Chapter 3
Nanomaterial and Nanoparticle: Origin and Activity

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3.1 Introduction

Nanomaterials are defined as materials with external dimensions in the nanoscale or with internal structure or surface structure in the nanoscale. This would qualify most of the materials as nanomaterials, as their internal structure is modulated at the nanoscale.

A nanoparticle can be defined as a particle with at least one external dimension in the nanoscale. The term nanoscale can be defined as a size range from about 1 nm to less than 1 μm (Buzea et al. 2007). Particles larger than nanoparticles are called microparticles, while the ones smaller than nanoparticles are atoms and molecules. One must emphasize that the properties of a material in nanoform can be quite different that those of its bulk (heat of fusion, melting temperature, band energy gap, electronic structure and catalytic activity, magnetic properties, fluorescence, tensile strength, etc.) (Auffan et al. 2009; Buzea et al. 2007). The size at which nanoparticles physical properties begin to deviate from its bulk counterpart is about 100 nm (Bakshi et al. 2015), however it is not always a rule (Buzea et al. 2007). Hence, some authors are trying to limit the size of nanoparticles to sizes for which the properties of particles differ from those of their bulk counterparts.

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3.2 Nanoparticle Classification

From the point of view of their dimensionality, nanomaterials encompass broadly three types: with one, two, and three dimensions in the nanoscale. Those with one dimension in the nanoscale are very thin films or coatings attached on a substrate. Those with two dimensions in the nanoscale can be porous films with nanoscale pores, long aspect ratio fibers, wires, or tubes. The third type nanomaterials are membranes with nanopores and nanoparticles. This chapter focuses only on nanoparticle and long aspect ratio particles.

From the point of view of their provenance, inorganic nanoparticles qualify as natural and anthropogenic, as seen in Fig. 3.1. Natural nanoparticles can have geologic sources, incomplete combustion, biochemical cycling, and abiotic chemical precipitation. Geological sources of natural nanoparticles encompass wind erosion, dust storms, glaciations, earthquakes, and volcanic activity. Natural nanoparticles are generated via incomplete combustion in forest fires and earthquakes. An example of abiotic chemical precipitation is sea spray. Biochemical cycling of nanoparticles can be mediated by bacteria, plants, or fungi. Anthropogenic sources of nanoparticles can be unintentional and intentional. The unintentional can be due to incomplete combustion from heating and cooking, automobiles, industry, wear, corrosion (such as tires or construction materials), and garbage disposal of products containing nanoparticles. The intentional nanoparticles are released as pesticides, fertilizers, water or soil remediation.

Sometimes is hard to predict the origin of environmental nanoparticle, however several markers elements can be used to determine the most probable source of inorganic nanoparticles, as shown in Table 3.1 (Calvo et al. 2013). For example, anthropogenic nanoparticles from the steel industry will have Cr, Ni and Mo markers, while the ones from the petrochemical industry those of Ni and V. Incomplete combustion from vehicle tailpipe have platinum group elements tracers, as well as Ce, Mo, and Zn.

Origins, composition, and morphology of various types of natural and anthropogenic nanoparticles are discussed in this chapter.

3.3 Natural Nanoparticles

The term "nanoparticle" is relatively a new one. One should keep in mind that when searching the earlier literature for publications on natural nanoparticle keywords other than nanoparticles should be used, as this term is a relatively new one. For instance to increase the search yield, particle, particulate matter, dust or the specific composition of mineral particles should be used.

When are think of nanoparticle we associate them mainly with nanotechnology and manufactured nanoparticles. However, naturally formed nanoparticles are ubiquitous in nature and can be found in 10,000 years old glacial ice cores or in

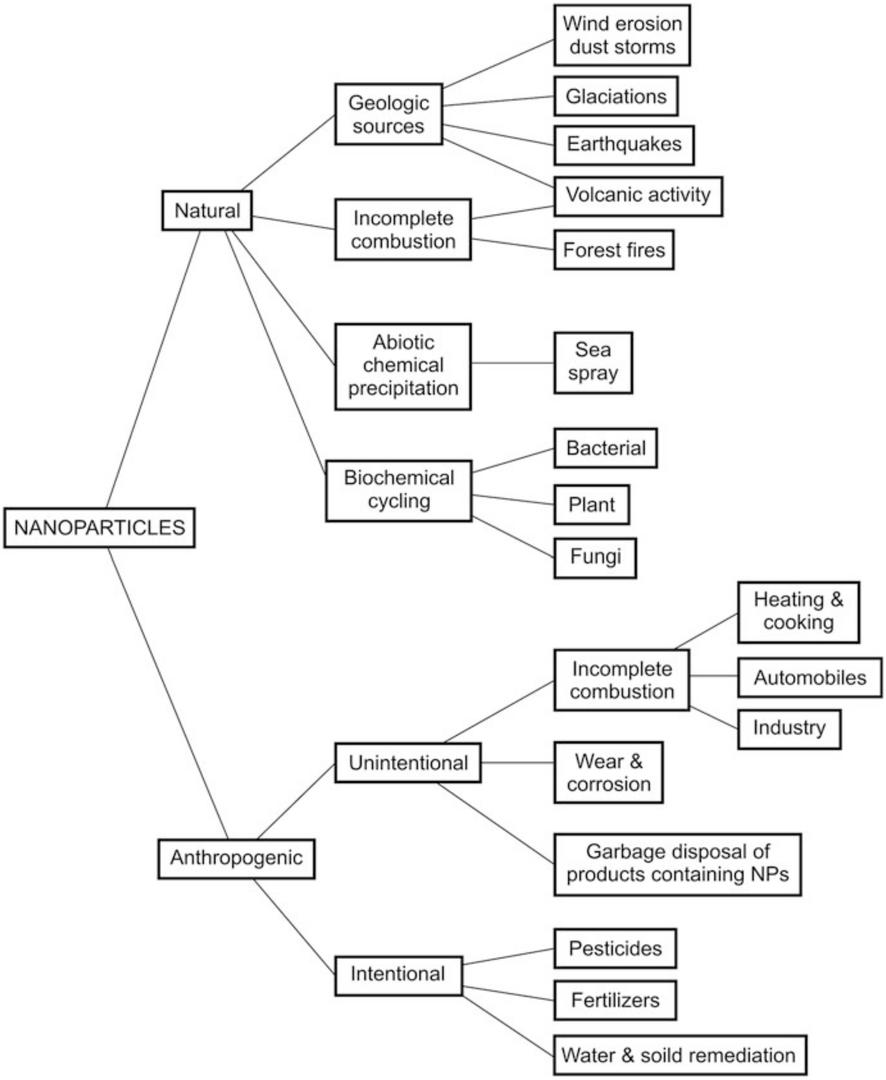


Fig. 3.1 Sources of natural and anthropogenic nanoparticles

the Cretaceous–Tertiary boundary layer (Murr et al. 2004; Verma et al. 2002; Handy et al. 2008a).

For example, studies of samples from the Cretaceous–Tertiary (K-T) boundary layer from Italy shows nanoparticles made of magnetically ordered iron materials, hematite, and a paramagnetic silicate, with a size of about 16–27 nm (Verma et al. 2002). It is believed that these nanoparticles formed due to the impact between Earth and a meteorite, and remained as aerosols for a long time before settling.

Table 3.1 Inorganic marker elements associated with emission sources or processes that generate nanoparticles

Tracers, secondary aerosols		Elements
Crustal or geological		Elements associated with feldspars, quartz, micas, and their weathering products (mostly clay minerals), i.e., Si, Al, K, Na, Ca, Fe and associated trace elements such as Ba, Sr, Rb, and Li. In addition, accessory silicates and carbonates, sulfates, oxides, hydroxides, and phosphates
Anthropogenic	Steel industry	Cr, Ni and Mo
	Copper metallurgy	Cu and As
	Ceramic industries	Ce, Zr, and Pb
	Heavy industry (refinery, coal mine, power stations)	Ti, V, Cr, Co, Ni, Zn, As, and Sb
	Petrochemical industry	Ni and V
	Oil burning	V, Ni, Mn, Fe, Cr, As, S, and SO_4^{2-}
	Coal burning	Al, Sc, Se, Co, As, Ti, Th, S, Pb, and Sb
	Iron and steel industries	Mn, Cr, Fe, Zn, W, and Rb
	Non-ferrous metal industries	Zn, Cu, As, Sb, Pb, and Al
	Cement industry	Ca
	Refuse incineration	K, Zn, Pb, and Sb
	Biomass burning	K and Br
	Firework combustion	K, Pb, Ba, Sb, and Sr
	Vehicle tailpipe	Platinum group elements, Ce, Mo, and Zn
	Automobile gasoline	Ce, La, Pt, SO_4^{2-}, and NO_3
	Automobile diesel	S, SO_4^{2-}, and NO^3
	Mechanical abrasion of tires	Zn
	Mechanical abrasion of brakes	Ba, Cu, and Sb

Adapted from Calvo A. I. et al., Research on aerosol sources and chemical composition: Past, current and emerging issues. Atmospheric Research, 2013, 120–121, 1–28, Copyright (2013), with permission from Elsevier (Calvo et al. 2013)

Natural nanoparticles can be organic and inorganic. The focus of this chapter is on inorganic nanoparticles. Natural nanoparticles sources can be classified as geologic, incomplete combustion, abiotic precipitation, and biochemical cycling. These sources of natural nanoparticles can involve bottom-up processes, which begin with molecular or ionic species, or top-down processes which begin with a larger precursor. Examples of bottom-up approaches are metallic nanoparticles formation via biomineralization or halide and hydrous sulfate nanoparticles from evaporation of sea spray (Sharma et al. 2015; Hochella et al. 2008). Examples of top-down approaches are nanoparticles generated by wind erosion in deserts, nanoparticles from incomplete combustion of matter.

Nowadays, the mineral dust generated by blowing wind from arid and agricultural lands constitutes probably the largest source of natural nanoparticles (Hochella et al. 2008). Other considerable source of natural nanoparticles are those generated by volcanoes and forest fires as ash, and biological debris (Bernhardt et al. 2010).

The composition of naturally generated nanoparticles is varied, ranging from: metals, metal oxides, and their compounds, alloys, carbon allotropes and silicates (Sharma et al. 2015; Guo and Barnard 2013; Hough et al. 2011). Noble metal nanoparticles are found in various environments. Figure 3.2 shows schematics, scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images of several types of natural nanoparticles: (a), (b) imogolite, a naturally occurring aluminosilicate nanotube in volcanic soils (Wilson et al. 2008; Yamamoto et al. 2005), (c) natural hydrous iron oxide aggregates on a mixture of organic fibrils found between 6.5 and 7.5 m in the water column (Taillefert et al. 2000), (d) weathered quartz fracture with Au nanoparticles (Hough et al. 2011), (e) bacteriomorphic gold (Brugger et al. 2013). Sometimes mineral nanoparticles can form in aqueous environments via nano-biomineralization, as aggregates with natural organic matter. Mineral weathering can generate nanoparticles of Fe and Mn oxides or ferrihydrite (Bakshi et al. 2015). Weathering reactions result in the formation of nanoparticle aggregates and coatings. Hence, nanoparticles in the environment have a dynamical chemical composition, size, and shape.

3.3.1 Nanoparticles from Wind Erosion and Dust Storms

Natural processes, such as weathering, can result in the formation of nanoparticles in soil, atmosphere, and aquatic environments. Weathering is a process of physical abrasion or chemical dissolution of rock material that results in the formation of nanoparticles and microparticles at the solid–air or solid–liquid interface. Weathering existed on Earth since 4 billion years from the time Earth was cold enough to have an atmosphere (Handy et al. 2008a). Today, the mineral dust generated by blowing wind from arid and agricultural lands constitutes probably the largest source of natural nanoparticles (Hochella et al. 2008).

Wind erosion is a top-down process of generating nanoparticles from larger precursors. Nanoparticle generation occurs via aeolian erosion in the desert, and on lands that is not covered by vegetation. Dust deposition occurs annually and increases with extended drought and land disturbance in source regions (Painter et al. 2007). Nanoparticles generated from dust storms are the largest amount of natural nanoparticles in the atmosphere.

