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Nanotechnologies — Health and safety practices in occupational settings relevant to nanotechnologies

Nanotechnologies — Pratiques de sécurité dans les arrangements professionnels relatifs aux nanotechnologies

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard (“state of the art”, for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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1. Introduction

The field of nanotechnologies is advancing rapidly and is expected to impact virtually every facet of global industry and society. International standardization on nanotechnologies should contribute to realizing the potential of this technology for the betterment and sustainability of our world through economic development, improving the quality of life, and for improving and protecting public health and the environment. One can expect many new engineered nanomaterials coming to the market place and work place. The introduction of these new materials into the workplace raises questions concerning occupational safety and health that should be addressed, as appropriate, by international standards. While such standards are being developed, it is important, through this Technical Report, to assemble and make available to users, useful knowledge on occupational safety and health practices in the context of nanotechnologies.

Nanotechnology involves materials at the nanoscale. As a working definition,[i] the “nanoscale” means size range from approximately 1 nm to 100 nm. A nanometer is 1×10^{-9} m or one millionth of a millimeter. It is difficult to fully appreciate these remarkably small scales. To give a sense of this scale, a human hair is of the order of 10,000 to 100,000 nm, a single red blood cell has a diameter of around 5,000 nm, viruses typically have a maximum dimension of 10 to 100 nm and a DNA molecule has a diameter of around 2 nm. The term “nanotechnology” can be misleading since it is not a single technology or scientific discipline. Rather it is a multidisciplinary grouping of physical, chemical, biological, engineering, and electronic processes, materials, applications and concepts in which the defining characteristic is one of size.

The distinctive and often unique properties which are observed with nanomaterials offer the promise of broad advances for a wide range of technologies in fields as diverse as computers, biomedicine, and energy. At this early stage the potential applications of nanomaterials seem to be limited only by the imagination. Articles appear daily in the scientific and popular press and on a host of websites dedicated to the field. New companies, often spin outs from university research departments, are being formed and are finding no shortage of investors willing to back their ideas and products. New materials are being discovered or produced and astonishing claims are being made concerning their properties, behaviors and applications. As of June, 2007, over 400 nano-enabled new products are listed in an inventory of products already utilizing nanotechnology compiled by the Woodrow Wilson Center's Project on Emerging Nanotechnologies (www.nanotechproject.org/inventories/consumer/). Another list of products can also be found on U. S. National Nanotechnology Initiative web-site at www.nano.gov/html/facts/appsprod.html. While much of the current “hype” is highly speculative, there is no doubt that worldwide, governments and major industrial companies are committing significant resources for research into the development of nanometer scale processes, materials and products.

Ordinary materials such as carbon or silicon, when reduced to the nanoscale, often exhibit novel and unexpected characteristics such as extraordinary strength, chemical reactivity, electrical conductivity, or other characteristics that the same material does not possess at the micro or macro-scale. A huge range of nanomaterials have already been produced including nanotubes, nanowires, fullerene derivatives (bucky balls).

A few engineered nanomaterials were developed already in the 19th and 20th centuries, at a time when the word “nanotechnology” was unknown. Among such nanomaterials are zeolites, catalyst supports such as $MgCl_2$, pigments and active fillers such as carbon black and synthetic amorphous silica. Market size of these commodity materials is well above the billion US dollars or million tons threshold.

Nanotechnologies are gaining in new commercial application. Nanomaterials are currently being used in electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, catalytic and materials applications. Areas producing the greatest revenue for nanomaterials are chemical-mechanical polishing, magnetic recording tapes, sunscreens, automotive catalyst supports, electro-conductive coatings and optical fibers.

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[i] Please note, that definitions used throughout this Technical Report are based on draft definitions developed by ISO TC 229 WG1 and might become obsolete if draft definitions change.

The occupational health and safety effects of new nanomaterials are mostly unknown. This can be attributed to the relatively recent development of the nanotechnology sector and, as a result, the lack of available information on human exposures and working conditions. As a consequence our abilities to accurately predict the impact of some nanomaterials exposures on worker health are limited at this time. In particular our abilities to measure nanoparticles in the workplace (or more generally) are limited by current technologies. Nanotechnology presents us with new challenges as the properties of nanomaterials now depend on size and shape as much as the more conventional factors of chemical structure and composition. Measuring these additional attributes will be necessary to accurately assess nanomaterials in the workplace. In addition, the capability of the human body to recognize and appropriately respond to most nanomaterials is essentially unknown at the moment. On the other hand, in the case of some nanostructured materials, such as carbon black and synthetic amorphous silica, toxicologic and epidemiologic data are available.

