Nanomaterial Safety

Introduction

Nanomaterials are defined as materials with at least one external dimension (length, width or depth) in the size range from approximately 1-100 nanometers. Nanoparticles are objects with all three external dimensions at the nanoscale. Nanoparticles can be formed naturally (commonly known as ultrafine particles) by nature such as dust and ash or they can be found as incidental by-products from processes such as welding, combustion, or diesel engines. Nanomaterials can be reagents, catalysts, or the desired product of research. Engineered nanomaterials are intentionally made for specific purposes, such as shape, size, properties, or content. They have unique properties and functions because of their nano-scale size and dimensions. Often, the behavior of nanomaterials may depend more on surface area than particle composition itself. Relative-surface area is one of the principal factors that enhance its reactivity, strength and electrical properties. Examples of engineered nanomaterials include carbon buckeyballs or fullerenes; carbon nanotubes; metal or metal oxide nanoparticles (e.g., gold, titanium dioxide); quantum dots. The different types of materials that are used in nanotechnology research and application vary widely; however, the more common ones include carbon, silver, gold, silica, titanium, and polymers. Nanomaterials can be suspended in a gas (nanoaerosol), suspended or dissolved in liquids, or can be incorporated into a larger matrix or substrate. Due to the size of these particles, they often exhibit unique properties that are quite different from similar larger sized materials.

Hazards/Controlling the Hazards

In dealing with health and safety of nanomaterials, the uncertainties are great because the characteristics of them may be very different from that of larger particle materials of the same composition. Studies have shown in rodents and cell cultures that the toxicity of nanomaterials is greater than those of larger particles of similar chemical composition. In addition to particle size and surface area, other particle characteristics may influence toxicity, such as the shape, surface coatings, solubility, etc. Existing toxicity information about a given material of larger particle size can provide a baseline for anticipating the possible adverse health effects that may occur from exposure to a nanoscale material that has some of the same physicochemical properties (e.g., chemistry, density). However, predicting the toxicity of an engineered nanomaterial based on its physicochemical properties may not provide an adequate level of protection. "Approaches to Safe Nanotechnology, Managing the Health and Safety Concerns Associated with Engineered Nanomaterials" is a guidance document authored by the Department of Health and Human Services, Centers for Disease Control and Prevention and National Institute for Occupational Safety and Health that should be consulted for further information.

Nanomaterial exposure can occur through inhalation, dermal absorption, or in some cases, ingestion. Inhalation is considered the primary route of potential exposure. Studies have concluded that discrete nanomaterials are deposited in the lungs more readily than larger particle sizes. Based on animal studies, discrete nanomaterials may enter the bloodstream from the lungs and translocate to other organ systems following penetration. Current scientific evidence indicates that nanomaterials may be more biologically reactive than larger particles of similar chemical composition and thus may pose a greater health risk when inhaled. Studies of carbon nanotubes (CNT) and nanofibers demonstrate adverse effects in the lungs including pulmonary inflammation, fibrosis or possibly mesothelioma.

Dermal or skin exposure is also a potential route of exposure. Studies have shown that particles less than 1 µm in diameter may penetrate intact skin. Studies conducted in vitro using primary or cultured human skin cells have shown that both single-wall carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) can enter cells and cause release of pro-inflammatory cytokines, oxidative stress, and decreased viability. Nanoparticles can cross cell membranes and interact with sub cellular structures where they have been shown to cause oxidative damage and impair function of cells in culture. It remains unclear, however, how these findings may be extrapolated to a potential occupational risk, given that additional data are not yet available for comparing the cell model studies with actual conditions of occupational exposure.

Nanomaterial can be ingested due to hand to mouth contact. Upon entry, the materials could transfer themselves to other organs in the body via the gastrointestinal tract. Ingestion may also accompany inhalation exposure because particles that are cleared from the respiratory tract via the mucociliary escalator may be swallowed. Little is known about possible adverse effects from the ingestion of nanomaterials.

