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Molecular Level Insight for Cu substitution on Hausmannite Nanoparticles: Environmental Implication for Nanocolloid Formation and Fate

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The Cu substituted hausmannite (Cu-Haus) nanoparticle was prepared with Cu(II) addition during the hydrothermal synthesis, and the physiochemical properties and transformation upon the environmental condition were investigated. The characterization includes X-ray diffraction (XRD), Transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS) and depth profile of X-ray photoelectron spectroscopy (DP-XPS). It reveals that bimodal crystallites using the XRD, which was identified as nanocluster (NC, < 3 nm) and nanoparticle (NP, ~30 nm). The XRD and TEM results implied that the size of NC and NP aggregates were increased with Cu(II) addition while the TEM with Energy dispersive X-ray spectroscopy showed even distribution on the NC, NP and aggregates. The Cu substitution mainly occurs at the tetrahedral site of hausmannite at low Cu(II) addition (x=0.01 and 0.02) while the substitution site was not characterized at high Cu(II) addition (x=0.05 and 0.10) due to additional formation of spertiniite and particle size effect. The DP-XPS results implied that the NCs on the surface were accumulated with spertiniite ($Cu(OH)_2$) and Cu-Haus NCs while the Cu(I) and Cu(II) were substituted the tetrahedral and octahedral sites, respectively. Such substitution increase the negatively charged surfaces, and the NCs and NPs had high level of colloidal mobility as the result, but the drying of samples easily make the aggregates of NCs and NPs, which had no colloidal property. The aging effect was monitored for the control (x=0) and Cu-Haus (x=0.2) by incubating at pH 4, 7 and 9 under oxic and anoxic conditions for 9 months. The proton addition readily transformed the samples into the NCs of a-MnO2 while no significant transformation was observed in the Cu-Haus at pH 7 and 9. It indicated that the surface accumulation of Cu-Haus NCs plays a significant role for protecting the haus NPs, and the transformation into the manganite rod work as the strings entangling the aggregates of NCs and NPs, which easily transport from the soil environment into the water system.