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Transformations of Nanomaterials in the Environment

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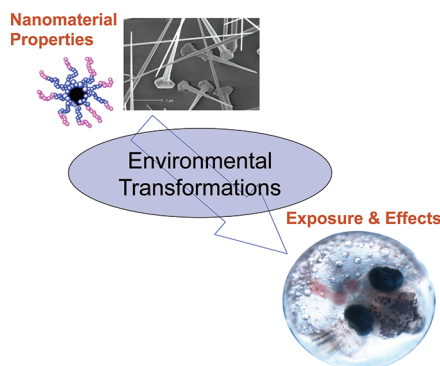
Increasing use of engineered nanomaterials with novel properties relative to their bulk counterparts has generated a need to define their behaviors and impacts in the environment. The high surface area to volume ratio of nanoparticles results in highly reactive and physiochemically dynamic materials in environmental media. Many transformations, e.g. reactions with biomacromolecules, redox reactions, aggregation, and dissolution, may occur in both environmental and biological systems. These transformations and others will alter the fate, transport, and toxicity of nanomaterials. The nature and extent of these transformations must be understood before significant progress can be made toward understanding the environmental risks posed by these materials.

■ INTRODUCTION

The nanotechnology field continues to grow rapidly and the increasing use of engineered nanomaterials (NMs) in commercial products translates into an increasing presence in the biosphere. Engineered NMs are manufactured materials having at least one dimension in the nanoscale (ca. 1−100 nm) dimension. Naturally occurring NMs are also ubiquitous in the environment, resulting from both natural processes and from anthropogenic impacts (e.g., flocculation of nanometer-scale metal oxides in acid mine drainage). The extremely small sizes of both naturally occurring and engineered NMs results in a high percentage of surface atoms which can result in novel properties and reactivity compared to a larger size material with the same chemical composition.[1,2] Examples of such engineered NMs include semiconductors like quantum dots which have different optical and electrical properties depending on their size,[3] and gold nanoparticles (NPs) that are typically inert but become catalytic as their size is decreased to a few nanometers.[4] NMs are becoming increasingly complex and include those with coatings that target specific cells in the body[5] or that

are engineered from more than one NM for optimized utility (e.g., carbon nanotubes (CNTs) doped with quantum dots[6]). These newly emergent materials that will soon enter manufacturing supply chains are unique and xenobiotic (e.g., metal oxide NP-decorated graphene sheets[7]). The lack of a natural analog for these new materials complicates the forecasting of their fate, transport, reactivity and toxicity in environmental systems. The uncertain effects resulting from the novel properties exhibited by NMs have given rise to concerns by citizens and governments throughout the world, and a justified increase in environmental health and safety (EHS) research aimed at assessing the potential for NMs to harm the environment or human health. An overall goal of these research activities is to correlate the properties of NMs to their behavior in the environment and their effects on living organisms.[8]

Assessing the environmental and human health implications of nanomaterials requires an understanding of the potential exposure routes and toxicological effects from acute and chronic exposures. To date, the predominant focus of the global research endeavor has been defining the fate, transport, and toxic properties of pristine or "as manufactured" nanomaterials. However, the high surface to volume ratio and reactivity of NMs makes them highly dynamic in environmental systems. The resulting transformations of the NMs will affect their fate, transport, and toxic properties. For example, metallic silver NPs will oxidize and may become sulfidized in the environment.[9] Sulfidation of the particles changes their aggregation state, surface chemistry, and charge, as well as their ability to release toxic Ag^+ ions[10] and therefore their persistence and toxicity. Similarly, the interaction between NMs and humic substances (HS) including natural organic matter (NOM) results in a nanoscale coating of the NMs,[11] analogous to protein coronas in mammalian systems,[12] that dramatically changes their aggregation, deposition, and toxic properties.[13,14]

Because environmental systems are dynamic and stochastic, the physicochemical changes that accompany engineered and incidental coatings, as well as subsequent reactions in the environment, greatly complicate the understanding of risks associated with the release of NMs in the environment. We currently lack sufficient knowledge of the types, rates, and extent of transformations expected for NMs in environmental and biological systems. By extension, we also fail to understand

the impact of those transformations on the fate, transport, and toxicity of NMs. To correctly forecast the environmental and human health risks associated with these materials, we must endeavor to broaden our knowledge of the transformations of NMs.

