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Novel Applications of Nanoparticles in Nature and Building Materials

Juyoung Ha

Abstract

Nanoparticles are assemblies of atoms in the size range less than 100 nanometers. At these length scales, the properties of particles may deviate significantly from those of the equivalent bulk material indicating that changes in physical and chemical properties of materials depend on the dimensions of the particle. The presence of mineral nanoparticles has been reported in a range of natural environments. Such nanoparticles can arise from a variety of mechanisms, including chemical weathering processes, precipitation from relatively saturated solutions in hydrothermal and acid mine drainage environments, evaporation of aqueous solutions in soils, and biological formation by a variety of different microorganisms. Furthermore, recent increased applications of nanoparticles in different types of industries, including construction and building material manufacturing, have caused prevalent occurrences of different types of synthetic nanoparticles in the environment. In this chapter, a comprehensive reviews on occurrences and observations of naturally and anthropogenically generated nanoparticles in the environment and their characterization techniques will be discussed along with directions and suggestions for the future research topics and areas for nanomaterials.

Keywords: nanoparticle, nanotoxicity, geopolymer, Scanning transmission X-ray microscopy (STXM), X-ray absorption fine structure (XAFS)

1. Introduction

Nanoparticles (NPs) are assemblies of atoms in the size range less than 100 nanometers (i.e., one nm = billionth of a meter, which is roughly ten times the size of an individual atom). Apart from size, NPs may also be classified by of their physical parameters, such as electrical charge, chemical characteristics, shapes, and origin (natural vs. artificial). Regardless of how NPs are classified and defined, at these length scales, the properties of particles may deviate significantly from those of the equivalent bulk material indicating that changes in physical and chemical properties of materials depend on the dimensions of the particle. For example, at the surface of nanoparticles, significantly greater fractions of atoms are expected to be exposed and disordered rather than confined in the bulk crystalline structure for nanoparticles. This structural modification causes the nanoparticles to be more reactive and prone to greater dissolution than the bulk materials. In addition, thermodynamic analyses illustrate that adsorption on smaller particles decrease the

free energy and the activation energy barrier of the system to a greater degree than adsorption on larger particles; thus, the driving force for adsorption onto smaller particles is larger and more favored. As a result, NPs possess higher surface reactivities than larger particles of the same phase, subsequently affecting the metal and organic ion availability and sequestration much more significantly than the larger particles of the same phase. However, more work still is needed to fully understand the chemical reactivity dependence on the particle size and the impact of the nano-sized particles in the environment.

The presence of mineral nanoparticles has been reported in a range of natural environments. Such nanoparticles can arise from a variety of mechanisms, including chemical weathering processes, precipitation from relatively saturated solutions in hydrothermal and acid mine drainage environments, evaporation of aqueous solutions in soils, and biological formation by a variety of different microorganisms [1–9]. When compared with larger particles of the same material, mineral nanoparticles possess a number of unique and potentially important physical, chemical, and magnetic properties. Interestingly, while a number of these unique features of mineral nanoparticles have been extensively studied with respect to their applications in the medicine, pharmacotherapies, semiconductor, microelectronics, and catalysis industries, comparatively little is known about the properties of nanoparticles with respect to their potential importance in natural environments (e.g., enhanced adsorption coefficients and chemical reactivities). Recent studies have reported a ubiquitous presence of different types of nanoparticles in virtually all water domains, including the oceans, surface waters, groundwater, atmospheric water, and even treated drinking water [10–16]. Wigginton et al. [17] reported these naturally occurring environmental nanoparticles can play a critical role in determining an important chemical characteristics and the overall quality of natural and engineered waters. Moreover, aquatic nanoparticles have the ability to influence environmental and engineered water chemistry and processes in a much different way than similar materials of larger sizes. Zhu et al. [18] reported toxic effects of a range of metal oxide nanoparticles on zebra fish while Li et al. [19] investigated ecotoxicological impacts of metal oxide nanoparticles released to aquatic environments on *Ceriodaphnia dubia*, a species of water flea. They reported chronic exposure of nanoparticles induced a significant increase of severe stress response. Pakrashi et al. [20] also reported that the aluminum oxide nanoparticles play a significant role in the cytotoxicity towards freshwater algae. They identified that the surface charge driven interaction between the aluminum oxide nanoparticles and the cell surface functional groups are the dominating reaction mechanism resulting in the cell membrane damage and increased oxidative stress. Their study also elucidated the dissolution of the nanoparticles and release of Al^{+3} ions into the solution caused enhanced cytotoxicity. The particle aggregation of NPs and ion release from the nanoparticles will significantly alter the solution phase dynamics and the subsequent change will cause challenging ecological problems in understanding the impact of NPs in an environmental matrices.

At a broader Earth ecosystem scale, naturally occurring iron nanoparticles have been found to significantly impact global biogeochemical of various metals and metalloid ions [21]. Iron nanoparticles are of particular interest since iron oxide nanoparticle surface chemistry and the subsequent reactions within the interface between the water and iron nanoparticles determine the long-term fate and transport behavior for nutrients and pollutants in natural systems [22–24]. Iron oxide nanoparticles have been shown to be an effective agent for hazardous waste site remediation [25]. Tagliabue et al. [26] have shown that iron nanoparticles can drive primary productivity of the ocean where its biogeochemical systems rely primarily on iron and suggested that iron nanoparticles can play an integral role

in global ocean biogeochemistry. Nowack and Bucheli [27] also provided evidence of ubiquitous presence of nanoparticles including those engineered ones in the aquatic environments and presented comprehensive results from ecotoxicological studies to show that only certain nanoparticles have effects on organisms under environmental conditions, though mostly at elevated concentrations. They argued that the assessment of the risks posed by nanoparticles in the environment should be re-considered and re-evaluated especially when the current available technology and analytical tools lack to measure materials in the nanometer scale. Recent article by Hyden et al. [21] reviewed the current analytical approaches that can be used to characterize natural Fe nanoparticles using a synchrotron-based X-ray spectro-microscopic techniques (more details in section). They measured suspended Fe nanoparticles collected from fluvial, marine, and lacustrine surface waters. They successfully identified different oxidative state Fe into ferrous, ferric and magnetite classes of Fe nanoparticles (10–100 nm). The heterogeneity of iron oxidation state within the collected samples was attributed to the possible presence of nanoparticle aggregates, and to the low degrees of crystallinity and ubiquitous presence of impurities in natural samples. Their results provided an important baseline for natural nanoparticle speciation in pristine aquatic systems and elucidated the importance of inter-particle variability, which should be considered as an important variable for making accurate biogeochemical models. Furthermore, their study suggests that the fate of released engineered or natural Fe nanoparticles must be considered as a time dependent kinetic reactions as they evolve and transform in natural systems.

This review covers recent advances made in identifying nanoparticles in aqueous phase from a variety of sources, and advances in understanding their very interesting properties and reactivity that affect the chemical characteristics and behavior of natural water and soil. More specifically, an overview of recent scientific advances enhancing the understanding of the (i) sources and (ii) fate of nanoparticles, (iii) the effects of nanoparticles in simplified studies, and (iv) how nanoparticles interact with biota in a more complex environment will be discussed.

