Environmental Impacts of Nanomaterials

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Abstract

Nanotechnology is currently one of the highest priority research fields in many countries due to its immense potentiality and economic impact. Nanotechnology involves the research, development, production, and processing of structures and materials on a nanometer scale in various fields of science, technology, health care, industries, and agriculture, and have contributed to the gradual restructuring of many present technologies. However, due to the uncertainties and irregularities in shape, size, and chemical compositions, the presence of certain nanomaterials may have adverse effect on the environment as well as human health. Concerns have thus been raised about the destiny, transport, and transformation of nanoparticles released into the environment. A critical evaluation of the current states of knowledge regarding the exposure and effects of nanomaterials on the environment and human health is discussed in this review. Recognizing the potential advantages and unintended dangers to the environment and human health are critically important for the future development and use of nanomaterials.

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1. Introduction

Nanomaterials (NMs) contain at least one structural dimension at the nanoscale (one nanometer is a billionth of a meter or 10^{-9} of a meter) and have attracted intense research interest due to their application potential in various fields of science and technology (OECD, 2014). As the characteristic structures of NMs are between single atoms and bulk materials, NMs generally exhibit unique and significantly improved but sometimes unpredictable physical, chemical, and biological properties different from their bulk materials (nano.DE-Report, 2013). Today's scientists are able to produce materials at the nanoscale such as nanoclays, nanofibers, carbon nanotubes, and graphene with lighter, stronger, and more expanded control on light spectrum as well as more prominent chemical reactivity (Khan et al., 2017).

Despite such progress in NMs technology, information regarding the possible effects of NMs on the human health is yet insufficient. As NMs may not be detectable after discharge into the environment, they can cause various types of environmental problems if remediation is not achieved. Therefore, additional study is required to systematically explain the structure-function relationships of NMs with respect to their chemistry fundamentals (e.g., functionality and toxicity). Moreover, full hazard appraisals should be performed on NMs that present a genuine exposure danger during manufacture or use. Hence, green nanoscience has been proposed to lessen conceivable environmental and human health hazards from the creation and utilization of NMs and to advance supplanting existing items with new nano-products that are more ecologically benevolent (Iavicoli et al., 2014). For applications of nanotechnology in various fields, a number of concerns remain including uncertain ecological impacts, environmental soundness, fouling properties, low detection limits, high expenses, regeneration, and environmental deposition. In this review, we outline the adverse effects of NMs on the human health as well as environment. Such efforts may be helpful for proper expansion of applications and research interest toward further development of nanotechnology.

2. Types and Properties of NMs

Structures with a dimension of 1 to100 nanometers are considered NMs (Guisbiers et al., 2012). Because of the big surface area-to-volume ratio and probable occurrence of quantum effects, NMs behave quite differently than their bulk counterparts (Ding et al., 2016). According to the European Commission, a NM is defined as a "natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 to 100 nm" (European Commission, 2016). Although there are already numerous kinds of NMs, it is expected that a variety of new forms will appear in the future. However, based on their construction, NMs are currently classified as (i) carbon-based, (ii) metal-based, (iii) dendrimers, and (iv) composites (Saleh, 2016).

Carbon-based NMs have gained extra attention in the scientific and engineering community because of their unique and exceptional physical, chemical, optical, mechanical, and thermal properties (Cha et al., 2013). Carbon-based NMs commonly take the shape of nano-particles, hollow spheres, ellipsoids, sheets, or tubes. Carbon nanotubes (cylindrical shape) are usually synthesized by arc discharge or chemical vapor deposition of graphite (Saleh, 2016). Carbon nanotubes are considered the most robust and stiffest materials as far as rigidity and flexible modulus are concerned (Kim et al., 2017). The chain of unbroken covalent carbon-carbon bonds makes them exceptionally strong materials (Kim et al., 2017). Graphene is a one atom-thick carbon layer arranged in a two-dimensional hexagonal lattice with excellent heat and electric conductivity along with optical transparency in the infrared and visible range (Edwards and Coleman, 2013). Moreover, because of graphene's robust yet highly flexible property with the capacity of binding other elements (e.g., gases and metals), it is a highly attractive option for various applications (Kulkarni, 2015). Various structures of carbon-based NMs are shown in Figure 1.

Metal-based NMs include quantum dots, nanogold, nanosilver, and nanometallic oxides (e.g., titanium dioxide, zinc oxide, and iron oxide) (Tourinho et al., 2012). Quantum dots are fluorescent semiconductors ranging from 2 to 10 nm (Libralato et al., 2017). Quantum dots are characterized by a broad absorption spectrum and intense narrow emission spectra in direct relation to their size (Libralato et al., 2017). Dendrimers are man-sized symmetric molecules with mono-dispersed structure consisting of tree-like branches built accross a molecule or a linear polymer core (Abbasi et al., 2014). The surface of a dendrimer has many chain ends and may experience changes in size, shape, and adaptability to another element (Mendes et al., 2017). Furthermore, three-dimensional dendrimers contain inside cavities into which different particles can be set for different applications in both biological and materials sciences (Mendes et al., 2017). The properties of composite NMs can be designed according to their application or requirement and are dependent on the choice of matrix, curing phase, shape, and orientation (Sahay et al., 2014).

Nanomaterials can also be classified based on their dimensionality: (i) zero-dimension (0D), (ii) one-dimension (1D), (iii) two-dimensions (2D), and (iv) three-dimensions (3D) NMs (Figure 2) (Tiwari et al., 2012). The majority of nano-particles are 0D NMs, which include NMs with all dimensions within the range of 1 to100 nm.1D NMs are needle or rod like-shaped with a length from 100 nm to 10 μm and include nanotubes, nanorods, and nanowires (Tiwari and Kim, 2011). 2D NMs display plate-like shapes including nanocoatings, nanofilms, and nanolayers (Tiwari and Kim, 2011). 0D, 1D, and 2D NMs can be used on a substrate or they can be distributed in fluid or solid matrixes.3D NMs can have three arbitrary dimensions and possess multilayer nano-crystalline structure (Tiwari et al., 2012). These NMs may consist of bulk powders, nanowire bundles, multi-nanolayers, dispersions of nanoparticles, and nanotubes.

3. Fate and Behavior of Nanoparticles in the Environment

The destiny of NMs in the environment is controlled by the combined effects of their physicochemical properties, and their interactions with other pollutants (Maiti et al., 2016). Nanomaterials found in the environment can come either from various natural activities (e.g., volcanic activities, forest fires, soil erosion, weathering, clay minerals, and dust storms) or from intentional/unintentional anthropogenic activities (e.g., burning fossil fuels, mining/demolition, automobile traffic, and NMs production and waste stream) (Figure 3) (Smita et al., 2012). After NMs are discharged into the environment, they accumulate in different environmental matrices, for example, air, water, soil, and sediments (Iavicoli et al., 2014). In this section, we discuss the fate of engineered nanomaterials (ENMs) in different environmental matrices. Table S1 lists different emission sources of ENMs in the environment and their respective applications.

