

Review

Fate of engineered nanoparticles: Implications in the environment



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ABSTRACT

The increased flux of engineered nanoparticles (ENPs) in consumer and commercial products has become a viable threat, particularly if their release affects the environment. The aim of this paper is to review the recent literature results pertaining to the underlying mechanisms initiating the transformations of ENPs for both biotic and abiotic processes. The transformation of ENPs is necessarily interrelated to multiple environmental aspects and many concepts overlap. Physicochemical, macromolecular, and biological pathways contribute to assessing the impact of the altered activities of ENPs on the surrounding environmental matrices. Transformations involving both organic and inorganic ligands are vital in soil and water systems. Energy-efficient biocatalytic pathways can easily facilitate biotransformation involving enzymatic reactions and biomolecules. The relationship between physicochemical and biological parameters triggers transformation, greatly affecting the bioavailability and aging of ENPs to various extents. Therefore, the interaction of ENPs in environmental matrices is significant in understanding the risk of potential exposure and/or uptake by biota.

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1. Introduction

It is well known that engineered nanoparticles (ENPs) are used widely in medical, energy, electronics, and environmental applications [1]. The extensive commercial application and production volume of ENPs raises concerns about their impact on the environment [2]. According to Amara's law, the growth of ENPs is predicted to form a large number of nano-products and, consequently, nano-wastes (Fig. 1) [3]. Therefore, exposure assessment is important, at least for the popular ENPs, because their environmental impact is poorly understood. ENPs are released into the biosphere, whether inadvertently or intentionally. For example, occupational or residential exposure to Ag nanoparticles (NPs) from consumer and hospital products has impacts on the aquatic environment through oxidative dissolution and sulfidation. Likewise, nanozerovalent iron (nZVI) is injected into groundwater polluted with chlorinated solvents at remediation sites where ENPs are released directly into water and soil [4]. Therefore, the influx of ENPs is a matter of balancing reward and risk in the environment.

The complex interaction between environmental matrices and ENPs is important. Abiotic and biotic pathways influence transformation, altering bioavailability and the aging process [5]. Different hydro-chemical parameters such as pH, ionic strength (IS), hardness (e.g. Ca^{2+} and Mg^{2+} ions), and O_2 -limiting conditions change aggregation kinetics [6]. Similarly, natural organic matter (NOM) alters stability through electrostatic and steric interactions [7,8]. Moreover, the (ad)sorption of molecules in surrounding environmental matrices indicates macromolecular level transformations [9]. ENPs are often functionalized by surface coatings for specific use, which results in altered activities [10]. For example, TiO_2 NP (Ti NP) composites showed hydrophilicity during the aging process and formed aggregates due to the oxidation and desorption of amphiphilic surface-coated molecules in an aqueous environment [11]. In addition, photochemical reduction of Ag^+ ions shows that ionic Ag bound to NOM facilitates the formation of Ag NPs under ambient light conditions in an aquatic system [12]. Similarly, biotic pathways including cellular degradation in matrices containing NOM, protein/polypeptide, and polysaccharide can alter the bioavailability of ENPs [13]. Bioavailability process controls the potential for transfer of ENPs from the environment to ecological receptors. So ENPs are not only affected by soil and water quality parameters but also by the presence of biomolecules including the biomass of plants and (micro)organisms [14]. Therefore, ENPs can

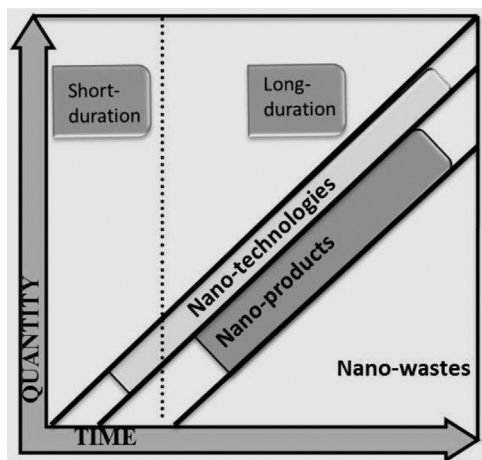


Fig. 1. Relationship of ENPs growth over time (Amara's law correlation of nanotechnological growth).

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change their behavior after being released into the environment by abiotic and biotic interactions [15].

The environmental implications and risks associated with nanotechnology have been addressed by various researchers. For example, specific reviews on silver [16], biotic mechanisms [17], and nanomaterial behavior and their fate [18–22] are a few of the valuable contributions to this field. This paper reviews the recent results in the wider literature concerning the mechanisms initiating the physicochemical, macromolecular, and biological transformations of ENPs through both the biotic and abiotic processes.

2. Transformation of ENPs

The characteristics of both the environment and ENPs are important in controlling the behavior of the released ENPs. The nature and degree of the transformation can be perceived in physicochemical, macromolecular interaction and biologically mediated reactions.

2.1. Physicochemical transformation

Abiotic pathways are generally based on physicochemical transformations. For example, the aggregation, stability, dissolution and deposition of ENPs are interrelated process. The natural pathways of sunlight-driven photochemical reactions are significant in controlling photo transformations. The adsorption of molecules readily occurs in the surrounding matrix of a natural system showing macromolecular transformations. The aerobic and anaerobic environment can also potentially alter the behavior of ENPs by differential affinity to the ligands, such as sulfidation in O_2 -limiting conditions.

2.1.1. Aggregation kinetics and stability

The colloidal stability of ENPs and their aggregation are explained through the interactions of colloid particles and adhering surfaces by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [23]. According to this model, the aggregation of ENPs is dependent on interaction forces such as electrostatic repulsion and van der Waals attraction. Non-DLVO theory interactions namely steric hindrance, magnetic and hydration forces may have significant influence on the adhering surface efficiency. According to the International Organization for Standardization (ISO, 2008), nanomaterials in the size range of 1–100 nm are nanosized in different dimensions, such as nanoparticles, nanoplates and nanofibers which are nanosized in all three-dimensions, one-dimension and two-dimensions, respectively [24]. ENPs are much smaller than conventional colloid particles ($<2\ \mu\text{m}$) and may not necessarily be spherical. They demonstrate wide variations in shape, such as triangular, icosahedral, ellipsoidal, and cylindrical forms. Two types of aggregation are relevant to ENPs in the environment: homoaggregation and heteroaggregation, which are the aggregations of similar and dissimilar ENPs. For example, aggregation of Ag NPs with Ag NPs is a homoaggregation whereas aggregation of Ag NPs with clay minerals is a heteroaggregation. Considering natural environment systems, heteroaggregation plays a significant role for ENPs transformation. Therefore core–shell structure, surface properties (which varies from hydrophobic to hydrophilic coatings), and the degree of transformation all alter the DLVO justification of the aggregation and stability of ENPs [25].

2.1.1.1. Effect of ionic strength.

2.1.1.1.1. Studies related to critical coagulation concentration. Ionic strength (IS) is known for its capability of ENPs transformation. The critical coagulation concentration (CCC) explains the 'required minimum electrolyte concentration' for favorable aggregation of ENPs by eliminating the electrostatic energy barrier.

Favorable and unfavorable aggregations depend on the aggregation attachment efficiency (α), which ranges from 0 to 1. In a reaction-limited (slow and unfavorable) regime, α is less than 1 and in diffusion-limited (fast and favorable) regime, α is equal to 1. Higher CCC values imply greater colloidal stability, whereas a lower CCC value indicates destabilization and higher aggregation of ENPs at a specific background solution. In environmental studies, attachment efficiency (α) and CCCs are the useful metric for predicting the degree of aggregation and stability in natural and engineered systems. For example, a CCC of 111.5 mM was noted for polyvinylpyrrolidone (PVP)-coated Ag NPs compared to a CCC of 47.6 mM for citrate-coated Ag NPs in NaCl electrolyte [26]. The lower CCC of the citrate-coated Ag NPs yielded a higher aggregation. Monovalent ions (Na^+/K^+) are on the order of <10 mM concentration in most natural freshwater bodies, including surface and ground water [27]. Therefore, the CCCs of ENPs were much higher than the typical monovalent salt concentration of freshwater. Consequently, in this case, they are mobile in an aqueous environment. Alternatively, some homo- or heteroaggregations could possibly occur due to high ENPs concentration, water flow condition that facilitates the frequent collision of ENPs with either ENPs or natural colloids. Zhou et al. have studied the role of clay minerals in affecting the aggregative stability of Ag and TiO_2 NPs in suspension at varying ionic strength showing aggregation increased with increasing ionic strength [28]. Afroz et al. have studied the heteroaggregation behavior of Au NPs in presence of pluronic acid modified single walled carbon nanotubes (SWCNTs) under a wide range of mono- and di-valent electrolyte conditions and concluded that slower aggregation at low electrolyte conditions and enhance heteroaggregation in presence of high electrolytes as presented in Fig. 2 [29].

In addition, ENPs can be immobile due to heteroaggregation between ENPs and soil/sediment particles. Alternatively, if the ion concentrations are well above the CCC, ENPs may still be mobile due to low ENP or particle concentrations and flow conditions that result in few collisions that can be further confirmed by other factors discussed below.

2.1.1.1.2. Capping agents and preparation methods. Capping agents and preparation methods have a strong impact on colloidal stability and the mechanism of aggregation. Surface oxidation can change CCCs, as various researchers have demonstrated. Yi and Chen [30] observed higher CCC values with more oxidized multi-walled carbon nanotubes (MWCNTs) reduced aggregation. Bouchard et al. have investigated the effect of surface coatings on the CCC values of coated and uncoated- C_{60} [31]. The phenyl alkyl ester-derived C_{60} showed considerably higher CCC at >500 mM NaCl than aqueous suspensions at 260 mM NaCl. The results showed that the surface coatings of fullerene inhibited aggregation, possibly through steric interference or differing particle-particle interaction energies. Li et al. have reported a lower CCC value at ~40 mM for uncoated Ag NPs causing higher aggregation in the absence of capping agents [32], thus surface coating may prevent the oxidative dissolution. Huynh and Chen prepared citrate-coated Ag NPs by cleaning an original stock suspension of Ag NPs and re-suspending it in citrate solution (CCC ~50 mM) [26]. He et al., instead, synthesized Ag NPs by reduction of Ag^+ to Ag^0 followed by the addition of citrate solution (CCC~300 mM NaCl) [33]. Both studies clearly showed stabilization by use of the same capping agent, but the much higher CCC value (He et al. [33]) suggests that both, the surface coating and the methodology used for the synthesis of ENPs have significant impacts on the aggregation and stability. Similarly, Table 1 comprises the lists of different capping agents (stabilizers) for ENPs.

Other researchers noticed impacts of different ENPs' preparation methods. Bouchard et al. [31] have reported a higher CCC for a stirred aqueous suspension of C_{60} at 260 mM NaCl compared to

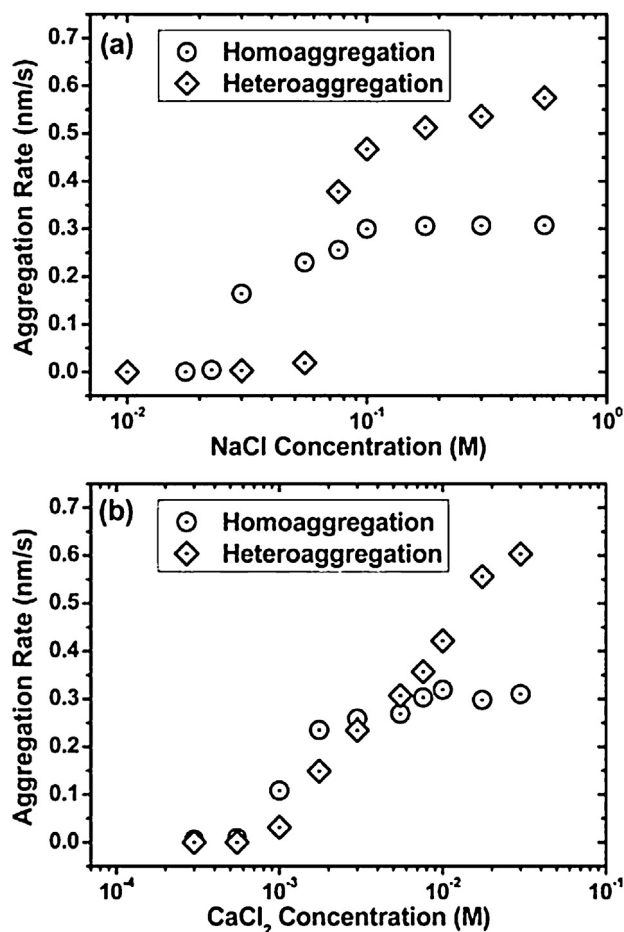


Fig. 2. Initial aggregation rates of homo- and heteroaggregation of Au NPs with (a) NaCl and (b) CaCl_2 . Measurements were carried out at pH of ~6.5 and a temperature of 20 °C.

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a solvent exchange suspension at 120 mM NaCl [34]. Furthermore, the reported CCC for sonicated and acid-treated MWCNTs was considerably lower CCC at 25 and 93 mM NaCl, respectively [35,36]. In addition, sonicated and stirred fullerenes showed CCC values of 40 and 166 mM KCl, respectively [37]. On the whole, the 'stirred process' of preparing fullerenes resulted in higher stability than the 'sonicated process', as demonstrated by the higher CCC values. Measurement of electrophoretic mobility (EPM) showed similar results, as there was a more negative charge on the stirred than on the sonicated fullerenes. This way the variation in natural growth and development of ENPs can be relevant in different matrices of the environment.

2.1.1.1.3. Cation valence and salt type. Cation valence and salt type also influence aggregation tendency of ENPs. Mono and divalent cations are common in aqueous and soil suspensions. French et al. have investigated the aggregation of Ti NPs by simulating the soil and surface water conditions [38]. Results showed that Ti NPs (4–5 nm) formed stable aggregates (50–60 nm) at 4.5 mM NaCl suspension. Further increase of IS up to 16.5 mM formed μ -sized aggregates at the same conditions. Ti NPs also rapidly formed μ -sized aggregates in CaCl_2 suspension at the higher IS of 12.8 mM. Larger aggregates were observed at a higher pH range (5.8–8.2) and IS (8.4–9.9 mM NaCl); so hardness enhanced aggregation in soil and surface water. Moreover, the stability of ENPs was correlated to salt type [36]. The CCC value of MWCNTs was observed at 93 mM (NaCl), 98 mM (Na_2SO_4), 1.8 mM (MgCl_2), and

Table 1
Prevalent capping agents (stabilizers) of ENPs (compiled from various literature studies).

