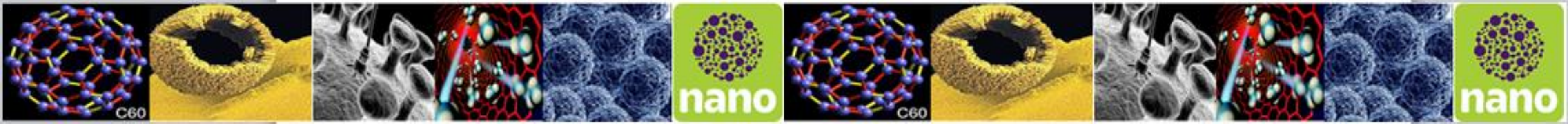

Nanomaterials Safety

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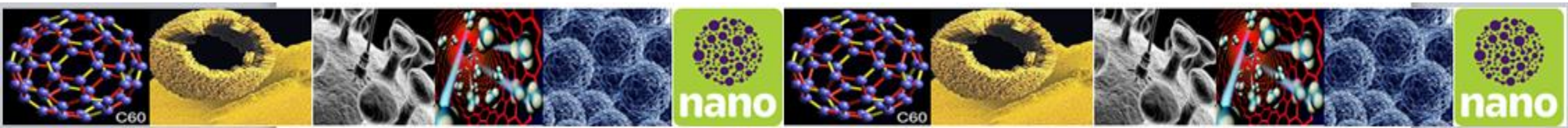
Wichita State University

April 25, 2014



Laboratory Safety Videos

https://www.youtube.com/watch?v=kqoXhAdAwrk Emergency Response (11:44min)

https://www.youtube.com/watch?v=vT8R6gYCn_0 Chemical Storage Hazards(11:16 min)

https://www.youtube.com/watch?v=fvYWY9In8fg Chemical Hazards (9:26min)

http://www.youtube.com/watch?v=fWBv9kDEcDQ Burning Nitrile glove with sulfuric acid (2:46min)

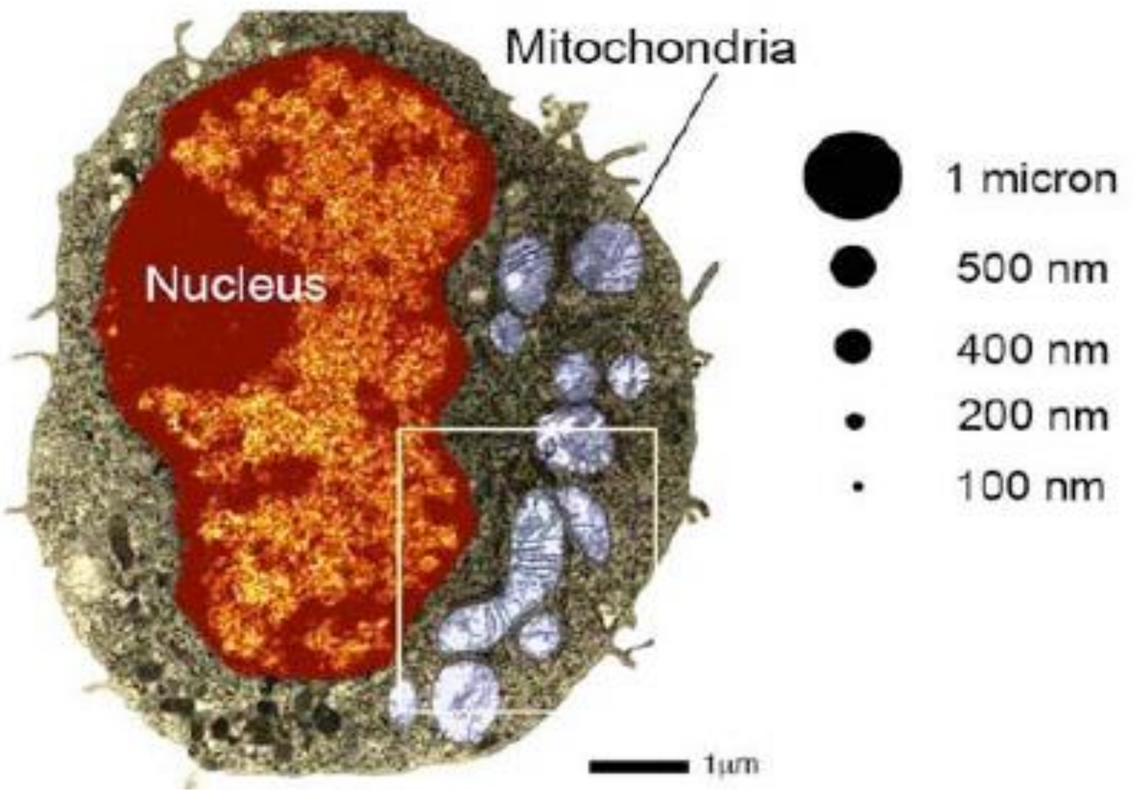
https://www.youtube.com/user/LabSafetyInstitute/videos

https://www.youtube.com/user/LabSafetyInstitute

http://blink.ucsd.edu/safety/research-lab/laboratory/videos.html

Training Objective

Provide information on the potential hazards and risks involved in nanotechnology and nanoproducts (or nanomaterials) and the control measures that should be utilized to limit exposures to student, staff and educator at WSU.

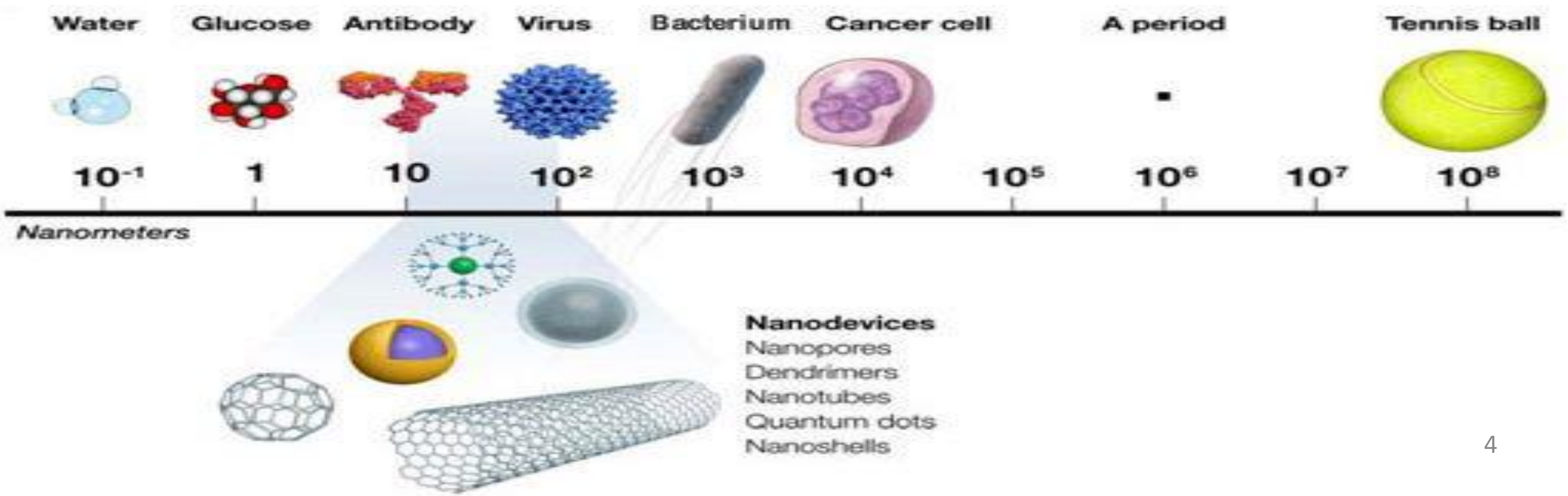


Real illustration of a cell with different micro and nanoparticles.