Dust storms originate in drylands, the main sources being the Sahara and Kalahari (Africa), Arabian desert (Middle East), Gobi desert (Asia), Patagonian desert (South America), Western US deserts (North America) and Great Victoria desert (Australia). Desert dust has an effect on human health and ecosystems

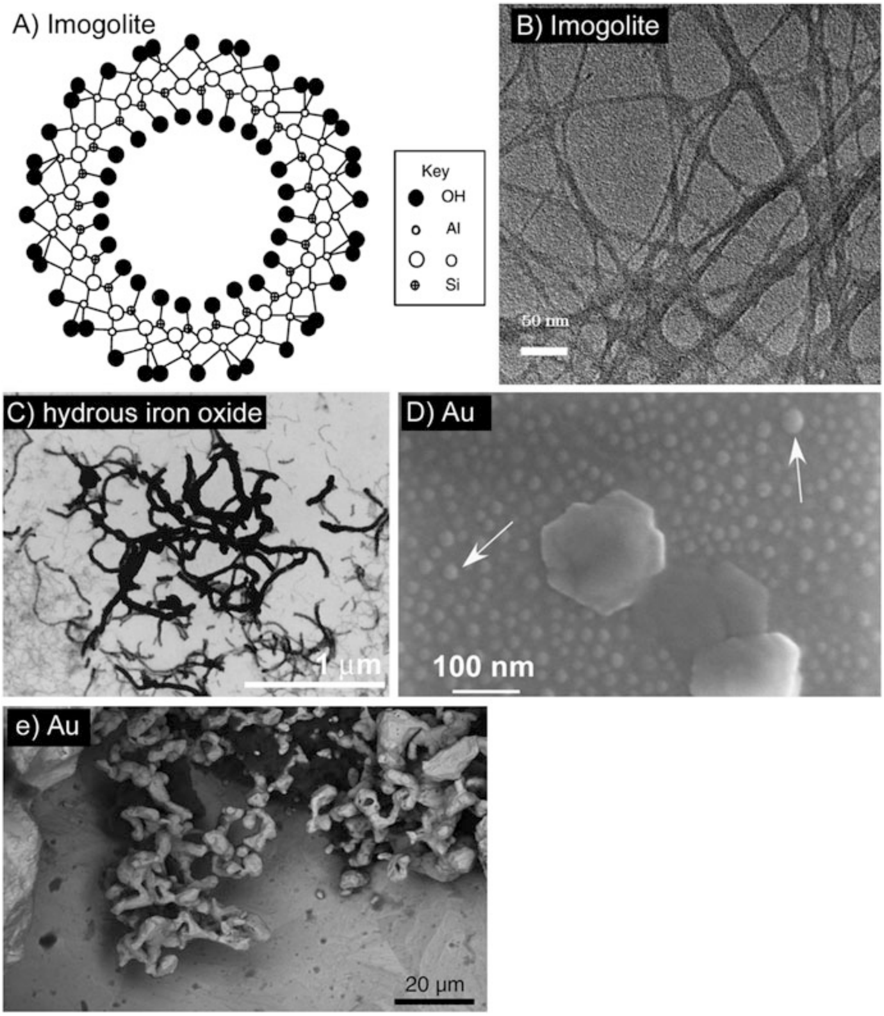


Fig. 3.2 (**a**) Schematics of imogolite structure. Reprinted from Wilson M. A. et al., Nanomaterials in soils. Geoderma, 146, 2008, 291–302. Copyright (2008), with permission from Elsevier (Wilson et al. 2008). (**b**) TEM image of imogolite, a naturally occurring aluminosilicate nanotube. Reprinted from Yamamoto K. et al., Preparation and properties of poly(methyl methacrylate)/imogolite hybrid via surface modification using phosphoric acid ester. Polymer, 2005, 46, 12386–12392. Copyright (2005), with permission from Elsevier (Yamamoto et al. 2005). (**c**) Natural hydrous iron oxide aggregates on a mixture of organic fibrils found between 6.5 and 7.5 m in the water column. Reprinted from Taillefert M. et al., Speciation, reactivity, and cycling of Fe and Pb in a meromictic lake. Geochimica Et Cosmochimica Acta, 2000, 64, 169–183, Copyright (2000), with permission from Elsevier (Taillefert et al. 2000). (**d**) Image of the surface of a weathered quartz fracture which shows 20 nm nanospheres (*white arrows*) in the background next to coarser Au nanoparticles. Reprinted from Hough R. M. et al., Natural gold nanoparticles, Ore Geology Reviews, 2011, 42, 55–61, Copyright (2011), with permission from Elsevier (Hough et al. 2011). (**e**) SEM image of bacteriomorphic gold on a gold grain from soil at the Platina Lead at Fifield. Reprinted from Brugger J. et al., Can biological toxicity drive the contrasting behavior of platinum and gold in surface environments? Chemical Geology 2013, 343, 99–110, Copyright (2013), with permission from Elsevier (Brugger et al. 2013)

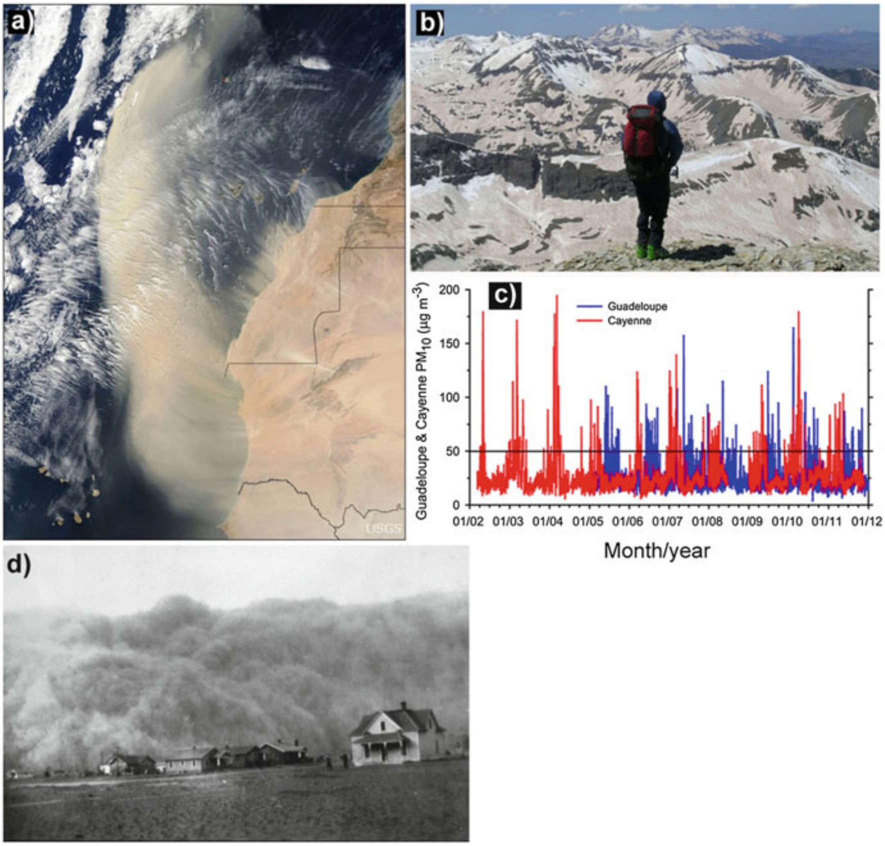
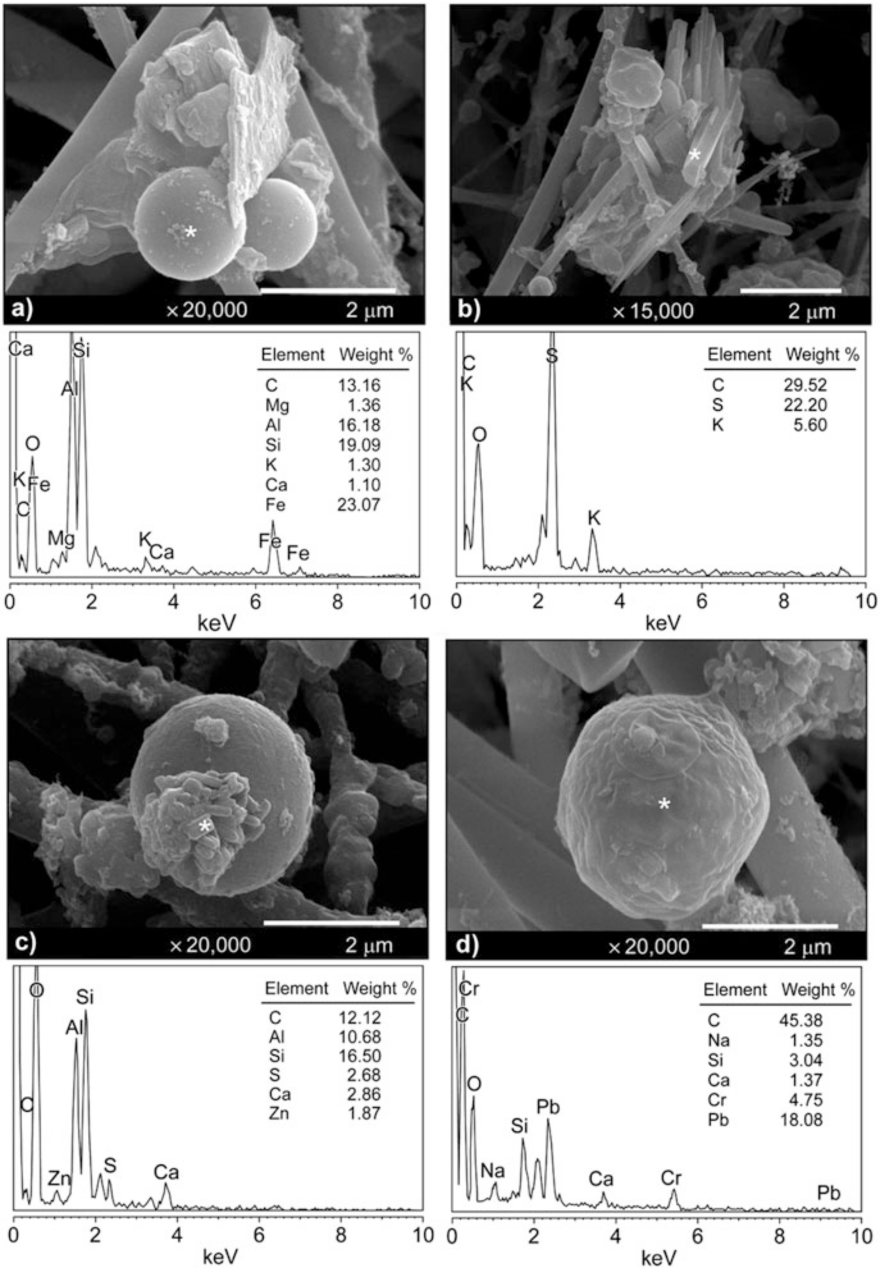


Fig. 3.3 (**a**) A large Saharan dust storm leaves the West African coast to move over the Atlantic Ocean. Courtesy Moderate Resolution Imaging Spectroradiometer (MODIS) aboard NASA's Terra satellite on March 2004. (**b**) Dust deposits on snow covered surface in the San Juan Mountains, Colorado, 12 March 2009. Courtesy of U.S. Geological Survey. (**c**) Plot of the daily average PM10 concentrations (µg/m^3) at Cayenne and Guadeloupe. The horizontal line is the World Health Organization value Air Quality Guideline for 24 h. Reprinted from Prospero J. M. et al., Characterizing the annual cycle of African dust transport to the Caribbean Basin and South America and its impact on the environment and air quality. Global Biogeochemical Cycles, 2014, 28, 757–773, Copyright (2014) with permission from John Wiley and Sons (Prospero et al. 2014). (**d**) Dust storm near Stratford, Texas, 1935. NOAA George E. Marsh Album. Reprinted from Morman S. A. and Plumee G. S., The role of airborne mineral dusts in human disease. Aeolian Research, 9, 203–212, Copyright (2013), with permission from Elsevier (Morman and Plumlee 2013)

specially those situate downwind (Goudie 2014). Dust storms occur many times throughout the year in many regions. Dust particles from dust storms are able to transport pollutants and allergens over immense distances across continents.

Naturally occurring nanoparticles from dust storms have not only a local or regional environmental effect, but also global consequences, as seen in Fig. 3.3.



a)

Element	Weight %
C	13.16
Mg	1.36
Al	16.18
Si	19.09
K	1.30
Ca	1.10
Fe	23.07

b)

Element	Weight %
C	29.52
S	22.20
K	5.60

c)

Element	Weight %
C	12.12
Al	10.68
Si	16.50
S	2.68
Ca	2.86
Zn	1.87

d)

Element	Weight %
C	45.38
Na	1.35
Si	3.04
Ca	1.37
Cr	4.75
Pb	18.08

Fig. 3.4 SEM images and composition determined by energy dispersive X-ray spectroscopy (EDS) of different particles from Asian dust storm samples. (**a**) Spherical particle of carbon enriched iron oxides of combustion origin. (**b**) Elongated particles containing sulfur. (**c**) Spherical particle with sulfur-containing nanoparticles, an anthropogenic signature, suggesting the possible adsorption of sulfates on the surface of wind-blown dust particles. (**d**) some heavy metals (e.g., Cr

Dust from dessert storms in Africa are transported across the oceans and seas and are able to affect ecosystems worldwide, as illustrated in Fig. 3.3a, c (Prospero and Mayol-Bracero 2013; Prospero et al. 2014). An example of dust deposition on mountain snow cover is shown in Fig. 3.3b. African mineral dust is transported to the Caribbean basin, showing a strong seasonal cycle, as seen in Fig. 3.3c (Prospero et al. 2014). The measurement of particulate matter at two different locations, at Cayenne (French Guiana) and Guadeloupe, show that the high levels of particles are almost entirely due to African dust.

