Nanomaterial Safety

Engineered nanomaterial/particles are particles that have at least one dimension between 1-100 nanometers. These very small particles often possess drastically different properties than larger particles of the same composition. Nanoparticles can be spheres, rods, tubes, and other geometric shapes (Fig. 1). The small particles may be bound to surfaces or substrates, put into solution or suspension, attached to a polymer, or in a few cases handled as a dry powder. Several nanoparticles can be created in the laboratory and some can be purchased from commercial vendors.

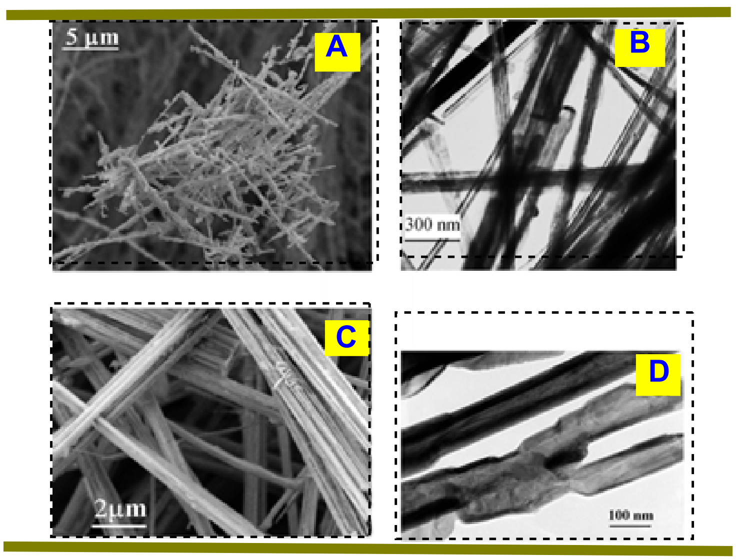

Fig. 1: SEM image of WS_2 nanotubes decorated with **WS_2** fullerene-like particles

Health and Physical Hazards

The potential for human and ecological toxicity associated with nanomaterials and ultrafine particles is a growing area of study as additional nanomaterials and products are advanced and brought into commercial use. The lung is a key target organ and so lung epithelial cells, macrophages, immune cells, and fibroblasts represent key cells for nanoparticle effects with specific regard to inflammation, immunopathology, fibrosis, genotoxicity, microbial defense, and clearance. Inhaled nanoparticles can be deposited in the respiratory system and may cause irritation and damage to lung cells and tissues.

Fig. 2: Nanomaterial hazards

Certain nanomaterials may enter cell membranes and may cause damage to intracellular structures and functions. In addition to health hazards; fire, and explosion risk, dangers of catalytic reactions are associated with many nanomaterials, certainly metal-based nanomaterials.

Potential Safety Concerns and Controls

Even though insufficient information exists to predict the fire and explosion risk associated with powders of nanomaterials, nanoscale combustible material could present a higher risk than sandier material with a similar mass concentration given its increased particle surface area and potentially unique properties due to the nanoscale. Some nanomaterials may initiate catalytic reactions depending on their composition and structure that would not otherwise be anticipated based on their chemical composition.

Use of an enclosed system such as Glovebox (Fig. 3a), enclosure, biological safety cabinet, chemical fume hood, and a cannula filtration method aids in isolating reactive nanomaterials from a solution (Fig. 3b). For most laboratory processes, the control of airborne exposure to nano aerosols can be accomplished using a variety of engineering control techniques comparable to those used in reducing exposure to common aerosols.