Very little is known about the safety risks that engineered nanomaterials might pose, beyond some data indicating that they possess certain properties associated with safety hazards in traditional materials. Depending on their composition and structure, some nanomaterials may initiate catalytic reactions that, based on their chemical composition, would not otherwise be anticipated. Decreasing the particle size of combustible materials can increase combustion potential and combustion rate, leading to the possibility of relatively inert materials becoming highly reactive in the nanometer size range. This can lead to exothermic reactions, fires and explosions depending upon the reactions that are catalyzed. In the case of some metals, explosion risk can increase significantly as particle size decreases. With this in mind, nanomaterials that can be aerosolized should be treated with extra caution as if they are highly flammable.

Nanomaterials fall under OSHA General Industry Standards, which includes established exposure limits for naturally occurring nanomaterials. Although there are currently no established (legal) exposure limits (US or International) for Engineered Nanomaterials, NIOSH has developed Recommended Exposure Limits (RELs) for carbon nanotubes (8-hr TWA 1 $\mu g/m^3$) and nano-titanium dioxide (8-hr TWA 0.3 mg/m^3). When controlling potential exposures within a workplace, NIOSH has recommended a hierarchical approach to reduce worker exposures. The philosophical basis for the hierarchy of controls is to eliminate the hazard when possible (i.e., substitute with a less hazardous material) or, if not feasible, control the hazard at or as close to the source as possible. At Central Michigan University, our policy is to follow current best practices as well as government recommendations in our handling of nanomaterials/nanoparticles.

Administrative Controls

All personnel are required to complete Laboratory Safety Training prior to working in a laboratory.

There must be an approved Standard Operating Procedure (SOP) in place before work begins with nanomaterials. Furthermore, all personnel shall read and fully adhere to this SOP when handling nanomaterials. Be sure to consult and review the Chemical Hygiene Plan and any SDS for chemicals used before performing any work in the laboratory. Instructions and a template for SOP development may be found in Section VII and Appendix K of the Chemical Hygiene Plan.

Training on lab-specific procedures, including the locations of fire extinguishers, safety showers, eyewashes, and fire alarms is required for all personnel working with these materials and must be documented. Laboratory-specific training for work with nanomaterials must include information on the hazards of working with nanomaterials, and on the uncertainty of health effects. Appendix I of the Chemical Hygiene Plan contains the Laboratory Safety Training Record form that must be completed for each worker in the laboratory.

As with all laboratory practices, be sure there is no food or drink in the laboratory. Wash hands frequently to minimize potential chemical or nanomaterial exposure through ingestion and dermal contact.

Keep working area clean and as dust free as possible. Use wet wipe-downs of the work area instead of dry sweeping. Be sure to wet-wipe down the floors and sides of hoods at the end of each day where nanomaterials are used.

Restrict access and post signs around designated areas where nanomaterials are in use or synthesized. Be sure the signs include Nanomaterials warnings, lists of hazards and required personal protective equipment (PPE). Labels for flasks and vials should also include Nanomaterials, name of materials, lists of hazards, date, etc.

Be sure all unattended reactions are properly posted or labeled with the following:

a) Researcher name
b) Faculty supervisor
c) Emergency telephone number
d) Date of reaction startup
e) Date of reaction completion
f) Brief description of reaction apparatus and chemicals involved

A template for unattended operations signage may be found in Appendix T of the Chemical Hygiene Plan.

Appropriate secondary containers must be in place around reaction vessels in order to contain any loss of primary containment or accidental release of hazardous chemicals.

Communicate with others in the building when working alone in the laboratory; let them know when you arrive and leave. Avoid working alone in the laboratory when performing high-risk operations.

Since the most likely route of exposure is inhalation, it is recommended that whenever nanomaterials are handled, that they are either in solutions/suspension or attached to substrates/matrix. Wet materials are less likely to give off air borne particles that can be inhaled. Be aware that sonication of liquids or vigorous agitation will produce airborne materials that can be potentially inhaled.

