



# TECHNICAL FACT SHEET - NANOMATERIALS

# At a Glance

- Diverse class of small-scale substances that have structural components smaller than 100 nanometers (nm) in at least one dimension (EPA 2011b). Nanomaterials (NMs) include nanoparticles (NPs), which are particles with at least two dimensions between approximately 1 and 100 nm.
- Can be categorized into three types: natural, incidental and engineered.
- Engineered NMs are used in a wide variety of applications, including environmental remediation, pollution sensors, photovoltaics, medical imaging and drug delivery.
- May be released through point and nonpoint sources, or introduced directly to the environment when used for remediation purposes.
- May be readily transported through media, usually over much greater distances than larger particles of the same composition. The mobility of NMs depends on factors such as surface chemistry and particle size, and on biological and abiotic processes in the media.
- May stay in suspension as individual particles, aggregate, dissolve or react with other materials.
- Characterization and detection technologies include differential mobility analyzers, mass spectrometry and scanning electron microscopy.
- Can be removed from air using air filters and respirators, and from water by flocculation, sedimentation and filtration.

### Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of nanomaterials (NMs), including their physical and chemical properties; potential environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet is intended for use by site managers and other field personnel who may need to address or use NMs at cleanup sites or in drinking water supplies.

Because of their unique properties, NMs are increasingly being used in a wide range of scientific, environmental, industrial and medicinal applications. However, there is a growing concern about the lack of environmental health and safety data.

#### What are nanomaterials?

- ❖ NMs are a diverse class of small-scale substances that have structural components smaller than 100 nanometers (nm) in at least one dimension. NMs include nanoparticles (NPs), which are particles with at least two dimensions between approximately 1 and 100 nm (EPA 2011b; Klaine and others 2008).
- NMs can be categorized into three types according to their source: natural, incidental and engineered. See Exhibit 1 for examples.
- Engineered NMs, designed with specific properties or composition, are intentionally produced through certain chemical processes, physical processes or both, such as self-assembly (from atoms and molecules) or milling (from their macro-scale counterparts). These NMs may be released into the environment primarily through industrial and environmental applications or improper handling (DHHS 2009; EPA 2007).
- Because of their novel nanoscale size, NMs may possess unique chemical, biological and physical properties compared with larger particles of the same material (Keiner 2008; Klaine and others 2008).
- The unique properties of NMs allow them to be used for various applications, as shown in Exhibit 1.
- As of 2013, more than 1,600 consumer products containing NMs are on the market (WWIC 2013).

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# **Technical Fact Sheet – Nanomaterials**

Exhibit 1: Properties and Common Uses of Nanomaterials (NMs)

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Types of NMs		Physical				
(Occurrence)	Example	Properties	Chemical Properties	Uses		
Carbon-based (Natural or Engineered) (EPA 2007, Klaine and others 2008)	Fullerenes/Buckyballs (Carbon 60, Carbon 20, Carbon 70), carbon nanotubes, nanodiamonds and nanowires.	Exist as hollow spheres (buckyballs), ellipsoids, tubes (nanotubes), 1-nanometer wires (nanowires) or hexagonal structures (nanodiamonds). Excellent thermal and electrical conductivity.	Carbon-based NMs are stable, have limited reactivity, are composed entirely of carbon and are strong antioxidants.	Biomedical applications, super- capacitors, sensors and photovoltaics.		
Metal Oxides (Natural or Engineered) (Klaine and others 2008)	Titanium dioxide, zinc oxide and cerium oxide.	Some have photocatalytic properties, and some have ultraviolet blocking ability. When used in sunscreen, nano-titanium dioxide and nano-zinc oxide appear transparent when applied on skin.	High reactivity; photolytic properties.	Photocatalysts, pigments, drug release, medical diagnostics, cosmetics, ultraviolet blockers in sunscreen, diesel fuel additive and remediation.		
Zero-Valent Metals (Engineered) (EPA 2008a; Klaine and others 2008)	Nanoscale zero- valent iron, emulsified zero-valent nanoscale iron and bimetallic nanoscale particles. Bimetallic nanoscale particles include elemental iron and a metal catalyst (such as gold, nickel, palladium or platinum)	Between 1 and 100 nanometers or greater, depending on the NM- type containing the zero-valent metal. Properties can be controlled by varying the reductant used and the reduction conditions.	High surface reactivity. Common starting materials used in production include ferric or ferrous salts with sodium borohydride.	Remediation of waters, sediments and soils to reduce contaminants such as nitrates, trichloroethene and tetrachloroethene.		
Quantum Dots (Engineered) (Klaine and others 2008)	Quantum dots made from cadmium selenide, cadmium telluride and zinc selenide.	Size: 10 to 50 nanometers. Reactive core controls the material's optical properties. The larger the dot, the redder (lower energy) its fluorescence spectrum.	Closely packed semiconductor whose excitons (bound electron-hole pairs) are confined in all three spatial dimensions. Possible metal structures include cadmium selenide, cadmium telluride, cadmium selenide telluride, zinc selenide, indium phosphide or lead selenide, for the core; cadmium sulfide or zinc sulfide for the shell.	Medical imaging, targeted therapeutics, photovoltaics, telecommunication and sensors.		
Dendrimers (Engineered) (EPA 2007; Watlington 2005)	Hyperbranched polymers, dendrigraft polymers and dendrons.	Size: 2 to 20 nanometers. Highly branched polymers. Common shapes include cones, spheres and disc-like structures.	Highly branched; multi- functional polymers.	Drug delivery, chemical sensors, modified electrodes and DNA transferring agents.		