2. Naturally occurring nanoparticles

From an environmental perspective, one of the most important features of mineral nanoparticles is their high characteristic surface area, which potentially allows them to act as powerful sink of contaminant ions through sorption processes. Higher mobility of nanomaterials in the environment is expected due to its colloidal properties and it implies a greater potential of exposure and persistence for nanomaterials in the environment. Classical thermodynamic forces such as attractive London-van der Waals and attractive or repulsive electrical double-layer forces (e.g., the classic Derjaguin, Landau, Verwey and Overbeek or DLVO forces) that are known to influence particle attachment deviate significantly when particle size gets small in the nanometer range as shown in **Figure 1**. The stability of colloidal nanoparticles is greatly influenced by the presence of adsorbed natural organic matter. Without any functionalized surface modification in water, colloidal nanoparticles will tend to grow to become larger particles through aggregation and flocculation in order to stabilize the disordered structure of surfaces and to reduce the excess surface energy. Hence, understanding the surface reactions on nanoparticles are of particularly important and deserve more investigations as current models and predictions do not apply and cannot accurately predict the fate and transport of the nanoparticles in the environment.

This review attempts to investigate the environmental impacts of naturally occurring nanoparticles by studying their unique properties and sorption reactions

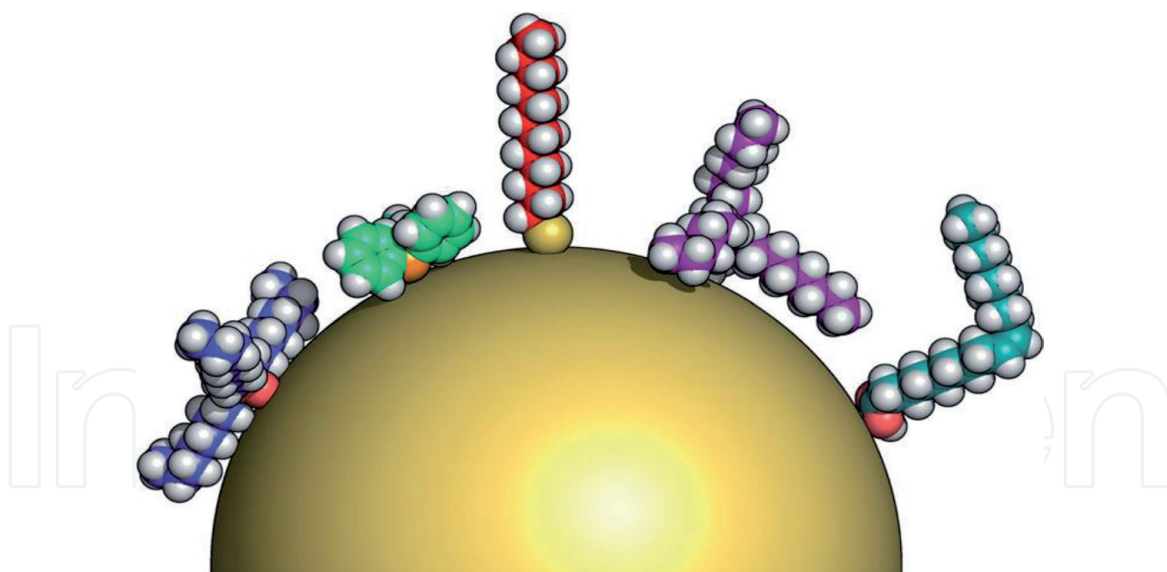


Figure 1.
A nanoparticle of 5 nm core diameter with different organic molecules drawn to scale.

with various environmental constituents and by comparing those results of the nanoparticles to that of microparticles to elucidate the role of nanoparticles in the environment. A wide range of nanoparticle phases has been reported in various environmental conditions as shown in **Table 1**. Of particular, the dependence of aquatic chemical reactivity of iron oxides on particle size is important because iron oxide plays a key role in the geocycling of elements, rock weathering and soil formation, as well as in the transport of aqueous metal species and contaminants. Iron oxide clusters are also found in living organisms (e.g., plants, bacteria, molluscs, fish, birds, and humans). They are also applied to (nano)technologies, including alternative energy, catalysis, electronics, optoelectronics, memory devices, corrosion protection, cleaning of waters and control of acid mine drainage, radioactive waste storage and disposal, flotation, pigments, magnetocaloric refrigeration, colour imaging, biochemical engineering, sensors, and other surface-based

Solid Phase	Typical size (nm)	Shape	Environments	Reference
Ferrihydrite	2–10	Irregular and spherical	Oxic surface water and soils, bacterial surfaces	[28]
Goethite	A few nm to micrometer	Acicular	Soils, water	[28]
Hematite	A few nm to micrometer	Rounded or platy	Oxic water, bacterial surfaces	[28, 29]
Magnetite	Several nm	Octahedron	Anoxic soils and sediments	[28]
Glauconite	A few nm to 100 nm	Acicular	Anoxic soils and sediments, bacterial surfaces	[28, 30]
Gold	< 200 nm	Platy	Groundwater, mining pits	[31]
Aluminum Oxide	< 200 nm	Rounded or platy		[32]
Manganese Oxide	A few to hundreds nm	Rounded or platy	Bacterial surfaces, anoxic soil and water	[33, 34]

Table 1.
Examples of naturally occurring nanoparticles in various environments.

applications. Such wide diversity in occurrence and application of iron oxides stems from the richness of their physical, chemical, and structural properties with continuous or sudden change between them, which in turn originates from the transition character of iron and the complex crystal and electronic structures of its compounds.

2.1 Iron oxide nanoparticles

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is one of the most naturally abundant iron oxide mineral phases [12, 22–24, 28]. It is also commonly present in a nanoparticle form, occurring in soils, acid mine drainage effluent, and on bacterial surfaces as well as in atmospheric dusts (**Figure 2**). Iron is one of the essential element in governing the biogeochemical cycling of nutrients in marines and sedimentary environments. During the iron cycling process in those environment, various nanostructures of iron oxides and oxyhydroxides form and persist under certain conditions, especially at redox and pH interfaces [29]. Recent surveys on the global budget of naturally occurring iron oxide nanostructures suggest 105 Tg (teragram) of iron oxide including hematite phase is introduced annually in soil by mass [30]. The ubiquitous existence of hematite nanoparticles has a significant implication on fate on toxic heavy metal contaminants. For example, heavy metals such as Cr and U that are introduced to environments by anthropogenic activities such as mining and spills can be effectively sequestered by iron oxide nanostructures through sorption and precipitation reactions due to the thermodynamically active nanomorphologies and crystallinity of the nanoparticulate phase. It has been shown that the adsorption capacities of Cr and U by ferrihydrite decrease remarkably with either increasing

