Nanoparticles in Research

A Health and Safety Overview

October 2016

About SLR: Nathan Redfern

- Employee owned International Company with 1,000 staff
- 200 staff & 13 Offices in Australia and New Zealand
- Established in Australia more than 30 years
- HSH Team has 30 staff in APAC
- Working with universities for more than 15 years
- Working regularly with Curtin since 2011

NATHAN REDFERN, COH CMFOH CChem ChOHSP
Technical Discipline Manager, Health Safety & Hygiene
& WHS Manager Asia Pacific

SLR: Our Role at Curtin University

- Hazardous Substances Infrastructure Manager engaged by Properties, Facilities and Development (Erin Poultney)
- Engagement with Properties stakeholders: HSEM, Laboratory staff, Researchers
- Development and maintenance of Project Design Guidelines which set out Curtin University design standards
- Nano-particles Design Guidelines

Nanomaterials: what are they?

Nanomaterials are usually considered to be materials with at least one external dimension that measures 100 nanometres or less or with internal structures measuring 100 nm or less.

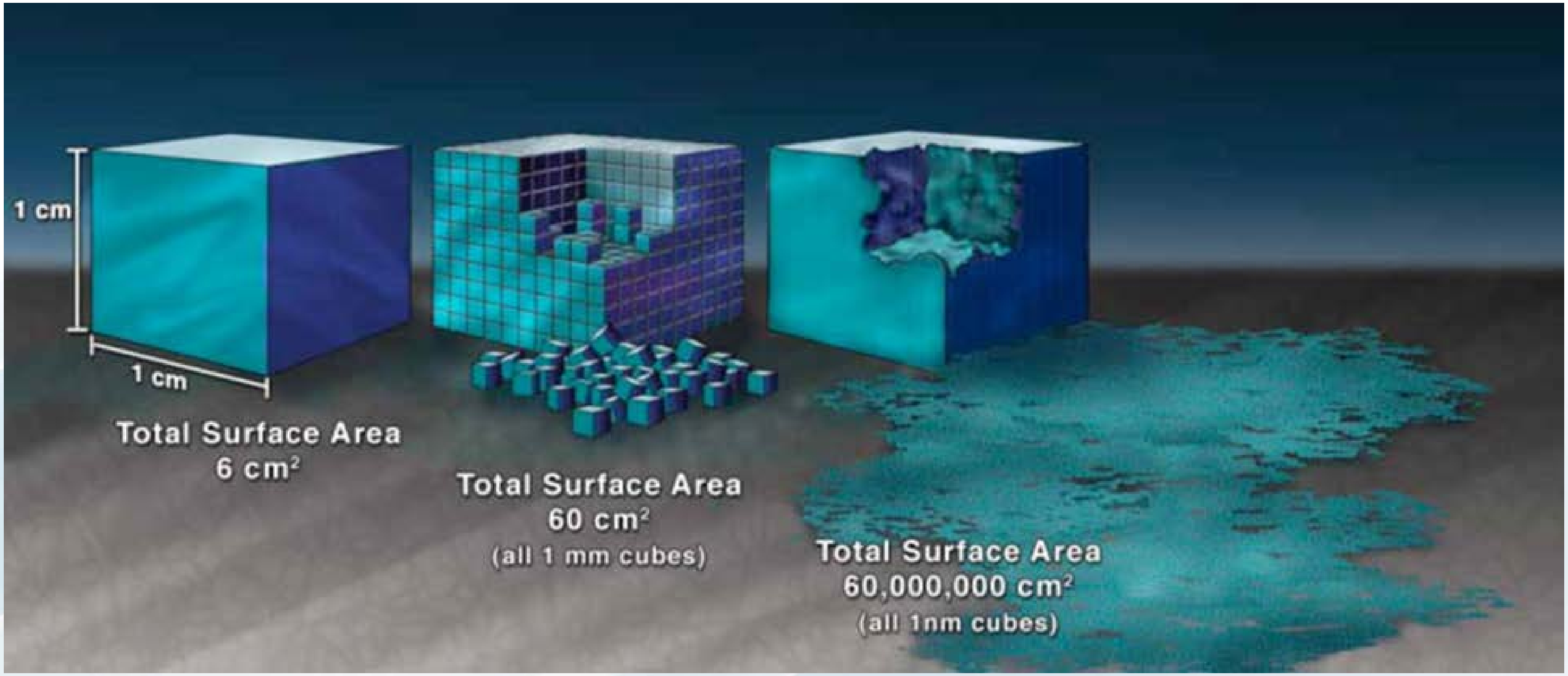
They may be in the form of particles, tubes, rods or fibres. The nanomaterials that have the same composition as known materials in bulk form may have different physico-chemical properties than the same materials in bulk form, and may behave differently if they enter the body.