3.1 Air

There are still large knowledge gaps with respect to NMs' environmental fate, especially after release into the air. Each step of an ENMs life cycle from generation, processing, transportation, handling, and application to end-of-life may prompt discharge into ambient air (Caballero-Guzman and Nowack, 2016). Atmospheric NMs are produced through road traffic exhaust, combustion, explosion, and oxidation of atmospheric gases (John et al., 2017).

Engineered nanomaterials exhausted into the atmospheric environment tend to be exposed to sunlight and UV wavelengths at significantly higher degrees than those released into other compartments

(Mitrano et al., 2015). This exposure is likely to increase the possible outcomes of photochemical changes to NMs. Nanomaterials can experience several transformations in the atmosphere such as condensation of low volatility compounds or decrease in the size through dissipation of adsorbed water or other volatiles. As such, particle size distributions can deviate without altering overall numeral concentrations (Soni et al., 2015). Moreover, the deposition of NMs from air relies upon gravitational settling velocities, which correspond to molecule size (Hartmann et al., 2014).

Emission of ENMs from waste incineration plants is greatly dependent on composition (Ounoughene et al., 2015). Carbonaceous and organic ENMs tend to burn out completely, while nanoclays appear to remain in combustion residues (Ounoughene et al., 2015). However, in many applications including cleaning, packing, sonication, mixing, and spraying, ENMs are released not at the nanoscale but in large aggregates (around 1 μm) (Ding et al., 2016). Furthermore, high volumes and concentrations of NMs may be released into air by accident (e.g., explosion, fire, and carrier leakage) (John et al., 2017).

3.2 Soil

Engineered nanomaterials can enter soils through different sources and pathways, for example, the use of fertilizers and plant protection products, biosolids, sewage water, and floodplains (Batley et al., 2013). Soil is a matrix of a multilayer and complex interface between diverse matters (e.g., gases-solid-water-organic/inorganic components) and organisms. Nanomaterials pass through soil pores and adhere to soil particles due to their high surface area (Mukhopadhyay 2014). Furthermore, vast aggregates of NMs can be immobilized by sedimentation, filtration, or straining in smaller pores (Mukhopadhyay 2014). The mobility of NMs in soils relies upon a number of variables (e.g., nanoparticle's physical–chemical properties, characteristics of the soil and environment, and interactions of NMs with natural colloidal material) (Jafar and Hamzeh, 2013). It was found previously that Ag NMs may form a soil-based sink for Ag^+ ions and that their aggregation is greatly influenced by Ag NMs concentrations (Klitzke et al., 2015). Previous studies have also reported that plants can take up and translocate NMs from soil, which may influence the germination and plant growth (Khodakovskaya, et al., 2009; Hong et al., 2014). Ge et al. (2011) found adverse effects of TiO_2 and ZnO NMs on the biodiversity of soil microorganism communities.

3.3 Water

Nanoparticles may enter aquatic environment instantly via industrial release, dumping of wastewater treatment effluents, and/or through surface runoff from soils (Batley et al., 2013). The fate of NMs in the aquatic system is thus affected by various processes, for example, accumulation, disaggregation, diffusion, interaction with other components (and aquatic organisms), biological degradation (aerobic and anaerobic), and abiotic degradation (including photolysis and hydrolysis) (Vale et al. 2015). In a previous study on citrate-(Cit-AgNPs) and polyvinylpyrrolidone-coated silver nanoparticles (PVP-AgNPs), the combined effects of size of the particle and coating material type were found to play vital roles in determining the fate of these nanoparticles in water (Jang et al. 2014). Nevertheless, NMs may interact with other suspended particulate matter, organic matter, and colloids, causing aggregation and probably sedimentation from solution (Rocha et al. 2015). Aggregation of NMs with other substances in water often leaves them related with different solids rather than being dispersed in suspensions (Grillo et al. 2015). Moreover, the degree of aggregation depends on the characteristics of the particles (i.e., size, type, and surface properties) and of the environmental system (i.e., ionic strength, pH, and dissolved organic carbon content) (Baker et al. 2014). Furthermore, aggregation can lead to a reduction in the particular surface region of the particles and the interfacial free energy, decreasing particle reactivity (Baker et al. 2014). Some studies have reported the adverse effects (e.g., DNA damage, mortality, oxidative stress, and growth reduction) of NMs exposure on aquatic organisms (Baker et al. 2014; Grillo et al. 2015; Rocha et al. 2015). However, these studies were conducted by acute laboratory exposure, whereas organisms in real ecosystems are more likely to experience chronic exposure to numerous NMs.

With a model parsimony approach, Hendren et al. (2013) developed a mass-balance equation to represent ENM behavior. Accordingly, significant differences in the removal of silver NMs can be expected based on the type of coatings used for their stabilization in suspension. For example, 95% of the estimated concentrations of nano-Ag in effluent and sludge fractions fell below 0.12 and 0.35 μg L^{-1}, respectively (Hendren et al., 2013). In another study, the predicted environmental concentrations (PEC) derived from a life-cycle perspective of ENM containing products were calculated for the U.S., Europe, and Switzerland (Gottschalk et al., 2009). The concentration for simulated modes of fullerenes and nano-TiO_2 were 0.003 and 21 ng L^{-1}, respectively, for surface waters, while the values were 4 ng L^{-1} and 4 μg L^{-1}, respectively for sewage treatment effluents (Gottschalk et al., 2009). It was predicted that the average NM removal efficiencies of Irish wastewater treatment plants (WWTPs) were 59.8% and 70.2%, while those for water treatment plants (WTPs) were between 0 and 96.95% (O'Brien and Cummins, 2010). The model proposed to estimate the behavior of nanomaterials (nanoscale TiO_2, Ag (metal and ionic forms), and CeO_2) in surface water and human exposure is shown in Figure 4.

4. Environmental Effects of NMs

Due to their unique properties (e.g., extremely small size and high surface-volume ratio), the impacts and toxicity of NMs on the environment with respect to their interaction with biological substances are still relatively poorly described. Increasing application of NMs in commercial purposes, as well as in different consumer products, tends to increase the possibility of their exposure to humans in both direct and indirect routes (Pattan and Kaul 2014). Concern has also been raised whether the manufacturing of NMs may generate additional hazards. In light of their significance, the positive and negative effects of nanotechnology on the environment are discussed in the following sections.

4.1 Positive Effects on the Environment

Nanotechnology promises significant social, environmental, and financial benefits. Nanotechnology may ultimately be developed to help decrease the human footprint on the environment by providing more efficient and energy saving innovations. As an example, NMs are used in aircrafts as a substitute of conventional composites to help reduce aircraft weight, saving thousands of tons of fuel (Kausar et al., 2017). Furthermore, NMs are applied in wind turbine blades to make them stronger and lighter, helping increase their energy conversion efficiency (Patel and Mahajan, 2017). Nanomaterials are progressively used in automotive exhaust systems and petroleum refining systems to boost chemical reactions while reducing pollution and expenses (Etim et al., 2018).