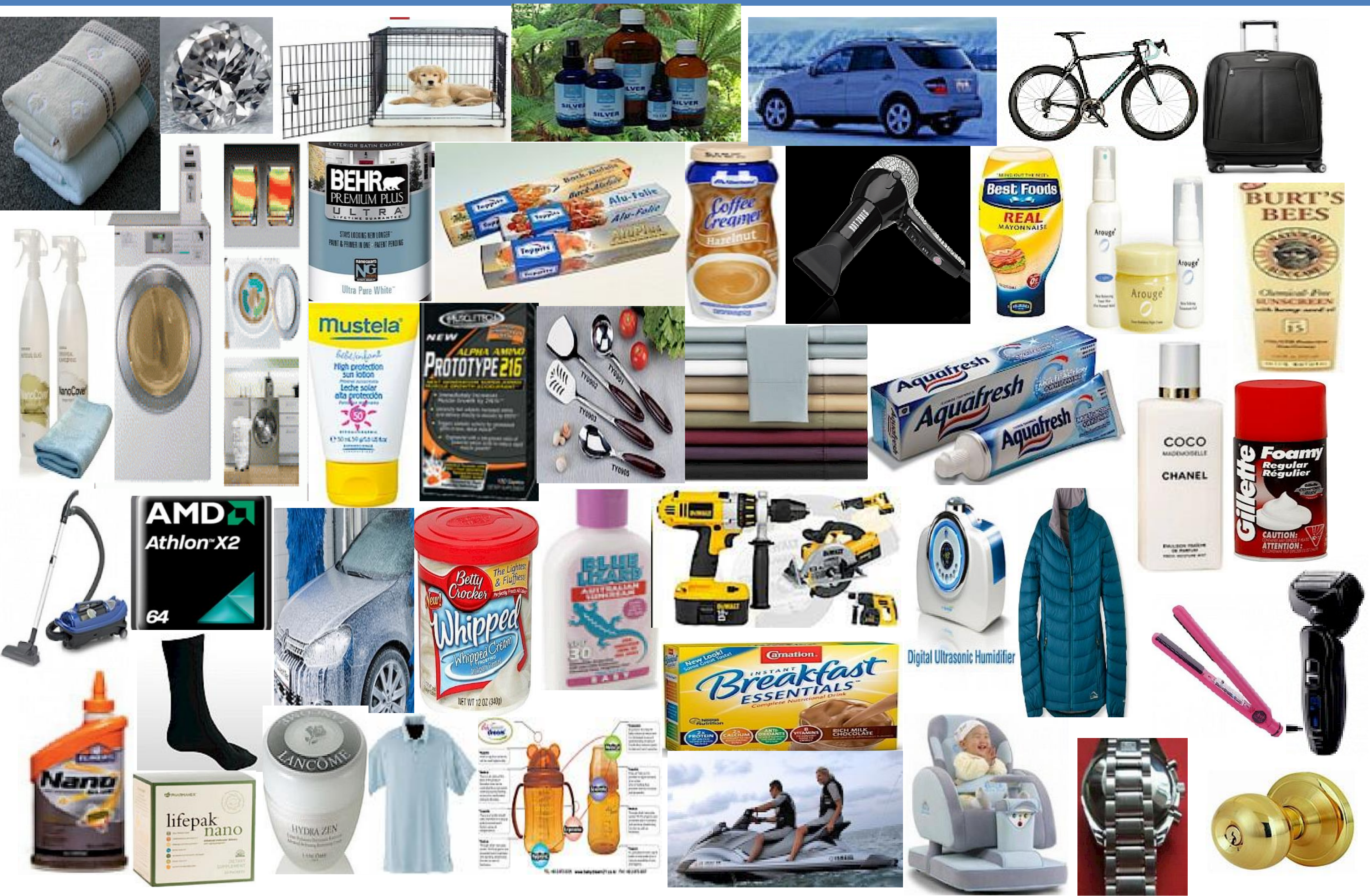
1 nm is invisible, but has highest surface area and energy to interact with cell DNA.

What is Nanotechnology?

- **Nanotechnology** is the manipulation of matter at an atomic, molecular, and/or supramolecular scale.
- Nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometers (1 nm = 10 Angstrom). A human hair is approximately 20,000 to 80,000 nm.
- At these length scales, materials begin to exhibit unique physical, chemical, physicochemical and biological properties that affect overall behavior of the materials.
- Variance in properties comes with both pros and cons.



Nanoproducts



Engineered Nanoparticles

Classifications	Examples
Dimensions	
3 dimensions < 100nm	Particles, quantum dots, hollow spheres, etc.
2 dimensions < 100nm	Tubes, fibers, wires, platelets, etc.
1 dimension < 100nm	Films, coatings, multilayer, etc.
Phase compositions	
Single-phase solids	Crystalline, amorphous particles and layers, etc.
Multi-phase solids	Matrix composites, coated particles, etc.
Multi-phase systems	Colloids, aerogels, ferrofluids, etc.
Manufacturing process	
Gas phase reaction	Flame synthesis, condensation, CVD, PVD, etc.
Liquid phase reaction	Sol-gel, precipitation, hydrothermal processing, etc.
Mechanical procedures	Ball milling, plastic deformation, etc.

