NANOMATERIAL SAFETY MANUAL

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1. Introduction:

Nanotechnology offers great promise of scientific advancement in different sectors including medicine, consumer products, energy, materials and manufacturing. Nanotechnology undoubtedly presents limitless possibilities like any new technology but it also brings new challenges to understanding, predicting and managing potential safety and health risks to workers/researchers.

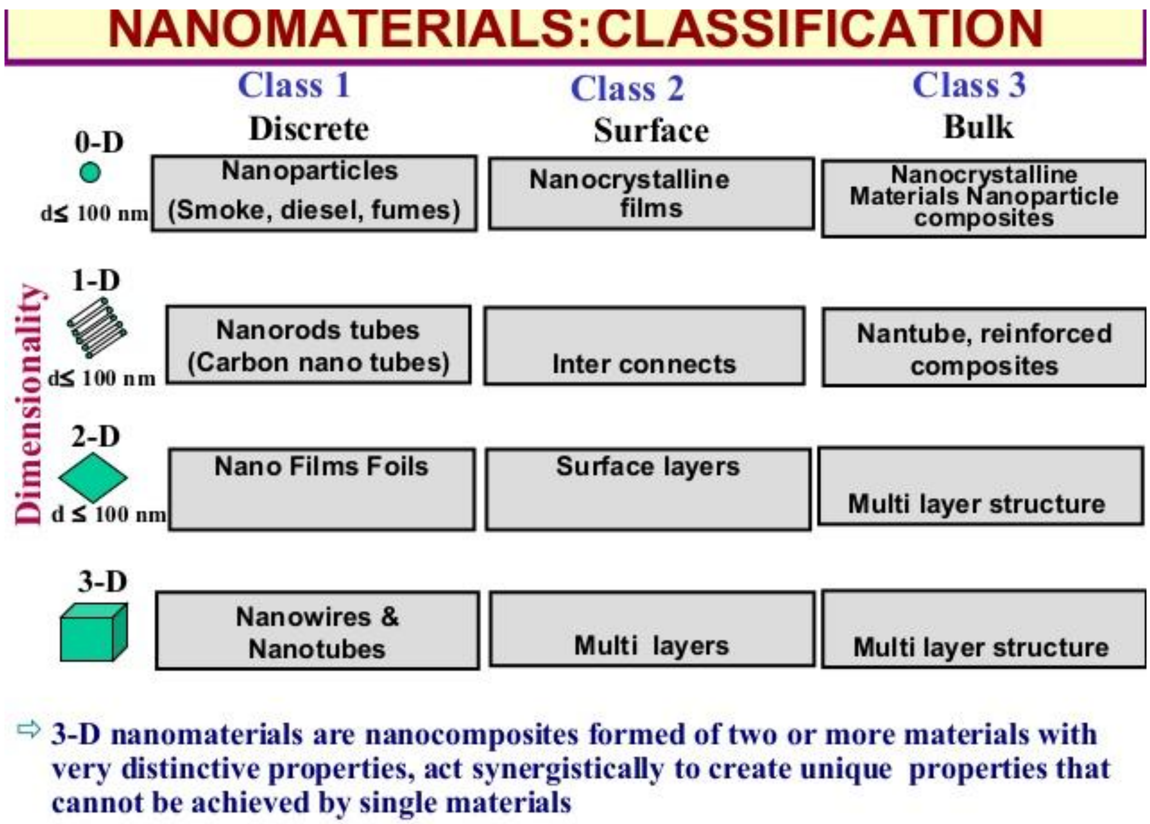
This manual is prepared with the intension to provide precautionary principles to be followed while working with the nanomaterials (NMs) or nanoparticles (NPs). Nanomission, DST, Government of India has come up with document on "Guidelines and Best Practices for Safe Handling of Nanomaterials in Research Laboratories and Industries" which is available at the link http://nanomission.gov.in/What_new/Draft_Guidelines_and_Best_Practices.pdf

2. Important Definitions:

a. Nanomaterial (NM): nano-sized material having at least one external dimension in the size range of 1-100 nanometers. NMs include nanoparticles (NPs), nanostructured materials and ultrafine particles, and their agglomerates and aggregates.
b. Nanoparticle (NP): NM having all three external dimensions in the size range of 1-100 nanometers and its physicochemical properties are distinctly different than its bulk material of the same composition.
c. Nanostructured material: NM having distinct structural elements with dimensions in the size range of 1 to 100 nm. Nanostructured materials include nano-sized clusters, nano-crystallites or molecular composites.
d. Ultrafine particles: Aerosolized NMs including incidental NPs derived from aerosols and their agglomerates are defined as ultrafine particles.
e. Agglomerates: group of NPs held together by weak interactions, such as Van der Waals forces, electrostatic forces and surface tension such that NPs are separated relatively easily with mild perturbation.

f. Aggregates: heterogeneous NPs in which various components are not easily separated as they are held together by relatively strong forces.

