

PROPERTIES, TRANSFORMATIONS, AND HEALTH IMPACTS OF ENGINEERED, INCIDENTAL, AND NATURAL NANOPARTICLES

GORDON E. BROWN, JR.^{1*}, CLEMENT LEYARD², A. CRISTINA CISMASU³, F. MARC MICHEL⁴,
GABRIELLE DUBLET¹, RUI MA⁵, YUHENG WANG⁶, GUILLAUME MORIN⁶,
AND GREGORY V. LOWRY⁵

¹Dept. of Geological & Environmental Sciences, Stanford University, Stanford CA 94305-2115, USA

²CEREGE, Europôle Méditerranéen de l'Arbois, BP 80, University of Marseilles III,
13545 Aix en Provence, Cedex 04, France

³Earth Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA 94720, USA

⁴Dept. of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA

⁵Dept. of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

⁶Institut de Minéralogie et de Physique des Milieux Condensés, 4 Place Jussieu, 75252 Paris, Cedex 05, France

Engineered nanoparticles (NPs) (*e.g.*, Ag(0), Au(0), C-nanotubes, TiO₂, Fe₃O₄, ZnO, CuO), have many beneficial uses ranging from catalysts used for efficient production of chemicals (*e.g.*, Au(0)) and photocatalytic degradation of organic pollutants (*e.g.*, TiO₂) to water treatment to remove As (*e.g.*, Fe₃O₄) and use as antibacterial agents (*e.g.*, Ag(0) and ZnO). I will review some of these uses, as well as some of the transformations that ENPs undergo in different environments (*e.g.*, sulfidation of Ag(0), CuO, and ZnO NPs), which can significantly alter their properties (*e.g.*, solubility) and result in lowered health impacts to organisms. For example, engineered Ag(0) NPs, which are commonly coated by polyvinylpyrrolidone (PVP), are readily transformed to Ag₂S and AgCl NPs or aqueous Ag-Cl species when exposed to aqueous solutions containing inorganic sulfide and chloride ions, respectively. Using solubility measurements, XPS, TEM, and high-energy synchrotron x-ray total scattering and pair distribution function analysis, we found that PVP-coated Ag(0) NPs transform to Ag₂S, forming a core-shell structure, which results in significantly lower release of Ag⁺ ions and thus lower toxicity to a variety of organisms. ZnO NPs when exposed to sulphide in aqueous solutions forms ZnS NPs; the transformation mechanism is dissolution followed by re-precipitation, which differs from that for Ag(0) NP sulfidation. When exposed to inorganic sulphide, CuO transforms to CuS (covellite), which results in higher release of Cu²⁺ to solution and higher toxicity. Incidental NPs (*e.g.*, black carbon, α -Fe₂O₃, CaO), and natural NPs (*e.g.*, 2-line ferrihydrite (2L-Fh), Fe₃O₄, ZnS) also interact with the environment in various ways. For example, incidental NPs such as α -Fe₂O₃ produced during combustion of coal in coal-fired electric power plants can adsorb As, Se, and Hg, which results in airborne transport of these toxic species. Natural 2L-Fh NPs from acid mine drainage environments are often associated with natural organic matter (NOM) and high concentrations of Al and Si. We used the same methods as listed above for engineered NPs, in addition to ²⁷Al NMR and scanning transmission x-ray microscopy (STXM), to study the structure and strain of 2L-Fh NPs and their interactions with Si and Al and found that Al can substitute for Fe³⁺, whereas no observable substitution of Si into 2L-Fh structural sites was found. We also found that synthetic 2L-Fh (Fe_{8.2}O_{8.5}(OH)_{7.4}•3H₂O) transforms to a more ordered form of different stoichiometry (Fe₁₀O₁₄(OH)₂•~1H₂O) and ultimately to hematite (α -Fe₂O₃) when exposed to citrate at elevated temperature (175°C). The effects of NOM coatings on the reactivity of 2L-Fh were examined by EXAFS studies of Zn(II)- and U(VI)-reacted 2L-Fh with and without NOM coatings and will be reviewed.