Nanotechnology has also been applied for the development of energy efficient and energy saving products in various applications. Scientists have put enormous efforts into developing carbon nanotube "scrubbers" to isolate carbon dioxide from power plant emissions (Bloch et al., 2013). In addition, researchers are working to develop low resistance wires with carbon nanotubes, which may be helpful to reduce transmission power loss (Azmi et al., 2017). Nanomaterials are playing a vital role in reducing the manufacturing cost and increasing the efficiency of solar panels, which are one of the cleanest energy sources. Furthermore, with NMs, solar panels can be made in flexible rolls instead of discrete panels and are even printable (Sumaiya et al., 2017). Nanomaterials are also being sought to convert the waste heat of automobiles, power plants, and computers into a usable source of electrical power.

Nanomaterials have been successfully implemented for the purification of air and water by means of adsorption, filtration, and oxidation techniques with greater efficiency than conventional techniques (Kunduru et al., 2017; Mohamed, 2017). One of the unique features of NMs is that they can be utilized to respond to pollutant contaminants, ultimately leading to conversion into nontoxic particles (Mohamed, 2017). Nanomaterials coating can resist pollutants and have self-cleaning features (Nica et al., 2016). Nanomaterials are also used in sensing technology to detect contamination at low concentrations. Nanotechnology could be used for precision manufacturing, which may lead to the generation of less waste and reduce the requirement for large industrial plants. A self-cleaning NMs surface coating technology could spare water, energy, and cleaning agents. Furthermore, nanotechnology has been used to make more efficient and environment friendly batteries (Sun et al., 2017). Additionally, by breaking down oil into biodegradable compounds, NMs may play an important role cleaning up oil spills (Daza et al., 2017). Figure 5 lists the positive impacts of NMs.

4.2 *Negative* Effects on the Environment

As the environmental impacts of NMs cannot be clearly diagnosed and there are too many variables to account for (e.g., NMs identification, low detection limits, and unknown environmental concentrations), it is very difficult to reach any conclusion about the ecological effects and environmental stability of NMs. Even a minor change in the chemical structure of NMs could radically change their properties, turning them into toxic compounds. According to the United States Environmental Protection Agency, “the toxicity of NMs is difficult to identify because they have unique chemical properties, high reactivity, and do not dissolve in liquid" (USEPA, 2016). As NMs are highly reactive, even the properties of NMs in environmental samples could change between collecting and analyzing the samples (USEPA, 2016). Sometimes it is very difficult to figure out the origin of the NMs in the samples as well. Recently, scientists have investigated the ecological effects of Ag_2S nanoparticles. Accordingly, it was found that plants (e.g., dicotyledonous cucumber (*Cucumis sativus*) and monocotyledonous wheat (*Triticum aestivum L.*)) may uptake nanosilver if available in soil (Wang et al., 2017). As the uptake of nanoparticles led to the upregulation of genes (associated with the ethylene signaling pathways), reduction in the plants growth was accompanied. Moreover, NMs facilitated the upregulation in plant defense system, which also contributed to decrease in plant growth. As the majority of the Ag_2S nanoparticles were accumulated at the leaves of the tested plants, such phenomenon increased the chances of trophic transfer of these structures through food chain. The transfer of certain nanoparticles such as TiO_2 was also seen to cause genotoxic effect (at low dose of 0.25 mM) to damage DNA (at higher concentrations) on the plants, e.g., *Allium cepa* and *Nicotiana tabacum* (Ghosh et al., 2010). The malondialdehyde level of *A. cepa* was found to increase in the presence of TiO_2, which was also suspected to cause DNA damage. The exact mechanism of toxicity associated with nanoparticles is yet unclear. However, a few groups claimed that the toxicity of nanoparticles is majorly associated with the dissolved material or metals leached from the nanoparticles (Chen et al., 2016). The fact was evidenced by testing the toxicity of nanostructures under different conditions such as nano-ZnO at 4.5 pH, nano-ZnO at >7 pH, and coated nano-ZnO on *Lemna minor*. The nano-ZnO at 4.5 pH exhibited much higher toxicity in comparison to the other two types of nano-ZnO due to easy and rapid dissolution of ZnO at pH 4.5. In contrast, the dissolution of nano-ZnO at pH >7 and coated nano-ZnO was negligible with the minimal effect on the growth of plant. The phytotoxicity effects of the NMs were also seen to be affected by the depends upon the type of NMs. For instance, nano Zn and nano-ZnO exerted negative impact on the seed germination and growth of ryegrass/corn, respectively (Lin and Xing, 2007). On the other hand, multi-walled carbon nanotube, aluminum, and alumina exhibited negligible effect on both seed germination and plant growth.

After the release of NMs to the environment, they may interact with other pollutants to form a mixture of materials. The toxicity of these mixtures should also be assessed to learn more about such combination. To this end, nano-ZnO and/or nano-CuO were blended either individually or as a mixture with either of three types of nanoparticles (i.e., nano-TiO_2, nano-Cr_2O_3, and nano-Fe_2O_3) for the assessment of toxicity on plants in terms of seed germination and root growth inhibition (Jośko et al., 2017). It was observed that the NMs in blended form exhibited less toxicity on tested plant species than those applied individually or as a mixture.

The presence of NMs was also demonstrated to exert low to high toxicity impacts on the aquatic life. According to the toxicological investigations, NMs may affect unicellular aquatic organisms and creatures (e.g., fish and Daphnia) (Gao et al., 2018). The effect of nano-Cd on the *Daphnia magna* was investigated to assess its toxicity level. The nano-Cd showed the dose dependent toxicity on *D. magna*. For instance, at low/medium concentration of nano-Cd, the activity of peroxidase, catalase, superoxide dismutase, and anti-superoxide anion increased. In contrast, oxidative damage on *D. magna* was observed at higher nano-Cd levels. The carbon nanotubes and their byproducts were also reported to exhibit toxic effects on marine organisms, e.g., *Thalassiosira pseudonana*, *Tigriopus japonicas*, and *Oryzias melastigma* (Kwok et al., 2010). The half maximal effective concentrations (EC_{50}) of CNTs for the growth inhibition of *T. pseudonana*, *T. japonicus* and *O. melastigma* were measured as 1.86, 0.1, and 10 mg/L, respectively. The exposure of CNTs also exerted negative impact on the larvae of marine organisms (Kwok et al., 2010). The CNTs are suspected to induce physical and oxidative stress due to their toxicity. Carbon nanotubes and their byproducts are reported to increase the mortality of some freshwater crab species (Khalid et al., 2016). Likewise, it was suggested that the nano-ZnO can actively affect the growth phase of algae (Li et al., 2017). Moreover, the NMs exhibited toxic effects on several aquatic microorganisms, e.g., *Escherichia coli* and *Aeromonas hydrophila* (Tong et al., 2015). Both nano-TiO_2 and nano-ZnO exerted toxic effects on the aquatic bacteria by damaging bacterial cell membrane. Likewise, NMs displayed anti-bacterial activity (especially against *E. coli*) to cause the death of microorganisms through the generation of oxygen species near bacterial surface (Lok et al., 2006; Li et al., 2010; Das et al., 2017). Apart from plant and aquatic systems, the effect of NMs on the life of soil organisms was also demonstrated. To evaluate the toxicity of NMs on soil organisms, nano-CeO_2 particles were applied at 1 to 100 nM concentration on *Caenorhabditis elegans* (Zhang et al., 2011). The nanoparticles caused oxidative damage through the accumulation of reactive oxygen species in *C. elegans*. The exposure of very low concentration of nano-CeO_2 (i.e., 1 nM) to the mentioned nematodes led to 12% decrease in their lifespan. On the other hand, 18% decrease in the lifespan of the nematodes was observed when exposed to enhanced concentration (100 nM) of nano-CeO_2.

