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Risk Management

OFFICE OF THE PRESIDENT
1111 Franklin Street, 10th Floor
Oakland, California 94607-5200

January 14, 2010

Jeffrey Wong, Ph.D.
Chief Scientist
Department of Toxic Substances Control
P.O. Box 806
1001 I Street
Sacramento, California 95812

DIRECTOR'S OFFICE
DEPT OF TOXIC SUBSTANCES CONTROL
JAN 19 2010
RECEIVED

Dear Dr. Wong:

This letter is in response to the Department of Toxic Substances Control's January 22, 2009 call-in letter to the University of California (UC) for chemical information regarding carbon nanotubes ("CNTs") (California Health and Safety Code §57018-57020).

UC's response to each call-in question is listed below. As one of the world's largest public teaching and research institutions, UC has thousands of research operations in millions of square feet of laboratory space. With ten campuses and one national laboratory, processes and procedures must vary to meet the individual operational needs of the facility and the specific research operation. Therefore the response to each call-in question has been worded in broad terms to reflect the wide operational variability between each UC campus and the national laboratory.

What is the value chain for your company? For example, in what products are your carbon nanotubes used by others? In what quantities? Who are your major customers?
UC, as the premier public teaching and research institution in the world, produces CNTs for research and development purposes within the existing campus/laboratory. UC does not enter CNTs into commerce. The UC system has approximately a total of 30 to 35 grams of CNTs which are used by researchers at the UC campuses and one national laboratory.

What sampling, detection, and measurement methods are you using to monitor the presence of your chemicals in the workplace and environment?
Some UC facilities have used direct reading instruments to monitor airborne levels of CNT in the laboratory environment, including the TSI 3007 condensation particle counter (concentration range - 0 to 1 $X10^5$ particles/cm^3; particle size range - 0.01 to >1 μm), the TSI 8525 P-Track particulate counter (concentration range - 0 to 5 $X10^5$ particles/cm^3; particle size range - 0.02 to >1 μm), the DustTrak aerosol monitor (TSI 8520). In addition, UCLA evaluated the response to laboratory generated CNT aerosols of several number and mass concentration technologies. These were simultaneously compared with the two bench top scanning mobility particle sizer (SMPS) models TSI 3786/3085 ultrafine water-based condensation particle counter (CPC) with a long differential mobility analyzer (DMA), and the TSI 3785/3081 water-based CPC with a nanoDMA. This study found that portable particle counters (in particular the TSI 8525 and 3007) generally under-reported aerosolized CNT concentrations. In addition, long term air samples were collected over a duration of several months using specially designed sampling chambers. High volume air sampling pumps were used to collect samples onto Teflon and quartz filters

and analyzed using ICP-MS and organic carbon/ elemental carbon (OC/EC) techniques, respectively. Results indicated that accurate CNT quantification and identification is not possible, probably related to low nanomaterial mass regardless of potentially high episodic number concentrations compared to ambient background urban dust. However, LBNL developed a portable clean room which attaches to the front of fume hoods and another smaller table top unit that shows promise in reducing high interfering background levels.

What is your knowledge about the current and projected presence of your chemical in the environment that results from manufacturing, distribution, use, and end-of-life disposal?
The quantities of CNTs which are manufactured and used for research at UC facilities are extremely small, in the microgram to less than one gram per year range. Due to the value of the CNTs, minuscule quantities, and the work practices/engineering controls used at UC facilities, the amount released to the environment would be negligible. The majority of the CNTs used in research projects are typically bound within the research product which is the subject of research and not disposed.

What is your knowledge about safety of your chemical in terms of occupational safety, public health and the environment?
Nanomaterials are novel materials and may undergo a number of modifications during research. Current toxicological research and EH&S related information is evolving and is focused on understanding general mechanisms of biological interaction with nanomaterials. In the absence of specific hazard information UC is handling all nanomaterials as hazardous. UC is extremely knowledgeable regarding the current information which is currently available regarding CNTs. Significant research initiatives on nanomaterials are housed at two UC campuses. The California NanoSystems Institute (CNSI), established in December 2000 through a state-wide initiative as one of four Governor Gray Davis Institutes for Science and Innovation, is a partnership between industry in California and the academic community. CNSI members include faculty from the life and physical sciences, engineering, and medicine from UCLA and UCSB. The primary CNSI facility, located at UCLA, includes 180,000 square feet of labs, clean rooms, analytical technology (including electron, atomic force, X-ray diffraction, and specialized optical microscopes) and high throughput robotics for molecular screening. Housed within the CNSI, the Center for the Environmental Implications of Nanotechnology (CEIN) is an interdisciplinary research center investigating the impact of engineered nanomaterials on a wide range of organisms in terrestrial, fresh water and sea water environments. By developing new screening and risk ranking methods, the CEIN aims to provide guidance on the safe design of engineered nanomaterials for the research community, industry, the public, and the regulatory community. Recent initiatives of the CEIN include forming a working group on regulating nanomaterials with the UCLA School of Law, and developing an online training module and written guidance document on the safe handling and disposal of nanomaterials for the research community.

Each UC facility has an Environment, Health and Safety (EH&S) program which oversees and advises researchers regarding health and safety issues. The UC system has an Industrial Hygiene (UCIH) Workgroup which meets regularly to discuss environment, health and safety issues, including CNTs. Members of the UCIH Workgroup have attended various conferences and seminars regarding CNT EH&S issues. Certain members of the UCIH Workgroup have been in direct contact with the nanomaterial experts at the National Institute for Occupational Safety and Health (NIOSH) to discuss and share information regarding the safe handling of nanomaterial, including CNTs. Lawrence Berkeley National Laboratory actively participates in the US Department of Energy Nanoscale Science Research Centers Environment, Health and Safety Working Group. Nanomaterial experts at NIOSH have requested the UCIH workgroup members and researchers at CEIN to review and comment on NIOSH publications and documents. A short bibliography of University of California nanomaterial publications is attached (Attachment 1).

What methods are you using to protect workers in research, development and manufacturing environment?
Each UC facility has developed facility/operation-specific training or written guidelines/factsheets for the safe handling of CNTs. The guidelines/factsheets list suggested engineering controls, work practices, and

personal protective equipment to control and limit exposure to CNTs. Attached are sample factsheets from UC Berkeley, UCLA CEIN, (Attachments 2 and 3), and Control Procedures for Engineered Nanomaterials developed by Lawrence Berkeley National Laboratory (Attachment 4).

When released, does your material constitute a hazardous waste under California Health and Safety Code provisions? Are discarded off-spec materials a hazardous waste? Once discarded are the CNTs you produce a hazardous waste? What are your handling practices for CNTs?
At certain facilities, no CNT-waste has been generated. At other facilities, unless known to be non-hazardous, the CNT-waste, along with its substrates, are managed as a hazardous waste under the California Health and Safety Code. Materials managed as hazardous waste are labeled and collected by authorized personnel, stored in a 90 day hazardous waste storage area until they are transferred to a hazardous waste disposal contractor to be disposed of at a permitted treatment, storage, and disposal facility.

In addition to responding to DTSC's call-in questions, UC has developed the attached "University of California Fact Sheet: Guidelines for Safe Research Practices", which includes standard operating procedures specific to CNT operations (Attachment 5). This document was developed in response to your request during your August 28, 2009 meeting with Ed Baylosis and Larry Wong.

If you have any additional questions regarding UC's response to DTSC's call-in for information, please contact Larry Wong at 510-987-9772 or larry.wong@ucop.edu.

Sincerely,

Grace M. Crickette, Chief Risk Officer
Office of Risk Services

Attachments:

1. UC Publications on Health Effects and Environmental Impacts of Carbon Nanotubes.
2. Nanotechnology: Guidelines for Safe Research Practices – University of California Berkeley
3. Interim Guidelines for Safe Handling and Disposal of Nanomaterials – University of California Center for Environmental Implications of NanoTechnology (CEIN)
4. Control Procedures for Engineered Nanomaterials, - Lawrence Berkeley National Laboratory
5. Fact Sheet: Guidelines for Safe Research Practices - University of California Lab Safety Workgroup, University of California Industrial Hygiene and Safety Steering Committee

cc: Frank Parr, CIH
Senior Industrial Hygienist
Department of Toxic Substances Control
9211 Oakdale Avenue
Chatsworth, CA 91311-6505

Vice President Steven Beckwith
Executive Director Ellen Auriti, Research Policy (RPAC)
EH&S Directors
Larry Wong, UCOP EH&S

Attachment 1

UC Publications on Health Effects and Environmental Impacts of Carbon Nanotubes

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Chen, X., Tam, U., Czlapinski, J.L., Lee, G.S., Rabuka, D., Zettl, A., Bertozzi, C.R. Interfacing Carbon Nanotubes with Living Cells. ***Journal of the American Chemical Society,*** 2006, 128 (19) 6292–6293. doi: 10.1021/ja060276s

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Attachment 2

Nanotechnology: Guidelines for Safe Research Practices

University of California Berkeley
Office of Environment, Health & Safety

EH&S FACT SHEET
Environment, Health and Safety Information for the Berkeley Campus

No. 73
Revised 11 /17/08

Nanotechnology:
Guidelines for Safe Research Practices

Introduction

This fact sheet provides environmental, health and safety information to UC Berkeley researchers working with engineered nanoparticles, and should be incorporated as a standard operating procedure in each laboratory's chemical hygiene plan. Given the evolving knowledge base regarding potential health effects of nanoparticles, this fact sheet may be updated. Always check the EH&S web site (http://ehs.berkeley.edu) for the latest version.

Nanoparticles are particles that have at least one dimension between 1-100 nanometers. Particles in this size range have always been present in Earth's air. Nanoparticles may be naturally occurring (such as in volcanic ash), produced as unintentional byproducts (such as in auto emissions) or intentionally created or engineered. These very small particles exhibit properties different from larger particles of the same composition, making them of interest to researchers and of potential benefit to society. This fact sheet focuses on lab practices researchers should follow to protect themselves from the potential hazards of engineered nanoparticles.

Nanoparticles can be spheres, rods, tubes, and other geometric shapes. 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.

Various nanoparticles can be created in the laboratory under experimental procedures, and some can be purchased from commercial vendors. In most research, the amount of material used is small, generally less than a gram.

Only limited information is currently available on the toxicity of a few types of nanoparticles. It is believed that some engineered nanoparticles may present health effects following exposure, based in part on air pollution studies that show smaller particles get deep into the lungs and can cause human illness. However, laboratory research most commonly involves handling nanoparticles in liquid solutions or other forms that do not become easily airborne, and even free formed nanoparticles tend to agglomerate to a larger size.

