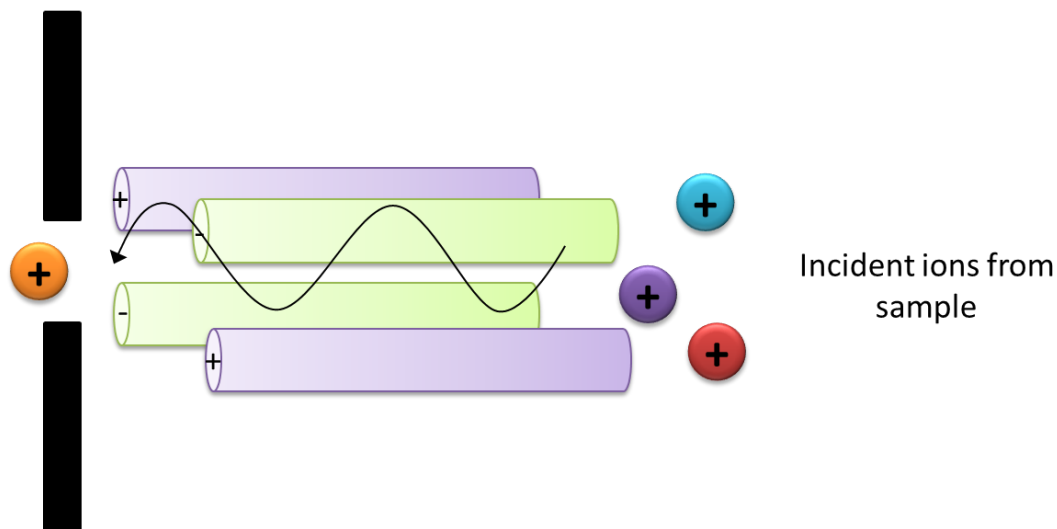
Figure 14. ***Schematic of a quadrupole mass filter.***

In a quadrupole mass filter, AC and DC voltages are applied to opposite pairs of the rods. These voltages are then rapidly switched along with an RF-field. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/e) to pass through the rods to the detector at a given instant in time. The ability to filter ions on their mass-to-charge ratio allows an ICP-MS to supply isotopic information, since different isotopes of the same element have different masses. Typical quadrupole mass spectrometers used in ICP-MS have resolutions between 0.7 - 1.0 amu. This is sufficient for most routine applications. However, there are some instances where this resolution is not sufficient to separate overlapping molecular interferences from the elemental isotope of interest. The use of high resolution or magnetic sector

mass spectrometers has become more common in ICP-MS, allowing the user to eliminate or reduce the effect of interferences due to mass overlap. This mass resolution will help users to identify contaminants on a surface.

Once the ions have been separated by their mass-to-charge ratio, they are detected or counted by a detector. The purpose of the detector is to translate the number of ions striking the detector into an electrical signal that can be measured and related to the number of atoms of that element in the sample via the use of calibration standards. Most detectors use a high negative voltage on the front surface of the detector to attract the positively charged ions to the detector. Once the ion hits the active surface of the detector, a number of electrons is released which then strike the next surface of the detector, amplifying the signal.

The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer, or by using a laser to directly convert solid samples into an aerosol. Once the aerosol is introduced into the ICP torch the elements in the aerosol are converted into gaseous atoms and ionized in the plasma. The ions produced are extracted in the sampling interface and separated by a mass spectrometer to determine elemental composition and concentrations. Our samples are digested with an acid prior to ICP-MS analysis. For a sample of silver nanoparticles, the sample is first digested with nitric acid to form silver ions. The number of silver ions present in a sample can be determined via ICP-MS and used to calculate the number of nanoparticles based on an average particle size determined by TEM analysis. Each element of the periodic table has at least one isotope that consists of a unique mass. In the case of silver, it has two isotopes, one at 106.9 μ and the other at 108.9 μ. In a typical ICP-MS analysis, the peak position corresponding to a particular mass to charge, m/z, ratio (x axis) identifies the isotope present, and the peak intensity (y axis) is proportional to the concentration. Similar to XRF, a calibration curve can also be created.

One of the most powerful analytical techniques for ultratrace analysis for a wide variety of samples is ICP-MS. Unlike many other techniques, ICP-MS is applicable to nearly all elements in the periodic table, and elements can typically be measured in a single analysis. Due to its high sensitivity, one major disadvantage of ICP-MS is that it's

also more susceptible to trace contaminants from glassware and reagents. The presence of some ions can also influence detection of other ions. This can lead to false information especially in the case when you are attempting to determine the presences of trace nanoparticle contamination.

A significant amount of time (e.g., hours to days) is required in the sample preparation for ICP analysis. Most samples must be digested with an acid. Hence this is a destructive technique. Choosing a specific acid for digestion also poses a concern as it may interfere with the results. [58] The objective of our research is to develop methods that are simple and quick to implement. The selected methods must also be relatively inexpensive for the analysis of multiple samples, and portable for implementation at the point-of-use of these nanomaterials. The need to develop these methods is for preventing potential hazardous workplace conditions from exposure to nanoparticles. Information about the nanoparticles could be utilized to simplify the task of discerning the presence of a contaminant. The workers will often know some information about the materials they are handling, such as the average size, shape and composition of the materials. Size and shape of the nanoparticle are not essential pieces of information if the composition of the nanoparticle is foreign (unique in) the workplace environment. There are a number of techniques that can quantitatively analyze a sample for its elemental composition. A number of these techniques are summarized in Table 1, each capable of analyzing samples for a wide range of elements. This evaluation included analysis of the: i) sensitivity; ii) capability of simultaneous detection of multiple elements; iii) required sample preparation time; iv) ability to potentially detect nanoparticles on various surfaces; v) time for analysis; vi) portability; and vii) cost to implement each technique. Many of these techniques require a relatively long time to obtain the data as samples must be introduced under vacuum for analysis.

A large variation is observed in the amount of time required for analysis (including sample preparation time) and for the cost of procuring equipment associated with each technique. The limit of detection also significantly varies between these techniques. The concentration of nanoparticles per area deemed to be safe in the workplace is beyond the scope of this study, and will require further analysis. However, based on the typical concentrations of nanoparticles in solution, our initial calculations suggest that the ideal method of analyzing nanoparticles in the workplace should at least

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detect concentrations as low as parts per million (ppm) levels. This estimate is supported by our studies to simulate spills of solutions containing nanoparticles. Keeping in mind each of the considerations outlined above, the top two techniques are laser-induced breakdown spectroscopy (LIBS) and x-ray fluorescence spectroscopy (XRF). These techniques are each relatively inexpensive, portable, sensitive to ppm levels without the need for sample preparation, and offer relatively fast sample analysis. However, analysis by LIBS can be locally destructive to ~100 nm of the surfaces under analysis, but is considered a non-destructive technique as this damage might not be discernable by eye. [59] We identified XRF as the desired system to pursue for these initial studies, but other analytical techniques such as LIBS might be of interest for future studies in the area of assessing nanoparticle contamination.

All of the analytical techniques in Table 1 will give elemental information about the sample of interest, but they do not offer insight into the size of the material (e.g., bulk or nanosized). Complementary analyses are required and imaging by electron microscopy is one way to obtain the necessary information to verify the presence of a nanomaterial. An alternative is to use dynamic light scattering (DLS) techniques. Typical applications of DLS are the characterization of colloidal particles, emulsions or large molecules (e.g., proteins) which have been dispersed or dissolved in a liquid. The Brownian motion of these particles or matter in the suspension causes an incident laser to scatter with an intensity pattern that varies spatially, which can be correlated with the dimensions and dielectric properties of the suspended material. Analysis of the variations in intensity of the results over time can provide a measure of the velocity due to Brownian motion of the scattering center and hence an estimate of particle size through the use of the Stokes-Einstein relation. [60] This technique can provide information on the nanoscale dimensions of a material. However, there are some limitations to this technique, such as its ability to process significantly large particles or non-uniform samples, as well as particles that are too dense (e.g., undergo significant settling during the course of a measurement), and the fact that the nanomaterial needs to be dispersible into solution and ideally colloidal. Each of these limitations can cause potential issues with an accurate interpretation of the light scattering measurement.

Table 1. *Comparison of selected methods for the analysis of nanoscale materials.†*

Method *	information provided	elements detected	detection limits	analysis time	portable?	relative cost
AES	chemical and elemental	Li – U	0.2 %	> 1 h	no	$$$$
EDX	elemental	Na – U	0.1 %	> 1 h	no	$$$
FAAS	elemental	Na – Bi	> μg g^{-1}	> 1 h	no	$
LA-ICP-MS	elemental	Na – U	> ng g^{-1}	minutes	no	$$$$
LIBS	elemental	Li – U	> μg g^{-1}	minutes	yes	$$
SIMS	elemental	H – U	> ng g^{-1}	> 1 h	no	$$$
XPS	chemical and elemental	Li – U	< 0.1 %	> 1 h	no	$$$$
XRF	elemental	Al – U	> μg g^{-1}	minutes	yes	$

† Adapted from Evans Analytical (www.cea.com) and J.S. Becker, Inorganic Mass Spectrometry: Principles and Applications, John Wiley & Sons, Ltd. 2007.
* Interpretation of abbreviations: AES – Auger electron spectroscopy; EDX – energy dispersion X-ray spectroscopy; FAAS – flame atomic absorption spectroscopy; LA-ICP-MS – laser ablation inductively coupled plasma mass spectrometry; LIBS – laser induced breakdown spectroscopy; SIMS – secondary mass spectroscopy; XPS – X-ray photoelectron spectroscopy; and XRF – X-ray fluorescence spectroscopy.

X-ray fluorescence spectroscopy is an ideal method for analyzing multiple samples throughout the workplace. [61], [62], [63] There are a number of commercially available portable XRF systems that are designed to be brought "into the field" for analyzing samples on site. [63], [64], [65] These developments have led to a number of advantages for using XRF technology to track nanoparticle contamination. The portable XRF technologies are manufactured with the knowledge that users may want to collect information on the samples that include time, date, sample number, and location. All of this information can be automatically logged by the system using an on-board data logger with an integrated global positioning system. These systems are not essential for

our studies, but for the proposed hypothetical analysis of 100 independent samples these capabilities would significantly reduce the time required to inspect a workplace for contamination. If each sample required 3 min to complete the analysis and logging of the data, it would still require ~2 days of analysis. Although this is a ~30x improvement in throughput compared to other analytical techniques available, it is clear that the analysis of nanoparticle contamination does require a relatively simple, quick and yet informative analytical technique.

From this process, the best solution to meet the needs of this proposed project is to implement X-ray fluorescence (XRF) technology, which can be field portable and brought to a work site. The sensitivity of XRF for detecting the presence of elements, and its low cost would mean that the system could be widely implemented. Potentially each user of nanoparticles could purchase their own system, or contract an independent analytical consultant to test the workplace for contamination. Analysis by XRF could be easily implemented on a regular basis by a worker or on an occasional basis by a third party. The regularity of inspection will be determined in part by the frequency with which the nanoparticles are used in a particular workplace. Methods need to be developed for the use of XRF technologies to detect nanoparticles on various surfaces found in the workplace. This technique has been used to detect the presence of toxic elements (e.g., Pb and Hg) in paints, toys, and other household items. [61] It has also been used to determine the composition of thin films, [62] and to analyze personal protective equipment (PPE) for particles generated from welding. [63] Clean-up of particles from welding has also been assisted by portable XRF technologies. [63] These demonstrations support the use of XRF for monitoring elemental contamination in the workplace, as well as developing best protocols that could be implemented in any workplace to minimize worker exposure to nanoparticles.

Aside from detecting the presence of nanoparticles, the other aspect of managing potential contamination is clean-up of a spill. The objectives of this research will include developing methods to decontaminate a surface. Techniques need to be implemented to prevent spreading of nanoparticles over a larger area, and to avoid the false sense of security in thinking that if a surface passes a visual inspection that it has been properly cleaned. The choice of cleaning materials is also important. Material choices could include the types of wipes (e.g., porosity, solvent retention, and

composition) and cleaning reagents (e.g., cleaning oils or surfactants). Remediation of contaminant requires removal of the contaminant from the environment of concern. Determining the success of a remediation process can, however, be difficult to discern. A contaminant that is spread over a larger area is still present, but might no longer be detectable. One approach might be to train individuals on appropriate methods of remediation. However, considering that unintentional contact might result in the spread of a nanoparticle contaminant it is equally important to establish a set of methods that can remediate nanoparticle contaminants while minimizing physical contact between the worker and the potentially hazardous particles. This research aims to promote early detection of nanoparticles in the workplace and to promote awareness of appropriate techniques (and excellent habits) for cleaning up spills containing nanoparticles.

3. Remediation of nanoparticle contaminants by encapsulation

Asbestos, a naturally occurring fibrous mineral, is a common material used in buildings due to its significant resistance to heat. [66] However, in the early 20th century, it was discovered that it was highly toxic when inhaled. Exposure to asbestos was a health risk and was linked to lung cancer. [67], [68] Exposure to even a low amount of asbestos can cause as much health damage as exposure to a higher level of asbestos. [67], [68] Many years later, scientist discovered that attempting to remove asbestos from a building is more harmful than simply covering it up. When asbestos has been disturbed, small particles drift into the air, quickly contaminating the air. The best solution is to manage asbestos by containing it using encapsulation techniques. [69] Remediation by encapsulation is the process of sealing the contaminated surfaces with a material such as a ceramic coating, to prevent the contaminant from releasing into the surroundings. Like asbestos, nanoparticles may not seem obviously toxic, but may have some long term harmful effects. Since nanoparticles can't be seen by the naked eye, it is important to minimize the spread of nanoparticle contamination. Learning from the ideas developed for the remediation of asbestos, we pursued the remediation of nanoparticle contaminants by encapsulation. Through the use of an encapsulant, a nanoparticle spill on a surface may also be removed in a similar manner by applying and removing a layer of encapsulant. By this process, the nanoparticles can be contained and easily sent for disposal or for further processing. Encapsulation would ideally provide an effective barrier between the worker and the nanoparticles, thus minimizing the potential for transfer of the contamination to other surfaces. The encapsulation would also provide a simple means to remove the particles; peeling the encapsulating layer away from the contaminated surfaces would, ideally, remove the particles from these surfaces as well.

3.1. Adhesive tapes
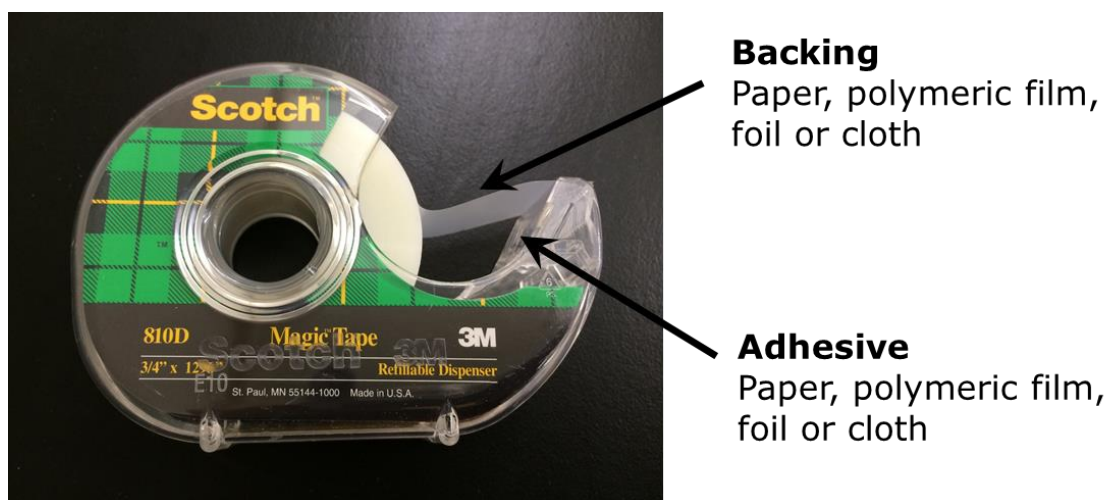
Figure 15.   Picture of a pressure sensitive adhesive tape.

One type of material that could be used for nanoparticle remediation are adhesive tapes. Adhesive tapes are materials that are coated with an adhesive typically used to temporarily or permanently join two or more objects. These tapes are used throughout our daily lives, serving a number of purposes. In this study, pressure sensitive adhesive tapes are pursued for the remediation of nanoparticles as it is relatively inexpensive and readily available. Pressure sensitive adhesive (PSA) tape can be defined as a continuous flexible strip of paper, plastic, metal or cloth, on one or both sides with a tacky adhesive, which will adhere to a variety of surfaces with light pressure (Figure 15). PSAs can be blends of natural or synthetic rubber and resin, acrylic, silicone or other polymer systems. Most common household tapes are single coated adhesives, such as masking, electrical, medical and Scotch™ tape. Most adhesive tapes contain four basic components. A mixture of either paper, polymeric film, foil, or cloth backing, which provides a non-adhesive side for ease of manipulating the pieces of tape and present a non-adhesive surface once the tape is adhered to the intended surface. An adhesive primer is applied to the backing to help the adhesive spread evenly and adhere securely to the backing material once applied. A thin layer of acrylic, rubber or silicone adhesive is sprayed onto this primed backing material, and the adhesive is also coated with an anti-cohesion material such as polyvinylcarbamate. [70] This release coating prevents cohesion at the surface of the tape so it can be unrolled easily. This final

coating also plays a role in both adhesion and cohesion. Adhesion arises from the interactions of one type of molecule with another type of molecule, whereas cohesion is the interaction of one type of molecule with itself. Molecules within the adhesive interact strongly with the molecules of substrates, or adhere, but these molecules also stick to each other or cohere. These are essential properties of adhesive substances that hold the material together and help it adhere to various surfaces. [70]