Mechanisms Behind Toxicity of Nanomaterials

Toxicity of nanomaterials is primarily dependent on their surface properties:

- Surface Chemistry (hydrophobicity, hydrophilicity, aggregation)
- Particle Size (the smaller the size, the higher the toxicity)
- Surface Charge (including zeta potential and surface potential)
- Surface Area (playing a major role in the interaction of the materials with cells)
- Oxidative Stress and reactive oxygen species

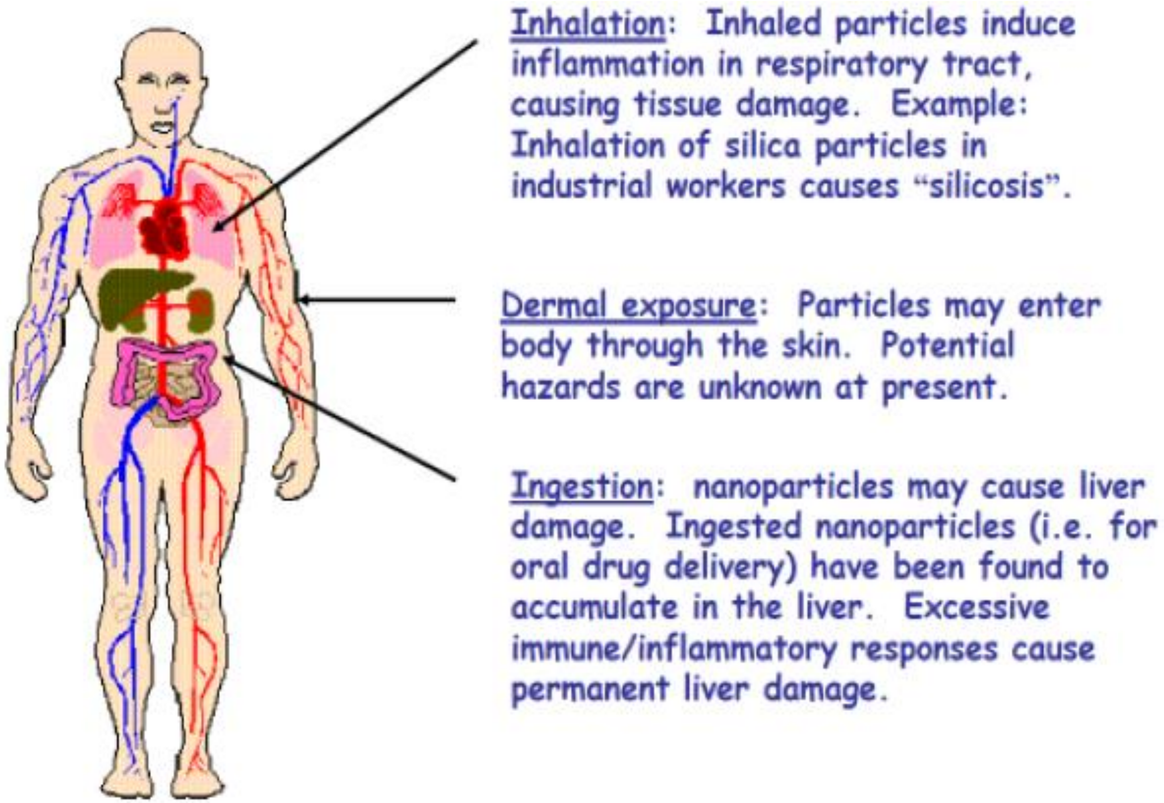
  In humans, **oxidative stress** is thought to be involved in the development of cancer, Parkinson's, and Alzheimer's diseases, heart failure, fragile X, autism, and many other genetic and chronic diseases.

Exposure Pathways

- Inhalation - most common.
- Ingestion - unintentional or swallowing particles cleared from respiratory tract.
- Dermal - possibly could penetrate skin.

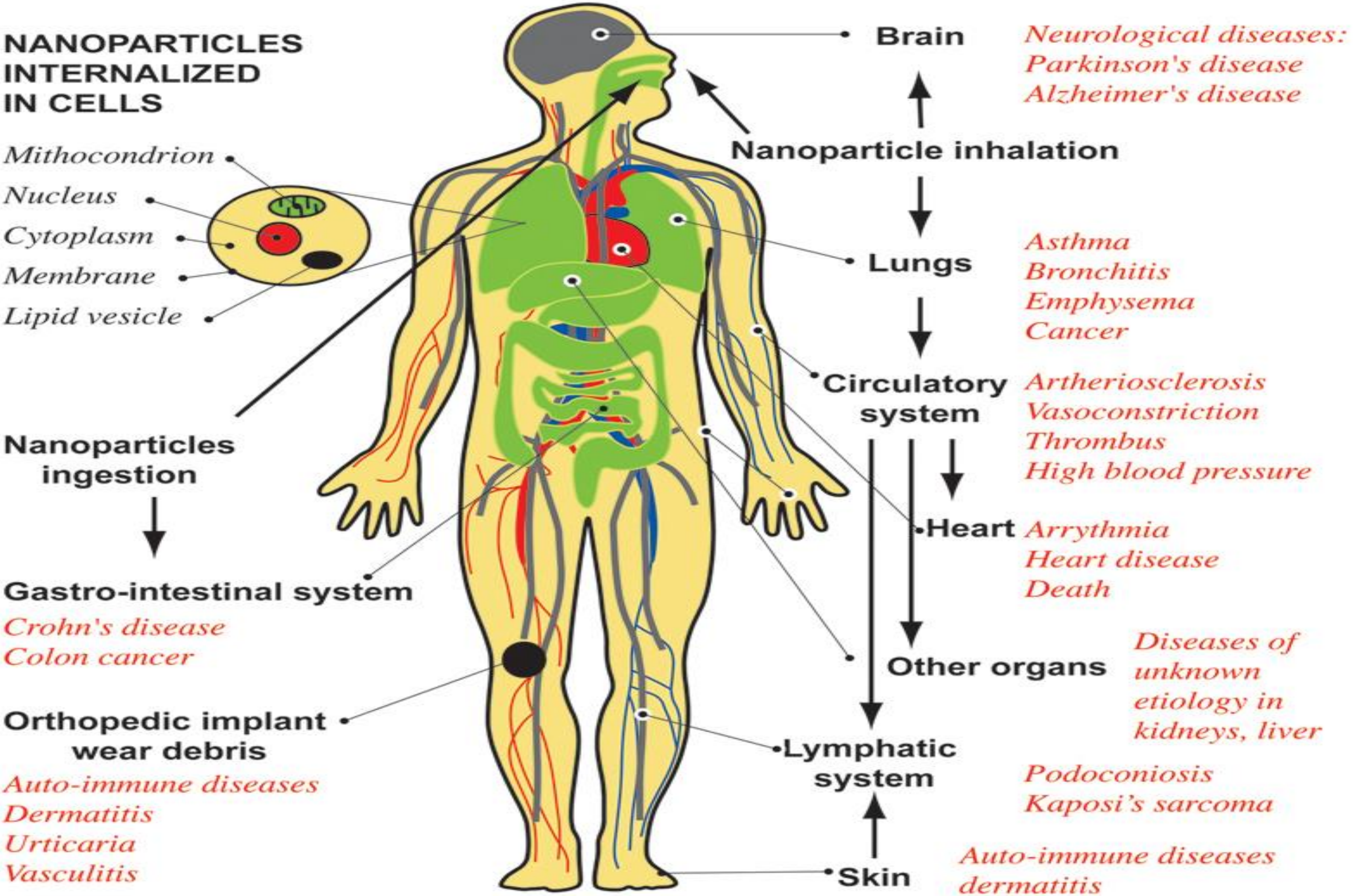
Exposure factors include:

1. Concentration
2. Duration
3. Frequency



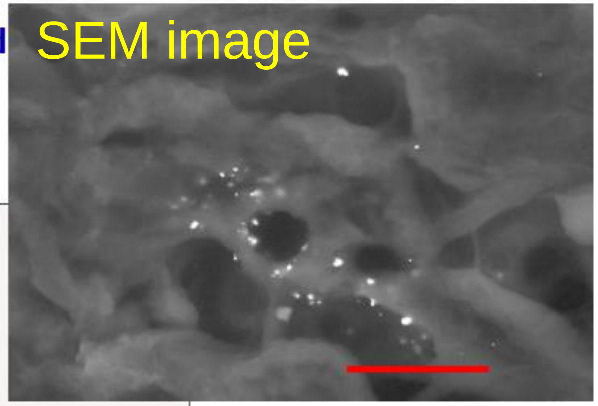
DISEASES ASSOCIATED TO NANOPARTICLE EXPOSURE

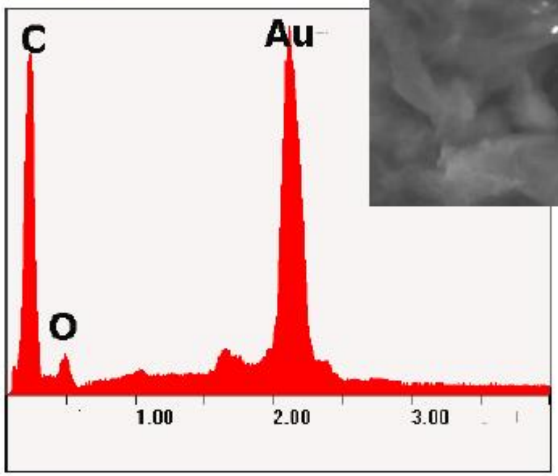
C. Buzea, I. Pacheco, & K. Robbie, Nanomaterials and nanoparticles: Sources and toxicity, Biointerphases 2 (2007) MR17-MR71



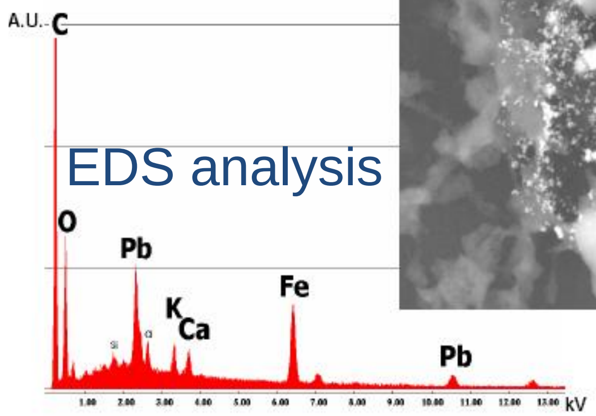
Nanomaterials in Body

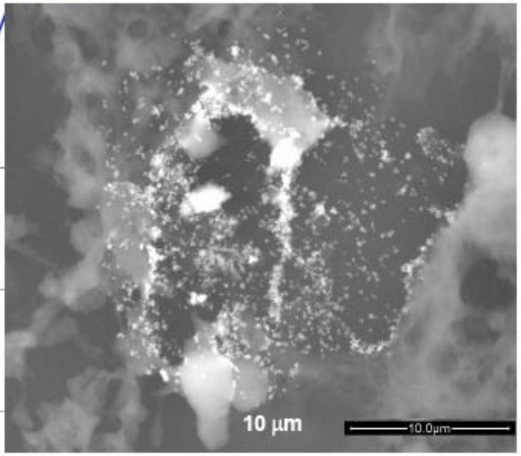
Nanoparticles of Gold in a liver granuloma.
The patient was treated with colloidal gold particles for knee arthrosis



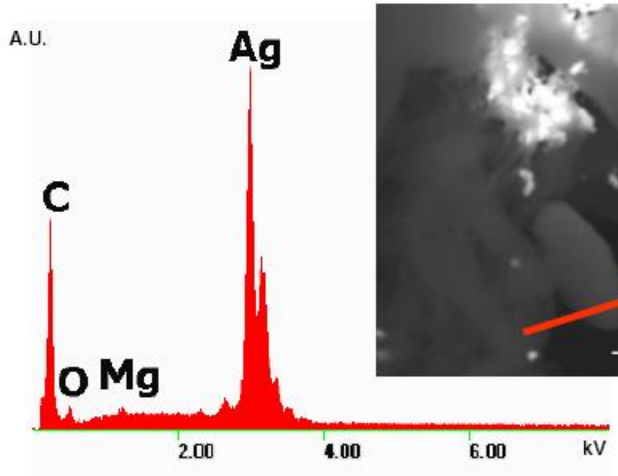


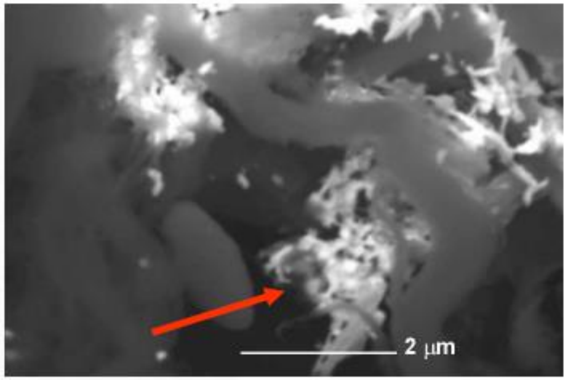
Nanoparticles of a Lead compound in the lung. The patient was affected by a multiorgan granulomatosis





Cancerogenic tissue of the colon with aggregates of nanoparticles of Silver-Magnesium





SEM / EDS analysis of nanoparticle exposed areas in human body.

Hazards of Nanoparticles

- Little information about hazards of nanomaterials and nanoparticles.
- OSHA currently has limited Occupational Exposure Limits (OELs) for nanomaterials.
  - OSHA recommends that worker exposure to respirable **carbon nanotubes** and **carbon nanofibers** not exceed 1.0 micrograms per cubic meter ($\mu g/m^3$) as an 8-hour time-weighted average, based on the National Institute for Occupational Safety and Health (NIOSH) proposed Recommended Exposure Limit (REL).
  - OSHA recommends that worker exposure to nanoscale particles of **TiO_2** not exceed NIOSH's 0.3 milligrams per cubic meter (mg/m^3) REL. By contrast, NIOSH's REL for fine-sized TiO_2 (particle size greater than 100 nm) is 2.4 mg/m^3.
- Concerns include **inhalation**, **ingestion** and **skin exposures**.
- Various Federal agencies (OSHA, NIOSH, EPA) are actively working to figure out how to protect workers and the environment.
- Nanoparticles have highest risk for exposure to a surface/organ.

Mineral dust composition can contain particles of crystalline silica, asbestos, carbon black and other molecules. These particles are the most common causes of particle-induced pulmonary fibrosis.