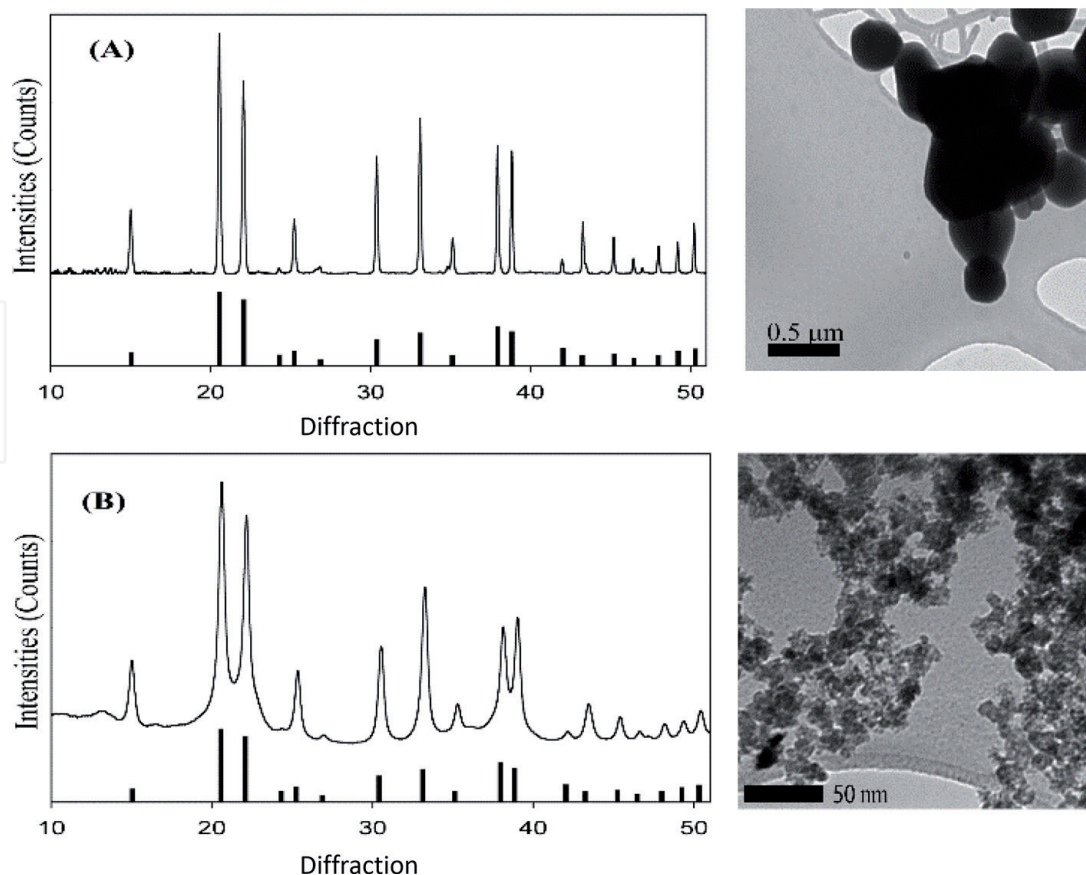


Figure 2. (A) Powder X-ray diffraction pattern of hematite microparticles (HM) compared with the reference XRD pattern of hematite and the TEM image of HM; (B) Powder X-ray diffraction pattern of hematite nanoparticles (HN) compared with the reference XRD pattern of hematite.

crystallinity or transformation to more crystalline phases (such as goethite or hematite) further confirming the effectiveness of the nanoparticle phases in contaminant removal [31–33].

Moreover, hematite nanoparticles recently has received much attention from industry for different applications due to their unique properties, such as extremely small size, high surface-area-to-volume ratio, surface modifiability, excellent magnetic properties and great biocompatibility. A range of environmental clean-up technologies have been proposed in wastewater treatment which applied iron oxide nanomaterials as nanosorbents and photocatalysts [34]. Nanoscale zero-valent iron (nZVI) is an example of extensively applied iron nanomaterials for groundwater and hazardous waste treatment. Over the past decade, nZVI synthesis and application have been comprehensively investigated for its remediation applications focusing on enhanced sequestration of a wide spectrum of contaminants in addition to the well-documented chlorinated solvents both in the laboratory and field experiments [25, 32, 35–37]. At least 50 successful field applications of nZVI for in-situ groundwater and soil cleanup worldwide were reported by recent reviews by Karn et al. [38] and Mueller et al. [39]. As the application of the nZVI gained more attention, colloidal stability and transport properties of nZVI in porous media, and the effects of nZVI amendment on the biogeochemical environment were also studied in order to understand the impacts of the nZVI in the environment once released [25, 35, 40]. Dong et al. [40] observed the presence of humic acid increases the stability of nZVI in the aqueous phase due to enhanced the electrosteric repulsion effect but it can also cause coagulation among nZVI particules via bridging effect if too much humic acid is present. Hence, the nanoparticle stability and transport behavior depends on the concentrations of other environmental constituents, especially organic acids, both in aqueous and soil environments. Further studies are needed to enhance the colloidal stability and transport properties of nZVI in porous media to fully understand effects of nZVI on the biogeochemical environment.

Lastly, iron oxide nanoparticles have received a great attention recently in biomedical applications due to their non-toxic role in the biological systems [41–43]. Iron oxide nanoparticles have both magnetic behavior and semiconductor property, which lead to multifunctional biomedical imaging applications. According to Chen et al. [41] gold coated nanoparticle of iron oxide has enhanced magnetic properties compared to the same phase of larger particles. Cheong et al. [43] similarly reported greater cellular MRI contrast enhancement of nanoparticles compared to iron oxides of a bigger size without increase in cytotoxicity. Iron oxide nanoparticles also became popular for its application in biomedical fields as antibacterial, antifungal and anticancer agents as well as bone marrow treatments and cell labelling activities for its unique biocompatibility, biodegradability, ease of synthesis and different magnetic behaviors [44].

In addition to the above reported laboratory synthesized nanoparticles, iron oxide nanoparticles exist in nature at low-temperature environmental conditions and places that have high degrees of supersaturation. The supersaturation condition is typically created by changing the physical and chemical conditions, such as influx of Fe(II)-rich hydrothermal vent fluids, mixing of highly acidic solutions with neutral pH water, and the evaporation of soil solutions [12, 22–24, 45, 46]. Once formed, iron oxide and oxyhydroxide nanoparticles are redistributed by rivers, glaciers, winds, and ocean currents into various ecosystems, where they can undergo continuous phase transformations, dissolution, and morphology changes. One potentially important role played by naturally occurring hematite nanoparticles is their interaction with various types of organic acids. In many natural environmental settings, ubiquitous presence of naturally occurring low-molecular weight (LMW) organic compounds and nanoparticles often controls the fate and transport

behavior of many heavy metal contaminants by sorption and/or co-precipitation processes. For example, mobile nanoparticles can serve as carriers for strongly sorbed contaminants and thereby facilitate contaminant transport in soils, groundwater aquifers, and fractured rocks [21, 25]. The colloidal stability of nanoparticles is greatly influenced by the presence of adsorbed natural organic matter. Recent studies have suggested that sorption of organic acids can dramatically enhance the particle-based transport of heavy metal contaminants by physically stabilizing contaminant-containing nanoparticles in aquatic environments [47, 48]. In addition, the organic matters typically bind strongly to common iron- and aluminum-(oxy)hydroxide minerals as well as to heavy metal contaminants (e.g., Pb, Hg, Cr, and Zn) under circumneutral to moderately acidic pH conditions [47, 49, 50]. Therefore, the nature of bonding between organic species and nanoparticle surfaces can substantially alter the properties of mineral nanoparticle-water interfaces and thereby affect the geochemical cycling of metals.

Ha et al. [51] studied the interaction of the L-lactate ion ($\text{L-CH}_3\text{CH(OH)COO}^-$, Lact^{-1}) with hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticles (average diameter 11 nm) in the presence of bulk water at pH 5. Their combined dissolution and ATR-FTIR spectroscopy data suggested different hydrogen bonding environments was found as Lact^{-1} surface coverage on hematite nanoparticle surfaces increases which resulted in a concomitant increase in Fe(III) dissolution from the hematite nanoparticles due to the inner-sphere complex formation as shown in **Figure 3**.