When research involves work with engineered nanoparticles for which no toxicity data is yet available, it is prudent to assume the nanoparticles may be toxic, and to handle the nanoparticles with precaution using the laboratory safety techniques outlined below.

E H & S UC BERKELEY
Office of Environment, Health & Safety
University of California
317 University Hall #1150
Berkeley, CA 94720-1150
http://www.ehs.berkeley.edu
(510) 642-3073

Potential Routes of Occupational Exposure to Researchers

There are four possible routes of workplace exposure to nanoparticles: inhalation, ingestion, skin absorption, and injection.

Skin absorption. In some cases nanoparticles have been shown to migrate through skin and be circulated in the body. If the particle is carcinogenic or allergenic, even tiny quantities may be biologically significant. Skin contact can occur during the handling of liquid suspensions of nanoparticles or dry powders. Skin absorption is much less likely for solid bound or matrixed nanomaterials. Researchers should double glove to protect themselves from skin absorption and to protect their research materials from being contaminated. Outer gloves should be removed inside a fume hood or under the influence of local exhaust ventilation and placed into a sealed bag. This will prevent the particles from becoming airborne in the lab.

Ingestion. As with any contaminant, ingestion can occur if good hygiene practices are not followed. Once ingested, some types of nanoparticles might be absorbed and transported within the body by the circulatory system. To prevent ingestion, eating and drinking are not allowed in laboratories outside of clearly designated areas. Also, spills of nanoparticles should be quickly and properly cleaned up, as detailed below.

Inhalation. Respiratory absorption of airborne nanoparticles may occur through the mucosal lining of the trachea or bronchioles or the alveoli of the lungs. Because of their tiny size, certain nanoparticles appear to penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles. Thus, whenever possible, nanoparticles are to be handled in a form that is not easily made airborne, such as in solution or on a substrate.

Injection. Exposure by accidental injection (skin puncture) is also a potential route of exposure, especially when working with animals or needles. To prevent this, wear double gloves and lab coats, and apply the standard practices for working with sharps.

Laboratory Safety Guidelines for Handling Nanomaterials

The practices for safely working with nanoparticles are essentially the same as one would use when working with any research chemical of unknown toxicity.

1. Use good general laboratory safety practices as stated in your chemical hygiene plan. Wear double gloves (preferably nitrile gloves), safety glasses or goggles, and appropriate protective clothing.

2. All personnel participating in research involving nanoscale materials need to be briefed on the potential hazards of the research activity, as well as on proper techniques for handling nanoparticles. The contents of this Fact Sheet can serve as a useful component of this training. As with all safety training, written records need to be maintained to indicate who has been trained on this topic.

3. Eating and drinking are allowed only in clearly designated and demarcated areas where chemicals or nanoparticles are not used.

4. When purchasing commercially available nanoscale materials, be sure to obtain the Material Safety Data Sheet (MSDS) and to review the information in the MSDS with all persons who will be working with the material. (Note that given the lack of toxicological data on the effects of nanoparticles, the information on an MSDS may be more applicable to the properties of the bulk material.)

5. In some cases, the making of nanomaterials involves the use of chemicals that are known to be hazardous or toxic. Be sure to consider the hazards of the precursor materials when evaluating the process hazard or final product. Users of any chemicals should make themselves familiar with the known chemical hazards by reading the MSDS or other hazard literature.

6. To minimize airborne release of engineered nanoparticles to the environment, nanoparticles are to be handled in solutions, or attached to substrates so that dry material is not released. Where this is not possible, nanoscale materials should be handled with engineering controls such as a HEPA-filtered local capture hood or glove box. If neither is available, work should be performed inside a laboratory fume hood. HEPA-filtered local capture systems should be located as close to the possible source of nanoparticles as possible, and the installation must be properly engineered to maintain adequate ventilation capture.

7. Use fume exhaust hoods to expel any nanoparticles from tube furnaces or chemical reaction vessels. Do not exhaust aerosols containing engineered nanoparticles inside buildings.

8. If you must work outside of a ventilated area with nanomaterials that could become airborne, wear a respirator with NIOSH-approved filters that are rated as N-, R-, or P-100 (HEPA). EH&S will work with researchers to provide the most appropriate type of respirator. See the following fact sheet for the procedures for obtaining and wearing a respirator at UC Berkeley: http://www.ehs.berkeley.edu/pubs/factsheets/48respiratoryprotect.html

9. Lab equipment and exhaust systems used with nanoscale materials should be wet wiped and HEPA vacuumed prior to repair, disposal or reuse. Construction/maintenance crews should contact EH&S for assistance.

10. Spills of engineered nanoparticles are to be cleaned up right away. The person cleaning up should wear double gloves and either vacuum up the area with a HEPA filtered vacuum or wet wipe the area with towels, or a combination of the two. For spills that might result in airborne nanoparticles, proper respiratory protection should be worn (see item 8 above). Do not brush or sweep spilled/dried nanoparticles. Place a Tacki-Mat at the exit to reduce the likelihood of spreading nanoparticles on footwear. For assistance with cleaning up any chemical spill contact EH&S.

11. Work surfaces should be wet-wiped regularly – daily is recommended. Because many engineered nanoparticles are not visible to the naked eye, surface contamination may not be obvious. Alternatively, disposable bench paper can be used.

12. All waste engineered nanoparticles should be treated as unwanted hazardous materials unless they are known to be non-hazardous. Dispose of and transport waste nanoparticles in solution according to hazardous waste procedures for the solvent. If you have questions on how to dispose a specific nanoparticle waste, call EH&S for more information.

Additional Information

For more information on Health and Safety of Nanotechnology visit the following web sites:

DTSC - California Department of Toxic Substances Control
http://www.dtsc.ca.gov/TechnologyDevelopment/Nanotechnology/nanoport.cfm

NIOSH - National Institute for Occupational Safety and Health
http://www.cdc.gov/niosh/topics/nanotech/

National Nanotechnology Initiative
http://www.nano.gov/

EPA - Environmental Protection Agency
http://www.epa.gov/oppt/nano/nano-facts.htm

Woodrow Wilson International Center for Scholars
http://nanotechproject.org/

For any questions on this Fact Sheet, please contact EH&S at 642-3073.

Attachment 3

Interim Guidelines for Safe Handling and Disposal of Nanomaterials

University of California Center for Environmental Implications of NanoTechnology

UCCEIN Center for Environmental Implications of NanoTechnology

INTERIM GUIDELINES FOR SAFE HANDLING AND DISPOSAL OF NANOMATERIALS

As a general rule, we have inadequate information on the toxicological mechanisms and methods for measuring exposures of nanomaterials, which makes it difficult to impossible to perform a rigorous risk assessment for these materials. The lack of information available for these materials requires that **extra precaution must be taken in handling nanomaterials. Developing and following a current chemical hygiene plan for hazardous materials is key to ensuring safety. Steps you should take include:**

- Obtain current toxicity and chemical reactivity information on nanomaterials in use to the best of your abilities.
- Use safe handling practices to prevent inhalation, ingestion, and dermal exposures
- Be careful to prevent laboratory and personal contamination during routine use (*e.g.,* via aggressive dust management and use of laboratory coats and other personal protective equipment).
- Prevent exposure during spills and during disposal.
- Prevent fire hazard if large quantities generated during reactions or production. Carbonaceous and metal dusts can self-heat, burn, and explode if an oxidant, such as air, and an ignition source are present

To obtain current toxicity and safety information on nanomaterials you are making or using:

- Contact the source or manufacturer of the nanomaterial you are using; be certain they are reputable in terms of reliability of their information and reproducibility of their samples.
- Keep in mind that Material Safety Data Sheets (MSDS's) supplied by manufacturers are intended for industrial uses and may be incomplete, particularly with respect to nanomaterials.
- Stay abreast of the current understanding of the toxicity of nanomaterials used in your lab
- Regularly check for new information on the following sites:
  - ICON (http://icon.rice.edu/)
  - NIOSH(http://www.cdc.gov/niosh/topics/nanotech/)
  - Pub Med

To prevent inhalation and ingestion exposures:

- Avoid handling nanomaterials on open lab benches; always wear a lab coat.
- In general, it is recommended that you handle nanomaterials in a fume hood, biosafety cabinet or other exhausted and filtered enclosure. However, you should be aware that when fume hood sashes are at low heights and the worker stands close to the hood, air currents can pull nanomaterials (and other airborne particles or volatile chemicals) out of the hood and into the breathing zone. Make sure that you know how to properly use the fume hood in your laboratory to minimize exposure.
- When you are handling dry powders (particularly ones that are flocculent), use a box lined with antistatic paper.

- Always transport nanomaterials in closed/sealed containers.
- When performing syntheses in a furnace or reactor, be sure to safely exhaust reactor gases:
  - Purge all gas before opening the reactor;
  - Provide local exhaust ventilation for emission points;
  - Perform any maintenance on reactor parts that are used to manufacture or manipulate nanomaterials in a fume hood.
- Use a fitted respirator when working with nanomaterials that can be aerosolized; make sure that you have been appropriately trained (*e.g.,* by your institution's Office of Environmental Health and Safety) and fitted prior to using the respirator.
- Never eat, drink, or apply of cosmetics in a laboratory where nanomaterials are used.

To prevent dermal exposures:

- Always use gloves when manipulating dry particulates and powders.
- Use gloves that you know are resistant to the solvent you are using if the nanoparticles are in suspension (*e.g.,* nitrile gloves).
- If skin contamination is likely, use double gloves or gloves with extended sleeves.
- Always wear a lab coat when working with nanomaterials; use a disposable coat with elastic at the wrists, if you are working with dry flocculent materials.
- Use appropriate eye protection (goggles).

To prevent laboratory and personal contamination:

- Use container sizes that minimize the number of transfers and volumes involved; disperse into liquids whenever the experiment design permits.
- Wet wipe hood and other lab surfaces at the end of each day; do not allow build-up of dust.
  - Never sweep or use compressed air to clean areas that may be contaminated with nanomaterials.
- Use bench liners and HEPA-filtered vacuum cleaners in areas where nanoparticles are used and change them regularly.
- Designate and label nanoparticle workspaces and storage areas.
- Wear lab coats when working with nanomaterials.