The idea is that by applying the PSA tape onto the contaminated surface, it will come into contact with and adhere to the nanoparticles. After lifting off the tape, the nanoparticles will be removed from the contaminated surface and, ideally, remain on the tape, as seen in Figure 16. The process of applying and removing the tape is repeated until quantitative analysis determines that the surfaces are clean or the contaminant concentration is down to a safe level. However, further studies will be required to determine occupational exposure limits to nanoscale materials. [71]

1) CONTAMINATED SURFACE

2) APPLY ADHESIVE TAPE

3) REMOVE ADHESIVE TAPE

4) REPEAT STEPS 2-3 WITH NEW PIECES OF ADHESIVE TAPE

5) REMEDIATED SURFACE
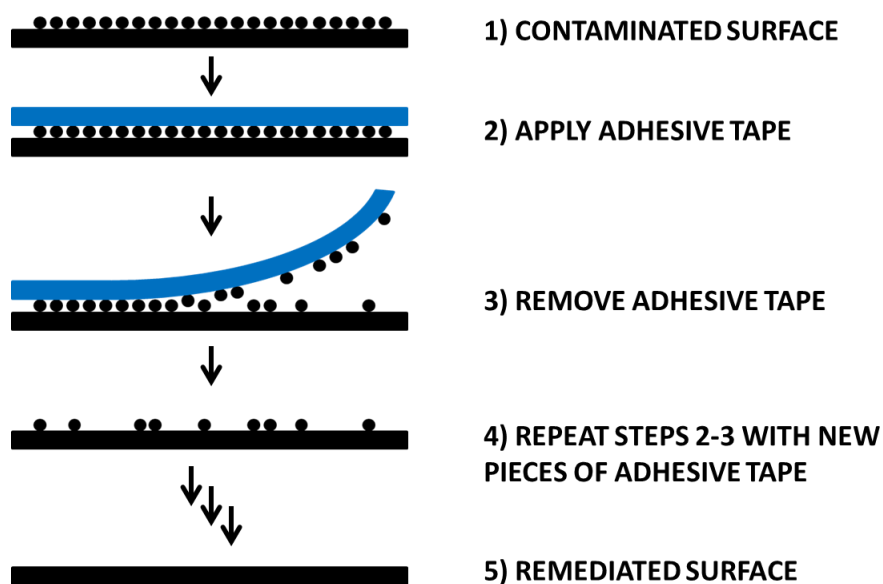
Figure 16. *Schematic depiction of the process to use adhesive tape to remediate surfaces contaminated with nanoparticles. The adhesive tape is applied onto the contaminated surfaces and subsequently peeled to remove the nanoparticles that adhere to the tape.*

Multiple applications of separate pieces of tape should be able to reduce the concentration of nanoparticles contaminating the surfaces. Unlike wiping a countertop, which may spread the nanoparticles over a larger area (Figure 17), the tape

encapsulates the nanoparticles in its adhesive layer, such that these particles are trapped and can be disposed of properly.

To determine the efficiency and effectiveness of using adhesive tape for this type of remediation, nanoparticles were deposited onto a variety of surfaces and multiple pieces of adhesive tape were consecutively applied and removed. After a set amount of applications and removal of tape, the surfaces were examined for traces of remaining contaminants.
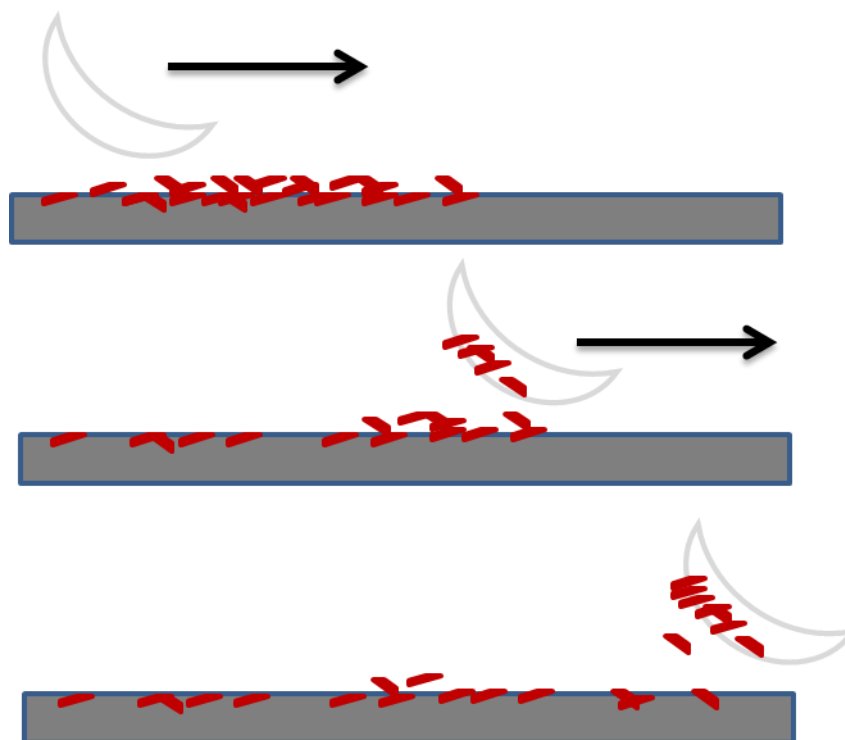
Figure 17. *Schematic of cleaning contaminated surfaces with a cloth. By dragging the cloth across surfaces, the area of contamination could increase.*

3.1.1. Methodology

In this nanoparticle remediation test, silver nanoparticles, a commonly used nanoparticle in the workplace, were chosen as the nanoparticle contaminant. The syntheses of silver nanoparticles were based on a procedure developed by Hiramatsu and Osterloh. [72] A small amount of silver acetate (99.9% purity), 0.05 g was dissolved in 19.00 mL of octadecene in a 250 mL round bottom flask. When silver acetate has

completely dissolved, 6.15 mL of oleylamine was added to the flask. The flask was then immersed into a silicone oil bath at 180 °C. After heating for approximately one hour, the flask was cooled to room temperature, divided into plastic centrifuge tubes, and mixed with chloroform at a 1:1 (v/v) ratio. Silver nanoparticles were then precipitated from solution after addition of methanol in a volume equivalent to that of the chloroform. This mixture was centrifuged at 8500 rpm for 25 min, the supernatant decanted and the isolated precipitate dispersed into methanol. This process of purification was repeated two more times, and the purified silver nanoparticles were dispersed into hexanes. The resulting nanoparticles were imaged with a Hitachi 8000 STEM with a lanthanum hexaboride thermionic source operating at 200 kV.

To be able to examine the success of using adhesive tape in remediation processes polished, silicon <100> wafers were chosen as the test substrate in order to be able to both quantitatively and qualitatively analyze the process. Prior to contaminating the silicon wafers, the wafers were cut into approximately 1 cm square pieces and in a solution of piranha and rinsed with high purity 18.2 MΩ·cm water. The piranha solution was prepared from a 7:2 (v/v) mixture of concentrated sulfuric acid and a 30 % by volume aqueous solution of hydrogen peroxide. The polished silicon pieces were immersed in Piranha for 15 min and rinsed at least three times with ~ 50 mL of 18.2 MΩ·cm deionized water. *CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.* A simulated spill was prepared by pipetting onto the polished silicon 10 µL of the synthesized nanoparticles, after purification in hexanes. The nanoparticles were then air dried for at least 30 minutes. Samples of a laboratory benchtop (Wilsonart D417-335-01) were also used for these studies to simulate, and extend these studies to, spill detection and clean-up from a potential workplace environment.

Selenium nanowires were also used as potential contaminants. Selenium nanowires were synthesized by following a procedure developed by Wang and Gates. [73], [74], [75] In a 250 mL round-bottom flask, 2.73 g of selenious acid was dissolved in 100 mL of 18.2 MΩ·cm water and cooled in an ice-water bath. Over a period of 2 min, 3 mL of hydrazine (50-60% water) was added to the solution drop wise while the reaction was maintained under magnetic stirring. After 15 min of reaction, a red precipitate was collected by filtration. The filtrate was rinsed with 200 mL of ice-cold high purity water to

remove residual hydrazine. The isolated red solid was stored in a desiccator under darkness to dry while protected from exposure to ambient light. Selenium nanowires were prepared by subsequently sonicating 1 mg of the red solid (amorphous selenium colloids) in 1 mL of ethanol for 1 min. The nanowires were stored in darkness over a period of 12 h and then centrifuged at 1500 rpm for 15 min. The supernatant was decanted and replaced with a mixture of hexanes. A 10 µL droplet of this solution was cast onto the test surfaces to simulate a spill. In this case, the test substrate was a 2004 Canadian copper penny that was cleaned by sonication in water for 30 min, briefly immersed in a 6 M hydrochloric acid bath and rinsed with 18.2 MΩ·cm high purity water. The sample was air dried in a desiccator until ready for use.

To remove the nanoparticle contaminants, a small piece of 19 mm wide 3M Scotch® Magic adhesive tape was placed over the contaminated surface. A plastic cylinder was used to apply an even pressure across the surface to ensure uniform adhesion between the tape and the contaminated surface. The adhesive tape was removed by peeling along the length of the tape, and the remediation process repeated as necessary with a new piece of adhesive tape each time. Samples were analyzed at regular intervals, such as after 1, 5, 10, 15, and 20 separate applications of tape to the substrate.

The success of the remediation process was monitored by electron microscopy imaging with a FEI Strata DB 235 field emission SEM and by further elemental analysis. Elemental analysis was performed using a Perkin Elmer SCIEX ELAN 6000 ICP-MS, or either a portable Delta or X-5000 XRF system from Olympus Innov-X. Samples were prepared for ICP analysis by digestion in 5 mL of 5% nitric acid (Anachemia Reagent Grade, diluted with 18.2 MΩ·cm deionized water). After a specific set of applications of tape, the samples were placed into individual plastic 10 mL centrifuge tubes and 5.00 mL of 5% nitric acid solution was subsequently added to digest the samples for a minimum of 1 h. The ICP-MS was set with a sample flow rate of approximately 0.1 mL / min. The presence of silver nanoparticles was monitored by signal of the mass to charge ratio of 106.9µ. The XRF analyses were performed using a portable Delta or X-5000 XRF system equipped with a tantalum anode x-ray tube from Olympus Innov-X. Each sample was set for an integration time of 45 s.

3.1.2. Remediating of nanoparticle contaminants with adhesive tape

In this nanoparticle remediation test, silver nanoparticles, a commonly used nanoparticle in the workplace, were chosen as the nanoparticle contaminant. A number of researchers are interested in silver for its bioactivity and ability to act as an antimicrobial material. [76], [77] TEM analysis of the nanoparticles indicates that the silver nanoparticles were polydisperse and ranged from 10 to 30 nm in diameter (Figure 18). Instead of monodisperse nanoparticles, a polydisperse nanoparticle solution was important for this study as it can help determine the feasibility of remediating a spill of nanoparticles that includes nanoparticle of a diverse range of sizes.
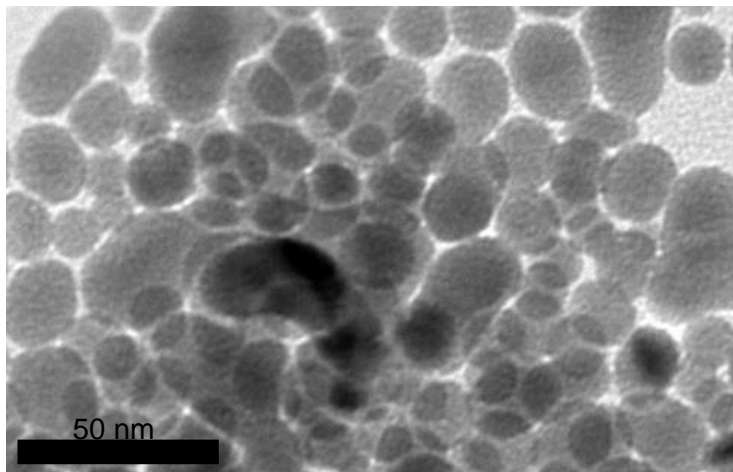
Figure 18. *Transmission electron image of silver nanoparticles synthesized and used in simulated remediation studies.*

To be able to examine the success of using adhesive tape in remediation processes polished, silicon <100> wafers were chosen as the substrate in order to be able to both quantitatively and qualitatively analyze the process. SEM images of a simulated, contaminated surfaces of silver nanoparticles on a silicon surface were obtained, Figure 19. Features in the image are large particles or clusters of silver nanoparticles. The surface of the silicon wafer is densely coated with these particles.

To remove the nanoparticle contaminants, a small piece of 19 mm wide 3M Scotch® Magic adhesive tape was placed over the contaminated surface. A plastic cylinder was used to apply an even pressure across the surface to ensure uniform adhesion between the tape and the contaminated surface. The adhesive tape was removed by peeling along the length of the tape, and the remediation process repeated as necessary with a new piece of adhesive tape each time. Samples were analyzed at regular intervals, such as after 1, 5, 10, 15, and 20 separate applications of tape to the silicon substrate. The success of the remediation process was monitored by electron microscopy imaging and elemental analysis.

Spot	Mag	FWD	E-Beam	Tilt	Det	HFW	100 μm
3	500 X	4.958	5.00 kV	-0.0°	SED	608 μm	
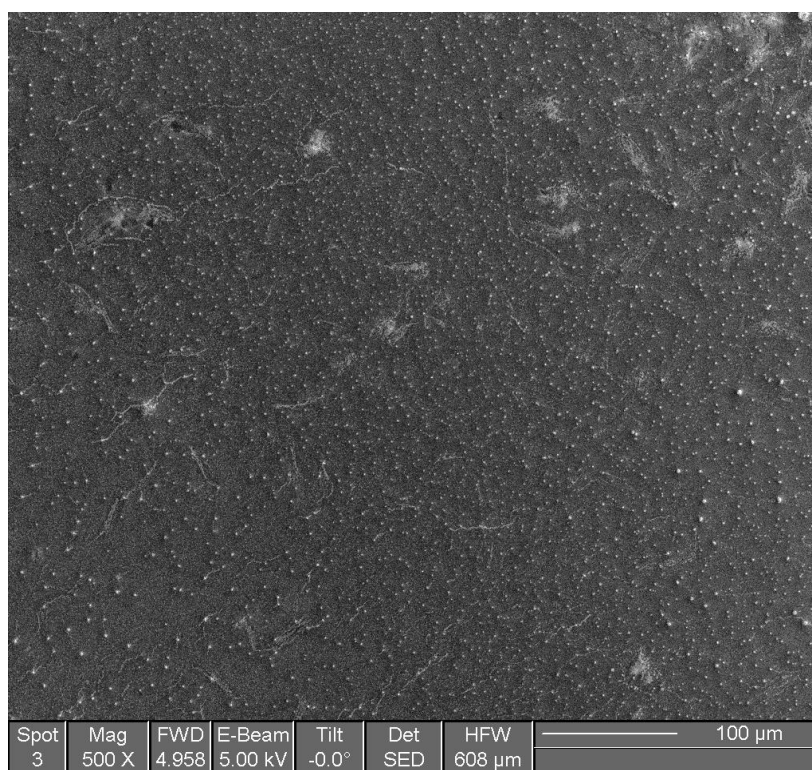
Figure 19.   Scanning electron microscope image of a silicon wafer contaminated with silver nanoparticles.