There are many gaps in current science about identifying, characterizing, and evaluating potential occupational exposures in the nanotechnology context. These gaps in our knowledge will best be addressed at a multidisciplinary level. Occupational health practitioners and scientists and practitioners in the toxicology field including medical scientists and environmental scientists have vital roles to play in safeguarding health in this fast-moving field. Collaborative studies - ideally with international coordination - are essential in order to provide the critical information required within a reasonable time frame.

2. Scope

This Technical Report describes health and safety practices in occupational settings relevant to nanotechnologies. The initial outline was prepared using U. S. NIOSH's Approaches to Safe Nanotechnology: An Information Exchange with NIOSH.[1] This Technical Report focuses on the occupational manufacture and use of engineered nanomaterials. It does not address health and safety issues or practices associated with nanomaterials generated by natural processes, hot processes and other standard operations which unintentionally generate nanomaterials, or potential consumer exposures or uses, though some of the information in this Technical Report might be relevant to those areas. For more general information on the environment, health and safety of nanotechnologies, the reader can refer to other existing well documented reviews.[2-7] Use of the information in this Technical Report could help companies, researchers, workers and other people to prevent adverse health and safety consequences during the production, handling, use and disposal of manufactured nanomaterials. This advice is broadly applicable across a range of nanomaterials and applications.

This Technical Report is based on current information about nanotechnologies, including characterization, health effects, exposure assessments, and control practices. The authors of the Technical Report have attempted to remain current with the use of terms and their definitions. However, definitions in this field are evolving and some terms have not yet undergone ISO consensus review. Therefore, the terms are intended to be used solely for the purpose of this Technical Report and not to be considered formal definitions beyond this Technical Report. It is expected that this Technical Report will be revised and updated and new safety standards will be developed as our knowledge increases and experience is gained in the course of technological advance.

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3. Nanomaterials: description and manufacturing

3.1. Engineered nanomaterials

Engineered nanomaterials are designed with specific properties in mind. Engineered nanomaterials encompass nano-objects and nanostructured materials. The former are defined as materials with one (nanoplate), two (nanorod) or three external dimensions (nanoparticle) in the nanoscale (i.e. between approximately 1 and 100 nm). Examples of nanostructured materials are nanocomposites composed of nano-objects embedded in a solid matrix or nano-objects bonded together in simple random assemblies as in aggregates and agglomerates or ordered as in crystals of fullerenes or carbon nanotubes.[1] Discussion in this Technical Report will focus primarily on nano-objects and their simple assemblies.

Relatively simple nanomaterials presently in use or under active development can be classified in terms of dimensionality and the primary chemical composition. However, even simple nanomaterials are often coated and have complex chemical and physical structure. Any attempt to classify nanomaterials is highly artificial with many materials falling into several classification categories. Thus, the following description is for organizational purposes only.

Quantum dots and fullerenes are confined to the three-dimensional nanoscale domain. Nanotubes, nanowires, nanofibers and nanofibrils have at least two nanoscale dimensions, while nanoscale surface coatings, thin films and layers have at least one nanoscale dimension. In the following subsections, nanomaterials are described according to the primary (or core) chemical composition of nano-objects: carbon containing nanomaterials (e.g. fullerenes, carbon nanotubes); oxides nanomaterials (e.g. TiO_2 and ZnO); metal nanomaterials (e.g. Au); semiconductor nanomaterials (e.g. quantum dots); organic polymeric nanomaterials (e.g. dendrimers); and bio-inspired nanomaterials (e.g. capsid nanoparticles). Within these classes, different nanomaterials are listed in the order of decreasing necessary number of dimensions in nanoscale from 3D particles to fibers to layers.

3.1.1. Carbon containing nanomaterials

3.1.1.1. Fullerenes

Fullerenes are chemical entities which can be envisioned as spherical cages built from carbon atoms chemically bonded to three nearest neighbors. The best known example is a soccer-ball shaped C_{60} fullerene. Fullerene molecules can contain from 28 to more than 100 carbon atoms with some experimental studies reporting molecules containing up to 1 500 atoms with 8.2 nm diameter.[2] Existence of even larger fullerene molecules has been postulated from theoretical considerations.[3] Multi-shell fullerene-like nanoparticles referred to as carbon nano-onions, can range in size between 4 and 36 nm.[4] Fullerenes are actively investigated for a wide range of potential applications including: lithium-ion batteries, solar cells, fuel cells, oxygen and methane storage materials, additives to plastics, oil and rubber, and cancer and AIDS treatments.