Nanomaterials: Properties?

Nanotechnology, the manipulation of matter at a nanometer scale to produce new materials, structures, and devices having new properties, may revolutionize life in the future.
It has the potential to impact medicine through improved disease diagnosis and treatment technologies and to impact manufacturing by creating smaller, lighter, stronger, and more efficient products. Nanotechnology could potentially decrease the impact of pollution by improving methods for water purification or energy conservation.

Although engineered nanomaterials present seemingly limitless possibilities, they bring with them new challenges for identifying and controlling potential safety and health risks to workers. Of particular concern is the growing body of evidence that occupational exposure to some engineered nanomaterials can cause adverse health effects.

Nanomaterials: what are they?



global environmental solutions

Curtin University

Nanomaterials: me?

"As with any new technology or new material, **the earliest exposures will likely occur for those workers conducting discovery research in laboratories** or developing production processes in pilot plants. The research community is at the front line of creating new nanomaterials, testing their usefulness in a variety of applications and determining their toxicological and environmental impacts. Researchers handling engineered nanomaterials in laboratories should perform that work in a manner that protects their safety and health"

General Safe Practices for Working with Engineered Nanomaterials in Research Laboratories. (2012) NIOSH

SLR

Legal Framework

Australian Regulators advise applying caution to nanotechnology processes, as there is insufficient information regarding the health effects of nanomaterials.

Current scientific research suggests that exposure to at least some nanomaterials, engineered nanoparticles, nanodevices, or the products of nanobiotechnology, may result in harm to human health and the environment.

The health effects and risks associated with exposure to these substances are not fully understood, as such a precautionary approach should be taken regarding exposure to engineered nanoparticles at workplaces.

The person in control of the nanotechnology work must ensure that health and safety is a priority during manufacture, use, handling, transport, storage, modification or generation of nanomaterials.

Legal Framework

Unlike most *simple* particles, a feature that sets nanoparticles apart is their relatively large surface area relative to their small size. This is an important aspect, because this relatively large surface area gives these particles an unusually high activity compared to their small size, and consequently their potential toxicity.

Nanotechnology is regulated through the OSH Act. Depending on the physicochemical properties and/or or **parent materials**, nanomaterials may be classified as hazardous chemicals.

Types of Nanoparticles

Nanoparticle Type

Research and development produces numerous engineered NPs

• Fullerenes: carbon-only molecules (hollow sphere, ellipsoid, tube, or plane)

• Carbon nanotubes (CNT): cylindrical fullerene (single or multi-walled, capped or uncapped)

• Metals & metal oxides: ultrafine powders (e.g. Ag, Au, ZnO, TiO2, CeO)

• Quantum Dots (QD): semi-conducting crystal core (e.g., CdS core, ZnS coat)

• Nanowires: large aspect ratio

• Nanocrystals: crystalline nanomaterial

• Others: dendrimers, graphene sheets, nanoscreen arrays; hybrids

Clearly NPs cannot be "lumped together", due to differences in size, shape, surface area & activity, nano-structure, etc. These also affect bioactivity & toxic potential.

Managing Nanomaterials

Persons working with nanomaterials are required to identify hazards, risks and controls for nanotechnology through:
Documenting hazards, risks and controls prior to commencing work.
Risk assessments should consider nanoparticle generating processes; activities which may produce nanoparticles as a by-product; and the safe handling, use, storage, transport and waste management of nanomaterials.