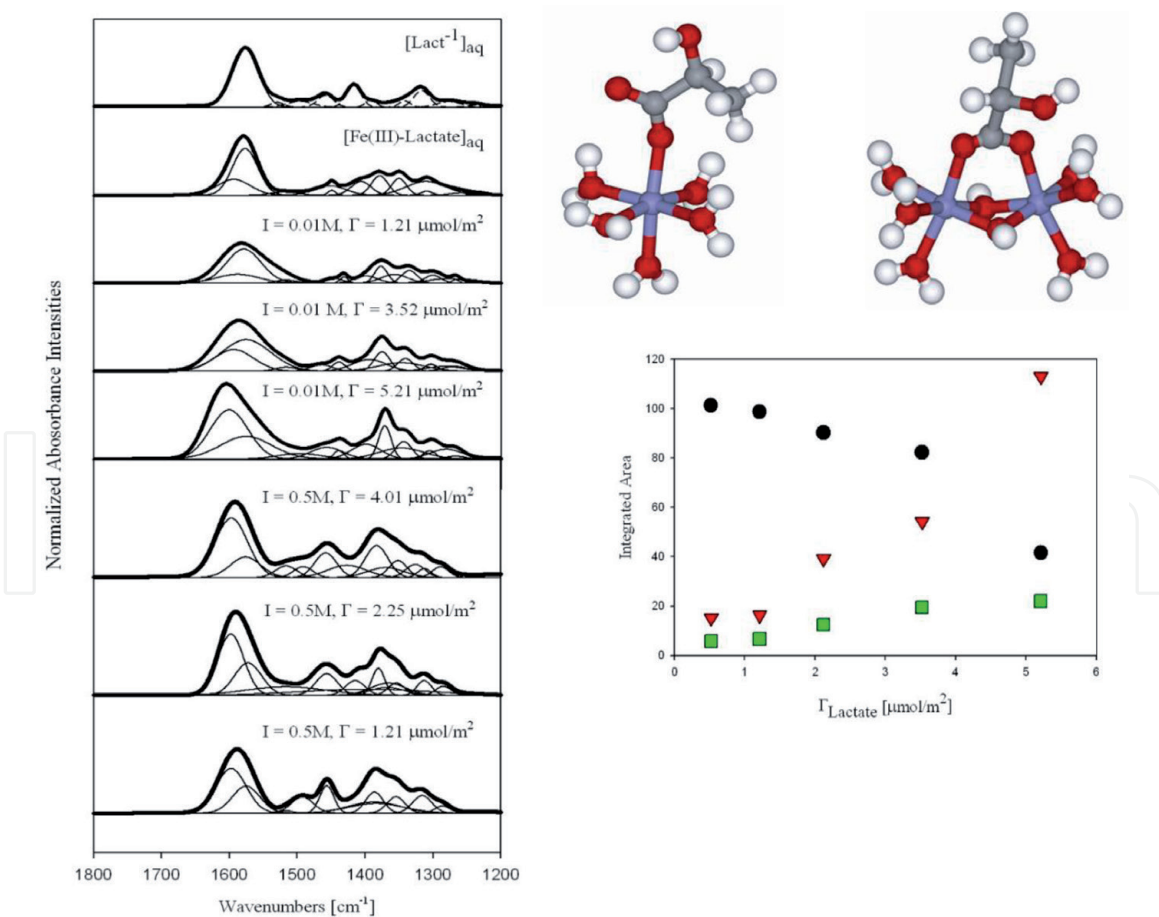


Figure 3. (Left) Fit of ATR-FTIR spectra of aqueous deprotonated lactate species, aqueous Fe(III)-lactate complex, and Lact⁻¹ species at the hematite/water interface at 25°C, pH 5.0 and 0.01 M and 0.5 M of NaCl for different Lact⁻¹ surface coverages. (Top Right) Molecular model for Lact⁻¹ sorption on monomer and dimeric Fe cluster unit. (Bottom Right) Fit of ATR-FTIR spectra of aqueous deprotonated lactate species, aqueous Fe(III)-lactate complex, and Lact⁻¹ species at the hematite/water interface at 25°C, pH 5.0 and 0.01 M and 0.5 M of NaCl for different Lact⁻¹ surface coverages demonstrating different surface complexation

Lenhart et al. [52] also reported the impacts of fumaric acid and maleic acid, which are naturally occurring dicarboxylic acids, on aggregation kinetics of nano-sized hematite. Interestingly, they found that the structure and orientation of the adsorbed dianion at the hematite surface, not the adsorption mechanism, defined the resulting effect. Maleate, which directed both carboxyl groups to the surface in the form of inner- and outer-sphere surface complexes, enhanced colloidal stability. Fumarate, however, which bounded to the hematite surface as an outer-sphere complex with just one carboxyl group only slightly influenced particle stability. Their research outcome suggested that subtle differences in the structure of adsorbed acids produced important differences in the physicochemical behavior of particles in dilute aquatic systems. Another study by Dickson et al. [47] similarly suggested that the surface chemical reactions and dissolution of the iron oxide nanoparticles strongly depend on the presence of organic molecules. They found significantly increased aggregation and sedimentation reactions of iron oxide nanoparticles in presence of humic acids regardless of different ionic strength of the solution. Their results suggested that understanding the effects of important environmental factors on the stability of nanoparticles is key to fully and accurately be able to predict the mobility of the nanoparticles in aquatic environment.

On the contrary, Palomino and Stoll [53] identified that iron oxide nanoparticle aggregation process significantly depends on the solution pH conditions even in the presence of fulvic acids. Dispersion and stability of the nanoparticles were maintained only at pH conditions of which the surface charge of the nanoparticles remained positive regardless of the fulvic acid concentrations. Their results showed that the examined environmentally relevant range of fulvic acid concentrations were expected to promote not only the nanoparticle stabilization but also the disaggregation of nanoparticle aggregates, but only at very low concentrations of fulvic acid and specific solution pH conditions. This finding suggests that hematite nanoparticle behavior in natural aquatic environments are much more complex and dynamic that it cannot generalized or linearly predicted based on a single parameter. A recent study by Xu et al. [50] presented laboratory experimental results to simulate more environmentally relevant conditions by investigating the hematite nanoparticles coated with naturally found peat humic acid and soil humic acid. Their model system reflects the fact that hematite nanoparticles exist naturally and ubiquitously in soil, and they are always associated with soil organic matter by forming organic–inorganic complexes. In this work, the organic coated hematite nanoparticles reacted with hydrophobic organic contaminants (HOCs) to simulate the sorption processes in soil. The sorption of HOCs on organic acid coated nanoparticles were inhibited with increasing pH values of solution due to the deprotonation reaction of the organic acid functional groups within the adsorbed humic acids. Their findings further elucidated the mechanisms involved in contaminant sorption processes by organic acids coated hematite nanoparticles are complex reactions governed both by the surface complex structures formed within the mineral-water interfaces as well as the solution chemistry of the aquatic environments. Results on sorption of a commonly occurring pollutant, Zn(II), on hematite nanoparticles in presence or absence of dicarboxylate organic compound, oxalate, also identified the complexity of the nanoparticle reactions with naturally occurring constituents [54, 55]. At higher concentrations of Zn(II), formation of surface precipitates on hematite nanoparticles was observed based on comparison of the EXAFS spectra of the sorption samples with that of zinc-bearing hydroxalcalcite ($\text{Zn}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$), Cauchy wavelet analysis, and fitting of the Zn K-edge EXAFS data. On the contrary, no surface precipitate was observed on the bigger size hematite particles even at the same concentrations of Zn(II) suggesting enhanced dissolution of hematite nanoparticles was promoted by the divalent metal ions in

solution (**Figure 4**). Similarly, different types of Zn(II) surface complex structures formed in the presence of oxalate on hematite nanoparticle surfaces. These studies provide a direct comparative and quantitative evidence that different surface chemical reactions on hematite nanoparticles persist.