Capping agents	Model ENPs	Studies
Organic molecules		
Citrate, Tannic acid, Ethylenediaminetetraacetic acid, Polyethylene glycol (PEG), Polyvinylpyrrolidone (PVP)	Ag	[161–165]
Citrate, Tannic acid, Cysteine, Biotin, Bovine serum albumin (BSA), Polypeptides, 11-Mercaptoundecanoic acid	Au	[166–173]
PVP, Tetraoctylammonium bromide	Cu ₂ O	[174,175]
Trioctylphosphine oxide, Oleate	CdS	[176]
Oleylamine, Mercaptoundecanoic acid, Glutathione	Pd	[177–179]
Dodecylamine, Mercaptosuccinic acid, PVP	Pt	[180–182]
PVP	Rh	[182]
PVP, Citrate, Hydrobenzamide	Sn	[183]
Oleic acid, Oleyl amine, Poly (acrylic acid)	TiO ₂	[184,185]
Hexadecanediol	Ir	[186]
Carboxymethyl cellulose, Xanthan gum	nZVI	[187,188]
Graphene	Ag/AgCl	[189]
Polysaccharides, 2-Mercaptoethanol, Triethanolamine, Acetate, PVP	ZnO	[190–194]
PEG, Alginate, Poly(acrylic acid), Poly (methacrylic acid), Dodecylamine, Oleic acid, BSA	Fe-oxide	[195–201]
Citrate, Poly(acrylic acid)	CdSe, CdS	[202,203]
Citrate	SnO ₂	[204]
Citrate, Tri-octylphosphine oxide and oleic acid, PVP, Oleic acid	CeO ₂	[204–206]
Cetyltrimethylammonium bromide (CTAB)	GaN	[207]
CTAB	Se	[208]
PEG, PVP	CNTs	[209,210]
Cetyltrimethylammonium chloride, Triton X-100, BSA	Fullerene	[211,212]
Polypropylene glycol, 3-Aminopropyl	SiO ₂	[213,214]
Arginine	Iron oxide/rGO	[215]
Citrate	Au/Graphene	[216]
Triethanolamine	TiO ₂ /graphene	[217]
Inorganic molecules/element/ion		
Au, Cl ⁻	Ag	[218,219]
Ag, Pd	Au	[220,221]
SiO ₂	Pd	[222]
Ag	Pt	[223]
Pt, Au, Ag	TiO ₂	[224–226]
Au, SiO ₂	Fe-oxide	[227,228]
SiO ₂ , Pt	ZnO	[229,230]
SiO ₂ , ZnS	CdSe	[231,232]
Si, TiO ₂	CNTs	[233,234]
Al, Ag	SiO ₂	[235,236]

1.2 mM (CaCl₂), showing that NaCl and Na₂SO₄ electrolytes measured almost similar CCCs. This study demonstrated the negligible influence of anions (Cl⁻ and SO₄²⁻) on the stability of negatively charged MWCNTs. Furthermore, divalent electrolyte revealed a higher level of aggregation [26]. Citrate-coated Ag NPs showed destabilization due to lower CCC values at 2.1 mM CaCl₂ and 2.7 mM MgCl₂, while for monovalent electrolyte (NaCl) a higher CCC of 47.6 mM was observed. In contrast, PVP-coated Ag NPs showed higher stability than citrate-coated Ag NPs in mono or divalent electrolytes due to steric repulsion by the large and non-charged polymeric groups. Therefore, cation valence and salt type showed impact on transformation potential by altering the aggregation and stability of ENPs in the environment.

The impact of the surface oxidation of ENPs on aggregation kinetics in mono- and divalent electrolytes has been studied [30]. High-oxidized MWCNTs (Ho-MWCNTs) showed higher stability than low-oxidized MWCNTs (Lo-MWCNTs) in NaCl electrolyte because of the higher surface charge density caused by negatively charged –CO₂H groups. A higher concentration of Na⁺ ions was thus required to screen sufficiently the surface charge of Ho-MWCNTs than for Lo-MWCNTs for favorable aggregation. In contrast, both oxidized carbon nanotubes showed a similar aggregation trend in CaCl₂ electrolyte. Ca²⁺ ions exhibited preferential affinity to form bidentate complexes with the adjacent –CO₂H group on Ho-MWCNTs than with an isolated –CO₂H group on Lo-MWCNTs. A larger fraction of the –CO₂H group was placed at close proximity to the Ho-MWCNTs than to the Lo-MWCNTs. Surface charge neutralization was more efficient for Ho-MWCNTs with the Ca²⁺ ions. Thus despite the difference in degree of surface oxidation, aggregation possibly was related to the spatial distribution of the functional

groups on ENPs. Thus, the physicochemical alterations of ENPs can change their behavior in the environment.

2.1.1.2. Effect of pH. Aggregation of ENPs can show variations due to changes in pH values. Chowdhury et al. have investigated the effect of pH on graphene oxide (GO) NPs in natural and synthetic water [39]. The hydrodynamic diameter (D_h) was ~250 nm in the pH range of 4–10, but increased sharply (>1000 nm) in more acidic conditions (pH < 4). A reduction in electrostatic repulsive forces between (GO) NPs was responsible for the increase in D_h . EPM values were fairly constant from pH 5 to 9 but increased significantly from pH 4 to 2 similar to that of D_h . The (GO)-containing functional groups (e.g. –OH and =CO) changed EPM values at both the ends of the pH scale [40]. Thus, electrokinetic or hydrodynamic properties did not significantly affect aggregation kinetics or stability of similar ENPs in a typical aquatic environment in a pH range of 5–9 [27].

The pH stability of citrate-capped and bovine serum albumin (BSA)-capped Ag NPs were studied by MacCuspie [41]. Citrate-capped Ag NPs were more stable at pH 7 and 9, whereas BSA-capped Ag NPs were stable at wider pH range (2, 3, 7 and 10) except pH 4 and 10. It is expected that the pH dependence of Ag NPs stability may be related to citric acid speciation and steric effect of BSA in citrate- and BSA-capped Ag NPs respectively. Such pH-dependent transformation can be relevant in industrial and municipal wastewaters that can potentially mediate the pH-specific transformations.

Rathnayake et al. have showed that pH dependent transformation resulted in structurally and morphologically heterogeneous end products [42]. Variations in pH determined the final speciation, structure, and morphology of ZnO NP (Zn NP) transformation

products. They transformed into two different morphological/structural phases due to pH dependence of phosphate-induced effect. Zn NP dissolution enhanced at pH 6, with the dissolved material re-precipitating as hopeite (a micrometer scale crystalline zinc phosphate phase). On the other hand, a nanoscale phase of a ZnO core with an amorphous $Zn_3(PO_4)_2$ shell obtained for Zn NPs aged at pH 8. Therefore, $Zn_3(PO_4)_2 \cdot 4H_2O$ was expected at thermodynamic equilibrium for both acidic and alkaline values but the complete transformation was kinetically limited. Loosli and Stoll have studied the effect of pH (3.7, 6.2 and 9.7) on heteroaggregation of TiO_2 NPs in latex suspension by a second order aggregation kinetics. Better aggregates were obtained at pH 3.7 than pH 6.2 and 9.7 due to charge neutralization of negatively charged latex suspensions with positively charged TiO_2 NPs [43]. These details are significant in environmental release scenarios in various environments, such as soils, surface and ground waters, and wastewater treatment processes at varying pH values.

2.1.1.2.1. Is the charge acquisition of fullerene pH-dependent?
The pH-dependent charge acquisition explained the higher stability of fullerene in water. Charge acquisition through adsorption of OH^- ions has been proposed via two mechanisms, charge acquisition for hydrophobic surfaces [44] and surface-mediated hydrolysis [45]. Aqueous fullerene acted as a potential electrophile (strong electron acceptor) that polarized the water at fullerene surfaces. The polarized water molecules provided the protons for adsorption of OH^- ions or were subjected to surface-mediated hydrolysis. Brant et al. have reported more strongly charged fullerenes by solvent exchange (using organic solvent) process than by extended mixing with water due to charge transfer from the guest solvent (oxygen acted as an electron donor) and surface hydrolysis reactions [46]. These mechanisms of charge acquisition for aqueous fullerene showed pH-dependence, particularly at pH <4 [31]; OH^- ions are adsorbed on surfaces more readily than H_3O^+ ions [47]. This possibly contributed to the negative surface charge of fullerenes. In contrast, Chen and Elimelech have reported that fullerene underwent faster aggregation at pH 2 since the ENPs were the least negatively charged [37]. They became more negatively charged showing slower aggregation as pH was increased. Therefore, aggregation was very slow at pH 12, resulting in higher stability. The overall results demonstrated that the surface hydrophobicity of fullerene NPs was altered with aqueous pH conditions [48]. These changes can be relevant in industrial wastewater processes or on acid mine sites.

Additionally, decrease in ζ -potential with slight increase in pH is consistent with NOM adsorption onto the surfaces of ENPs. For example, Considine et al. have investigated that NOM adsorbed to Si NPs through acid-base functional group H-bonding of organic acids and the $-OH$ groups of Si-surfaces at relatively high pH [49]. Significantly, less adhesion was reported for free NOM due to protonation at pH <4.8. So NOM coating was influenced by ionization equilibrium as adsorbed NOM ionized with increasing pH. As a result, NOM can introduce new ingredients, the environmental fate of which is still ambiguous. Aforementioned studies highlighted the potential environmental transformations of ENPs in terms of the sensitivity of the process to environmental variables.

2.1.2. Dissolution behavior

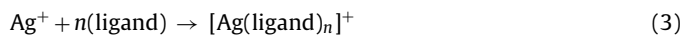
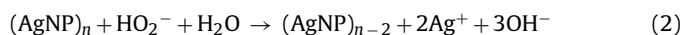
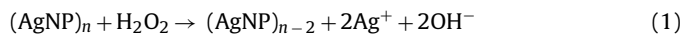
ENPs can be divided in two categories, (i) dissolvable (e.g. Ag, Zn and CuO, ZnO) and (ii) non-dissolvable (e.g. graphene, CNTs). In dissolution studies, carbon NPs can be virtually insoluble in natural waters; fullerene, for example, shows very low solubility at 10^{-18} mol/L [50]. However, C_{60} suspensions can form a highly oxidized water soluble fullerene oxide in aerobic conditions [51]. Similarly, oxidative treatment such as ultrasonication and adsorption of organic help to produce stabilized CNTs dispersions [52]. Zn NPs and Ag NPs are the most soluble ENPs [53]. For example, Franklin

et al. have demonstrated rapid dissolution of Zn NPs with solubility saturation. The Zn NPs produced ~ 8 mg/L dialyzed (dissolved) zinc concentration within 6 h and a much higher equilibrium concentration of 16 mg of Zn/L after 72 h [54]; observed rate of dissolution and saturation solubility was 19% of total Zn concentration.

The important role of dissolution of ZnO and CuO were indicating their toxicity to algae and bacteria [55,56]. Dissolution of ENPs will help them to persist for a longer time in the environment; a detailed discussion on dissolution of Ag NPs follows.

The rate of dissolution indicates that metal ions tend to participate in redox and complexation reactions. Ho et al. have investigated that dissolution was 9 times faster when the size of spherical Ag NPs decreased from ~ 20 to ~ 5 nm [57]. The Ag NPs with capping agents (PVP or tannic acid) presented similar behavior on dissolution [58]. Smaller Ag NPs (5 nm) dissolved more rapidly than larger Ag NPs (50 nm) in aqueous systems which could be due to larger fraction of surface atoms (higher specific surface area) in smaller Ag NPs or due to lower redox potentials of smaller Ag NPs than large size particles.

Oxidative and reductive dissolution reactions greatly influence the metal speciation and its transport in the environment [59]. Oxidative dissolution by the reactive oxygen species in aerobic systems was investigated by Ho et al. [57]. Oxidation of Ag NPs by either H_2O_2 or HO_2^- ions was thermodynamically feasible, based on the standard redox potentials [60]. Surface atoms of Ag NPs (Ag^0) oxidized to Ag^+ ions and concurrently, H_2O_2 reduced to OH^- ions followed by a rapid complexation of Ag^+ ions with the ligands (or solvent molecules). Kinetic expression of the overall steps of oxidative dissolution is presented below (Eqs. (1)–(3)):



A possible thin layer of Ag_2O over the surfaces of Ag NPs in aerobic systems was demonstrated in several cases [61,62]. Thus, the electrochemical passivity of surface oxide controlled Ag^+ ion release. Such oxidative dissolution pathways are significant for understanding the nano-bio interface chemistry between living cells and ENPs [63].

Furthermore, the presence of Cl^- ions affects Ag NPs dissolution and strongly associated with a varying Cl/Ag molar ratio. At low Cl/Ag ratio, the presence of Cl^- ions significantly decreases or inhibits the dissolution of Ag NPs [32,57]. Levard et al. highlighted the enhanced dissolution of Ag NPs at high Cl/Ag ratio [64]. The rate of release of aqueous Ag increased at high Cl/Ag molar ratio (26,750) in short time (≤ 10 h), but the rate reported at Cl/Ag ratio was slower (≤ 2675). On increasing the Cl/Ag ratio ($\geq 26,750$), soluble species, $AgCl_x^{(x-1)-}$ begin to dominate as compared to solid AgCl. The soluble species may include Ag^+ , $AgCl_{aq}$, $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$ ions. Thermodynamic data showed $AgCl_2^-$ (51%), $AgCl_3^{2-}$ (27%), and $AgCl_4^{3-}$ (22%) speciation at 2×10^{-5} and 0.5 M concentration of Ag NPs and NaCl, respectively. In other case, AgCl (solid) was the main species at a Cl/Ag ratio of ≤ 2675 in the reaction vessel. Thus dissolution was mainly dependent on the $[AgCl(\text{solid})/AgCl_x^{(x-1)-}]$ ratio. The dissolution rate increased with decreasing $[AgCl(\text{solid})/AgCl_x^{(x-1)-}]$ ratios and vice versa.