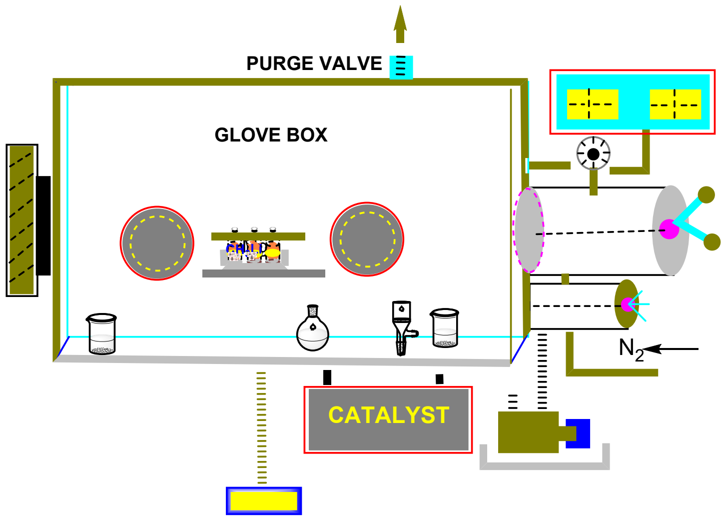

Figure 3a. Manipulation of Nanomaterials Using a Glovebox

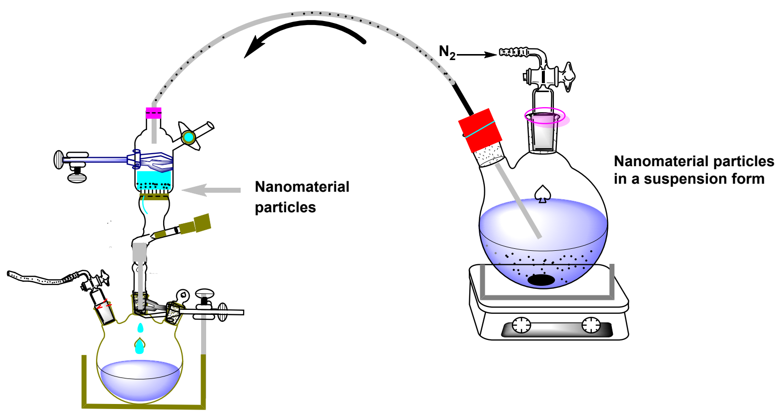

Figure 3b. Isolation of Pyrophoric Nanomaterials Using a Stainless-Steel Cannula and the Schlenk Line Technique

The following workplace activities can increase the risk of exposure to nanoparticles:

- Working with nanomaterials in **liquid media** without adequate PPE
- Working with nanomaterials where a **high degree of agitation** is involved
- Syntheses of nanoparticles in **non-enclosed systems**
- Handling (e.g., **weighing, blending, spraying**) powders of nanomaterials
- Maintenance on equipment and processes used to produce or fabricate nanomaterials and the cleaning-up of spills and waste material containing nanomaterials

- Cleaning of **dust collection** systems used to capture nanoparticles
- **Machining, sonication, sanding, drilling, or other mechanical disruptions** of materials containing nanoparticles.

Hierarchy of Controls

Controlling exposures to nanomaterials is the fundamental method of protecting researchers and students. Conventionally, a hierarchy of controls has been used as a resource of determining how to implement feasible and effective control solutions.

One representation of this hierarchy (Fig. 4) is as follows:

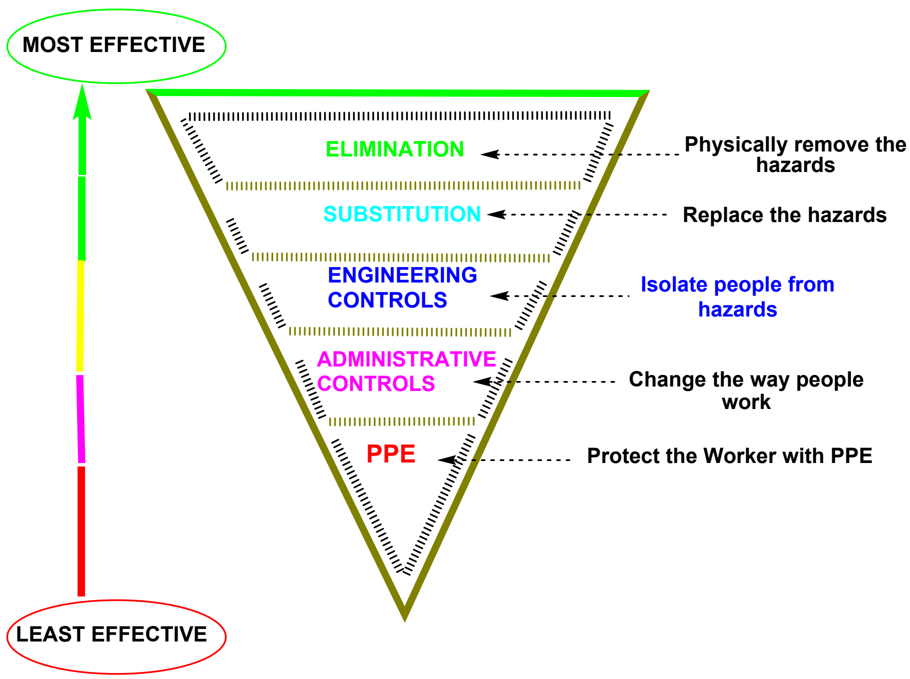

Figure 4. Hierarchy of Controls

Hazard Assessment: Nanomaterial Manipulations

Proper hazard assessment and prudent laboratory practices in research labs will assist users to minimize the potential of any physical and exposure hazards. Researchers/students must appraise the specific nanomaterial used in the research project, experiment, or protocol. Other precautions may be essential.

Before manipulating any nanomaterials in laboratories, a proper hazard assessment (Fig. 5) should be conducted. Also, developing a standard operating procedure (SOP) for nanomaterial manipulations can assist researchers to decide about the appropriate controls and manipulation techniques. The SOP should be tailored to be specific to the proposed experimental procedure. Consider the hazards of the precursor materials in evaluating the process using a **checklist or a what-if analysis** method (Table 1 & 2). Special consideration should be given to the high reactivity of some nanopowders concerning potential fire and explosion (Table 2).

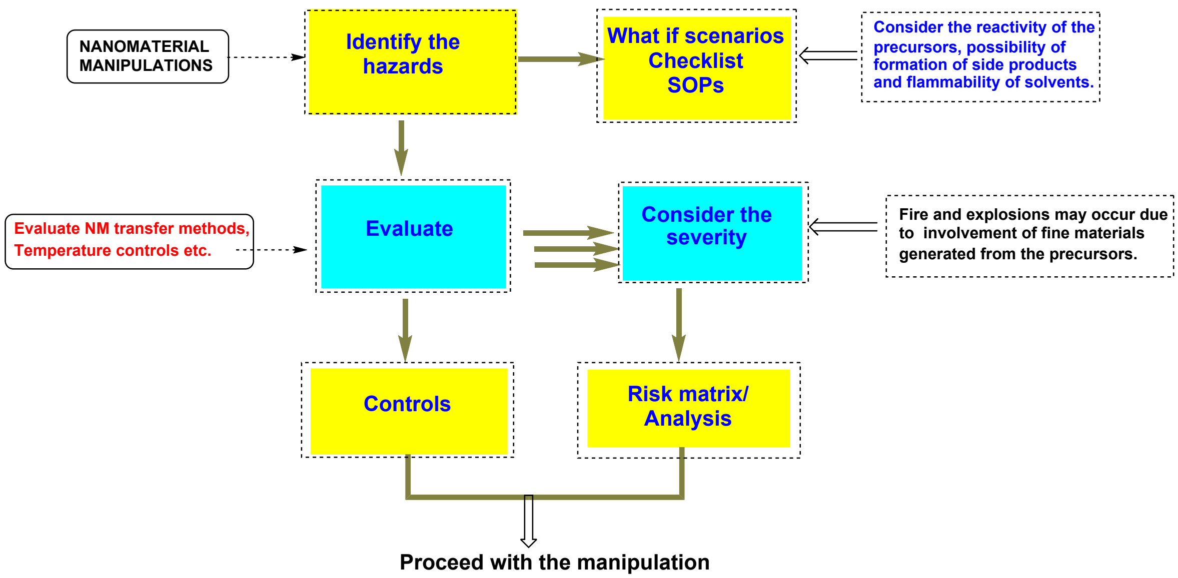

Figure 5: Hazards Assessment and Hazard Analysis for Nanomaterial Manipulations

Table 1: Laboratory Scale Checklist When Working with Nanomaterials

Items	Y	N*
Are you fully aware of the properties of the precursors used for nanomaterial synthesis? And have you alerted all other potentially exposed people to those properties? (This includes everyone being aware of both what is known and what is NOT known about these chemicals and nanoparticles.)		
Has the engineering devices inspected for proper function		