Nanomaterials are also reported to exert negative impact on the air system. The NMs played an important role in the formation of dust clouds after being released into the environment (Turkevich et al., 2015). The drawbacks associated with the applications of NMs are shown in Figure 6. The negative impacts of NMs and ENMs on marine animals, microorganisms, plants, soil, water, and air are presented in Table S2 (Doshi et al., 2008; Lee et al., 2008; Ghosh et al., 2010; Clément et al., 2013; Tang et al., 2015; Tong et al., 2015; Chen et al., 2016; Li et al., 2017). Overall, NMs exerted negative effects on environment by complicating the different environmental systems. The NMs not only affected the life of aquatic and terrestrial systems but also degraded the quality of air. In other word, NMs can affect all the environmental media, i.e., air, water, and land. The negative impacts of NMs are listed in Table S2.

5. Human and Other Mammals Health Impacts of NMs Exposure

There is growing concern regarding the toxicity and exposure of NMs as they can pass through and absorb in the cell membranes of mammalians. The absorption rate of the NMs in cells depends upon their size, aggregation, and sedimentation characteristics (Binderup et al., 2013). Cellular absorption of NMs happens by endocytosis or phagocytosis (Mallapragada et al., 2015). Exposure routes of NMs are diverse and include oral, dermal, inhalation, and/or gastrointestinal tract while using products such as sunscreen, skin care products, paints and coatings products, food and health supplements, food additives, and food colorings (Ma et al., 2015; Mackevica and Foss, 2015). Additionally, in some cases, ENMs are intentionally injected into the human body for medical applications. By generation of reactive oxygen species (ROS) and oxidative injury, NMs cause antagonistic health effects (Liou et al. 2012). NMs may also act as allergens during early stages of life, which may trigger the immune system to respond with allergic inflammation in later stages of life (Sly and Schüepp, 2012).

Scientists have found connections between NMs exposure during neonatal (the first month after birth) with increased asthma exacerbation, decreased lung function, and wheezing and coughing without infection (Meldrum et al., 2017). However, nanotechnology may provide a great opportunity for treatment of pediatric diseases, with substantial promise in the field of imaging and therapeutical applications (Zare-Zardini et al., 2015). Inhaled NMs can distribute throughout the body through the blood stream (Terzano et al., 2010). Epidemiological studies have reported that harmful cardiovascular consequences like changing blood coagulation, which may cause alternation in cardiac frequency and function, could occur because of NMs exposure (Araujo and Nel 2009; Quan et al., 2010; Liou et al., 2012). Further, chronic exposure to NMs could reduce forced expiratory volume (FEV1) and forced vital capacity (FVC) (Bonner, 2010). In an animal model study, Becker et al. (2011) concluded that carbon nanotubes and nanoscale TiO_2 particles may induce tumors. Engineered nanomaterials have toxic effects on fibroblasts and epidermal keratinocytes and, furthermore, can alter gene or protein expression (Haliullin et al. 2015).

In a few studies, the effect of NMs on the human cells was examined to understand the basic aspects of their interactions. To this end, Nguyen et al. (2015) found that cadmium telluride quantum dot (CdTe-QD) could create multifarious toxicity to human hepatocellular carcinoma HepG2 cells by altering mitochondrial morphology and structure. Further such nanostructure was capable of reducing their capacity and stimulating their biogenesis. The CdTe-QDs were further suspected to severely affect the mitochondrial membrane potential and cellular respiration, increase the intracellular level of calcium, and decrease synthesis of adenosine triphosphate. These findings were helpful to prove that human system can be damaged severely, if exposed to NMs. Due to oxidative stress, exposure to NMs may pose distinct effects on interstitial fibrosis and airway inflammation in animal model (Smita et al., 2012). Nanomaterials may also prompt the initiation of ROS by altering mitochondrial functioning and/or by inducting cell signaling pathways (Liu et al., 2013). Although some animal studies have reported potential impacts of silver NMs on reproduction and development systems, those studies were conducted with extensive dose levels (15 to 1000 mg kg^{-1}) and sizes (6.45 to 323 nm) that are not relevant to environmental exposure (Ema et al., 2017).

A few NMs and ENMs have exhibited toxic effects on human cells and organs by generating oxidative stress, DNA damage, cell membrane damage, glutathione depletion, mitochondria morphology/structure alteration, and inflammation (Sayes et al., 2006; Li et al., 2008; Lin et al., 2009; Akhtar et al., 2010; Mittal and Pandey, 2014; Chen et al., 2015; Fede et al., 2015; Ng et al., 2017). For instance, the presence of nano-ZnO induced the elevation of reactive oxygen species in human bronchoalveolar carcinoma-derived cells (A549), which caused the oxidative stress, cell membrane leakage, lipid peroxidation, and oxidative DNA damage (Lin et al., 2009). The cell viability was tested on A549 cell lines at varying concentration levels (i.e., 2-16 µg/mL) of nano-ZnO. Accordingly, it was reduced most significantly at the maximum level of nano-ZnO (16 µg/mL). The negative impacts of these NMs on human health are also listed in Table S2.

In addition to the specific NMs used for diverse applications, some NMs are unknowingly generated in the environment to severely affect the human health. For instance, due to excessive use and inappropriate disposal of plastics, the level of nano-plastics is increasing in alarming rate, especially in aquatic and air system (Bouwmeester et al., 2015; Galloway, 2015; Prata, 2018). Due to the presence of these nano-plastics in marine and air system, they can be easily accommodated or transferred into food chain. After entry into food chain or in human system, the nano-plastics can impose their negative impact on human health by releasing monomers/additives and through accumulation in the body.