XRF results of 5 different samples each containing various concentrations of silver nanoparticles were deposited onto a polished silicon wafer can be seen in Figure 20. The number of separate applications of tape between each XRF analysis varied from 1, 5, 10, 15 and finally 20 times of adhering and peeling separate pieces of tape. Each step used a brand new piece of tape. The graph in Figure 20 represents the intensity of the silver signal detected by XRF. It can be seen that after 15 applications of tape, the

intensity decreased significantly from the initial values and leveled off to an approximately constant value for some of the samples to background intensities (10±4).
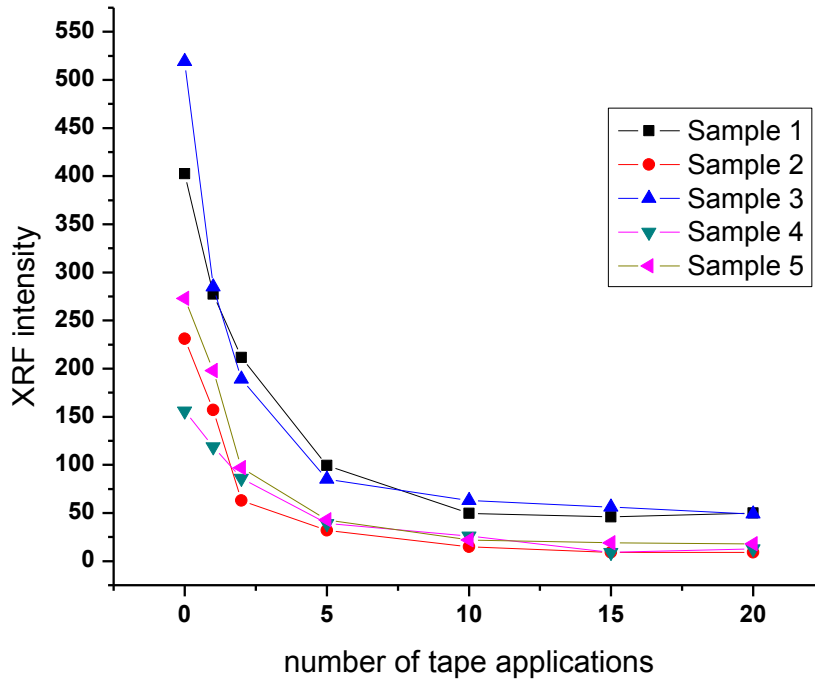
Figure 20. **Peak silver Kα intensities detected by portable x-ray fluorescence (XRF) spectroscopy for the remediation of silver nanoparticle contamination as simulated on silicon wafers. Signals obtained from the five samples were tested, each at slightly varied amounts of silver nanoparticles loaded onto the silicon wafer. The silver nanoparticle contamination is remediated through a series of 20 steps of applying adhesive tape to the surfaces, removing the tape, and repeating this process with new pieces of adhesive tape each time. Background intensity for a clean polished silicon wafer gave intensity reading of 10 ± 4.**

The decreasing intensity signifies that silver nanoparticles are being removed after each application of adhesive tape to the contaminated surfaces. This can also been seen in the SEM images in Figure 21. In these images, it can be seen that the initial contamination prior to any remediation treatment covered the entire silicon wafer and after multiple applications of separate pieces of tape, it became hard to visually confirm the presence of nanoparticles. After application of 5 tapes, there is a steady intensity

that could indicate a plateau in the ability to remediate remaining contaminants or potentially nanoparticle levels are below the limits of detection of the XRF system.

After a single application and removal of tape, a significant amount of silver nanoparticles is removed. What is noticeable in both Figure 20 and Figure 21 was that after approximately 15 applications of tape, no significant change was noticed. However, in Figure 21D and Figure 21E where more applications of tape have been applied, there are additional features that are not present in the clean or the initial contaminated silicon wafer. These features are perhaps residuals left behind from the adhesive tape, such as those seen in the optical image in Figure 22. The non-reflective features in the bright field image are residues left behind after applying and removing 20 separate pieces of adhesive tape on a clean polished silicon <100> surface. This residue may explain the plateau observed in Figure 20. The adhesive tape leaves residual adhesives on the surfaces of the silicon. This residual adhesive can potentially trap some of the nanoparticles resulting in a decrease in the effectiveness of remediation steps, which could also explain the differences seen in the plateau levels between higher initial concentrations compared to lower initial concentrations of nanoparticles on a surface. For the samples that initially started with a lower amount of contamination, the final intensity after 20 applications of tape reached approximately 18±4 counts. This value was close to the limit of detection of the XRF (i.e. 10±4 counts). However, with higher starting concentrations of nanoparticles (samples 1 and 2), the intensity levels plateaued off around 55±4 counts. This is possibly due to the potential presence of tape residue encapsulating the nanoparticles after multiple applications of the tape. The initial applications of tape remove a fair amount of nanoparticles, but as more tape is applied, more tape residue is left behind on the surfaces, resulting in the potential for encapsulation of the remaining nanomaterials. After this encapsulation any subsequent applications of tape would interact primarily with the tape residue and not with the contaminant of interest. Starting with high concentrations of contaminant in samples 1 and 2, the application of tape for the remediation may only be effective up to a certain number of applications of tape. The background intensity for a clean silicon wafer was approximately 10±4 counts. However, as seen in Figure 20, after 15 tape applications, the intensity was 60 or less, which according to our calibration, resembles an approximately 2-3 nm thick layer of silver. With multiple applications of adhesive tape, it

was possible to bring the level of silver nanoparticle content down to a range close to the limit of detection of the XRF instrument, the level of concentration at which the presence of an element in a sample can be detected above background.

Since the intensity of silver levels reached the limit of detection of the XRF after the application of 20 pieces of adhesive tape, a more sensitive analytical method was used to confirm the capability of adhesive tape to remediate nanomaterials. Hence, a thorough analysis with ICP-MS was performed. However, as mentioned in Chapter 2, unlike XRF, ICP-MS is a destructive method, therefore further examination after each application of tape on a single sample is not possible. As a result, multiple trials were performed to achieve a representative trend for the remediation of silver nanoparticles by use of adhesive tape. In this study, a total of 25 separate pieces of contaminated surfaces were prepared. The samples were subdivided in groups of 5 for analysis. Each group varied for the number of applications of tape. After a specific set of applications of tape, the samples were placed into individual plastic 10 mL centrifuge tubes and 5.00 mL of 5% nitric acid solution was subsequently added to digest the samples for a minimum of an hour. The samples were then analysed via a Perkin Elmer SCIEX ELAN 6000 ICP-MS set with a sample flow rate of approximately 0.1 mL / min.
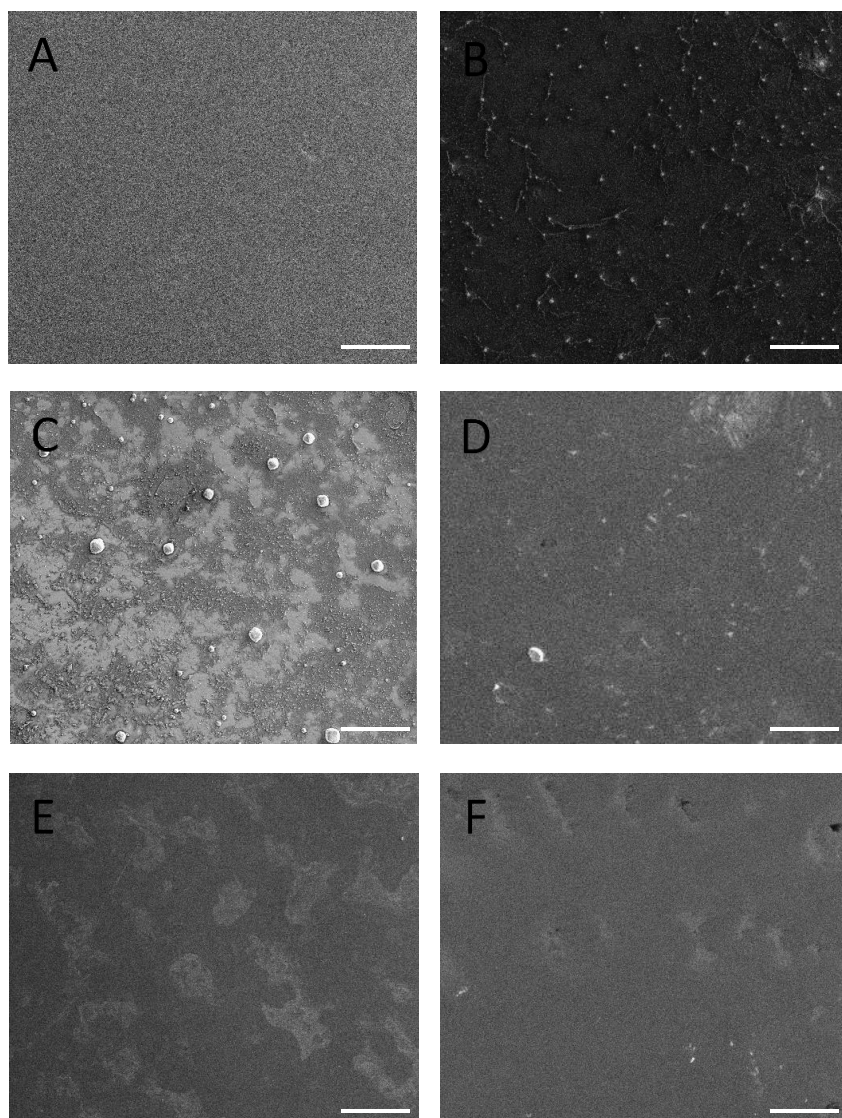
Scale Bars: 50 µm

Figure 21. ***SEM images of a silicon wafer A) prior to any treatment, B) after deposition of silver nanoparticles, C) after 1x tape remediation, D) after 5x tape remediation, E) after 15x tape remediation and F) after 20x tape remediation.***
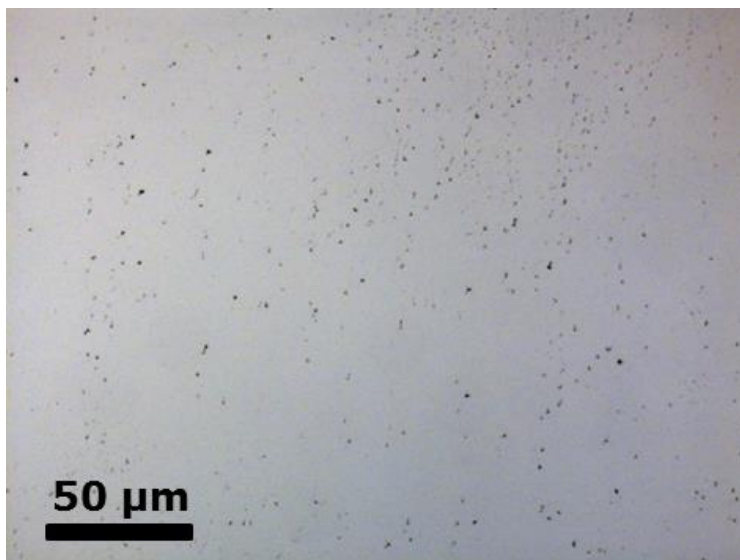
Figure 22.   ***Bright field optical microscope image of a polished silicon wafer surface after 20 applications of separate pieces of adhesive tape. Non reflective markings indicate residue left behind on the surface.***

From the data obtained by ICP-MS analysis, the maximum intensities were analyzed and compared with a standard calibration to obtain concentrations of silver present in each sample. By determining the concentrations of silver present in a sample, the approximate number of particles can be determined. Since each of the samples that were digested in 5.00 mL of 5% nitric acid were approximately 1 cm^2. The number of atoms remaining on the surfaces is determined by the ICP-MS analysis. In addition, assuming that all the silver nanoparticles averaged 25 nm in diameter and that all the nanoparticles were spherical in shape (Figure 18), the approximate number of silver atoms per nanoparticle could be estimated. From these two calculations, we were able to assess the number of nanoparticles per mm^2 on each sample. The results obtained from the ICP-MS analysis of 25 different samples each with a different number of applications of adhesive tape were combined to obtain an average of 5 different samples for each data point (Figure 23). From these results, the initial concentrations were on average over 3 billion silver nanoparticles per mm^2, and after 15 successive applications of adhesive tape the nanoparticle density remaining on the surface of the sample reduced to 13 ± 6 million silver nanoparticles per mm^2. Similar to the results obtained by XRF analysis, 15 separate applications of adhesive tape significantly reduced the number of contaminants remaining on the silicon surface. However, additional studies are required to determine if it is possible to further reduce the number of nanoparticles

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with more applications of tape. This would also require the use of an instrument with a lower limit of detection. Although both analytical techniques lead towards a plateau, comparing Figure 20 and Figure 23 the point in which it begins to plateau varies. This is most likely due to the detection limits of the instruments. In other words, the higher the detection limit, the sooner the plateau begins. With this study, we did however, demonstrate that it was possible to reduce the number of nanoparticles down to the detection limit of XRF.
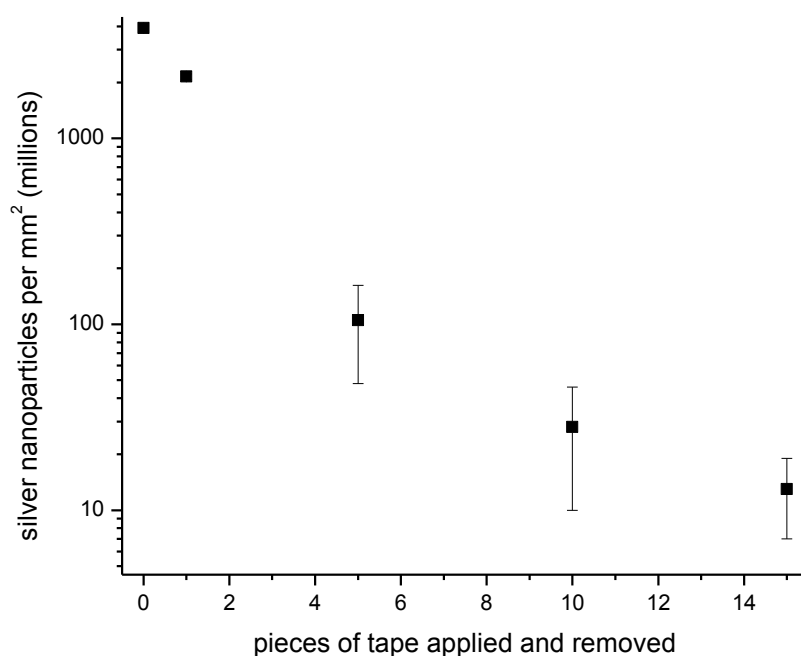
Figure 23. *Average number of silver nanoparticles per mm^2 remaining on silicon wafer surface as determined by ICP-MS. Error bars on these plots were calculated from multiple measurements, and depicted one standard deviation of these measurements.*

One of our initial concerns was that the adhesive tape would leave too much residue on the contaminated surfaces; thus hindering the success for nanoparticle remediation. However, by observing the quantitative results obtained from ICP-MS (Figure 23), the silver residue after the first step of remediation (i.e. one application and removal of adhesive tape) demonstrated a significant decrease in the amount of silver relative to the contaminated surfaces. However, after subsequent steps of adhesive tape

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application, the effectiveness of this remediation process decreased. In fact, the preparatory treatments performed to clean the polished pieces of silicon could have increased the bonding strength interactions between the silicon surfaces and both the nanoparticles and the adhesive tape. This could also lead to non-uniform contact between the adhesive tape and the surfaces, which arise from the method used to apply the adhesive tape or due to topography resulting from multiple layers of nanoparticles. These factors should be even more significant when applying the adhesive tape to rougher surfaces. This model system, however, confirms that off-the-shelf adhesive tape can be used in the remediation of nanoparticle contamination.

Although we have shown that it is possible to remediate silver nanoparticles on a silicon wafer, not all workplace surfaces are smooth like silicon. Different types of surfaces will have different surface energies, which can affect the adhesion between the surfaces and the adhesive tape. Adhesion results from molecular forces of attraction between materials. The strength of this attraction can be correlated with the surface energies of the materials. The higher the surface energy, the greater the potential attraction. The lower the surface energy, the weaker the attractive forces. A high surface energy material will draw the adhesive closer in contact, creating a higher apparent bond strength. In addition, some surfaces, such as wood, cement, or vinyl, may be rough and possibly porous as depicted in Figure 24. With porous surfaces, it could be easy for nanoparticles to embedded deep into the surface, making the remediation process more difficult. Similar to asbestos, one can simply leave the nanoparticles embedded deep in the porous surface since the nanoparticles will not typically come into contact with workers. However, there could be concerns when or if the surface breaks apart, exposing the nanoparticles to the surrounding environment and to future workers.

nanoparticle residue | nanoparticle residue | nanoparticle residue

clean surfaces | flat surfaces | rough surfaces | porous surfaces
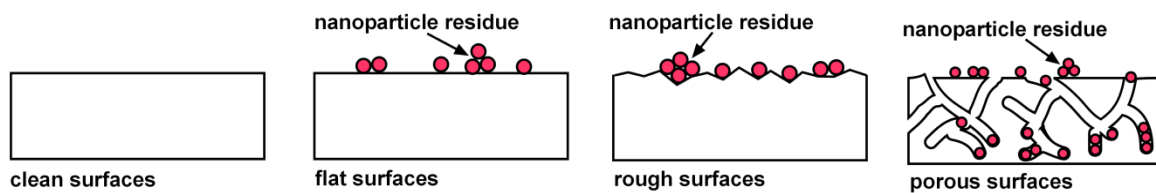
Figure 24. ***Cross-sections of typical surfaces that may be encountered in the workplace environment and a demonstration of how nanoparticles may become trapped on these surfaces.***

Testing the use of adhesive tape to remove nanoparticles from a rough surface, We initially used a Canadian copper penny because of the ease of imaging the remediation process. Due to surface roughness, it was hard to image the spherical nanoparticles. Therefore, another type of contaminant was pursued. Selenium nanowires were chosen to show proof of concept of the technique on a rougher surface. These nanowires were selected for their aspect ratio that assist in visualizing these materials by electron microscopy. Selenium nanowires were also prepared to simulate the remediation of a semiconducting nanomaterial. Selenium is also an element that is common to many types of quantum dots, and nanoparticles pursued in the literature or commercially available as contrast agents for biological imaging or in solar cells. [78], [79], [80], [81] This nanomaterial, therefore, contains an element that might be common to a number of work environments.