Figure 3.4 shows examples of scanning electron microscope images and composition of particles from Asian dust storm samples (Kim et al. 2012). Carbon and crustal elements magnesium, aluminum, silicon and calcium are major components in most particles.

3.3.2 Nanoparticles from Volcanic Activity

A class of natural nanoparticle are those generated by volcanic activity. During a volcano eruption gases and large amounts of ash, composed of nanoparticles and microparticles, are ejected in high in the atmosphere, up to a height of 18,000 m (Buzea et al. 2007). During a single volcanic eruption hundreds of tons of ash can be ejected. Due to the air circulation in the upper troposphere and stratosphere, ash can distribute worldwide, blocking and scattering sun radiation. Figure 3.5 shows examples of scanning electron microscope images of volcanic ash and the 2011 Eruption of Shinmoedake volcano in Japan.

Figure 3.6 shows transmission electron microscope images of nanoparticles trapped in ice core drilled from Greenland and estimated to be about 10,000 years old. Some of these core samples include particles related to volcanic eruptions and dust-fall (Murr et al. 2004). Interesting to note that the arctic airborne particulate matter as well as carbon dioxide and methane concentrations are highly correlated. The ice cores of glacier ice are able to shed some light on their concentrations and antiquity (Murr et al. 2004). Various techniques can allow the identification of the time of the ice cores, ranging from 100 years to several millions years old ice identified in Antarctica. The study of particulate matter trapped in ice cores drilled from Greenland from a depth of 506 m, estimated to be about 10,000 years old, showed the composition of nanoparticles to be of carbon, including carbon nanotubes, silica, alumina, and iron-based compound, among others (Murr et al. 2004). Some clusters had a much more complex chemistry, including C, O, Na, S,

◄

Fig. 3.4 (continued) and Pb) on the surface of spherical nanoparticles. The *asterisk* (*) in the photographs indicates the position where EDS analysis was carried out. Reprinted from Kim W. et al., Asian dust storm as conveyance media of anthropogenic pollutants. Atmospheric Environment, 2012, 49, 41–50. Copyright (2012), with permission from Elsevier (Kim et al. 2012)

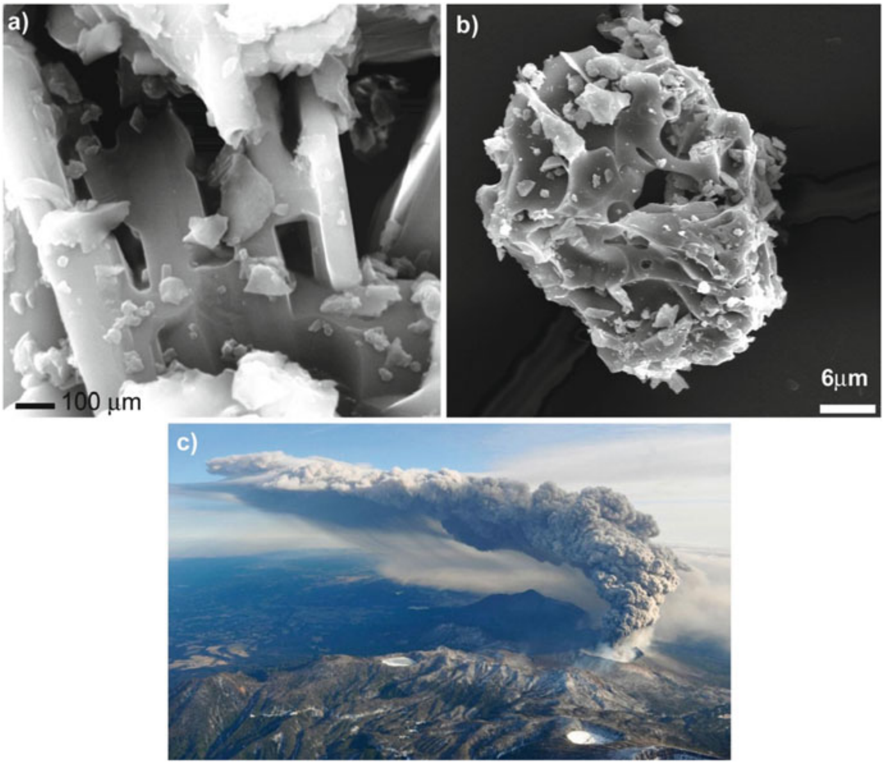


Fig. 3.5 (**a**) Scanning electron microscope image of volcanic ash from the first volcanic eruption of Mount St. Helen, Washington state, USA in 1980. Courtesy Louisa Howard, http://remf.dartmouth.edu/imagesindex.html. (**b**) SEM image of ash microparticle with nanoparticles on its surface. The ash particle was erupted by Augustine volcano in 2006 and collected during the ashfall in Homer, Alaska by John Paskievitch, AVO. The image was acquired by PavelIzbekov using ISI-40 Scanning Electron Microscope at the Advanced Instrumentation Laboratory, University of Alaska Fairbanks. (**c**) 2011 Eruption of Shinmoedake, Japan. Courtesy U. S. Geological Survey

Cl, K, Ca, Cu, and Zn. The carbon nanotubes are indicative of incomplete combustion processes, such as burning natural gas, while alumina is indicative of weathered alumino silicates (Murr et al. 2004).

3.3.3 Nanoparticle Weathering

Research on aerosol sources and their chemical composition shows that aerosol particles may be removed from the atmosphere by dry and/or wet deposition (Calvo et al. 2013). They can enter soil, interact with the substances from soil, release ions and be available for uptake by plants (Coutris et al. 2012). The size of aerosol

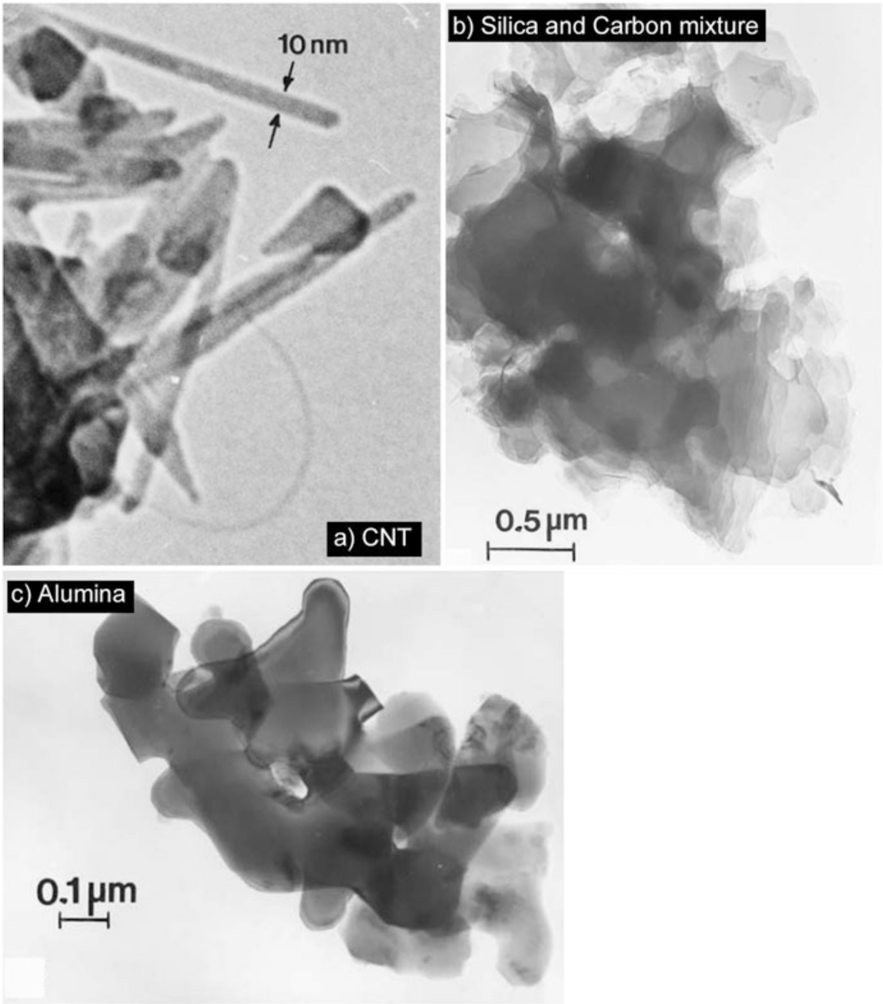


Fig. 3.6 TEM images of nanoparticles trapped in ice core drilled from Greenland and estimated to be about 10,000 years old. (**a**) carbon nanotubes. (**b**) silica SiO_2 and carbon C mixture, and (**c**) Alumina Al_2O_3 nanoparticles. Reprinted from Murr L. E. et al., Chemistry and nanoparticulate compositions of a 10,000 year-old ice core melt water. Water Research, 2004, 38, 4282–4296, Copyright (2004), with permission from Elsevier (Murr et al. 2004)

particle varies from a few nanometers to several tens of microns (Calvo et al. 2013). Size is an important parameter that dictates its environmental behavior.

In many cases, nanoparticles occur via a combination of processes. An example would be weathering, which is a combination of mechanical processes, such as erosion, combined with dissolution and precipitation (an example is shown in Fig. 3.7), or volcanic activity that involves fast cooling of fumes and explosions.

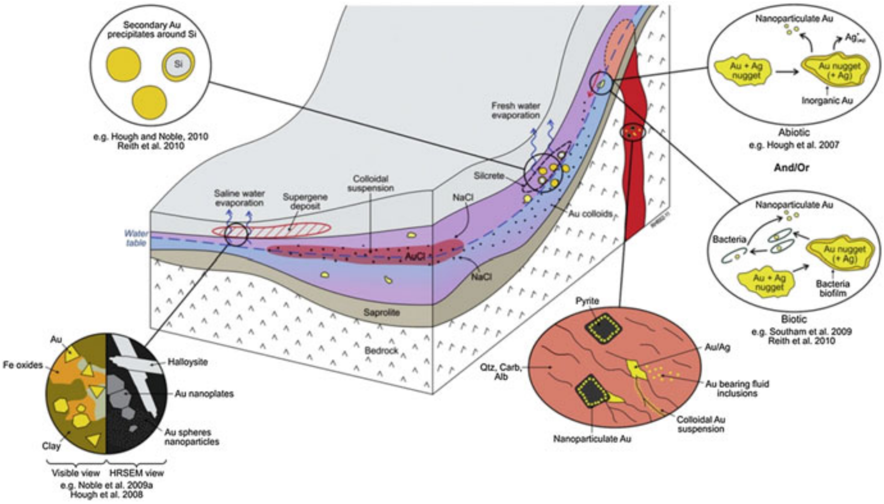


Fig. 3.7 The formation of hydrothermal and supergene gold deposits via gold nanoparticle weathering. Reprinted from Hough R. M. et al., Natural gold nanoparticles, Ore Geology Reviews, 2011, 42, 55–61, Copyright (2011), with permission from Elsevier (Hough et al. 2011)

Usually nanoparticles form at phase boundaries, such as wind erosion at a solid–gas interface, evaporation of sea spray, at a liquid–gas interface, and weathering of rocks at a solid–liquid interface (Sharma et al. 2015).

The formation of new nanoparticles from dissolved species is called authigenesis or neoformation (Handy et al. 2008a). This process occurs when the concentration of dissolved species is high enough and exceed the saturation in solution of a phase, and results in the nucleation and growth of nanoparticles. An example of nanoparticles formed by authigenesis are clay and iron oxyhydroxide nanoparticles.

3.3.4 Biogenic Nanoparticles: From Bacteria

Organisms, especially microorganisms, generate a large amount of inorganic nanoparticles in the environment, such as iron, silicon and calcium based minerals (Sharma et al. 2015). These biogenic nanoparticles are ubiquitous. The morphology of these particles varies from wires, see for example Fig. 3.8 (Leung et al. 2013), to spherical or cuboidal shapes, as seen in Fig. 3.9 (Fairbrother et al. 2013; Reith et al. 2014; Lengke et al. 2006; Alphandéry 2014).