Known nano/micro particle hazards include:

- **Asbestos:** Asbestos is a toxic, naturally-occurring fibrous mineral that is mined and processed for use in a number of industrial and commercial products. Respirable asbestos fibers range in size from .01 µm to 20.0 µm wide. That is, asbestos fibers are naturally-occurring nanoparticles
- **Coal mine dust:** Known for over 1000 years
- **Silica:** Known for over 5000 years
- Assume all nanoparticles are hazardous!

Toxicity Information for Nanomaterials

- Be aware that many Safety Data Sheets (SDSs) currently shipped with nanomaterials refer to the bulk material toxicity information, which is inappropriate for the nanomaterial.

- If no information is available for your materials or the toxicity information is limited or uncertain, handle the material as if it is toxic.

- The best place to keep up to date is the International Council on Nanomaterials (ICON) database which collects toxicity and environmental information by nanoparticle type (see references for link).

Preplan Ahead of Time

- Preplan the experiments and determine equipment and procedures needed for preventing inhalation, skin or ingestion exposures, laboratory contamination, and for properly dispose of all nanomaterial waste.

- Have appropriate spill materials on hand before beginning your work. Equipment setup may require additional exhaust ventilation and installation or the use of respirators.

- All users of respirators must be fit tested to insure they are wearing the proper size. Contact the EHS Office for ventilation changes and respirator fit testing.

Job Related Activities

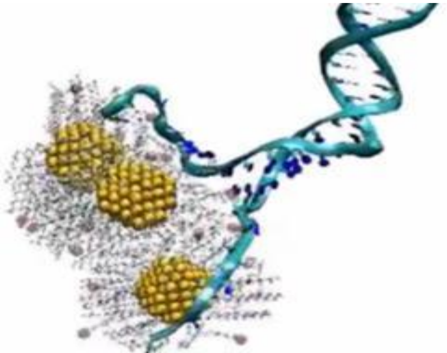
- Handling powders of nanomaterials.
- Working with nanoparticles in liquid media without appropriate protection.
- Generating nanoparticles in open systems.
- Maintenance on equipment and processes used for fabrication.

Ventilation, fume hood, filters

Risk Assessment

- Base your risk assessment on the type of nanomaterial (composition, shape, size, surface area, physical status)
- The Nanomaterial Risk Level (NRL) summary chart is a helpful tool to use for your initial risk assessment.
- Reference Safety Data Sheet (SDS).
- Utilize the proper engineering controls.
- Utilize personal protective equipment (PPE).
- Institute work practice controls.
- Contact EHS (978-3347) if assistance is needed.

DNA nanoparticle interactions

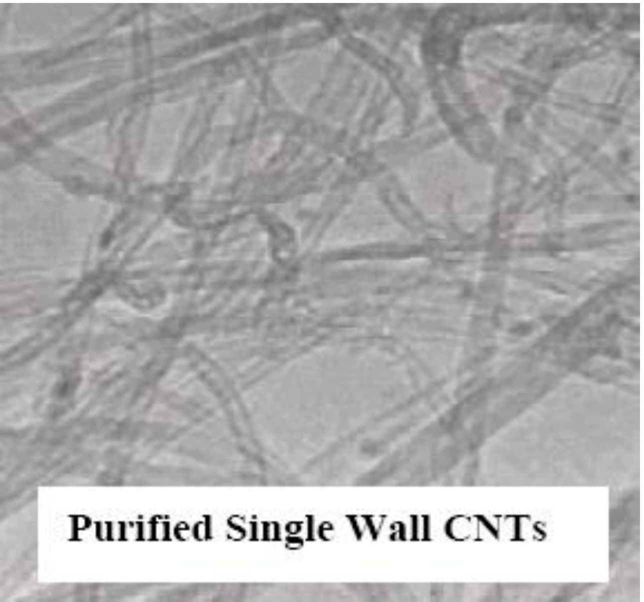


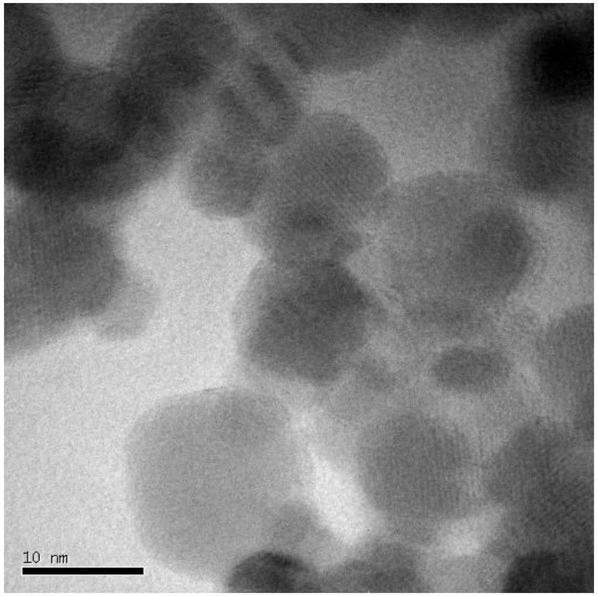
Nanomaterial Risk Level (NRL)

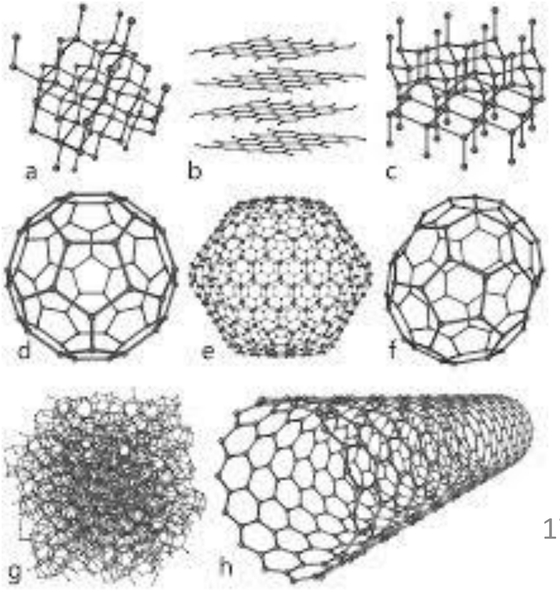
NRL	Type of Nanomaterial	Practices	Engineering Controls	Personal Protective Equipment (PPE)
1	Polymer matrix	Standard Laboratory Practices including: • Lab Safety Plan should be updated with NRL defined • Labeling of storage containers of nanomaterials with both the chemical contents and the nanostructure form	Fume hood or biological safety cabinet (Class II Type A1, A2 vented via a thimble connection, B1 or B2)	Standard PPE (lab coat, gloves, safety glasses with side shields)
2	Liquid dispersion	NRL-1 practice plus: • Use secondary containment for containers that store nano-materials • Wipe contaminated areas with wet disposable wipes • Dispose of contaminated cleaning materials as segregated nanomaterial waste	Fume hood or biological safety cabinet (Class II Type A1, A2 vented via a thimble connection, B1 or B2) or approved vented enclosure (e.g., Flow Sciences vented balance safety enclosure [VBSE])	NRL-1 practice plus: • Nitrile gloves • Safety goggles
3	Dry powders or aerosols	NRL-2 practice plus: • Vacuum with HEPA-equipped hand vacuum cleaner • Label work areas with "Caution Hazardous Nanoscale Ma-terials in Use"	Fume hood or biological safety cabinet (Class II Type A1, A2 vented via a thimble connection, B1 or B2) or approved vented enclosure (e.g., Flow Sciences vented balance safety enclosure [VBSE]). HEPA fil-tered exhaust preferred for fume hoods containing particularly "dusty" operations.	NRL-2 practice plus: N95 respirators are required if work operation must be done outside of containment
4	Dry Powders or aerosols of parent materials with known toxicity or hazards	NRL-3 practice plus: • Baseline medical evaluation or employees including physi-cal exam, pulmonary function test (PFT) and routine blood work. • Access to the facility should be permitted only to persons who are knowledgeable about the hazards of the material and the specific control measures implemented to avoid exposures and/or environmental releases. These control measures should include work practices (SOPs), engineer-ing controls, spill and emergency procedures, personal protective equipment, disposal procedures, and decon-tamination/clean up procedures. Department procedures should address the designation and posting of the labora-tory, how access will be controlled, and any required entry and exit protocols.	Fume hood or biological safety cabinet (Class II Type B1 or B2) or glove box or approved vented enclosure (e.g., Flow Sciences vented balance safety enclosure [VBSE]). HEPA filtered exhaust with Bag-In/Bag-Out capability preferred for hoods, BSCs, and gloveboxes.	NRL-3 practice plus: Need determined and respirator selected with refer-ence to the engineering controls in use and potential for aerosol generation