A 10 µL droplet of prepared selenium nanowire solution was cast onto a cleaned 2004 Canadian copper penny to stimulate a spill. Small pieces of 19 mm wide 3M Scotch® Magic adhesive tape was used to remediate the nanowires. Figure 25 contains SEM images showing the selenium nanowires on a 2004 copper penny and the results for multiple applications of tape. After 10 subsequent removals of the adhesive tape, it became apparent that over 80% of the nanowires have been removed. However, under higher magnifications, after 20 applications of adhesive tape, small amounts of nanowires were remaining on these surfaces (inset of Figure 25).

Since adhesive tape was able to remediate nanowires on a copper penny, adhesive tape was examined on a more common workplace surface. Instead of using a silicon wafer as the surface, approximately 1 cm^2 sections of laboratory bench top (Wilsonart D417-335-01) were used to represent a typical rough workplace surface

(example shown in Figure 26). A laboratory benchtop is one of the most common places for a spill in a workplace environment, as well as the most likely place for a worker to be exposed to contaminant that can be transferred onto their skin from contact with the spill. Although bench tops and counter tops can be easily replaced, it could be fairly costly especially in a lab environment where spills (even on a small scale) are likely to happen frequently. We focused on simulating the contamination of workplace countertops. Other surfaces in the laboratory could also become contaminated with nanoparticles, but the primary route of contamination is most likely from accidental spills when handling solutions of nanoparticles. Future work may extend this analysis to flooring materials, glass windows in the workplace and glass sashes in fume hoods, and clothing materials that include laboratory coats.
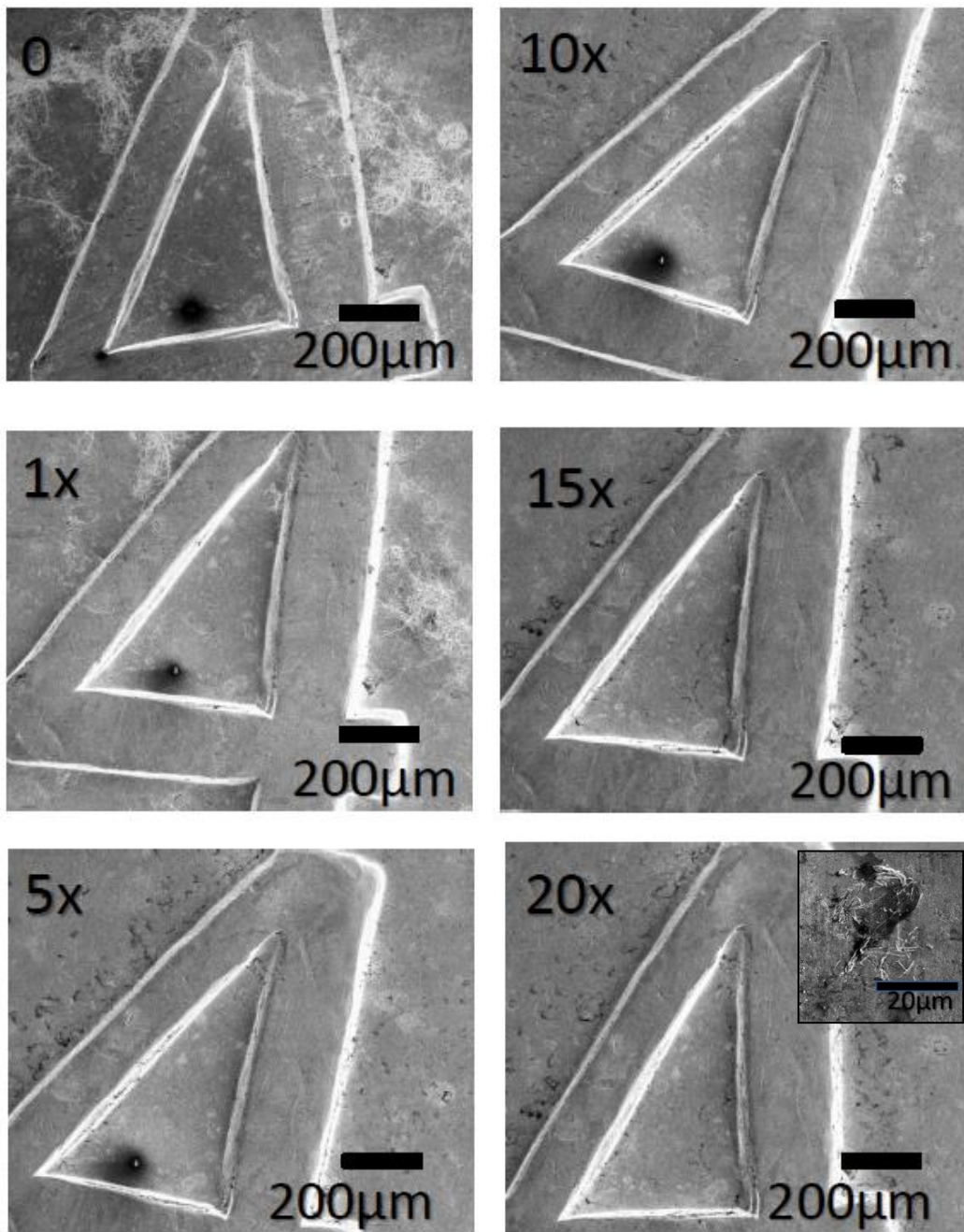
Figure 25.   *Selenium nanowires deposited onto a Canadian penny, simulating contamination on a rough surface. These SEM images show these surfaces after multiple, separate treatments (0 to 20x) with scotch tape.*
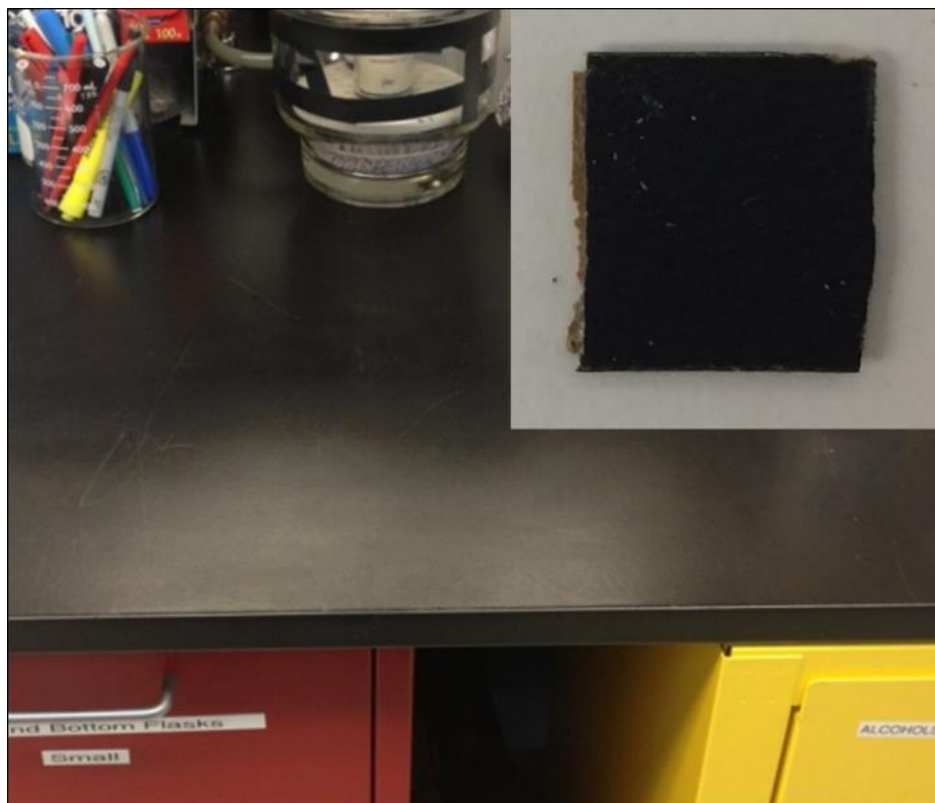
Figure 26. ***Picture of a sample laboratory countertop (rough material used for
analysis) taken by a digital camera. Inset shows a piece of
laboratory bench top initially contaminated with silver nanoparticles.***
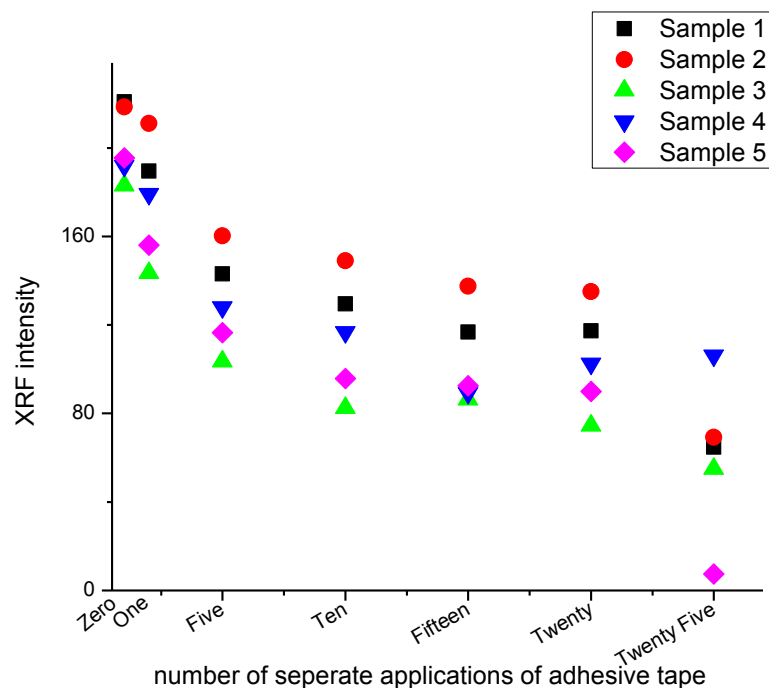
Figure 27. *Remediation of silver nanoparticles from a section of countertop. Peak silver Kα intensities were obtained from 5 separate samples and analyzed at various steps of the remediation process.*

Similar to the results seen for the remediation of silver nanoparticle on silicon wafers, Figure 27 shows a general trend in the process of the remediation. All five samples were prepared by drop casting 10 µL of a solution containing silver nanoparticles. Variation in the initial concentrations or amount of nanoparticles applied to each material were due to errors in the methodology, which include non-uniform application and/or evaporation of the solvent. The degree of remediation plateaus after a number of trials. The intensity count by XRF decreases. However, a noticeable difference is that this progress required more applications of adhesive tape to reduce the number of particles to the same intensity level as achieved on the smooth surfaces after 15 applications of tape. As the countertop could not be imaged directly by SEM due to sample charging, a surface profile of the countertops was obtained to assess their roughness (Figure 28). We measured the vertical profiles (to assess this roughness) of multiple locations on the countertop samples by profilometry and determined a variation in vertical features of >20µm. *(I acknowledge Him Wai Ng for his assistance in the collection of profilometry data.)* This variation in feature height provides further insight

into the potential for non-uniform contact between the countertops and the adhesive tape. With this roughness, it may be difficult for the adhesive tape to conform to the surfaces. In order to achieve effective remediation it may require more applications of adhesive tape to increase the chances for the adhesive to come into contact with the nanoparticles.
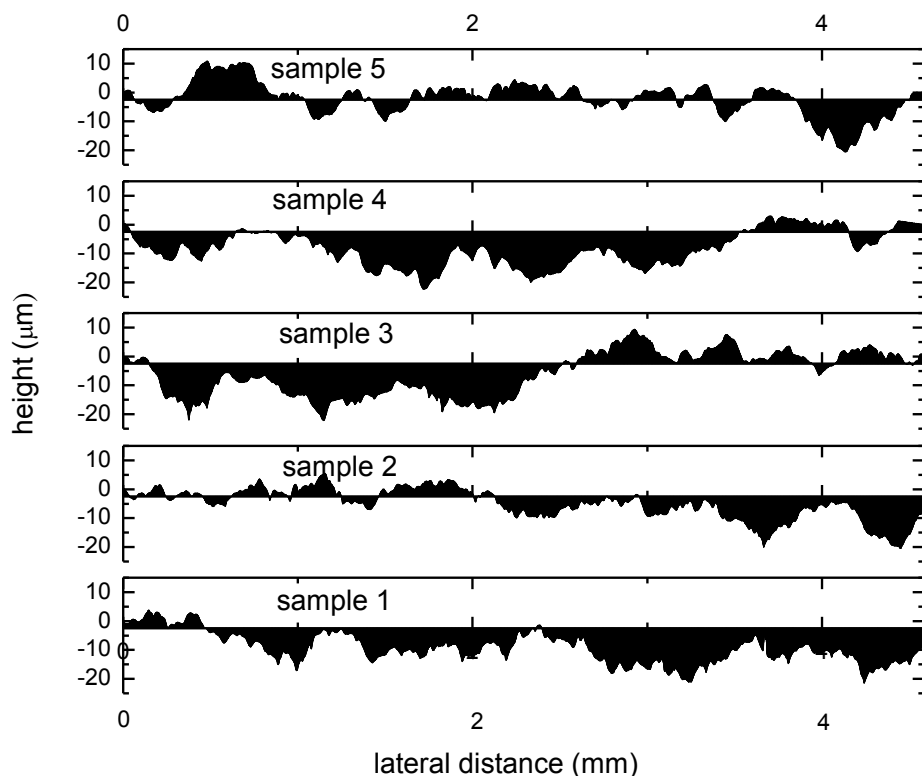
Figure 28. *Surface profiles (cross-sections obtained by scanning profilometry) of 5 different samples of a laboratory bench countertop.*

In addition, there is a large variance in the measured intensity between each sample. This variance may largely be due largely to the rough surfaces of the bench countertop. It was hypothesized that the measured values could vary depending on the orientation of the sample due to scattering of the incident excitation and resulting signals during XRF analysis.

The resulting XRF signal could depend on loss of signal due to this scatter of the incident excitation or resultant emission. [82] To help elucidate this potential variation in response within the same sample, we setup a test scenario with pristine and

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contaminated pieces of countertop. These samples were analyzed by XRF at four independent positions of rotation of the substrate relative to the XRF system; each piece of countertop was analyzed by XRF, subsequently rotated 90 degrees, and the process repeated. The measurements (Figure 29) portrayed a significant variation in signal intensity with the angle of rotation. The variations in silver signal within the contaminated sample could be attributed in part to local variations in concentration of nanoparticles due to the effects of solvent evaporation. [83] These results suggest a correlation between the orientation of the substrate and the detector within the portable XRF system. We kept the samples level and maintained a uniform separation between the XRF system and our samples throughout these studies, which could have otherwise lead to further variations in the signal intensities. Scatter does arise from the interaction of both the excitation source and emitted signal with the roughened surfaces of the countertop. As mentioned above, the countertop had a large variation in the height of features. This variation in feature height also provides further insight into the potential for non-uniform contact between the countertops and the adhesive tape as mentioned above.
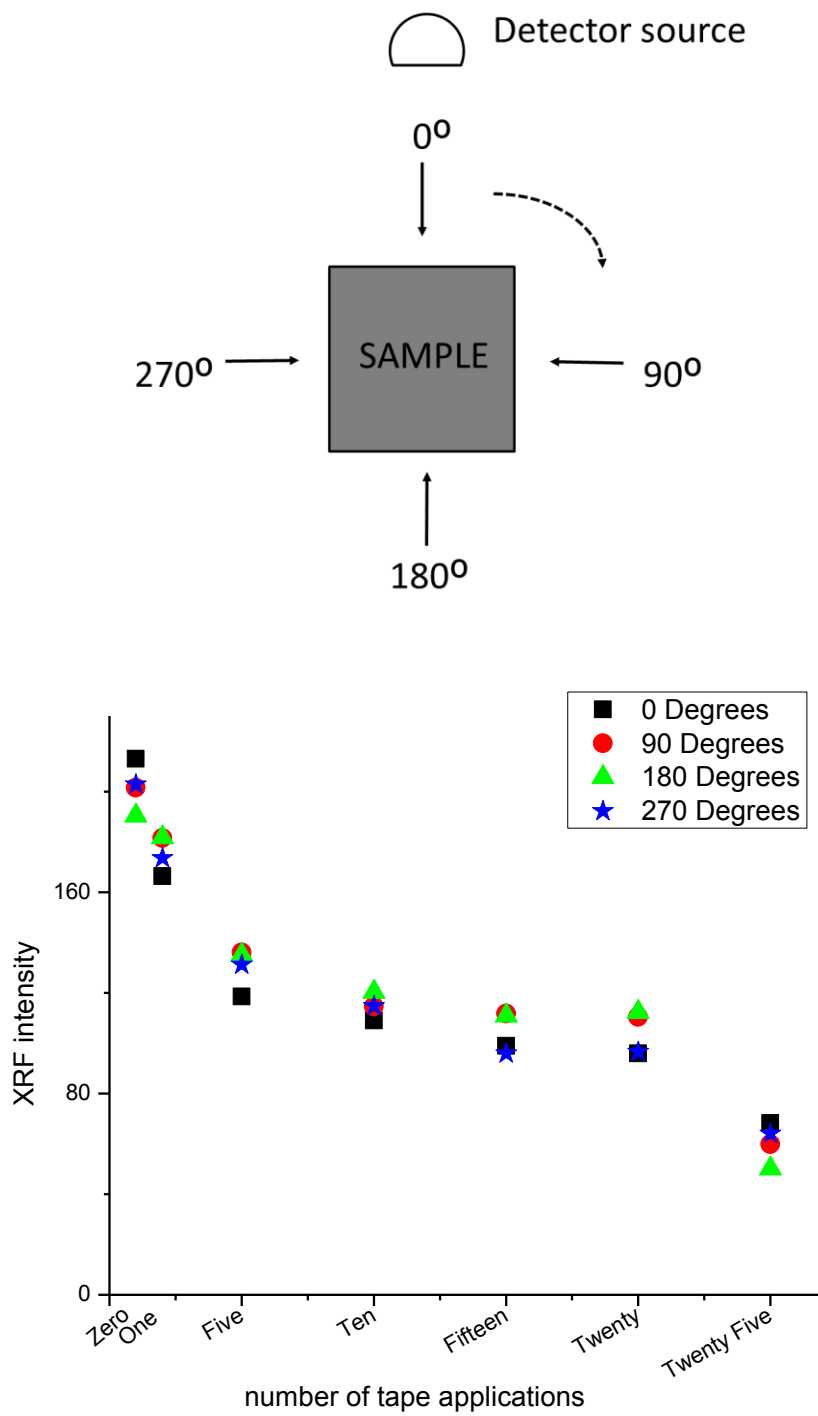
Figure 29. ***Measured peak XRF silver Kα signals from the remediation of Ag on
countertop while orienting the sample at 0, 90, 180 and 270 degrees
relative to the detector.***