Microorganisms that produce nanoparticles are bacteria, fungi, and yeast (Prasad et al. 2016). Table 3.2 gives some examples of microorganisms able to synthesize nanoparticles and the composition of nanoparticles. The composition of nanoparticles produced by microorganism is varied, ranging from precious metals to magnetic materials, such as Au, Ag, Ba, Hg, Se, Cd, Te, CdS, Cu, U, Tc, Cr, Co,

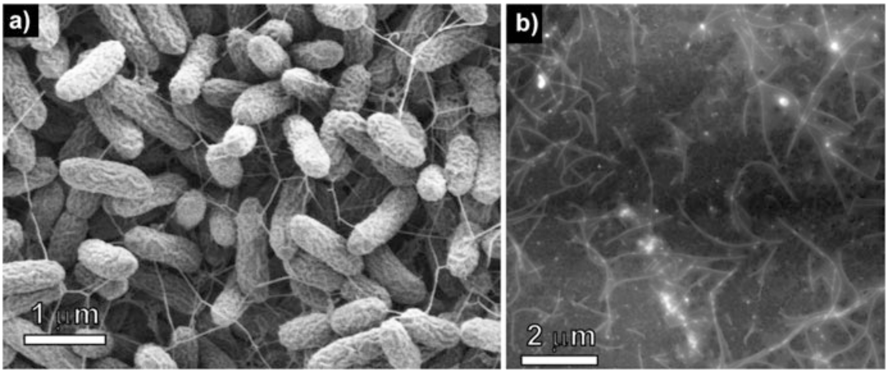


Fig. 3.8 Nanowires generated by *Shewanella oneidensis* MR-1 strain. (**a**) SEM image of *S. oneidensis* exhibiting large amounts of nanowires. (**b**) atomic force microscopy image of nanowires onto a flat surface. Reprinted with permission from Leung K. M. et al., Shewanella oneidensis MR-1 Bacterial Nanowires Exhibit p-Type, Tunable Electronic Behavior. Nano Letters, 2013, 13, 2407–2411. Copyright (2013) American Chemical Society (Leung et al. 2013)

Mn, Pd, Pt, Zr, Fe_3O_4, Fe_3S_4, Zn, TiO_2, among other (Nath and Banerjee 2013; Quester et al. 2013).

Some types of bacteria, as a response to environmental stresses (such as toxicity of metal ions), have developed a defense mechanism that allows them to survive and grow in environments with high metal ion concentrations (Quester et al. 2013; Prasad et al. 2016). As a result, many bacterial species are currently used to produce metallic nanoparticles as an alternate route to simple chemical synthesis. This method of nanoparticle biosynthesis can use intact cells and cell extracts. In Table 3.2 are presented types of bacteria used to produce a large variety of metallic nanoparticles. The synthesis of nanoparticles by bacteria can be an intracellular or extracellular process, depending on the type of bacteria and material.

Biologically induced mineralization (BIM) is one of the processes involved in nanoparticle formation by organisms (Sharma et al. 2015). During this process nanoparticles are formed as a result of metabolic processes, the nanoparticles having no particular function in the functioning of the organisms, being only in a substrate attached to bacteria, or interacting with bacterial cell wall.

Biologically controlled mineralization (BCM) is another process when, in contrast to the previously discussed one, the growth of the nanoparticles is controlled by the organisms, being usually formed inside the cells (Sharma et al. 2015). Nanoparticles formed during this process are usually crystalline with a narrow particle-size distribution and serve different functions within the organisms, such as iron storage, tissue hardening, electron transfer mediators to promote oxidation and reduction under anaerobic conditions. For example, magnetotactic bacteria generates magnetite nanoparticles that are used for navigation, or in *Shewanella oneidensis* hematite nanoparticles facilitate respiration (Sharma et al. 2015).

Some bacteria developed a strategy for efficient electron transfer and energy distribution by generating electrically conductive appendages having the shape of

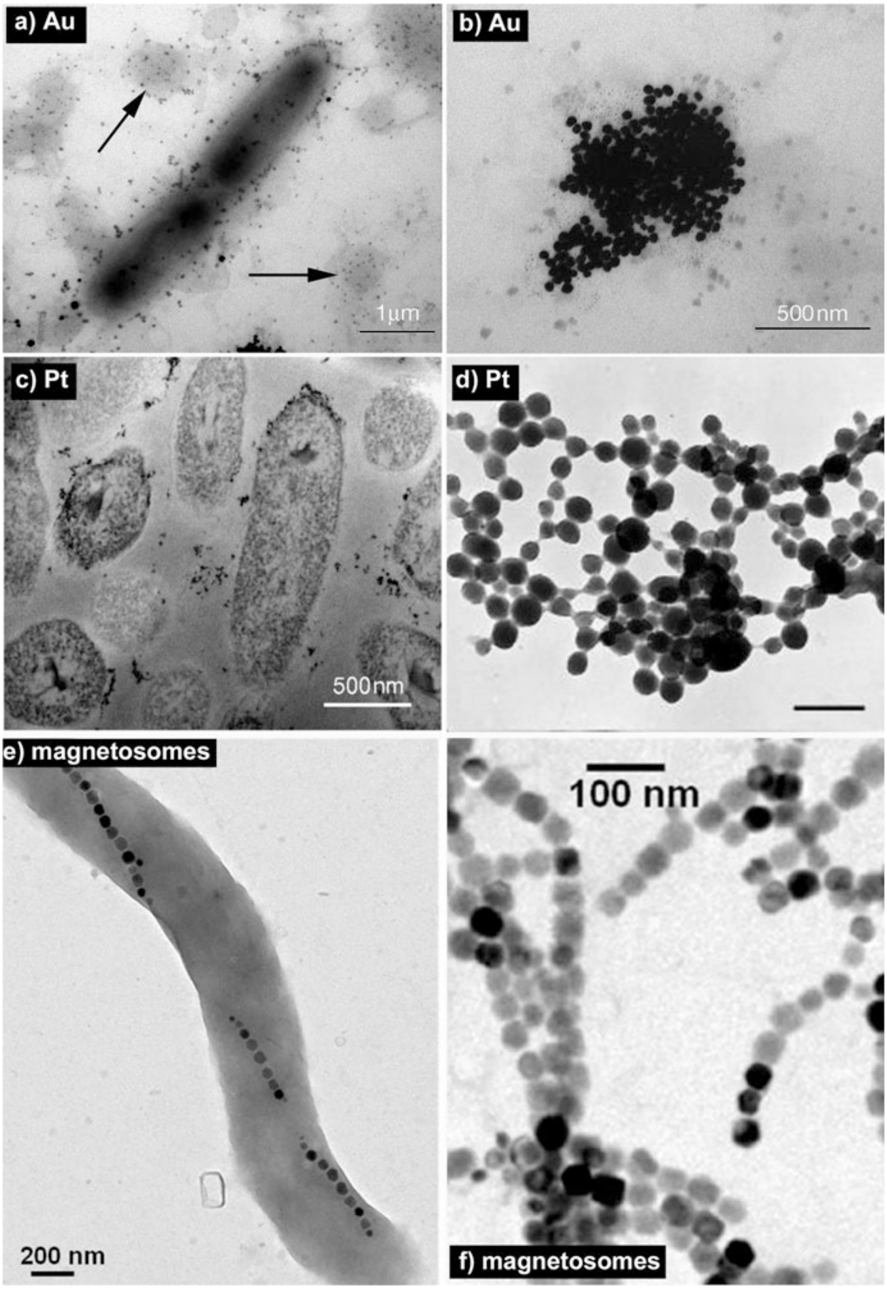


Fig. 3.9 (**a**) TEM of *Cupriavidus metallidurans* bacterium capable of precipitating gold nanoparticles from aqueous gold complexes. (**b**) agglomerate of Au nanoparticles synthesized by *Cupriavidus metallidurans* bacterium. Images (**a**) and (**b**) are reprinted with permission from Fairbrother L. et al., Biomineralization of Gold in Biofilms of *Cupriavidus metallidurans*. Environmental Science & Technology, 2013, 47, 2628–2635. Copyright (2013) American Chemical Society (Fairbrother et al. 2013). (**c**) TEM image of *C. metallidurans* exposed to Pt(II)-chloride

nanowires (Gorby et al. 2006). This is the case for the mesophilic bacterium *Shewanella oneidensis*, cyanobacterium Synechocystis PCC6803, and the thermophilic bacterium Pelotomaculum (Gorby et al. 2006; Leung et al. 2013).

Magnetosomes are nanoparticles synthesized intracellularly by magnetotactic bacteria, as seen in Fig. 3.9e, f (Alphandéry 2014). Magnetotactic bacteria use the magnetosomes as tiny compasses to navigate using the geomagnetic field. These bacteria are ubiquitous in sediments of fresh water, marine and hypersaline habitats, being found on all continents (Lefevre and Bazylinski 2013). The structure of a magnetosome is composed of a magnetic nanoparticle surrounded by lipid bilayer membrane. The magnetic nanoparticles are morphologically uniform, with a size between 35 and 120 nm, with a narrow size distribution, for the most studied species of magnetotactic bacteria. The composition of the core nanoparticle is high purity and crystallinity magnetite (Fe_3O_4) or greigite (Fe_3S_4) (Lefevre and Bazylinski 2013). The magnetosome has usually a single domain magnetic nanoparticle, as opposed to chemically synthesized iron oxide nanoparticles which are usually multidomain. As shown in Fig. 3.9e, the magnetosomes are ordered in chains inside the magnetotactic bacteria. The magnetic nanoparticles are coated by lipids and proteins, which gives it a total negative charge and good water dispersability.

Via their interactions with some metals, microorganisms are involved in metal cycling, determining their mobility in surface environments (Brugger et al. 2013). For example Au has a high mobility in many near-surface environments due to their interaction with metal-resistant bacteria.

3.3.5 Biogenic Nanoparticles: From Plants

Plants have different behavior towards excess metals present in the growth media. Metal-tolerant ones limit the uptake of nanoparticles into the photosynthetic tissue by restricting the transport of metals across the root endodermis and storing them on the root cortex (Manceau et al. 2008). Hyper-accumulating plants uptake and translocate excess amounts of metals in harvestable parts (Manceau et al. 2008).

Fig. 3.9 (continued) showing Pt nanoparticles in the cytoplasm and periplasm. Reprinted from Reith F. et al., Platinum in Earth surface environments. Earth-Science Reviews, 2014, 131, 1–21, Copyright (2014), with permission from Elsevier (Reith et al. 2014). (**d**) TEM image of Pt nanoparticles forming long beadlike chains in cyanobacteria-PtCl4° systems. Scale bar 0.25 μm. Reprinted with permission from Lengke M. F. et al., Synthesis of Platinum Nanoparticles by Reaction of Filamentous Cyanobacteria with Platinum(IV)−Chloride Complex. Langmuir, 2006, 22, 7318–7323. Copyright (2006) American Chemical Society (Lengke et al. 2006). (**e**) Magnetosomes inside a magnetotactic bacteria. (**f**) magnetosomes extracted from the magnetotactic bacteria. Images (**e**) and (**f**) are reprinted from Alphandery E., 2014, Applications of Magnetosomes Synthesized by Magnetotactic Bacteria in Medicine, Frontiers in Bioengineering and Biotechnology, 2, 5 (Alphandéry 2014)

Table 3.2 Microorganisms able to synthesize nanoparticles and the composition of nanoparticles (NPC)

NPC	Bacteria and actinomycetes	Fungi	Yeast
Au	*Brevibacterium casei*, *Bacillus licheniformis*, *Bacillus subtilis*, *Brevibacterium casei*, *Candida utilis*, *Cupriavidus metallidurans*, *Escherichia coli*, *Desulfovibrio desulfuricans*, *Neurospora crassa*, *Plectonema boryanum*, *Pseudomonas stutzeri*, *Pseudomonas aeruginosa*, *Rhodococcus* sp., *Rhodopseudomonas capsulate*, *Sargassum wightii*, *Shewanella algae*, *Shewanella oneidensis*, *Streptomyces hygroscopicus*, *Thermomonospora* sp., *Yarrowia lipolytica*	*Alternaria alternata*, *Aspergillus niger*, *Colletotrichum* sp., *Coriolis versicolor*, *Fusarium oxysporum*, *Neurospora crassa*, *Rhizopus oryzae*, *Trichoderma viride*, *Verticillium luteoalbum*, *Volvariella volvaceae*	*Pichia jadinii* (*Candida utilis*), *Yarrowia lipolytica*
Ag	Aeromonas spp., *Aspergillus flavus*, *Aspergillus fumigatus*, *Brevibacterium casei*, *Bacillus cereus*, *Bacillus subtilis*, *Bacillus licheniformis*, *Bacillus thuringiensis*, *Brevibacterium casei*, *Corynebacterium glutamicum*, *Escherichia coli*, *Fusarium oxysporum*, *Geobacter sulfurreducens*, *Lactobacillus* sp. from yoghurt, Morganella sp., *Morganella psychrotolerans*, *Neurospora crassa*, *Shewanella oneidensis*, *Phaenerochaete chrysosporium*, *Plectonema boryanum*, *Proteus mirabilis*, *Staphylococcus aureus*, *Streptomyces albidoflavus*, *Streptomyces hygroscopicus*, *Trichoderma viride*, *Ureibacillus thermosphaericus*	*Amylomyces rouxii* KSU-09, *Aspergillus clavitus*, *Aspergillus flavus*, *Aspergillus fumigatus*, *Aspergillus terreus*, *Aspergillus niger*, *Cladosporium cladosporioides*, *Coriolis versicolor*, *Fusarium oxysporum*, *Neurospora crassa*, *Penicillium fellutanum*, Penicillium strain J3, Phanerochaete, *Phoma glomerata*, *Pleurotus sajor caju*, *Rhizopus stolonifera*, *Streptomyces* sp., *Chrysosporium*, *Trichoderma asperellum*, *Trichoderma viride*, *Verticillium*, *Volvariella volvaceae*	Yeast strain MKY3
Ba		*Fusarium oxysporum*	
Hg	Enterobacter sp.	*Aspergillus versicolor*	
Se	Shewanella sp.		
Cd	*Escherichia coli*	*Fusarium oxysporum*	