To prevent personal exposure in everyday work, when cleaning up spills or handling waste:

- Have a spill kit on hand before you start your work.
- Wet wipe when cleaning dry spills; be sure to wear gloves while cleaning spills.
- Use an appropriate absorbent for liquids with nanoparticles in suspension.
- Use a HEPA-filtered vacuum to clean larger spills. Use a respirator during vacuuming large amounts.
- Use a respirator (disposable P100 or elastomeric half mask with P100 cartridges) if inhalation exposure is possible; note that you must be specifically trained and fitted prior to using a respirator; contact your local Environmental Health and Safety officer if you think that you need to use a respirator.

- Make sure that solid and liquid wastes containing nanomaterials and materials used to contain spills of nanomaterials are placed in closed containers, labeled appropriately, and disposed of according to the hazardous waste disposal policies of your institution.

To prevent fire hazards:

- Be aware that carbonaceous and metal dusts can burn and explode if an oxidant such as air and an ignition source are present; self heating may occur when reactive moieties, such as double bonds, are constituents of the carbonaceous material.
- Prior to starting work, assess whether large quantities/high concentrations of nanoparticles will be generated
- Verify that appropriate chemical fire extinguishers available and in working order before starting work

Know your institutional Environmental Health & Safety (EH&S) contacts:

- For UCLA researchers, the EH&S Web site is: http://map.ais.ucla.edu/portal/site/UCLA/menuitem.2bceb61fc98129c1ae13e110f848344a/?vgnextoid=064ae6ffe0e1e010VgnVCM100000db6643a4RCRD
- UCLA's Environment, Health and Safety (EH&S) phone number is: (310) 825-5689.

Bottom Line:

Until we know what properties of nanomaterials correlate with hazards, it is important to use caution and good chemical hygiene practices when working with nanomaterials.

References:

- Woodrow Wilson Institute Project on Emerging Nanotechnologies (http://www.nanotechproject.org/inventories/consumer)
- NIOSH (http://www.cdc.gov/niosh/topics/nanotech)
- DOE Nanoscale Science Researcher Centers: Approach to Nanomaterial ES&H (www.sc.doe.gov/bes/DOE_NSRC)

Attachment 4

Control Procedures for Engineered Nanomaterials

Lawrence Berkeley National Laboratory

Attachment 4

CONTROL PROCEDURES FOR ENGINEERED NANOMATERIALS

Engineered Nanomaterials (ENMs) are defined as:

- Discrete materials having structures with at least one dimension between 1 and 100 nanometers (nm).
- Intentionally created, as opposed to those that are naturally or incidentally formed.

Engineered Nanomaterials do not include:

- Larger materials that may have nanoscale features, for example etched silicon wafers.
- Biomolecules (proteins, nucleic acids, and carbohydrates),
- Materials with occupational exposure limits (OELs) that address nanosized particles for that substance.

Nanoparticles are a type of engineered nanomaterials that:

- Are not bound to a surface or weakly bound to a surface and therefore are or may become dispersible
- Have two or three dimensions between 1 and 100 nm.

Exposures to engineered nanomaterials may occur through inhalation, dermal contact, or ingestion. Because of their tiny size, engineered nanomaterials can penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles.

The nanoparticulate forms of some materials show unusually high reactivity, especially for fire, explosion, and in catalytic reactions. Depending on their composition and structure, some engineered nanomaterials may initiate catalytic reactions that would not otherwise be anticipated from their chemical composition.

In general, laboratory personnel should treat all new compounds, including engineered nanomaterials of unknown toxicity, as though they could be acutely toxic in the short run and chronically toxic over time. Engineered nanomaterials whose hazards have been studied should be managed in a manner consistent with the observed risks.

Control Measures

Training and Information

- Employees who either handle or who may be exposed to the hazards of engineered nanomaterials must indicate this on their Job Hazards Analysis, must complete Chemical Hygiene and Safety Training (EHS 348) and Safe Handling of Engineered Nanoscale Particulate Matter (EHS 344) and must comply with requirements listed in the Job Hazards Analysis.

- All employees in the work area must be trained in the specific hazards and controls of these materials. Area-specific training is a line management responsibility. EH&S Industrial Hygienists are available to provide assistance.

Engineering Controls

- Conduct work that could generate engineered nanomaterials in gloveboxes, glove bags, laboratory fume hoods, or other negative-pressure or isolation enclosures. If a process (or subset of a process) cannot be enclosed, then use other engineered systems to control fugitive emissions of engineered nanomaterials or hazardous precursors that might be released. For example, use a local exhaust system like a "snorkel hood."
    - With regard to gloves worn in glove boxes: Consider using an inner pair of different colored gloves to detect small tears in glovebox gloves and/or wearing an outer pair of gloves to prevent degradation of glovebox gloves. Refer to the Personal Protective Equipment Section for selecting chemically resistant gloves.
- Avoid exhausting effluent air reasonably suspected to contain engineered nanomaterials whose hazards are not well understood. Whenever practical, filter it or otherwise clean (scrub) it before release. High Efficiency Particulate Arresting (HEPA) filtration appears to effectively remove engineered nanomaterials from air.
- Do not use horizontal laminar-flow hoods ("clean benches") that direct a flow of air into the laboratory to control exposure to engineered nanomaterials.
- Consider exhausting Type II biological safety cabinets, in which free engineered nanomaterials are handled, directly to the exterior (hard-ducted) or through a thimble connection over the cabinet's exhaust.
- Evaluate laboratory equipment and exhaust systems for contamination before removing, remodeling, or repairing them.

Administrative Controls

Housekeeping

- Insofar as practicable, maintain all working surfaces (i.e., benches, glassware, apparatus, exhaust hoods, support equipment, etc.) free of engineered nanomaterial contamination. Some engineered nanomaterials fluoresce under ultraviolet light, which can be useful in locating areas of contamination.
    - Designated Areas: Conduct all work involving free unbound ENMs in designated areas. Requirements may be found in the section entitled "Designated Areas."
    - Clean up dry engineered nanomaterials, using:
        - A dedicated HEPA vacuum-tested and certified by EH&S
        - Wet wiping
        - Other methods that do not involve dry sweeping or the use of compressed air.
    - Dispose of used cleaning materials and wastes as hazardous waste (see below).
- Clean up dry engineered nanomaterials, using:
    - A dedicated HEPA vacuum-tested and certified by EH&S
    - Wet wiping
    - Other methods that do not involve dry sweeping or the use of compressed air.
- Dispose of used cleaning materials and wastes as hazardous waste (see below).

Chemical Inventory

- *Enter all containers of commercially obtained engineered nanomaterials into the Chemical Management System (CMS).* The CMS has a check box for engineered nanomaterials to allow easier identification of storage and use locations. Ensure this is checked when entering the material into the inventory.

Marking, Labeling, and Signage

- Post signs indicating hazards, minimum personal protective equipment requirements, and administrative control requirements at entry points into areas where engineered nanomaterials are handled. The section entitled: Posting Area Entrances has specific posting requirements and instructions.
- Designated areas shall be posted and controlled as described above.
- *Primary and secondary containers must be labeled with the identity of the substance and its hazards.* Label containers to plainly indicate that the contents are in engineered nanoparticulate form, e.g., "nanoscale zinc oxide particles" or other identifier, rather than just "zinc oxide."
- There may be practical limitations to carrying out these labeling requirements to small containers such as sample vials and tubes. Alternatives such as numbering or coding are permissible provided that the material's identity and hazards are readily accessible (e.g., by means of a lab notebook, a spreadsheet, or some other equivalent means).
- When engineered nanomaterials are being moved outside the work area, also include label text that indicates that the particulates may be unusually reactive and are potentially more toxic, quantitatively and qualitatively, than normal-scale forms of the same material.

Storage

- Storage requirements are provided below: The section entitled Storage Guidelines provides additional information and chemical incompatibilities. Consult the chemical's Material Safety Data Sheet for specific storage and incompatibility requirements.
- Follow the storage guidelines in Control Procedures for Flammable and Combustible Liquids if the material is either flammable or combustible. Also consider the properties of the solvent if the engineered nanomaterial is dissolved or suspended.
- Separate incompatible chemicals from one another.
- Store engineered nanomaterials in a cool, dry environment, away from light and free from extremes of temperature and humidity. Storage cabinets that are connected to the ventilation system provide the best means of storage. It is Laboratory policy that chemical storage cabinets installed as part of new facilities construction and laboratory renovations will be connected to the facility's exhaust ventilation system.
- All engineered nanomaterials should be stored in sealed, air-impermeable containers. Dark amber glass containers with tight-fitting caps may be necessary if the engineered nanomaterial or its solvent is light sensitive. Containers with loose-fitting lids or glass stoppers should not be used.
- Use secondary containment for all liquids.

Personal Protective Equipment

Skin and eye contact shall be prevented. Wear PPE appropriate to the hazard, as identified through the Job Hazard Analysis process. Obtain a hazard assessment from an EH&S Industrial Hygienist to determine the selection and use of PPE. PPE required for a wet-chemistry laboratory, which is often appropriate for handling engineered nanomaterials, includes:

- Laboratory coats
- Eye protection, e.g., safety glasses with side shields, face shields, chemical splash goggle, or other safety eyewear appropriate to the type and level of hazard. NOTE: Face shields or safety glasses alone do not provide sufficient protection against unbound, dry materials that could become airborne.
- Closed-toe shoes made of a low- permeability material.
- Protective gloves
    - Store gloves in a clean area outside of fume hoods and away from equipment that could potentially contaminate them.
    - Wear polymer (e.g., nitrile rubber) gloves when handling engineered nanomaterials and particulates in liquids. Choose gloves only after considering the resistance of the glove to the chemical attack both by the engineered nanomaterial and, if suspended or dissolved in liquid, the liquid. Consult the glove selection guides in the Personal Protective Equipment Section. Disposable gloves may be appropriate
    - Change gloves often to minimize potential exposure hazards. Alternatively, double-glove.
    - For glove box gloves: Consider using an inner pair of different colored gloves to detect small tears in glovebox gloves and/or wearing an outer pair of gloves to prevent degradation of glovebox gloves.
    - Wash hands and forearms after wearing gloves.

Keep potentially contaminated clothing and PPE in the laboratory or change out area to prevent engineered nanomaterials from being transported into common areas. Use disposable lab coats if feasible, and discard of them as hazardous waste (see below) when they become unusable. If cloth lab coats are used, do not send them to a laundry unless the laundry (such as the LBNL contract lab coat provider) has specifically agreed to handle engineered nanomaterial-contaminated clothing.