Loza et al. have observed the effect of different inorganic anions (Cl^- and PO_4^{3-}) and organic solutes (glucose and cysteine) on dissolution of Ag NPs in aerobic condition [65]. Chloride ion alone or in combination with phosphate ion slows down the dissolution of Ag NPs with the formation of silver chloride on nanoparticle surface. Glucose has only a small effect on the dissolution rate, but in presence of cysteine, the dissolution is quantitatively inhibited.

Metal oxides may undergo reductive dissolution in presence of organic and inorganic solutes, in anaerobic conditions [59,66]; iron

oxide has been studied where Fe(III) reduces to Fe(II) using organic ligands. Cwiertny et al. have used photochemical reductive dissolution and observed the enhanced rate of Fe(II) production in nanorods α -FeOOH systems over microrods in presence of oxalate and hence greater dissolution of nanorods [67].

Li et al. have studied the effect of different anions (Cl^- , SO_4^{2-} , NO_3^- , and HPO_4^{2-}) on nano-ZnO dissolution behavior [68]. Increasing concentration of Cl^- , SO_4^{2-} and NO_3^- , increased the dissolution of nano-ZnO due to increasing ionic strength, while HPO_4^{2-} ion inhibit the dissolution and free Zn^{2+} concentration decreased from 0.23 to 0.04 mg L^{-1} at 5 mM HPO_4^{2-} concentration. Furthermore, Stumm have reported that oxoanions, such as phosphate, arsenate and borate are efficient inhibitors for metal oxide dissolutions because they form bi- or multinuclear inner sphere surface complexes that can bridge two or more metal centers in the surface lattice [69]. Overall, the results indicate that the dissolution of ENPs is a regulating process for particle/ion partitioning in the aquatic environment.

2.1.3. Deposition behavior

Deposition is the retention behavior and occurs when molecules settle on a solid surface from a solution. It can be viewed as the reverse process to dissolution. Influence of surface coating on ENPs mobility in porous media is well studied but its influence on ENPs deposition and their environmental fate have received meager attention [70,71]. Wang et al. have investigated the influence of a surface coating polymer, polyacrylic acid-octylamine, which may exist both in the free aqueous phase and as a surface-bound coating, on the deposition behavior of quantum dots (QD) (e.g., CdSe/CdZnS nanocrystals) in water-saturated quartz sand [70]. The retention profile of QD clearly demonstrates that a free polymer was preferentially adsorbed onto the solid surface near the column inlet, thereby preventing QD attachment, whereas in the down-gradient portion of the column, QDs attached to the solid phase without competition from the polymer. Hence, it is important to account for the influence of coating on nanoparticle deposition, which demonstrates their need in assessing nanoparticle mobility in porous media. Ikuma et al. have investigated the deposition characteristics of ENPs (e.g., hematite and silica) onto surfaces coated with polysaccharides [71]. ENPs deposition characteristics suggest that electrostatic interactions were the major driving force in governing the initial surface deposition of ENPs onto polysaccharide-coated surfaces. In addition, the distribution and heterogeneity of charges across the surface can play an important role in the ENPs deposition, which needs more study for better prediction of ENPs attachment onto environmental surfaces. Li et al. have quantified the deposition kinetics of oleic acid coated iron oxide NPs (OA-IONPs) using hydrophilic silica and relatively hydrophobic polystyrene in the presence of electrolytes [72]. The relative higher deposition attachment efficiencies of engineered OA-IONPs onto the polystyrene than the silica surface indicate that the transport and fate of these nanoparticles will be greatly influenced by the hydrophobic surfaces in the environment (e.g., oil or natural organic matter). They observed no deposition of OA-IONPs onto silica sensor surface in the absence of salt and at higher electrolyte concentrations close to or higher than the CCC values and decrease in deposition rate was observed as presented in Fig. 3 [72].

2.1.4. Macromolecular interaction

Macromolecular interaction occurs in soil and water matrices. NOM and (bio)macromolecules show the potential to facilitate ENP transformation pathways in the environment.

2.1.4.1. Natural organic matter. NOM is regarded as a heterogeneous macromolecule consisting of biopolymers and degraded products with great variability in composition and molecular

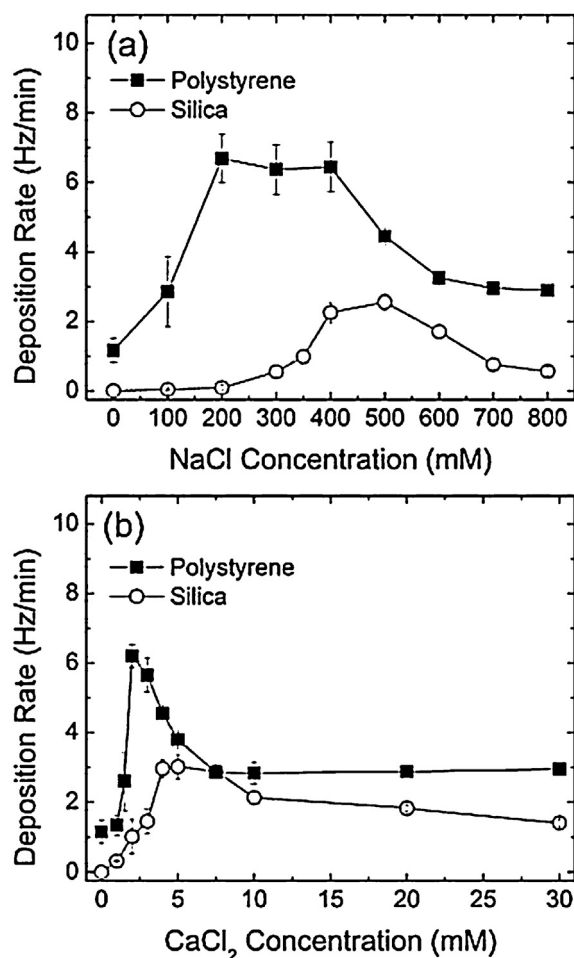


Fig. 3. Deposition rates (frequency shift rates) of OA-IONPs in the presence of (a) NaCl and (b) CaCl_2 onto silica and polystyrene sensor surfaces. Each data point shows the average of duplicate or triplicate measurements, where the error bars represent standard deviations.

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weight [73]. The humic acid (HA) and fulvic acid (FA) fractions of NOM are ubiquitous degraded materials, local to the aquatic environment, typically of 'anionic character' due to their extremely high carboxylic and phenolic constituents. NOM demonstrates anionic influence in natural water due to the auto-dissociation of weak organic acids.

Various studies have indicated that NOM stabilized ENPs through electrostatic and steric interactions [74,75]. The ζ -potential is increasingly negative with NOM for Ti NPs and Fe NPs such as hematite [9,76]. Both, the electrostatic and steric effects, were considered primary determinants of the stabilization of ENPs such as Ti NPs. Saleh et al. have reported that the EPM values of MWCNTs remained unchanged in presence of the typical NOM (Suwannee River Humic Acid or SRHA), validating steric stabilization [35]. Similar steric stabilization was documented for fullerene and colloidal suspensions [77,78].

Furthermore, the stability of fullerene was enhanced by humic acid (HA), except in the presence of elevated concentrations of CaCl_2 (>10 mM) [77]. Complexation promoted intermolecular bridging between HA and ENPs through Ca^{2+} ions, which caused aggregation at high concentrations of CaCl_2 . Chowdhury et al. have also demonstrated the effect of NOM on carbon-based NPs (e.g. (GO) NPs) [39]. Ground and/or surface water conditions at 1–10 mg/L (total organic carbon) exhibited insignificant difference

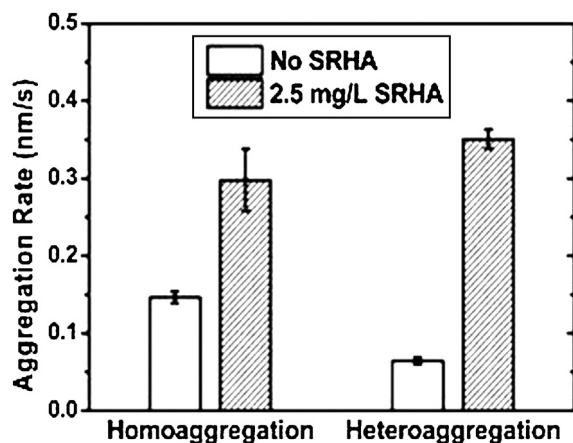


Fig. 4. Aggregate rate for homo- and heteroaggregation of Au NPs in presence of 7 mM NaCl + 1 mM CaCl₂ and with and without the presence of Suwannee river humic acid (SRHA). Measurements were carried out at pH of ~6.5 and a temperature of 20 °C.

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in ζ -potential for different salt types (NaCl, CaCl₂, and MgCl₂), similar to CNTs and fullerenes [79,80]. With SRHA, the monovalent salt type was highly efficient in increasing stability of (GO) NPs, whereas the divalent salt type showed higher efficiency in the formation of large aggregates on account of Ca²⁺ ions bridging with hydroxyl and carbonyl functional groups of GO [39]. The sorption of the SRHA on (GO) NPs surface significantly improved the stability of (GO) NPs in water due to steric repulsions, similar to the steric repulsion observed for CNTs [39,81,82].

Huynh et al. have investigated the effects of organic matter on the heteroaggregation behavior of CNTs and hematite NPs. In lower range of CNT/hematite NPs ratio (<0.01), the presence of humic acid (0.15 and 0.25 μ g/L) elevate the aggregation and at highest humic acid concentrations (500 μ g/L), completely inhibit heteroaggregation regardless of CNT/hematite ratio [83]. Afrooz et al. observed enhanced homo- and heteroaggregation in presence of SRHA as presented in Fig. 4 [29].

Aromaticity improved stabilization compared to aliphatic surfactants such as sodium dodecyl sulfate [84]. Also, the –CO₂H functional group enhanced the dispersibility of NOM-ENPs complexes, which largely depended on their source and age in a local aqueous environment [84,85]. The aromatic fraction of NOM stabilized ENPs by π - π interactions [86]. Macromolecular bonding of NOM with MWCNTs and fullerenes showed π - π interactions between cross-linked aromatic network of molecules and aromatic rings of ENPs. A similar interaction between the ENP and organic ligand was predicted to improve stability of ENPs in natural systems [87,88].

Generations of NPs using abiotic pathways by natural organic matter has been studied well. For example, reduction of silver ions (Ag⁺) in the presence of aquatic or sedimentary or soil humic acids were investigated to form Ag NPs [89]. The formation of AgNPs at elevated temperature (90 °C) completed within 3 h compared to 2–4 days at 22 °C. The time required for generation of NPs varied depending upon the type and concentration of HA, as well as temperature. The natural formation of Ag NPs was also investigated by fulvic acid fractions of NOM [90]; stable AgNPs were formed through the Ag⁺-fulvic acid under environmentally relevant conditions. The Ag NPs was stable for many months, suggesting surfaces of NPs are sufficiently coated, thus inhibiting the dissolution by oxygen to release Ag⁺. This way, the humic acid or fulvic acid-induced abiotic pathways can be the potential routes

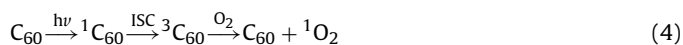
for the natural formation of NPs under environmental conditions from ionic metal sources.

2.1.4.2. (Bio)macromolecules. (Bio)macromolecules can be the controlling factors in stability and transformation changes [91]. For example, the effect of polysaccharide (e.g. alginate), protein (e.g. bovine serum albumin or BSA), and cell culture (e.g. Luria-Bertani [LB] broth) were examined for SWCNTs aggregation [82]. (Bio)macromolecules significantly inhibited ENP aggregation. BSA protein reduced the aggregation rate most effectively, followed by LB and alginate. Steric repulsions originating from the adsorbed biomolecules caused the slow aggregation. Furthermore, Deguchi et al. have investigated the adsorption of protein and dispersion stability of C₆₀ NPs [92]. ENP coagulation was completely suppressed at concentrations of >1 mg/mL of human serum albumin (HSA). Because of adsorption, the D_h of C₆₀ NPs increased slightly from 152 nm to 154.5, 155, and 153.6 nm at 1, 5, and 10 mg/mL of HSA, respectively. The adsorbed HSA molecule formed a protective layer onto surfaces of C₆₀ NPs, preventing coagulation. Such stabilization is vital between living cells and ENPs; the association of adsorbed protein coatings and ENPs produced protein coronas in biological fluids [93,94]. Yet little is known about the impact of ENPs on biomolecules, specifically for protein/peptide, DNA, and cell membranes.

Computational studies have explored the interaction of structures and dynamics of ENPs with peptide/protein [95,96], nucleotide/nucleic acid [97,98], and cell membranes [99,100]. The relationship between size, shape and surface chemistry of ENPs and intracellular and in vivo bio-distribution is still insufficiently understood [101]. Computer modeling of spatial and temporal resolutions has enabled the investigation of ENP interactions with biomolecules [102]. Typical cellular components are on the same size scale as ENPs, so significant interatomic interaction occurred between ENPs and biomolecules, such as peptide and DNA-functionalized Au NPs [103] and DNA-CNTs arrays [104]. The surfaces of carbon NPs were favored by hydrophobic interactions with π - π stacking of aromatic side chains [105]. The insertion process of CNTs into the DNA molecules is controlled by van der Waal forces [106]. Adsorption onto graphene partially disrupted the tertiary structure of proteins [107]. ENPs such as QDs, CNTs, and CeO₂ showed protein fibrillation by nucleation-dependent kinetics leading to protein unfolding [108]. Hydrophobic ENPs (e.g. CNTs and fullerenes) were also able to transverse the lipid bilayer [109]. Au NPs showed the potential to adhere, repel, or penetrate the lipid bilayers depending on the density and surface charge of ENPs [110]. Thus, biotic macromolecules potentially influence the transformation of ENPs. Overall, available data show that the interaction of ENPs with biological matter is a crucial factor in their transformation and bioavailability studies.