(continued)

Table 3.2 (continued)

NPC	Bacteria and actinomycetes	Fungi	Yeast
			Candida glabrata, *Schizosaccharomyces pombe*
Te	*Escherichia coli*		
CdS	*Escherichia coli*, *Lactobacillus* sp., *Rhodopseudomonas palustris*	*Fusarium oxysporum*	*Candida glabrata*, *Schizosaccharomyces pombe*
Cu	*Mycobacterium smegmatis*		
U	*Pyrobaculum islandicum*		
Tc	*Pyrobaculum islandicum*		
Cr	*Pyrobaculum islandicum*		
Co	*Pyrobaculum islandicum*		
Co_3O_4	*Brevibacterium casei*		
Mn	*Pyrobaculum islandicum*		
Pd	*Bacillus sphaericus*, *Cupriavidus metallidurans*, *Cupriavidus necator*, *Desulfovibrio desulfuricans*, *Desulfovibrio fructosovorans*, *Shewanella oneidensis*, *Paracoccus denitrificans*, *Plectonema boryanum*, *Pseudomonas putida*		
Pt	*Shewanella algae*, *Plectonema boryanum*	*Fusarium oxysporum*	
Zr			Yeast
Fe_3O_4	Actinobacter spp., Shewanella sp., *Thermoanaerobacter ethanolicus*, Thermoanaerobacter sp., various magnetotactic bacteria		
Fe_3S_4	Actinobacter spp., various magnetotactic bacteria		
ZnS	*Rhodobacter sphaeroides*		
Zn		Fusarium spp.	
ZnO	*Bacillus cereus*		
TiO_2	*Bacillus subtilis*, Lactobacillus sp., Lactobacillus sp. from yoghurt	*Aspergillus flavus*	
UO_2	*Anaeromyxobacter dehalogenans*, *Shewanella oneidensis*		

(continued)

Table 3.2 (continued)

NPC	Bacteria and actinomycetes	Fungi	Yeast
TcO_2	*Anaeromyxobacter dehalogenans*		

Data adapted with permission from Nath and Banerjee (2013) and Quester et al. (2013)

Hydraulic lift of nanoparticles by deep-rooted vegetation is a mechanism of transport of nanoparticles from deeper sediments to the earth surface (Lintern et al. 2013). It has been shown that Eucalyptus trees are able to translocate Au from mineral deposits at more than 30 m depth (Lintern et al. 2013). Gold nanoparticles were found in the foliage of the studied Eucalyptus tree.

Rice (*Oryza sativa*) uptakes silica from the soil as silicic acid and accumulates around cellulose micro-compartments (Mohammadinejad et al. 2016). As the second largest farmed crop in the world, rice has the potential to become a significant source of silica nanoparticles (Mohammadinejad et al. 2016). Rice husks are considered an important agricultural residue, 1 t of husks for every 5 t of rice. Some authors suggest the use of rice husks as a source of silica nanoparticles (Mohammadinejad et al. 2016). Silica nanoparticles derived from burning the husks is about 20 % of the dry weight of their weight.

Common wetlands plants can transform cationic copper into nanoparticles in and near their roots with the help of fungi when grown in contaminated soils (Manceau et al. 2008). Table 3.3 shows examples of plants that are able to synthesize nanoparticles together with the composition of nanoparticles (Nath and Banerjee 2013; Quester et al. 2013).

3.4 Anthropogenic Nanoparticles

3.4.1 Examples of Engineered Nanoparticles

Engineered nanoparticles can have different compositions: carbon based, metals and their oxides, polymers, etc. Carbon based nanomaterials encompass carbon different allotropes: carbon black, an amorphous form of carbon, graphite, nanodiamonds, carbon nanotubes (CNTs), and fullerenes, such as C60, C70 (Bhatt and Tripathi 2011; Nowack and Bucheli 2007). Examples of carbon allotropes that can be found in nanoform are shown in Fig. 3.10 (Balasubramanian and Burghard 2005). The size of these nanomaterials can range from smaller than 1 nm, 0.7 nm for fullerenes, while carbon nanotubes can have diameter of about 1 nm and varying lengths. Carbon nanotubes can be single walled carbon nanotubes (SWCNTs), or multi-walled carbon nanotubes (MWCNTs) (Balasubramanian and Burghard 2005). SWCNTs are formed of rolled up single-layered graphene sheets while MWCNTs can have several concentric layers with varying diameter, as shown in Fig. 3.10e, g, respectively.

Table 3.3 Plants that synthesize nanoparticles and the composition of nanoparticles

Nanoparticle composition	Plants	Algae
Au	Alfalfa plant (*Medicago sativa*), *Aloe vera*, *Avena sativa*, *Azadirachta indica*, black tea, *Camelia sinensis*, *Camelia sinensis*, *Cassia fistula*, *Cinnamomum camphora*, *Citrus paradisi*, *Coriandrum sativum*, *Cymbopogon flexuosus*, *Diopyros kaki*, *Emblica officinalis*, *Hibiscus rosasinensis*, *Magnolia kobus*, *Pelargonium graveolens*, *Psidium guajava*, *Sesbania drummondii*, *Terminalia chebula*	*Chlorella vulgaris*, *Fucus vesiculosus*, *Sargassum myriocystum*, *Sargassum wightii*
Ag	Alfalfa plant (*Medicago sativa*), *Aloe vera*, *Annona squamosa*, *Azadirachta indica*, Black tea, *Brassica juncea*, *Camellia sinensis*, *Camellia sinensis*, *Capsicum annum*, *Cinnamomum camphora*, *Cinnamomum zeylanicum*, *Citrullus colocynthis*, *Citrus sinensis*, *Coccinia grandis*, *Dioscorea bulbifera*, *Emblica officinalis*, *Ficus racemose*, *Helianthus annus*, *Hibiscus rosasinensis*, *Jatropha curcas* (latex), *Lippia citriodora*, *Mimosa pudica*, *Murraya koenigii*, *Musa paradisiaca*, *Musa paradisiaca*, *Nelumbo nucifera*, *Origanum vulgare*, *Pandanus odorifer*, *Pelargonium graveolens*, *Punica granatum*, Purified Apiin (from henna leaves), *Rhizophora mucronata*, *Solanum torvum*, *Syzygium cumini*, *Terminalia chebula*, *Tribulus terrestris*, *Vinca rosea*	*Chlorella vulgaris*, *Sargassum wightii*, Urosporasp.
Ni	Alfalfa plant (*Medicago sativa*), *Brassica juncea*, *Helianthus annus*	
Zn	Alfalfa plant (*Medicago sativa*), *Brassica juncea*, *Helianthus annus*	
Cu	Alfalfa plant (*Medicago sativa*), *Brassica juncea*, *Helianthus annus*, *Calotropis procera*	
Co	Alfalfa plant (*Medicago sativa*), *Brassica juncea*, *Helianthus annus*	
Pd	*Gardenia jasminoides* Ellis	
Ti	Alfalfa plant (*Medicago sativa*)	
TiO_2	*Annona squamosa*	
Sm	Alfalfa plant (*Medicago sativa*)	
Se	Lemon plant	
FeO	Alfalfa plant (*Medicago sativa*)	

Data adapted with permission from Nath and Banerjee (2013) and Quester et al. (2013)

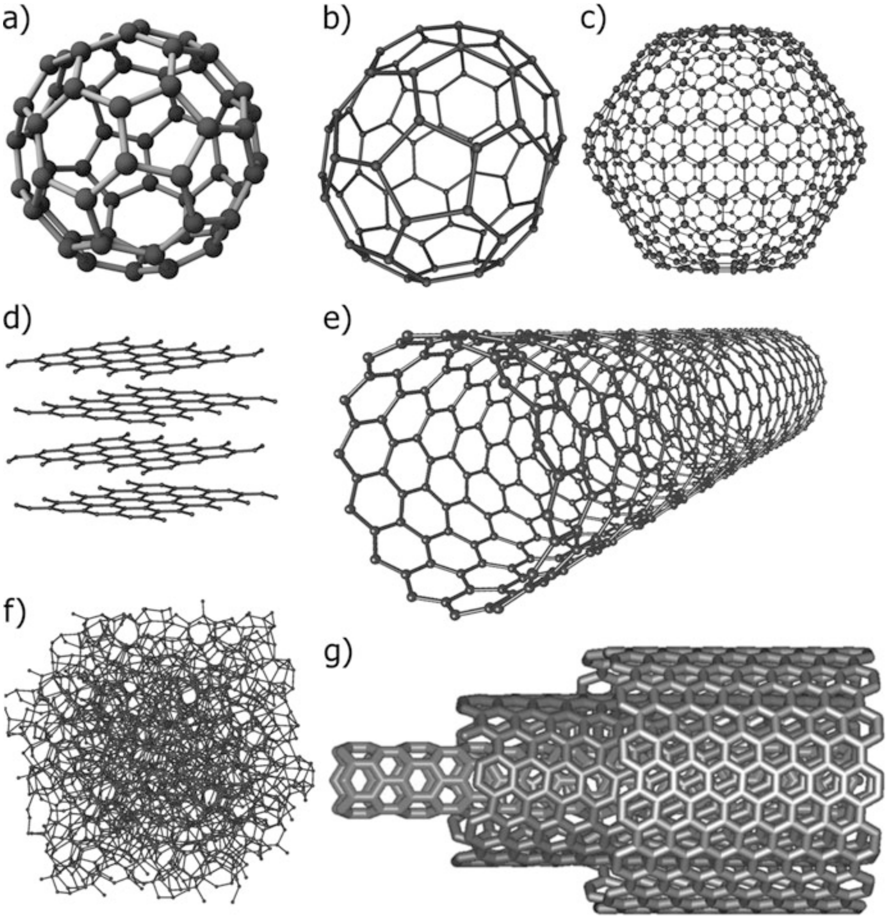


Fig. 3.10 Structure of various carbon allotropes in nanoform. (**a**) fullerene C60, (**b**) C70, (**c**) C540, (**d**) graphite, (**e**) single-walled carbon nanotube SWCNT, (**f**) amorphous carbon, (**g**) multi-walled carbon nanotubes. Image (**a**) courtesy of James Hedberg, images (**b**), (**c**), (**d**),(**e**), and (f) courtesy of Michael Ströck, (**g**) reproduced with permission from Balasubramanian and Burghard (2005), John Wiley and Sons

Various types of nanoparticles are currently synthesized for various applications. They range from metals, metal oxides (such as TiO_2 and ZnO), non-metals, such as carbon and silica. Figure 3.11 shows transmission electron microscope images of various anthropogenic nanoparticles: rattle-type Au/CdS nanostructures (Xia and Tang 2012), MWCNTs (Larue et al. 2012), silica nanoparticles (Nair et al. 2011), cobalt oxide nanoparticles, zinc oxide nanoparticles (Ghodake et al. 2011), ceria nanoparticles (Zhang et al. 2011), and rare earth oxides nanoparticles La_2O_3, Gd_2O_3, Yb_2O_3 (Ma et al. 2010).