3. Classification of nanomaterials:



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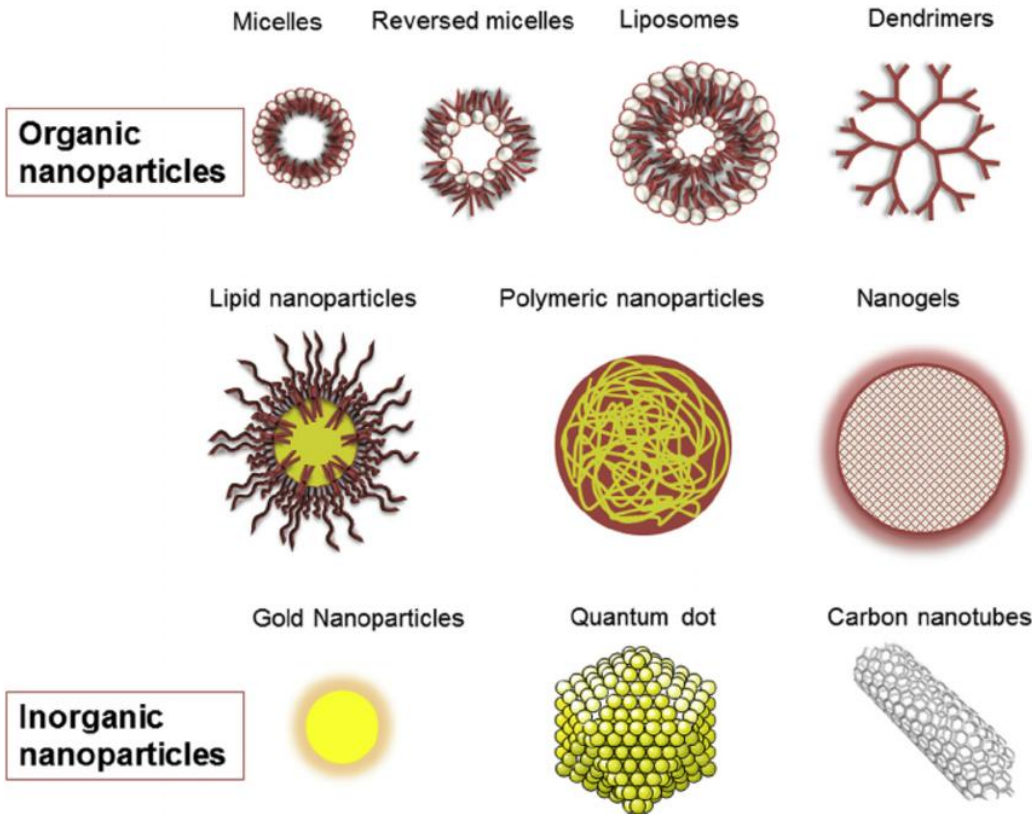