3.1.1.2. Carbon black

Carbon black consists of partially amorphous material, organized into spherical or near-spherical particles fused together to give aggregates, weakly interacting to form agglomerates, usually further organized into macroscopic pellets.[5] Furnace black accounts for 98 % of the worldwide production and has an average aggregate diameter of 80-500 nm and an average primary particle size of 11-95 nm. The main industrial uses of carbon black are as a pigment and as reinforcing filler for rubber articles, in particular, tires.

3.1.1.3. Carbon nanofibers

Carbon nanofibers (CNFs) are cylindrical or conical structures that have diameters ranging from a few to one hundred nanometers and lengths ranging from under micrometer to several millimeters. The internal structure is comprised of stacked curved graphite layers (or graphene sheets, see also section 3.1.1.5) that form cones (herringbone structure), cups (bamboo structure), rods (solid structure), or tubes (hollow structure).[6] The main distinguishing characteristic of nanofibers from nanotubes is the stacking of graphene sheets which make a non-zero angle with the fiber axis. When graphene sheets are parallel to the fiber axis, they form carbon nanotubes (see next section). Since there are “in-plane” and “interplane” components of transport and mechanical properties along the fiber axis, as well as presence of unsaturated bonds similar to graphite, carbon nanofiber characteristics differ from those of carbon nanotubes.

Carbon nanofibers are produced during chemical vapor deposition processes from carbon rich gases such as hydrocarbons over metal catalysts.[7] A greater control over carbon nanofiber structure and composition can be achieved with catalytic plasma-enhanced chemical vapor deposition.[8] Carbon nanofibers are produced on an industrial scale and find applications as polymer additives, gas storage materials and catalyst supports.[9]

3.1.1.4. Carbon nanotubes

Carbon nanotubes (CNTs) represent a diverse family of carbon-based materials based on a graphene sheet rolled up in the form of a tube. CNTs can be made up of one sheet (Single-Walled) or several sheets (Multi-Walled). Single-walled CNT can be open- or closed-ended depending on whether they are capped with fullerene halves at each end. Carbon nanotubes can have a diameter as small 0.4 nm and reach several centimeters in length.[10,11] Multi-walled form can reach 100 nm in diameter.[12]

Single-walled carbon nanotubes display metallic or semiconductive properties depending on how the graphene sheet is rolled up, and their electronic response can be tuned using elemental subsitution.[13] Carbon nanotubes have been predicted to be as much as sixty times stronger than steel and six times lighter.[14] They are considered excellent heat conductors, have a great capacity for molecular absorption and are chemically and thermally very stable.[15]

Applications which are currently being investigated include; polymer composites, electromagnetic shielding, electron field emitters, super capacitors, batteries, hydrogen storage and structural composites. Main synthesis methods for carbon nanotubes fall into two classes: those in which elemental carbon is vaporized typically by a laser or an electric arc and those in which the carbon is derived at lower temperature from a carbon source usually assisted by a catalyst or plasma.[16]

Commercial manufacturing and supply of carbon nanotubes at a large-scale production rate appears to be taking place in a number of countries.

3.1.1.5. Graphene nanosheet

Graphene sheet is a single layer of graphite structure which can be described as a hexagonal network of carbon atoms bonded to three nearest neighbors. Microscopic roughening through out-of-plane deformations makes graphene sheet effective thickness of about 1 nm. Graphene was shown to possess unique electronic, magnetic, optical and mechanic properties and might find applications in flat flexible electronic devices and coatings.[17] Micromechanical cleavage is presently the main method used to prepare this material.

3.1.2. Oxides

Metal oxide nanostructured materials in the form of agglomerated and aggregated nanoparticles are used mostly as paint and sunscreen additives and often coated to achieve desired properties. Main production methods are spray pyrolysis, laser ablation and solution phase synthesis.

Metal oxide nano-objects can be grown with a variety of simple shapes such as nanorod, nanotubes,[18] nanoflakes, and more complex structures such as nanobrushes, nanosprings, and nanobelts.[19] These nanostructures exhibit unique electronic properties and can find novel applications in optoelectronics, sensors, transducers, and medicines.