When samples were rotated 90 degrees, the detected XRF intensity varied. A rough surface presents a heterogeneous surface to the incident and detected x-rays, and is influenced by the incident angle of the x-ray beams. Therefore, care must be taken when sampling on rough surfaces as these orientations of the XRF beam will have an effect on the results. Taking into consideration the roughness of the samples, measurements were obtained at multiple rotations and averaging them together. These results and their standard deviation were plotted as shown in Figure 30.
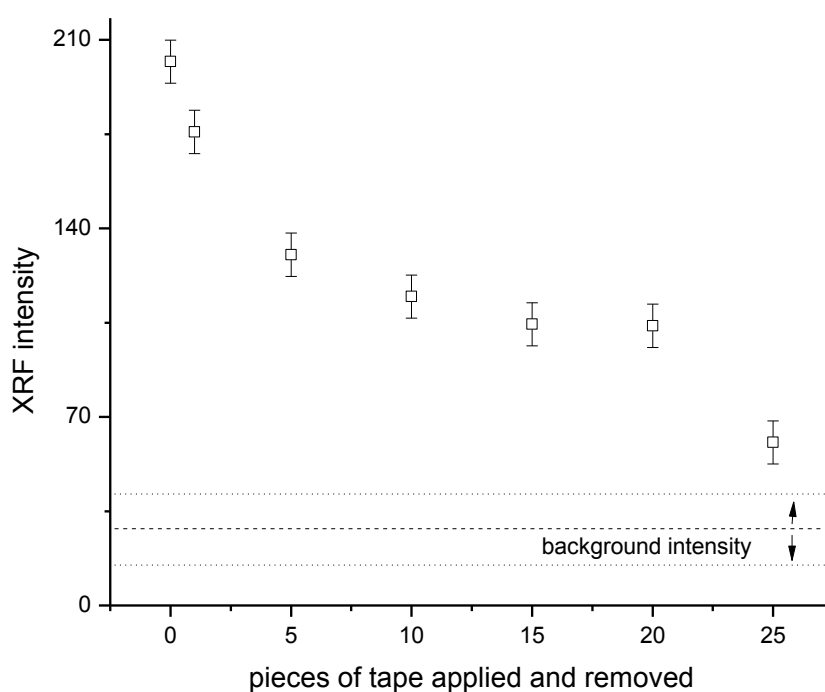
Figure 30. **Peak intensities detected by a portable x-ray fluorescence (XRF) spectroscopy for the remediation of silver nanoparticles as simulated on a section of countertop. The silver nanoparticle contamination is remediated through a series of 25 steps of applying separate pieces of adhesive tape to the surfaces, removing the tape, and repeating the process. Background intensity for a clean piece of counter had an XRF intensity of 30 ± 10 (dotted lines).**

After each application of adhesive tape application, the adhesive tape was removed and adhered onto a piece of paper. Figure 31 contains images of the adhesive tapes used after each application and removal on a contaminated surface. It can be

seen that the intensity of the colored film transferred to the adhesive tape is higher at the beginning and decreases significantly after 5 separate applications of adhesive tape. After these 5 sequential steps of applying and removing tape, the coloration in the tape became significantly harder to visually identify by naked eye, and harder to determine if there were further contaminants being removed from the surfaces. XRF analyses were performed on the pieces of adhesive tape removed from the contaminated silicon surface. Intensity counts of 150±4 and 37±4 were observed for the first piece and second piece of tape, respectively. This observed trend correlates with the data in Figure 20 for sample #2 whereby the first applications of tape remove a larger amount of silver than the subsequent applications of tape. Placing the tape onto a piece of white paper, the nanoparticles were encapsulated within the tape's adhesive and could be handled for proper disposal while minimizing potential health concerns. Even though no apparent signs of nanoparticles are visible to the human eye on the tape, from the XRF and ICP analyses, particles are being removed with each subsequent application of a new piece of tape.
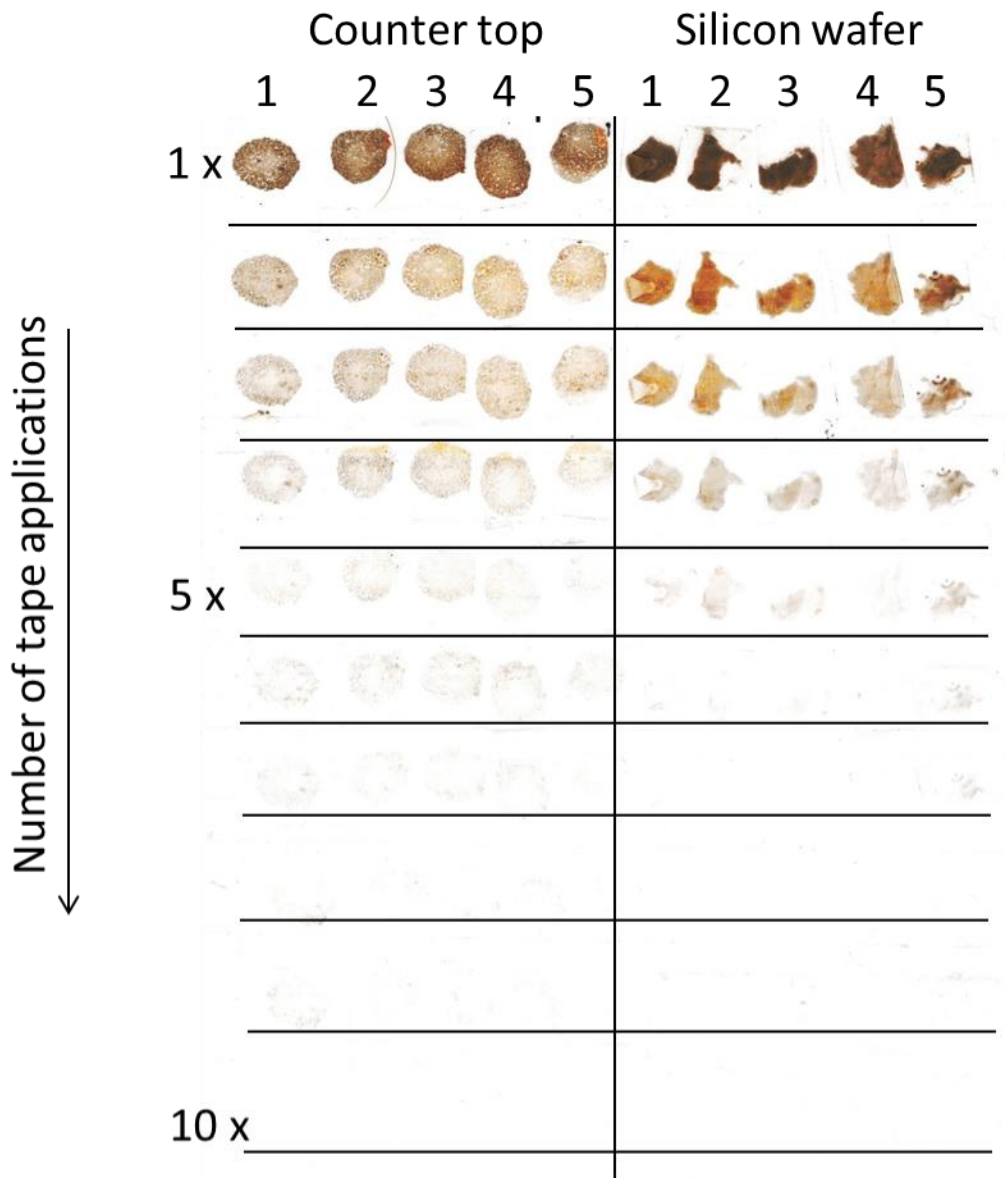
Figure 31. *Images of the adhesive tape after each application and removal from a rough countertop (left) and from a smooth silicon wafer (right) contaminated with silver nanoparticles.*

The first five applications of adhesive tape decreased the silver concentration by approximately half. Subsequent steps of remediation with adhesive tape were, however, less effective than these initial steps. In fact, complete remediation requires more than 10 applications of adhesive tape. There are a number of factors that may play a role in the effectiveness of this process. Although silver nanoparticles are removed in the first step of the remediation, subsequent steps may be hindered due to residual adhesive left

on the surfaces from the first application of the adhesive tape. Since the silicon surfaces were polished, the interaction between the nanoparticles and the adhesive tape could be more favourable relative to a rougher surface. This potential difference could also arise from a non-uniform contact between the adhesive tape and the surfaces, which arise from the method used to apply the tape or the topography resulting from multiple layers of nanoparticles. These factors could be even more significant when applying the adhesive tape to rougher surfaces, such as the laboratory countertops. As the adhesives in these studies used were pressure sensitive adhesive tapes, pressure across the surfaces may not have been evenly applied that results in some areas being less well remediated. Applying firm pressure to the bonding surface can increase adhesive flow and contact for a more secure bonding. Time and temperature can also further increase contact and adhesion values. An alternative method to pursue in the future is to potentially use a roller, similar to a lint roller. The process would be to simply roll over the contaminated area, to remove the outer tape layer and repeat if necessary as depicted in Figure 32. This would allow for a uniform pressure to be applied. This method would make the remediation process quick and simple to use. Heating of the tape backing can also be tested to assist in the adhesiveness between the material and tape. Alternative tapes can also be investigated as different adhesive materials will "wet" and penetrate a substrate better. A low surface energy solid adhesive translates into an adhesive with fairly mobile molecules under standard conditions, resulting in an adhesive that freely flows, relative to other adhesives, even though it's in a solid form, into the pores of the contacting surfaces. It's better ability to conform with the substrate, the stronger the resulting physical bond. In addition, molecules in adhesive tapes can exhibit strong dipole moments, inducing corresponding dipole moments within the molecules of the substrate. Oppositely charged molecules or aligned dipoles of the adhesive and the substrate form strong interactions upon contact, such as through electrostatic and van der Waal's forces which augments the strength of the surface wetting-based adhesion.

Overall, the silver nanoparticles were, however, remediated to near background levels detected by XRF on the pieces of countertop after 25 consecutive steps of applying and removing separate pieces of adhesive tape. Further steps of remediation may be necessary to remove trace quantities of silver, but these steps are below the detection limit of the XRF system used in these studies. However, this experiment

confirmed that off-the-shelf adhesive tapes can be used in the remediation of nanoparticle contamination.

1) CONTAMINATED SURFACE

2) APPLY TAPE ROLLER

3) REPEAT STEP 2 MULTIPLE TIMES WITH NEW SHEETS OF TAPE

4) REMEDIATED SURFACE
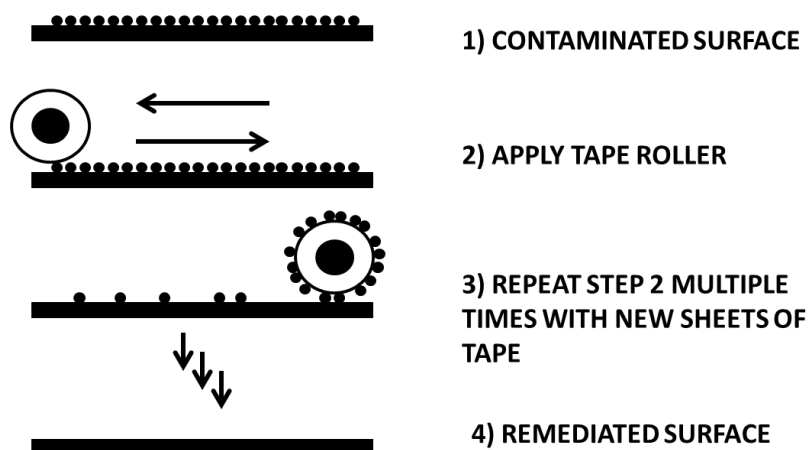
Figure 32. *Schematic of process using a roll of adhesive tape for nanoparticle remediation.*

3.2. Synthetic rubber encapsulants

As demonstrated in section 3.1, the use of adhesive tape works well for removing nanoparticle spills from smooth surfaces, but when working with rough surfaces, more time and applications of tape are required. A better alternative to adhesive tape is whereby the material used in remediation wouldn't adhere and conform to the rough surfaces, such that it can have better contact with the surfaces and the nanoscale contaminants. In search of an alternative remediation material to encapsulate the nanoparticle contaminants, we identified a number of criteria that we also wanted to include as desirable attributes in the potential product. First among our criteria was to identify a material that could be cast against surfaces of varying roughness, and yet retain its material integrity (i.e. not pull apart) upon release from these surfaces (e.g., a stretchable material). A similar criterion was to find a material that could temporarily coat various surfaces and upon removal leave no observable residue. The final set of criteria was that the material should be easily obtainable, but also have an easily distinguishable coloration that can be used to indicate the presence of a spill in the process of being remediated.

For this second approach to encapsulating a spill of nanoparticles, we chose a synthetic rubber that could be cast or sprayed onto a variety of surfaces. The material of choice contained a bright orange pigment to clearly identify the location of the spill; a spill might be initially identified through the use of XRF technology and then marked by coating with the synthetic rubber. The synthetic rubber that we chose was an off-the-shelf product commonly used to coat plastics, metals and other materials, Plasti Dip. Plasti Dip is a commercially available multi-purpose, specialty rubber coating. It can be easily applied by dipping, brushing, or spraying onto a surface. Plasti Dip is known best for its ideal protective coating against moisture, acids, abrasion, corrosion, and skidding/slipping, as well as providing a comfortable, controlled grip. [84] Plasti Dip remains flexible and stretchable over time, and will not crack or become brittle in extreme weather conditions. It has been tested and proven to be in temperatures from -30°F to 200°F. [84] The resulting rubber coating can be removed from surfaces and will stretch during removal without pulling apart into smaller pieces. Plasti Dip coating comes in many colors and one of the benefits for the use of Plasti Dip coatings is the use of bright colors to indicate to workers around the workplace that a spill has occurred and remediation is underway. Ideally, when there is a nanoparticle spill or contamination on a surface, Plasti Dip can be applied using an aerosol spray can to coat a layer of colored rubber encapsulant. As seen in Figure 33, the brightly colored coating can easily indicate to others that a spill has occurred, giving a signal to stay away from that area. After air drying, the layer of rubber can be removed and along with it, hopefully, the nanoscale contaminants. In the case where potential aerosols can spread the nanoparticle contaminants, a liquid paint version of Plasti Dip can be used.
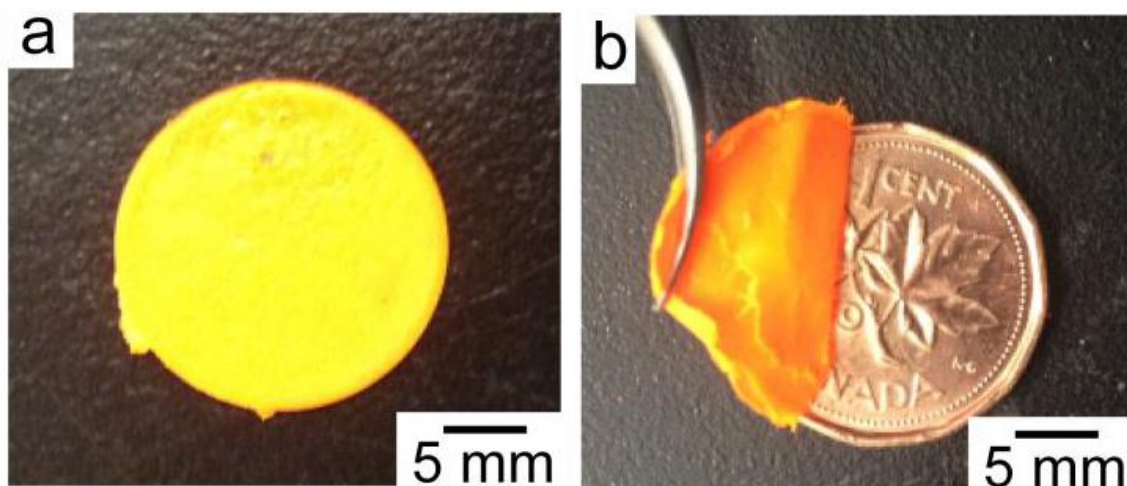
Figure 33. *Simulated remediation of surfaces contaminated with selenium nanowires. (a) A bright orange colored synthetic rubber is coated onto the contaminated surfaces (in this case the surface of a Canadian penny) placed on a black countertop. (b) The rubber coating is cured and peeled away from the coin using hand-held tweezers.*

In order to more quantitatively identify, track, and assess the remediation of nanoparticle spills from a rough surface we changed the substrate to a Canadian copper penny. This substrate contained easily identifiable features and topography, and was conducive to further investigation by electron microscopy. The previous remediation method demonstrated the utility of XRF to identify the presence of a spill and monitoring its remediation, but for the purposes of this study we wanted to understand how well the encapsulating material removed the contaminant relative to adhesive tape. Figure 34 shows the schematic of the process for remediating nanoscale contaminants with a synthetic rubber encapsulant.