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Types of NMs (Occurrence)	Example	Physical Properties	Chemical Properties	Uses
Composite NMs (Engineered) (EPA 2007; Gil and Parak 2008)	Produced using two different NMs or NMs combined with larger, bulk-type materials. They can also be made with NMs combined with synthetic polymers or resins.	Composite NMs have novel electrical, magnetic, mechanical, thermal or imaging features.	Multifunctional components, catalytic features.	Potential applications in drug delivery and cancer detection. Also used in auto parts and packaging materials to enhance mechanical and flame-retardant properties.
Nanosilver (Engineered) (Klaine and others 2008; Luoma 2008)	Forms include colloidal silver, spun silver, nanosilver powder and polymeric silver.	Size: 10 to 200 nanometers. Made up of many atoms of silver in the form of silver ions.	High surface reactivity, strong antimicrobial properties.	Medicine applications, water purification and antimicrobial uses. They are used for a wide variety of commercial products.

### How can nanomaterials affect the environment?

- NMs in solid wastes, wastewater effluents, direct discharges or accidental spills may be transported to aquatic systems by wind or rainwater runoff (Klaine and others 2008).
- NPs fate and transport in the environment are largely dependent on material properties such as surface chemistry, particle size and biological and abiotic processes in environmental media. Depending on these properties, NPs may stay in suspension as individual particles, aggregate forming larger sized NMs, dissolve or react with other materials (EPA 2009; Luoma 2008).
- Because of their small size and slower rate of gravitational settling, some NMs may remain suspended in air and water for longer periods and may be readily transported over much greater distances than larger particles of the same material (EPA 2007, 2009).
- The mobility of NMs in porous media is influenced by their ability to attach to mineral surfaces to form aggregates. For example, NMs that readily attach to mineral surfaces may be less mobile in groundwater aquifers (Wiesner and others 2006); smaller NMs that can fit into the interlayer spaces between soil particles may travel longer distances before they become trapped in the soil matrix (EPA 2007); and soils with high clay content tend to stabilize NMs and allow greater dispersal (EPA 2008a).

- A field study demonstrated that once nanoscale zero-valent iron (nZVI) is emulsified to form emulsified zero-valent iron (EZVI), the nZVI particles generally agglomerate and the size of the particles is significantly greater than nanoscale, thereby reducing the mobility of nZVI in the subsurface (ESTCP 2010).
- ❖ The surface chemistry and therefore the mobility of NMs in porous media may be affected through the addition of surface coatings. For example, nano-titanium dioxide (TiO₂) can be harmless in soil, but could be problematic in water or once a surface coating is added. In addition, uncoated nZVI can aggregate more rapidly in soil and water compared with coated nZVI, thereby reducing the NM's environmental transport in soil and water (EPA 2008a; Keller and others 2012; Lubick 2008).
- Some NMs are reported to be photoactive, but their susceptibility to photodegradation in the atmosphere has not been studied (EPA 2007).
- The potential mechanisms of biodegradation of NMs are the subject of current investigation. Some fullerenes such as C60 and C70 have been found to biodegrade after several months. Many NMs containing inherently non-biodegradable inorganic chemicals such as metals and metal oxides may not biodegrade as readily (EPA 2007).