A good number of studies were carried out to estimate the effect of NMs exposure on human human cell lines and other mammals. The indirect estimation of NMs exposure on human health can be assessed by analyzing the effect of NMs on these biological bodies. However, the exact effect of NMs exposure on the human health can only be estimated by testing on higher animals and humans. At present, the lack of direct study on humans and higher animals is restricting researchers such as emphasis on the prediction of their adverse effect. However, according to the toxicological studies on human cell lines and lower animals, it was estimated that NMs can exert harmful effects on human body by generating oxidative stress and DNA damage.

Numerous studies have examined the health impacts of NMs exposure. However, these studies have several limitations including small population groups, unclear dose response relationship, heterogeneity of NMs, and misclassification of exposure. In fact, most toxicological reports on NMs exposure are conflicting and inconsistent. Thus, the toxic effects of NMs should be assessed by more objective means (e.g., nonbiased in vivo toxicological models) using state-of-the-art methodologies.

6. Regulations

New technology or products should go through extensive testing for adverse environmental and health consequences before introduction. Kriebel et al. (2001) outlined the precautionary principles for environmental decision making as “1) taking preventive action in the face of uncertainty; 2) shifting the burden of proof to the proponents of an activity; 3) exploring a wide range of alternatives to possibly harmful actions; and 4) increasing public participation in decision-making.” However, such principles were not followed before the introduction of NMs, leaving uncertainty about the dangers versus advantages of NMs. Even though there is dispute among the scientific community regarding proper safety assessment of NMs exposure for governance and regulation, governments and regulatory authorities are working to adopt considerable regulation about NMs. While there are always disputes among employers, scientists, and regulatory groups about the acceptable range of hazards, until now there have been no standardized methods for the determination and characterization of NMs, which makes it very difficult to make any appropriate assessment. Except for a few exceptions, there are no specific regulations about NMs exposure. After a decade of critical revisions, EC recently admitted that NMs are “difficult to regulate” because of their complexity and lack of knowledge (OECD, 2016).

Some organizations, however, have proposed tentative occupational exposure limits (OELs) for NMs. For example, the United States National Institute for Occupational Safety and Health (NIOSH) suggested recommended exposure limits (RELs) of carbon nanotubes as 1 $\mu g\text{-}m^{-3}$ for 8 h time-weighted average (TWA) (NIOSH, 2013). NIOSH also proposed RELs for ultrafine (nanoscale) and pigmentary (>100 nm) titanium dioxide as 0.3 and 2.4 $mg\text{-}m^{-3}$ for 10 h TWA per day, respectively (NIOSH, 2013). Moreover, manufacturers should provide detailed information (e.g., specific chemical identity, manufacturing methods, processing, production volume, exposure and release information, use, and available health and safety data) on NMs to the United States Environmental Protection Agency (US EPA) for review to ensure that products do not pose any human and/or environmental risks (EPA, 2017). The British Standard Institute (BSI) has suggested NM "benchmark levels" for insoluble, highly soluble, and substances classified as hazardous as 0.066, 0.5, and 0.1× OEL of the corresponding micro-sized material, respectively (BSI, 2007). Further, the proposed BSI benchmark level for fibrous NMs is 0.01 fibres-mL^{-1} (BSI, 2007). According to the German Institute for Occupational Safety and Health (IFA), the benchmark level for metals, metal oxides, and bio-persistent granular NMs (density > 6,000 kg-m^{-3}) is 20,000 particles-cm^{-3} and for biopersistent granular NMs (density < 6,000 kg-m^{-3}) is 40,000 particles-cm^{-3} (IFA, 2011). For provisional fibers, the proposed IFA benchmark level is 10,000 fibres-cm^{-3} (IFA, 2011). Table S3 lists the NMs exposure regulation set by different organizations.

However, such OELs of NMs may not be adequate for protection from health risks. Therefore, it is preferable to keep the exposure limit as low as possible by practicing proper control measures like safety data sheets, labelling, and signage. According to the European Union (EU) regulation 1272/2008, NMs considered as hazardous should be classified and labeled accordingly (EC, 2008). Through the Cefic-LRI project, Read et al. (2016) mapped the governance landscape for nanotechnology by considering the existing regulatory frameworks, reporting schemes, standardizations, and best practice guidance. Furthermore, voluntary schemes in European countries for data submission on NMs is helping to gather information regarding toxicity levels as well as insight into production and market distribution (Hermann et al., 2014).

7. Conclusion

There is no doubt that cutting edge nanotechnology has been successfully utilized in various fields for the welfare of mankind. However, any new unproven technology comes with a few downsides. There are concerns about NMs' potential harmful effects on the environment and human health. There are reasons to believe that use of NMs is increasing. Till now, these wonder structures have been explored for countless applications in diverse sectors including catalysis, sensing, photovoltaic, energy, environment, and biomedical. However, due to lack of proper disposal guidelines, the level of NMs in the environment is consistently increasing. The results of preliminary studies revealed that these structures are affecting the environment by a number of routes, e.g., 1) by increasing the pollution level of air, water, and soil, 2) by accumulating in the environmental system (which may pose both short term and long term effects), and 3) by affecting the life-cycle of living systems present in environment.

The majority of studies on the effect on NMs on environment are based on short-term effects. The future studies with special focus on accelerated or long-term effect of NMs, if carried out, can help in estimating the exact toxicological profile of these structures on environment. As the NMs are highly reactive structures, these structures could interact with other pollutants to generate more/less toxic structures. Such studies should also be included in the future research to prepare disposal regulations of NMs. The adverse effects of NMs on higher animals and human are scantily studied. However, the toxicological profile of these structures on lower organisms and human cell lines demonstrated that the toxicity profile of the structure would not favor the human health. The proper guidelines and regulations for the use and disposal of NMs should be prepared to avoid any future complications. Environmental scientists, engineers, authorities, governmental and non-governmental organizations can only speculate about the impact of NMs. Therefore, it is very important to conduct proper life cycle evaluation and risk assessment analyses for NMs before wide application. Much more research is needed in this field as harmless bulk materials could become toxic and reactive substances at nano-levels. By reducing the huge gaps in knowledge about the nature of interactions of NMs, we will have proper guidelines regarding the processing, applications, and regulation of NMs in the future.