2.1.5. Photocatalytic transformation

Phototransformation is a significant process in regulating the fate and behavior of ENPs. They are linked to the reactive transients of various excited states and reactive oxygen species (ROS) of source and sink which can mediate the photoreactions. As an example, fullerene showed an easy transformation by different steps of photo-oxidation in aqueous solution [111]. When ground-state C₆₀ was photo-excited to singlet state (¹C₆₀), a rapid intersystem crossing (ISC) transformed it from singlet state to triplet state (³C₆₀), then quenched by O₂ molecules through energy transfer to generate the singlet oxygen (¹O₂) [112]. The singlet oxygen reacted with ³C₆₀ to form C₆₀-epoxides (C₆₀O) [113]. The phototransformation of C₆₀ is shown below (Eqs. (4) and (5)):



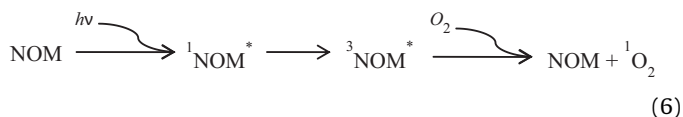


The photocatalytic exposure of ENPs was investigated in the generation of ROS species. Chen and Jafvert have reported the sunlight-driven production of ROS species by photoactive CNTs [114]. Functionalized SWCNTs (carboxyl and polyethylene glycol derivatives) generated radical species including singlet oxygen, superoxide radical anion ($\text{O}_2^{\bullet-}$), and hydroxyl radical ($\bullet\text{OH}$) in the solar spectrum (300–410 nm). However, the aqueous dispersion of uncoated SWCNTs under solar light conditions for several days led to insignificant formation of ROS. Amorphous carbon and metal impurities within different SWCNT preparations contributed to ROS generation.

Surface coatings can affect phototransformation. Li et al. have investigated the photokinetics of Ag NPs under ultraviolet (UV) irradiation (UV-365) [115]. Uncoated Ag NPs produced ROS species ($\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$), but citrate-coated Ag NPs yielded only $\text{O}_2^{\bullet-}$, and ROS were undetected for PVP-coatings. The maximum time-dependent release (5 h) of Ag^+ ions was observed for uncoated Ag NPs. Sterically stabilized PVP-coated Ag NPs showed a higher level of persistence than electrostatically citrate-stabilized Ag NPs. Further investigations highlighted the role of polymer surface coatings in shielding against the ENP photocorrosion process. For example, the Ag NPs with polymer coatings (e.g. PVP or Tween) showed higher stability than citrate or gum arabic coatings in forming aggregates in sunlight [116,117]. Oscillating dipole–dipole interaction formed larger aggregates whereas UV-irradiation formed smaller fragments of Ag NPs [118].

Phototransformation with cellular systems has been the subject of various investigations. Xia et al. have reported that ROS generation was promoted by the interaction of Zn NPs with living cells [63]. Crystal lattice imperfection and surface defects caused the generation of ROS [119]. Photoactive Zn NPs and Ti NPs have enhanced the production of ROS causing oxidative stress at several folds, resulting in phototoxicity to the ecological receptors [120]. Similarly, the photocatalytic activity of Ti NPs induced oxidative stress to *Escherichia coli* via the formation of $\bullet\text{OH}$ radicals leading to lipid peroxidation in bacterial inactivation [121]. Clearly, light-induced formation of ROS caused changes to cellular systems.

2.1.5.1. NOM-mediated photoreactions. NOM have caused variations in photoreaction pathways. Mostafa and Rosario-Ortiz have investigated the photochemical behavior of organic matter (OM) in wastewaters [122]. Wastewater OM acted as a photosensitizer facilitating the formation of ROS species including $\bullet\text{OH}$ and ${}^1\text{O}_2$. Dong and Rosario-Ortiz have reported higher formation of $\bullet\text{OH}$ in wastewater OM compared to OM isolates, so the concentration of ${}^1\text{O}_2$ is higher in wastewater-impacted systems than the unimpacted ones [123]. Thus, significant transformation can occur in a non-conventional wastewater treatment plant without the addition of disinfectant or other energy or chemically mediated processes (Eq. (6)):



Kong et al. have investigated the impact of NOM (e.g. HA and FA) on photokinetics [124]. The photoreaction of C_{60} in water (aqua/ $n\text{C}_{60}$) was quenched by NOM. Quenching decelerated the reactions through NOM adsorbed in aqua/ $n\text{C}_{60}$, leading to slow deposition attachment onto the surfaces of ENPs [125]. Solar irradiation caused the oxidation of $n\text{C}_{60}$ surfaces with negative surface charge and hydrophobicity. Consequently, fullerene is more stable due to aggregate inhibition and the photoreaction rate. In

contrast, the photoreaction of hydrophilic fullerene (fullerenol) was sensitized by NOM. Photosensitization accelerated the reactions by triplet excited state intermediates. So, both the photosensitization and the quenching of ENPs were influenced by NOM. The generation of Ag NPs and Au NPs were investigated by HA (as a model for dissolved organic matter (DOM)) under natural sunlight [126]. HA acted as a reductant and a coating agent to stabilize NPs in the sunlight-driven photoreduction of Ag^+ and Au^{3+} ions in environmental waters. Thus, the formation of AgNPs or AuNPs from ionic species through the NOM-mediated photoreduction procedure is highly possible in environment.

The cycle of chemical oxidation of Ag NPs to release Ag^+ and reformation to form Ag NPs is expected to occur in aquatic environment due to the oxidation of AgO and reduction of Ag^+ . Yu et al. have proposed a three-stage pathway for the transformation of highly dynamic PVP-coated Ag NPs under light irradiation [127]. Rapid oxidation of Ag NPs and release of Ag^+ (dissolution) occurred by light induced photodegradation of PVP (capping agent). Then, re-adsorption of Ag^+ on the Ag NP surface and reformation of small particles ensued. Finally, NPs participated in various cross-linking structures, forming aggregates and precipitation of Ag nanostructures. Therefore, Ag NPs can undergo oxidation and reduction simultaneously, along with release of Ag^+ , regeneration of secondary NP, and morphology changes from dispersed spherical NPs to larger aggregates, tiny particles, or settle down under environmentally relevant conditions. Aforementioned research demonstrates the easy photocatalytic transformation pathways of ENPs in the environment.

2.1.6. Aerobic and anaerobic environments

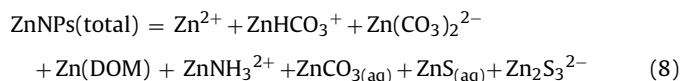
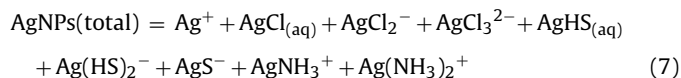
The predominant ligand species depend on the redox state and abundance, in both aerobic and anaerobic soil and natural waters [17]. Chloride and S^{2-} ions are often present in natural water and biological growth media and have a strong affinity for oxidized metals (e.g. Ag). Thermodynamically, oxidized Ag NPs typically react with reduced S-groups or Cl^- ions. Reactions of the Ag^+ ions, released from Ag NPs, with Cl^- ions are more favorable in aerobic than in anaerobic systems due to production of HS^- in many anaerobic system. Increased interactions between Ag^+ and HS^- ions makes the interface of Ag^+ ions with Cl^- less important in anaerobic system [64] and the sulfidation of Ag NPs was observed in anaerobic environments [128].

The formation of ENPs is potentially significant at the sites of high metal concentrations. For example, the formation of Ag NPs in surface water was influenced by wastewater or acid mine drainage [129,130]. Similarly, Ag NPs leached from certain consumer textiles after repeated washing [131] and Ag NPs (up to 70–90%) from tested sock fabrics were noted in dissolute ionic form that could possibly end up in sewage treatment plants (STPs). Moreover, Li et al. have reported the effect of Cl^- ions on stability of Ag NPs [32]. A passive layer of AgCl on the surfaces of Ag NPs inhibited dissolution. Furthermore, the oxidative dissolution of Ag NPs significantly decreased at a low Cl/Ag ratio, but a high Cl/Ag ratio enhanced dissolution rate due to soluble $\text{AgCl}_x^{(x-1)-}$ species [57], highlighting a potential route of transformation.

Environmental oxysulfidation reaction is important because they mediate the transformation. ENP oxysulfidation produces metal sulfide by the reaction of metal NPs with sulfide and an oxidant simultaneously. Therefore, this process transforms metal NPs to metal sulfides and metal-sulphydryl species to various extents [132]. For example, the Ag NPs rapidly transformed to stable Ag_2S in anaerobic environments [128], most likely in the mixing zone where both oxygen and sulfide co-exist.

Leachate-produced waste consisting of aqueous phase dynamic heterogeneous materials can also affect the behavior of ENPs. For example, Bolyard et al. have examined the interaction of common

ENPs and components of landfill leachates [133]. According to the chemical speciation model, Ag potentially was chelated with sulfide and ammonia species. Moreover, Ag predominately reacted with ammonia [Ag(NH₃)₂⁺] or chloride [AgCl₂ and AgCl (aq)] along with free ions at low sulfide concentration. The majority of Zn NPs associated with DOM, CO₃²⁻/HCO₃⁻, and Zn²⁺ ions. Yet ENPs were also observed with solid waste mass through adsorption. The main chemical species of Ag NPs and Zn NPs in the mobile aqueous phase of leachate are shown below (Eqs. (7) and (8)):



Time-dependent changes in the transformation of Ag NPs into environmental matrices were rapid [128]. Major Ag₂S (>90% was observed at concentration of 0.5 mg/L (~170 mg Ag/kg of total suspended solid) in anaerobic tanks during a short time period (<2 h). Furthermore, the ~60% fraction of Ag₂S transformed within 2 h at a high Ag concentration of 5 mg/L (~1700 mg Ag/kg of total suspended solid) but this fraction did not increase further even after 5 h, indicating the available sulfide was completely exhausted in the transformation process. Thus, the environmental setting of aerobic and anaerobic conditions can affect transformation pathways.

2.2. Biotic pathways for NP formation

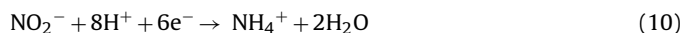
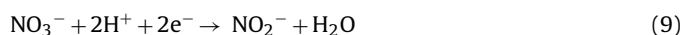
The natural environment is a source of crude unprocessed extracts from the tissues of different flora and fauna. Consequently, understanding the role of biomolecules is important in order to identify biotransformation. Biopolymers from plant and microbial cell extracts possess reductive enzymes and reducing functional groups, which can transform metal ions into the corresponding NP in a short time [134]. The natural growth of living organisms is a common bottom-up approach to ENP formation. The development of NPs is controlled by process variables such as reducing capacity, precursor concentration, solvent polarity, and stabilizer. As an example, ascorbic acid (a natural reducing agent) shows the potential to transform metal ions in the formation of NPs [135].

Various plant species have ability to form NPs according to their reducing abilities. Dubey et al. have demonstrated a simple protocol for the formation of Ag NPs and Au NPs (~20 to 50 nm) using leaf extracts from different plants [136]; tansy leaf mediated Au NPs showed the most stable forms due to their high negative ζ-value (-41.7 mV). Generally, the reduction and stabilization of NPs are attributed to the phenolic and/or hydroxyl-substituted functional groups and various metabolites of terpenoids and reduced sugar in the plants. They can act both, as reducing and stabilizing ligands in the development of NPs. Redox ability is primarily due to a complex system of phenolic compounds, which act as hydrogen donors, singlet oxygen quenchers and metal chelating agents in NP formation [137].

The biotransformation potential of mesophytic (*Cyperus sp.*), hydrophytic (*Hydrilla sp.*), and xerophytic (*Bryophyllum sp.*) plants were investigated for Ag NP development [138]. Mesophytic plants demonstrated tautomerization of three types of benzoquinones including cyperoquinone, dietchequinone and remirin in nano-transformations. Furthermore, reactive hydrogen liberated from ascorbic acid in the hydrophytes and catechol transformed into protocatechuic aldehyde and protocatechuic acid. Thus, the released

reactive hydrogen contributed to the formation of Ag NPs. In addition, organic acids are generated regularly in the xerophytic leaves due to redox reactions. So, the reaction of CO₂ with phosphoenol pyruvate (PEP) by the enzyme PEP carboxylase formed oxaloacetic acid and the emodin molecules underwent tautomerization (keto-enol conversions), thereby facilitating the reduction of Ag⁺ ions in plant extracts. Consequently, the redox changes in plants lead to biotransformation of Ag NPs (Fig. 5).

The metal transformation ability of microorganisms has been explored. Generally, O₂ is the preferred e⁻ acceptor. However, alternative e⁻ acceptors are depleted thermodynamically by Gibb's free energy as: O₂ > NO₃⁻ > Mn(IV) > Fe(III) > SO₄²⁻ > CO₂ [139]. As an example, in biosynthesis of Ag nanoparticles by cyanobacteria, it is expected that Ag⁺ reduced by an intracellular electron donor system through the reduction of nitrate to nitrite and then to ammonium (Eq. (9)–(11)) [140]:



The literature shows that the extracellular development of NPs is more common than intracellular pathways in microorganisms. For example, the archaeobacterium *Pyrobaculum islandicum* formed extracellular spherical NPs of different metallic ions (U⁶⁺, Tc⁷⁺, Cr⁶⁺, Co³⁺, and Mn⁴⁺) [141]; their reducing power was dependent on the presence of cell suspensions and availability of hydrogen (e⁻ donors) in transformations.

Similarly, many fungi including *Verticillium sp.*, *Cladosporium cladosporioides*, *Trichoderma asperellum* and *Volvariella volvacea*, and some species of *Aspergillus*, *Penicillium* and *Fusarium* have been investigated for the transformation of metal into their NP form. For example, Ahmad et al. have investigated the extracellular formation of bimetallic (Au-Ag) NPs by *Fusarium oxysporum* biomass [142]. Basavaraja et al. have reported the extracellular reduction of Ag⁺ ions through nitrate-dependent reductase enzymes and shuttle quinine using *Fusarium semitectum* [143]; amino acid and peptide acted as potential stabilizers in the bio-inspired production of Ag NPs. In addition, several algae including *Nannochloropsis oculata*, *Dunaliella salina* and *Chlorella vulgaris* were reported to assist the formation of Ag NPs [144]. *Neurospora crassa* produced fairly monodispersed mono- and bimetallic NPs (Ag and Au) by both the intra- and extracellular pathways [145]. Similarly, the marine alga *Sargassum wightii* was used to reduce aqueous AuCl₄⁻ ions into Au NPs [146].

Most of the biopolymeric NPs are derived from polysaccharide, protein, or polypeptide, which undergoes a wide range of biotransformations in natural systems. Various biopolymeric molecules in the bioconjugate chemistry of NPs are summarized in Table 2. They have the ability to form highly functionalized NPs [147]. Biologically derived ENPs often have one or more additional functional groups that can affect the modification of surfaces (e.g. carboxyl, hydroxyl and amine molecules). Hence, the natural systems of almost all living organisms including plant biomass and microorganisms are well suited for the biochemical metal transformation of NPs. As a result, the risks associated with the impact of transformation encourage the study of bioavailability and related processes.