Engineered Nanomaterial-Bearing Waste Streams

Consider any material that has come into contact with dispersible engineered nanomaterials (and that has not been decontaminated) as belonging to an engineered nanomaterial-bearing waste stream. This includes gloves, other PPE, wipes, blotters and other disposable laboratory materials used during research activities.

Do not put material from engineered nanomaterial-bearing waste streams into the regular trash or down the drain.

Collect engineered nanomaterial-bearing waste in a plastic bag or other sealing container. Until the container is sealed, keep it in the laboratory hood. This bag must remain sealed unless adding waste to it. It should be managed as hazardous waste, including completing the Hazardous Waste label when accumulation begins, and placing it in an identified Satellite Accumulation Area. The identity of the waste must be given on the label. For example, *"Wipes contaminated with trace levels of carbon nanotubes"* provides an appropriate level of description. When the bag is full, close it, take it out of the hood and place it into a second plastic bag or other sealing container in a Satellite Accumulation Area.

Characterize and manage engineered nanomaterial-bearing waste streams per the requirements of the LBNL hazardous waste program. Be sure to consider the properties of all components, for example, solvents in which the engineered nanomaterials may be dissolved or suspended.

Emergency Procedures and Spills

Refer to the section entitled "Emergency Procedures and Equipment" for LBNL policy and response procedures for chemical spills. Spills containing engineered nanomaterials are generally handled in a manner similar to spills of other potentially hazardous materials, with the following additional requirements:

- Clean the spilled material using wet wiping methods. Characterize, collect, and dispose of spill cleanup materials as engineered nanomaterial-bearing waste.
- Only HEPA vacuums that have been tested and certified by EH&S may be used to vacuum nanomaterials. Do not dry-sweep or use compressed air.
- Consider using a walk off mat such as a clean room mat or "sticky mat" at access/egress points to reduce the likelihood of spreading nanoparticles. These are available through McMaster – Carr via the Lab's Procurement web site.

Attachment 5

Fact Sheet

Nanotechnology: Guidelines for Safe Research Practices

University of California Lab Safety Workgroup, University of California Industrial Hygiene and Safety Steering Committee

FACT SHEET

Nanotechnology: Guidelines for Safe Research Practices

Introduction

This fact sheet provides environmental, health and safety information to researchers working with engineered nanoparticles, and should be incorporated as a standard operating procedure in each laboratory's chemical hygiene plan. Given the evolving knowledge base regarding health effects of nanoparticles, this fact sheet may be updated. Always check with your campus EH&S office for the latest information.

Nanoparticles are particles that have at least one dimension between 1-100 nanometers. Particles in this size range have always been present in Earth's air. Nanoparticles may be naturally occurring (such as in volcanic ash), produced as unintentional byproducts (such as in auto emissions) or intentionally created or "engineered." These very small particles often possess radically different properties than larger particles of the same composition, making them of interest to researchers and of potential benefit to society. This fact sheet focuses on lab practices researchers should follow to protect themselves from the hazards of engineered nanoparticles.

Nanoparticles can be spheres, rods, tubes, and other geometric shapes. 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.

Various nanoparticles can be created in the laboratory under experimental procedures, and some can be purchased from commercial vendors. In most research, the amount of material used is small, generally less than a gram.

Only limited information is currently available on the toxicity of a few types of nanoparticles. It is believed that some engineered nanoparticles may present health effects following exposure, based in part on air pollution studies that show smaller particles get deep into the lungs and can cause human illness. However, laboratory research most commonly involves handling nanoparticles in liquid solutions or other forms that do not become easily airborne, and even free formed nanoparticles tend to agglomerate to a larger size.

When research involves work with engineered nanoparticles for which no toxicity data is yet available, it is prudent to assume the nanoparticles may be toxic, and to handle the nanoparticles using the laboratory safety techniques outlined below.

Potential Routes of Occupational Exposure to Researchers

There are four possible routes of workplace exposure to nanoparticles: inhalation, ingestion, skin absorption, and injection.

Skin absorption. In some cases nanoparticles have been shown to migrate through skin and be circulated in the body. If the particle is carcinogenic or allergenic, even tiny quantities may be biologically significant. Skin contact can occur during the handling of liquid suspensions of nanoparticles or dry powders. Skin absorption is much less likely for solid bound or matrixed nanomaterials. Researchers should double glove and use nitrile gloves to protect themselves from skin absorption and contamination, and to protect their research materials from being contaminated. Outer gloves should always be removed inside the hood or under the influence of a local exhaust ventilation and placed into a sealed bag. This will prevent the particles from becoming airborne.

Ingestion. As with any material, ingestion can occur if good hygiene practices are not followed. Once ingested, some types of nanoparticles might be absorbed and transported within the body by the circulatory system. To prevent ingestion, eating and drinking and chewing gum are not allowed in laboratories, outside of designated areas. Also, spills of nanoparticles should be quickly and properly cleaned up, as detailed below.

Inhalation. Respiratory absorption of airborne nanoparticles may occur through the mucosal lining of the trachea or bronchioles, or the alveolus of the lungs. Because of their tiny size, certain nanoparticles appear to penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles. Thus, whenever possible, nanoparticles are to be handled in a form that is not easily made airborne, such as in solution or on a substrate.

Injection. Exposure by accidental injection (skin puncture) is also a potential route of exposure, especially when working with animals or needles. To prevent this, wear double nitrile gloves and lab coats, and apply the standard practices for working with sharps.

Laboratory Safety Guidelines for Handling Engineered Nanoparticles

The current practices for working with engineered nanoparticles safely are essentially the same as one would use when working with any research chemical of unknown toxicity.

1. Use good general laboratory safety practices as stated in your chemical hygiene plan. Wear double gloves (preferably nitrile gloves), safety glasses or goggles, and appropriate protective clothing. Place Tacki-Mat (or similar sticky walk-off mat) at the exit to reduce the likelihood of spreading nanoparticles.

2. All personnel participating in research involving nanoscale materials need to be briefed on the potential hazards of the research activity, as well as on proper techniques for handling nanoparticles. The contents of this Fact Sheet can serve as a useful component of this training. As with all safety training, written records need to be maintained to indicate who has been trained on this topic.

3. **Eating and drinking are allowed only in designated areas where chemicals or nanoparticles are not used.**

4. When purchasing commercially available nanoscale materials, be sure to obtain the Material Safety Data Sheet (MSDS) and to review the information in the MSDS with all persons who will be working with the material. Note, however, that given the lack of extensive data on nanoparticles, the information on an MSDS may be more applicable to the properties of the bulk material.

5. Be aware of the fire risk when working with reactive nanomaterials. Under certain conditions, combustible nanomaterials may present a higher risk when exposed to air due to their large surface area and overall small size. Carbonaceous and metal dusts can burn and explode if an oxidant such as air and an ignition source are present; self-heating may occur when reactive moieties, such as double bonds, are constituents of the carbonaceous material. Prior to starting work, assess whether large quantities/high concentrations of nanoparticles will be generated. Verify that appropriate chemical fire extinguishers are available and in working order before starting work.

6. In some cases, the manufacture of nanomaterials involves the use of chemicals that are known to be hazardous or toxic. Be sure to consider the hazards of the precursor materials when evaluating the process hazard or final product. Users of any chemicals should make themselves familiar with the known chemical hazards by reading the MSDS or other hazard literature.

7. To minimize airborne release of engineered nanoparticles to the environment, nanoparticles are to be handled in solutions, or attached to substrates so that dry material is not released. Where this is not possible, nanoscale materials should be handled with engineering controls such as a HEPA-filtered local capture hood or glove box. If neither is available, work should be performed inside a laboratory fume hood. HEPA-filtered local capture systems should be located as close to the possible source of nanoparticles as possible, and the installation must be properly engineered to maintain adequate ventilation capture.

8. Use fume exhaust hoods to expel any nanoparticles from tube furnaces or chemical reaction vessels. Do not exhaust aerosols containing engineered nanoparticles inside buildings.

9. If you must work outside of a ventilated area with nanomaterials that could become airborne, wear a respirator with NIOSH-approved filters that are rated as N-, R- or P-100 (HEPA). EH&S will work with researchers to provide the most appropriate type of respirator. Refer to your campus' Respiratory Protection Program for requirements.

10. Lab equipment and exhaust systems used with nanoscale materials should be wet wiped and HEPA vacuumed prior to repair, disposal, or reuse. Construction/maintenance crews should contact EH&S for assistance.

11. Spills of engineered nanoparticles are to be cleaned up right away.
    a. The person cleaning up should wear double nitrile gloves and either vacuum up the area with a HEPA-filtered vacuum or wet wipe the area with towels, or combination of the two.
    b. For spills that might result in airborne nanoparticles, proper respiratory protection should be worn (see item 8 above). For assistance with cleaning up any chemical spill contact EH&S.
    c. Do not brush or sweep spilled/dried nanoparticles.
    d. Place Tacki-Mat at the exit to reduce the likelihood of spreading nanoparticles.

12. Work surfaces should be wet-wiped regularly – daily is recommended. Because many engineered nanoparticles are not visible to the naked eye, surface contamination may not be obvious. Alternatively, disposable bench paper can be used.

13. All waste engineered nanoparticles should be treated as unwanted hazardous "toxic" materials unless they are known to be non-hazardous. Dispose of and transport waste nanoparticles in solution according to hazardous waste procedures for the solvent. If you have questions on how to dispose a specific nanoparticle waste, call EH&S for more information.

For more information on Health and Safety of Nanotechnology visit the following web sites:

NIOSH (http://www.cdc.gov/niosh/topics/nanotech/)

National Nanotechnology Initiative (http://www.nano.gov/)

EPA (http://www.epa.gov/oppt/nano/nano-facts.htm)

Woodrow Wilson International Center for Scholars (http://nanotechproject.org/)

Rice University (http://cnst.rice.edu/)

This fact sheet was developed by the University of California Lab Safety Work Group, a subcommittee of the University of California Industrial Hygienists and Safety Steering Committee.

Revised January 2010. September 2008

Attachment 5 Appendices

Standard Operating Procedures – Carbon Nanotubes

Appendix A

UC Irvine Standard Operating Procedure for Working with Carbon Nanotubes (CNT)

Appendix B

Safe Handling of Dry Carbon Nanotube Powder

UCLA School of Public Health, Industrial Hygiene Program

Appendix C

Evaluation of Novel Electrocatalyst Materials for Fuel Cells

University of California Riverside

Appendix A

UC Irvine Standard Operating Procedure for Working with Carbon Nanotubes (CNT)

UC Irvine Standard Operating Procedure for Working with Carbon Nanotubes (CNT)

Prerequisites

All users of nanomaterials must:

- complete the Laboratory Safety Core hazard awareness training class through EH&S
- have reviewed the attached UC document titled Nanotechnology: Guidelines for Safe Research Practices
- read and reviewed the Material safety Data Sheets
- prepared and reviewed the SOP with their Principal Investigators.