There are still many open questions regarding the ability of surface reactions to alter the fate and toxicity of nanoparticles in the environment. Evidence so far suggests that surface coatings and complexation with organic acids affect nanoparticle fate and transport mechanisms hence consequently impact nanoparticle toxicity in the environment. However, as surfactant adsorption on silica nanoparticle studies revealed that such surface complexation reaction can be readily reversible so that desorption can be kinetic reactions whereas adsorption for high molecular weight polymers is essentially an irreversible process [56, 57]. Clearly, the fate of nanomaterials in the environment is highly dependent on their surface coatings and reactions, hence, it is imperative to understand the fate of these coatings and surface reactions of organic matter with nanoparticles in the environment.

2.2 Nanoparticles and microorganisms

Bacteria can be considered as another extension of organic compounds in the natural environment. Similar to LMW organic acids, they have been shown to exhibit a strong affinity for heavy metal contaminants and metal (oxyhydr)oxide surfaces through reactions such as sorption, bioaccumulation, and precipitation [52, 58–60]. With their estimated biomass close to the total amount of carbon in plants [61], they can potentially passivate naturally occurring mineral surfaces

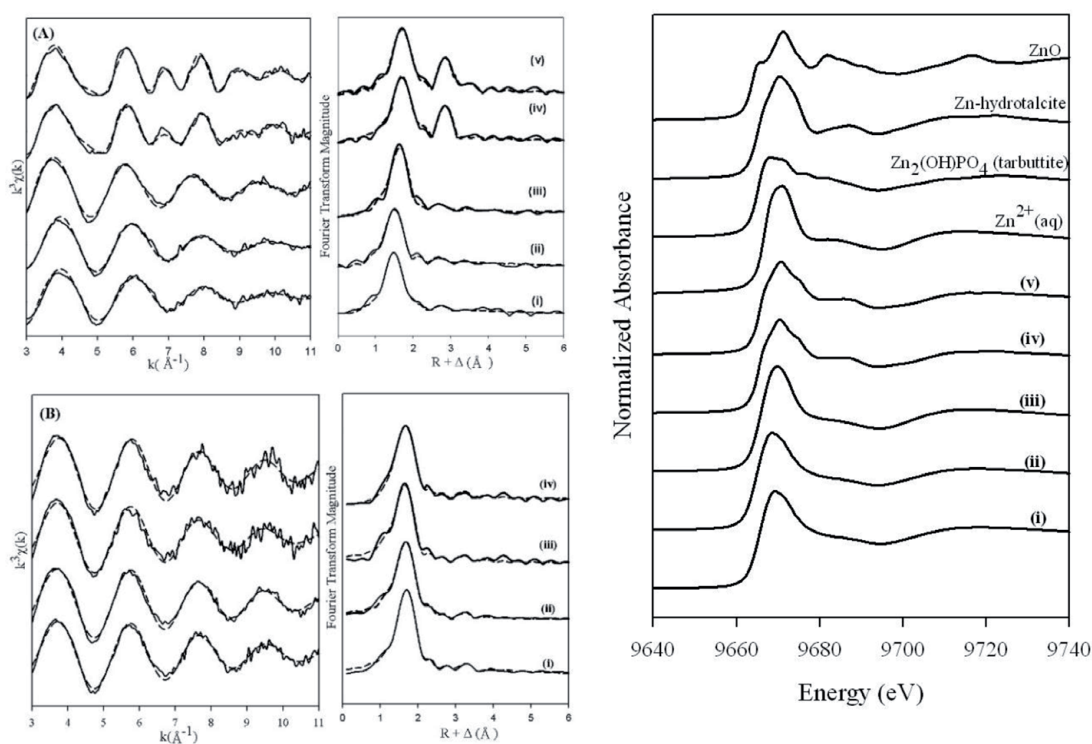


Figure 4.

(Left) (A) Background-subtracted, normalized, and k^3 -weighted Zn K-edge EXAFS spectra of Zn(II) sorbed on hematite nanoparticles (HN) at different Zn surface coverages, and corresponding Fourier transforms (not phase-shift corrected) of sorption samples with following surface concentration: (i) 68.35 micromol/g; (ii) 195.80 micromol/g; (iii) 384.92 micromol/g; (iv) 568.49 micromol/g; (v) 640.19 micromol/g; (B) Background-subtracted, normalized, and k^3 -weighted Zn K-edge EXAFS spectra of Zn sorbed on hematite microparticles (HM) at similar Zn surface coverages, and corresponding Fourier transforms (not phase-shift corrected) of sorption samples. (Right) Zn K-edge XANES spectra of Zn/HN sorption samples and four reference compounds: (i) 68.35 micromol/g; (ii) 195.80 micromol/g; (iii) 384.92 micromol/g; (iv) 568.49 micromol/g; (v) 640.19 micromol/g.

either hindering or enhancing the reactivity of the underlying mineral surfaces. The resulted the cell-mineral surface interactions occurring in natural soil and water environments can retain pollutants in great extent [62, 63]. Therefore, the presence of microorganisms can result in significant modification of metal speciation or contaminant sequestration and transport, and hence, investigating the interfaces of bacteria-metal and bacteria-mineral surfaces is essential in predicting the mobility of heavy metal contaminants accurately and quantitatively.

More importantly, understanding the dynamics of the bacterial interaction with engineered and/or naturally occurring NPs have received significant attention because the fate and transport reactions and mechanisms of them in the terrestrial and aquatic environments strongly depend on the nature and extent of the bacterial sorption and reduction of the nanoparticles [64]. For example, Schwegmann et al. [65] observed iron oxide nanoparticle sorption on microorganisms (*Saccharomyces cerevisiae* and *Escherichia coli*) significantly shifted the point of zero charge for bacteria. Their results imply that overall electrostatic interaction between dissolved heavy metal contaminants and bacteria can be considerably altered due to the presence of the nanoparticles. Another study showed an enhanced removal of the heavy metals from the solution phase in conventional activated sludge wastewater treatment plants when nanoparticles were added to reactors including different types of bacteria. This study suggested that the production and transformations of the surface properties of biomass due to NP would be key factors in determining the fate of the waste toxic metals in the environment [66]. Droz et al. [67] observed biogenic MnO₂ nanoparticles affected a wide range of metal fate and transport in natural and engineered systems by strongly sorbing metals ions.

Of particular importance, the dissimilatory microbial iron reduction is one of the important processes in determining the biogeochemical cycling of iron under anaerobic conditions and has significant influences on the aqueous geochemistry and mineralogy of sedimentary environments [68, 69]. Iron cycling has dramatic implications for trace element and heavy metal contaminant mobility, and the complex interplay of biological and chemical processes determine the extent and reaction pathways of iron cycling in the environment [69]. Past studies have identified many different chemical and biological factors controlling the microbial reduction of iron oxides, yet the role of nanoparticles in determining the extent and reaction pathways for dissimilatory iron reduction are still poorly understood. Despite the important roles of nanoparticles, current molecular-level understanding on the interaction of organic compounds, metals, and microorganisms with nanoparticle surfaces and the resulting impacts on pollutant speciation at nanoparticle-water interfaces are very limited. One of the main reasons for this limitation is lack of appropriate tools with high resolution and/or high sensitivity to molecular structural changes occurring on nanometer scales. In addition, ability to study the materials in situ, i.e., in presence of water with minimal alteration of the sample from its natural state, has been limited. For many environmental samples, especially those involving interactions at solid-water interfaces, the presence of water plays a critical role.