The U.S. National Research Council has recently proposed a new framework for nano EHS research.[8] This committee recommended that research should focus on understanding "critical elements of nanomaterial interactions", needed for assessing exposure, hazards, and hence risks posed by engineered nanomaterials (Figure 1). These critical elements include physical, chemical, and
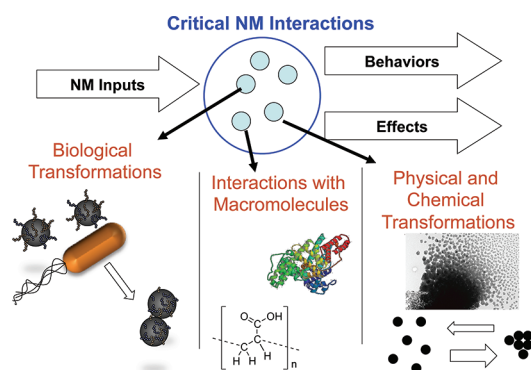

Figure 1. Nanomaterial transformations are critical processes affecting NM interactions. Transformations include physical and chemical transformations, biologically mediated transformations, and interactions with macromolecules and biomacromolecules. Adapted from ref 8.

biological transformations that ultimately influence NM persistence, bioavailability/biouptake, reactivity, and toxicity.

Oxidation and reduction (redox) reactions, dissolution, sulfidation, aggregation, and adsorption of macromolecules and molecules/ions all readily occur in the environment and in biological systems. These transformations greatly impact NM behavior. In some cases, these transformations may enhance toxicity potential (e.g., chemical weathering of the shell of a Cd–Se quantum dot that releases toxic ions from the particle core).[15] In other cases, these transformations have been shown to decrease effects (e.g., adsorption of NOM decreased the short-term bactericidal effects of C_{60}, Ag NPs, and Fe(0) NPs,[13,14,16] but increased bioaccumulation[17]). Some transformations can potentially limit NM persistence in the environment (e.g., dissolution of ZnO NPs).[18] There is still a great deal of uncertainty about the role that transformations have on both exposure and biological effects across the whole life cycle of NMs.

Nanomaterials are commonly produced with an organic capping agent or stabilizer, often a small anion or polymer (Table 1). Transformations of the material can therefore affect the core material, the capping agent, or both. For example, the simple coordination of ZnS nanoparticles (NPs) with water molecules can alter their crystalline phase and properties.[19] The capping agent may be bioavailable and removed by bacteria.[20] Indeed, the rate, extent, and type of transformations possible will depend on the properties of the initial NM, its coating, and its surrounding chemical and biological environment. Importantly, many transformations are slow or effectively irreversible and cannot necessarily be predicted using thermodynamics. Here, we briefly review what is known about chemical, physical, and biologically mediated transformations of NMs in natural systems and their effects on the resulting NM behavior. We also discuss state-of-the-science knowledge and instrumentation gaps preventing us from quantifying and predicting these transformations in biological and environmental media.

■ NM TRANSFORMATIONS AND THEIR EFFECT ON NM BEHAVIOR

Chemical Transformations (Figure 2a). Reduction and oxidation are coupled processes in natural systems and involve the transfer of electrons to and from chemical moieties. A number of NMs may be composed of or contain constituents that undergo reduction, oxidation, or both in aquatic and terrestrial environments. These include elemental metal NMs such as silver[21,22] and iron.[23] Ceria NPs can contain both Ce(III) and Ce(IV) and subsequent sorption of macromolecules can alter the ratio of Ce(III)/Ce(IV) on the NP surface.[24] The sulfur and selenium in some metal sulfides and metal selenides, major components of quantum dots, are also susceptible to oxidation that may release soluble toxic metal ions such as Cd.[2,25] In some cases, oxidation may result in the accumulation of a relatively insoluble oxide surface coating on the NP that passivates the surface and reduces subsequent oxidation, while also forming metal-oxide phases with a high capacity for binding ions from solution. In other cases, (e.g., Ag NPs), oxidation of Ag(0) to Ag(I) is required to dissolve and release bactericidal Ag^+.[22] Natural waters and aerated soils are predominantly oxidizing environments, while carbon-rich sediments and groundwater may be depleted of oxygen and result in NM reduction. In dynamic redox environments such as tidal zones one may well encounter cycling of NMs between different redox states.