Health Effects

Exposure to engineered nanoparticles may cause adverse health effects similar to well characterized ultrafine particles that have similar characteristics. Recent animal inhalation studies indicate CNTs may cause inflammation and fibrosis.

Be sure to consider the hazards of the precursor materials when evaluating the process hazard or final product.

It is prudent to assume that nanomaterials may be toxic and to follow the safe handling practices outlined below.

Safe Work Practices

1. Follow the general laboratory safety procedures outline in the Chemical Hygiene Plan.
2. Safety glasses, lab coats, nitrile gloves and closed toe shoes are required in the laboratory. Consider using disposable lab coats where there's a possibility of significant contamination and dispose of as hazardous waste.
3. Weighing dry, loose carbon nanoparticles must be done in a fume hood or a glove box.
4. Dry, loose carbon nanomaterials should be stored in sealed containers to avoid accidental dispersion of materials into the air and to avoid fire hazard.
5. Routine handling of dry, loose carbon nanomaterials should be carried out in fume hoods or glove boxes until such time as the material is dissolved or suspended in liquid or become physically attached to a solid material.
6. If it is necessary to manipulate dry, loose carbon nanomaterials outside of the fume hood, a job hazard analysis will be required to assess the hazards, evaluate the need for P100 respiratory protection, and clean up procedures.
7. Avoid skin contact with nanoparticles or nanoparticle-containing solutions by using appropriate PPE.

8. Use fume hood to expel fumes from tube furnaces or chemical reaction vessels.

Clean-up / Decontamination Disposal

To prevent accumulation of nanomaterials on work area surfaces, routine cleaning is necessary. Bench surfaces and other work areas should be routinely damp-wiped daily.

1. Accidental spills must be cleaned up immediately. Always have a bottle of liquid with surfactant and laboratory wipes handy. Standard approaches to cleaning up powder and liquid spills include the use of HEPA-filtered (High Efficiency Particulate Air filter) vacuum cleaners, wetting agents, using dampened cloths to wipe up powders, and applying absorbent materials.
2. Dispose of nanomaterials and cleaning materials as hazardous waste.
3. Lab equipment and exhaust systems should be wetted with water/surfactant and wiped down then HEPA vacuumed prior to their removal, remodelling or repair.
4. For larger spills, the use of a HEPA filtered vacuum cleaner is recommended. Contact EH&S for assistance. Use Tacki mats to reduce the spread of spilled materials.
5. Dry sweeping or pressurized gas hoses should not be used for cleaning as these will distribute nanoparticles in the air. Cleanup should be performed in such a way as to prevent personal contact with any waste material.
6. Researchers should wash their hands before leaving the area.
7. All waste that contains (or may contain) nanoparticles is to be disposed of in a clearly labelled container and is to be treated as hazardous waste through EH&S.

<u>Potential for workplace exposure</u>

Devices comprised of nanostructures, such as integrated circuits and composite materials, pose a minimal risk of exposure to nanoparticles during handling.

- If such materials are subject to machine working (e.g., cutting or grinding), or go through degradation processes that lead to the release of nanoparticles, then exposure may occur by the inhalation, ingestion, and/or dermal penetration of these particles.

Some workplace factors that can increase the potential for exposure include:

- Working with nanoparticles in liquid or solid form during mixing operations such as crushing or sonication may result in exposure.

- Generating nanoparticles in the gas phase in open systems may increase the chances of aerosol release to the workplace.

- Handling nanoparticles powders outside the fume hood may lead to the possibility of skin and inhalation exposure.

- Maintenance on equipment and processes used to produce or fabricate nanomaterials may pose a potential exposure risk to workers performing these tasks.

- Cleaning of dust collection systems used to capture nanoparticles may pose a potential for both skin and inhalation exposure.

Additional Information: Chemical Vapor Deposition (CVD) Deposition of CNTs

Chemical Vapor Deposition is a general technique of deposition of materials using chemical reaction of vapor on the surfaces of the sample. In carbon nanotubes or nanofibers deposition, this is usually aided with a transition metal catalyst e.g. nickel, iron, cobalt.

The procedure involves putting a catalyst coated substrate (usually silicon wafer) into the chamber. The CNT growth involves heating up the substrate under an inert gas atmosphere, introduction of a hydrocarbon gas e.g. acetylene, methane, etc for desired amount of time, and cooling of the sample under an inert gas..

The process is safer than bulk nanomaterials handling because:

- The nanotubes are attached to the substrate,
- The chamber is operated in vacuum and purged with inert gases and
- Cooling stage is typically over an hour under inert gas environment.

Additional Precautions:

- Ensure chamber temperature is less than the autoignition temperature of the flammable gas in use before venting to the atmosphere.
- Ensure chamber is purged with an inert gas before venting the system to atmosphere.
- Chamber is then cleaned using heat and oxygen. All carbon nanomaterials would be etched away during the process.

FACT SHEET

Nanotechnology: Guidelines for Safe Research Practices

Introduction

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Only limited information is currently available on the toxicity of a few types of nanoparticles. It is believed that some engineered nanoparticles may present health effects following exposure, based in part on air pollution studies that show smaller particles get deep into the lungs and can cause human illness. However, laboratory research most commonly involves handling nanoparticles in liquid solutions or other forms that do not become easily airborne, and even free formed nanoparticles tend to agglomerate to a larger size.

When research involves work with engineered nanoparticles for which no toxicity data is yet available, it is prudent to assume the nanoparticles may be toxic, and to handle the nanoparticles using the laboratory safety techniques outlined below.

Potential Routes of Occupational Exposure to Researchers

There are four possible routes of workplace exposure to nanoparticles: inhalation, ingestion, skin absorption, and injection.

Skin absorption. In some cases nanoparticles have been shown to migrate through skin and be circulated in the body. If the particle is carcinogenic or allergenic, even tiny quantities may be biologically significant. Skin contact can occur during the handling of liquid suspensions of nanoparticles or dry powders. Skin absorption is much less likely for solid bound or matrixed nanomaterials. Researchers should double glove and use nitrile gloves to protect themselves from skin absorption and contamination, and to protect their research materials from being contaminated. Outer gloves should always be removed inside the hood or under the influence of a local exhaust ventilation and placed into a sealed bag. This will prevent the particles from becoming airborne.

Ingestion. As with any material, ingestion can occur if good hygiene practices are not followed. Once ingested, some types of nanoparticles might be absorbed and transported within the body by the circulatory system. To prevent ingestion, eating and drinking and chewing gum are not allowed in laboratories, outside of designated areas. Also, spills of nanoparticles should be quickly and properly cleaned up, as detailed below.

Inhalation. Respiratory absorption of airborne nanoparticles may occur through the mucosal lining of the trachea or bronchioles, or the alveolus of the lungs. Because of their tiny size, certain nanoparticles appear to penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles. Thus, whenever possible, nanoparticles are to be handled in a form that is not easily made airborne, such as in solution or on a substrate.

Injection. Exposure by accidental injection (skin puncture) is also a potential route of exposure, especially when working with animals or needles. To prevent this, wear double nitrile gloves and lab coats, and apply the standard practices for working with sharps.

Laboratory Safety Guidelines for Handling Engineered Nanoparticles

The current practices for working with engineered nanoparticles safely are essentially the same as one would use when working with any research chemical of unknown toxicity.

1. Use good general laboratory safety practices as stated in your chemical hygiene plan. Wear double gloves (preferably nitrile gloves), safety glasses or goggles, and appropriate protective clothing. Place Tacki-Mat (or similar sticky walk-off mat) at the exit to reduce the likelihood of spreading nanoparticles.

2. All personnel participating in research involving nanoscale materials need to be briefed on the potential hazards of the research activity, as well as on proper techniques for handling nanoparticles. The contents of this Fact Sheet can serve as a useful component of this training. As with all safety training, written records need to be maintained to indicate who has been trained on this topic.

3. Eating and drinking are allowed only in designated areas where chemicals or nanoparticles are not used.

4. When purchasing commercially available nanoscale materials, be sure to obtain the Material Safety Data Sheet (MSDS) and to review the information in the MSDS with all persons who will be working with the material. Note, however, that given the lack of extensive data on nanoparticles, the information on an MSDS may be more applicable to the properties of the bulk material.

5. In some cases, the manufacture of nanomaterials involves the use of chemicals that are known to be hazardous or toxic. Be sure to consider the hazards of the precursor materials when evaluating the process hazard or final product. Users of any chemicals should make themselves familiar with the known chemical hazards by reading the MSDS or other hazard literature.

6. To minimize airborne release of engineered nanoparticles to the environment, nanoparticles are to be handled in solutions, or attached to substrates so that dry material is not released. Where this is not possible, nanoscale materials should be handled with engineering controls such as a HEPA-filtered local capture hood or glove box. If neither is available, work should be performed inside a laboratory fume hood. HEPA-filtered local capture systems should be located as close to the possible source of nanoparticles as possible, and the installation must be properly engineered to maintain adequate ventilation capture.

7. Use fume exhaust hoods to expel any nanoparticles from tube furnaces or chemical reaction vessels. Do not exhaust aerosols containing engineered nanoparticles inside buildings.

8. If you must work outside of a ventilated area with nanomaterials that could become airborne, wear a respirator with NIOSH-approved filters that are rated as N-, R- or P-100 (HEPA). EH&S will work with researchers to provide the most appropriate type of respirator. Refer to your campus' Respiratory Protection Program for requirements.

9. Lab equipment and exhaust systems used with nanoscale materials should be wet wiped and HEPA vacuumed prior to repair, disposal, or reuse. Construction/maintenance crews should contact EH&S for assistance.

10. Spills of engineered nanoparticles are to be cleaned up right away.

    i)The person cleaning up should wear double nitrile gloves and either vacuum up the area with a HEPA-filtered vacuum or wet wipe the area with towels, or combination of the two.

    ii) For spills that might result in airborne nanoparticles, proper respiratory protection should be worn (see item 8 above). For assistance with cleaning up any chemical spill contact EH&S.

    iii) Do not brush or sweep spilled/dried nanoparticles.

    iv) Place Tacki-Mat at the exit to reduce the likelihood of spreading nanoparticles.