3. Bioavailability potential

The bioavailable species of ENPs are potentially taken up by aquatic and terrestrial biota resulting in bioaccumulation and biomagnification in food chains. For example, the soluble metal ion released from ENPs can render them bioavailable to ecological receptors [148]; transformation pathway of ENPs changes their

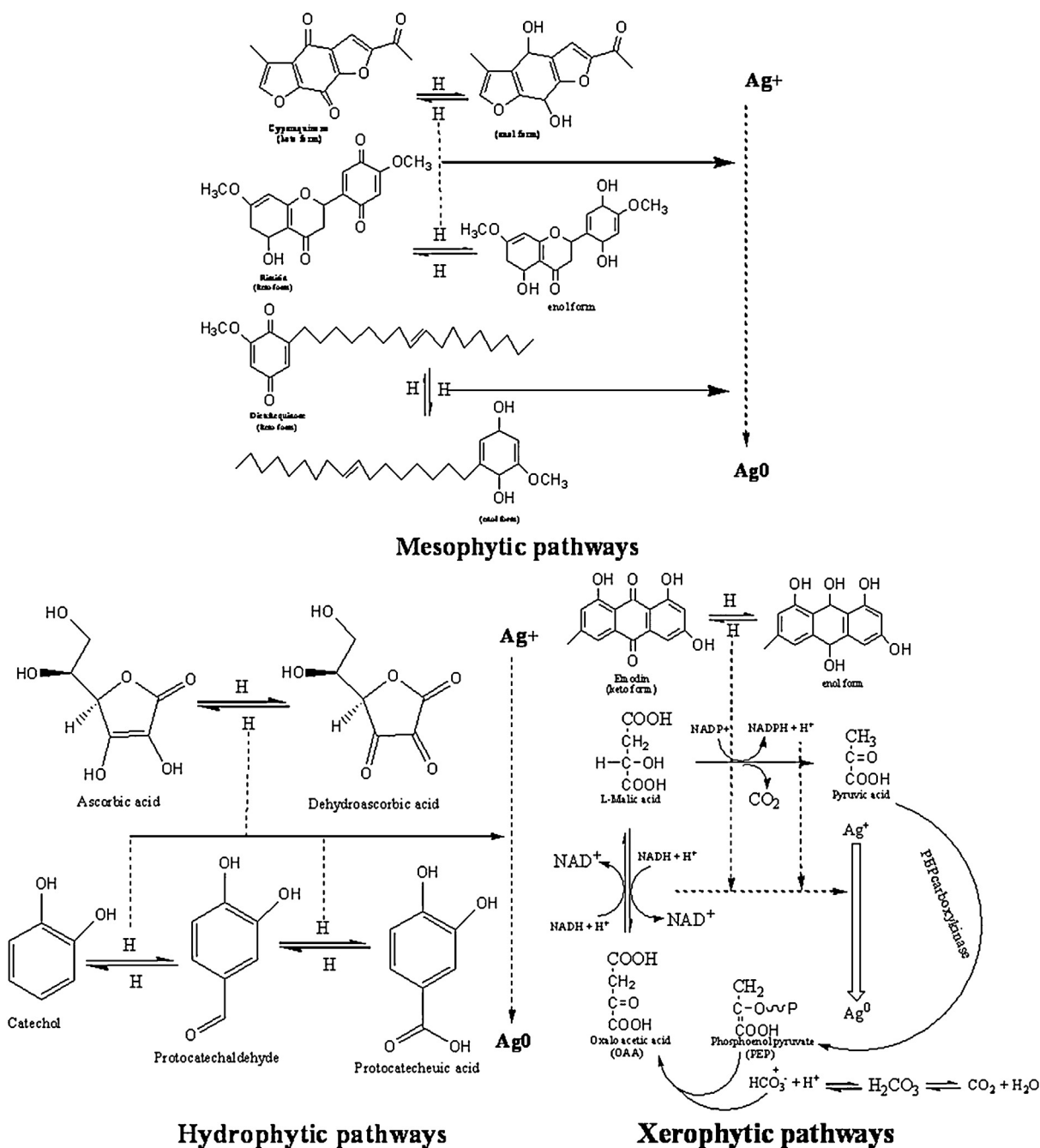


Fig. 5. Plant-mediated pathways of Ag NPs formation.

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bioavailability to different plants or organisms. Lowry et al. have investigated the transformation of Ag NPs with distribution in soil and sediment in freshwater mesocosms [15]; Ag NPs transformed to Ag_2S (52%) in soil compared to 55% in subaquatic sediment. Sulfidation was greater in aquatic sediment due to the anoxic conditions and favorable geochemical phase for Ag [149]. Concurrently, erosion and runoff were observed to release Ag NPs from terrestrial soil to sediment. In addition, in terrestrial plant biomass, mosquito fish and chironomids, Ag concentrations of 0.17 mg/kg and 0.5–3.3 mg/kg, respectively were observed, showing the potential bioavailability of Ag NPs even after significant sulfidation. How long does Ag remains bioavailable and what the bioavailable species are remains unclear, however, studies show that transformation products including ions, sulfide, or sulfhydryl classes or

products with (un)known compositions may be part of the explanation.

ENP size, their bulk composition, and surface coating all influence their bioavailability and aging. For example, Urine et al. have showed that smaller Au NPs (20 nm) were more bioavailable than larger ones (55 nm) due to the extent of their aggregation in soil pore water [150]. The absorption of Au NPs showed nanoparticulate forms rather than ionic species in the bio-distributed tissues of earthworms (*Eisenia fetida*). ENPs clearly showed biomagnification and trophic transfer in terrestrial food chains [151]. Furthermore, Li et al. have reported that surface coatings of HA, FA and alginate enhanced bioavailability of Zn NPs compared to coating with tannic acid [152]; variations in coatings showed a differential affinity to Zn^{2+} ions in complex formation with NOM. Mudunkotuwa

Table 2
Various biopolymeric molecules in formulation of NPs.

Biopolymer	Description	Studies
Polysaccharide		
Cellulose	Abundant renewable polymer, structural components of primary cell walls of higher plants, hydrophilic	[237]
Starch	Renewable polymer, storage energy source of majority of plants	[238]
Chitosan	Product of deacetylation of chitin, linear cationic, structural component of the exoskeletons (e.g., crustaceans and fungal cell walls)	[239]
Heparin	Anionic, highly sulfated glycosaminoglycan, highest negative charge density of any known biomolecule	[240]
Alginate	Linear anionic, extracted from seaweeds, capacity to absorb water quickly	[239]
Hyaluronate	Anionic, non-sulfated glycosaminoglycan linear chain, component of extracellular matrix of humans.	[241]
Dextran	Branched polysaccharide of many glucose units	[242]
Protein		
Collagen	Abundant macromolecules of proteins in mammals, main component of fibrous tissues (e.g., fibroblast cells)	[243]
Albumin	Most abundant plasma protein in mammals, e.g. human serum albumin (HSA) and bovine serum albumin (BSA)	[244]
Casein	A phosphoprotein source of mammalian milk, forms casein micelles by Ca ²⁺ ions and hydrophobic interactions	[245]
Gelatin	Derived from the hydrolysis of collagen, gelling agent as stabilizer and thickener	[246]
Heat shock proteins (HSPs)	Induced by heat shock, named according to molecular weight (e.g., HSP60, HSP70, HSP 90), triggers when cells are exposed to higher temperature or stress factors	[247]
Protamine	Small nuclear protein, Arg-rich amino acid residues	[248]
Ferritin	Intracellular Fe-storage protein, produced by nearly all living organisms	[249]

et al. have investigated Cu-based NPs of different oxidation levels including Cu (new), Cu (aged), and CuO (oxide form) for the adsorption of organic acids [153]. Apart from the new Cu NPs, the other two samples showed sorption by organic acids (citric and oxalic acid). The enhanced concentrations of Cu complexation with organic acids varied the bioavailability of ENPs. Moreover, smaller ENPs showed higher solubility and stability, whereas aged Cu NPs increased in size due to coalescence and coarsening under ambient environmental conditions. Thus, a greater colloidal stability of ENPs resulted in their potential bioavailability and increased residence time in the aqueous environment.

The exposure period can further affect bioavailability [154]. For example, Lombi et al. have reported the rapid transformation of Zn NPs to ZnS within one day during the anaerobic treatment of wastewater sludge [155]. A high volume of ZnS (67–96% of total Zn) was noted in fresh biosolids, compared to nil in aged biosolids. The age of the biosolids affected the speciation of Zn NPs due to their degree of transformation. Similarly, the uptake of CNT conjugates was very rapid, occurring within minutes in the vascular bundles of tomato plants [156]. Moreover, Reinsch et al. have noted that the faster rate of oxidation of nZVI resulted in the rapid loss of Fe⁰, within one day [157]. Samples aged six-month showed different oxide mineral phases and sulfate species. Therefore, the rapid depletion of Fe⁰ and oxide phases slowed down aggregation [158]. Consequently, the transformation and aging of nZVI facilitated bioavailability to aquatic or terrestrial biota.

3.1. Plant species specific changes

The uptake dissimilarity of ENPs between plants suggests changes in bioavailability. Judy et al. have investigated the differences in bioavailability of monocot and dicot plants [13]. The size of Au NPs and surface coatings altered bioavailability to plants. In dicot plants, accumulation of different sizes (10, 30, and 50 nm) of Au NPs was found for tobacco, whereas in monocot plants no accumulation for any sizes of Au NPs was found for wheat, although Au NPs adsorbed to the surfaces of wheat root. Apparently, the Au NPs showed greater aggregation in wheat than in tobacco plants. As an example, wheat plants showed 88.3% and 93.3% larger aggregates

(>80 nm) for tannate-coated and citrate-coated Au NPs, respectively, but just 61.4% and 67.9% for tobacco plants, with 10 nm Au NP treatment to both plants. The variation in GNP aggregation was due to the differences in root exudates for different compounds.

The bioavailability of ENPs was examined further through biotic and abiotic interactions on different plants. Recently, Glenn and Klaine highlighted a four-way interaction using two abiotic and two biotic factors [6]. Bioavailability was investigated depending on the size of Au NPs (4-, 18- and 30-nm), dissolved organic carbon (DOC) presence/absence, root presence/absence, and aquatic macrophytes; absorption of Au NPs was plant species specific. The free-floating plant *Azolla caroliniana* has an increased surface area of roots, which were in contact with water due to the root hairs. Submerged plants (*Myriophyllum simulans* and *Egeria densa*) were either rooted or free-floating, showing the absence or presence of root structures. The presence of DOC showed a complex of Au NPs-DOC with Au NP sizes of 4 and 18 nm, leading to reduced aggregation and inhibited absorption of Au NPs by aquatic plants; DOC reduced the bioavailability for both sizes of Au NPs. Interestingly, the same effect was not observed with larger Au NP treatments (30 nm). Both DOC and roots played an important role in tissue concentration of Au NPs in *A. caroliniana*. Consequently, the bioavailability is easily affected by the abiotic and biotic interactions in natural systems.

Research shows that the environmentally induced changes in transformation, bioavailability, and related processes (such as aging) are closely interrelated. Fig. 6 summarizes this complex interplay of physicochemical and biological interactions on the transformation pathways of ENPs.

4. Current perspective

Natural NP in the aquatic and terrestrial environment differs from those in synthetic media due to the presence of natural and colloidal materials [10]. Aggregation and dissolution are important processes of synthetic ENPs in laboratory conditions [38,55,159]. In contrast, natural NPs are complex moieties of natural growth and chemical heterogeneity; as an example, the biotic and abiotic growth of iron oxide demonstrates different optical and catalytic

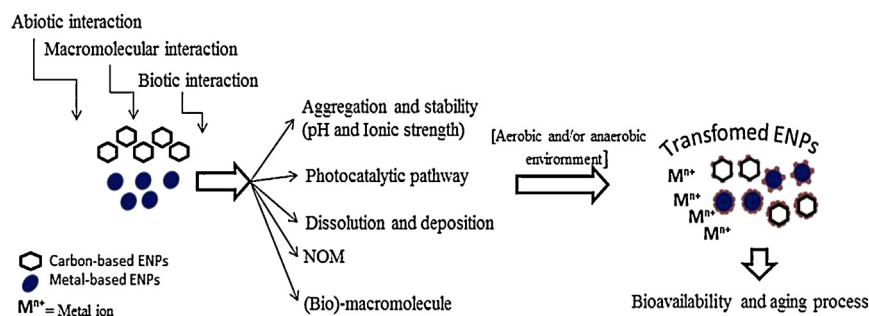


Fig. 6. Summary of ENPs transformation pathways.

properties [160]. Various processes such as immobilization, metal binding, organic transformation and contaminant uptake may be coupled with natural NPs. Accordingly, data generated under standard laboratory conditions cannot translate directly into the natural systems. Additionally, experimental uncertainty in studies of particle concentrations (typically in the $\mu\text{g/L}$ or $\mu\text{g/kg}$ range) presents a major challenge to investigation at the environmentally relevant concentrations. Furthermore, the 'core-shell' model of ENPs shows that transformation affects the core, shell or both in the environment [15]. However, many transformation studies consider core, shell separately and seldom consider core-shell structure together [17].

The results in the literature provide essential tools in order to determine the most important issues for research over the next few years. However, many questions still need to be addressed more carefully before a consensus can be reached on the transformation of ENPs. For example, what transformations are expected at varying electrolyte types and concentrations; solution pH; NPs' particle size and coating; interactions with the environmental macro, micro, nano-species and different physical conditions including flow rate, temperature, etc. How do the acquired and inherited properties of ENPs alter transformation pathways? How is transformation influenced by media composition and biotic interaction? What are the possible stable species of transformed ENPs (aged ENPs) in natural systems? The current awareness of such issues is rather limited.