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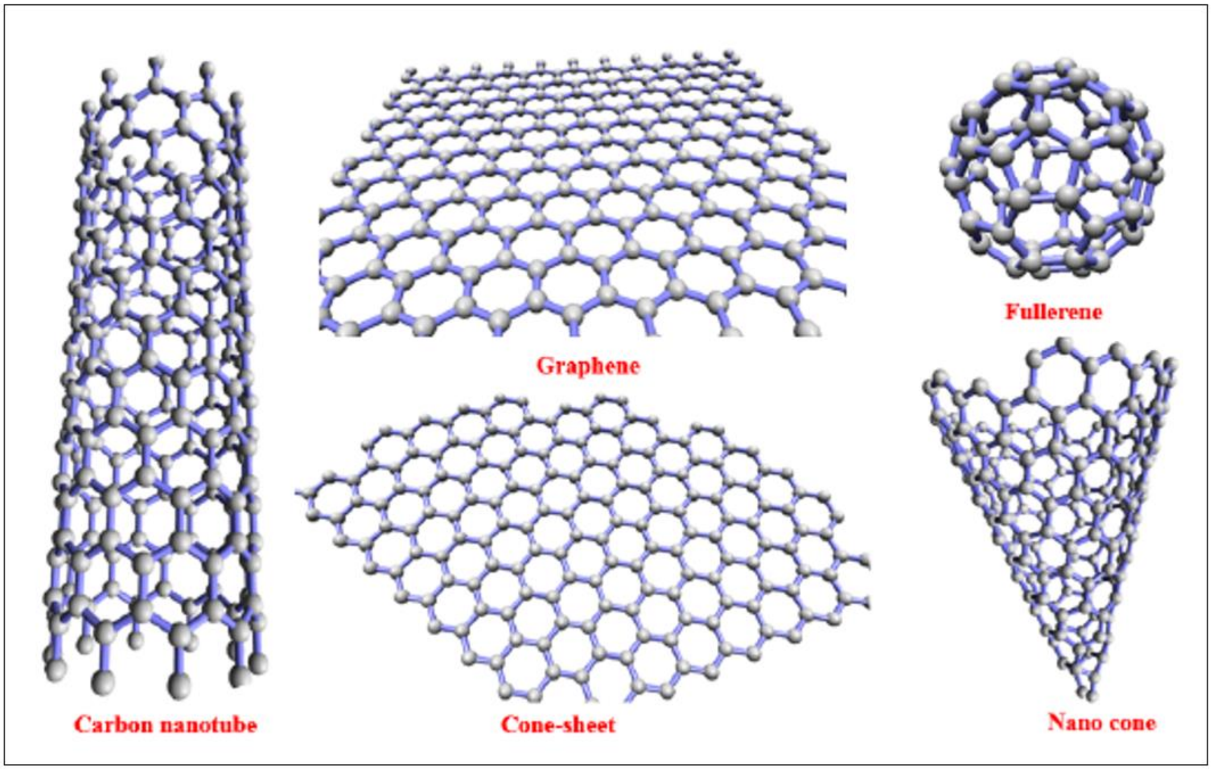


Figure 1. Various structures of carbon-based nanomaterials (Saleh, 2016).

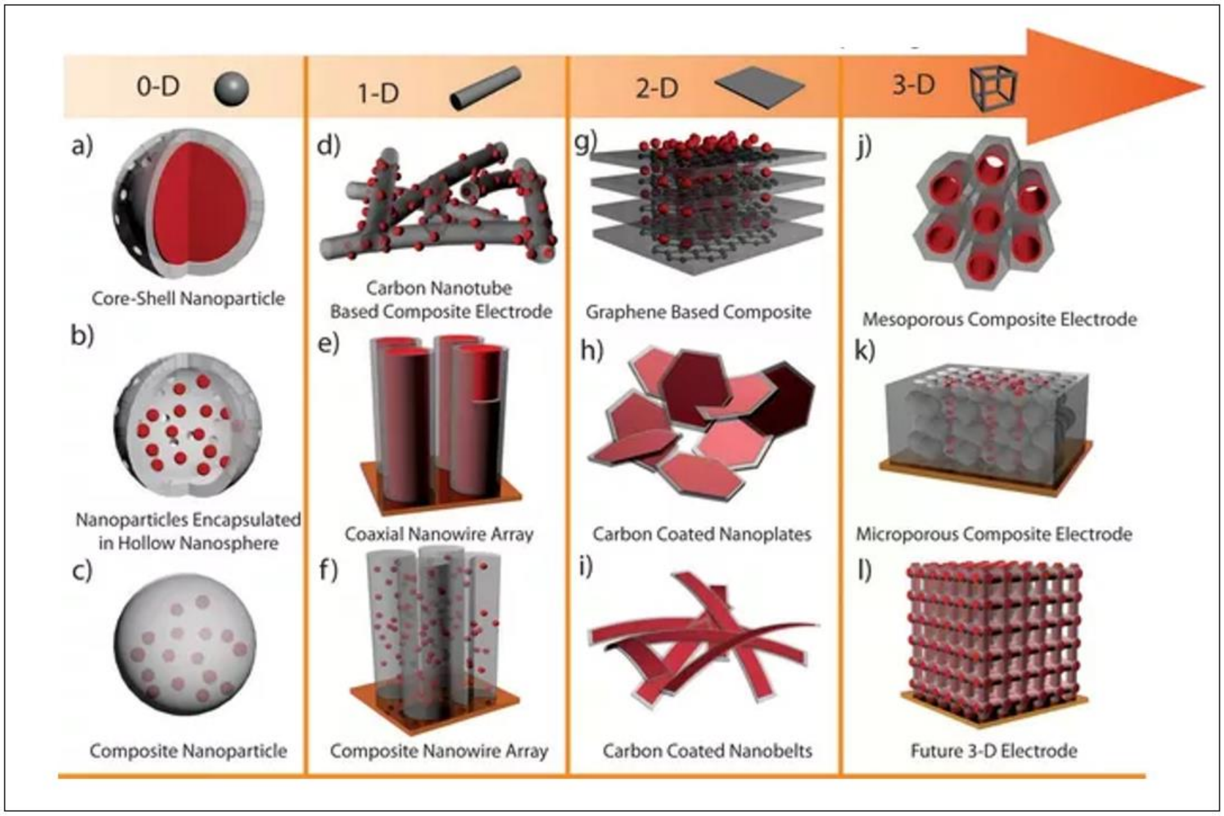


Figure 2. Classification of nanomaterials according to dimension (Tiwari et al., 2012).

