Structure transformation of core-shell Mn oxide nanowires by removal of Mn(II) from aqueous solution

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The coexistence of aqueous Mn ions and Mn oxides/(oxyhydr)oxides is common at the interfaces between the hydrosphere and the lithosphere and/or biosphere. In natural systems, Mn oxidation is mediated by microbes or catalyzed by various transition metal oxide nanoparticle surfaces. The products of oxidation typically consist of Mn oxides of lower stability, and they undergo the abiotic transformation into secondary Mn oxides of higher stability as a result of continuous interaction with Mn^{2+}_{aq}. This process may closely relate to the ability of Mn oxides to attenuate heavy metals in the environments. Previous wet chemistry studies provided a macroscopic view of structural transofmration caused by the reaction between Mn^{2+}_{aq} and crystalline Mn oxides. A direct observation of the mineral-fluid interfacial reaction would provide indispensable experimental evidences to elucidate what kind of structural changes of Mn oxide nanoparticles take place and how the changes proceed.

Here, we characterized the transformation of hausmannite (Mn_3O_4) to manganite (γ-MnOOH) in the presence of Mn^{2+}_{aq} and hematite nanoparticles under circumneutral conditions using scanning transmission electron microscopy (STEM) as well as convenient liquid TEM. The hausmannite nanoparticles are initially formed by hematite catalyzed Mn^{2+}_{aq} oxidation [1]. After 48 hours of reaction, the manganite nanowires dominate the products. Both high resolution TEM observations and STEM-electron energy loss spectroscopy analysis of manganite nanowires revealed that they have a core-shell structure with a hausmannite-like outer layer. Most of the Mn oxide nanowires are not in contact with the hematite nanoparticle catalysts. The results indicate that the hausmannite nanowires formed by the hematite catalyzed Mn oxidation, and are then transformed into manganite as a result of continous oxidation under the presence of Mn^{2+}_{aq}.

[1] Veeramani et al., (2013) ACS Sustainable Chemistry & Engineering, 1, 1070-1074.