Magnetic nanoparticles are being used extensively in various fields, ranging from medicine to water remediation. Examples of magnetic nanoparticles are Fe,

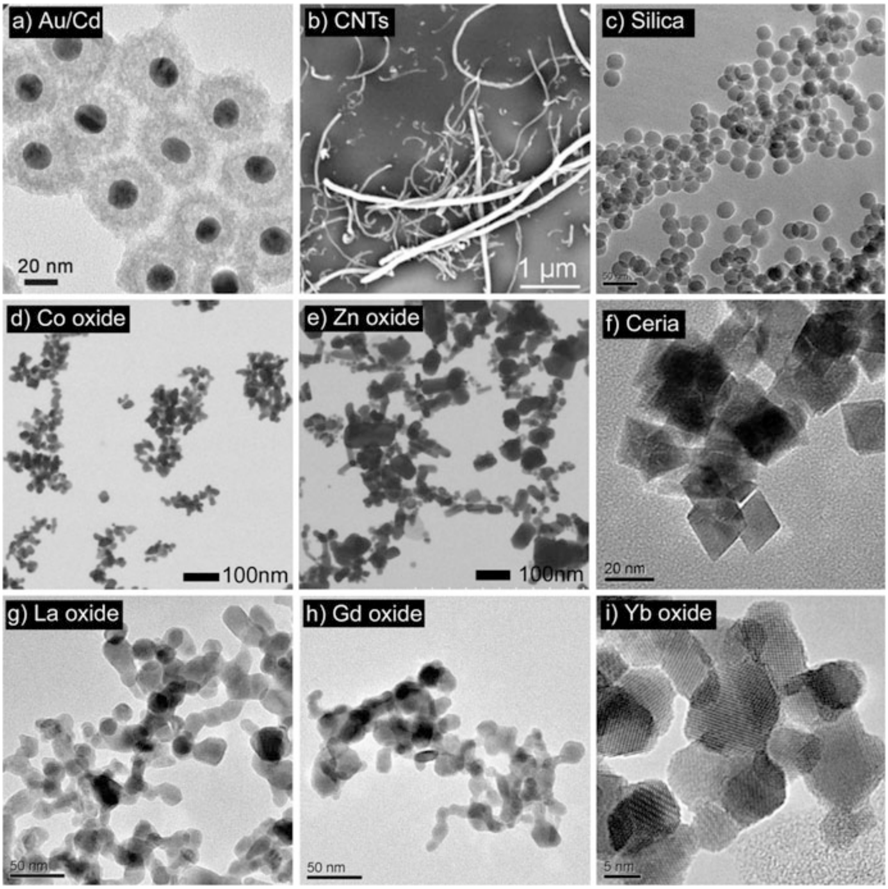


Fig. 3.11 TEM images of various anthropogenic nanoparticles. (**a**) Rattle-type Au/CdS nanostructures. Reprinted from reference (Xia and Tang 2012) with permission from John Wiley and Sons. (**b**) MWCNTs. Reprinted from Larue C. et al., Quantitative evaluation of multi-walled carbon nanotube uptake in wheat and rapeseed. Journal of Hazardous Materials, 227, 155–163, Copyright (2012), with permission from Elsevier (Larue et al. 2012). (**c**) Silica nanoparticles. Reprinted from Nair R. et al., Uptake of FITC Labeled Silica Nanoparticles and Quantum Dots by Rice Seedlings: Effects on Seed Germination and Their Potential as Biolabels for Plants. Journal of Fluorescence, 21, 2057–2068. Copyright (2011). With permission from Springer (Nair et al. 2011). (**d**) Cobalt oxide nanoparticles. (**e**) Zinc oxide nanoparticles. Images (**d**) and (**e**) are reprinted from Ghodake G. et al., Hazardous phytotoxic nature of cobalt and zinc oxide nanoparticles assessed using Allium cepa. Journal of Hazardous Materials, 186, 2011, 952–955, Copyright (2011), with permission from Elsevier (Ghodake et al. 2011). (**f**) Ceria nanoparticles. Reproduced from Zhang Z. Y. et al., Uptake and distribution of ceria nanoparticles in cucumber plants. Metallomics, 2011, 3, 816–822 with permission of The Royal Society of Chemistry (Zhang et al. 2011). (**g**) La_2O_3, (**h**) Gd_2O_3, (**i**) Yb_2O_3. Images (**g**), (**h**), and (**i**) are reprinted from Ma Y. et al., Effects of rare earth oxide nanoparticles on root elongation of plants. Chemosphere, 78, 273–279, Copyright (2010), with permission from Elsevier (Ma et al. 2010)

Co, Ni, Fe_3O_4, $CoFe_2O_4$, $HoMnO_3$, $MnFe_2O_4$, FePt (Kolhatkar et al. 2013; Chekli et al. 2016). Interesting to note that nanoparticles made of materials that are not magnetic in bulk form may acquire magnetic properties when in nanoform (Buzea et al. 2007). This is the case for nanoparticles with size of few nanometers made of Au, Pd (Hori et al. 1999), Pt (Sakamoto et al. 2011).

Quantum dots are a class of nanoparticles made of semiconductor nanocrystals with special optical properties, usually covered in a shell (silica). The role of the shell is to protect the core from oxidation and to mitigate the quantum dots toxicity. The core can be made of cadmium selenide CdSe, cadmium telluride CdTe, indium phosphide InP, or zinc selenide ZnSe (Farre et al. 2011).

Nowadays engineered nanoparticles are fabricated in industrial amounts. Each class of materials, such as SWCNTs exceed 1000 t per year (Klaine et al. 2008). Nanotechnology is one of the most rapidly growing fields of application. Given this, the entry of nanoparticles in the environment is unavoidable and its implication on the ecosystem health is becoming an increasing concern.

3.4.2 Pesticides and Fertilizers

A major way to introduce engineered nanoparticles in agricultural fields is the intentional use of nanoparticles as agrichemicals for crop protection and soil remediation (Deng et al. 2014). Agrichemicals encompass nanosystems that act as delivery devices for specific target tissues, pesticides additives that enhance solubility of active ingredients (Deng et al. 2014). Nanotechnology in the pesticide field comprise either very small particles of pesticides, nanocages, or small nanoparticles with pesticidal properties when in nanoform (Khot et al. 2012). Pesticides containing silver nanoparticles are used for their properties of supressing harmful organisms.

Nanoparticles with compositions of TiO_2, ZnO, Ag, Zn, Au are being developed for pesticide remediation due to their photocatalytic activity (Aragay et al. 2012; Gogos et al. 2012; Kah and Hofmann 2014). Other nanomaterials, such as Fe_3O_4, are being used for pollutant removal due to their magnetic properties (Aragay et al. 2012). Some research papers study the effects of carbon nanotubes and fullerenes on some pesticide uptake by agricultural plants (De La Torre-Roche et al. 2013).

The idea that nanomaterials can be applied in agriculture started to evolve about a decade or so ago, after the year 2000 (Gogos et al. 2012). There is an increasing number of research papers and patents involving nanomaterials for plant protection or fertilizers, as shown in Table 3.4 (Gogos et al. 2012; Aragay et al. 2012; Kah and Hofmann 2014; Servin et al. 2015). The composition of these nanomaterials is carbon-based (carbon nanotubes, liposomes, organic polymers), titanium dioxide, silver, silica, and alumina (Gogos et al. 2012). They serve as additives (for controlled release) and as active constituents.

Gogos et al. analyzed publications and patents of nanomaterials used for plant protection and fertilization (Gogos et al. 2012). They found that nanomaterials can be in the form of solid nanoparticles or nonsolid structures (lipid or polymer). As

Table 3.4 Nano-enabled products/patents in agriculture

Name of product/patent	Product type	Nanoparticle composition	Patent number	Inventors
Active nano-grade organic fine humic fertilizer and its production	Active organic Fertilizer	Nano-fermented active organic fertilizer	CN1472176-A	Wu (2002)
Application of hydroxide nano rare earth to produce fertilizer products	Fertilizer	Hydroxide of nano rare earth	CN1686955-A	Wang et al. (2007)
Application of oxide nano rare earth in fertilizer	Fertilizer	Nano rare earth	CN1686957-A	Wang et al. (2005)
Environment-friendly carbon-nano synergistic complex fertilizers	Fertilizer	Carbon nanomaterials	US 0174032-A1	Jian and Zhiming (2011)
Nano-composite superabsorbent containing fertilizer nutrients used in agriculture	Fertilizer	Nano-composite carbohydrate graft copolymer	US 0139347-A1	Barati (2010)
Nano-diatomite and Zeolite ceramic crystal powder	Fertilizer	Nano diatomite and zeolite	US 0115469 -A1	Yu (2005)
Nano-leucite for slow-releasing nitrogen fertilizer and Green environment	Fertilizer	Potassium aluminum silicate (Leucite) NPs occluded by calcium ammonium nitrates	US 0190226-A1	Farrukh and Naseem (2014)
Nano long-acting selenium fertilizer	Fertilizer	Nano-selenium	US 0326153-A1	Ying et al. (2012)
Nano-micron foam plastic mixed polymer fertilizer adhesive coating agent preparation method	Fertilizer	Nano-micron-foamed plastic organic compound mixed polymer	CN1631952-A	Zhang (2006a)
New method for preparation of controlled release special fertilizer comprises mixing and granulating Ximaxi clay minerals, coating with various fertilizers, trace elements, and additives	Fertilizer	Nano-clay	CN1349958-A	Li (2002)
Nonmetallic nano/microparticles coated with metal, process and applications	Fertilizer	Core of the nonmetallic nano/microparticles is selected from inorganic material such as silica and barium sulfate The metal coating is selected from Ag or	US 0047546-A1	Malshe and Malshe (2010)

(continued)

Table 3.4 (continued)

Name of product/patent	Product type	Nanoparticle composition	Patent number	Inventors
		transition/noble metals Cu, Ni, Ag, Pd, Os, Ru, Rh		
Process compromises combining soil repairing technique and nanobiological fertilizer to promote growth of microbes, improve soil, and remove residual herbicides	Biological Fertilizer	Nano-class biological fertilizer	CN1413963-A	Min (2003)
Production of novel precision customized control release fertilizers	Controlled release fertilizers	Transition metal silicates	US 8375629 B2	Prasad (2013)
Production technology of nano-clay–polyester mixed polymer fertilizer coating cementing agent	Controlled releasing fertilizer; soil improver	Nano-clay polyester mixed polymer	CN1414033-A	Zhang (2004b)
Production technology of coating cement for nanosulfonate lignin mixture fertilizer	Coating cement for Controlled release Fertilizer	Nano-sulfonated lignin mixture water solution	CN1417173-A	Zhang (2004a)
Preparation of nanometer-scale olefin/starch mixed polymer fertilizer covering agent	Slow release Fertilizer	Nano-level nonhomogeneous phase mixed polymer of hydroxyethylmethacrylate	CN1546543-A	Zhang (2006b)
Silicon nanocarrier for delivery of drug, pesticides, and herbicides, and for wastewater treatment	Pesticide	Nano-silicon carrier	US 0225412-A1	Sardari et al. (2013)
HeiQ AGS-20	Pesticide	Silver–silica composite material	US 0294919-A1 *Product available in the market	Jaynes et al. (2012)
Nano-Argentum 10	Fertilizer/antifungal/bug repellent	Silver	*Product available in the market	(Nano-Argentum)

Reproduced from Journal of Nanoparticle Research, A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield, Servin A. et al., 17, 2015. Copyright (2015). With permission of Springer (Servin et al. 2015)

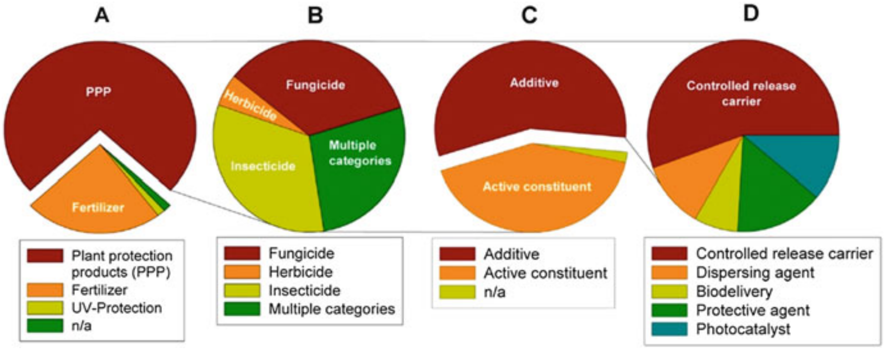


Fig. 3.12 Nanomaterials applications in agriculture (**a**), types of plant protection products—PPP containing nanoparticles, (**b**), general functions of nanomaterials in PPP (**c**), and tasks of nanomaterials additives in PPP (**d**). Reprinted with permission from Gogos A. et al., Nanomaterials in Plant Protection and Fertilization: Current State, Foreseen Applications, and Research Priorities. Journal of Agricultural and Food Chemistry, 2012, 60, 9781–9792. Copyright (2012) American Chemical Society (Gogos et al. 2012)

seen in (Fig. 3.12a), plant protection products were the topic of 74 % of all papers, with the rest on fertilizers and UV protection. 35 % of the plant protection products were used as fungicides, 33 % as insecticides, and 27 % had multiple function (Fig. 3.12b). Nanomaterials were the active component in 41 % of the plant protection products, and additives in 57 %, acting as controlled release carriers (Fig. 3.12c, d).

Another suggested application of nanoparticles in agriculture that is still in the developmental stages is for genetically modified crops with nanoparticles acting as vectors for DNA (Kah et al. 2013). The increase interest for the utilization of nanoparticles in agriculture should be addressed by regulatory bodies in order to control their use as nanopesticides or fertilizers (Kookana et al. 2014). A large number of patents involving nanoparticles have been already filed in agriculture and food industry and many research papers explore the use of nanoparticles for improved seed germination and crop yield. For example, carbon nanotubes are researched for improving the germination of some seeds (Alexandru et al. 2012). However, note should be made that multiple studies have proved that carbon nanotubes are quite toxic to humans and animals. Thus, the true benefit of carbon nanotubes in agriculture seems quite controversial and perhaps dangerous.

In the future, it is reasonable to speculate that the unregulated use of engineered nanoparticles in agriculture and food industry may pose a threat to food safety and health of unawares consumers. The accumulation of nanoparticles in soils and groundwater may potentially lead to accumulation of nanoparticles in plants. The long term effects of nanoparticle accumulation in plants is still largely unknown, but as research suggest, they may undergo morphological, physiological, genetic, and epigenetic changes that may alter plant growth and nutritional status. The introduction of engineered nanoparticles in the food chain from plants grown in contaminated soils may have serious repercussion upon the health of animals and humans.