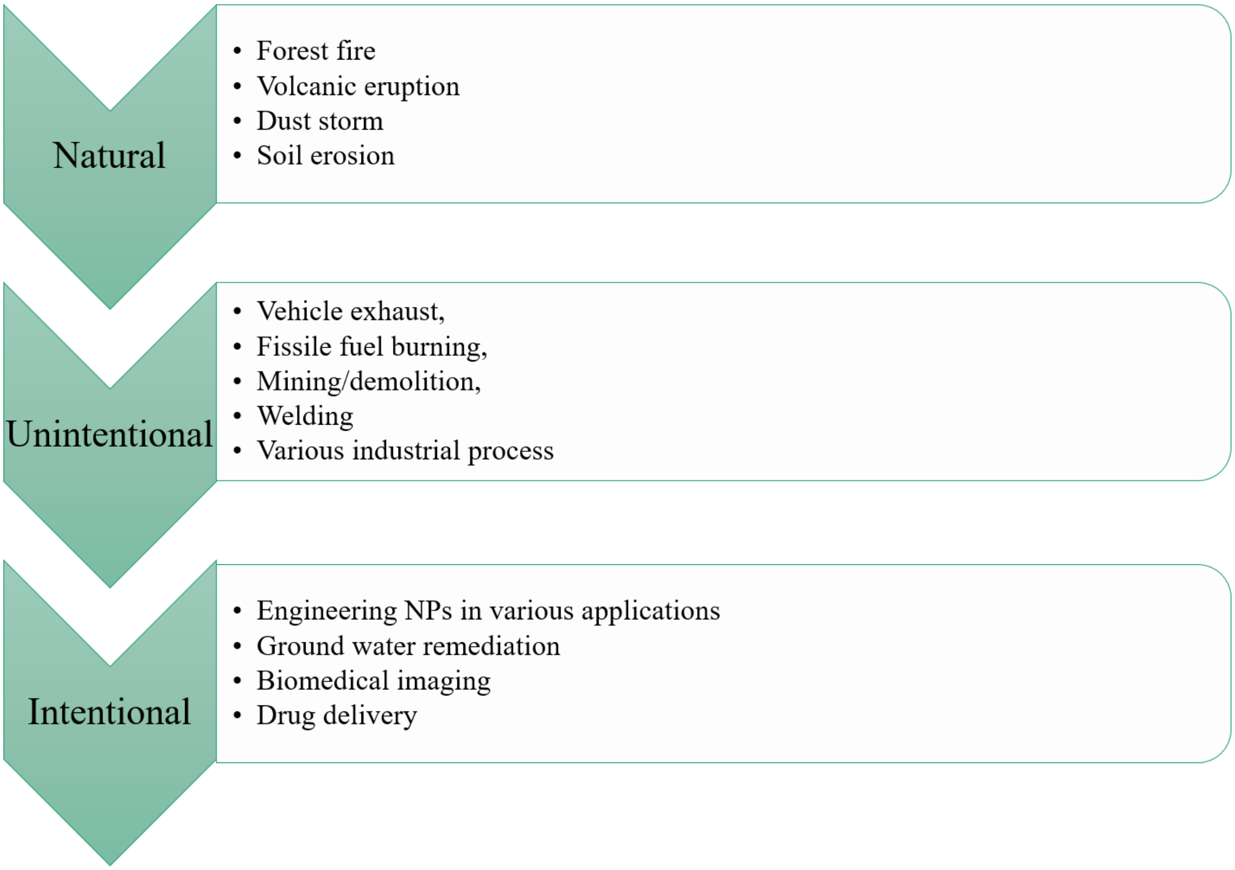


Figure 3. Common sources of nanomaterials in the environment.

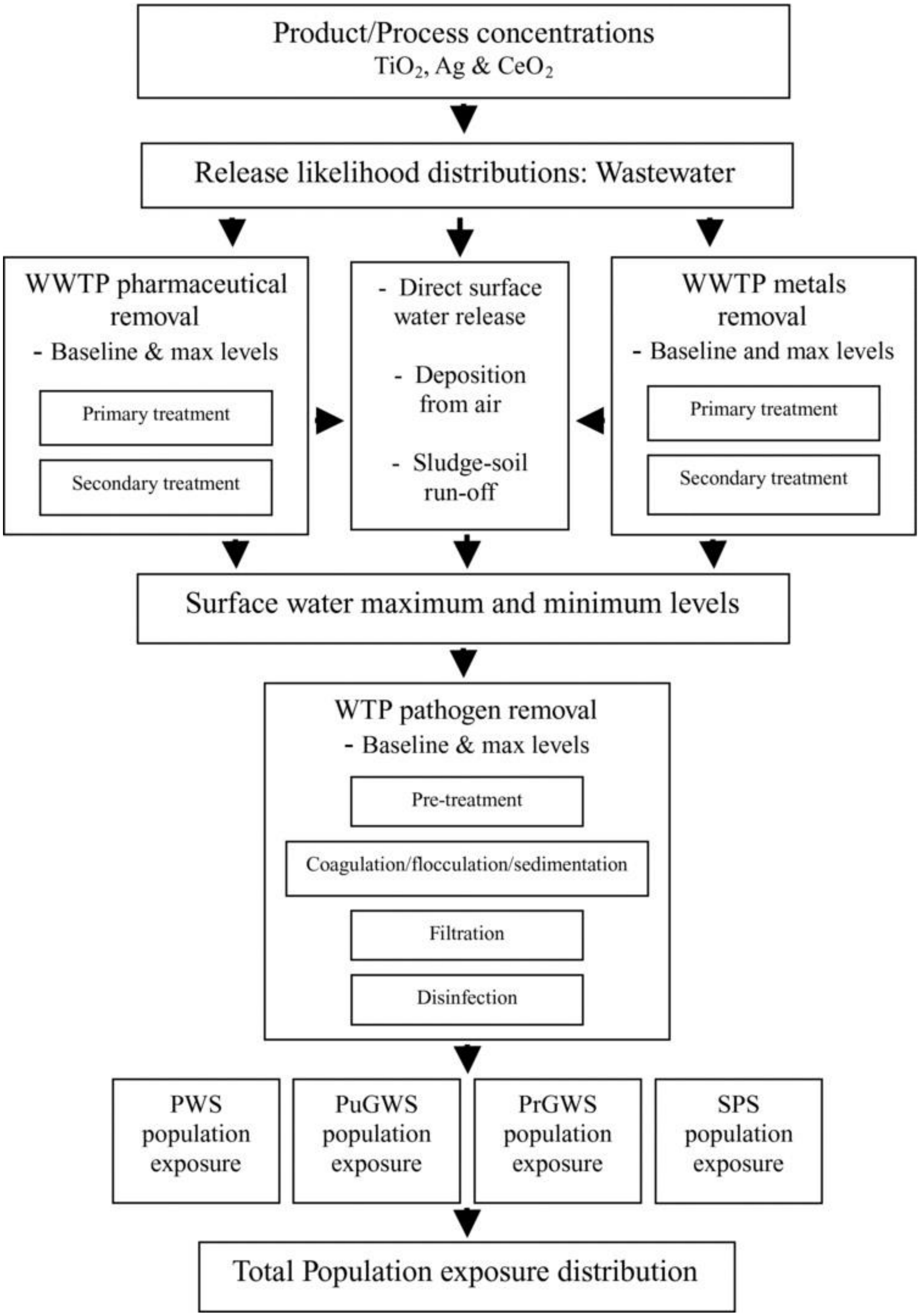
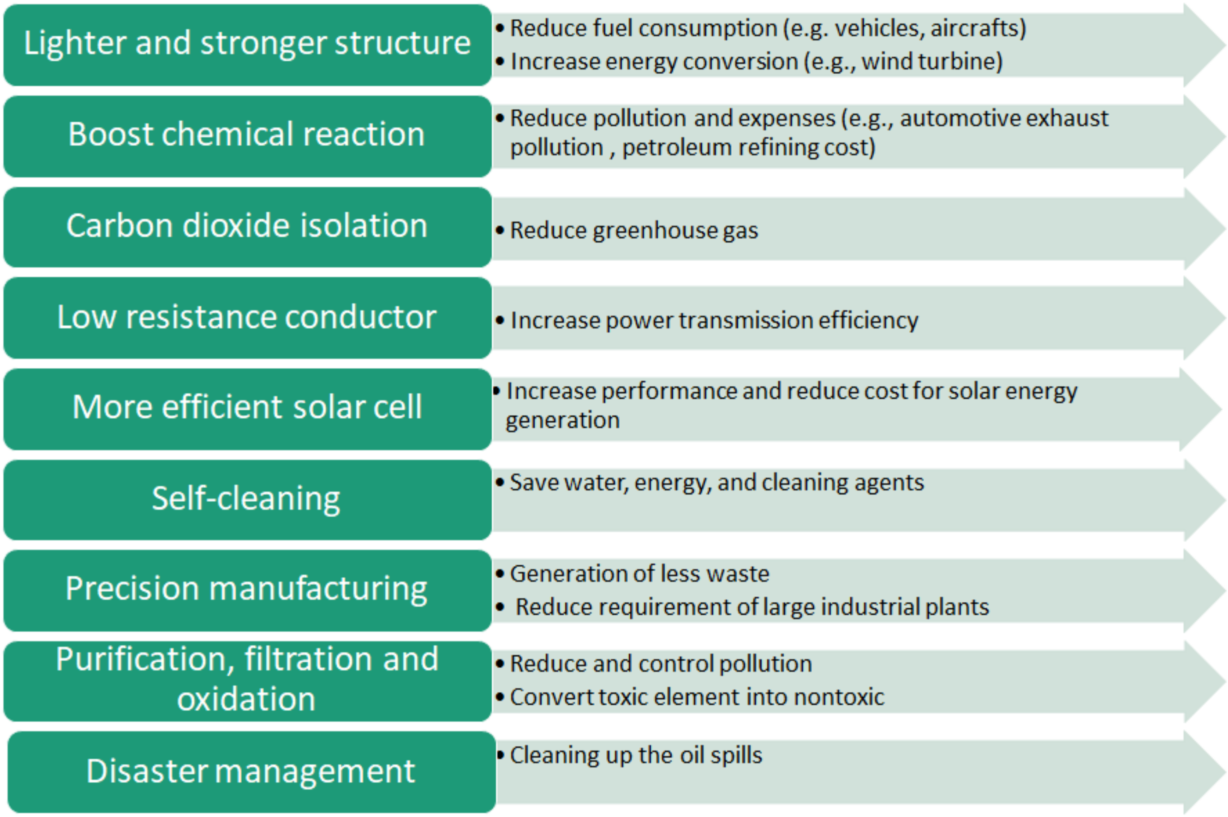