Sunlight-catalyzed redox reactions (photooxidation and photoreduction) may prove to be very important transformation

Table 1. Representative Nanomaterials and Capping Agents/Coatings

| nanomaterial	typical capping agents/coatings	
	inorganic and small organic molecules	synthetic and organic macromolecules
zinc oxide	2-mercaptoethanol, triethoxycarprylsilane, triethanolamine, acetate	polyvinylpyrrolidone (PVP), polysaccharides,
silver	citrate, decanethiol, tannic acid, ethylenediaminetetraacetic acid (EDTA)	polyethylene glycol (PEG), PVP, gum arabic
gold	citrate, octanethiol, cetyltrimethyl ammonium bromide (CTAB), cysteine, tannic acid	biotin, bovine serum albumin (BSA), polypeptides
cerium oxide	oleic acid	PVP, poly(acrylic acid)-octyl amine
titanium dioxide	oleic acid	Poly(acrylic acid)
quantum dots (CdSe, CdS)	Silica (inorganic), zinc sulfide (inorganic), citrate, mercaptopropionic acid	PEG, aminodextran
iron oxide	dodecylamine, oleic acid	BSA, poly(acrylic acid), poly(methacrylic acid), PEG
zerovalent iron (ZVI)	Au, Pd, Pt, Ni	carboxymethyl cellulose, xanthan gum, polypropylene glycol
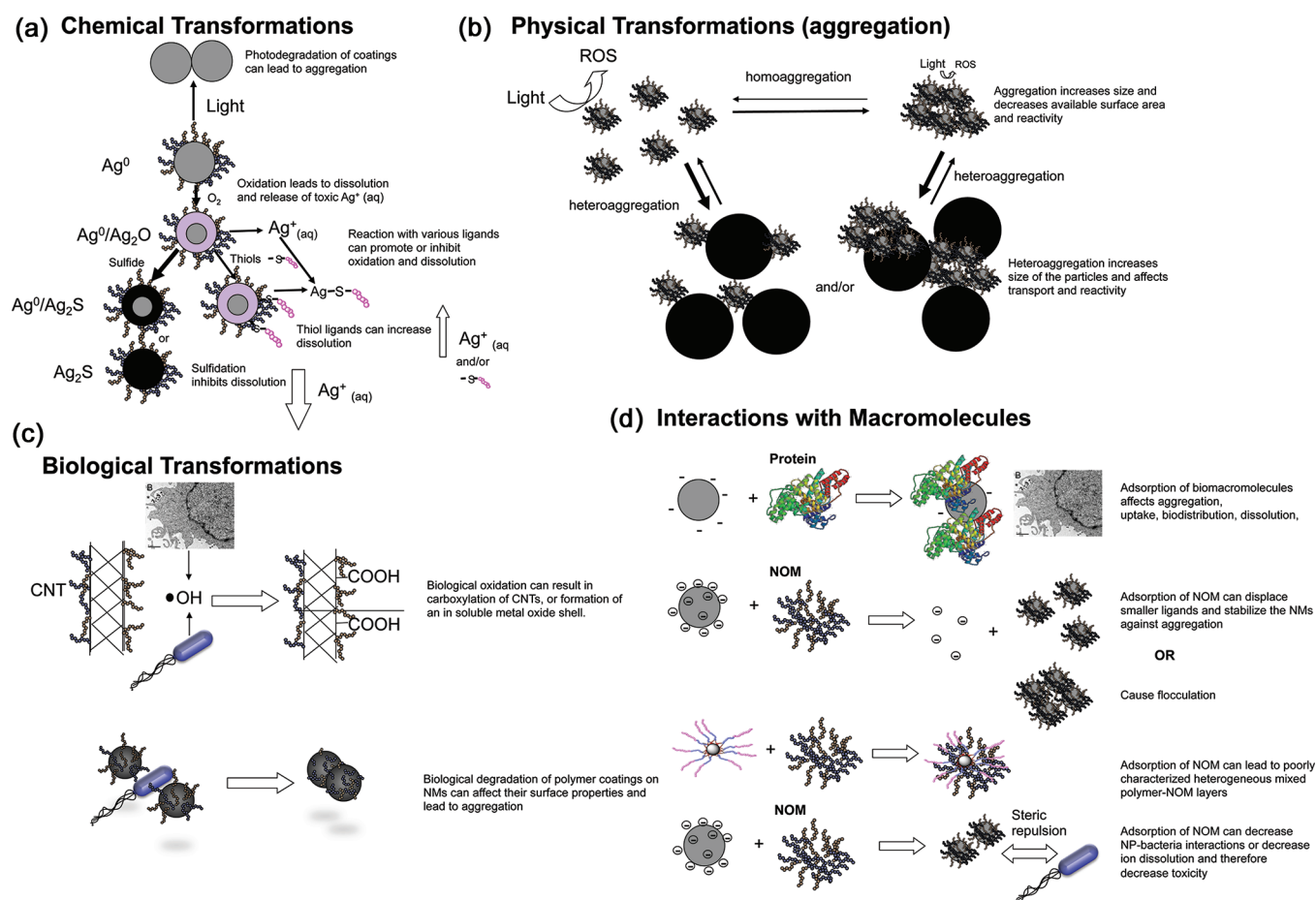
Figure 2. (a) Representative chemical transformations of metal nanomaterials and the potential impacts on their behavior and effects in the environment. AgNPs are used to exemplify the types of transformations that may occur. The magnitude of arrows approximately correlates with potential for these processes to occur as determined from the limited data available on these processes. (b) Effects of physical transformations including aggregation and heteroaggregation on the reactivity and transport of nanomaterials. The magnitude of arrows approximately correlates with potential for these processes to occur as determined from the limited data available on these processes. (c) Biologically mediated transformations of nanomaterials and their coatings, and the subsequent impact on fate, transport, and effects. Arrows do not indicate the relative potential for these processes to occur due to the limited data currently available for that assessment. (d) Effects of nanomaterial interactions with macromolecules such as proteins and natural organic matter. Adsorbed macromolecules can affect aggregation, nanoparticle-biointeractions, biouptake, and fate, transport, and effects in the environment. Arrows do not indicate the relative potential for these processes to occur due to the limited data currently available for that assessment.