3.4.3 Water and Soil Remediation

Nanoparticles are prospected for pollution remediation, water treatment and purification due to their high surface area, high adsorption capacity and unique structure and electronic properties (Gupta and Saleh 2013). They are able to remove organic and inorganic contaminants. Several types of materials are used for their adsorption of pollutants: metal-containing particles, carbon nanotubes, fullerenes, and zeolites (Gupta and Saleh 2013).

The magnetism of some nanoparticles makes them unique agents for water treatment (Xu et al. 2012). Adsorption processes together with magnetic separation makes some magnetic nanoparticles extensively used in water treatment and environmental cleanup. Most commonly used in soil remediation is nano-zero-valent iron due to its high reactivity (high surface area) and its ability to detoxify a wide range of contaminants, such as chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls (Deng et al. 2014).

The composition of nanoparticles used as heavy metals pollutant adsorbents include Fe_2O_3, Fe_3O_4, SiO_2, and Al_2O_3 (Bakshi et al. 2015). Nanoparticles of Fe and Al oxides or oxyhydroxides can be useful in the removal of As from water (Bakshi et al. 2015).

Recently, carbon nanomaterials, like carbon nanotubes and fullerene, are being broadly used for advanced treatment of wastewaters and are being researched as promising adsorbents for water treatment (Gupta and Saleh 2013). There is ongoing research regarding CNTs adsorbent properties against organic compounds such as pesticides, polycyclic aromatic hydrocarbons (PAHs), antibiotics, herbicides. They are also able to adsorb metal ions (Cu, Ni, Co, V, Ag, Cd and rare earth elements).

3.4.4 Incomplete Combustion

Accidental release of anthropogenic nanoparticles near urban areas is a result of traffic (such as exhaust emission due to incomplete combustion, road surface abrasion, brake and tire wear), industrial activities (incomplete combustion emissions from power plants, oil refineries, dust from mining), building (dust from excavations and demolitions) and from housing (incomplete combustion particles from heating and cooking) (Buzea et al. 2007). The anthropogenic particles in rural areas are mainly from biomass burning and various farming activities.

Nanoparticles generated via incomplete combustion of vehicle fuel are a large source of pollutants. In addition to the inherent release of nanoparticles due to incomplete burning of the fuel, nanocerium nanoparticles are being used as fuel additives to improve fuel efficiency and to reduce emissions of fine particulate matter, carbon monoxide, nitrogen oxides, and hydrocarbon species (Erdakos et al. 2014). The concentrations of cerium oxide is estimated to be between 0.32 and 1.12 μg/g at a distance of 26 m from the edge of highway, and 0.28–0.98 μg/g for a distance of 96 m from the highway (Park et al. 2008).

Nanoparticles synthesized by incomplete combustion are also used in different products (Heiligtag and Niederberger 2013). For example, carbon black, produced by the incomplete combustion of natural gas, is produced worldwide in huge amounts (10 million metric tons) and it is used as rubber reinforcement in car tires (Heiligtag and Niederberger 2013).

3.4.5 Particles in the Environment and their Long Range Transport

In environmental sciences particles are labeled as a function of their size. For example, particulate matter with components having diameters less than 0.1 μm (100 nm) is labeled $PM_{0.1}$ (often called ultra-fine particles) and results mainly from combustion processes. PM_{10} is particulate matter having a diameter smaller than 10 μm while $PM_{2.5}$ has size smaller than 2.5 μm. PM_{10} and $PM_{2.5}$ are mainly aggregates of ultra-fine particles and larger particles mostly mechanically generated (Buzea et al. 2007).

The particulate air matter may change its properties and chemical composition during its transport and aging. Its lifetime in the atmosphere can range from hours to weeks (Sielicki et al. 2011). The particulate matter in the atmosphere varies in amount and composition depending on its geographical location (Sielicki et al. 2011). The anthropogenic contribution to particulate matter is considerable, especially in highly populated areas of the globe. For example, in Netherlands between 70 and 95 % of particulate matter, with agriculture, transportation, and industry being the major sources of pollution (Hendriks et al. 2013).

Anthropogenic nanoparticles generation has an important effect not only locally, but also globally. They can be transported over large distances. For example, measurements of the dustfall in the high snowfields of the Caucasus is correlated to the European and Soviet industrialization, with little variation from 1790 to 1930, followed by an enormous 19-fold increase from 1930 to 1963 and a leveling off during World War II (Murr et al. 2004).

Due to their adverse effect on human health, particulate matter aerosols are monitored around the world. In order to protect human health, maximum thresholds standards are set by governments around the world for the fraction of particles with aerodynamic diameter smaller than 2.5 μm (Calvo et al. 2013). For example, in Europe a maximum threshold value of 20 $\mu g/m^3$ must be attained by 2020.

3.4.6 Nano-Waste

Many human activities generate nano-waste, such as research and development or various industries (Yadav et al. 2014). Nano-waste can also enter the environment from the disposal of consumer products that contain nanomaterials discarded via municipal or industrial waste treatment plants. Nanoparticles from waste water are not efficiently removed in water treatment plants, therefore they can enter the environment (Yadav et al. 2014; Aziz et al. 2015; Brar et al. 2010). The sludge from the waste water treatment plants is an important exposure source of engineered nanomaterials (Cornelis et al. 2014).

A study that model the flows of nanoparticles in the recycling system in Switzerland showed that occupational exposure, release of nanoparticles in landfills and incineration plants are the most important factors to be considered in the risk assessment (Caballero-Guzman et al. 2015).

Atmospheric nanoparticles can enter the water reservoir and the soil. Drinking water treatment does not remove entirely nanoparticles from the water. A study reported that only 2–20 %, 3–8 %, and 48–99 % of Ag, TiO_2, and ZnO nanoparticles are removed by a conventional drinking water treatment (Chalew et al. 2013). Therefore, a large amount of nanoparticles are still detectable in finished water.

3.4.7 Nanoparticles in the Construction Industry

Nanoparticles are also used in the construction industry (Pacheco-Blandino et al. 2012). Nanoparticles can be incorporated as nanocomposites in concrete. Silica, alumina, and zinc oxide nanoparticles nanocomposites in concrete confer it increased strength, water penetration and accelerated hydration. Titanium dioxide nanoparticles is used in concrete for their self-cleaning, antimicrobial, and pollution remediation properties. The incorporation of carbon nanotubes in concrete, polymers, or glass may result in a nanocomposite with improved properties, such as self-sensing, electromagnetic field shielding, and increased strength. Iron oxide nanoparticles incorporated in construction materials can offer self-sensing capabilities as well. Coating with different nanoparticles can greatly improve the properties of the covered material (Pacheco-Blandino et al. 2012). For example, photocatalytic TiO_2 and ZnO nanoparticles are used for pollution remediation, for their antifog, anticorrosion, and antimicrobial properties. Cu and Zn nanoparticles in coatings are anticorrosive, while Ag, Cu nanoparticles are antimicrobial. Silica nanoparticle coatings are scratch resistant, fireproof, and antireflective, while W_2O_3 can be used in coatings to adjust light transmittance (Pacheco-Blandino et al. 2012).

3.4.8 Nanoparticles in the Food Industry

Nanotechnology is becoming widely used in the food industry (Dasgupta et al. 2015). The use of nanotechnology in foods and dietary supplements encompasses food additives, food contact materials, and encapsulation (Prasad et al. 2014).

Nanoparticles of Ag, ZnO, TiO_2 are used as antimicrobial coating for refrigerators, storage containers, equipment for food processing (Rossi et al. 2014; Chellaram et al. 2014).

Smart packaging incorporates sensors that inform on the existence of specific chemicals and mitigate their effects, and can give information on the product shelf life. The smart packaging industry is about 80 % composed of oxygen, pathogen scavengers, moisture absorbers and barrier packing product (Chellaram et al. 2014).

Active food packaging serves as a passive barrier and also as active components via a desirable direct interaction with the food (antimicrobial or antioxidative agent) (Dasgupta et al. 2015). Food packaging with nano-coatings improve barrier properties. Food packaging uses mostly nanoparticles of clay or silver. Fewer products use silicon dioxide and titanium dioxide (Bouwmeester et al. 2014). Some nanoparticles are added to the matrix to confer antimicrobial activity or preservation via oxygen absorption. Nanoclays are used in polymers to improve barrier protection and preserve food by maintaining it in a low oxygen environment in order to inhibiting microbial growth (Chellaram et al. 2014).

Antibacterial nanoparticles are incorporated in food packaging which may extend food shelf life (Chellaram et al. 2014). For example the incorporation of silver or titania nanoparticles into food packaging serves as antimicrobial. The sunlight initiates photocatalysis of titania nanoparticle which promotes peroxidation of cell membrane phospholipids of bacteria (Dasgupta et al. 2015). Titania nanoparticles incorporated into food packaging can also act as O_2 scavengers, reducing food browning and rancid flavors. Silver is one of the most used nanomaterial in food industry and packaging. Silver can be used in refrigerators and food storage boxes due to its antibacterial properties. Nanoparticles can migrate from food packaging coatings into food, such as the case of Ag nanoparticles into food samples that were stored in contact with nano-silver coated surfaces (Metak et al. 2015).

Nanocomposites containing polymer incorporated nanoparticles are used to improve the strength of materials, durability, and biodegradation.

Some nanoparticles used as food additives have been available in products on the market for a long period of time, such as silicon dioxide SiO_2—E551, titanium dioxide TiO_2—E171, and Ag—E174, and are permitted as food additive without a definition of the particle size (Rossi et al. 2014; Bouwmeester et al. 2014; Lim et al. 2015; Wang et al. 2013). Silver nanoparticles can be used as food colorant (Wang et al. 2013). The anatase crystalline phase of titanium dioxide is mostly used as whitening agent and for texture (Wang et al. 2013). Silica is utilized in the

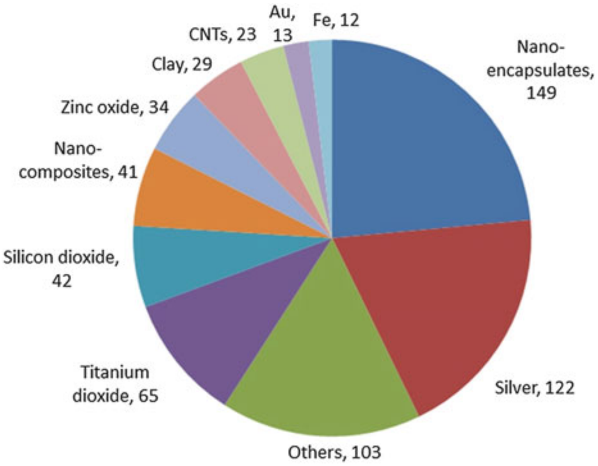


Fig. 3.13 Overview of the inventory of currently used and foreseen applications of nanomaterials in agriculture and food/feed production, including the number of records. Adapted from Aschberger et al. (2015). doi:10.1088/1742-6596/617/1/012032

production process of beer and wine, as a clearing, anticaking, and anti-clumping agent (Wang et al. 2013; Dekkers et al. 2011; Lim et al. 2015).

Other metals in nano-form marketed as food or health supplements are selenium, calcium, iron, copper, gold, platinum, silver, molybdenum, palladium, titanium, and zinc (Bouwmeester et al. 2014).

European Food Safety Authority (EFSA) commissioned an inventory of currently used and reasonably foreseen applications of NM in agriculture and food/feed production, published in 2015 (Aschberger et al. 2015). The majority of applications of nanotechnology are used in food (about 90 %), mostly as food additives and food contact materials. About 9 % are used in agriculture and 3 % in feed. The report found 55 types of inorganic and organic nanomaterials, of which the most used are nano-encapsulates, silver and titanium dioxide. This information is depicted in Fig. 3.13 (Aschberger et al. 2015).

Table 3.5 shows examples of nanomaterials and nanoparticles used in food, food additives and food packaging (Blasco and Pico 2011; Pico and Blasco 2012). Studies had shown that nanoparticles are in general toxic to humans and they are associated with a multitude of diseases (Buzea et al. 2007), therefore food contamination with nanoparticles or the environmental pollution via inadvertent release of nanoparticles from food packaging is highly undesirable.