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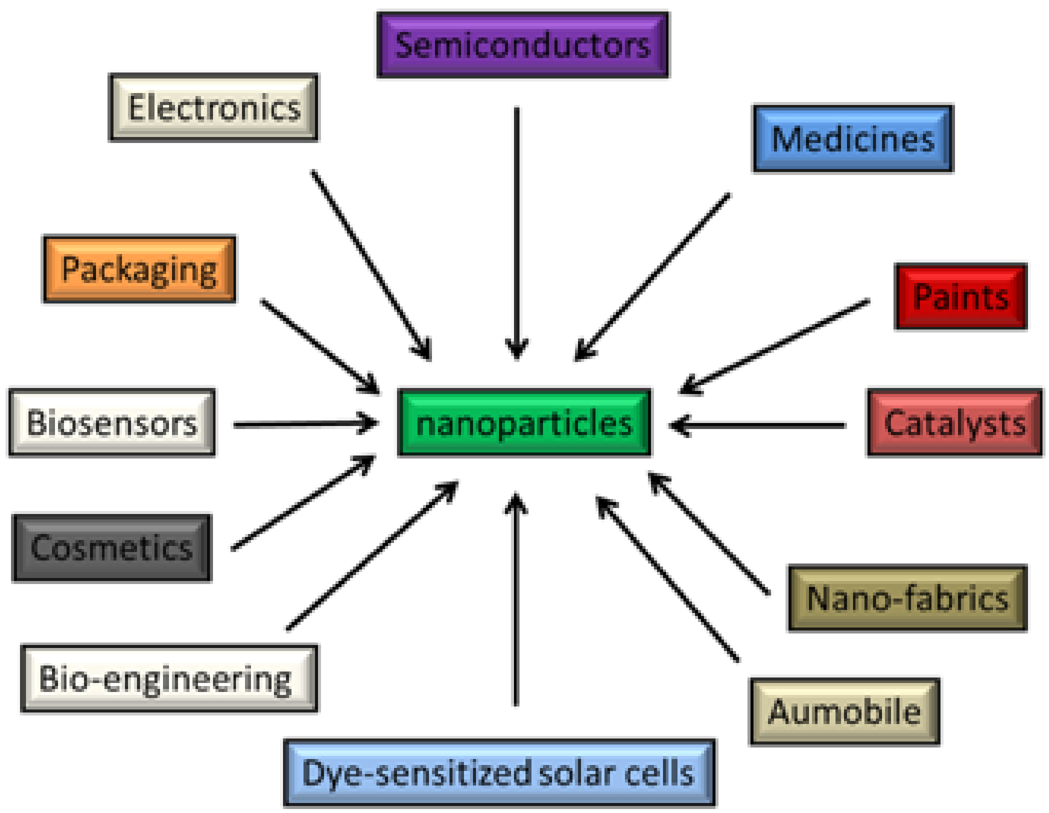
4. Applications of nanomarticles:

Table 1: Applications

Applications	Nanomaterials used
Electronics, ICT and photonics	Carbon nanotubes, fullerenes
Pharmaceuticals and medicine	Nanomedicines and carriers
Cosmetics and personal care	Titanium dioxide, zinc oxide, fullerenes, gold
Catalysts and lubricants	Cerium oxide, platinum, molybdenum trioxide
Paints and coatings	Titanium dioxide, gold, quantum dots
Environmental and water remediation	Iron, polyurethane, carbon nanotubes silica as carrier
Food packaging	Gold, nanoclays, titanium dioxide, silver



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5. **Why precautions with Nanoparticles?**

Though there is lack of scientific proof on nanoparticle hazards and health effects exists, it shouldn't be taken as an excuse to postpone the practice of safety measures that could prevent human exposure and environmental release. Following are the important points to be noted when working with NMs or NPs. Also safety measures to be developed and practiced in order to minimize the exposure to the nanoparticle hazards.

1. NMs impart greater toxicity than micro-sized bulk materials of the same composition.
2. NMs in insoluble form(s) can impart greater toxicity in the human body than micro-sized materials of the same chemical composition that are solubilized in water.
3. NMs with fresh active surfaces are more reactive than encapsulated NMs (treated to reduce chemical reactivity of surface).
4. Unbound or free NPs can pose a more severe health hazard than the bound or embedded NMs.

5. The duration, magnitude of exposure, and persistence of NMs in the human body can have adverse health effects.

6. What we know about nanoparticle/nanomaterial health hazard?

Limited information from research and animal studies on nanomaterials has identified some potential safety hazards and health effects. Inhalation of nanoparticles may be deposited in the respiratory tract and may cause inflammation and damage to lung cells and tissues.

Ex: Carbon nanotubes/nanofibres, might make their way to the lungs and cause mesothelioma.

Titanium dioxide (TiO2), which has many commercial applications (in paint, paper, cosmetics, food industry), can be produced and used in varying particle sizes, inhalation of these particles is believed to be an occupational carcinogen.

Nanotechnology is a rapidly emerging field; more information will likely become available about potential health hazards associated with nanomaterials.

7. Exposure

Table 2: Route of entry, pathway and safety measures

Route of entry	Pathway	Safety measure
Dermal	Nanoparticles can migrate through skin and circulate in the body while handling nanoparticle suspensions or dry powders. Skin absorption is much less likely for solid bound or matrixed nanomaterials	Wear gloves and lab coat while handling the nanoparticles.
Ingestion	Ingestion can occur if good hygiene practices are not followed. Nanoparticles might be absorbed and transported	Eating and drinking are not allowed in laboratories. Spills of nanoparticles should be quickly and properly cleaned-

	within the body by the circulatory system	up; Use masks.
Injection	Exposure by accidental injection (skin puncture), when working with animals or needles.	Wear gloves and lab coats, and apply the standard practices for working with sharp objects.
Eyes	Exposure to airborne nanoparticles placed near the eye, accidentally splashed onto the eye or transferred from hands during rubbing of eyes.	Wear safety glasses, goggles, full face piece respirator (Recommended when there is exposure to solvent or hot material). Do not wear contact lenses at work place.