processes affecting NM coatings, oxidation state, generation of reactive oxygen species (ROS), and persistence. The oxidation and mineralization of fullerenes dispersed in water by natural sunlight may attenuate carbon-based nanomaterials.[26] Sunlight exposure caused the degradation of gum arabic coatings on Ag NPs and induced aggregation and sedimentation from solution.[27] Many NMs will be innately photoactive (e.g., TiO_2 and CNTs), potentially producing ROS when exposed to sunlight.[28] Others may be oxidized or reduced by sunlight, changing their redox state, charge, and therefore potential for toxicity.

Dissolution and sulfidation are important processes affecting NP surface properties, toxicity, and persistence. This is especially true for NMs made from Class B soft metal cations (e.g., Ag, Zn, and Cu) because they form partially soluble metal-oxides, and because they have a strong affinity for inorganic and organic sulfide ligands. Class B metal NMs commonly express toxicity through dissolution and release of toxic cations, such that persistence is reduced but toxicity is increased. Complete dissolution may allow prediction of their impact using existing models for metal speciation and effects. However, Class B metals' affinities for electron-dense sulfur molecules make them

highly reactive with sulfur-containing biomacromolecules and inorganic sulfur in sediments, soils, and air. Formation of a relatively insoluble metal-sulfide shell on the particle surface can alter the surface charge and induce aggregation.[10] Determining the particle properties (e.g., particle size, capping agent, etc.) and environmental conditions (redox state and availability of free sulfide) that affect their dissolution and/or sulfidation rates are important for assessing their potential to release toxic metal cations, and their ultimate toxicity[29] and persistence in the environment.[30]

Adsorption of macromolecules or organic and inorganic ligands on NM surfaces can significantly affect their surface chemistry and resulting behavior in biological and environmental systems. For example, adsorption of polymer coatings on NPs generally decreases their attachment to silica surfaces, suggesting greater mobility in the environment and potentially less effective removal in drinking water treatment.[31] Adsorption of biomacromolecules is a particularly important transformation and is treated separately below. Adsorption of organic ligands or metal cations or oxo-anions can occur on either the surface of the core NM or within the organic macromolecular coating

of the particle. Organic ligands, such as those containing thiol groups may affect NM dissolution, charge, and stability against aggregation.[32,33] Organics present in the atmosphere can also condense onto airborne NMs, altering their surface chemistry.[34] Understanding the effects of organic ligands and adsorbed cocontaminants on NM toxicity is needed to fully assess the potential for harm.