Due to the small size of particles, different mechanisms and processes have been observed when bacteria interacts with nanoparticles. For example, a greater bio-availability of iron was observed when iron nanoparticle reacted with *Pseudomonas mendocina* bacteria [70] because of the possible penetration of the nanoparticles through the cell membrane and proximity of the particles to the bacteria. Sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) also showed different metabolic responses in presence of iron oxide nanoparticles and generated biogenic pyrrhotite formation suggesting a potential impact of iron oxide nanoparticles on geomagnetic

field behavior of sediments. Different dissimilatory reduction of hematite nanoparticles and microparticles were also observed for *Shewanella oneidensis* bacteria [71]. Results show that proximity and encapsulation of the nanoparticles near the cell membrane allowed different iron oxide reductive mechanisms resulting in a significantly enhanced iron oxide reductive transformation rates by *Shewanella oneidensis* (Figure 5). Clearly different reaction pathways and microbial responses toward nano-meter materials are present compared to the larger particle size even for the same mineral phases.

Nanoparticles are also generated by a biogenic enzymatic process and used as engineered materials. The development of eco-friendly technologies in material synthesis has become important and widely applied. Synthesis of nanoparticles using different microorganisms, and their applications in many cutting-edge technological areas have been explored. Recent study shows that biogenically generated iron(III) (oxyhydr)oxide ($\text{Fe}(\text{OH})_3$) clusters by gram positive bacteria *Clostridium* could be used to create lithium storage capacity [72]. This study provides another potential use of hematite nanoparticles as a substitute for an industrial product. Other studies also have found that many microorganisms can produce different types of inorganic nanoparticles through either intracellular or extracellular routes, and such biosynthesized nanoparticles have been used in a variety of applications including drug carriers for targeted delivery, cancer treatment, gene therapy and DNA analysis, antibacterial agents, biosensors, enhancing reaction rates, separation science, and magnetic resonance imaging (MRI) [50, 73–75]. As shown, there have been tremendous developments in the field of microorganism-produced nanoparticles and their applications over the last decade. However, much work is needed to improve the synthesis efficiency and the control of particle size and morphology.

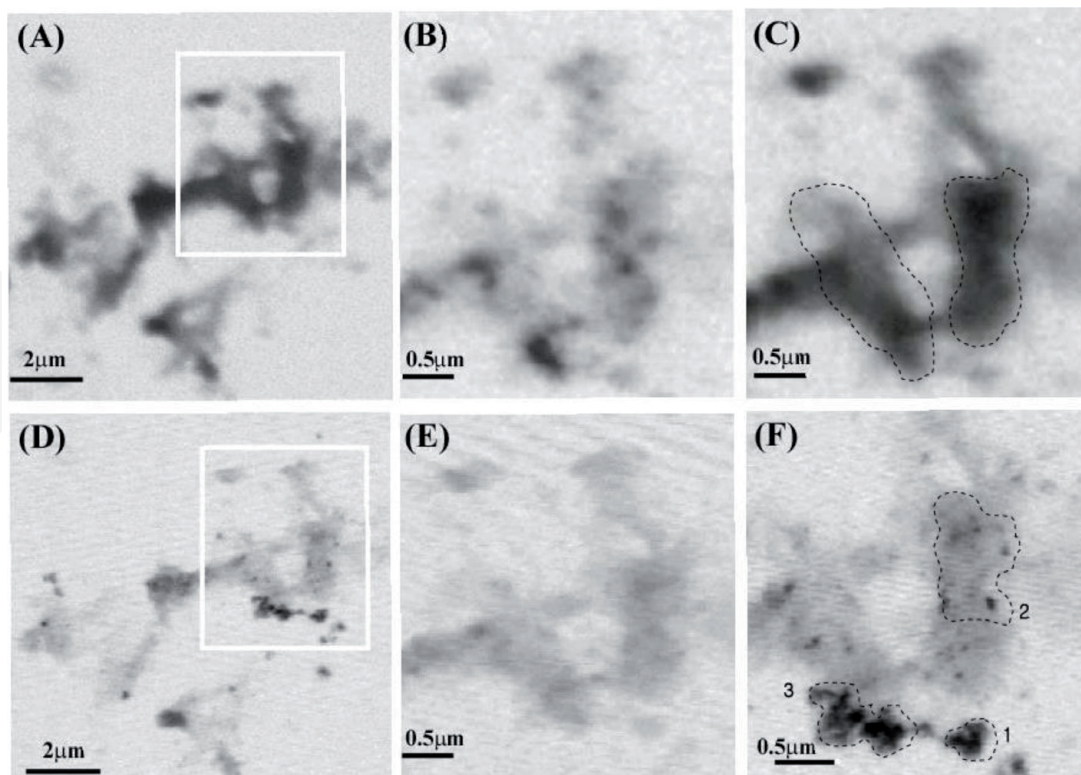


Figure 5. STXM images of *S. oneidensis* WT strain and hematite nanoparticle reacted for 98 hr under anaerobic condition at initial hematite concentration of 1mM in an aqueous suspension measured at (A) C K-edge (288.2 eV) and (D) Fe L-edge (709.5 eV). The outlined areas labeled in (A) and (D) are shown in higher magnification at (B) below C K-edge (280.0 eV), (C) C K-edge (288.2 eV), (E) below Fe L-edge (700.0 eV), and (F) Fe L-edge (709.5 eV).

2.3 Spectroscopic and theoretical tools used to study nanoparticle-water interface

Synchrotron-based [32, 54, 55, 71]. X-ray absorption spectroscopy (XAS) is one of the most structurally and chemically sensitive tools probing solid-water interface [32, 54, 55, 71]. It has been used in many different scientific research fields such as material sciences, chemistry, and environmental sciences [76–79]. Because XAS is non-destructive and element sensitive, it allows to probe the interface between the solid and liquid phases in-situ to elucidate the chemical coordination of metal ions in many different matrices. Furthermore, XAS can simultaneously characterize both the amorphous and crystalline portions of samples which makes it to be one of the most suitable tools to investigate biological and environmental samples because many samples involving nanoparticles and/or environmental matrices are often either non-crystalline or in a solution matrix [80–82]. Much advances in molecular understanding of the interactions of ions in solution with nanoparticle surfaces and the structures of complexes are made since XAS has been used as a research tool. XAS spectroscopy consists of two different complimentary techniques, extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) [76, 78, 80, 83–85]. XANES provides information on the oxidation state, three-dimensional geometry, and coordination environment of the element under investigation while EXAFS provides information on the coordination environment and nearest neighboring atoms to the atom of interest. Of particular, the Extended X-ray absorption fine structure (EXAFS) analyze the oscillatory variation of the X-ray absorption as a function of photon energy beyond an absorption edge. The absorption, normally expressed in terms of absorption coefficient (μ), can be determined from a measurement of the attenuation of X-rays upon their passage through a material. When the X-ray photon energy (E) is tuned to the binding energy of some core level of an atom in the material, an abrupt increase in the absorption coefficient, known as the absorption edge, occurs. For isolated atoms, the absorption coefficient decreases monotonically as a function of energy beyond the edge. For atoms either in a molecule or embedded in a condensed phase, the variation of absorption coefficient at energies above the absorption edge displays a complex fine structure called EXAFS. This is how EXAFS can be used to probe the molecular sorption complex of different metal ions on various surfaces.