8. How to control the hazard exposures:

A. A hazard assessment should be performed to control and minimize the exposures to research staff and laboratory personnel.

B. The hazard assessment includes evaluation of material identity, process description, availability of engineer controls, typical quantity of NMs used per operation, anticipated airborne concentration levels outside the engineering controls (if any), duration and frequency of exposure and toxicity levels.

C. Develop standard operative procedures for the lab and train the researchers for safe handling of nanomaterials.

D. Prevent or control the risks using appropriate engineering controls /PPEs /and best practices.

E. Engineering controls:

- Research Laboratory must have exhaust ventilation system with high-efficiency particulate air (HEPA) filters for capturing airborne nanoparticles.
- Use glove bags, glove boxes, fume hoods, or other containment or exhausted enclosures when there is a potential for aerosolization, such as: handling powders; creating nanoparticles in gas phase; pouring or mixing liquid media which involves a high degree of agitation.
- DO NOT use horizontal laminar flow hoods (clean benches), as these devices direct the air flow towards the worker.
- Use fume hoods or other local exhaust devices to exhaust tube furnaces and or chemical reaction vessels.
- Air lock and sealed containers are to be used for collecting nanomaterials from reactors.
- Use of distillation system for evaporating solvent from a colloidal dispersion within an explosion-proof enclosure.
- Remote control set up for nanomaterial production equipment is advised.

F. PPE: Personal Protective Equipments (PPE)

Wearing PPE is one of the best methods for avoiding exposure to the nanoparticles. Typical protective clothing should include:

- Long sleeved shirt.
- Nitrile gloves with extended sleeves. (Note: Advisable to use two pairs of gloves, as in case of carcinogenic material, to exercise abundant caution).
- Closed-toed shoes made of a low permeability material
- Long pants.

- Chemical splash goggles, safety glasses and full-face shields are recommended for eye protection when there is potential for exposure to nanomaterials.
- Respiratory air filters (N100 recommended or N95).

G. **Labeling: Labeling and signage:**

- Store NPs/NMs in a well-sealed container, preferably one that can be opened with minimal agitation of the contents.
- Label all chemical containers with the name of the content (avoid abbreviations/ acronyms) include term “nano” in descriptor (e.g., “nanozinc oxide particles” rather than just “zinc oxide.” Hazard warning and chemical concentration information should also be included.
- Use cautious judgment when leaving operations unattended:
- Post signs to communicate appropriate warnings and precautions,

H. **Spill cleanup:** Very important part of safety management, one should be very careful about exposure during cleaning operations.

- Wear PPE
- If needed, monitor the lab air nanomaterial concentrations during clean-up.
- Wear respiration protection when working outside a fume hood or in an open fume hood and consider overall protection.
- All contaminated material must be disposed of as chemical waste.

Materials and surfaces can be cleaned by following techniques:

- o Wiped with a wet cloth (use water or solvent) where possible, rinsing off the cloth with water or disposing it off.
- o Vacuum cleaned, where the exhaust of the vacuum cleaner is equipped with a HEPA filter and is not equipped with a pressure relief valve that bypasses this HEPA filter if blocked. Monitor the exhaust of the vacuum cleaner during operation. A malfunctioning filter can increase the exposure by dispersing the nanomaterial in the air.

  - HEPA-filtered vacuum cleaners with combination of wet wiping are more suitable for most nanomaterial clean-up.
  - Dry cleaning or use of compressed air should be prohibited.
    - Collect spill cleanup materials in a tightly closed container.
    - Manage spill cleanup debris as hazardous waste.

Nanoparticle spill kit containing the following items must be readily available to respond to spills.

- No Entry sign
- Latex or nitrile gloves.
- Disposable N100 (best rated filter by the CDC and WHO and is recommended for ultimate protection, have a minimum filter efficiency of 99.97% of particulate matter of average particle size less than 0.3 micron.) respirators.
- Adsorbent material
- Wipes
- Sealable plastic bags
- Dry materials

➢ Do not dry sweep spilled accumulations of dry nanomaterials. Small quantities of dry materials (i.e., gram quantities) can be cleaned up with wet wipes. Dispose of the wipes as hazardous waste, as described above. Significant spills should be vacuum cleaned. Use only HEPA-filtered vacuum cleaners to clean up nanoparticles.

