Facet-Dependent Changes in Crystallinity and Atom Exchange of Hematite Nanocrystals during Fe(II)-Accelerated Recrystallization

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It is well established that the chemical and catalytic activity of crystalline materials can strongly depend on the types and proportions of their exposed facets. Hematite(α-Fe_2O_3) is one such material which exhibits various crystal morphologies include platy, rhombohedral, and rounded, often based upon (001), (012), (110), and (104) facets. To obtain a detailed understanding of facet-specific mechanisms and atom exchange in the Fe(II)-accelerated recrystallization of hematite, we used two different structurally well-defined hematite nanoparticle morphologies reacted with ^{57}Fe(II)*aq* as a tracer at neutral pH. After reaction with ^{57}Fe(II), we observed partial suppression of the Morin transition of hematite to below 13 K. This is significantly lower than the Morin temperature (TM) of ~210 K measured for hematite nanoparticles. And the abundance of weakly ferromagnetic (WF) phase at 13 K for nanoplates dominated by {001} facets and nancubes dominated by {012} facets were 73.6% and 38.0% (based on the Mössbauer spectra area), respectively. {001} facets induced more iron atom exchange than {012} facets, indicating that the Fe(II)-accelerated recrystallization process was mediated by exposed facets of hematite. And facet-spefic differences appear to be not directly linked with the simple aerial cation site density, while with their extent of under-coordination. High resolution transmission electron microscopy (HR-TEM) and fast Fourier transforms (FFT) showed that the {001} facets has the same lattice spacing (2.5 Å) before and after reacted with Fe(II), while the lattice spacing of {012} facets changed from 4.6 Å to 3.7Å. Our results resolving Fe(II)-Fe(III) reaction fronts across multi-faceted crystals provide a clear correlation between recrystallization and particle surface structure.