1) CONTAMINATED SURFACE

2) SPRAY SYNTHETIC RUBBER SOLUTION

3) AIR DRY 10-15 MIN AND RECOAT

4) REMOVE RUBBER COAT AND REPEAT STEPS 2-3 IF NECESSARY
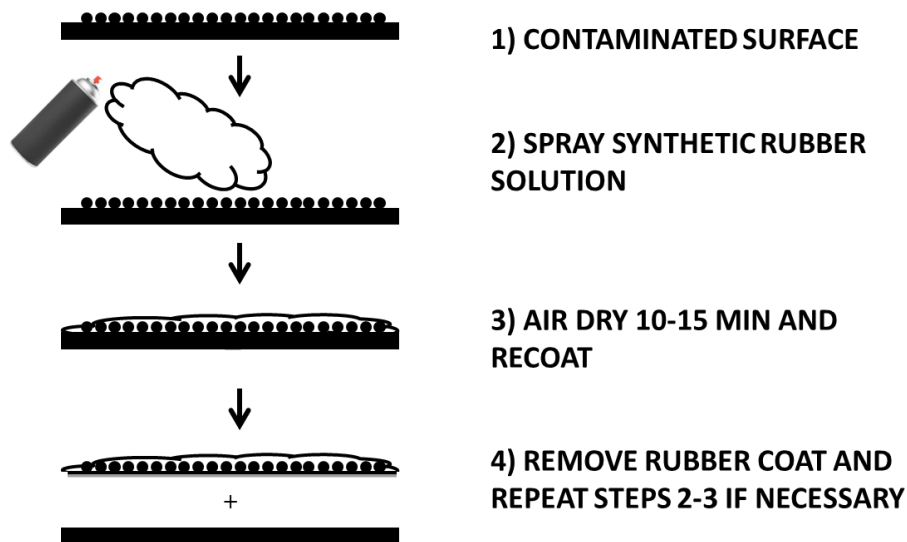
Figure 34.   Schematic of synthetic rubber coating based remediation technique.

3.2.1.   Methodology

As in section 3.1.1, selenium nanowires were deposited onto a 2004 Canadian penny and then evaluated for remediation from this test substrate. However, instead of using an adhesive tape, Plasti Dip was used in this example. An orange aerosol Plasti Dip spray was applied by holding the spray can one foot away from the contaminated surfaces and spraying a continuous layer onto these surfaces. The solution was vigorously shaken and applied as a thin coating, sufficient to cover all exposed surfaces of the contaminated surfaces. This coating was dried for 10 min before adding a second, top coat. After an additional 30 min, the rubber coating was gently removed using handheld tweezers for proper disposal. The samples were analyzed by scanning electron microscopy (SEM) analysis and energy dispersion x-ray spectroscopy (EDS). This data was acquired with an FEI Strata DB 235 field emission SEM operating at 5 kV. Samples for SEM and EDS analysis were prepared by drop-casting a solution of nanowires onto the coin, and evaporating the solvent before further analysis or remediation by encapsulation with a rubber Plasti Dip coating.

3.2.2. Remediation of nanoparticles from countertops using synthetic rubber encapsulants
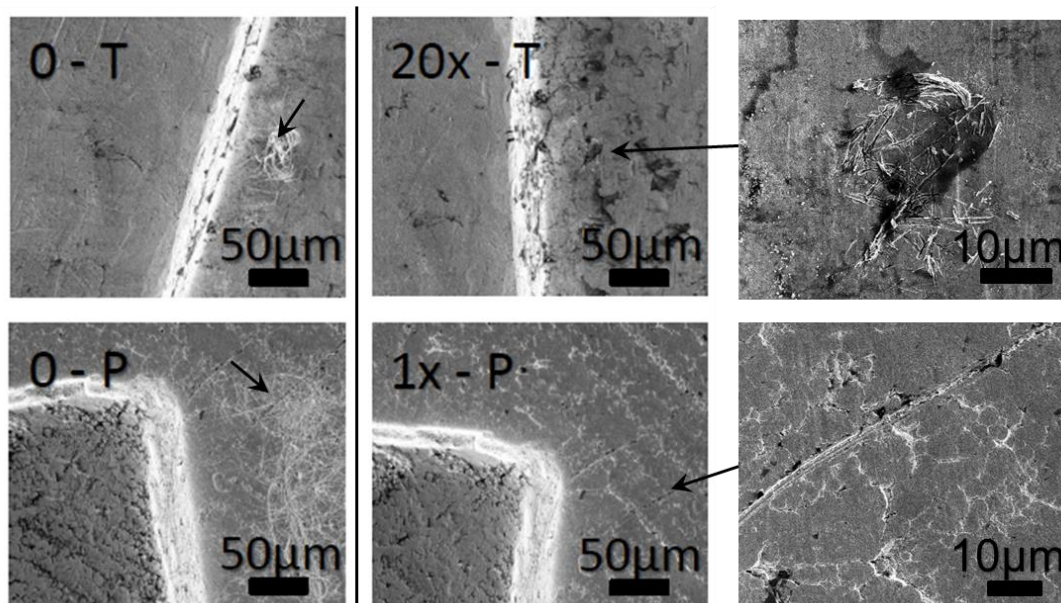
Figure 35. *Selenium nanowires were deposited onto a Canadian penny, simulating contamination on a rough surface. SEM images shows the presence of nanowires before remediation (left); after adhering and removing 20 pieces of scotch tape, the presence of selenium nanowires were significantly reduced (top-right); after applying and removing one layer of Plasti Dip rubber coating, presence of selenium nanowires could not be seen (bottom-right).*

In order to assess the ability of the synthetic rubber to serve as a potential encapsulant, an initial test was performed with selenium nanowires on a Canadian penny. Figure 35 are SEM images showing the presence of nanowires before remediation (left) and after application of an adhesive tape 20 times (top-right) and after application of a synthetic rubber coating once (bottom-right). Arrows within this figure indicate the regions from which the higher magnification SEM images were obtained, corresponding to areas originally containing selenium nanowires. From the SEM images, it can be seen that even after 20 applications of adhesive tape, there are still nanowires present in the samples. However, after a single application of a synthetic rubber coating, the presence of selenium nanowires could no longer be observed. This successful remediation was also confirmed by performing energy dispersive spectroscopy on the

samples. Figure 36 are the EDS spectra of samples after the application of adhesive tape for 20 consecutive times or once using a rubber coating. The spectra indicates that even after tape removal, selenium is still detected, but only background values were detected when using the rubber coating method to remove these nanomaterials. In addition to the detection of copper, nickel is also present as Canadian Pennies after 2000 contained 1.5% nickel. [85]
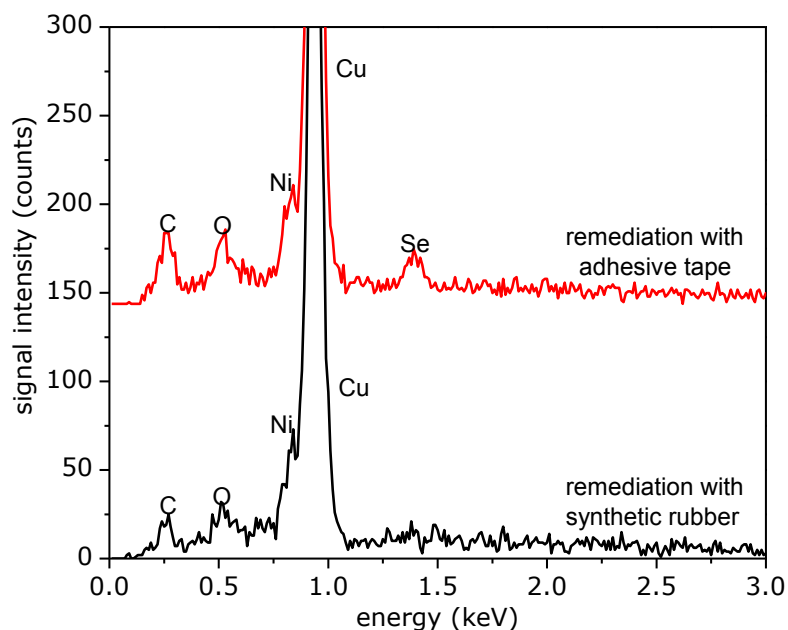
Figure 36. *Spectroscopic analysis following the remediation of a simulated spill containing selenium nanowires on the surfaces of a Canadian penny. Contaminated surfaces were monitored by energy dispersive x-ray spectroscopy (EDS). The surfaces remediated by casting adhesive tape (red, top trace) contain residual selenium, whereas those surfaces remediated by coating with the synthetic rubber (black, bottom trace) show no signs of residual selenium.*

The remediation with synthetic rubber encapsulant was also performed on a section of laboratory countertop for evaluating the practicality of this method. Once again, silver nanoparticles were deposited onto multiple 1 cm^2 pieces of countertop. A 1.5 cm^2 mask was made out of paper and placed around the individual samples. This helps prevent over spraying the counter, as well as a means for easy removal of the rubber coating from the surfaces.

Figure 37 contains XRF results obtained from an average of 5 samples for both the adhesive tape and synthetic rubber remediation methods. It can be seen that for a rough surface, the use of a rubber coating that is flexible and able to conform to rough surfaces can remediate more efficiently and effectively than adhesive tape. After two applications of the rubber coating, the intensity level has reached almost its limit of detection or levels that can be seen after 20x adhesive tape on a smooth surface.
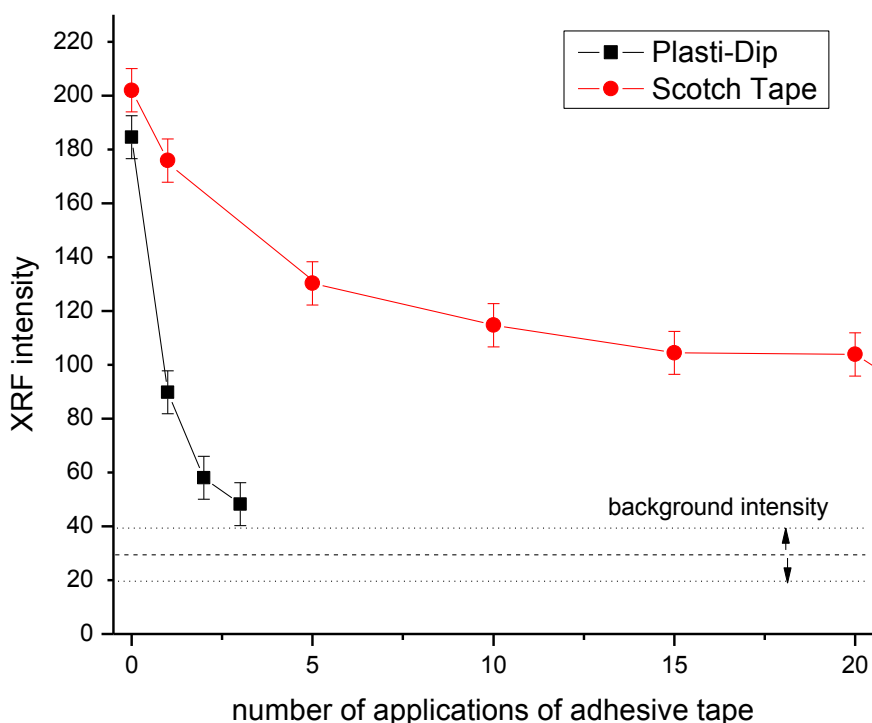
Figure 37. **XRF results of the remediation of silver nanoparticles contaminated on a laboratory countertop using Plasti Dip or scotch tape to remove these particles through multiple separate applications of the rubber or adhesive. Background intensity for a clean piece of counter had an XRF intensity of 30 ± 10 (dotted lines).**

3.3. Polymer encapsulants*

Since commercially available rubber coatings could sufficiently remediate silver nanoparticles on a rough surface, polymer based encapsulants were also examined and tested on a different type of nanomaterial. Instead of using silver nanoparticles as the contaminant, gold nanoparticles were used. Over the past decade, there has been a significant interest in gold nanoparticles due to its' tunable and specific optical properties. When exposed to light, the oscillating electromagnetic field of the light causes a collective oscillation of the free electrons (conduction electrons) of gold nanoparticles. The amplitude of the oscillation is at a maximum at specific frequencies, which are referred to as the surface plasmon band. [7], [8] Gold nanoparticles also have photothermal properties; [8] these particles are able to convert light energy (photons) into thermal energy (phonons). The resultant thermal energy can allow for selective release of molecules and the potential for the release of drugs for cancer patients. [7], [8]

The polymer encapsulant chosen for this study is The New-Skin® Liquid Bandage (NSLB), which is used as an antiseptic. As its name suggests it is a liquid and can be used directly on a person's skin to form a thin film over an incurred cut. The active ingredient is 5-Hydroxiquinoline in an alcohol containing solvent. After application over a small cut or abrasion, the solution dries quickly, on the order of a minute, depending on how much of the fluid is applied to a given area. In our application of this material, the inherent film forming property is exploited to mould to a nanoparticle contaminated surface and the nanoparticle adhesion to the NSLB formed film is evaluated. The initial trials consisted of testing the film forming capability of the NSLB, and subsequent removal when dry from a structured surface. The surface chosen for testing was a laboratory counter top surface (Wilsonart D417-335-01) where presumably a nanoparticle spill is likely to occur. All sections of countertop used in this study were cut into ~1 cm^2 pieces.