11. Work surfaces should be wet-wiped regularly – daily is recommended. Because many engineered nanoparticles are not visible to the naked eye, surface contamination may not be obvious. Alternatively, disposable bench paper can be used.

12. All waste engineered nanoparticles, including wafers containing nanomaterials, should be treated as unwanted hazardous "toxic" materials unless they are known to be non-hazardous. Dispose of and transport waste nanoparticles in solution according to hazardous waste

procedures for the solvent. If you have questions on how to dispose a specific nanoparticle waste, call EH&S for more information.

For more information on Health and Safety of Nanotechnology visit the following web sites:
NIOSH (http://www.cdc.gov/niosh/topics/nanotech/)
http://www.cdc.gov/niosh/docs/2009-125/pdfs/2009-125.pdf
National Nanotechnology Initiative (http://www.nano.gov/)
EPA (http://www.epa.gov/oppt/nano/nano-facts.htm)
Woodrow Wilson International Center for Scholars (http://nanotechproject.org/)
Rice University (http://cnst.rice.edu/)
This fact sheet was developed by the University of California Lab Safety Work Group, a subcommittee of the University of California Industrial Hygienists and Safety Steering Committee.
September 2008

These training resources were provided by a variety of sources. It is your responsibility to customize the information to match your specific operations. These resources were prepared solely for the use of the Regents of the University of California. Neither the University of California nor any of its employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the University of California, and shall not be used for advertising or product endorsement purposes.

Appendix B

Safe Handling of Dry Carbon Nanotube Powder

UCLA School of Public Health, Industrial Hygiene Program

Safe Handling of Dry Carbon Nanotube Powder

by Nancy Jennerjohn, Arantza Eiguren-Fernandez and Nola Kennedy
UCLA School of Public Health, Industrial Hygiene Program

Dry carbon nanotube (CNT) powder is lightweight and extremely low density, and as a result CNTs have a tendency to escape into air currents. In addition, CNTs are electrostatically charged, making them attracted to nearby objects and thereby difficult to control. This document outlines safe handling procedures to help control the release of CNTs during typical experimental handling procedures, such as weighing and container transfer.

CNTs should always be handled in a fume hood, but the relatively strong air current of the fume hood can create additional airborne releases of CNTs. To prevent this, this guidance document outlines a method for handling CNTs to reduce employee exposure and product loss. Requirements for personal protective equipment are also included.

PPE Requirements

Before you begin handling CNTs, assemble and don the following PPE:

- A lab coat, preferably made of a non-woven material and with gathered/non-woven wristbands
- Double nitrile or latex gloves pulled over the sleeves of your labcoat
- A minimum of P-100 respiratory protection.

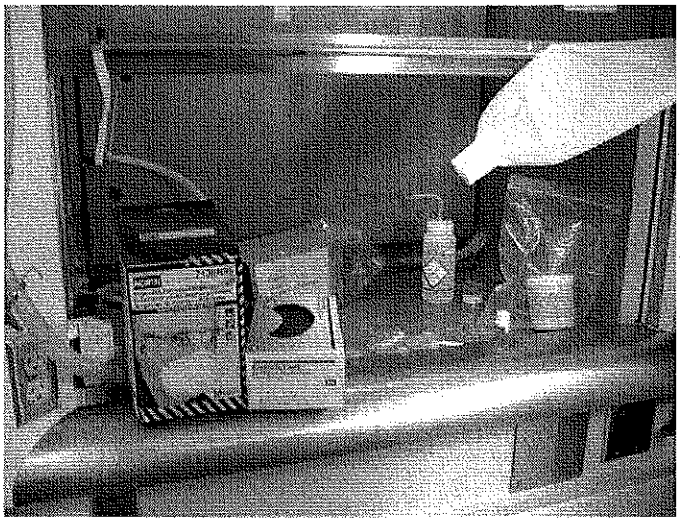


Figure 1: Equipment gathered in and near the fume hood prior to transferring nanotubes from one container to another.

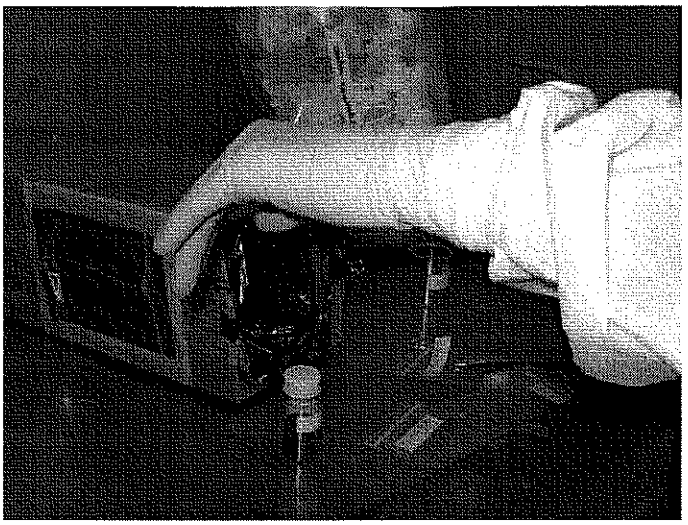


Figure 2: Gloves pulled over the sleeves of a lab coat to prevent dermal contact with nanotubes.

Preventing CNT Release During Container Opening

Opening a container filled with nanotubes inside a fume hood may cause significant spontaneous loss of product. Manufacturers' nanotube product containers are often overfilled, and there is frequently no label warning of this. Therefore never open a container of nanotubes, especially a previously unopened one, outside a fume hood without wearing the required PPE.

Weighing and Transferring CNTs

The following procedure is designed to minimize releases of CNTs:

- Do not stand too close to the front of the fume hood, or lean against the sash. Close proximity to the fume hood entrance creates eddies which may draw particles out of the fume hood and into the breathing zone.

- Empty the fume hood of unnecessary equipment so that any CNT flakes that may escape inside the fume hood do not lodge onto nearby equipment. Equipment contamination that occurs may not be visible, resulting in a release of nanotubes when the equipment is removed from the fume hood and releasing CNTs into the ambient air.

- Place the static control box, described in the next section, inside the fume hood.

- Place a large labeled plastic bag, preferably with a zipper lock, into one corner of the fume hood for hazardous waste. This bag must be large enough to accommodate a lab coat if your gown becomes soiled with nanotubes.

- Place tissues and a wash bottle filled with the solvent of your choice inside the fume hood. Place the plastic-lined box, with the open end facing out, on its side, deep inside the fumehood, but not so deeply that you cannot manipulate both containers while one of your

hands is inside the box.

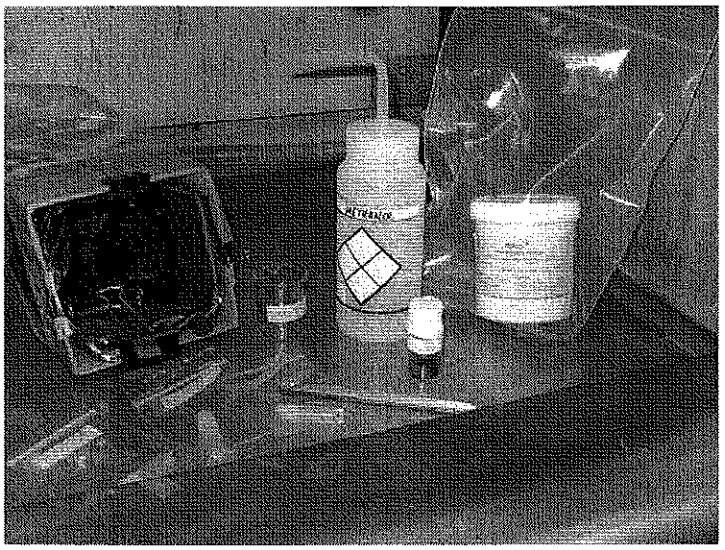
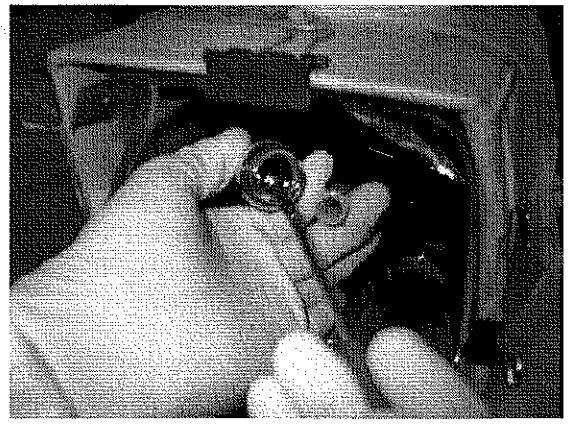


Figure 3: Place the lined box deeply into the fumehood, together with the other equipment.

- Pre-weigh the new container and its lid, if desired. Place the new container, its lid, the original un-opened container, and a clean transfer spatula into the plastic-lined box. Don gloves, gown and mask. Loosen the lid on the container containing nanotubes. With your non-dominant gloved hand inside the box, pick up and hold both containers between your fingers if possible, deep inside the box, so the mouths of both containers are close together and both containers are tilted slightly toward you.

- Keeping both containers deep inside the box to prevent loss of product, remove the lid of the container containing nanotubes with your other hand. Place this "dirty" lid on the bottom of the box. Both containers are now open. Carefully transfer the desired mass of nanotubes, using the spatula, into the new container, transferring only manageable quantities that you can carefully control at one time.



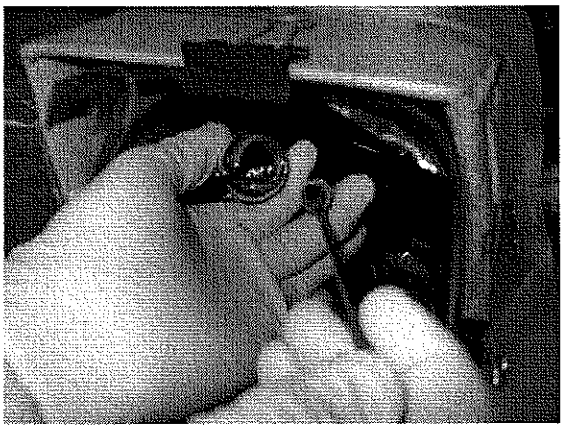


Figure 4: Transfer of carbon nanotubes taking place between two relatively small containers.

