Nanomaterials Guidance Document

Nanomaterials are metals, ceramics, polymeric materials, or composite materials with at least one dimension ranging from 1 to 100 nanometers (1 nanometer is 1 billionth of a meter = 10−9 or 0.000000001 m.) Particles created at the nanoscale have different chemical and physical properties than larger particles of the same material.

Examples of Nanomaterials

Carbon Based: Buckyballs or Fullerenes, Carbon Nanotubes (CNT), Dendrimers
Metals and Metal Oxides: Titanium Dioxide (Titania), Zinc Oxide, Cerium Oxide (Ceria), Aluminum oxide, Iron Oxide, Silver, Gold, and Zero Valent Iron (ZVI) nanoparticles
Quantum Dots (QDs): ZnSe, ZnS, ZnTe, CdS, CdTe, CdSe, GaAs, AlGaAs, PbSe, PbS, InP

Health & Safety Concerns

Health Hazards

Epidemiological data is limited for occupational exposure to nanoparticles. The available data suggests humans and laboratory animals exposed to nanoparticles may experience adverse health effects associated with chronic exposure. The observed effects are dependent on the route of exposure and the particular nanoparticle to which the individual has been exposed. Nanoparticle surface characteristics, functional groups, charge, and induced charge, create unique properties that may result in genotoxic interactions. In particular, radicals may form on the particle surface generating reactive oxygen species that have been shown to interact with DNA.

The size and shape of nanoparticles can enable them to interact with DNA, and thus have potential to promote DNA damage or cancer. Carbon nanotubes (CNTs) are thought to cause cellular toxicity by a non-specific association with hydrophobic regions of the cell surface and internalization by endocytosis, and accumulation in the cytoplasm of the cell. DNA then wraps around the CNTs resulting in cell death.

Nanoparticles have the potential to penetrate deep into the lungs because of their small size. These deposits can aggravate existing respiratory conditions, such as asthma or bronchitis, and may even lead to the formation of granulomas. Inhaled nanoparticles have been shown to cross the alveolar wall into the bloodstream and translocate from the lungs toward other organs within 24 hours after exposure. This may lead to inflammation, altered heart rate and function, and oxidative stress. Inhaled nanoparticles may reach the brain through the olfactory nerve. Until long-term study results become available, as a prudent precaution, nanomaterials should be treated as “Highly Toxic.” Research also shows that:

- Metal nanoparticles have been shown to penetrate damaged or diseased skin.
- Iron oxide, nanotubes, TiO_2, and silver have been shown to inhibit cell proliferation.
- Nanotubes affect cell morphology.
- Fullerenes damage cell membrane.

Fire Hazards

Oxidation of nanoparticles can result in a fire hazard. Due to the high surface area to volume ratio and protective coating layers, nanoparticles can also have explosive potential. Due to oxidation sensitivity, even very small quantities of nanoparticles may cause fires and explosions. Nanoparticles freshly manufactured in an inert atmosphere display a significantly higher sensitivity to oxygen. This property can manifest itself by self-heating. Metallic nanoparticles may be more likely to self-heat when they form agglomerates and aggregates. Some metallic nanoparticles like aluminum, magnesium and titanium are pyrophoric, and will ignite on contact with air, requiring specialized handling precautions.

Exposure Concerns

Exposure Routes and Factors

Nanomaterial exposure potential is determined by the likelihood for airborne release, as inhalation is the most hazardous exposure. Solids bound to a substrate or matrix have a lower exposure potential than solids in the form of powders or pellets. Liquids in water-based suspensions or gels have a lower exposure potential than liquids in solvent-based suspensions or gels.

Active handling of nanoparticles as powders in non-enclosed systems poses the greatest risk for inhalation exposure. The level of inhalation hazard corresponds to the ability of nanoparticles to be dispersed as a dust (e.g., a powder) or an airborne spray or droplets. Aerosolization of nanoparticles should be avoided. Tasks that may generate aerosols of nanoparticles include: production of slurries, suspensions, or solutions; mechanical disruptions such as machining, sanding and drilling; cleanup and disposal, if not properly handled; and maintenance and cleaning of production systems or dust collection systems, if deposited nanoparticles are disturbed. These activities should only be done with proper engineering controls or personal protective equipment, while following the safe work practices below.

Exposure Limits

The evaluation of nanomaterial effects on human health is ongoing. Research that has been done may not apply to all types of nanomaterial, and there are few defined exposure limits. Because of this, it is prudent to limit exposure to the lowest level achievable.