3.3.1. Methodology

The nanoparticle contaminant chosen for the detection of nanoscale remediation was gold nanorods. As a spill of these particles could not be seen by human eyes, a fluorescent molecule, Rhodamine B was attached to the surfaces of the gold nanorods through the use of a covalent linker (a thiol modified poly(ethylene glycol) with a terminal amine). [86] The dye contaminated countertop will fluoresce when appropriately excited

and will be detectable with an optical microscope equipped with a mercury lamp and an appropriate filter set, as well as a spectrometer. The fluorescent tag will be able to track the position of the nanoparticles on various surfaces. To prepare the gold nanorods, [84] 24 µL of an aqueous seed solution containing 0.5 mM $HAuCl_4$ (5 mL), 0.2 M cetyl trimethylammonium bromide (CTAB) (5 mL), and 10 mM of cold $NaBH_4$ (600 µL) was mixed into a transparent growth solution containing 1 mM $HAuCl_4$ (10 mL), 0.2 M CTAB (10 mL), 4 mM 99.9 % $AgNO_3$ (500µL), and 78.7 mM ascorbic acid (140 µL). *All chemicals used were purchased from Fisher Scientific.* The mixed solution was then maintained at 37 °C for 3 h. The resulting solution was a faint red coloration. To purify the gold nanorods, the solution was centrifuged for 20 mins at 8500 rpm and the supernatant was decanted and replaced with high purity water (18.2 MΩ·cm water purified using a Barnstead Nanopure Diamond Life Science water filtration system). This purification process was repeated for two additional times to remove excess CTAB from the gold nanorod solution. A product of approximately 40 nm long and 10 nm wide gold nanorods (Figure 38) was verified by transmission electron microscopy (TEM) analysis using either an FEI Tecnai G2 F20 scanning TEM (STEM) with a field emission gun thermionic source operating at 200 kV or a Hitachi 8000 STEM with a lanthanum hexaboride thermionic source operating at 200 kV.
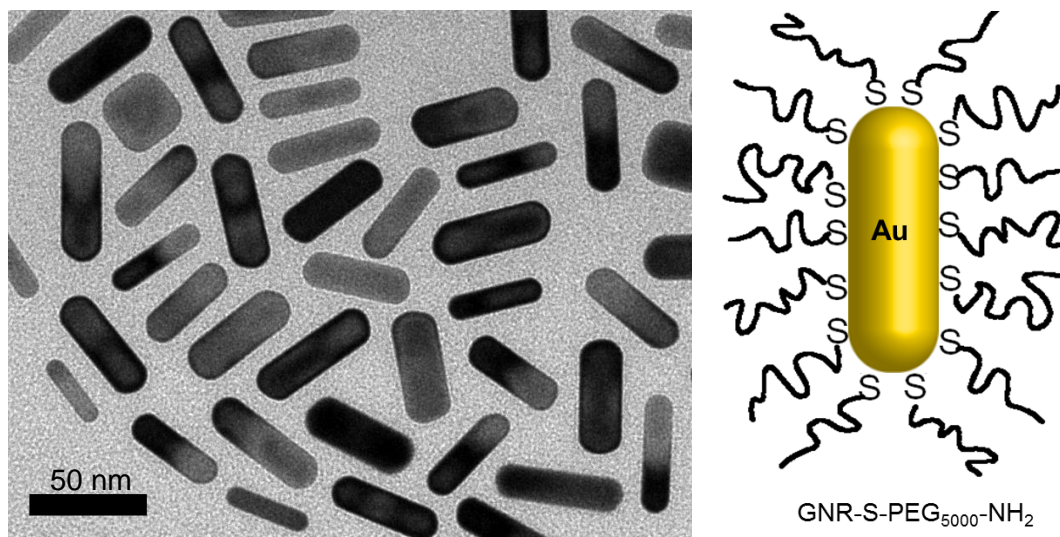
Figure 38. *Transmission electron microscope image(left) and schematic image (right) of gold nanorods coated with a tag, HS-PEG$_{5000}$-NH$_2$.*

In order to easily track the gold nanoparticles during the remediation process, a fluorescent molecule was tagged onto the surface of the gold nanorods. This tag, HS-PEG$_{5000}$-NH-Rhodamine B consisted of a long chain poly(ethylene glycol), or PEG, terminated on one end with Rhodamine B and the other with a thiol that would bind to the gold surfaces. In order to prepare HS-PEG$_{5000}$-NH-Rhodamine B molecules, 42 mg of HS-PEG$_{5000}$-NH$_2$ and 9 mg of Rhodamine B – isothiocyanate was dissolved in 500 µL of N,N=diisopropylethylamine and allowed to stir for 3 hours at room temperature. The solution was purified by dialysis (MW: 7000) with 18.2 MΩ·cm high purity water. A solution of the HS-PEG$_{5000}$-NH-Rhodamine B was mixed with CTAB coated gold nanorods at room temperature for 2 days and stored in the dark to minimize exposure to ambient light. The mixture was purified by size exclusion chromatography using a column of Sephadex G-25 gel. Elution with 18.2 MΩ·cm high purity water and pressurized air removed unreacted CTAB coated gold nanorods and any unbounded HS-PEG$_{5000}$-NH-Rhodamine molecules. Subsequent elution with PBS buffer (pH 7.4) yielded the desired product of gold nanorods tagged with Rhodamine dye (GNR-S-PEG$_{5000}$-NH-Rhodamine B).

To simulate nanoparticle spills on a countertop, 2 µL of the GNR-S-PEG$_{5000}$-NH-Rhodamine B with an optical density of 1.71 at 754 nm was drop cast onto a 1 cm^2 countertop piece and allowed to air dry. As the spill cannot be seen by the naked eye, a

Zeiss Axio M1m Microscope equipped with a filtered HBO 100 mercury lamp was used to excite the Rhodamine B (filter set purchased from Chroma Technology: #41002 – TRITC (Rhodamine)/DiI/Cy3TM) and to track the spill on the pieces of counter top. Fluorescence images such as those in Figure 39 39, were captured with a Zeiss Axio Cam MRc5 Camera, and fluorescence spectra from the samples collected using a Princeton Instrument Acton spectrometer equipped with a PIXIS 400 CCD detector cooled to -72°C. Fluorescence spectra were acquired from 300 to 700 nm using Winspec 32 software, a shutter speed of 100 ms and a slit width of 20.5 µm. Spectral position of the fluorescence spectra were calibrated using the emission lines of the HBO mercury lamp. The background spectrum (e.g., detector white noise) is depicted in the purple trace (bottom trace) for Figure 39e. The process of remediating the spill of gold nanoparticles is tracked by using fluorescence images and fluorescence spectra (λ_{ex} = 546 nm). The spill is first remediated by wiping the countertop with a wet paper towel containing tap water and using either a linear or circular motion to wipe the contaminated surface.

3.3.2.   Remediation of nanoparticles on countertops with a polymer encapsulant

Using a combination of extinction spectroscopy and ICP techniques, the number of gold nanorods in solutions was quantified. Each 2 µL droplet contained approximately 4.5 x 10^8 nanoparticles for an average surface density of approximately 72 x 10^6 nanoparticles/mm^2. However, as seen in Figure 39a, a coffee ring pattern existed indicating a non-uniform distribution of particles as spills solvent evaporates from a spill. This is due to capillary flow where there is a differential evaporation rate across the droplet of contaminated solution. Remediation of the simulated contamination by gold nanorods were pursued first by a traditional method of wiping. Wiping the sample with a paper towel in a linear motion, spread the particles over the countertop, as indicated by the increase in fluorescence signal in the region outside of the original droplet (Figure 39b). After additional wipes of the countertop surface with a new paper towel, fluorescence was still observed (Figure 39c). Wiping in a circular fashion did not improve the removal of the nanoparticles either (Figure 39d). As seen in Figure 39e, fluorescence spectra associated with the original spill and the samples after wiping were acquired.

The spectrum indicates that although a significant decrease in the fluorescence occurred, the signal intensity did not decrease to the background values after multiple wipes of the spilled area. This suggests that a wiping method does not effectively remediate the nanoparticles and an alternative method is necessary.

As mentioned above, an alternative approach is to cast a solution of liquid bandage onto the spill. Once the film of solution dries, a polymer layer is formed and could be easily peeled away from the countertop. This film did encapsulate the fluorescently tagged gold nanoparticles Figure 40a and Figure 40b, but some of the particles still remain attached to the countertop. It is also seen in Figure 40c that the first application and removal of the polymer film was not as efficient as subsequent applications. This is likely due to the coffee ring effect. As the contaminated solution dries, the nanoparticles gather in a gradient leading to a potential variation in height. With the first application of the thin film, it will reach the contaminants in the outermost layers of this "ring" of material. After subsequent applications, it is able to remove more contaminants. In addition, there could be other surface contaminants present that can compete with the contaminants of interest in the first application of the polymer film. It was also observed that the technique for separating the polymer film from the countertop played a crucial role in the success of the remediation. If the polymer film was peeled too quickly or if the physical stress on the film was too great, the film would pull apart making it more difficult to remove from the countertop. A polymer frame (e.g., adhesive tape) was also established to strengthen and provide support to the polymer film while it was separated from these surfaces (Figure 41). A variety of methods to remove the polymer are tabulated in Table 2.
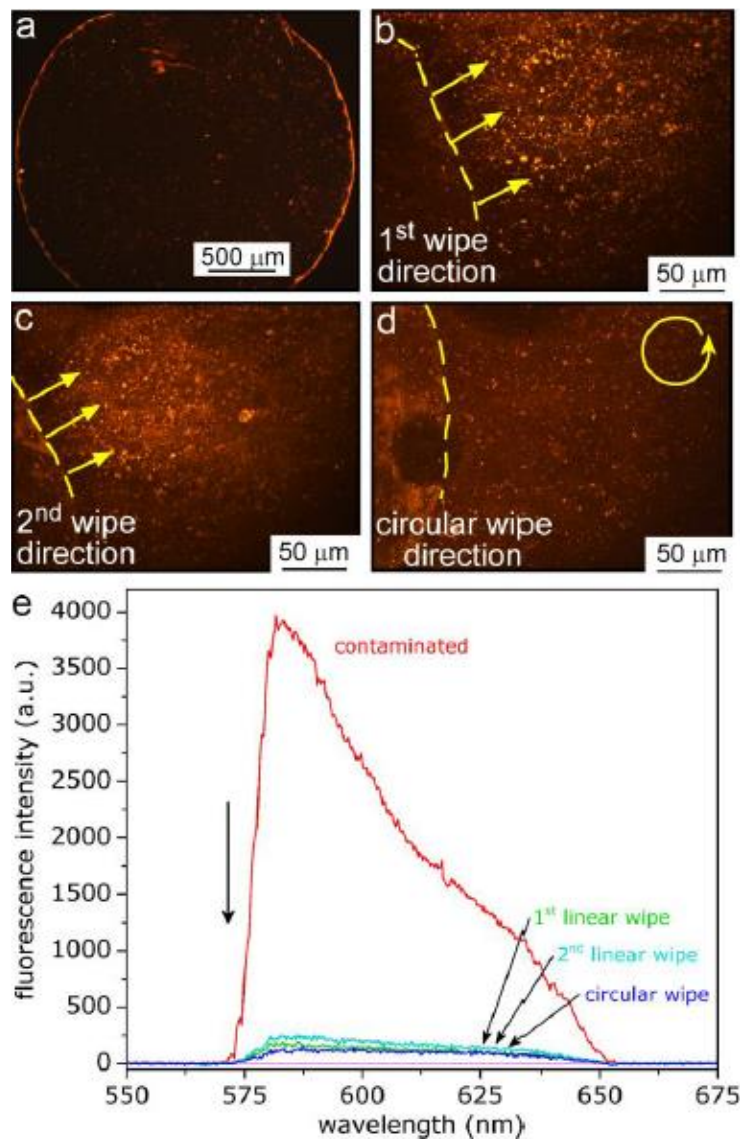
Figure 39. *(a) Fluorescent microscopy image of a simulated spill of a 2 µL solution containing gold nanoparticles coated with poly(ethylene glycol) terminated with a Rhodamine dye, on a section of countertop. The process of remediating this spill of gold nanoparticles is tracked using (b-d) fluorescence images and (e) fluorescence spectra (λ_{ex} = 546 nm). The spill was remediated by wiping the countertop with a paper towel wet with water using either (b,c) a linear motion or (d) circular motion in a direction indicated by the yellow arrows relative to the spill (outlined with the yellow, dotted line). (e) Fluorescence spectra obtained by optical microscopy from the original, contaminated surfaces and those surfaces remediated by wiping the spill with a paper towel. The background spectrum (e.g. detector white noise) is depicted in the purple trace (bottom trace).*

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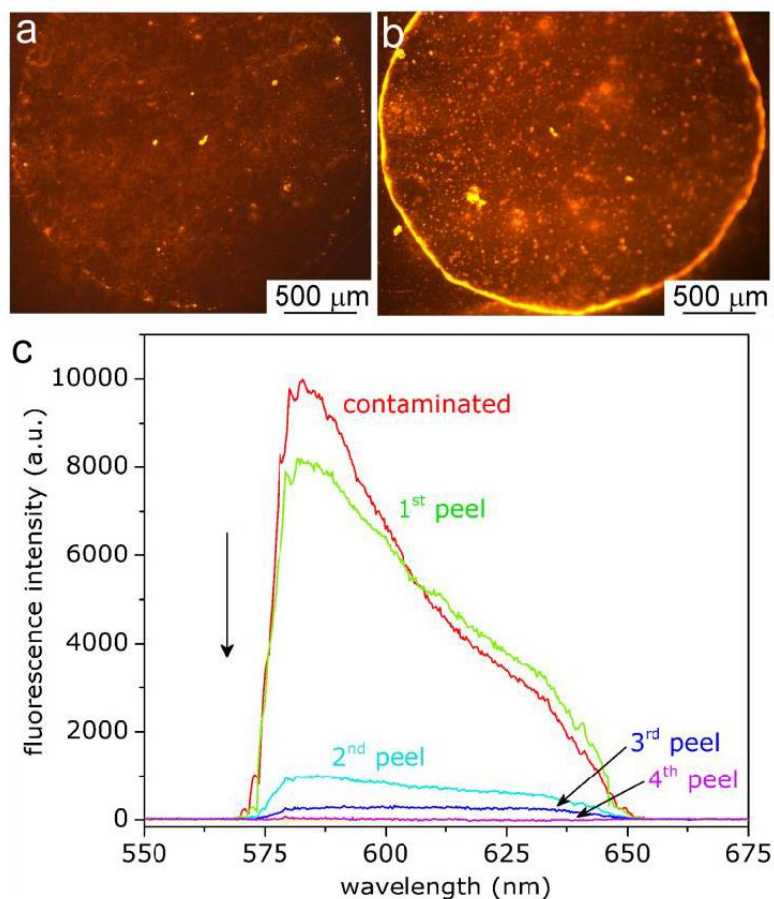
Figure 40. *Remediation of nanoparticle contaminated countertop through the use of casting a polymer solution onto the surfaces, evaporating the solvent, and peeling the polymer away from the surfaces. Fluorescence microscopy (λ_{ex} = 546 nm of the (a) countertop and (b) polymer film after separating the polymer from the countertop depict the transfer of contaminant, gold nanoparticles coated with poly(ethylene glycol) terminated with a Rhodamine dye, to the cast polymer. The remediation process is tracked by fluorescence spectroscopy, where (c) the fluorescence intensity from the substrate returns to baseline values (equivalent value to that of the countertop surfaces before contamination) after casting and peeling the fourth polymer film.*
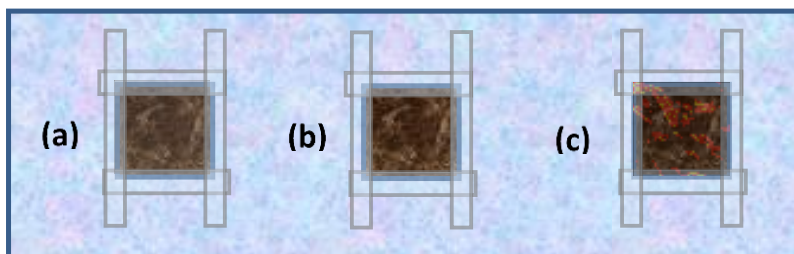
Figure 41. *Sketch of test set-up for particle detection and remediation from 1 cm² sections of laboratory countertop surfaces. Glass slide with 3 samples secured with Scotch tape and covered with a layer of New Skin: (a) Au-Nanorods-PEG-Rhodamine-B contaminant, (b) benchtop control, and (c) PEG-Rhodamine-B contaminant control.*

Repeating this process of casting, drying and peeling of the polymer film can remove more nanoparticles from the countertop than by wiping. After four consecutive sequences of adhering and removal of a polymer layer, the nanoparticles are removed to a level below the detection limits of the fluorescence spectrometer. An alternative methods, such as XRF or ICP-MS are required to further verify the presence (or absence) of nanoparticles following this process as the limit of detection of fluorescence spectrometer is not as sensitive.

