Ph.D. THESIS DEFENSE

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Chemical transformations of lithium cobalt oxide nanoparticles in model environmental systems
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Nanostructured cobalt-containing metal oxides are important materials for catalysis, energy storage, and water purification. These nanomaterials are being rapidly incorporated into numerous commercial products, however, the potential impact to the environment upon improper disposal is still unknown. A commonly overlooked aspect when assessing the environmental and biological safety of engineered nanomaterials is transformation in aqueous systems. Such transformations are poorly understood, and yet will dictate the environmental fate and biological impact of these nanomaterials. We present a comprehensive analysis of the interaction of an environmentally relevant oxyanion, phosphate, with complex metal oxide nanomaterial lithium cobalt oxide (LiCoO$_2$), through the implementation of complementary in situ analytical techniques to probe the reactions occurring at the nanoparticle-liquid interface. Attenuated total reflectance – FTIR (ATR-FTIR) elucidates irreversible binding of inorganic phosphate to the surface of LiCoO$_2$ nanoparticles. This adsorption is significant even at environmentally relevant concentrations, altering LiCoO$_2$ surface charge, and therefore dispersibility in solution. Analysis of the thermodynamics of interaction using flow calorimetry reveals two distinct time regimes where surface reactions between phosphate and LiCoO$_2$ occur at circumneutral pH. Complementing these results with two-dimensional cross correlation analysis of time-course ATR-FTIR spectra elucidates how the vibrational modes of phosphate evolve on the LiCoO$_2$ surface, and the combination of these results allows us to propose a mechanism of phosphate adsorption. These studies highlight the power of using multiple in situ techniques in tandem to tackle complex research questions at the nanoparticle-liquid interface. Forward-looking studies illustrate the promise of using this analytical toolkit to assess chemical transformations of LiCoO$_2$ nanoparticles in model systems of increasing complexity. This work is important for understanding, predicting and controlling the fate and transport of engineered complex metal oxide nanomaterials in the environment.