### How can nanomaterials affect the environment? (continued)

- Research is still being conducted on the effects of NMs on wildlife species. Some studies have reported oxidative stress and pathological changes in aquatic species, specifically trout, after exposure to nano-TiO<sub>2</sub> (Federici and others 2007). Additionally, study results indicate potential hepatic effects in rainbow trout after exposure to nanosilver and potential toxic effects to phytoplankton species after exposure to some forms of nZVI (Keller and others 2012; Monfared and Soltani 2013).
- A recent study compared the toxic effects of zinc oxide (ZnO) NPs and ion zinc toward *Dunaliella*

- tertiolecta, a type of marine algae. Results found the ZnO NPs affected the growth rate of the algae and suggested that the ZnO NPs were more toxic to the marine algae than bulk ZnO (Manzo and others 2012).
- Although nZVI is widely used in site remediation, information is limited on its fate and transport in the environment. While increased mobility because of the smaller size may allow for efficient remediation, research is ongoing to determine whether these NMs could migrate beyond the contaminated plume area and persist in drinking water aquifers or surface water (EPA 2008a).

## What are the routes of exposure to nanomaterials?

- Human exposure to NMs may occur through ingestion, inhalation, injection and dermal exposure, depending on the source and activities of the person. In the workplace, inhalation is a widely recognized route of human exposure (DHHS 2009; EPA 2007; Watlington 2005).
- The small size, solubility and large surface area of NMs may enable them to translocate from their deposition site (typically in the lungs) and interact with biological systems. Circulation time increases drastically when the NMs are water-soluble. With smaller NM sizes, the likelihood of greater pulmonary deposition and potential toxicity exists (DHHS 2009; SCENIHR 2009).
- ❖ Studies have shown that NMs, as a result of their small size, have the potential to pass through both the blood-brain barrier (BBB) and the placenta. For example, a recent study showed that nanoanatase TiO₂ may pass the BBB of mice when mice are injected with high doses (DHHS 2009; Liu and others 2009).
- Some types of NMs that translocate into systematic circulation may reach the liver and spleen, the two major organs for detoxification and further circulatory distribution. Various cardiovascular and other extra pulmonary effects

- may also occur (Nel and others 2006; SCENIHR 2009).
- Animal studies indicate that nano-TiO<sub>2</sub> may accumulate in the liver, spleen, kidney and brain after it enters the bloodstream through various exposure routes (Chang and others 2013).
- In humans, although most inhaled NMs remain in the respiratory tract, less than 1 percent of the inhaled dose may reach the circulatory system (SCENIHR 2009).
- ❖ Use of sunscreen products may lead to dermal exposure to NMs (TiO₂ and ZnO), depending on the properties of the sunscreen and the condition of the skin. In healthy skin, the epidermis may prevent NM migration to the dermis. However, damaged or flexed skin may allow NMs to penetrate the dermis and access regional lymph nodes, as suggested by quantum dots and nanosilver (EPA 2010; Mortensen and others 2008; Nel and others 2006).
- Ingestion exposure may occur from consuming NMs contained in drinking water or food (for example, fish) or from unintentional hand to mouth transfer of NMs (DHHS 2009; Wiesner and others 2006).

#### What are the health effects of nanomaterials?

- Further epidemiological studies are needed to determine whether NMs, under realistic exposure scenarios, may present adverse health effects to humans (Chang and other 2013).
- The potential health effects of NMs are variable, depending on their characteristics. Clinical and experimental animal studies indicate that NMs can induce different levels of cell injury and oxidative
- stress, depending on their charge, particle size and exposure dose. In addition, particle coatings, size, charge, surface treatments and surface excitation by ultraviolet (UV) radiation can modify surface properties and thus the aggregation and potential biological effects of NMs (Chang and others 2013; Nel and others 2006).

## What are the health effects of nanomaterials?(continued)

- EPA is researching how NMs interact with biological processes important to human health and identifying the unique properties that regulate their activity (EPA 2013).
- Some NMs may generate reactive oxygen species (ROS), which can lead to membrane damage, including increases in membrane permeability and fluidity. As a result, cells may become more susceptible to osmotic stress or impaired nutrient uptake (Klaine and others 2008).
- ROS production may also lead to DNA damage. For example, study results indicate that C60 fullerenes and nano-TiO<sub>2</sub> may impair the structure, stability and biological functions of DNA (EPA 2007; Jaeger and others 2012; Klaine and others 2008).
- When cultured cells are exposed to NMs of various metals (such as NMs containing titanium and iron), NMs may be absorbed and gain access to tissues that the metals alone cannot normally reach. The uptake-and-damage mechanism is frequently called the "Trojan Horse effect," where the NMs appear to "trick" the cells to let them enter, and once inside, the toxic metals can significantly increase the damaging action of such materials (Limbach and others 2007).
- Metal-containing NMs may cause toxicity to cells by releasing harmful trace elements or chemical ions. For example, silver NMs may release silver ions that can interact with proteins and inactivate