Figure 4. Nanomaterial exposure model (O'Brien and Cummins, 2010)).



Lighter and stronger structure	• Reduce fuel consumption (e.g. vehicles, aircrafts) • Increase energy conversion (e.g., wind turbine)
Boost chemical reaction	• Reduce pollution and expenses (e.g., automotive exhaust pollution , petroleum refining cost)
Carbon dioxide isolation	• Reduce greenhouse gas
Low resistance conductor	• Increase power transmission efficiency
More efficient solar cell	• Increase performance and reduce cost for solar energy generation
Self-cleaning	• Save water, energy, and cleaning agents
Precision manufacturing	• Generation of less waste • Reduce requirement of large industrial plants
Purification, filtration and oxidation	• Reduce and control pollution • Convert toxic element into nontoxic
Disaster management	• Cleaning up the oil spills

Figure 5. Positive impacts of nanomaterials on the environment.

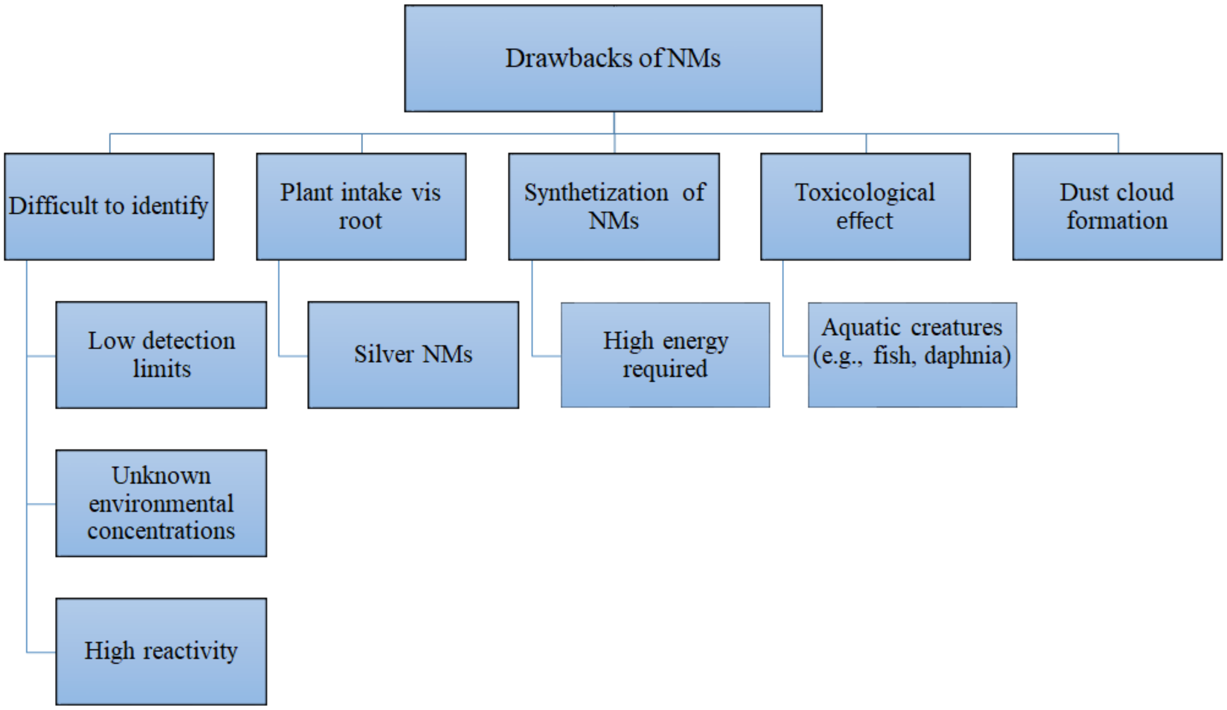


Figure 6. Downsides of nanomaterials.