THE GEODYNAMICS SEMINAR Nº 548

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Venue: Zoom
A link will be sent @grc-all within 30 minutes before the beginning of the seminar.

Mn(II) oxidation catalyzed by nanohematite surfaces and structural evolution of product Mn oxyhydroxides by self-catalytic reaction.

Mn is considered a minor element in the Earth's crust, but the redox reactions of Mn play a significant role in the geochemical cycling of elements in near-surface environments. We investigated the solid products of heterogeneous catalytic oxidation of aqueous Mn(II) by O_2 in the presence of nanohematite using transmission electron microscopy (TEM), scanning TEM (STEM), and electron energy-loss spectroscopy (EELS). The mechanisms of product Mn oxide nanoparticle evolution were elucidated with a special emphasis on the electron transfer process across the semiconducting nanoparticle.

During 48 h of reaction, a single-phase manganite (a Mn oxyhydroxide) nanowire was formed by way of metastable polymorphs of manganite. Between 48 and 168 h, the manganite further altered to core-shell structured nanowires with hausmannite (a mixed valent Mn oxide) outer-shell on the manganite wire core. The initial formation of Mn oxyhydroxide nanowires was catalyzed by the nanohematite surface. On the other hand, the core-shell structured nanowires are most likely to be formed by the reactions catalyzed by the manganite nanowires themselves. This study shows that the structure of Mn oxide nanowires changes continuously as a result of both nanohematite- and self-catalyzed Mn(II) oxidation. The formation of an outer-shell on the manganite nanowires will change the redox chemistry and phase stability, suggesting that self-catalyzed reactions of product nanowire are as important as nanohematite-catalyzed reaction. Microscopic investigation of interfacial changes in structure and chemistry at the nanoscale is key to understand the kinetic and thermodynamic phenomena in complex, heterogeneous systems such as natural environments.

Keywords:
1. Mn(II) oxidation, 2. HRTEM, 3. Interfacial catalysis

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