Engineering Controls

Dry boxes, glove bags, or fully enclosed systems are recommended ways to handle and synthesize nanomaterial. Avoid handling nanomaterials in open air. Nanomaterials that are brought outside a hood or glove box should be in sealed containers.

Perform work inside a designated chemical fume hood, lining the work area with an absorbent pad. Make sure the hood is in proper working order, not cluttered and the face velocity setting is between 80-120 ft. /min. OLFS recommends (but does not require) that hoods have High-Efficiency Particulate Air systems. Portable bench top HEPA units are also recommended.

It is highly recommended that secondary containers be used around all reaction vessels, apparatus, or equipment when nanomaterials are being synthesized or stored.

When working with powders, use antistatic paper and floor sticky mats.

A designated ventilated weighing balance should be used for the weighing of nanomaterials. This allows the operator to weigh out and use nanomaterials in a non-turbulent environment.

The most probable route of exposure is inhalation. Wet wipe and/or HEPA-vacuum work surfaces, equipment, glassware or apparatuses used that may be potentially contaminated with nanomaterials at the end of each operation. Perform regular maintenance activities such as cleaning/replacing filters or dust collecting systems. Dry box traps should also be changed with care. Be aware that nanomaterials trapped in filters can be reactive. Also, be aware of possible exposure while cleaning or replacing of filters or dry box traps.

The properties of nanomaterials, along with the unique methods that may be employed for producing them, may mean that traditional exhaust ventilation may be more energetic than necessary for removing incidentally released nanoscale particles. For this reason, engineering controls need to be applied judiciously to ensure protection of workers without compromising production.

Safety Equipment and Personal Protective Equipment

Know the location and proper use of emergency equipment, such as safety showers, fire extinguishers, fire alarms, and spill clean-up kits.

Eye protection and lab coats must be worn while in the laboratory. All eye protection equipment must be American National Standards Institute (ANSI) approved and appropriate for the work being done.

Based upon the uncertainty of the health effects of dermal exposure to nanomaterials, it is prudent to consider using protective equipment, clothing, and gloves to minimize dermal exposure, with particular attention given to preventing exposure of nanomaterials to abraded or lacerated skin. Gloves are to be used whenever nanomaterials are handled. Use appropriate gloves, (such as nitrile), that meet the chemical resistance needed. Extended or 9 inch disposable gloves should be used because they cover the wrist area, preventing exposure to the skin. Be sure to change gloves routinely. Dispose of gloves in a proper disposal unit: either a sealed bag or sealed container. Remove gloves when leaving the laboratory in order to prevent contamination of doorknobs or other common use objects such as phones, multiuser computers, etc. Wash hands immediately after removing gloves.

See Chemical Hygiene Plan, Appendix E: glove selection.

If materials are used inside a glove box, the operator does not need a respirator until the material is removed from that environment. When the potential exists that workers may inhale nanomaterials due to a lack of effective engineering controls or during activities with higher nanomaterials exposure potential (e.g., emergencies), appropriate respirators are required. During initial SOP review, OLFS staff will conduct a dermal and respiratory hazard assessment of the procedure and determine the appropriate level of PPE, including any required respirator, needed for the specific procedure. Contact OLFS prior to wearing a respirator to schedule training, fit testing, and a medical evaluation. Do not wear a respirator until approved by the OLFS office. Respirators must be maintained and cleaned on a regular basis, replacing old or damaged respirators as needed. Dust masks should not be used in place of NIOSH-approved respirators for protection against nanomaterials.

Emergency Procedures

When a spill occurs, personal safety should always come first. Alert and clear everyone in the immediate area where the spill occurred. Inhalation exposure and dermal exposure will likely present the greatest risks. Consideration will therefore need to be given to appropriate levels of personal protective equipment. Inhalation exposure in particular will be influenced by the likelihood of material re-aerosolization. In this context, it is likely that a hierarchy of potential exposures will exist, with dusts presenting a greater inhalation exposure potential than liquids, and liquids in turn presenting a greater potential risk than encapsulated or immobilized nanomaterials and structures. If spilled material is flammable, turn off ignition and heat sources. Do not light Bunsen burners or turn on other switches.