Maintaining a register of nanomaterials, including the type of research, work and manufacture involved. It is recommended that you use a template available in the *Register of nanomaterial use and storage (Qld Gov).*
The SDS should be created by the designer/manufacturer of the new nanomaterial (this may include the principle researcher).
Evaluating the effectiveness of current nanoparticle exposure controls.

Exposure: Inhalation

The greatest risk of exposure is through inhalation of airborne nanomaterials. The amount of material released depends on the type of nanomaterial and how it is being used. The following table lists three common forms and their potential for release of airborne nanomaterials: Once nanomaterials are released into the air, they can remain suspended for days **or even weeks**.

Form	Risk for release into air	Potential routes for Inhalation Exposure
Nanomaterial embedded into a solid matrix or tightly bound to a surface	low	Mechanically working on the material such as cutting, sanding, drilling.
Suspensions	Moderate	Formation of aerosols through agitation such as sonicating, stirring, centrifuging of open containers holding suspensions
Dry powder	High	Any open handling of powder

Exposure: Inhalation

The Australian WHS regulations require that no person at the workplace is exposed to a substance or mixture in an airborne concentration that exceeds the Australian workplace exposure standards.

Currently there are only a limited number of exposure standards for nanoscale material, however overseas agencies have recommended or proposed a number of exposure limits which are summarised in table 1.

Table 1: Exposure Standards for Some Nanoparticles

Exposure: Inhalation

Table 1: Exposure Standards for Some Nanoparticles

Substance	Type of standard	Size of material	Exposure standard (8 hr TWA mg/m^3)
Carbon black	Australian WES	Nanomaterial	3
Carbon nanofibers including CNT's	NIOSH	Nanomaterial	0.007
Fullerenes	AIST	Nanomaterial	0.39
Crystalline Silica	Australian WES	Respirable	0.1
Amorphous Silica	Australian WES	Inhalable	10
Fumed Silica	Australian WES	Nanomaterial	2
Titanium dioxide	Australian WES	Inhalable	10
Titanium dioxide	NIOSH REL	Fine size fraction	2.4
Titanium dioxide	NIOSH REL	Nanomaterial	0.3

Exposure: Dermal

The ability of nanoparticles to penetrate skin remains unclear. As such gloves should be worn when handling particulates or particles in solution.

In all cases the material and thickness of the gloves should be considered. Some studies suggest a minimum thickness of 3mm provide better protection. If this is not possible, then double-gloving may be necessary.

Exposure: Health Risks

There is experimental evidence of a range of possible interactions with biological systems and health effects of manufactured nanoparticles.

All these effects would depend on nanoparticles' fate in the body. Only a minimal amount of nanoparticle doses escape the lungs or intestine, but long-term exposure could still mean a large number are distributed round the body. Most are held in the liver or the spleen, but some appear to reach all tissues and organs. There may also be entry into the brain via the membranes inside the nose.

The long-term health effects of such exposures are not known. Nanotubes or rods with similar characteristics to asbestos fibres pose a risk of the mesothelioma (a form of cancer of the pleura).

Risk Assessment: Basis

Existing risk assessment methods are generally applicable to NPs but specific aspects need more development.

- Much uncertainty about the toxic potential of many engineered NM;
- There is a lack of knowledge regarding the quantitative (surface) structure activity and toxicology studies
- Nanotechnology research activities generate many NM's, most of which are only briefly studied and then discarded

Risk assessment requires a detailed examination of properties, including:

• **Particle size**	**Surface area**	**Stability**
• **Surface properties**	**Solubility**	**Chemical reactivity**

Comparisons with well-known existing hazards may help inform risk assessment. They include those from airborne fine particles, and asbestos fibres.

Risk Assessment: Basis

Existing Method using Hierarchy of Control and Consequence vs Likelihood etc

global environmental solutions

Curtin University

Control Banding: Alternative RA

Detailed risk assessments for unusual or high risk nano-particles require an experienced occupational hygienist or exposure scientist.