There are a few defined limits available. NIOSH recommended exposure level (REL) for elemental carbon particles (primarily from carbon nanotubes CNT and fibers CNF) are set at 7$\mu g/m^3$ in 8-hr time weighted average (TWA). Also, due to the risk of developing lung cancer, nano-titanium dioxide is subject to a proposed permissible exposure limit (PEL) of 0.3 mg/m^3 in 8-hr TWA.

If airborne exposure to any type of nanomaterial is suspected, stop work and contact DEHS for assistance in conducting a hazard assessment and determining mitigation and monitoring protocols.

Safe Work Practices

The following work practices are recommended to limit worker exposures to nanomaterials.

Selection of Materials

- Select nanomaterials which are bound in a substrate, a matrix, in a water-based suspension, or a gel in order to decrease the risk of inhalation.
- Ensure metallic nanoparticles are coated with organic substances (this method is only used in solution) or electrostatically charged (reduces self-heating fire risk).

- Choose nanomaterials that are not pyrophoric, such as nanosilver or non-metallic nanoparticles. Avoid materials with a high degree of oxygen sensitivity such as freshly manufactured metallic nanomaterials.

Table 1: Risk Level and Recommended Controls for Nanoparticles

Risk Level	Recommended Controls
Low Risk of Exposure *No potential for airborne release (when handling)* **Material State** **Solid:** bound in substrate or matrix **Liquid:** water-based liquid suspensions or gels **Gas:** with no potential for release into air. **Activities:** • Non-destructive handling of solid engineered nanoparticle composites or nanoparticles permanently bonded to a substrate	• **Storage and labeling:** Store in sealed container and secondary containment with other compatible chemicals. Label chemical containers with the identity of contents (include the term "nano" in descriptor). • **Housekeeping:** Clean all surfaces potentially contaminated with nanoparticles (i.e., benches, glassware, and apparatus) at the end of each operation using a HEPA vacuum and/or wet wiping methods. DO NOT dry sweep or use compressed air. • **Hygiene:** Wash hands frequently. Upon leaving the work area, remove any PPE and wash hands, forearms, face, and neck. • **Notification:** If you will be dosing animals with the nanomaterial, work closely with Research Animal Resources (RAR) to make sure staff are notified appropriately and to fulfill cage labeling/management requirements • **Eye protection:** Wear proper safety glasses with side shields (for powders or liquids with low probability for dispersion into the air). • **Face protection:** Use face shield if there is a potential for splashing. • **Gloves:** Wear disposable gloves to match the hazard, including consideration of other chemicals used in conjunction with nanomaterials. Gauntlet-type/wrist-length gloves with extended sleeves are recommended. Double glove as risk increases. Change gloves at least every 2 hours, as particles can permeate through deformations caused by wearing gloves. o For CNTs wear nitrile over Latex. For TiO_2, wear PT Latex, Nitrile or Neoprene. For Graphite use Latex, Nitrile, Neoprene or Vinyl. • **Body protection:** Wear laboratory coat and long pants (no cuffs).
Moderate Risk of Exposure *Moderate potential for airborne release (when handling)* **Material State** **Solid:** powders or pellets **Liquid:** solvent-based liquid suspensions or gels **Air:** potential for release into air (when handling) **Activities** • Pouring, heating, or mixing liquid suspensions (e.g., stirring or pipetting), or operations with high degree of agitation involved (e.g., sonication) • Weighing or transferring powders or pellets • Changing bedding out of laboratory animal cages	**Follow recommended controls for "Low Risk of Exposure" and the following, as appropriate:** • **Fume Hood, Biosafety Cabinet, or Enclosed System:** Perform work in a laboratory-type fume hood, biosafety cabinet (must be ducted if used in conjunction with volatile compounds), powder handling enclosure, or enclosed system (i.e., glove box, glove bag, or sealed chamber). • **Preparation:** Line workspace with absorbent materials. • **Transport:** Use sealed containers with secondary containment when moving material between laboratories or buildings • **Signage:** Post signs in area indicating nanomaterials in use. • **Materials:** Use antistatic paper and/or sticky mats with powders. • **Eye protection:** Wear proper splash goggles (for liquids with powders with moderate to high probability for dispersion into the air). • **Body protection:** Wear laboratory coat made of non-woven fabrics with elastic at the wrists (disposable Tyvek®-type coveralls preferred). • **Clean-up:** At the end of each operation, decontaminate all work surfaces potentially contaminated with nanoparticles (e.g., benches, glassware, apparatus) using a wet wipe and/or HEPA-vacuum. Do not use dry sweep or use compressed air. • **Respiratory Protection:** If working with engineering controls is not feasible, respiratory protection may be required (i.e., N95 respirator, or one fitted with a P-100 cartridge). Consult DEHS at (612) 626-6002 for more information

Risk Level	Recommended Controls
High Risk of Exposure *High potential for airborne release (when handling)* **Material State** **Solid:** powders or pellets with significant potential for release into air **Gas:** suspended in gas **Activities** • Generating or manipulating nanomaterials in gas phase or in aerosol form. • Furnace operations • Cleaning reactors • Changing filter elements • Cleaning dust collection systems. • High speed abrading / grinding nanocomposites.	**Follow recommended controls for "Moderate Risk of Exposure", and the following:** • **Enclosed System:** Perform work in an enclosed system (i.e., glove box, glove bag, or sealed chamber). • **Body protection:** Wear disposable Tyvek®-type coveralls with head coverage.