For dry spills, standard approaches for cleaning include using HEPA-filtered vacuum cleaners if available, but contact OLFS (774-4474) before proceeding. If vacuum cleaning is employed, care should be taken that HEPA filters are installed properly and bags and filters changed according to manufacturer's recommendations. Energetic cleaning methods such as dry sweeping or the using of compressed air should be avoided or only used with precautions that assure that particles suspended by the cleaning action are trapped by HEPA filters. Alternately, wipe up the powder using damp cloths or by wetting the powder with a suitable solvent prior to dry wiping. Do not sweep up materials with a broom, as this will lead to more airborne materials. Liquid spills are typically cleaned by applying absorbent materials.

Damp cleaning methods with soaps are preferred. Cleaning cloths should be properly disposed of; drying and reusing contaminated cloths can result in re-dispersion of particles and is not recommended. Use of commercially available wet or electrostatic microfiber cleaning cloths may also be effective in removing particles from surfaces with minimal dispersion into the air. Do not put any nanomaterial contaminated waste in regular trash or down the drain.

For an actual chemical exposure/injury:

Flush exposed eyes or skin with water for at least 15 minutes, and then seek medical attention
Note: In case of inhalation, seek medical attention.

Report all work related accidents, injuries, illnesses or exposures. Appendix M of the Chemical Hygiene Plan contains the University's Procedure to be followed in case of an injury on campus.

Storage

Store all nanomaterials in a well-sealed container. Label all chemical containers with the identity of the contents (do not use abbreviations/acronyms); include term "nano" in descriptor (e.g., "nano-zinc oxide particles) rather than just "zinc oxide." Include hazard warning and chemical concentration information, if known.

When transporting nanomaterials from one laboratory to another, the materials should be in a sealed container. The sealed container should also be secured inside a sealed secondary container. Bio-Safe Carriers from VWR (56609-112) are an example of a sealed secondary carrying container.

Disposal

All nanomaterials/materials should be treated as hazardous chemical waste. Contaminated solid waste (papers, gloves, wipes, pipettes, filters, etc.) should be collected in a sealed solid waste container and separated from other chemical waste. Liquid nanomaterials (suspensions, solutions, contaminated solvents) should also be collected in a sealed container, separated from other chemical waste. All waste should be labeled as “Hazardous Waste”. List the chemical contents of the nanomaterials, other chemical contaminants, solvents, hazards, etc. with percentages of each material according to the CMU chemical hygiene plan section VIII Chemical Distribution/Storage/Inventory/Disposal/ Subsection H “Hazardous Waste Disposal” and note that it is nanomaterial. Do not put any nanomaterial contaminated waste in regular trash or down the drain.

For further waste management questions, contact the CMU Hazardous Waste Manager at 774-2770.

Contact OLFS, 108 Foust Hall, at 774-4474, with questions/concerns regarding nanomaterials.

References and Further Information

1. Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials, Department of Health and Human Services, National Institute for Occupation al Safety and Health (NIOSH), March 2009 http://www.cdc.gov/niosh/docs/2009-125/pdfs/2009-125.pdf

2. NIOSH Current Intelligence Bulletin 65: Occupational Exposure to Carbon Nanotubes and Nanofibers; April 2013. http://www.cdc.gov/niosh/docs/2013-145/pdfs/2013-145.pdf

3. OSHA Fact Sheet: Working Safely with Nanomaterials, U.S. Department of Labor. April 2013. https://www.osha.gov/Publications/OSHA_FS-3634.pdf

4. 29 CFR 10 1910; (OSHA) Nanotechnology. https://www.osha.gov/dsg/nanotechnology/nanotech_standards.html