Physical Transformations (Figure 2b). Aggregation of NPs reduces the surface area to volume effects on NM reactivity. This increase in aggregate size in turn affects their transport in porous media, sedimentation, reactivity, uptake by organisms, and toxicity. Over time, aggregation of NPs into clusters is inevitable without engineered or incidental coatings to decrease aggregation. Aggregation may take on two forms: homoaggregation between the same NMs, or heteroaggregation between a NM and another particle in the environment. In most cases, the greater concentration of environmental particles compared to NMs will result in heteroaggregation. Where aggregation occurs, the number concentration of NMs in the suspension decreases, with a concomitant increase in their effective (aggregate) size. For example, 30−70 nm diameter Fe(0) NPs rapidly aggregate in water to form micrometer-sized aggregates,[35] greatly decreasing their mobility in the subsurface and likely pathways of exposure to sensitive receptors. Heteroaggregation between NMs and comparatively larger particles (e.g., clay) could change NM behavior if the NM−clay heteroaggregates ultimately move more like a clay particle that the NM.[36]

Aggregation can also decrease the "available" surface area of the materials, thereby decreasing reactivity. However, the decrease in specific surface area will depend on particle number, size distribution, and the fractal dimensions of the aggregate.[37] Aggregation can therefore decrease toxicity when the toxic response is a result of a surface area-mediated reaction such as ROS generation or dissolution. Aggregation may also serve to increase the persistence of the NM if aggregation decreases the rate of dissolution or degradation, albeit in a different location compared to the dispersed NPs. The size of a NP may also affect its bioavailability to organisms. When aggregates or heteroaggregates become too large for direct transport across the cell wall and/or membrane, uptake may be prevented. Phagocytosis and similar mechanisms may also be affected. Conversely, heteroaggregation with soft biogenic particles might increase NM bioavailability (e.g., uptake by filter feeders who preferentially remove larger particles). Delineating the effects of aggregation on uptake and any subsequent toxicity will be challenging since it is a dynamic process, uptake will be highly dependent on both the species examined and its aqueous chemical environment and metabolic state, and because instruments for tracking NMs in situ or in vivo are lacking.

Biologically Mediated Transformations (Figure 2c). Biological transformations of NMs are inevitable in living tissues (both intracellular and extracellular) and environmental media (e.g., soils). Redox reactions are fundamental to growth in all biological systems. These reactions take place in the cytoplasm, cell wall, cell membrane, and extracellularly via redox-labile enzymes and cytochromes or through ancillary intracellular ROS production such as hydroxyl radicals or H_2O_2. The redox reactions between bacteria and naturally occurring, nanoscale iron oxide are well understood.[38] Moreover, bacteria such as *Geobacter* and *Shewanella* spp. were recently demonstrated to produce nanoscale silver particles by reduction of Ag^+ from solution.[39]

Biologically mediated transformations of both the underlying NM core and the coatings are possible, and these transformations can affect the behavior of the NMs including surface charge, aggregation state, and reactivity, which ultimately can affect transport, bioavailability, and toxicity. The oxidation and carboxylation of CNTs by OH radicals produced from the horseradish peroxidase enzyme has been demonstrated.[40] This oxidation increases the surface charge of the CNTs and stability against aggregation while decreasing hydrophobicity. Moreover, this biological oxidation and surface functionalization may affect the toxic potential of CNTs.[41]

Biotransformation of polymer coatings used on many NMs for biomedical applications is also feasible. Covalently bound poly(ethylene glycol) (PEG) coatings on engineered NMs, for instance, were shown to be bioavailable to microorganisms isolated from an urban stream.[20] Moreover, the biotransformation of the PEG coating caused the NMs to aggregate. Biological transformations of NMs, especially carbon-based ones, and their organic coatings may ultimately act to attenuate their concentrations in the environment or to affect transport, but it remains to be seen if these processes occur at rates that are high enough to be important. Perhaps the most critical biotransformation of NMs is adsorption of biomacromolecules on their surfaces as discussed next.