5. Conclusions

The transformation process for ENPs is altered by a confluence of factors depending on the characteristics of ENPs and of the receiving medium. The interaction of ENPs with both, organic and inorganic ligands, results in changes at the physicochemical, macromolecular and biological levels. Surface coatings including ions, polysaccharide/protein, and NOM can potentially affect the transformation. Electrostatic and steric effects are key determinants in the stabilization process. Aromatic NOM increases stability due to typical π - π interactions, similar to electrokinetic measurements for an increase in negativity of ζ -potential of ENPs. The reactive transients of excited states and generation of ROS species (e.g. $^1\text{O}_2$, $\text{O}_2^{\cdot-}$, and $\cdot\text{OH}$) assist phototransformation. In addition, the aerobic and anaerobic conditions have a putative impact through their differential affinity to ligands, such as sulfidation in anaerobic phase resulting in transformed products. Biopolymers from plants and microorganisms have complex enzyme systems that potentially mediate biotransformation. Plants, bacteria, algae and fungi are all reported to mediate such transformation by a simple energy-efficient process. ENPs show bioavailability potential dependent on the extent of transformation and aging in the environment. The overall study suggests that in this era of nanotechnology, behavior of ENPs remains a critical factor in improving the existing environmental safety framework. Transformations of

ENPs depend strongly on characteristic properties of the ENPs and their respective environment. Hence, it is necessary to explore each NP's property and its environmental interactions to find that particular ENPs' fate in a particular environment considering that none of them will exist to a single composition in ever changing environment.

6. Disclaimer

The U.S. Environmental Protection Agency, through its Office of Research and Development, collaborated in the research described herein. It has been subjected to the Agency's administrative review and has been approved for external publication. Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of the Agency, therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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References

- [1] T. Kurniawan, M. Sillanpää, M.K. Sillanpää, *Crit. Rev. Environ. Sci. Technol.* 42 (2012) 1233–1295.
- [2] C.O. Hendren, X. Mesnard, J. Droge, M.R. Wiesner, *Environ. Sci. Technol.* 45 (2011) 2562–2569.
- [3] P.G. Bystrzejewska, J. Golimowski, P.L. Urban, *Waste Manage.* 29 (2009) 2587–2595.
- [4] P.G. Tratnyek, R.L. Johnson, *Nano Today* 1 (2006) 44–48.
- [5] J.B. Glenn, S.J. Klaine, *Environ. Sci. Technol.* 47 (2013) 10223–10230.
- [6] C. Levard, B.C. Reinsch, F.M. Michel, C. Oumahi, G.V. Lowry, G.E.J. Brown, *Environ. Sci. Technol.* 45 (2011) 5260–5266.
- [7] I. Chowdhury, D.M. Cwiertny, S.L. Walker, *Environ. Sci. Technol.* 46 (2012) 6968–6976.
- [8] R. Grillo, A.H. Rosa, L.F. Fraceto, *Chemosphere* 119 (2015) 608–619.
- [9] K.V. Hoecke, K.A.C.D. Schamphelaere, S. Ramirez-Garcia, P.V. Meeren, G. Smaghe, C.R. Janssen, *Environ. Int.* 37 (2011) 1118–1125.
- [10] H.P. Jarvie, S.M. King, *Nano Today* 5 (2010) 248–250.
- [11] M. Auffan, M. Pedeutour, J. Rose, A. Masion, F. Ziarelli, D. Borschneck, C. Chaneac, C. Botta, P. Chaurand, J. Labille, J.Y. Bottero, *Environ. Sci. Technol.* 44 (2010) 2689–2694.
- [12] W.C. Hou, B. Stuart, R. Howes, R.G. Zepp, *Environ. Sci. Technol.* 47 (2013) 7713–7721.
- [13] J.D. Judy, J.M. Unrine, W. Rao, S. Wirick, P.M. Bertsch, *Environ. Sci. Technol.* 46 (2012) 8467–8474.
- [14] G.V. Lowry, K.B. Gregory, S.C. Apte, J.R. Lead, *Environ. Sci. Technol.* 46 (2012) 6893–6899.
- [15] G.V. Lowry, B.P. Espinasse, A.R. Badireddy, C.J. Richardson, B.C. Reinsch, L.D. Bryant, A.J. Bone, A. Deonarine, S. Chae, M. Therezien, B.P. Colman, H. Hsu-Kim, E.S. Bernhardt, C.W. Matson, M.R. Wiesner, *Environ. Sci. Technol.* 46 (2012) 7027–7036.

- [16] C. Levard, E.M. Hotze, G.V. Lowry, G.E. Brown, *Environ. Sci. Technol.* 46 (2012) 6900–6914.
- [17] A.E. Nel, L. Madler, D. Velegol, T. Xia, E.M.V. Hoek, P. Somasundaran, F. Klaessig, V. Castranova, M. Thompson, *Nat. Mater.* 8 (2009) 543–557.
- [18] B. Nowack, J.F. Ranville, S. Diamond, J.A. Gallego-Urrea, C. Metcalfe, J. Rose, N. Horne, A.A. Koelmans, S.J. Klaine, *Environ. Toxicol. Chem.* 31 (2012) 50–59.
- [19] S.J. Klaine, P.J.J. Alvarez, G.E. Batley, T.F. Fernandes, R.D. Handy, D. Lyon, S. Mahendra, M.J. McLaughlin, J.R. Lead, *Environ. Toxicol. Chem.* 27 (2008) 1825–1851.
- [20] K.L. Garner, A.A. Keller, J. Nanopart. Res. 16 (2014) 2503.
- [21] G.E. Batley, J.K. Kirby, M.J. McLaughlin, *Acc. Chem. Res.* 46 (2013) 854–862.
- [22] B. Nowack, T.D. Bucheli, *Environ. Pollut.* 150 (2007) 5–22.
- [23] Z. Adamczyk, P. Weronksi, *Adv. Colloid Interface Sci.* 83 (1999) 137–226.
- [24] International Organization of Standardization, *Nanotechnologies – Terminology and Definitions for Nano-Objects*, ISO/TS 27687:2008(E), ISO, Geneva, Switzerland, 2008.
- [25] E.M. Hotze, T. Phenrat, G.V. Lowry, *J. Environ. Qual.* 39 (2010) 1909–1910.
- [26] K.A. Huynh, K.L. Chen, *Environ. Sci. Technol.* 45 (2011) 5564–5570.
- [27] J.C. Crittenden, W.H. Montgomery, *Water Treatment Principles and Design*, John Wiley & Sons Inc., Hoboken, NJ, 2005.
- [28] D. Zhou, A.I. Abdel-Fattah, A.A. Keller, *Environ. Sci. Technol.* 46 (2012) 7520–7530.
- [29] A.R.M.N. Afroz, I.A. Khan, S.M. Hussain, N.B. Saleh, *Environ. Sci. Technol.* 47 (2013) 1853–1860.
- [30] P. Yi, K.L. Chen, *Langmuir* 27 (2011) 3588–3590.
- [31] D. Bouchard, X. Ma, C. Isaacson, *Environ. Sci. Technol.* 43 (2009) 6597–6600.
- [32] X. Li, J.J. Lenhart, H.W. Walker, *Langmuir* 26 (2010) 16690–16798.
- [33] D. He, M.W. Bligh, T.D. Waite, *Environ. Sci. Technol.* 47 (2013) 9148–9150.
- [34] K.L. Chen, M. Elimelech, *Langmuir* 22 (2006) 10994–11001.
- [35] N.B. Saleh, L.D. Pfefferle, M. Elimelech, *Environ. Sci. Technol.* 42 (2008) 7963–7970.
- [36] B. Smith, K. Wepasnick, K.E. Schote, A.R. Bertele, W.P. Ball, C. O'Melia, D.H. Fairbrother, *Environ. Sci. Technol.* 43 (2009) 819–825.
- [37] K.L. Chen, M. Elimelech, *Environ. Sci. Technol.* 43 (2009) 7270–7280.
- [38] R.A. French, A.R. Jacobson, B. Kim, S.L. Isley, R.L. Penn, P.C. Baveye, *Environ. Sci. Technol.* 43 (2009) 1354–1360.
- [39] I. Chowdhury, M.C. Duch, N.D. Mansukhani, M.C. Hersam, D. Bouchard, *Environ. Sci. Technol.* 47 (2013) 6288–6290.
- [40] M.C. Duch, G.R.S. Budinger, Y.T. Liang, S. Soberanes, D. Urich, S.E. Chiarella, L.A. Campochiaro, A. Gonzalez, N.S. Chandel, M.C. Hersam, G.M. Mutlu, *Nano Lett.* 11 (2011) 5201–5210.
- [41] R.I. MacCusprie, *J. Nanopart. Res.* 13 (2011) 2893–2900.
- [42] S. Rathnayake, J.M. Unrine, J. Judy, A.-F. Miller, W. Rao, P.M. Bertsch, *Environ. Sci. Technol.* 48 (2014) 4757–4760.
- [43] F. Loosli, S. Stoll, *J. Colloid Sci. Biotechnol.* 1 (2012) 1–9.
- [44] K.G. Marinova, R.G. Alargova, N.D. Denkov, O.D. Veliev, D.N. Petsev, I.B. Ivanov, R.P. Borwankar, *Langmuir* 12 (1996) 2045–2050.
- [45] G.V. Andrievsky, V.K. Klochkov, A.B. Bordyuh, G.I. Dovbeshko, *Chem. Phys. Lett.* 364 (2002) 8–17.
- [46] J. Brant, H. Lecoanet, M. Hotze, M. Wiesner, *Environ. Sci. Technol.* 39 (2005) 6343–6350.
- [47] R. Zimmermann, S. Dukhin, C. Werner, *J. Phys. Chem. B* 105 (2001) 8544–8550.
- [48] W. Zhang, C.W. Isaacson, U. Rattanaudompol, T.B. Powell, D. Bouchard, *Water Res.* 46 (2012) 2992–3000.
- [49] R.F. Considine, C.J. Drummond, D.R. Dixon, *Aust. J. Chem.* 58 (2005) 837–844.
- [50] M.H. Abraham, C.E. Green, W.E. Acree, *J. Chem. Soc. Perkin Trans. 2* (2000) 281–286.
- [51] J.D. Fortner, D.-I. Kim, A.M. Boyd, J.C. Falkner, S. Moran, V.L. Colvin, J.B. Hughes, J.H. Kim, *Environ. Sci. Technol.* 41 (2007) 7497–7502.
- [52] E.J. Petersen, L. Zhang, N.T. Mattison, D.M. O'Carroll, A.J. Whelton, N. Uddin, T. Nguyen, Q. Huang, T.B. Henry, D.R. Holbrook, K.L. Chen, *Environ. Sci. Technol.* 45 (2011) 9837–9856.
- [53] K. Aschberger, C. Micheletti, B. Sokull-Klütgen, F.M. Christensen, *Environ. Int.* 37 (2011) 1143–1156.
- [54] N.M. Franklin, N.T. Rogers, S.C. Apte, G.E. Batley, P.E. Casey, *Environ. Sci. Technol.* 41 (2007) 8484–8490.
- [55] M. Heinlaan, A. Ivask, I. Blinova, H.-C. Dubourgier, A. Kahru, *Chemosphere* 71 (2008) 1308–1316.
- [56] V. Aruoja, H.-C. Dubourgier, K. Kasemets, A. Kahru, *Sci. Total Environ.* 407 (2009) 1461–1468.
- [57] C.M. Ho, S.K.W. Yau, C.N. Lok, M.H. So, C.M. Che, *Chem. Asian J.* 5 (2010) 285–293.
- [58] J. Dobias, R. Bernier-Latmani, *Environ. Sci. Technol.* 47 (2013) 4140–4146.
- [59] A.T. Stone, J.J. Morgan, in: W. Stumm (Ed.), *Aquatic Surface Chemistry: Chemical Processes at the Particle Water Interface*, John Wiley & Sons, Inc., New York, 1987, pp. 221–254.
- [60] J.P. Hoare, in: A.J. Bard, R. Parsons, J. Jordan (Eds.), *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, 1985.
- [61] R. Kumar, H. Munstedt, *Biomaterials* 26 (2005) 2081–2088.
- [62] J.Y. Liu, R.H. Hurt, *Environ. Sci. Technol.* 44 (2010) 2169–2175.
- [63] T. Xia, M. Kovochich, J. Brant, M. Hotze, J. Sempf, T. Oberley, C. Sioutas, J.I. Yeh, M.R. Wiesner, A.E. Nel, *Nano Lett.* 6 (2006) 1794–1807.
- [64] C. Levard, S. Mitra, T. Yang, A.D. Jew, A.R. Badireddy, G.V. Lowry Jr., G.E. Brown, *Environ. Sci. Technol.* 47 (2013) 5738–5745.
- [65] K. Loza, J. Diendorf, C. Sengstock, L. Ruiz-Gonzalez, J.M. Gonzalez-Calbet, M. Vallet Regi, M. Köller, M. Eppler, *J. Mater. Chem. B* 2 (2014) 1634–1643.
- [66] G. Bondietti, J. Sinniger, W. Stumm, *Colloids Surf.* A 79 (1993) 157–167.
- [67] D.M. Cwiertny, G.J. Hunter, J.M. Pettibone, M.M. Scherer, V.H. Grassian, *J. Phys. Chem. C* 113 (2009) 2175–2186.
- [68] M. Li, D. Lin, L. Zhu, *Environ. Pollut.* 173 (2013) 97–102.
- [69] W. Stumm, *Colloids Surf.* A 120 (1997) 143–166.
- [70] Y. Wang, M.D. Becker, V.L. Colvin, L.M. Abriola, K.D. Pennell, *Environ. Sci. Technol.* 48 (2014) 10664–10671.
- [71] K. Ikuma, A.S. Madden, A.W. Decho, B.L.T. Lau, *Environ. Sci.: Nano* 1 (2014) 117–122.
- [72] W. Li, D. Liu, J. Wu, C. Kim, J.D. Fortner, *Environ. Sci. Technol.* 48 (2014) 11892–11900.
- [73] S. Metsämuuronen, M. Sillanpää, A. Bhatnagar, M. Mänttäri, *Sep. Purif. Rev.* 43 (2014) 1–61.
- [74] A. Fernandez-Nieves, F.J.D. Nieves, *Colloids Surf.* A 148 (1999) 231–243.
- [75] S.E. Mylon, K.L. Chen, M. Elimelech, *Langmuir* 20 (2004) 9000–9006.
- [76] K.L. Chen, S.E. Mylon, M. Elimelech, *Environ. Sci. Technol.* 40 (2006) 1516–1523.
- [77] K.L. Chen, M. Elimelech, *J. Colloid Interface Sci.* 309 (2007) 126–134.
- [78] J. Buffle, K.J. Wilkinson, S. Stoll, M. Filella, J.W. Zhang, *Environ. Sci. Technol.* 32 (1998) 2887–2899.
- [79] K.L. Chen, M. Elimelech, *Environ. Sci. Technol.* 42 (2008) 7607–7614.
- [80] C.W. Isaacson, D.C. Bouchard, *Environ. Sci. Technol.* 44 (2010) 8971–8976.
- [81] I. Chowdhury, M.C. Duch, C.C. Gits, M.C. Hersam, S.L. Walker, *Environ. Sci. Technol.* 46 (2012) 11752–11760.
- [82] N.B. Saleh, L.D. Pfefferle, M. Elimelech, *Environ. Sci. Technol.* 44 (2010) 2412–2418.
- [83] K.A. Huynh, J.M. McCaffery, K.L. Chen, *Environ. Sci. Technol.* 46 (2012) 5912–5920.
- [84] H. Hyung, J.D. Fortner, J.B. Hughes, J.H. Kim, *Environ. Sci. Technol.* 41 (2007) 179–184.
- [85] K.A. Thorn, D.W. Folan, P. MacCarthy, *Characterization of the international humic substances society standard and reference fulvic and humic acids by solution state carbon-13 (¹³C) and hydrogen-1 (¹H) nuclear magnetic resonance spectrometry*, U.S. Geological Survey, Water-resources investigations report 89-4196, USGS, Denver, CO, 1989, pp. 93.
- [86] Y. Tan, D.E. Resasco, *J. Phys. Chem. B* 109 (2005) 4454–4460.
- [87] M. Terashima, S. Nagao, *Chem. Lett.* 36 (2007) 302–303.
- [88] B. Xie, Z.H. Xu, W.H. Guo, Q.L. Li, *Environ. Sci. Technol.* 42 (2008) 2853–2859.
- [89] N. Akaighe, R.I. MacCusprie, D.A. Navarro, D.S. Aga, S. Banerjee, M. Sohn, V.K. Sharma, *Environ. Sci. Technol.* 45 (2011) 3895–3901.
- [90] N.F. Adegboyega, V.K. Sharma, K. Siskova, R. Zboril, M. Sohn, B.J. Schultze, S. Banerjee, *Environ. Sci. Technol.* 47 (2013) 757–764.
- [91] S.M. King, H.P. Jarvie, *Environ. Sci. Technol.* 46 (2012) 6959–6967.
- [92] S. Deguchi, T. Yamazaki, S. Mukai, R. Usami, K. Horikoshi, *Chem. Res. Toxicol.* 20 (2007) 854–858.
- [93] T. Cedervall, I. Lynch, S. Lindman, T. Berggard, E. Thulin, H. Nilsson, K.A. Dawson, S. Linse, *Proc. Natl. Acad. Sci. U. S. A.* 104 (2007) 2050–2055.
- [94] I. Lynch, K.A. Dawson, *Nano Today* 3 (2008) 40–47.
- [95] C.C. Chiu, G.R. Dieckmann, S.O. Nielsen, *Biopolymers* 92 (2009) 156–163.
- [96] J. Klein, *Proc. Natl. Acad. Sci. U. S. A.* 104 (2007) 2029–2030.
- [97] R.R. Johnson, A.T. Johnson, M.L. Klein, *Nano Lett.* 8 (2008) 69–75.
- [98] X. Zhao, A. Striolo, P.T. Cummings, *Biophys. J.* 89 (2005) 3856–3862.
- [99] R. Qiao, A.P. Roberts, A.S. Mount, S.J. Klaine, P.C. Ke, *Nano Lett.* 7 (2007) 614–619.
- [100] J. Wong-Ekkabut, S. Baoukina, W. Triampo, I.M. Tang, D.P. Tieleman, L. Monticelli, *Nat. Nanotechnol.* 3 (2008) 363–368.
- [101] H.C. Fischer, W.C.W. Chan, *Curr. Opin. Biotechnol.* 18 (2007) 565–571.
- [102] A.J. Makarucha, N. Todorova, I. Yarovsky, *Eur. Biophys. J.* 40 (2011) 103–115.
- [103] Y.W. Lin, C.W. Liu, H.T. Anal, *Methods* 1 (2009) 14–24.
- [104] G. Lu, P. Maragakis, E. Kaxiras, *Nano Lett.* 5 (2005) 897–900.
- [105] W.H. Noon, Y.F. Kong, J.P. Ma, *Proc. Natl. Acad. Sci. U. S. A.* 99 (2002) 6466–6470.
- [106] H.J. Gao, Y. Kong, D.X. Cui, C.S. Ozkan, *Nano Lett.* 3 (2003) 471–473.
- [107] L.J. Liang, Q. Wang, T. Wu, J.W. Shen, Y. Kang, *Chin. J. Chem. Phys.* 22 (2009) 627–634.
- [108] S. Linse, C. Cabaleiro-Lago, W.F. Xue, I. Lynch, S. Lindman, E. Thulin, S.E. Radford, K.A. Dawson, *Proc. Natl. Acad. Sci. U. S. A.* 10 (2007) 8691–8696.
- [109] W.R. Yang, P. Thordarson, J.J. Gooding, S.P. Ringer, F. Braet, *Nanotechnology* 18 (2007) 412001.
- [110] J. Lin, H. Zhang, Z. Chen, Y. Zheng, *ACS Nano* 4 (2010) 5421–5429.
- [111] W.C. Hou, C.T. Jafvert, *Environ. Sci. Technol.* 43 (2009) 362–367.
- [112] J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz, R.L. Whetten, *J. Phys. Chem.* 95 (1991) 11–12.
- [113] L. Juha, V. Hamplova, J. Kodymova, O. Spalek, *J. Chem. Soc. Chem. Commun.* 21 (1994) 2437–2440.
- [114] C.Y. Chen, C.T. Jafvert, *Carbon* 49 (2011) 5099–5100.
- [115] Y. Li, W. Zhang, J. Niu, Y. Chen, *Environ. Sci. Technol.* 47 (2013) 10293–10300.
- [116] Y. Cheng, L. Yin, S. Lin, M. Wiesner, E. Bernhardt, J. Liu, *J. Phys. Chem. C* 115 (2011) 4425–4430.
- [117] X. Li, J.J. Lenhart, *Environ. Sci. Technol.* 46 (2012) 5378–5380.
- [118] J.M. Gorham, R.I. MacCusprie, K.L. Klein, D.H. Fairbrother, R.D. Holbrook, *J. Nanopart. Res.* 14 (2012) 1–16.
- [119] G. Applerot, A. Lipovsky, R. Dror, N. Perkas, Y. Nitzan, R. Lubart, A. Gedanken, *Adv. Funct. Mater.* 19 (2009) 842–852.