In the last 15 years, X-ray absorption spectroscopy (XAS) has found wide application in determination of the local atomic and electronic structures of absorbing centers (atoms) in materials science, physics, chemistry, biology, and geophysics. With its elemental specificity and ability to determine the molecular-scale speciation in situ even at the parts per million concentration range, EXAFS has become a useful method for the analysis of environmentally relevant elements in natural sediment and soils, and in laboratory model system studies involving nanoparticles [83, 86–88]. Quantitative measures of interatomic distances and coordination numbers for the first and second coordination neighbors around specific elements can be obtained based on EXAFS analysis, and these information, especially of the second-shell coordination, provide the means to construct surface complex structures in which an adsorbate ion is bonded to a sorbent surfaces. Sheng et al. [89] studied nanoparticle zero-valent iron (NZVI) interaction with uranium using EXAFS. They found that reduction of highly toxic and mobile UO_2^{2+} into less toxic and mobile UO_2 could be enhanced using NZVI. Their EXAFS analysis provide evidence to support the proposed detailed reaction mechanisms the iron nanoparticles sequester insoluble products like UO_2 , and thus more reactive sites could be used for U(VI) reduction and increase the rate and extent of the overall reductive reactions. Others also successfully characterized CuO nanoparticles and

nanocomposites crystal structures and the detailed local electronic structures using X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy [85]. Frenkel [90] also demonstrated that mono- and heteroatomic nanoparticles can be modeled using EXAFS experimental data and theory the multiple-scattering FEFF6 theory. Combined with the results of other experimental evidence such as transmission electron microscopy and electron diffraction, EXAFS analysis can be used to determine the size and shape of the nanoparticles with much higher accuracy than any other experimental tools.

Synchrotron-based scanning transmission x-ray microscopy (STXM) is another powerful spectroscopic tool capable of both imaging and spectroscopic speciation for samples with ~30 nm spatial resolution under fully hydrated conditions [91–94]. The emergence of combination of microspectroscopic and fluorescence-based techniques with imaging has permitted investigations of carbon containing materials such as microorganisms at nanometer scale. Imaging of nanoparticle samples coupled with X-ray absorption near edge structure (XANES) spectroscopy provides an excellent opportunity to identify and fingerprint the fine structures of carbon and directly image micro to nanometer sized environmental samples with nanometer spatial resolution. More recently, STXM and NEXAFS spectromicroscopic analyses has been effectively employed to investigate soil carbon and mineral associations at a nanometer scale. For example, using the STXM technique, Obst et al. [92] found that cyanobacteria produced an amorphous or nanocrystalline calcium carbonate phase with a short-range structure order. STXM results provided direct evidence that the bacteria induced the formation of the nanocrystalline as part of their metabolic activity on the extracellular polymeric substances (EPS). Because of the spectral data and mapping information provided by STXM technique, they were able to discriminate the nucleation of the amorphous aragonite-like nanoparticles were taking place within the cyanobacteria cell wall structure. Lawrence et al. [95] also reported for the first time the spatial correlation between the copper nanoparticles and natural river biofilms based on the STXM experimental data. Their results of copper nanoparticles dissolved and redistributed in the biofilm lipid and polymers have significant implications on the fate and transport mechanism of the metal particulates in the natural environments. Several other studies were also carried out successfully using STXM to elucidate the nanomaterial sorption reaction with subsequent dissolution and/or re-sorption chemodynamics with bacterial surfaces [96, 97]. Leuf et al. [97] used STXM and identified iron-reducing bacteria accumulate ferric oxyhydroxide nanoparticle aggregates that may support planktonic growth suggesting the aquatic food chain can be substantially altered due to the presence of the nanoparticles. Clearly, the advances in the spectroscopic and microscopic tools and techniques enhance our understanding of the nanoparticle dynamics with other environmental constituents and their roles in the ecosystem as well as the subsequent effects on the long term fate and transport of other metal contaminants.

3. Nanoparticle applications

Nanomaterials have gained much attention due to their unique properties. Many engineered nanoparticles, such as nano silver (nano-Ag), nano TiO₂ (nano-TiO₂), nano aluminum oxide (nano-Al₂O₃) and carbon nanotubes (CNT), have found potential commercial applications in catalysis, biomedical researches, medicinal applications, etc. Their subsequent impending effects on the ecosystem have also raised concerns over human health and environments as evidence has suggested that engineered nanomaterials are likely to present potential risks. Numerous

active research and studies are carried out to analyze the health and environmental risk assessments. Although none of the analytical techniques employed provide unequivocal evidence as to the nature and impacts of the nanoparticles, advances in the analytical tools and techniques allowed to significantly enhance our understanding on the properties and roles of nanoparticles. One of the recent emerging fields for nanoparticle applications is agriculture and construction. In this review, examples of nanoparticle usages in these two fields of practices to date and the challenges associated with nanoparticle applications are introduced.

3.1 Nanoparticle and biochar

Biochar (BC) is a carbon-rich product generated by pyrolysis of biomass such as wood, crop residues, and manure in a closed container with little or no oxygen. Creating biochar is a carbon-negative process because synthesizing BC utilizes naturally decaying organic matters to turn into useable sustainable materials while bypassing the release of CO₂ into the atmosphere. Studies have shown that BC can substantially enhance physicochemical and biological properties of the soil to increase the plant and crop yields [98–101]. A number of remediation strategies using BC as sorbents are developed to remove toxic contaminants from polluted soils because of the high surface areas and presence of various carbon functional groups in BC. Furthermore, chemical structure of BC is stable and highly resistant to microbial degradation due to the recalcitrant nature of BC hence allowing BC to be an alternative growing medium or substrates for agronomic applications. For example, in 2010, the American Society of Agronomy Soil Science Society of the American Environmental Quality Division identified the agronomic applications of BC to be one of the immediate challenges and solutions to address the global food shortage. Clearly, more research on BC and its application to agronomic industry is urgently necessary for globally sustainable agricultural practices.

Recent report by Saxina et al. [102] provided evidence of biochar contains carbon nanoparticles. Presence of these carbon nanoparticles in the biochar significantly enhanced the soil fertility and nutrient retention compared to the ones without the carbon nanoparticles. Others also reported the properties of biochar containing the NPs differ from the properties of their macro-counterparts [103]. Different zeta potential, cation exchange capacity, elemental compositions, and aromaticity/polarity not only based on the type of biochars, but also the regularities in the differences between their macro- and nano-structure were observed suggesting the nanoparticles have substantial impacts on governing the overall properties of the biochar. They accounted that the larger surface area and smaller pore sizes than the corresponding macro-biochars are the main physicochemical properties. On the contrary, Chen et al. [104] reported nanoscale biochar particles may carry the inherent contaminants along the soil profile, posing a potential risk to the groundwater. Their study on the transport and retention of wood chip-derived biochar nanoparticles (NPs) in water-saturated columns packed with a paddy soil identified mobility of biochar NPs in natural soils must be taken into consideration for accurately assessing their environmental impacts. **Figure 6** illustrates the effects of different type of nanoparticle modifications on biochars to enhance the contaminant removal and transformation reactions of a wide range of environmental and anthropogenically abundant toxic matters.