Safety Data Sheet (SDS)

- Carbon black, graphite, diamonds, buckyballs, and carbon nanotubes are all pure carbon just different molecular configurations (allotropes)!
- SDS for some commercially available carbon nanotubes refers to graphite Permissible Exposure Limit (PEL) .
- Graphite is composed of coarse particles.
- Carbon nanotubes are shaped like fibers and behave much differently - graphite PEL is not applicable!
- The SDS is not always accurate because it may reference base chemical and not formulation or grade specific to nanomaterial.







Best Practices

The following are the best practices currently being recommended by a number of universities:

1. Know the existing toxicity information available for your nanomaterial

2. Preplan the experiments and determine equipment and procedures needed

3. Prevent Inhalation Exposure during All Handling of Nanomaterials

Fume Hoods, Biosafety Cabinets , Ventilation for furnaces and reactors, Ventilation for large equipment or engineering processes, Nanomaterial Transport in the Lab

5. Prevent Dermal Exposure to Nanomaterials

6. Use Eye Protection

7. Signage and Labeling

8. Be Aware of Possible Fire and Explosion Hazards

9. Prevent Contamination of Laboratory Surfaces

10. Spill Cleanup

11. Nanomaterial Waste Management

12. Transportation of Nanomaterials Off-Site

13. Exposure Monitoring

Reducing Exposure in Workplace

Methods for controlling potential exposures to airborne and liquid materials in the workplace include **process design** and **engineering controls** such as containment and ventilation systems, work practices, administrative actions, and personal protective equipment. The adequacy of exposure controls for exposure to free nanomaterials is greater than for embedded nanomaterials.

Work Practice Controls

- Standard Operating Procedures (SOPs) should be in place for working with specific nanomaterials. Check list for SOP
- Clean-up using HEPA vacuum and wet methods.
- Designated food/drink areas away from nanomaterials handling.
- Restrict areas to authorized personnel only.

Chemistry Laboratory Safety Rules(2.44min)

https://www.youtube.com/watch?v=GOPv9qjRUQQ

Steps to protect workers / students

Steps to Protect Workers Involved with Nanotechnology

NIOSH Focus

Hazard Identification
Is there reason to believe this could be harmful?

- Toxicologic Research
- Health Effects Assessment
- Safety Research

↓

Hazard Characterization
How and under what conditions could it be harmful?

- Toxicologic Research
- Field Assessment

↓

Exposure Assessment
Will there be exposure in real-world conditions?

- Metrology Research
- Field Assessment
- Control Technology Research
- Personal Protective Equipment (PPE) Research

↓

Risk Characterization
Is the substance hazardous *and* will there be exposure?

- Risk Assessment
- Dose Modeling
- Exposure Characterization

↓

Risk Management
Develop procedures to minimize exposures.

- Risk Communication
- Guidance Development for Controls, Exposure Levels, PPE, and Medical Surveillance
- Information Dissemination

Personal Protective Equipment (PPE)

- Essential for minimizing exposures when handling nanomaterials. Basic PPE should always include:
- Gloves
- Eye protection
- Lab coat
- Respirators may be required for certain work operations (Surgical type masks are not respirators!).

PPE: Respirators

- Filtration efficiency P100 recommended (NIOSH-approved)
- Studies show they are good down to 2.5nm
- Fit testing is required ensures no face seal leakage
- Critical because of nanoparticle size

Prevent Inhalation Exposure

- All free particulate nanomaterials should be examined within exhausted enclosures, such as fume hoods, glove boxes, Class II Type A2, B1 or B2 biosafety cabinets, reactors and furnaces.
- Manipulation of free nanoparticulate on the lab bench should be avoided. Work with suspensions of nanoparticles that are subjected to processes that generate aerosols should be performed in exhausted enclosures.
- **Fume Hoods** When using a fume hood to contain dust or aerosols of nanomaterials, follow good fume hood use practices which is available on http://www.youtube.com/watch?v=A4AHxLnByts (3.37min)

Biosafety Cabinets (BSCs) Only Class II type A2, B1 or B2 biosafety cabinets which are exhausted into the building ventilation system may be used for nanomaterials work. BSCs that recirculate into the room may not be used. There is recirculation of air inside type A2 and B1 cabinets, so care should be taken not to perform **extremely dusty processes** in these cabinets as the internal fans of the BSC are not explosion proof. The air in the type B2 cabinet is 100% exhausted and standard amounts of nanomaterials and solvents may be used in this type of enclosure.

Prevent Inhalation Exposure (cont'd)

- **Ventilation for furnaces and reactors** should be provided to exhaust gasses generated by this equipment. If possible, the exhaust gasses should be run through a liquid filled bubbler to catch particulate before it enters the building ventilation system.
- **Ventilation for large equipment or engineering processes:** Equipment that is too large to be enclosed in a fume hood can be set up such that specially designed local exhaust ventilation can capture contaminants at points where emission is possible.
- **Nanomaterial Transport in the Lab** Nanomaterials removed from furnaces, reactors, or other enclosures should be put in sealed containers for transport to other locations. If nanomaterial product from a reactor is bound or adhered to a substrate, the substrate may be removed and put in a transport container. If the nanomaterials product is unbound and easily dispersible (such as in CNT synthesis using aerosolized catalyst), the removal from a reactor should be done with supplementary exhaust ventilation or a glove bag connected to a HEPA vacuum.