Have you completed a hazard assessment (HA) on your process that includes the precursors and any emissions from the process including the nanoparticles themselves?		
Have you secured the latest SDS versions from the vendors for the chemicals of interest?		
Are safety glasses, goggles, flame retardant (for PP chemicals) lab coats and face shields available?		
Have you prepared your emergency response procedure and cleared it with EH&S or potential responders? Are Class B & Class D fire extinguishers available in the lab?		
Is a laboratory chemical fume hood or secured space available to conduct the experiment?		
Is the chemical fume hood free of clutter (solvent bottles, samples, combustible materials)?		
Is inert gas (dry nitrogen or argon) available in the hood or where the reaction is being conducted?		
Is an inert gas delivery system (Schlenk line) or manifold available in the hood?		
Is a vacuum pump available to evacuate the equipment, if this technique is selected?		
Have you prepared your emergency response procedure?		
Is sufficient time available to complete the experiment?		

***NOTE:** Please do not proceed in case any items are noted with NO.

Table 2: Hazard Assessment: What if Analysis Examples

What if?	Answer	Result	Consequences	Recommendations
Glassware is not moisture-free for manipulating metal nano particles	Possibility of a runaway rxn due to moisture	A fire or an explosion	Likelihood of loss of material, and property loss, and chemical exposures	Glassware should be flame-dried under vacuum or assembled after being dried in the oven and allowed to cool to room temperature under vacuum.

Pyrophoric nanomaterial container opened in the air without N2	Introduction of Into container	A fire and explosion can occur	Product and undesired events	All small-nanomaterials should be handled under an inert atmosphere.

Prudent Practices for Nanomaterial Handling

- Administrative controls, such as proper signage and labels, access control, and a lab-specific chemical hygiene plan, including SOPs, are critical parts of good laboratory practices. These are a fragment of a hierarchy of controls (Fig. 3) supporting the implementation of feasible and effective control solutions.
- Housekeeping is an important aspect to prevent any exposures to nanomaterials. The work area and equipment should be cleaned regularly to avoid any exposure. Immediately clean spills involving nanomaterials according to written protocols or SOPs and using proper personal protective equipment. Typical methods for cleaning spills can be used for cleaning surfaces contaminated with dry powder nanomaterials. Never use flammable solvents for cleaning nanomaterials with flammable or pyrophoric properties. Clean dry nanomaterials with damp cloths, or by wetting the powder before wiping. Avoid using compressed air or other high-energy techniques, such as brushing or shaking, to remove nanomaterials from clothing.

- Educate the students/researchers on the safe manipulations of engineered nanomaterials or nano-object-containing materials to minimize the possibility of inhalation exposure and skin contact.
- The use of nanopowders that are pre-mixed in a liquid may reduce the potential for airborne exposure if they are compatible with the process.
- Avoid skin contact with nanoparticles or nanoparticle-containing solutions by using appropriate personal protective equipment. The NIOSH-PPE program has the most up-to-date information on appropriate personal protective methods for researchers/staff safety.
- Dry sweeping or air hoses should NOT be used to clean work areas. Cleanup should be conducted in a manner that prevents worker contact with wastes.
- Avoid handling nanomaterials in the open air in a ‘free particle” state.
- Store dispersible nanomaterials, whether suspended in liquids or in a dry particle form in closed (tightly sealed) containers whenever possible.
- Provide information, as needed, on the hazardous properties of the precursor materials and those of the resulting nanomaterials product with instruction on measures to prevent exposure.
- A flame-retardant lab coat is recommended when manipulating metal nanoparticles.
- When nanomaterials are present in an organic solvent, glove choice should be based on the suitability of the glove for protection against the particular solvent.

- Ensure that engineered nanomaterials are not transported outside the work area without secondary containment.
- Gloveboxes should be maintained at slightly negative pressure so leaks are into the box rather than out of the box.
- Utilize NIOSH-approved respirator filters that are rated as N-, R- or P-100 (HEPA) for respiratory protection where airborne exposure to engineered nanomaterials is expected (e.g. cleanout of systems used for the growth of carbon nanotubes).
- If you are using needles and cannula for nanomaterial manipulations, clean properly them using either vacuum or nitrogen pressure before drying as shown in Fig. 6.