- [120] H. Ma, A. Brennan, S.A. Diamond, *Environ. Toxicol. Chem.* 31 (2012) 2099–2100.
- [121] K. Pathakoti, S. Morrow, C. Han, M. Pelaez, X. He, D.D. Dionysiou, H.M. Hwang, *Environ. Sci. Technol.* 47 (2013) 9988–9990.
- [122] S. Mostafa, F.L. Rosario-Ortiz, *Environ. Sci. Technol.* 47 (2013) 8179–8180.
- [123] M.M. Dong, F.L. Rosario-Ortiz, *Environ. Sci. Technol.* 46 (2012) 3788–3790.
- [124] L. Kong, B. Mukherjee, Y.F. Chan, R.G. Zepp, *Environ. Sci. Technol.* 47 (2013) 6189–6190.
- [125] X. Qu, P.J.J. Alvarez, Q. Li, *Environ. Sci. Technol.* 46 (2012) 13455–13460.
- [126] Y.G. Yin, J.F. Liu, G.B. Jiang, *ACS Nano* 6 (2012) 7910–7920.
- [127] S. Yu, Y. Yin, J. Chao, M. Shen, J. Liu, *Environ. Sci. Technol.* 48 (2014) 403–411.
- [128] R. Kaegi, A. Voegelin, B. Sinnet, S. Zuleeg, H. Hagenlocher, M. Burkhardt, H. Siegrist, *Environ. Sci. Technol.* 45 (2011) 3902–3910.
- [129] A.D. Tappin, J.L. Barriada, C.B. Braungardt, E.H. Evans, M.D. Patey, E.P. Achterberg, *Water Res.* 44 (2010) 4204–4210.
- [130] L.-S. Wen, P.H. Santschi, G.A. Gill, D. Tang, *Environ. Toxicol. Chem.* 21 (2009) 2040–2050.
- [131] T.M. Benn, P. Westerhoff, *Environ. Sci. Technol.* 42 (2008) 4133–4140.
- [132] J.Y. Liu, K.G. Pennell, R.H. Hurt, *Environ. Sci. Technol.* 45 (2011) 7345–7350.
- [133] S.C. Bolyard, D.R. Reinhart, S. Santra, *Environ. Sci. Technol.* 47 (2013) 8114–8120.
- [134] A.D. Dwivedi, K. Gopal, *Colloids Surf., A* 369 (2010) 27–33.
- [135] N.R. Jana, L. Gearheart, C.J. Murphy, *Chem. Mater.* 13 (2001) 2313–2320.
- [136] S.P. Dubey, A.D. Dwivedi, M. Lahtinen, C. Lee, Y.-N. Kwon, M. Sillanpää, *Spectrochim. Acta A* 103 (2013) 134–142.
- [137] Y. Kumarasamy, M. Byres, P.J. Cox, A. Delazar, M. Jaspars, L. Nahar, M. Shueb, S.D. Sarker, *Chem. Nat. Compd.* 40 (2004) 122–128.
- [138] A.K. Jha, K. Prasad, K. Prasad, A.R. Kulkarni, *Colloids Surf. B* 73 (2009) 219–223.
- [139] E.A. Seagren, J.G. Becker, *Practice Period. Hazard. Tox. Radio. Waste Manag.* 6 (2002) 156–172, [http://dx.doi.org/10.1061/\(ASCE\)1090-025X\(2002\)6:3\(156\)](http://dx.doi.org/10.1061/(ASCE)1090-025X(2002)6:3(156)).
- [140] F.M. Lengke, E.M. Fleet, G. Southam, *Langmuir* 23 (2007) 2694–2699.
- [141] K. Kashefi, D.R. Lovley, *Appl. Environ. Microbiol.* 66 (2000) 1050–1056.
- [142] A. Ahmad, P. Mukherjee, S. Senapati, D. Mandal, M.I. Khan, R. Kumar, M. Sastry, *Colloids Surf. B* 28 (2003) 313–318.
- [143] S. Basavaraja, S.D. Balaji, A. Lagashetty, A.H. Rajasab, A. Venkataraman, *Mater. Res. Bull.* 43 (2008) 1164–1170.
- [144] M. Mohseniazar, M. Barin, H. Zarredar, S. Alizadeh, D. Shanehbandi, *Biolm-pacts* 1 (2011) 149–152.
- [145] E. Castro-Longoria, A.R. Vilchis-Nestor, M. Avalos-Borja, *Colloids Surf. B* 3 (2011) 42–48.
- [146] G. Singaravelu, S.J. Arockiamary, G.V. Kumar, K. Govindaraju, *Colloids Surf. B* 57 (2007) 97–101.
- [147] K.E. Sapsford, W.R. Algar, L. Berti, K.B. Gemmill, B.J. Casey, E. Oh, M.H. Stewart, L.L. Medintz, *Chem. Rev.* 113 (2013) 1904–2074.
- [148] E. Navarro, F. Piccapietra, B. Wagner, F. Marconi, R. Kaegi, N. Odzak, L. Sigg, R. Behra, *Environ. Sci. Technol.* 42 (2008) 8959–8964.
- [149] T.W. Bober, A.W. Andren (Eds.), *Silver in the Environment: Transport, Fate, and Effects*, Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, FL, 2002, pp. 27–64.
- [150] J.M. Unrine, S.E. Hunyadi, O.V. Tsyusko, W. Rao, W.A. Shoultz-Wilson, P.M. Bertsch, *Environ. Sci. Technol.* 44 (2010) 8308–8313.
- [151] J.D. Judy, J.M. Unrine, P.M. Bertsch, *Environ. Sci. Technol.* 45 (2011) 776–781.
- [152] M. Li, S. Pokhrel, X. Jin, L. Madler, R. Damoiseaux, E.M.V. Hoek, *Environ. Sci. Technol.* 45 (2011) 755–761.
- [153] I.A. Mudunkotuwa, J.M. Pettibone, V.H. Grassian, *Environ. Sci. Technol.* 46 (2012) 7001–7010.
- [154] E.E. Connor, J. Mwamuka, A. Gole, C.J. Murphy, M.D. Wyatt, *Small* 1 (2005) 325–327.
- [155] E. Lombi, E. Donner, E. Tavakkoli, T.W. Turney, R. Naidu, B.W. Miller, K.G. Scheckel, *Environ. Sci. Technol.* 46 (2012) 9089–9096.
- [156] D.A. Nedoskin, M.V. Khodakovskaya, A.S. Biris, D. Wang, Y. Xu, H. Villagarcia, E.I. Galanzha, V.P. Zharav, *Cytom. Part A* 79 (2011) 855–865.
- [157] B.C. Reinsch, B. Forsberg, R.L. Penn, C.S. Kim, G.V. Lowry, *Environ. Sci. Technol.* 44 (2010) 3455–3461.
- [158] T. Phenrat, N. Saleh, K. Sirk, R.D. Tilton, G.V. Lowry, *Environ. Sci. Technol.* 41 (2007) 284–290.
- [159] Y.G. Wang, Y.S. Li, K.D. Pennell, *Environ. Toxicol. Chem.* 27 (2008) 1860–1867.
- [160] N.S. Wigginton, K.L. Haus, M.F. Hochella Jr., *J. Environ. Monit.* 9 (2007) 1306–1316.
- [161] C.Y. Flores, A.G. Miñán, C.A. Grillo, R.C. Salvarezza, C. Vericat, P.L. Schilardi, *ACS Appl. Mater. Interf.* 5 (2013) 3149–3159.
- [162] F. Cataldo, O. Ursini, G. Angelini, *Eur. Chem. Bull.* 2 (2013) 700–705.
- [163] V.V. Malkar, T. Mukherjee, S. Kapoor, *Mater. Sci. Eng. C* 44 (2014) 87–91.
- [164] A. Mandal, S. Sekar, N. Chandrasekaran, A. Mukherjee, T.P. Sastry, *Proc. Inst. Mech. Eng. H* 227 (2013) 1224–1236.
- [165] Q. Wei, B. Li, C. Li, J. Wang, W. Wang, X. Yang, *J. Mater. Chem.* 16 (2006) 3606–3608.
- [166] X. Zhang, M.R. Servos, J. Liu, *Langmuir* 28 (2012) 3896–3902.
- [167] S.A. Aromal, D. Philip, *Phys. E* 44 (2012) 1692–1696.
- [168] N.S. Sarangi, A.M.P. Hussain, S.N. Sahu, *Appl. Phys. Lett.* 95 (2009) 073109.
- [169] X. Li, K. Tamada, A. Baba, W. Knoll, M. Hara, *J. Phys. Chem. B* 110 (2006) 15755–15762.
- [170] P. Murawala, S.M. Phadnis, R.R. Bhande, B.L. Prasad, *Colloids Surf. B* 73 (2009) 224–228.
- [171] R. Levy, N.T.K. Thanh, R.C. Doty, I. Hussain, R.J. Nichols, D.J. Schiffrin, M. Brust, D.G. Fernig, *J. Am. Chem. Soc.* 126 (2004) 10076–10084.
- [172] T. Laaksonen, P. Ahonen, C. Johans, K. Kontturi, *ChemPhysChem* 7 (2006) 2143–2149.
- [173] M.M. Chilil, V.S.R.R. Pullabhotla, N. Revaprasadu, *Mater. Lett.* 65 (2011) 2844–2847.
- [174] M. Sampath, R. Vijayan, E. Tamilarasu, A. Tamilselvan, B. Sengottuvelan, *J. Nanotechnol.* 2014 (2014), Article ID 626523, 7 pages.
- [175] V.V. Nikesk, A.B. Mandale, K.R. Patil, S. Mahamuni, *Mater. Res. Bull.* 40 (2005) 694–700.
- [176] A.G. Young, N. Al-Salim, D.P. Green, A.J. McQuillan, *Langmuir* 24 (2008) 3841–3849.
- [177] Y. Xu, J. Ma, Y. Xu, L. Xu, L. Xu, H. Li, H. Li, *RSC Adv.* 3 (2013) 851–858.
- [178] J.K. Das, N. Das, *ACS Appl. Mater. Interf.* 6 (2014) 20717–20728.
- [179] S. Sharma, B. Kim, D. Lee, *Langmuir* 28 (2012) 15958–15965.
- [180] D. Fenske, H. Borchert, J. Kehres, R. Kroger, J. Parisi, J. Kolny-Olesiak, *Langmuir* 24 (2008) 9011–9016.
- [181] M. Irfan, N. Eshuis, P. Spanning, M. Tessari, M.C. Feiters, F.P.J.T. Rutjes, *J. Phys. Chem. C* 118 (2014) 13313–13319.
- [182] Y. Borodko, H.S. Lee, S.H. Joo, Y. Zhang, G. Somorjai, *J. Phys. Chem. C* 114 (2010) 1117–1126.
- [183] Y. Kwon, M.G. Kim, Y. Kim, Y. Lee, J. Cho, *Electrochem. Solid-State Lett.* 9 (2006) A34–A38.
- [184] T.T. Vu, F. Mighri, T.O. Do, A. Ajji, *J. Nanosci. Nanotechnol.* 12 (2012) 2815–2824.
- [185] M.A. White, A. Maliakal, N.J. Turro, J. Koberstein, *Macromol. Rapid Commun.* 29 (2008) 1544–1548.
- [186] C.A. Stowell, B.A. Korgel, *Nano Lett.* 5 (2005) 1203–1207.
- [187] J. Fatisson, S. Ghoshal, N. Tufenkji, *Langmuir* 26 (2010) 12832–12840.
- [188] E.D. Vecchia, M. Luna, R. Sethi, *Environ. Sci. Technol.* 43 (2009) 8942–8947.
- [189] M. Zhu, P. Chen, M. Liu, *Langmuir* 29 (2013) 9259–9268.
- [190] V. Khatri, K. Halász, L.V. Trandafilović, S. Dimitrijević-Branković, P. Mohanty, V. Djoković, L. Csóka, *Carbohydr. Polym.* 109 (2014) 139–147.
- [191] N. Padmavathy, R. Vijayaraghavan, *Sci. Technol. Adv. Mater.* 9 (2008) 035004, 7 pages.
- [192] A.K. Singh, *Adv. Powder Technol.* 21 (2010) 609–613.
- [193] S.A. Oh, X.W. Sim, S. Tripathy, *Proc. SPIE* 7155, Ninth International Symposium on Laser Metrology, 71551Y October 03, 2008.
- [194] L. Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge, G.K.L. Wong, *Appl. Phys. Lett.* 76 (2000) 2901–2903.
- [195] J.Y. Park, P. Daksha, G.H. Lee, S. Woo, Y. Chang, *Nanotechnology* 19 (2008) 365603–365610.
- [196] H.L. Ma, X.R. Qi, Y. Maitani, T. Nagai, *Int. J. Pharm.* 333 (2007) 177–186.
- [197] C.L. Lin, C.F. Lee, W.Y. Chiu, *J. Colloid Interface Sci.* 291 (2005) 411–420.
- [198] H. Zhang, R. Wang, G. Zhang, B. Yang, *Thin Solid Films* 429 (2003) 167–173.
- [199] M. Aslam, E.A. Schultz, S. Tao, T. Meade, V.P. Dravid, *Cryst. Growth Des.* 7 (2007) 471–475.
- [200] T. Hyeon, S.S. Lee, J. Park, Y. Chung, H.B. Na, *J. Am. Chem. Soc.* 123 (2001) 12798–12801.
- [201] D.K. Bora, P. Deb, *Nanoscale Res. Lett.* 4 (2008) 138–143.
- [202] M. Hu, H. Yu, F. Wei, G. Xu, J. Yang, Z. Cai, Q. Hu, *Spectrochim. Acta A* 91 (2012) 130–135.
- [203] C. Zhai, H. Zhang, N. Du, B. Chen, H. Huang, Y. Wu, D. Yang, *Nanoscale Res. Lett.* 6 (2011) 31.
- [204] Y.J. Kim, Y.S. Kim, S.Y. Choi, D.H. Cha, Y.S. Choi, W.I. Lee, *New J. Chem.* 31 (2007) 260–264.
- [205] A. Fotopoulos, J. Arvanitidis, D. Christofilos, K. Papaggelis, M. Kalyva, K. Triantafyllidis, D. Niarchos, N. Boukos, G. Basina, V. Tzitzios, *J. Nanosci. Nanotechnol.* 11 (2011) 8593–8598.
- [206] X. Wang, Z. Jiang, B. Zheng, Z. Xie, L. Zheng, *Cryst. Eng. Commun.* 14 (2012) 7579–7582.
- [207] K. Sardar, C.N.R. Rao, *Adv. Mater.* 16 (2004) 425–429.
- [208] S.K. Mehta, S. Chaudhary, K.K. Bhasin, *J. Nanopart. Res.* 11 (2009) 1759–1766.
- [209] S. Liu, A.C.-T. Ko, W. Li, W. Zhong, M. Xing, *J. Mater. Chem. B* 2 (2014) 1125–1135.
- [210] J. Hua, Z. Wang, J. Zhao, L. Xu, J.I. Zhang, R. Li, X. Sun, *J. Macromol. Sci. B* 50 (2011) 679–687.
- [211] D.M. Guldli, *J. Phys. Chem. A* 101 (1997) 3895–3900.
- [212] B. Belgorodsky, L. Fadeev, J. Kolsenik, M. Gozin, *ChemBioChem* 7 (2006) 1783–1789.
- [213] B.P. Binks, P.D. Fletcher, M.A. Thompson, R.P. Elliott, *Langmuir* 29 (2013) 5723–5733.
- [214] I. Slowing, B.G. Trewyn, V.S. Lin, *J. Am. Chem. Soc.* 128 (2006) 14792–14793.
- [215] T.-Y. Lin, D.-H. Chen, *RSC Adv.* 4 (2014) 29357–29364.
- [216] R.S.S. Siddhardha, V.L. Kumar, A. Kaniyoor, V.S. Muthukumar, S. Ramaprabhu, R. Podila, A.M. Rao, S.S. Ramamurthy, *Spectrochim. Acta A* 133 (2014) 365–371.
- [217] B.Y.S. Chang, N.M. Huang, M.N. Anant, A.R. Marlinda, Y. Norazriena, M.R. Muhamad, I. Harrison, H.N. Lim, C.H. Chia, *Int. J. Nanomed.* 7 (2012) 3379–3387.
- [218] A.P.Z. Stevenson, D.B. Bea, S. Civit, S.A. Contera, A.I. Cerveto, S. Trigueros, *Nanoscale Res. Lett.* 7 (2012) 151.
- [219] J. An, B. Tang, X. Zheng, J. Zhou, F. Dong, S. Xu, Y. Wang, B. Zhao, W. Xu, *J. Phys. Chem. C* 112 (2008) 15176–15182.