In addition to the laboratory studies on biochar nanoparticles, field-scale experiments were carried and provided promising evidence on the impacts of the biochar nanoparticles to increase food production and remediation. Su et al. [105] synthesized biochar-supported zero-valent iron nanoparticles and used in the remediation of Cr(VI)-contaminated soil. They found removal of Cr(VI) was significantly

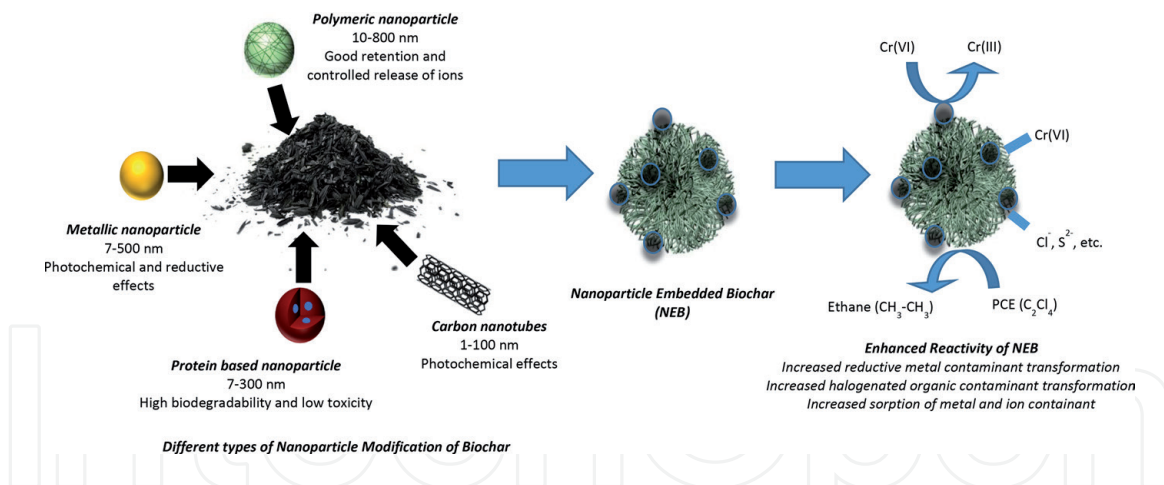


Figure 6. Schematic representation of biochar modifications by different types of nanoparticles and the subsequent enhanced reaction mechanisms in transformation of the contaminants in the environment.

improved and observed substantially increased cabbage mustard growth as the phytotoxicity of Cr(VI) and Fe in the seedlings was effectively decreased by the biochar nanoparticle treatment in the field. Yue et al. [106] also demonstrated that application of the biochar nanoparticles on the rice plants significantly alleviated the phytotoxicity of Cd²⁺. However, their study reported that the nano-biochar significantly increased the contents of antioxidative enzyme activities indicating that nano-biochar could also induce oxidative stress in the rice plants. These results indicate that nano-biochar could greatly reduce the uptake and phytotoxicity of Cd²⁺, but its potential risk should not be overlooked during the environmental and agricultural applications of biochar. Clearly more studies are needed before fully applying nanoparticles in biochar synthesis or application to the fields especially focusing on the the interaction between biochar nanoparticles and plant roots in the rhizosphere where most of the physico-chemical reactions between the plants and nutrients occur.

3.2 Nanoparticle and cement

Portland cement based materials like concrete, mortar, fiber reinforcement and others are widely used building materials. About 4.1 billion metric tons of cement were produced in 2020 worldwide and a continuously increased demand is expected, elevating the environmental impacts related with this worldwide industry. Efforts have been made to mitigate the environmental impacts of cement production by creating different synthesis approaches and alternative methods for production. For example, geopolymers are developed and commercially produced to reduce the carbon footprint of cement production, while also being highly durable and comparable to the traditional cements [107–110]. Recently, nano-engineered cement based materials is also actively studied because materials, such as nano-SiO₂, nano-TiO₂, nano-Fe₂O₃, nano-Al₂O₃, nano-CaCO₃, nano-ZnO₂, nano-cement particles of C₂S and C₃S phases, nano-clays, and Carbon Nanotubes, can work as effective binder to improve the cement based materials performance [111]. The addition of nanoparticles in cementitious materials can act as a filler agent, producing a dense matrix and reduce the growth of micro pores. Some nanoparticles also help in the secondary reactions forming cement composite and contribute to the strength development. Moreover, with the advancement on the analytical tools, the current knowledge of the microstructure, mechanical strength and durability of cementitious materials when incorporating different types of nanoparticles increased during the past decades [112–114].

For example, Said et al. [115] demonstrate a wide range of nanoparticles like Al_2O_3 , C-S-H-phase, and quartz have the best potential as accelerators for cement hydration and therefore are most suitable for cement production based on their result of heat flow calorimetry measurements, particles size of nanomaterials and their percentage in the cement paste. Gaitero et al. [116] also identified that the addition of small amounts of silica nanoparticles to the cement paste could substantially slow down a degradation process due to the progressive dissolution of the cement paste. Nazari and the co-workers [111] also identified nano-phase Al_2O_3 particles with the average diameter of 15 nm increased flexural strength of fresh concrete and the extent of this positive effects of nanoparticles amplified as the content of Al_2O_3 nanoparticles increased. It is concluded that partial replacement of cement with nanophase Al_2O_3 particles improves the split tensile and flexural strength of concrete but decreases its setting time. Kawashima et al. [112] combined two nanomaterials, namely calcium carbonate nanoparticles and nanosilica, to synthesize cementitious materials and observed the mixture can offset the negative effects of fly ash (i.e., precursor for cements) on early-age properties to facilitate the development of a more environmentally friendly, high-volume fly ash concrete. Lastly, Land and his co-workers [113] also investigated the effects of colloidal nano-silica on concrete incorporating cement binders and found that the concentrations of nano-silica determined the micro-structural and thermal property changes. Many studies to date suggest that utilizing nanoparticles in cement synthesis can benefit the system by improving many of the structural properties. Further in-depth study on the mechanisms underlying the influence of nanoparticles on the compressive strength gain and other physical properties of cement systems need to be carried out to fully assess the impacts of nanoparticles.

Lastly, another example of where nanotechnology made a tremendous impact on commercial building materials is synthesis of nano-paint. For example, Krishnamoorthy et al. [117] developed a multifunctional graphene oxide (GO) nanopaint by incorporating GO sheets in an alkyd resin of the paint. The prepared GO nanopaint exhibited enhanced corrosion-resistant behavior in both acidic and high-salt-content solutions as well as substantial inhibition of the bacterial growth on its surface. This in-situ biofouling test results demonstrated incorporating the nanoparticles into the conventional paint materials produce significant performance benefits. Another study also concluded that preparation of titanium oxide (TiO_2) nanopaint by embedding the TiO_2 nanoparticles in alkyd resin matrix exhibited substantially enhanced antibacterial properties against a wide range of different types of bacterial strains [118]. Others also reported similar findings of enhanced corrosion-resistant behavior and anti-bacterial properties of nanoformulated paints [119–124]. Clearly, results from various studies demonstrate that these new coating formulation of nanopaint to be of tremendous value to researchers and industry. In conclusion the result of nanopaint characterization and performance evaluation opens up a new promising field of study and building materials for next generation.

4. Conclusion

This review highlights the diversity in naturally occurring and engineered nanoparticle in various environments. Given the production of engineered nanoparticles is expected to increase significantly in forthcoming years with more applications and productions, the information provided herein review provide an important baseline from which to interpret future environmental change. Clearly the impacts and effects of nanoparticles on the bacterial toxicity, cement materials,

agricultural practices, and sequestration of contaminants cannot be generalized because the physico-chemical reactions occurring at the nanoparticle surfaces depend on a wide range of environmental conditions. Further work should continue to focus on the speciation, biogeochemical behavior and ecotoxicological impacts of both natural and engineered nanoparticles to understand the long-term effects as well as fate and transport behavior of them in the nature.

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