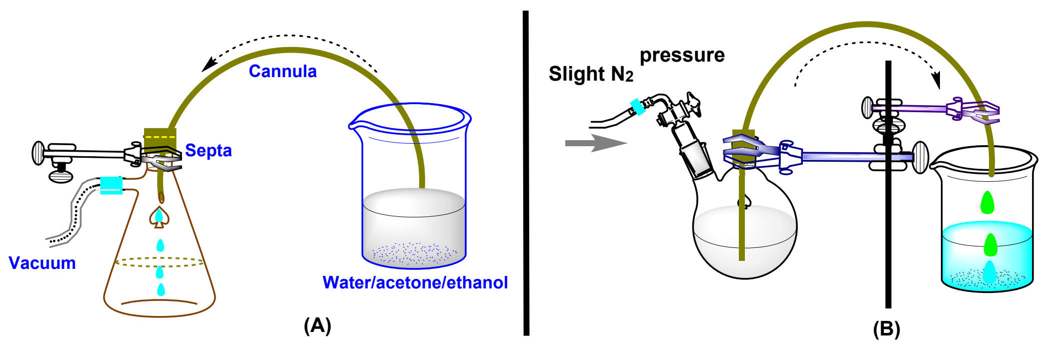

Figure 6. Cleaning Cannulas Using Vacuum and Nitrogen

- Avoiding storing and consuming food or beverages in workplaces where nanomaterials are handled.

Personal Protective Equipment

Face: Chemical splash goggles, use of a face shield is recommended when working with reactive precursors and pyrophoric nanomaterials.
Body: A lab coat with long sleeve (to the wrist) and closed toed shoes.
Gloves: Nitrile, butyl, latex or viton/butyl. Please remember, nitrile gloves are combustible.

Training

Make sure that the students and researchers have both general safety training and lab-specific training relevant to the nanomaterials and associated hazardous chemicals used in the process/experiment. Prior to working with any nanomaterials, the PI or lab

CHOs/manager must provide training to his/her laboratory personnel specific to the hazards involved in working with the precursors, chemical manipulations, and emergency procedures.

NOTE: *EH&S is available to assist in the education and training of personnel concerning safe work practices.*

Emergency Procedures

The following emergency measures are recommended when dealing with nanomaterial related emergencies.

- The students or researchers should be:
  - Trained to recognize critical conditions and hazards associated with the materials.
  - Given precise shut-down instructions in the event of critical conditions.
  - Fire-extinguishing equipment, Class D, in case a pyrophoric material is generated during manipulation.

Disposal

The nanomaterials generated in labs may have unique physical and chemical properties which may affect disposal routes. The best plan is to work with chemical safety (608-265-5700) before generating waste to plan for future disposal. As a general rule of thumb, all unused nanomaterial, solutions, that contained stock, unused material, spill clean-ups, and grossly contaminated items shall be disposed of through the EH&S. Collect and store waste/unwanted materials in a tightly closed container. Include information describing the nanomaterial nature of the materials on the waste tag (e.g. “contains nanosilver material”).

References and Important Links

The following references and links provide additional information on the hazards associated with nanomaterials and safe work practices:

1. Approaches to safe nanotechnology, https://www.cdc.gov/niosh/docs/2009-125/pdfs/2009-125.pdf (Accessed on 05/27/2021)
2. WS_2 Nanobuds as a New Hybrid Nanomaterial, https://pubs.acs.org/doi/pdf/10.1021/nl0719426

3. Controlling Health Hazards When Working with Nanomaterials: Questions to Ask Before You Start https://www.cdc.gov/niosh/docs/2018-103/pdfs/Nano_MP2_2018-103_508.pdf?id=10.26616/NIOSHPUB2018103 (Accessed on 06/27/2022)
4. Hill, R. H, Jr.; Finster, D. C. Laboratory safety for chemistry students, 2nd ed.; Wiley: Hoboken, NJ, **2016**.
5. Nanomaterials, https://ehs.stanford.edu/wp-content/uploads/Working-Safely-with-Engineered-Nanomaterials.pdf (Accessed on 06/27/2022)
6. ACS-Committee on chemical safety, Nanotechnology safety resources, https://www.acs.org/content/acs/en/about/governance/committees/chemical-safety/publications-resources/nanotechnology-safety-resources.html (Accessed on 06/27/2022).
7. The Chemical Safety: https://ehs.wisc.edu/labs-research/chemical-safety/

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