- [220] M.-T. Wang, M.-H. Liu, C.R.C. Wang, S.Y. Chang, *J. Am. Soc. Mass Spectrom.* 20 (2009) 1925–1932.
- [221] J.-W. Hu, J.-F. Li, B. Ren, D.-Y. Wu, S.-G. Sun, Z.-Q. Tian, *J. Phys. Chem. C* 111 (2007) 1105–1112.
- [222] F. Lu, Q.-H. Zhang, Y. Wang, H.-L. Wan, *Acta Chim. Sinica* 62 (2004) 1713–1716.
- [223] M.E. Grass, Y. Yue, S.E. Habas, R.M. Rioux, C.I. Teall, P. Yang, G.A. Somorjai, *J. Phys. Chem. C* 112 (2008) 4797–4804.
- [224] W.-N. Wang, W.-J. An, B. Ramalingam, S. Mukherjee, D.M. Niedzwiedzki, S. Gangopadhyay, P. Biswas, *J. Am. Chem. Soc.* 134 (2012) 11276–11281.
- [225] A. Dawson, P.V. Kamat, *J. Phys. Chem. B* 105 (2001) 960–966.
- [226] H. Cao, X. Liu, F. Meng, P.K. Chu, *Biomaterials* 32 (2011) 693–705.
- [227] A.J. Wagstaff, S.D. Brown, M.R. Holden, G.E. Craig, J.A. Plumb, R.E. Brown, N. Schreiter, W. Chrzanowski, N.J. Wheate, *Inorg. Chim. Acta* 393 (2012) 328–333.
- [228] S. Santa, C. Tapeç, N. Theodoropoulou, J. Dobson, A. Hebard, W. Tan, *Langmuir* 17 (2001) 2900–2906.
- [229] Z. Cao, Z. Zhang, F. Wang, G. Wang, *Colloids Surf., A* 340 (2009) 161–167.
- [230] L.C. Tien, P.W. Sadik, D.P. Norton, L.F. Voss, S.J. Pearton, H.T. Wang, B.S. Kang, F. Ren, J. Jun, J. Lin, *Appl. Phys. Lett.* 87 (2005) 222106.
- [231] M. Vibin, R. Vinayakan, A. John, F.B. Fernandez, A. Abraham, *Cancer Nanotechnol.* 5 (2014) 1.
- [232] M.A. Hines, P. Guyot-Sionnest, *J. Phys. Chem.* 100 (1996) 468–471.
- [233] J. Zhou, Y. Hu, X. Li, C. Wang, L. Zuin, *RSC Adv.* 4 (2014) 20226–20229.
- [234] H. Liu, K. Zuo, C.D. Vecitis, *Environ. Sci. Technol.* 48 (2014) 13871–13879.
- [235] K. Watanabe, M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, S. Hirai, *J. Electrochem. Soc.* 148 (2001) B473–B481.
- [236] H. Guo, S. Tao, *Sens. Actuators B* 123 (2007) 578–582.
- [237] S. Dong, M. Roman, *J. Am. Chem. Soc.* 129 (2007) 13810–13811.
- [238] C.K. Simi, T.E. Abraham, *Bioprocess Biosyst. Eng.* 30 (2007) 73–80.
- [239] E. Azizi, A. Namazi, I. Haririan, S. Fouladdel, M.R. Khoshayand, P.Y. Shotorbani, A. Nomani, T. Gazori, *Int. J. Nanomed.* 5 (2010) 455–461.
- [240] X. Wang, J. Li, Y. Wang, L. Koenig, A. Gjyzezi, P. Giannakakou, E.H. Shin, M. Tighiouart, Z. Chen, S. Nie, D.M. Shin, *ACS Nano* 5 (2011) 6184–6194.
- [241] M. Bodnar, L. Daroczi, G. Batta, J. Bako, J.F. Hartmann, J. Borbely, *J. Colloid Polym. Sci.* 287 (2009) 991–1000.
- [242] T.T. Beaudette, J.A. Cohen, E.M. Bachelder, K.E. Broaders, J.L. Cohen, E.G. Engleman, J.M. Frechet, *J. Am. Chem. Soc.* 131 (2009) 10360–10361.
- [243] M. Nicklas, W. Schatton, S. Heinemann, T. Hanke, J. Kreuter, *Drug Dev. Ind. Pharm.* 35 (2009) 1384–1388.
- [244] D.J. Naczynski, T. Andelman, D. Pal, S. Chen, R.E. Riman, C.M. Roth, P.V. Moghe, *Small* 6 (2010) 1631–1640.
- [245] Y.D. Livney, *Curr. Opin. Colloid Interface Sci.* 15 (2010) 73–83.
- [246] C.-L. Tseng, W.-Y. Su, K.-C. Yen, K.-C. Yang, F.-H. Lin, *Biomaterials* 30 (2009) 3476–3485.
- [247] M.L. Flenniken, D.A. Willits, A.L. Harmsen, L.O. Liepold, A.G. Harmsen, M.J. Young, T. Douglas, *Chem. Biol.* 13 (2006) 161–170.
- [248] J.O. Liu, S.G. Guo, Z.H. Li, J.R. Gu, *Colloids Surf. B* 73 (2009) 36–41.
- [249] S.-E. Kim, K.-Y. Ahn, J.-S. Park, K.R. Kim, K.E. Lee, S.-S. Han, J. Lee, *Anal. Chem.* 83 (2011) 5834–5843.