3.4.9 Cosmetics

Nanoparticles have been used in cosmetics since ancient times, as powders or hair-dyes. Currently several types of nanoparticles are incorporated in cosmetics due to

Table 3.5 Nanomaterials and nanoparticles used in food, food additives, and food packaging

Product name	Manufacturer	Nanomaterial	Claim
Food packaging materials			
Durethan KU 2-2601	Bayer	Silica in a polymer-based nanocomposite	Nanoparticles of silica in the plastic prevent the penetration of oxygen and gas of the wrapping, extending the product shelf life
Hite brewery beers: three-layer, 1.6 L beer bottle	Honeywell	Honeywells Aegis OX nylon-based nanocomposite	Oxygen and carbon dioxide barrier, Clarity, Recyclability, Ease of Perform, Processability, Flavor/odor/aroma barrier, Structural integrity, Delamination resistance
Millar beers: Lite Genuine draft Ice house	Nanocor	Imperm nylon/nanocomposite barrier technology produced by Nanocor	Imperm is a plastic imbedded with clay nanoparticles that makes bottles less likely to shatter and increases shelf life to up to 6 months
Nano plastic wrap	Songsing Nanotechnology	Nano zinc light catalyst	Biodegradable after use, Compostable to European standards EN13432, Made from renewable and sustainable resources (non-GM corn starch), Water dispersible, will not pollute local groundwater systems or waterways, In use since 2002
Constantia multifilm N-COAT	Constantia Multifilm	Nanocomposite polymer	A clear laminate with outstanding gas-barrier proprieties developed primarily for the nuts, dry food, and snack markets
DuPont light stabilizer 210	Du Pont	Nano TiO_2	UV-protected plastic food packaging
Adhesive form MacDonalds burger containers	Ecosynthetix	50–150 nm starch nanospheres	The adhesive requires less water as well as less time and energy to dry
Food additives AdNano	Evonik (Degussa)	Nano ZnO (food grade)	
Aerosil, Sipernat	Evonik (Degussa)	Silica (food grade)	Free flow add for powdered ingredients in the food industry
AquaNovaNovaSol	AquaNova	Product micelle (capsule) of lipophilic, water-insoluble substances	An optimum carrier system of hydrophobic substances for a higher and faster intestinal and dermal

(continued)

Table 3.5 (continued)

Product name	Manufacturer	Nanomaterial	Claim
			resorption and penetration of active ingredients
Bioral Omega-3 nanocochleates	BioDelivery Sciences International	Nano-cochleates as small as 50 nm	Effective means for the addition of omega-3 fatty acids for use in cake, muffins, pasta, noodles, soup, cookies, cereals, chips, and candy bars
NanoCoQ10	Pharmanex	Nano coQ10	Nanotechnology to deliver highly bioavailable coenzyme Q10, making it up to 10 times more bioavailable than other forms of CoQ10
Nano self-assembled, structured liquids	Nutralease	Nanomicelles for encapsulation of nutraceuticals	Improved bioavailability means nutraceuticals are released into membrane between the digestive system and the blood
Solu E 200 BASF	BASF	Vitamin E nanosolution using NovaSOl	Solubilization of fat-soluble vitamins
Synthetic Lycopene	BASF	LycoVit 10 % (<200 nm synthetic lycopene)	
Food and beverages			
Nano tea	Shenzen Become Industry & Trading Co	Nanoparticles (160 nm)	Patent No.: 0100033.3—Three-step preparation method and its application for nanotea. Patent No.:02100314.9/ 00244295.7—Multi-layer, swinging nano-ball milling procedures
Nano slim	Nano Slim	Nano-diffuse Technology	Orosolic acid (derived from the *Lagerstroemia speciosa* plant)
Nanoceuticals slim shake chocolate and vanilla	RBC Lifescience	Nanodusters	
Fortified fruit juice	High Vive.com	300 nm iron (SunActive Fe)	
Daily Vitamin Boost	Jamba Juice Hawaii	300 nm iron (SunActive Fe)	22 essential vitamins and minerals and 100 %, or more of your daily needs of 18 of them!
Oat chocolate nutritional drink mix and	Toddler Health	300 nm iron (SunActive Fe)	Toddler health is an all-natural balanced nutritional drink for children

(continued)

Table 3.5 (continued)

Product name	Manufacturer	Nanomaterial	Claim
oat vanilla nutritional drink mix			from 13 months to 5 years. One serving of Toddler Health helps little ones meet their daily requirements for vitamins, minerals, and protein
Canola active oil	Shemen	Nano-sized self-assembled structured liquid micelles	
Maternal water	La posta del Aguila	Nanoparticle colloidal silver ions	Especially for the baby and the mother in pregnancy period, the mineral water is without chemical treatments, by using technology nanoparticle colloidal silver ions

Reprinted from Blasco C and Pico Y, 2011, Determining nanomaterials in food, Trends in Analytical Chemistry, 30, 84–99, Copyright (2011), with permission from Elsevier (Blasco and Pico 2011). The data from the last row in the table is taken from Pico and Blasco (2012)

their special properties (Borowska and Brzoska 2015). For example, Ag and Au nanoparticles are used in face and body care products, while Cu-Silica nanoparticles are used in deodorants due to their antibacterial properties. Alumina nanoparticles are incorporated in mineral foundations and concealers due to their properties of diffusing light. Many sunscreens contain titanium dioxide and zinc oxide due to their properties of UV filtering.

3.4.10 Engineered Nanoparticles Applications and Environmental Accumulation

While there is an increasing number of products containing nanoparticles on the market, the assessment of risk posed by nanomaterials and related legislations that should limit the use of toxic nanoparticles in products are in lagging behind. Many consumer products contain nanoparticles that will most likely enter the environment after improper recycling and disposal of consumer products. The buildup of engineered nanoparticles in the environment may affect soil-based food crop quality and yield. The effect of nanoparticle on edible plants is very important because of their uptake by plants. Once nanoparticles entered the food chain, they may potentially affect the health of humans and animals in ways that we cannot predict empirically.

Table 3.6 Engineered nanoparticles, their common applications, and possible environmental accumulation

Type of nanoparticle	Applications	Environmental accumulation			
		Soil	Water	Waste	Air
Carbon black	Additives to tyres, rubber, paints	+	+	+	+
CNTs	Electronics, sensors, conductive coatings, supercapacitors, catalysts, battery, fuel cell electrodes, additives to tyres, lubricants, plastics, water purification systems, orthopedic implants, adhesives and composites, sporting goods, components in aircrafts, aerospace, automotive industry, adsorption of contaminants	+	+	+	+
Fullerenes	Cosmetics, sorption of organic compounds (e.g., naphthalene), for the removal of organometallic compounds, in medicine	+	+	+	–
Fe and its oxides	Cosmetics and personal care products, environmental remediation of water, sediments, and soils, bioremediation for some pesticides and herbicides, concrete additives, biochemical assays, bio-manipulation	+	+	+	+
Ag	Antimicrobial agent in various products: toothpastes, baby-products, wound dressings, socks, and other textiles, in air filters, air conditioning, vacuum cleaners, and washing machines, paints, coatings, food packaging, plastics, varnish	+	+	+	+
Au	In tumor therapy, catalyst, flexible conducting inks or films	+	+	+	–
TiO_2	In cosmetics, skin care products, sunscreen lotions, solar cells, paints and coatings, environmental remediation, for the removal of various organics	+	+	+	–
ZnO	In cosmetics and skin care products, sunscreens, in bottle coatings, paints	+	+	+	–
CeO_2	Fuel catalyst, gas sensors, solar cells, oxygen pumps In lubricants and fuel additives In metallurgical and glass/ceramic applications	+	+	+	+
Pt, Pd	Catalysts, lubricants and fuel additives, automotive exhaust converters	+	+	+	+
Sn	Paints	+	+	+	–
Al and Al_2O_3	Metallic coatings and plating, batteries, grinding, fire protection, metal and biosorbent, flame retardant paints	+	+	+	+
Cu	Microelectronics, environmental remediation	–	–	+	–
Se	Nutraceuticals, health supplements	+	+	+	–
Ca	Nutraceuticals, health supplements	+	+	+	–
Mg	Nutraceuticals, health supplements	+	+	+	–

(continued)

Table 3.6 (continued)

Type of nanoparticle	Applications	Environmental accumulation			
		Soil	Water	Waste	Air
MoS_3	Catalyst, lubricants and fuel additives	+	+	+	+
QD	Medical imaging and targeted therapeutics, solar cells, photovoltaic cells, security inks, photonics, telecommunications	+	+	+	–
SiO_2	In porous form as a carrier (agrochemicals) Fireproof glass, UV-protection, flame retardant paints, coatings, varnish, ceramics, electronics, pharmaceutical products, dentistry, polishing	+	+	+	+

Data adapted from references: (1) Bhatt I and Tripathi B. N., 2011, Interaction of engineered nanoparticles with various components of the environment and possible strategies for their risk assessment. Chemosphere, 82, 308–317, Copyright (2011), with permission from Elsevier (Bhatt and Tripathi 2011), (2) Boxall et al. (2007), (3) Brar et al. (2010), (4) Gladkova and Terekhova (2013), (5) Gottschalk et al. (2015), (6) Hincapie et al. (2015), (7) Khin et al. (2012), (8) Tang and Lo (2013), (9) Bystrzejewska-Piotrowska et al. (2009)

Table 3.6 shows some of the most used engineered nanoparticles, their applications and possible environmental accumulation in soil, water, waste, and air (Bhatt and Tripathi 2011; Boxall et al. 2007; Brar et al. 2010; Gladkova and Terekhova 2013; Gottschalk et al. 2015; Hincapie et al. 2015; Khin et al. 2012; Tang and Lo 2013; Bystrzejewska-Piotrowska et al. 2009). The interaction, transport, and ecotoxicology of nanoparticles are dynamically altered by abiotic factors (pH, salinity, water hardness, temperature) (Handy et al. 2008b).

3.5 Nanoparticle Relative Toxicity Index on Humans and Animals

There are already various studies on the effects of nanoparticles on plants, with most of them reporting detrimental effects, and a minority showing some beneficial effects. While some plants exhibit benefits from a type of nanoparticle, other plants are negatively impacted by the same nanoparticles. Moreover, many nanoparticles are found to be extremely toxic to humans and animals and even though they might show some minor benefits for the growth of some plants, they may lead to detrimental effects if these plants containing nanoparticles were to be ingested by humans or animals. For example, Ag nanoparticles that are starting to be used increasingly in agriculture have a toxicity index higher than those of asbestos in animal cells, as shown in Table 3.7 (Soto et al. 2005). Also, carbon nanotubes, which have similar morphologies and sizes with asbestos, as shown in Fig. 3.14

Table 3.7 The relative toxicity index (RCI) on murine macrophage cells of nanoparticles varies with composition, their particle and mean aggregate size

Material	Mean aggregate size (μm)	Mean particle size (nm)	RCI (at 5 μg/ml)	RCI (at 10 μg/ml)
Ag	1	30	1.5	0.8
Ag	0.4	30	1.8	0.1
Al_2O_3	0.7	50	0.7	0.4
Fe_2O_3	0.7	50	0.9	0.1
ZrO_2	0.7	20	0.7	0.6
TiO_2 rutile	1	Short fibers 5–15 nm diam	0.3	0.05
TiO_2 anatase	2.5	20	0.4	0.1
Si_3N_4	1	60	0.4	0.06
Asbestos Chrysotile	7	Fibers 20 nm diam. Up to 500 aspect ratio	1	1
Carbon black	0.5	20	0.8	0.6
SWCNT	10	100 nm diam.	1.1	0.9
MWCNT	2	15 nm diam.	0.9	0.8

Adapted with permission from Soto K. F. et al., 2005, Comparative in vitro cytotoxicity assessment of some manufactured nanoparticulate materials characterized by transmission electron microscopy, Journal of Nanoparticle Research, 7, 145–169. Copyright (2005) Springer (Soto et al. 2005)

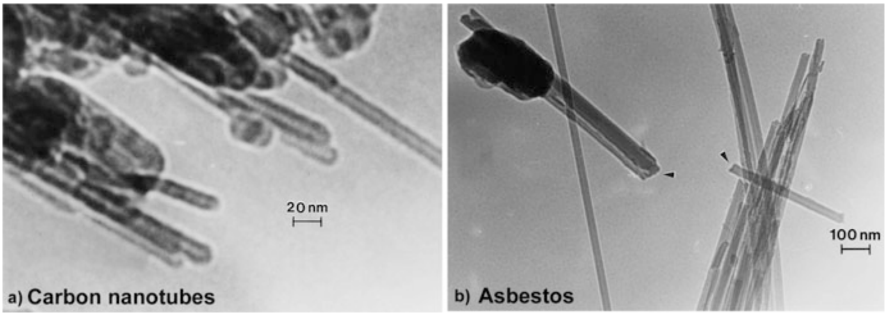


Fig. 3.14 TEM bright-field images of (**a**) carbon nanotube aggregates extracted from a natural gas flame exhaust, (**b**) chrysotile asbestos fibers. Reproduced from Murr L. E. & Soto K. F., TEM comparison of chrysotile (asbestos) nanotubes and carbon nanotubes. Journal of Materials Science, 2004, 39, 4941–4947. Copyright (2004). With permission from Springer (Murr and Soto 2004)

(Murr and Soto 2004), have similar toxicities in animal cells (Soto et al. 2005). For a comprehensive review of nanoparticles toxicity on humans see reference Buzea et al. (2007).

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