Synthetic amorphous silica can be manufactured as a nanostructured material via gas-phase synthesis or wet chemical processes, such as precipitation or sol-gel process. The nanostructured material consists of primary particles within a range of 5-10 nm forming hard aggregates (1-40 µm). Primary particles do not exist as individual units; aggregation and agglomeration are predominant in particle formation and growth. Synthetic amorphous silica is currently used in a wide variety of industrial applications. Most of them are related to the reinforcement of various elastomers, the thickening of various liquid systems, the free-flow of powders or as a constituent of matting, absorbents and heat insulation material.[20,21]

3.1.3. Metals

Gold nanoparticles are one of the most extensively studied. Gold nanoparticles are characterized by a prominent optical resonance in the visible range, which is sensitive to environmental changes, size, and shape of the particles as well as to local optical interactions in resonant systems. This unique property of gold nanoparticles is utilized in a number of applications such as optical markers and as thermal targeted cancer treatment agent in medicine. Silver nanoparticles are produced in largest volumes among metal nanoparticles and used in numerous applications ranging from wound dressings to washing-machine disinfectant for its anti-microbial activity.[22]

Metal nanoparticles with well-defined size and shape can be synthesized using metal reduction from a solution phase.[23]

Metal nanowires such as cobalt, gold and copper-based can be conductive or semiconductive and could be used as interconnectors for the transport of electrons in nanoelectronic devices.[16] Nanowires are typically manufactured by involving a template followed by the deposition of a vapor to fill the template and grow the nanowire.[16] Deposition processes currently include Electrochemical Deposition and Chemical Vapor Deposition. The template might be formed by various processes including etching, or the use of other nanomaterials such as nanotubes.[16]

3.1.4. Quantum dots

Spherical nanocrystals from 1 to 10 nm in diameter composed of semiconductor materials often possess unique optical properties due to quantum effects, hence they are often called quantum dots. The number of atoms in quantum dots makes them neither an extended solid structure nor a molecular entity. The light emitted can be adjusted to the desired wavelength by changing the overall dimension. [24]

Quantum dots are used, among other purposes, as fluorescent probes in diagnostic medical imaging and in therapeutics; they are used for these purposes due to their optical properties and our ability to coat and modify their surfaces with peptides, antibodies, nucleic acids and other biologically important molecules.[25]

Currently, chemistry, physics and material science have provided methods for the production of quantum dots and are allowing tighter control on factors such as particle growth and size, solubility and emission properties. The most common method to produce quantum dots is by wet chemical colloidal processes. [16]

3.1.5. Organic polymeric nanomaterials

3.1.5.1. Dendrimers

Dendrimers are a new class of controlled-structure multi-branched polymers with nanoscale dimensions. They allow precise, atomic-level control of the synthesis of nanostructures according to the desired dimensions, shape and surface chemistry. They can display both hydrophilic and hydrophobic characteristics and can accommodate a wide variety of functional groups for medical applications. They are expected to be used in the medical and biomedical field.[26] Most syntheses of dendrimers involve the repetitious alternation of a growth reaction and an activation reaction such as the more traditional Michael reaction, or the Williamson ether synthesis, and more modern solid-phase synthesis, organo-metallic chemistry, organo-silicon chemistry, and organo-phosphorus chemistry.[26]

3.1.5.2. Fibers

Nanofibers can be made of a wide variety of polymeric materials. The main manufacturing techniques are electrospinning and gas-blowing. These techniques allow for great flexibility in controlling chemical composition and physical parameters such as fiber diameter and length. Nanofiber scaffolds can be used in a number of applications such as sensors and ultrafiltration devices for liquid and gas phase.[27] Biodegradable polymer nanofibers can find numerous applications in medicine as scaffolds for tissue engineering, in controlled drug release, wound dressings, molecular separation, and bone restoration.[28]

3.1.6. Bio-inspired nanomaterials

Bio-inspired nanomaterials are generally materials in which a biological substance is trapped, encapsulated or adsorbed on the surface. They include a wide range of engineered assemblies of biological building blocks such as lipids, peptides and polysaccharides utilized as carriers for drugs, receptors, nucleic acids and imaging agents. Examples are polymeric micelles, protein cage architectures, viral-derived capsid nanoparticles, polyplexes, and liposomes[29] used in transport and optimal targeting of drugs. A number of formulations are under development for drug delivery via gastrointestinal and inhalation routes and skin applications.