Macromolecule NM Interactions (Figure 2d). There are an endless number of biomacromolecules in living cells (e.g., proteins) and in the environment (e.g., NOM, polysaccharides). Adsorption of these macromolecules can occur in all environments. On uptake by biological organisms, NMs may be transformed through their interaction with biomacromolecules which can coat and thereby transform their outer surfaces.[42] Adsorbed protein coatings, also known as protein coronas, form in biological fluids for several classes of NMs.[12,43,44] The coronas result from the adsorption of a wide range of proteins and are dynamic in nature, with the proteins capable of exchanging between free and bound forms. However, many proteins and other macromolecules are effectively irreversibly adsorbed over relevant time scales,[45,46] and therefore in part determine the "identity" of the NM (e.g., size, electrophoretic mobility, and surface composition) and subsequent environmental behavior and biological response. The adsorbed proteins may also offer a way of entry for NMs into cells through the process of receptor-mediated endocytosis.[44] The presence of biomacromolecules can affect their dissolution rate, ROS production, and may determine the fate of the material in the organism (e.g., excretion vs accumulation in specific organs). Therefore, the types of biomacromolecules present on the surface can affect important processes such as bioaccumulation and toxicity.

Once discharged into the environment, uncoated or coated NMs will be subjected to alterations through interactions with naturally occurring biomacromolecules or geomacromolecules including proteins, polysaccharides, and humic substances (HS). NOM concentrations are typically orders of magnitude higher in concentration than manufactured NMs and so are likely to substantially modify the properties and behaviors of the manufactured NMs. The observed interactions are analogous to the interactions with proteins and the formation of "protein coronas" in biological systems, which have been the subject of more intensive research reaching similar conclusions; the behavior and impacts of NMs depends highly on the types and amounts of these biological and environmental components attached to their surfaces.

Most work to date on NM−NOM interactions has been performed using extracted humic substances (HS), which will displace weakly bound synthetic capping agents on the particle surface to form nanoscale coatings which can be either coherent (i.e., fully coating the NM surface) or noncoherent. They can form relatively "flat" monolayers or more extended (thick) monolayers or multilayers. The coherence and thickness depend on the particle properties and the conditions (e.g., pH and ionic strength) during interaction. NOM provides both charge and steric stabilization of NMs,[11,47] although they may also result in bridging flocculation,[24] so their effects are complex and can be difficult to predict. In addition, deagglomeration may occur in the presence of NOM.[48] For larger MW polymeric coatings that are strongly bound mixed polymer−NOM layers may form on NMs, however, in some cases interactions with NOM may be minimal.[49,50] The conditions under which mixed layers form and the influence of those layers on NM behavior has yet to be explored.

NOM coatings on NMs will affect the attachment to surfaces, and therefore both homoaggregation and heteroaggregation described previously. However, determining the interaction between NMs and every type of environmental surface (various clay surfaces, iron oxides, quartz, etc.) is not feasible. The problem may be simplified, however, if the NOM coatings on the NM (and on the environmental surfaces) are relatively coherent. Then all surfaces would be expected to behave similarly and complex heteroaggregation phenomena may be treated as simpler homoaggregation processes, at least to a first approximation. The influence of the underlying NM properties and the NOM−NM interactions on the resulting forces affecting attachment must be determined to test this hypothesis.

In addition to changes in aggregation and disaggregation, interaction with NOM has been shown to reduce short-term bacterial toxicity for fullerenes,[14] Ag(0),[13] and Fe(0),[51] while increasing bioaccumulation in biofilms.[17] In all cases, presumably the NOM had the effect of "masking" the NP effect, either by directly coating the surface or by minimizing dissolution. NOM have also been known to alter surface chemistry, for instance altering ceria NM oxidation state.[24] Changing the redox state of the NM can affect its toxicity and mechanisms of action as described above.