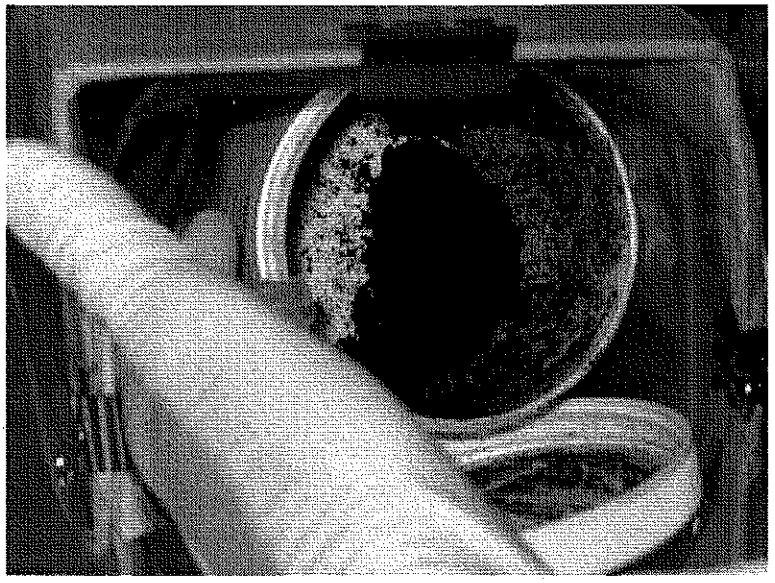


Figure 5: Transfer of carbon nanotubes from a large to a small container.

- When all the nanotubes have been transferred, place the lids on both containers and close tightly. Place the now dirty spatula inside the bottom of the box.

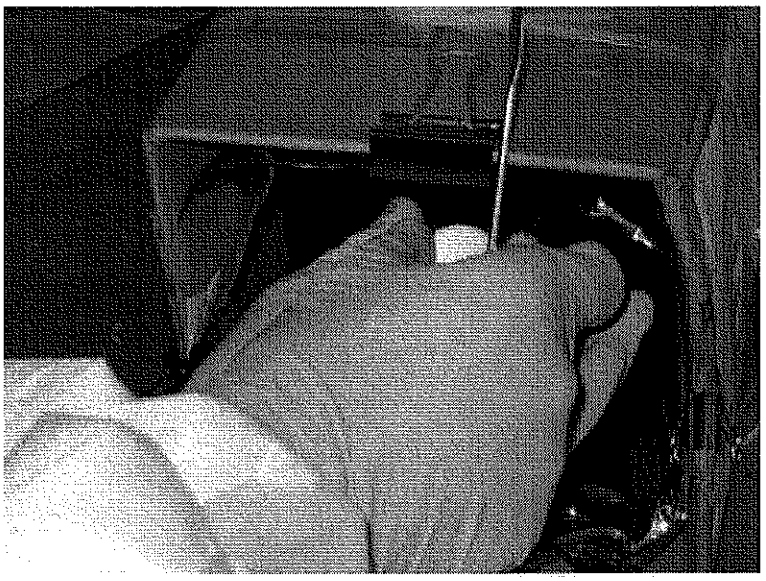


Figure C6: Tight closure of the containers containing carbon nanotubes.

- Remove both closed containers from the box, and set them down inside the fume hood.

Clean-up and Waste Disposal Practices

- Examine the outsides of both containers and your gloved hands and the sleeves of your labcoat. If there are visible CNTs on the outside of either container, rinse them off, making sure the rinse water is collected into a hazardous waste container inside the fume hood. When both containers are clean, set them down inside the fume hood to dry.

- If there are visible CNTs on the spatula, rinse it off, again collecting the rinse water. If nanotubes have adhered to your gloves, the gloves must be removed in an inside-out manner (Figure 7) and discarded in the hazardous waste bag inside the fume hood—Never remove soiled gloves from the fume hood unless they are enclosed inside the hazardous waste bag.

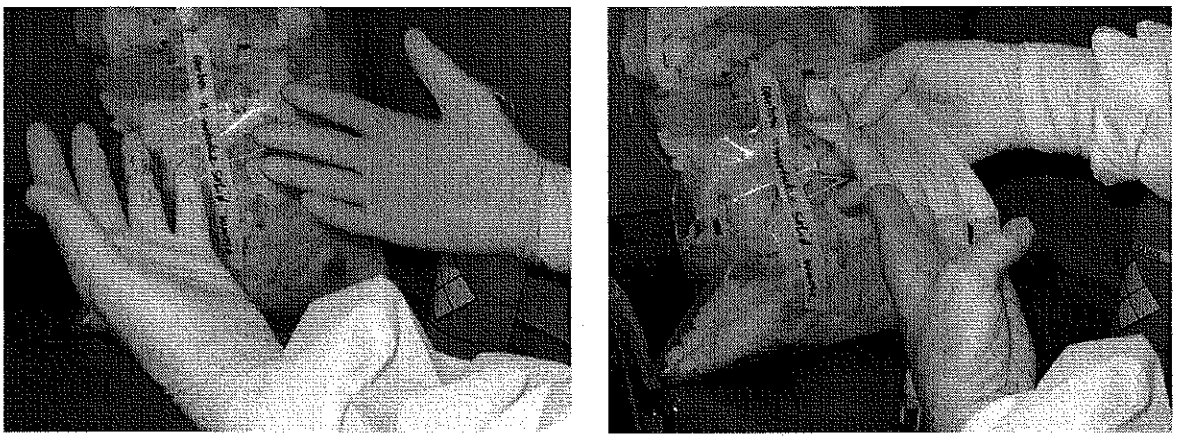


Figure 7: Examination of both gloved hands after nanotube transfer, and removal of gloves in an inside out manner to prevent dermal contamination.

- Without removing your hands from the fume hood, make sure no nanotubes have adhered to your sleeves. If they have, remove the gown carefully in an inside-out manner so no nanotubes touch your skin, and so that the entire gown ends up in a tightly rolled ball inside the fume hood. Place the entire gown in the hazardous waste container.

- If, upon weighing the new container, not enough nanotubes were obtained, repeat the entire procedure until the correct mass is obtained. Label and dispose of all hazardous waste in a timely manner.

Construction of an Anti-static Box for Transferring Carbon Nanotubes

Nanotubes are often electrostatically charged, so implementing some static control measures can help reduce product releases during material transfer. Obtain a cardboard box large enough to hold one hand, the bulk container and the new, with some room to spare. A 6 x 6 x 9 inch box may be large enough if both containers are small.

Remove the box's flaps, or secure its flaps to the box's sides, so that only one side of the box is open, and the box is firmly intact. Line the inside of the box with non-electrostatic airtight plastic. This plastic may be able to be obtained from an outside vendor, or is sometimes found as a large bag surrounding newly acquired electronic equipment. An electronics store may have a supply. The bag can be secured to the box using clamps if desired, as shown:

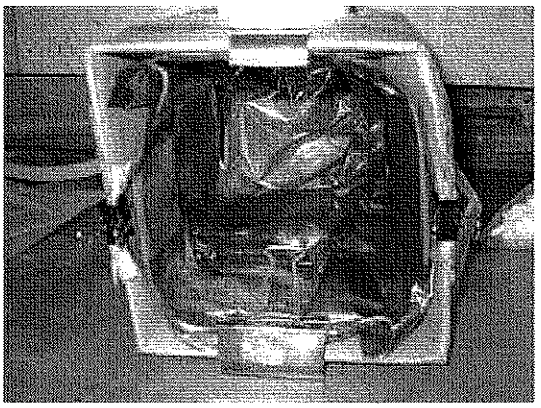


Figure 9: Cardboard box containing non-electrostatic airtight bag.

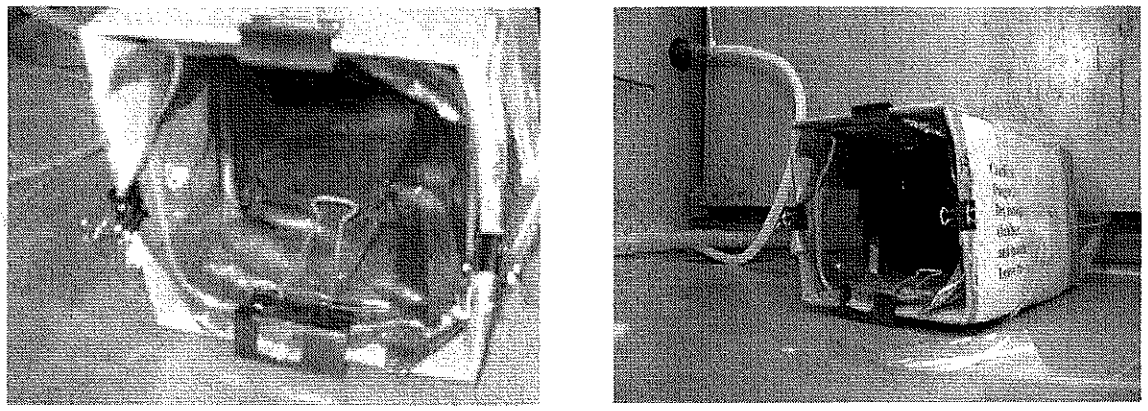


Figure 10: Non-electrostatic bag secured to the cardboard box using clamps.

When you are done using the box, label it, place it inside double plastic bags, and store it outside the fumehood.

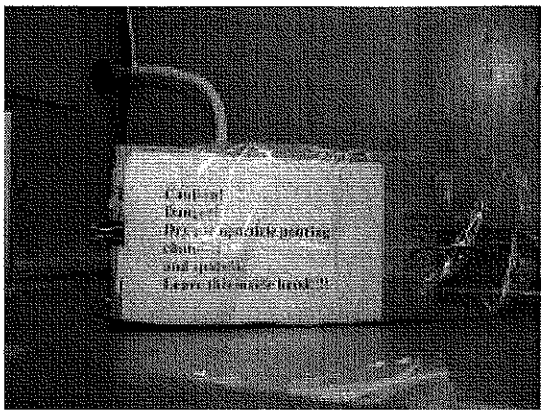


Figure 11: Cardboard box, now contaminated with carbon nanotubes, carefully labeled, placed inside an airtight bag and sealed. This box in its closed bag will be stored inside another air-tight bag, for long-term storage and eventual re-use.