- vital enzymes. The lead and cadmium used in quantum dots are known reproductive and developmental toxins. However, estimates of releases of these metals from NMs are crude because of varying factors such as the concentration of metal in the source (Klaine and others 2008; Luoma 2008; Powell & Kanarek 2006).
- Research has shown that NMs may stimulate or suppress immune responses (or both) by binding to proteins in the blood (Dobrovolskaia & McNeil 2007).
- Study results suggest that certain NMs may pose a respiratory hazard after inhalation exposure. For example, rodent studies indicate that single-walled carbon nanotubes may cause pulmonary inflammation and fibrosis. Exposures to nano-TiO<sub>2</sub> have also resulted in persistent pulmonary inflammation in rats and mice (EPA 2007; NIOSH 2011, 2013a; OSHA 2013b).
- Based on the results of available animal inhalation and epidemiologic studies, the National Institute for Occupational Safety and Health (NIOSH) has concluded that nano-TiO<sub>2</sub> may have a higher mass-based potency than larger particles and should be considered as a potential occupational carcinogen. Additional data and information are needed to assist NIOSH in evaluating potential occupation and health issues (NIOSH 2011).

# Are there any federal and state guidelines or health standards for nanomaterials?

- Federal standards and guidelines:
  - Many currently available nano-products fall under the U.S. Food and Drug Administration's (FDA) regulation (such as foods, cosmetics, drugs, veterinary products and sunscreens). FDA regulates these products based on a safety assessment of the bulk material ingredients or product. For example, FDA regulates nZVI the same as all forms of iron and carbon nanotubes the same as all forms of carbon (FDA 2012).
  - FDA has proposed guidelines on the evaluation and use of NMs in FDA-regulated products. In June 2011, FDA published the "Draft Guidance for Industry: Considering Whether an FDA-Regulated Product Involves the Application of Nanotechnology." In April 2012, FDA issued two new draft guidelines for manufacturers of food substances and cosmetics (FDA 2012).
- The presence of a NM in a pesticide may affect EPA's assessment under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of whether the product causes unreasonable adverse effects on the environment. In 2011, EPA issued a notice announcing the proposed plan for gathering information on NMs present in pesticide products and their potential effects on humans or the environment (EPA 2007, 2011b).
- Many NMs are regarded as "chemical substances" under the Toxic Substances Control Act (TSCA) and therefore are subject to the requirements of the Act. EPA has already determined that carbon nanotubes are subject to reporting under Section 5 of TSCA. Under TSCA, EPA may also regulate NMs considered as existing chemicals (EPA 2008b, 2011a).

# Are there any federal and state guidelines or health standards for nanomaterials?(continued)

- Federal standards and guidelines (continued):
  - EPA is developing a Significant New Use Rule (SNUR) under TSCA Section 5(a)(2) that would require persons who intend to manufacture, import or process new NMs based on chemical substances listed on the TSCA Inventory to submit a Significant New Use Notice (SNUN) to EPA at least 90 days before that activity commences (EPA 2011a).
  - If NMs enter drinking water or are injected into a well, they may be regulated under the Safe Drinking Water Act (EPA 2007). However, currently no maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) have been established for NMs based solely on their size. MCLGs and MCLs are established for the macro-sized forms of NMs.
  - Risks from NMs at waste sites may be evaluated and addressed under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA) (EPA 2007).
  - Discharges to waters of the United States that contain NMs may require authorization under a Clean Water Act (CWA) permit pursuant to Section 402 of the CWA. EPA can establish compound-specific effluent limits in permits under the CWA (EPA 2007).
  - NMs may also be regulated under the Clean Air Act if their use or manufacture results in emissions of pollutants that are or could be listed as criteria air pollutants or hazardous air pollutants (EPA 2007).
  - Some Occupational Health and Safety Administration (OSHA) standards may apply to situations where workers handle or are exposed to NMs. In addition, OSHA has approved plans for 25 states, Puerto Rico and the Virgin Islands that enable them to adopt federal safety standards for workers in private industry. These