Comparing Figure 39 and Figure 40, it may seem that wiping with a cloth is just as effective as the use of a polymer encapsulant, it is important to note that by wiping you may reduce the fluorescent signal of the contaminated area, but you will likely be spreading the contaminant over a greater area (diluting the spill of nanomaterials, but not effectively removing it from the surfaces) as seen in the fluorescent microscopy images. Remediation by casting a polymer film onto a countertop establishes the technique of encapsulating the nanoparticle contaminants and removal of these contaminants by separating the polymer from the countertop without spreading the contaminant to a larger area. There are, however, a number of limitations with this method that can be improved upon by other methods of encapsulation. These limitations include the technical difficulty in reproducibly casting the polymer film, such that the polymer has consistent properties. For example, the polymer film can easily pull apart while peeling it away from the countertop if the material is too thin, or the polymer film is not consistent, or if the method of peeling is too forceful as described in Table 2. Although the fluorescence spectra were taken from nearly the same location within the

coffee ring pattern of the dried solution of the nanoparticles, any variance from position can increase or decrease the overall intensity. In addition, quenching can also be a concern when dealing with fluorescence measurements. Quenching can occur from processes that include oxidative damage, intermolecular electron transfer at high concentrations, and/or when the molecules are in close proximity to the surfaces of the gold nanoparticles. [88] This absence in fluorescence can lead to inaccurate readings as there maybe nanoparticles but an absence of fluorescence signal. Benefits of the chosen experimental design include the ease of use of the fluorescence signal for imaging (and tracking) the location of the nanoparticles on various surfaces, and that the ease of use, compatibility with most surfaces and availability (an off-the-shelf product) of the encapsulating polymer material chosen for these studies. [89]

Table 2. *Comparison of methods for removing polymer films from countertops.*

	film support	apply heat	peel direction	peel speed	comments*
1	no	no	top-to-bottom	evenly	all films came off from the countertop
2	no	no	corner -to corner	evenly	about 1/3 of blank sample and most of dye sample were left on countertop
3	no	no	top-to-bottom	fast	most of NR-PEG-Dye sample and ~15-20% of other 2 samples were left on countertop
4	no	no	corner -to-corner	fast	most of dye sample, about 1/2 of blank sample, and a small corner of NR-PEG-Dye sample were left on the countertop
5	no	yes	top-to-bottom	evenly	all films came off from the countertop
6	no	yes	corner -to-corner	evenly	~15% of blank area of NR-PEG-Dye sample left on the countertop; others came off
7	no	yes	top-to-bottom	fast	all films came off from the countertop
8	no	yes	corner -to-corner	fast	most came off from the countertop; ~15-20% of blank areas from the NR-PEG-Dye sample & dye sample were left on counter
9	yes	no	top-to-bottom	evenly	all films came off from the countertop
10	yes	no	corner -to-corner	evenly	most of NR-PEG-Dye sample did not come off from the countertop; other 2 did
11	yes	no	top-to-bottom	fast	dye film did not come off from the countertop; other 2 did
12	yes	no	corner -to-corner	fast	all films came off from the countertop
13	yes	yes	top-to-bottom	evenly	all films came off from the countertop
14	yes	yes	corner -to-corner	evenly	all films came off from the countertop
15	yes	yes	top-to-bottom	fast	all films came off from the countertop
16	yes	yes	corner -to-corner	fast	all films came off from the countertop

* This analysis compares samples that included a blank or pristine countertop, a countertop coated with the Rhodamine B dye (dye), and countertops coated with GNR-S-PEG$_{5000}$-NH-Rhodamine B.

3.4. Remediation by encapsulation: conclusions and prospects for future work

The methodologies introduced here were to remediate nanoparticles by a process of encapsulation. We pursued a number of different methods of encapsulation that could be adapted to many different types of surfaces found throughout the workplace. The encapsulation process provides a simple means to contain the nanoparticles and minimize and/or prevent further contact between the worker and the contaminant. Although some encapsulating layers might remain in place, our aim was to completely remove the potentially hazardous material from the workplace and to not physically or chemically alter the countertops and other surfaces in the workplace. A secondary feature of the encapsulation process is that the encapsulating material could be color coded to indicate to other workers the potential presence of contamination by nanoparticles. We have identified methods that can encapsulate the nanoparticles, communicate the presence of these contaminants, and effectively remove the particles when the encapsulating layer is peeled away from the contacting surfaces.

Further work will be necessary in the field of nanoparticle contamination in the workplace. The outlook could include further development of better materials and methods to encapsulate or otherwise bind the nanoparticles, as well as optimizing the use of analytical instrumentation (e.g., XRF, LIBS) for the detection of nanoparticles. The on-going studies will, however, require further collaboration to establish the potential health impact of nanoparticle contaminants on surfaces found in the workplace. This work will include determining the potential correlations between the level of contamination, type of contamination, duration of exposure, and the immediate and long-term health of a worker. We are, however, pursuing outreach activities to promote further discussion, discovery, and development in this field.

Methods for remediation of nanoparticle contaminants need to be simple, easy to implement, efficient, and effective. Remediation may be pursued either through on the job training or through a third party contracted to clean-up a work environment. The same third party could be contracted for assessment of the workplace environment for potential contaminants as an assessment of the health impacts of the site. Whatever the approach to detection, assessment and remediation of the workplace from nanoparticle

contaminants, further work is also necessary to determine the potential acute and long-term health impacts of nanoparticles in the workplace.

There remain many unanswered questions in dealing with nanoparticle contamination. What level of contamination is acceptable? How do the levels of contamination in a common workplace, rather than the simulated environments here, correspond to health concerns of the worker? What types of materials are of the highest concern for remediation? Presumably there should be a correlation to the reactivity of a material in the ambient environment and/or with a worker that might come into contact with the material. How often should a workplace be inspected for potential contamination? This will likely correlate with the particular habits of a workplace, such as how often, how much, and what types of nanoparticles are used by workers. To answer these important questions further analysis is required from a broad spectrum of investigators. It would be most efficient to build a larger team of scientists to collect data to address some of these questions. The outcome of these investigations and the implementation of policies surrounding nanoparticle contamination in the workplace should be driven by data. Too many questions remain to draw a conclusion at this time on the importance or not of nanoparticle contamination in the workplace. However, in the exclusion of sufficient data it is prudent to avoid or otherwise minimize a worker's exposure to nanoparticles.

In summary, the findings of these studies suggest that simple methods can be implemented to contain and remediate nanoparticle contaminants from the workplace. Simple techniques can also be implemented to communicate the presence of nanoparticle contaminants. A number of analytical techniques could be used to determine the presence of nanoparticle contaminants, but the technique(s) should be chosen according to the needs of the remediation effort. Certain analytical techniques will only provide elemental analysis and won't be able to distinguish contaminants as nanoparticles or bulk. It is important that these techniques be supplemented by other techniques to confirm the type of contaminant of concern. Further work is required to establish appropriate techniques for implementation in the workplace, but a foundation has been laid that demonstrates the importance of worker training for proper methods of handling nanoparticles and cleaning up potential spills.

4. Summary and future directions

Further work is necessary to develop methods and materials for the remediation of spills containing nanoparticles. Some promising encapsulation materials have been demonstrated in the studies presented herein. A variety of contaminants were also demonstrated, but further work is necessary to extend it to other contaminants and to other surfaces that may become contaminated in the workplace. However, remediation by encapsulation of the spill has been demonstrated to be an effective means of clean-up and XRF technology could be used to track unseen spills in the workplace. It remains to be seen if these methods would be adopted in the work environment, and if they would be properly implemented to be effective. In addition, it would be beneficial to continue to seek alternatives to encapsulating the nanoscale materials that were pursued in this study. Further developments could produce a method that is further optimized for remediation of nanoparticles.

Future research will require extending remediation techniques to other nanoscale materials. The variety of nanoscale materials used in the workplace is vast. Some nanoscale materials may require further adaptations of the remediation techniques presented herein in order to be effective. In addition, the types of surfaces found in the workplace are also very diverse. We evaluated countertops as a common place of contamination throughout many workplaces. Other possible places for contamination may include laboratory coats and other proper protective equipment. Another common surface for contamination might be the metal or glass parts of a fume hood. Of equivalent concern might be the various plastic, metallic, or ceramic surfaces of common equipment found in the workplace and utilized for a wide variety of tasks (e.g., hotplates, pipettors). Detecting the presence of nanoparticle contaminants on each of these surfaces presents its own set of challenges.

4.1. Implications for future research on occupational health

Avoidance is the best measure of prevention, but when there is a potential of contact with nanoparticles that are unavoidable, then appropriate actions are necessary to ensure the safety of workers. This work seeks to further improve the health and safety of workers, visitors, and first responders when they are exposed to nanoscale particles in the workplace. A significant amount of work is necessary to assess the hazards associated with these materials. Of particular importance are the diversity of nanoparticles being produced, and the correlations between their shape, size, surface chemistry, concentration and the accompanying hazards. A key area for further development in order to appropriately assess these hazards will be establishing standards along with reliable physical and chemical data on nanoscale particles.

A primary recipient of the knowledge learned through these studies are occupational health and safety workers who represent the front-line of defense in promoting a safe and healthy work environment, and who may perform their own research in this field. These individuals can inform workers of the potential concerns regarding the use of nanoparticles in the workplace. This can include educating workers on the potential hazards associated with nanoparticles and exposures to spills of nanoparticles. They can also provide information on the techniques available to the worker for identifying the presence of nanoparticle contaminants in the workplace and best practices for clean-up of spills containing nanoparticles. These techniques are not universally ready for dissemination as the results of the techniques demonstrated herein may vary depending on the type of contamination and the type of surfaces that are contaminated. Occupational health and safety workers performing research in the area of nanomaterials could, however, assist in performing initial studies into the current practices in the workplace and assist in evaluating a more widespread implementation of techniques described herein. The method used to remediate a nanoparticle spill is of particular importance to avoid contaminants being spread throughout the laboratory environment. It is also important that the workers learn to communicate the use of nanoparticles and potential spills to other workers. As a start, the proposed signage described within can be implemented in a small community such as Simon Fraser University, whereby researcher or students within the university may come into contact

with nanoscale materials. As further work is needed to assess the potential biotoxicity and ecotoxicity of the types of nanoscale materials used in the workplace, the simple hazard sign indicating nanoscale materials are present can be implemented first. All this information can be delivered in general safety training. Feedback surveys should be performed to determine the effectiveness of the sign and further modifications can be performed.

In addition, regulatory bodies should be formed or be part of the occupational and health team. They can enforce laboratory inspections as a means of assessing workplace habits, and to reinforce best practices for remediation of nanoparticle contaminants (and many other trace contaminants for that matter). Habits could be adopted that suggest that something which is out of sight (e.g., nanoparticles spilled onto a countertop) is also out of one's mind, or in other words an unseen contamination is not of concern. The techniques outlined presented herein, offer a relatively simple mean for analysis of numerous locations throughout the workplace. The analytical techniques, such as XRF, could be brought into the workplace to assist in a real-time assessment by acquiring the data of the potential presence of and extent of nanoparticle contamination in the workplace. Performing spot checks of a workplace could be performed at regular intervals. There is, however, limitation to detecting low concentrations of nanoparticle contaminants using such portable techniques. These portable devices themselves will require adjustments and fine tuning to perform the task required.

The Olympus Innov-X x-ray fluorescence systems used in these studies were the Delta handheld and X-5000 desktop systems. Other XRF systems from Olympus Innov-X or another manufacturer might perform differently in the analysis of surface contamination by nanoparticles. The development of analytical techniques that are purpose-built for detecting the presence of nanoparticle contaminants in the workplace should be done in partnership with manufacturers of analytical equipment. An example is the optimization of a portable XRF unit with appropriate excitation energies and electronic gains for detecting and quantifying the presence of nanoparticle contaminants on various workplace surfaces; these tools are often pre-set at the factory and optimized for bulk materials, such as alloys and pure metals. Equipment manufacturers are driven by the demands of the market. The implications for regulatory bodies could be to

encourage companies to competitively build and offer equipment optimized for this new market.

4.2. Establishing protocol for remediating nanoparticle contamination

Aside from developing and expanding into new materials and techniques focused on nanoparticle remediation from surfaces in the workplace, there is a need for further work to assess the ability of workers to implement the detection and remediation processes on a regular basis. Appropriate training and simplicity of the procedures are each essential components to creating a solution that would be picked up and upheld by workers. The techniques do, however, need to be evaluated for their ease of use in the workplace and tested under a variety of laboratory conditions. There are many things to consider when determining the best method to remediate nanoparticles. Sometimes you may require the use of multiple remediation methods and sometimes it might be impossible to remove all of the contaminants or remove the contaminant down to a safe level. In this case more extensive measures may be required. Below is a general flow chart to follow for remediation of spills containing nanoparticles. One must first clean-up large spills until the contaminant cannot be seen by the human eyes, and then use a variety of steps to remediate the remaining trace amounts of contaminant. If there is a decrease in contamination, the process is repeated until the contaminant is no longer detectable; otherwise alternative methods are required for remediation. A protocol similar to Figure 42 should be created to guide users on the procedure to deal with nanoparticle spills.
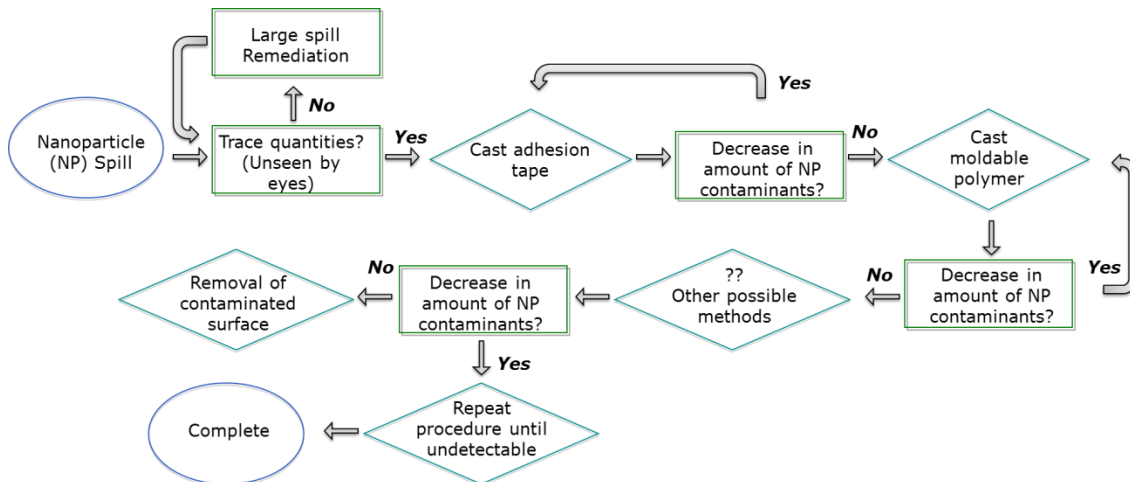
Figure 42.   **Protocol for remediating nanoparticle spills.**

4.3. Reactive membranes for nanoparticle remediation

An alternative to remediating nanoparticle spills by encapsulation is through the use of reactive membranes. One proposed approach is to make a 'stamp' similar to that shown in Figure 43. The stamp is composed of a handle and a reactive porous layer on the opposite side that is encapsulated for protection from unwanted damage or accidental contact by the user. The stamps will be designed for ease of fabrication and handling, but also for their ability to protect the end user from contact with the reacted material within the porous layer. A thin layer of porous silica or an appropriate polymer will encapsulate the reactive sponge-like layer. These layers will be deposited by solution processing or vapor processing techniques. In addition, to assist with providing a contact of the material within the stamp onto roughened surfaces, an elastomer such as polydimethylsiloxane can be incorporated into the top layer of the sponge. The elastomer will increase the flexibility of the stamp, as well as serving as a barrier between the user and the reactive sponge-like layer. A top handle will serve as an additional barrier and provide ease of handling. In summary, my idea is to develop a device for removing contaminants by a combination of stamping and reactive remediation techniques. The goal is to develop technologies that will irreversibly contain various contaminants after adsorbing these materials as a sponge would for the retention of water. Taking advantage of the high surface area of nano- and microporous materials, the reactive sponge layer will consist of materials that are specific to react with

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certain nanomaterials. The reactive layers of choice to start should be in accordance with particular particles that are commonly used in the workplace. As described in the work within, these particles include silver nanoparticles. Using materials such as a mesh of selenium nanowires encased within a porous layer of silica could be tested as a potential sponge for remediating silver nanoparticles. Selenium will react with the silver through an irreversible process, which is essential for complete removal of the contaminant. Once clean-up of the silver has been optimized, the technique can extend to the remediation of other nanoscale materials such as those that are being used in commercial products. Limitations of this alternative technique may include the migrations of nanoparticles into the sponge. In addition, the rate of reaction may change for all types of remediation process as each chemical reaction may occur at different rates.
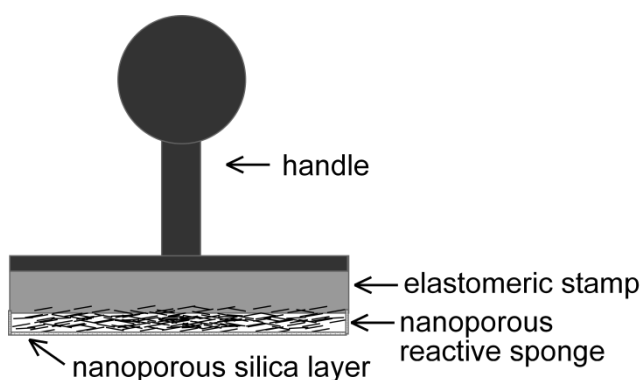
Figure 43.   *A stamp designed for ease of implementation by workers involved in the clean-up and remediation of contamination by heavy metals and nanoparticles in the workplace environment. This stamp is designed to specifically adsorb and react with contaminants of interest. A porous reactive 'sponge' serves as a layer to retain the contaminants and an elastomeric backing assists the stamp in conforming to the rough terrain of various surfaces.*

In addition, since XRF analysis alone cannot distinguish materials between those of nanoscale dimensions or bulk, the stamp can be composed of material that will specifically react or bind only with nanomaterials. Certain materials, such as platinum and gold, can be highly catalytic when prepared as nanosized materials, but when in bulk, they are not catalytic. [90] Taking advantage of the unique chemical properties of nanomaterials the sponge can be tailored such that it could be used as a method for both nanomaterial detection and remediation. The use of a stamp as part of the

remediation process can be used in conjunction with XRF and other analysis techniques being developed. One important aspect of this study will be to determine how much material can be loaded into each stamp and to quantify the trace levels of contaminant that may be left behind on the surfaces of interest. These studies will be essential for determining the best practices for using these stamps in the workplace.

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