Micelles are formed in solution as aggregates in which amphiphilic molecules are arranged in a spheroidal structure with hydrophobic cores shielded from the water by a mantle of hydrophilic groups. These dynamic systems, which are usually below 50 nm in diameter, are used for the systemic delivery of water-insoluble drugs. Drugs or contrast agents might be trapped physically within the hydrophobic cores or can be linked covalently to component molecules of the micelle.[29]

Liposomes are closed lipid bilayer vesicles that form by hydration of dry phospholipids. Drug molecules can be either entrapped in the aqueous space or intercalated into the lipid bilayer of liposomes, depending on the physicochemical characteristics of the drug. The liposome surface is amenable to modification with targeting ligands and polymers.[29]

Polyplexes are assemblies, which form spontaneously between nucleic acids and polycations or cationic liposomes (or polycations conjugated to targeting ligands or hydrophilic polymers), and are used in transfection protocols. The shape, size distribution, and transfection capability of these complexes depends on their composition and charge ratio of nucleic acid to that of cationic lipid/polymer. Examples of polycations that have been used in gene transfer/therapy protocols include poly-L-lysine, linear- and branched-poly(ethylenimine), poly(amidoamine), poly-ß-amino esters, and cationic cyclodextrin.[29]

Protein cage architectures and viral-derived capsid nanoparticles are formed by self-assembly of certain proteins.[29]

Building blocks of bio-inspired nanomaterials can be obtained from natural materials and using synthetic microbiology techniques,[30] while self-assembly often takes place in a liquid phase.

3.2. Production processes

3.2.1. Typical production processes

Methods typically used for the manufacturing of nanomaterials are:

- Aerosol generation such as flame pyrolysis, high temperature evaporation and plasma synthesis;
- Vapor deposition;
- Liquid phase methods: colloidal, self-assembly, sol-gel;
- Electropolymerization and electrodeposition;
- Electro-spinning for polymer nanofiber synthesis;
- Mechanical processes including grinding, milling and alloying.

3.2.2. Aerosol generation methods

The aerosol generation method is used to produce a wide range of nanomaterials. This method is based on homogeneous nucleation of a supersaturated vapor and subsequent particle growth by condensation, coagulation and capture. The formation of vapor typically occurs within an aerosol reactor at elevated temperatures where often a super saturate of a solid is cooled into a background of gas. The methods used to produce nanomaterials are usually categorized by the heating or evaporation process and include:[16]

- Flame pyrolysis
- Furnace/hot wall reactors
- Laser induced pyrolysis

3.2.3. Vapor deposition methods

These methods are traditionally based on already well known and established methods for the manufacture of semiconductors. Here, vapor is formed in a reaction chamber by pyrolysis, reduction, oxidation and nitridation. The first step is the deposition of a few atoms. These first atoms form islands which spread and coalesce into a continuous film. Later, growth continues until thicker film develops.[16]

These methods have been used to produce nanofilms including TiO_2, ZnO and SiC.[16] Vapour deposition processes mediated by a catalyst are used to produce carbon nanotubes commercially.

3.2.4. Colloidal/self-assembly methods

The colloidal methods are also well established conventional wet chemistry precipitation processes in which solutions of different ions at required concentrations are mixed under controlled conditions of temperature and pressure which form insoluble precipitates.[16]

Recently, a rapidly expanding sub-set of colloidal methods called sonochemistry methods, where acoustic cavitation is used to control the process.[31] Here molecular precursors undergo chemical reactions because of the application of ultrasound radiation. It is the creation, growth and rapid collapse of a bubble that is formed in the liquid which is the main event. In this process, high temperatures and high cooling rates accompany the collapse of the bubble and nucleation centers formed whose growth is limited by the rapid collapse.[16]

Chalcogenides, metals and alloys including gold, cobalt and nickel as well as carbon and titania nanotubes have been produced using this method.[16]

3.2.5. Electrodeposition

Polymer nanofiber and metal nanowire films can be fabricated on an substrate through a controlled electropolymerization (polymers) or electrodeposition (metals) process.[32,33]

3.2.6. Electro-spinning

Electro-spinning method is a major method in the manufacture of polymer nanofibers. It utilizes electrical force to produce polymer fibers from polymer solutions or melts.[34]

3.2.7. Attrition methods

In attrition methods, size reduction is accomplished by grinding and milling and production of materials such as clay, coal and metals have been made.[16] Production rates in the order of tons per hour can be obtained using these methods.

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4. Hazard characterization

4.1. Health effects

The potential health risk of a substance is generally associated with the magnitude and duration of the exposure, the persistence of the material in the body, the inherent toxicity of the material, and the susceptibility or health status of the person. Since nanotechnology is an emerging field, there are uncertainties as to whether the unique properties of engineered nanomaterials also pose unique occupational health risks. These uncertainties arise because of gaps in knowledge about the factors that are essential for evaluating health risks (e.g., routes of exposure, translocation of materials once they enter the body, and interaction of the materials with the body's biological systems). An important issue is whether the nanoscale version of a particular material poses risks that are significantly different in type or intensity than the macroscale forms of the same material.