➢ Ensure that the functioning of the HEPA filters is properly tested as frequently as the manufacturer's recommends. HEPA vacuums for nanomaterials should be dedicated and labeled "For Use with Nanomaterials Only".

➢ Used HEPA filters must be appropriately characterized, collected, and disposed of as hazardous or potentially hazardous waste based on the material involved.

9. Waste management:

A specific guideline for the waste disposal of nanomaterials is not yet in practice. Research data proves time to time the possible toxic effects of nanomaterials. Hence researcher should make every effort to prevent the release of Nanomaterials to the environment.

- ✓ A Milligram or above quantities of nanomaterials (powders, colloids) should be treated as hazardous chemical waste, if the particle solubility in water is very small (inorganic materials like metals, metal oxides etc.).
- ✓ Do not put engineered nanomaterials waste in the regular trash or dump it down the drain.
- ✓ All nanomaterials waste should be collected in labeled, enclosed hazardous waste containers with secure caps or covers. The waste Tag should include a description of the waste and prominently the words "contains nanomaterials".
- ✓ Sharps and needles should be disposed of separately in the sharp containers.
- ✓ Collect paper, wipes, PPE and other items with loose contamination in a plastic bag or other sealable container and store it in waste collection area of the laboratory, put waste Tag with words 'contains nanomaterials', securely tie or seal it, and dispose of it as hazardous waste following the standard procedures. Principal Investigator can discuss with chemical/Biological Safety office to decide final disposal of nanomaterial waste from the campus.

10. Best work practice:

i. Good Housekeeping:

- Good housekeeping practices in laboratories where nanomaterials are handled can minimize the risk of exposure.
- Clean all working surfaces potentially contaminated with nanoparticles (i.e., benches, glassware, apparatus, exhaust hoods, support equipment) at the end of each day using industrial vacuum cleaner equipped with HEPA filters.

ii. Hygiene:

- Do not consume or store food and beverages, or apply cosmetics where chemicals or nanomaterials are used or stored since this practice increases the likelihood of exposure by ingestion.
- Do not use mouth suction for pipetting or siphoning.
- Wash hands frequently to minimize potential chemical or nanoparticle exposure through ingestion and dermal contact.
- Remove gloves when leaving the laboratory, so as not to contaminate doorknobs, or when handling common use objects such as phones, multiuser computers, etc.

iii. Work practices:

- Whenever possible, handle nanomaterials in solutions or attached to substrates to minimize airborne release.
- Consult the material safety data sheet (MSDS), if available or other appropriate references prior to using a chemical or nanomaterial.
- While working with nanomaterials in liquids:

✓ Avoid spreading of the liquid by working in a spill container.

✓ Wear gloves that are suited for the liquid being handled.

✓ Avoid the dispersion of liquid droplets in the lab air.

✓ Directly clean up spills, before evaporation or further spreading occurs.

- While working with nanomaterials in gas phase reactors

✓ Work in a closed reaction vessel, preferably around atmospheric or lower than atmospheric pressure.

✓ Make sensitive leak checks between runs.

✓ When working with systems under positive pressure obey the standard safety rules for pressurized vessels and put the vessel into an enclosed safety vessel.

✓ For small positive pressure set-ups a closed fume hood is sufficient.

- ✓ Mount a HEPA filter (e.g. Emflon PFR filter from pall, > 3 nm) on the exhaust side of the process before leading into the fume hood and the outside air.
- While working with nanomaterial powders
- ✓ Handle free nanomaterial powder exclusively in a closed fume-hood or an enclosed vessel (glove box).
- ✓ If handling outside a closed environment cannot be avoided, wear class P3 (Filters at least 99.95% of airborne particles) certified respiratory filters.
- ✓ For characterization purposes such as XRD analysis, use a drop of oil to contain the powder and preventing it from becoming airborne.
- ✓ Clean all parts that have been in contact with nanoparticles and spills after using appropriate protection.

iv. Workplace monitoring:

- Reported studies have proved that the work place monitoring is important because it can significantly help the research group or organizations to describe the nanomaterial risk. The work place monitoring includes.
- Monitoring the particle concentrations at the working place using different types of particle counters, condensation particle counters, scanning mobility particle sizers or other means of particle collections, such as witness plates and particle size analysis by electron microscopy.

v. Storage:

- Storing nanoparticles might involve special protection to safeguard the products and to ensure workplace health and safety.
- Storage containers of nanoparticles should accommodate different granulometric characteristics and reactivity of particles.
- In order to avoid oxidation or explosion in case of certain metal nanoparticles, they are often needed to be protected from exposure in air and stored under inert gas/liquid bath.

References:

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