- plans allow states to adopt guidelines to manage the risks of NMs in the workplace (OSHA 2013a, 2013b).
- NIOSH has developed interim guidelines on the occupational safety and health implications and applications of NMs, including the use of effective control technologies, work practices and personal protective equipment (NIOSH 2013b).
- NIOSH has established a recommended exposure limit (REL) of 1.0 micrograms per cubic meter (μg/m³) as an 8-hour time-weighted average (TWA) for carbon nanotubes and carbon nanofibers. In addition, NIOSH established a REL of 2.4 milligrams per cubic meter (mg/m³) for fine TiO₂ (primary particle diameter between about 100 nm and 3,000 nm) and 0.3 mg/m³ for ultrafine (primary particle diameter less than 100 nm including engineered nanoscale) TiO₂ as a 10-hour TWA (NIOSH 2011, 2013a).
- State and local standards and guidelines:
  - In 2006, Berkeley, California, adopted the first local regulation specifically for NMs, requiring all facilities manufacturing or using manufactured NMs to disclose current toxicology information, as available (Berkeley 2006).
  - In 2010 and 2011, the California Department of Toxic Substances Control (CA DTSC) issued formal request letters to the manufacturers of certain carbon nanotubes, nanometal oxides, nanometals and quantum dots requesting information related to chemical and physical properties, including analytical test methods and other relevant information (CA DTSC 2013).
  - Several other states may have community rightto-know laws that authorize reporting or disclosures broader than the federal law; this may provide authority to require reporting when facilities use or produce NMs (Keiner 2008).

# What detection and characterization methods are available for nanomaterials?

- The detection, extraction and analysis of NMs are challenging because of NM's small size, unique structure, physical and chemical characteristics, surface coatings and interactions in the environment, including agglomeration and sequestration (EPA 2007).
- The analysis of NMs in environmental samples often requires the use of multiple technologies in tandem. Analysis can include use of size separation technologies combined with particle counting systems, morphological analysis and chemical analysis technologies (EPA 2007, 2010).

# What detection and characterization methods are available for nanomaterials? (continued)

- Aerosol mass spectrometer provides chemical analysis of NMs suspended in gases and liquids by vaporizing them and analyzing the resulting ions in a mass spectrometer (SCENIHR 2009).
- Aerosol fractionation technologies (differential mobility analyzers and scanning mobility particle sizers) use the mobility properties of charged NMs in an electrical field to obtain size fractions for subsequent analysis. Multi-stage impactor samplers separate NM fractions based on the aerodynamic mobility properties of the NMs (EPA 2007).
- Expansion condensation nucleus counters measure and derive NM density in gas suspension through adiabatic expansion followed by optical measurement. Currently available instruments can detect NPs as small as 3 nm (Saghafifar and others 2007).
- Size-exclusion chromatography, ultrafiltration and field flow fractionation can be used for size fractionation and collection of NM fractions in liquid media (EPA 2007).
- NM fractions may be further analyzed using dynamic light scattering for size analysis and mass spectrometry for chemical characterization (EPA 2007).

- One of the main methods of analyzing NM characteristics is electron microscopy. Scanning electron microscopy and transmission electron microscopy can be used to determine the size, shape and aggregation state of NMs below 10 nm (EPA 2007; SCENIHR 2006).
- Atomic force microscopy can provide single particle size and morphological information at the nanometer level in air and liquid media (EPA 2007).
- Dynamic light scattering is used to characterize manufactured NMs and provides information on the hydrodynamic diameter of NMs in suspensions. It is capable of measuring NPs from a few nm in size (EPA 2010).
- Other analytical techniques include X-ray diffraction to measure the crystalline phase and X-ray photoelectron spectroscopy to determine the surface oxidation states and chemical composition of NMs (EPA 2010).
- Additional research is needed to determine methods to detect and quantify engineered NMs in environmental media. EPA is currently researching practical methods for detecting, quantifying and characterizing NMs in the environment (EPA 2013).

# What technologies are being used to control nanomaterials?

- Limited information is available about which technologies can be used to control NMs in water and wastewater streams.
- Air filters and respirators are used to filter and remove NMs from air. A study found that membrane-coated fabric filters could provide an NP collection efficiency above 95 percent (Tsai and others 2012; Wiesner and others 2006).
- NMs in groundwater, surface water and drinking water may be removed using flocculation, sedimentation and sand or membrane filtration (Wiesner and others 2006).
- A recent study stabilized silver NPs using different capping agents to control the transport of the NPs in porous media (Badawy and others 2013).

### Where can I find more information about nanomaterials?

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