Spill Information

Personnel Exposure Procedures

1. Flush contamination from eyes/skin for a minimum of 15 minutes. Remove any contaminated clothing.
2. Take a copy of the Safety Data Sheet (SDS) of any chemical(s) involved with you when seeking medical treatment.
3. Report potential exposures to your Principal Investigator/Laboratory Supervisor.
4. File an incident report.

Spill Response Procedures

1. **Notify:** Alert workers near spill to avoid entering the area. Post signs in area or on door of lab. Eliminate sources of ignition. Report spill to your Principal Investigator/Lab Supervisor.
2. **Assess:** Are you able to clean up the spill yourself?
    a. If yes, proceed with spill cleanup. This is appropriate if it is a small spill, you are knowledgeable about the hazards of the spill, it can be cleaned up within 15 minutes, and there are cleanup supplies available.
    b. If no, obtain spill assistance. Contact DEHS at (612) 612-6002.
3. **Protect Yourself:** Don appropriate PPE (NOTE: Respiratory protection may be required if spill / release is outside the engineering control device. If you are not fit-tested for respiratory protection and you feel it is necessary, do not clean up the spill - instead, contact DEHS at (612) 626-6002 for assistance).
4. **Cleanup Spill:** Use methods listed below. Avoid dry sweeping or using compressed air.
5. **Dispose:** Dispose of used cleaning materials and wastes as hazardous waste.
6. **Report:** File incident report.

For powders:

- Use a dedicated, approved HEPA vacuum whose filtration effectiveness has been verified.
- Consider possible pyrophoric hazards associated with vacuuming up nanoparticles.
- Do not sweep dry nanoparticles or use compressed air.
- Wet wipe using damp cloths with soaps or cleaning oils, or commercially available wet or electrostatic microfiber cleaning cloths.
- Be sure to consider any possible incompatibilities of nanoparticles with the cleanup solvent.

For liquid dispersions:

- Apply absorbent material (appropriate for the solvent in the dispersion) to liquid spill.

Chemical Waste

Dispose of excess nanomaterials, solutions and unwanted labware that has not been de-contaminated as hazardous waste.

General Nanomaterial Waste Management Practices

1. Manage according to hazardous waste program requirements at the University.
2. Label nanomaterial waste containers at all times. Specify the nanomaterial and its hazard characteristic (or the hazard characteristic of the parent material) on container labels; make sure to include the word “nano” as a descriptor.
3. Keep containers closed at all times when not in use.
4. Maintain containers in good condition and free of exterior contamination.

Solid waste (dry nanoparticle product, filter media containing nanoparticles, debris / dust from nanoparticles bound in matrix):

- Follow the General Nanomaterial Waste Management Practices, listed above.
- Collect waste in rigid container with tight fitting lid.

Liquid waste (suspension containing nanoparticles):

- Follow the General Nanomaterial Waste Management Practices, listed above.
- Indicate both the chemical constituents of the solution and their hazard characteristics, and the identity and approximate percentage of nanoparticles on container labels.
- Use leak proof containers that are compatible with all contents.
- Place liquid waste containers in secondary containment and segregate from incompatible chemicals during storage.

Laboratory trash with trace nanomaterials (PPE, mats or pads, spill cleanup material):

- Follow the General Nanomaterial Waste Management Practices, listed above.
- Dispose of in double clear plastic bags, folded over and taped at the neck.
- Avoid rupturing the bags during storage and transport.

Solid Matrix embedded with nanomaterials (intact and in good condition):

- Consult with DEHS Chemical Waste Program at (612) 626-1604, as these materials may be non-hazardous.

References

Nanotoolkit Working Safely with Engineered Nanomaterials in Academic Research Settings

Safe Nanotechnology in the Workplace

UNT Nanoparticle Safety Training

Nanoparticles - Handle with Care

Virginia Commonwealth University Nanoparticles and Nanotechnology

Fire and explosion properties of synthetic nanomaterials- Swiss Office of the Environment

GoodNanoGuide

Resources

Midwest Emerging Technologies Public Health and Safety Training Program (METPHAST Program)

Nano-Link