◼ KNOWLEDGE GAPS AND MEASUREMENT CHALLENGES

Engineered NMs in natural systems are subject to a dynamic physical and chemical environment that will drive the particles away from their pristine or "as manufactured" state, toward largely unknown end points and products. Characterizing and predicting environmental transformations can pose a tremendous challenge for several reasons. First, the types of transformations expected will depend on the solution conditions (e.g., pH, redox state, organic matter content, types of serum components present); even slight variations between systems may lead to different behaviors. Second, many of the transformations are dynamic but not readily reversible and therefore the history of the NM will affect its properties and state in the environment. For example, a Ag NP might be readily sulfidized in wastewater treatment plants to a Ag_2S NP.[52] However, the resulting Ag_2S NP is likely stable against reoxidation so release of these particles to an oxic water column might not necessarily result in the thermodynamically predicted end member NP (e.g., AgCl). Similarly, adsorbed macromolecules are almost never at their final equilibrium state

because the arrangement on the surface to reach the final conformation is slow. Third, NMs will likely undergo multiple transformations simultaneously (e.g., interaction with NOM and oxidation or reduction), or successive irreversible transformations (e.g., irreversible adsorption of different proteins upon successive exposures to plasma and intercellular materials).[53] Therefore, answering the question of how a specific NM will behave in the environment requires information about the environment properties and the history of the NM over time scales of interest. We will have to address this using a well-planned (and likely multidimensional) matrix of representative materials and media, as opposed to a case by case basis, because the large number of permutations of NMs and environmental systems makes the latter impossible in practice. Simplification may be possible by measuring transformations in specific representative environments, i.e. environmental and biological matrices, at both short times and long times to capture the end member behaviors expected.

There are many instruments available to measure the properties of NMs such as chemical composition, size, and charge. However, most of these techniques are generally not capable of measuring these properties in situ and in vivo or in environmentally relevant concentrations and conditions. Equally importantly, methods are needed to better track the rate and extent of transformations of NMs under realistic conditions, especially for those where multiple transformations occur. Method validation and development are required to take this forward and greater collaboration between metrological and analytical researchers with environmental scientists and environmental chemists is needed. In some cases, transformations of NMs will occur over time scales of months or years. Understanding these transformations completely will require an ability to recover the NMs from environmental and biological matrices and measure the properties of these partially transformed NMs, or to measure them in vivo/in situ. A recent NRC report provides more specific suggestions for tools and instrumentation that are needed to advance nano EHS research.[8]

◼ IMPLICATIONS OF NM TRANSFORMATIONS ON NANO EHS RESEARCH

Transformations of NMs will readily occur in the environment and in vivo, which greatly affects their properties, behavior, and effects. However, most toxicity, fate, and transport studies to date have used relatively pristine materials, which will behave differently than the transformed ones. While the effects measured for relatively pristine materials may be representative of human exposures occurring at manufacturing or processing sites where direct exposure to relatively pristine NMs is possible, environmental exposures to aquatic organisms and to humans (e.g., via drinking water or food ingestion) will be to transformed NMs so data regarding fate and effects of pristine NMs may not be particularly informative. The research community instead needs to focus on understanding the reactivity, fate, mobility, persistence, and effects of the "aged" or transformed NMs where the "aging" process best represents the history of the NM prior to the exposure.

Environmental exposures to NMs are likely to be chronic and at low concentration. Therefore, slow transformations of NMs will need to be assessed to understand the ultimate fate and distribution in the environment and potential for harmful effects. Some transformations, e.g. adsorption of biomacromolecules or dissolution of metal NPs, are fundamental processes

that will affect NM behavior both in the environment and in vivo. Virtually nothing is presently known about the *rates* of these transformations under relevant conditions. Determining the potential for these fundamental processes to occur, and the rates of these processes, should be a research priority because advances in this area will benefit multiple nano EHS research communities, e.g. fate and transport, toxicology, and sustainable/green nanotechnology.

Classifications of NMs are desirable for regulatory purposes. Because most NMs are highly reactive, and because those transformations dramatically affect their fate and effects, it may be possible to classify NMs, at least in part, by their expected environmental transformations, although incorporating this into current legislation and regulatory practice will be challenging. Some NMs may require more than one classification depending on the environment in which they reside. Transformations can lead to materials that can be more heterogeneous than the parent NM, making characterization difficult. However, it is also possible that transformations may decrease heterogeneity if ubiquitous transformations (e.g., coating with humic acids, NOM, or proteins, or sulfidation) lead to NMs with behaviors that are less influenced by the NM core than by the coating. Transformations and the properties of the transformed NM will ultimately depend on the environment that they enter, and on the order of the environments in which they are exposed. This fact, and the uncertainty regarding use and release scenarios, makes the determination of risk challenging.

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Notes
The authors declare no competing financial interest.

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