Control banding for NMs involves a simplified form of the risk management approach, where specific controls are recommended based on process risk. For example all CNT's are considered to be hazardous, therefore the recommended controls are based on the potential level of exposure.

Control banding can be used when handling and manufacturing processes are well understood and managed, potential exposure routes are known and safe work procedures (SWP's) are developed and followed.

If a process or research project produces intermediates or new processes are undertaken Control Banding has limitations.

Control Banding: Alternative RA

This method of controlling risks involves the following 4-step approach. This is a precautionary approach, developed using practical experience at CSIRO.

Step 1. Determine the 'Exposure Potential' i.e. the amount of NM that are likely to be airborne, using the information in tables (amound handled, activity and likelihood)
Step 2. Use the matrix below to find the Control Band (1-4) depending on quantities used and task exposure
Step 3. Apply the controls indicated for the appropriate Control Band (Table 4)
Step 4. Monitor, review and validate the effectiveness of the controls used to manage risk.

SLR

Control Banding: Alternative RA

Assessed Exposure	Example of Tasks/Scenarios	Control
High	• Tasks that are likely to produce airborne CNTs • CNTs are handled in dry state or powder form, e.g. weighing and measuring • Manufacture of CNTs - e.g. synthesis, growing • Scraping and packing of dry CNTs • Opening bags of dry CNTs	**Isolated processing, negative pressure** work areas where operators work from a **remote control booth** and secure access into the workplace, e.g. **electronic swipe card access** into high risk areas.
Moderately High	• Blending CNTs into polymers • CNTs are mechanically manipulated, e.g. weave, knit, twist, pull, cut, grind, scrape, etc • Cutting/grinding polymers containing CNTs • CNTs in solution which are likely to be atomised	**Negative pressure** work areas with good local exhaust **ventilation with HEPA filtration, process enclosure,** secure access into the workplace, e.g. **electronic swipe card access,** and an appropriate **PPE** regime.
Moderately Low	• Extruding and manipulating polymers containing NMs • Processing, shaping, moulding of polymers containing CNTs • Cutting/grinding polymers containing non CNT NPs • Solutions containing NPs are mixed or agitated	Good **local exhaust ventilation with HEPA filtration,** comprehensive **administrative controls** and an appropriate **PPE** regime

Quantity	
A	
B	above 100 grams to 1 kilogram
C	above 10 grams to 100 grams
D	micrograms to 10 grams

global environmental solutions

Curtin University

Control Banding

Exposure Potential			
Determining the exposure potential, and hence the recomm on the quantity of CNTs handled, and the likelihood that CN			
	High Assessed Exposure	Moderately High Assessed Exposure	Mod A E
Quantity A	4	4	
Quantity B	4	3	
Quantity C	4	3	
Quantity D	3	2	

Control Band 3		
Inhalation Controls	**Dermal Controls**	**Environmental Controls**
Normal operations • Intrinsically safe electrical system for high exposure potential situations • Sealed glove box or biological cabinet for measurement or physical manipulation • Negative pressure work area • Local flexible exhaust ventilation (LEV) for ‘Quantity A’ (>1kg) with moderately low exposure risk • P2 Particulate - Half face respirator reusable or disposable when working with LEV • Wet cutting of solid articles containing CNTs **Emergencies (e.g. spills)** • P3 Particulate - Full Face respirator (PAPR) **Clean-up & maintenance** • Specific training required • JSA required to determine level of control and use of either P2 or P3 respirator **Exhaust air** • Single pass through HEPA	**Normal operations** • Tyvek lab coat • Close fitting safety glasses • Nitrile gloves – change regularly • Long trousers – no cuffs **Clean-up & maintenance** • Tyvek lab coat • Protective eyewear • Disposable over-booties for shoes • Nitrile gloves – change regularly • Long trousers – no cuffs **Emergencies (e.g. spills)** • Full Tyvek coverall and hood • Double nitrile gloves • Disposable over-booties for shoes • Protective eye wear • Long trousers – no cuffs	• Bunds and drain covers readily accessible • Emergency clean-up SWP documented and clean-up materials readily available, e.g., sealed containers, spades, mops, mist or fog generating equipment