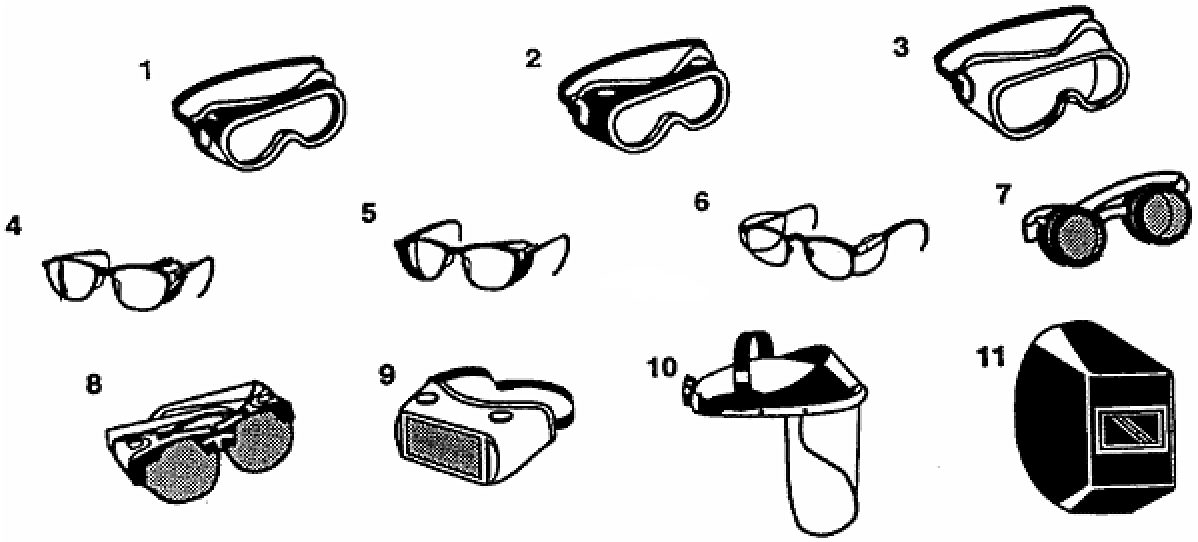
Prevent Dermal Exposure to Nanomaterials

PPE:GLOVES

- The ability of nanoparticles to penetrate the skin is uncertain at this point, so gloves should be worn when handling particulate and suspensions containing particulate.
- If working with dry particulate, a sturdy glove with good integrity should be used.
- If the nanoparticulate is in suspension, a glove having good resistance to the solvent should be used. Nanoparticles suspended in liquid may be more easily absorbed through the skin and represent more of an exposure hazard, so choose gloves appropriate to the solvent.
- Disposable nitrile gloves commonly used in many labs would provide good protection from nanoparticles for most procedures that do not involve extensive skin contact.
- Double gloving (for extensive skin contact).
- Gloves with gauntlets or extended sleeve nitrile gloves are useful in preventing contamination of lab coats or clothing.
- Change gloves routinely when using nanomaterials or if contamination is suspected.
- Keep contaminated gloves in plastic bags or sealed containers in your waste Satellite Accumulation Area until disposal.
- Wash hands and forearms thoroughly after handling nanomaterials. If contamination of clothing is a concern, use disposable lab coats and dispose of through hazardous waste pickup.
- Chemical resistance of gloves are available on the [chemical resistance guide]

PPE: Eye Protection

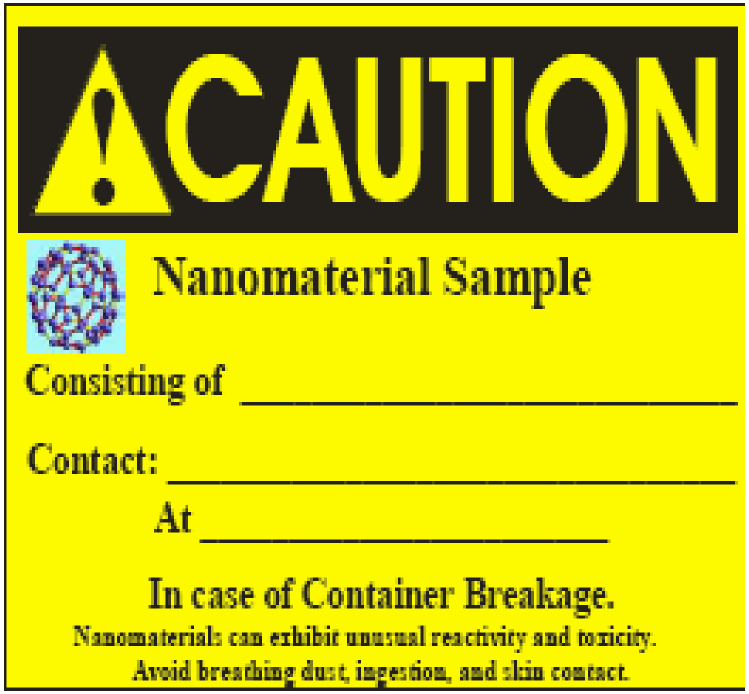
- Wear eye protection appropriate to the experimental conditions (for example, safety glasses, goggles, or face shields).
- Safety glasses or face shields alone cannot protect against aerosols released with pressure, so goggles may be necessary for some nanomaterial processes.



A variety of eye protections for nanosafety.

Transportation and Labeling Requirements

- The inner package must be labeled as nanomaterial.
- Inner containers must be a tightly sealed, rigid, and leak proof. Use tape on the cap to prevent the container from being unintentionally opened.
- Place the inner container in 6 mil(~152micron) plastic bag.
- The outer package must be filled with absorbent material to protect the inner container and absorb liquids during an inner container failure.



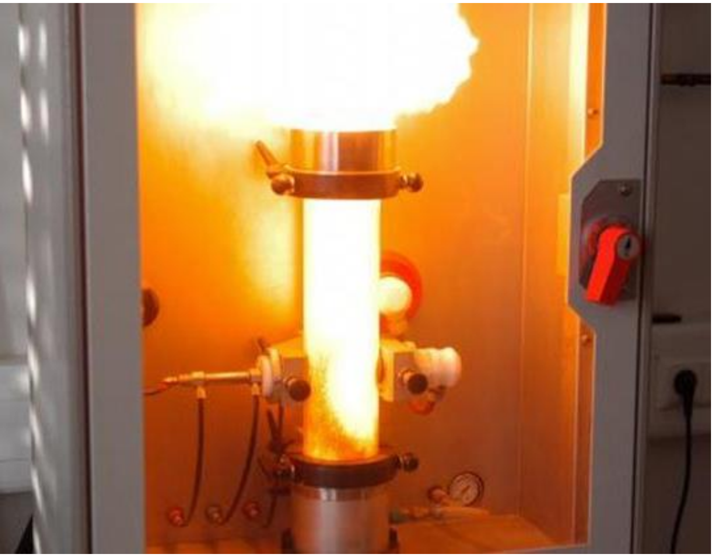
In areas where easily dispersible nanoparticles are in use, post signs indicating the hazards, control procedures, and personal protection equipment that is required.