**Special thanks to Camilla Ben-Levi for assistance with photography.

Appendix C

Evaluation of Novel Electrocatalyst Materials for Fuel Cells

University of California Riverside

Appendix A

Evaluation of Novel Electrocatalyst Materials for Fuel Cells

PI: Robert C Haddon, University of California at Riverside

TASKS TO BE PERFORMED

Task 1: Processing of carbon nanotube (CNT) powder

1. Purified carbon nanotube powder will be obtained from commercial source
2. Surface treatment of carbon nanotubes to enhance catalyst binding
3. Deposition of catalyst metals on carbon nanotubes

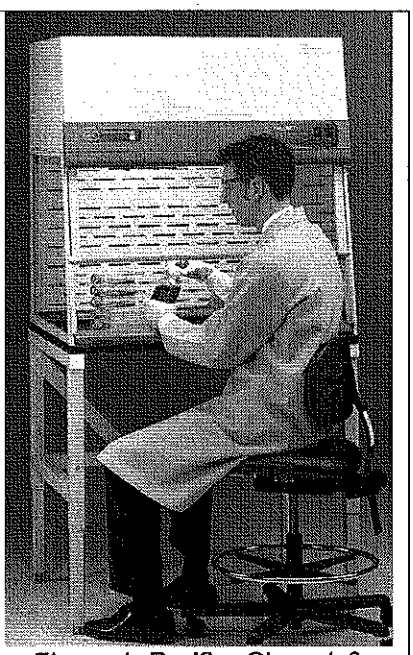


Figure 1. Purifier Class 1 & HEPA Filtered Enclosure
Catalog Number: 3980402

Safety measures:

- Only persons with sufficient awareness of the hazards and adequate training on the procedures will be allowed to work with the dry CNT powder
- Containers of CNT powder will be handled inside a bio-safety cabinet with HEPA filter (Figure 1).
- The personnel protective equipment (PPE) used by the individuals handling the CNT powders and others present in the vicinity consist of lab coats, nitrile gloves and safety glasses.
- If at anytime the carbon nanotubes are handled dry outside of the HEPA filtered enclosure, all personnel in the area will wear N95 filtering face pieces or respirators with HEPA filters.
- The weighing and transferring of the CNT powder will be carried out in the bio-safety cabinet.
- The CNT powder will be transferred to a suitable liquid medium and dispersed within the bio-safety cabinet, to avoid the escape of air-borne particulate matter.
- The CNT dispersion will be transferred from the bio-safety cabinet to a standard laboratory fume hood for further processing.
- Any spills of the CNT power outside of the HEPA filtered enclosure will be treated as a hazardous aerosol release; the room evacuated and EH&S called to respond with a HEPA vacuum and respiratory protection
- Any spills of dispersed CNT will be treated as a spill of the solvent, unless allowed to dry, then they become a CNT powder spill.

Task 2: Characterization of carbon nanotubes

Safety measures:

- CNT powders for characterization will be obtained by drying a dispersion of carbon nanotubes in a bio-safety cabinet.
- Carbon nanotubes and related nanoparticles will be supported on a suitable substrate which does not release individual nanotubes to the atmosphere for characterization by spectroscopy, electrochemistry or microscopy.
- Transportation of dried CNT dispersions will be in a secondary container with a tight fitting lid such as 'Tupperware'.

Task 3: Preparation of CNT thin films and their application

Safety measures:

- Thin films of carbon nanotubes will be prepared by a filtration technique which will leave the CNTs attached to a substrate to avoid the generation of air-borne particles.
- Devices comprised of carbon nanotube thin films will be isolated so as to avoid human contact and tested in the device configuration.

Storage:

The as-received and processed powders of CNTs will be stored in an air tight container in a designated cabinet

Disposal:

UCR EHS policy will be followed in disposing of waste containing nanomaterials

Appendix B

http://ucih.ucdavis.edu/pages/docs.cfm

Nanotechnology: Guidelines for Safe Research Practices

Introduction

This fact sheet provides environmental, health and safety information to researchers working with engineered nanoparticles, and should be incorporated as a standard operating procedure in each laboratory's chemical hygiene plan. Given the evolving knowledge base regarding health effects of nanoparticles, this fact sheet may be updated. Always check with your campus EH&S office for the latest information.

Nanoparticles are particles that have at least one dimension between 1-100 nanometers. Particles in this size range have always been present in Earth's air. Nanoparticles may be naturally occurring (such as in volcanic ash), produced as unintentional byproducts (such as in auto emissions) or intentionally created or "engineered." These very small particles often possess radically different properties than larger particles of the same composition, making them of interest to researchers and of potential benefit to society. This fact sheet focuses on lab practices researchers should follow to protect themselves from the hazards of engineered nanoparticles.

Nanoparticles can be spheres, rods, tubes, and other geometric shapes. 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.

Various nanoparticles can be created in the laboratory under experimental procedures, and some can be purchased from commercial vendors. In most research, the amount of material used is small, generally less than a gram.

Only limited information is currently available on the toxicity of a few types of nanoparticles. It is believed that some engineered nanoparticles may present health effects following exposure, based in part on air pollution studies that show smaller particles get deep into the lungs and can cause human illness. However, laboratory research most commonly involves handling nanoparticles in liquid solutions or other forms that do not become easily airborne, and even free formed nanoparticles tend to agglomerate to a larger size.

When research involves work with engineered nanoparticles for which no toxicity data is yet available, it is prudent to assume the nanoparticles may be toxic, and to handle the nanoparticles using the laboratory safety techniques outlined below.

Potential Routes of Occupational Exposure to Researchers

There are four possible routes of workplace exposure to nanoparticles: inhalation, ingestion, skin absorption, and injection.

Skin absorption. In some cases nanoparticles have been shown to migrate through skin and be circulated in the body. If the particle is carcinogenic or allergenic, even tiny quantities may be biologically significant. Skin contact can occur during the handling of liquid suspensions of nanoparticles or dry powders. Skin absorption is much less likely for solid bound or matrixed nanomaterials. Researchers should wear gloves to protect themselves from skin absorption and contamination, and to protect their research materials from being contaminated. Gloves should always be removed inside the hood or under the influence of a local exhaust ventilation and placed into a sealed bag. This will prevent the particles from becoming airborne.

Ingestion. As with any material, ingestion can occur if good hygiene practices are not followed. Once ingested, some types of nanoparticles might be absorbed and transported within the body by the circulatory system. To prevent ingestion, eating and drinking and chewing gum are not allowed in laboratories, outside of designated areas. Also, spills of nanoparticles should be quickly and properly cleaned up, as detailed below.

Inhalation. Respiratory absorption of airborne nanoparticles may occur through the mucosal lining of the trachea or bronchioles, or the alveolus of the lungs. Because of their tiny size, certain nanoparticles appear to penetrate deep into the lungs and may translocate to other organs following pathways not demonstrated in studies with larger particles. Thus, whenever possible, nanoparticles are to be handled in a form that is not easily made airborne, such as in solution or on a substrate.

Injection. Exposure by accidental injection (skin puncture) is also a potential route of exposure, especially when working with animals or needles. To prevent this, wear gloves and lab coats, and apply the standard practices for working with sharps.

Laboratory Safety Guidelines for Handling Engineered Nanoparticles

The current practices for working with engineered nanoparticles safely are essentially the same as one would use when working with any research chemical of unknown toxicity.

1. Use good general laboratory safety practices as stated in your chemical hygiene plan. Wear double gloves (preferably nitrile gloves), safety glasses, and appropriate protective clothing.
2. All personnel participating in research involving nanoscale materials need to be briefed on the potential hazards of the research activity, as well as on proper techniques for handling nanoparticles. The contents of this Fact Sheet can serve as a useful component of this training. As with all safety training, written records need to be maintained to indicate who has been trained on this topic.
3. Eating and drinking are allowed only in designated areas where chemicals or nanoparticles are not used.
4. When purchasing commercially available nanoscale materials, be sure to obtain the Material Safety Data Sheet (MSDS) and to review the information in the MSDS with all persons who will be working with the material.
5. In some cases, the manufacture of nanomaterials involves the use of chemicals that are known to be hazardous or toxic. Be sure to consider the hazards of the precursor materials when evaluating the process hazard or final product. Users of any chemicals should make themselves familiar with the known chemical hazards by reading the MSDS or other hazard literature.
6. To minimize airborne release of engineered nanoparticles to the environment, nanoparticles are to be handled in solutions, or attached to substrates so that dry material is not released. Where this is not possible, nanoscale materials should be handled with engineering controls such as a HEPA-filtered local capture hood or glove box. If neither is available, work should be performed inside a laboratory fume hood. HEPA-filtered local capture systems should be located as close to the possible source of nanoparticles as possible, and the installation must be properly engineered to maintain adequate ventilation capture.
7. Use fume exhaust hoods to expel any nanoparticles from tube furnaces or chemical reaction vessels. Do not exhaust aerosols containing engineered nanoparticles inside buildings.
8. If you must work outside of a ventilated area with nanomaterials that could become airborne, wear a respirator with NIOSH-approved filters that are rated as HEPA. EH&S will work with researchers to provide the most appropriate type of respirator. Refer to your campus' Respiratory Protection Program for requirements.
9. Equipment used to create or handle nanoscale materials should be cleaned or evaluated for potential contamination prior to disposal or reuse.

10. Lab equipment and exhaust systems should be evaluated prior to repair, remodeling, or removal, and construction/maintenance crews need to be alerted to the potential exposure to nanoparticles. Contact EH&S for assistance with this notification.
11. Spills of engineered nanoparticles are to be cleaned up right away. The person cleaning up should wear gloves and either vacuum up the area with a HEPA filtered vacuum or wet wipe the area with towels, or combination of the two. For spills that might result in airborne nanoparticles, proper respiratory protection should be worn (see item 8 above). For assistance with cleaning up any chemical spill contact EH&S.
12. Dispose of and transport waste nanoparticles in solution according to hazardous waste procedures for the solvent. All waste engineered nanoparticles should be treated as unwanted hazardous "toxic" materials unless they are known to be non-hazardous. If you have questions on how to dispose of a specific nanoparticle waste, call EH&S for more information.

References

For more information on Health and Safety of Nanotechnology visit the following web sites:

- NIOSH (http://www.cdc.gov/niosh/topics/nanotech/)
- National Nanotechnology Initiative (http://www.nano.gov/)
- EPA (http://www.epa.gov/oppt/nano/nano-facts .htm)
- Rice University (http://cnst.rice.edu/)
- Woodrow Wilson International Center for Scholars (http://nanotechproject.org/)

This fact sheet was developed by the University of California Lab Safety Work Group, a subcommittee of the University of California Industrial Hygienists and Safety Steering Committee.
September 2008