Control Banding: Further Info

The *Work health and safety assessment tool for handling engineered nanomaterials* should be utilised as part of the risk management / assessment process, with reference to the *Nanomaterial control banding tool worksheet.*

http://www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/at201008workhealthandsafetyassessmenttool

https://www.worksafe.qld.gov.au/__data/assets/pdf_file/0005/110975/nanotechnology-**control-banding**-tool.pdf

SLR

Handling and Storage

Every effort should be made to avoid releasing nanomaterials into the air. Because they can remain suspended for a long time, any release poses a hazard to everybody entering the laboratory.

Perform all work with nanomaterials inside a well-ventilated enclosure such as a chemical fume hood, glove box, biosafety cabinet, or an enclosure made especially for nanomaterial use.
Protect yourself from skin contact by wearing standard laboratory attire such as closed-toe shoes, long pants, a lab coat, safety glasses, and gloves when handling nanomaterials.

If a respirator is required for certain procedures, remember that other people working in the laboratory who are not wearing respirators are at risk, and nanoparticles may remain in the air after the work is done.

SLR

Handling and Storage

Some nanomaterials, carbon nanotubes in particular, are difficult to handle in a chemical fume hood because the air flow is often too high to contain the material inside its container.
Enclosures specifically made to contain nanomaterials are available. If possible, dedicate an enclosure for nanomaterial use.

Always wet-wipe the area where dry nanomaterials are used. If the wipes are contaminated, collect them in a sealed plastic bag and dispose of as hazardous waste.

A vacuum cleaner with HEPA filter can be used to clean areas that are difficult to wipe.

Store Nano materials as per their DG/GHS advice on the SDS. Ensure all containers are tightly sealed. Label the container with the chemical identity of the material and add the term “nano.”

Disposal

Nanomaterial waste must never be disposed as general waste or flushed

Dry nanomaterial waste should be contained in a sealed container that will remain closed.

When disposing of nanomaterial waste, including contaminated items, consideration should be given to the nature of the nanomaterial, the solvent and the parent or base material.
If the nanoparticles are suspended in solution, consideration should be given to the nature of the carrier solution or solvent (e.g. flammable solvents are handled as flammable waste materials) as well as the parent or base material of the nanoparticles.

Labelling of nanomaterial waste must include both the carrier solution and the parent or base material, and identified as containing nanoparticles.

Collect nanomaterial in a separate waste stream and dispose of through ToxFree as hazardous waste

Nano-Spills

When developing procedures for cleaning up nanomaterial spills consideration must be given to the potential for exposure during clean-up.

Inhalation exposure and dermal exposure will likely present the greatest risks.

Personnel need to follow safe working procedures relevant to their tasks and should ensure that they are using appropriate PPE to protect against possible exposure. An example of a specific task which may give rise to potential exposure is a filter replacement.

Wet methods are preferred for the clean-up of Nanomaterial spills. Methods for wet cleaning up are:
Mist smaller areas with water containing mild detergent. Wipe with light coloured disposable wipes until clear then double bag wipes for disposal.
Larger areas, such as floors, should be cleaned using a wet vacuum with HEPA filtration or wet mopping technique with a disposable mop head.

Myths and Reality

Nanomaterials are similar to normal chemicals/substances in that some may be toxic and some may not: the dose is decisive.

Nanomaterials are not necessarily new and innovative.

Not all innovative nanotechnology contains nanomaterials.

They are everywhere now - from, sunscreens and sunglasses to car tires, clothing and cosmetics.

Some nanomaterials are toxic whilst others can be life saving.

Treat Nanoparticles like Asbestos !

Nanomaterials should be treated like other chemicals. Where there is some doubt, precautionary principles apply – just like with new and intermediary chemicals or products in research.

SLR

Contact Health and Safety – Thank you

Nathan Redfern
Principal Technical Advisor

Erin Poultney
SLR Representative: Curtin University

national safe work month

Curtin University