If necessary, use the Chemical Hygiene Plan "Designated Area" sign available from the EHS Office to label the fume hood, lab bench, or lab itself.

Nanomaterial storage containers should have a designation that the material is "nanoscale" or a "nanomaterial", such as "nanoscale titanium dioxide".

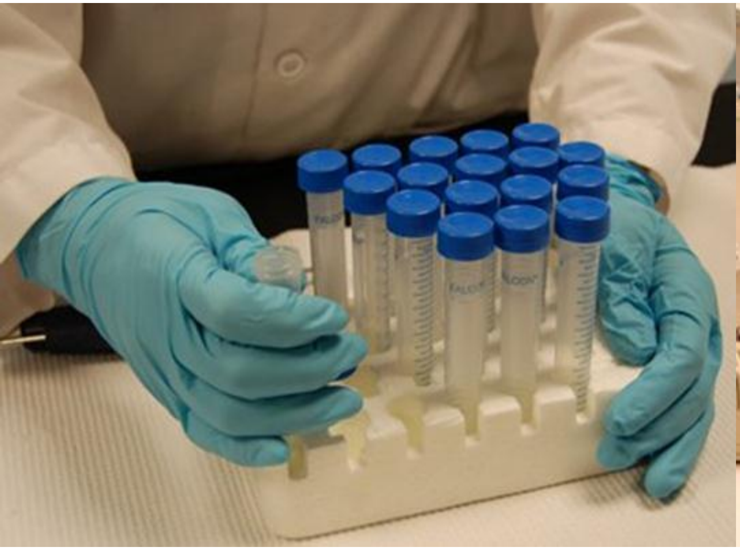
Fire and Explosion Hazards

- Nanoparticulate can be anticipated to have a greater potential for explosivity than micron sized particles, because of their increased reactivity.
- They may also have greater catalytic potential. Fire and explosions may be expected to be of greatest concern when reactions are scaled up to pilot plant levels.
- Both carbonaceous and metal dusts can burn and explode if an oxidant such as air or an ignition source is present.
- Determination of lower flammability limits using standard test bomb protocols may be necessary before scale-up. Contact the EHS Office for information on flammability testing protocols.



Prevent Contamination of Laboratory Surfaces

- Fume hood or enclosure surfaces should be wet-wiped after each use or at the end of the day.
- Alternatively use of bench liners would also prevent contamination. Bench liners, if contaminated, must be disposed of as hazardous waste. Do not dry sweep or use compressed air for cleanup.



Spill Cleanup

- Depending upon the quantity of nanomaterials in use in the lab, each lab should consider having the following items in a nanoparticle spill kit: barricade tape, nitrile gloves, disposable P100 respirators, adsorbent material, wipes, sealable plastic bags, walk-off mat (e.g. Tacki-MatTM).
- Minor spills or small quantities of nanomaterial can be wiped up using wet wiping for solid material and absorbent wipes for suspensions.
- Larger spills can be cleaned using a vacuum cleaner specially fitted with a HEPA filter on the exhaust to prevent dispersion into lab air. A reliable model of HEPA vacuum is the Nilfisk GM80CR. A log of HEPA vacuum use should be maintained so that incompatible materials are not collected on the HEPA filter. HEPA filter change-out should be done in a fume hood.

Waste Handling

- Currently there are no specific EPA regulations or guidelines for the proper disposal of nanomaterials.
- WSU will handle all nanomaterial waste as hazardous waste.
- DO NOT put material from nanomaterial – bearing waste streams into the regular trash or down the drain.
- Contaminated paper, PPE, wipes, tips should be collected in leak tight poly bags and submitted as hazardous solid waste.
- Pure nanomaterials in solid or powder form should be containerized and submitted as hazardous waste.
- Nanomaterials dissolved in solvents or formulations should be collected and submitted as a hazardous waste mixture.
- Submit all hazardous waste using the online form available on the EHS website.

Exposure Monitoring

Instruments and techniques for monitoring nanoparticle emissions in nano-manufacturing workplaces

Metric	Instrument	Remarks
Aerosol concentration	**CPC**	**Real-time measurement. Typical concentration range of up to 400,000 particles/cm^3 for stand-alone models with coincidence correction; 100,000 particles/cm^3 for hand-held models.**
	DMPS	**SMPS often uses a radioactive source. FMPS uses electrometer-based sensors. Concentration range from 100−107 particles/cm^3 at 5.6 nm and 1−105 particles/cm^3 at 560 nm.**
Surface area	**Diffusion charger**	**Need appropriate inlet pre-separator for nanoparticle measurement. Total active surface area concentration up to 1,000 $\mu m^2/cm^3$.**
	ELPI	**Real-time size-selective detection of active surface area concentration. 2×104–6.9×107 particles/cm^3 depending on size range/stage.**
Mass	**Size selective static sampler**	**Low pressure cascade impactors. Micro-orifice impactors.**
	TEOM	**EPA standard reference equivalent method.**
Aerosol concentration by calculation	**ELPI**	
Surface area by calculation	**DMPS**	
DMPS and ELPI used in parallel		**Surface area is estimated by difference in measured aerodynamic and mobility diameters.**
Mass by calculation	**ELPI**	**Calculated by assumed or known particle charge and density.**
	DMPS	**Calculated by assumed or known particle charge and density.**

CPC=condensation particle counter; DMPS=differential mobility particle sizer; SMPS=scanning mobility particle sizer; FMPS=fast mobility particle sizer; ELPI= electric low pressure impactor; TEOM=tapered element oscillating microbalance

Summary

- The safety of researchers and workers advancing the field of nanotechnology is as important as the field itself.
- Assume all nanoparticles are hazardous.
- Minimize your risk by handling nanoparticles in solution to prevent the generation of dust/aerosols that could lead to inhalation.
- Understand the risks and implement measures to keep yourself safe!
- EHS at WSU is here to help you and your students against the potential hazards of nanotechnology and nanoproducts.

Future Studies

- Overall characterization of nanomaterial processes
- Prudent work practices to minimize and manage exposure to nanomaterials engineering controls and PPE
- Worker training that addresses potential hazards that may be associated with nanomaterials
- Evaluation of analytical instruments and methods used to measure exposure to nanomaterials
- Quantitative and qualitative measurements of exposure to nanomaterials

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- Nanotechnology Safety (Online Available March 10,2014) http://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0CCsQFjAB&url=http%3A%2F%2Fehs.unc.edu%2Ftraining%2Fself_study%2Fnano%2Fdocs%2Fnano.ppt&ei=IcdU5qYNse62wXO_oHoDA&usg=AFQjCNEB_L_arHvH6XhgArKZwbDBW4LFwQ
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- Proper use of fume hood (Online Available February 6,2014)

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Stay Safe

Thank You