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A size dependent phase map and phase transformation kinetics for iron(III) oxide nanomaterials (γ →ε→α pathway)

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Nanometric iron(III)-oxide has been of great interest in a wide range of fields due to magnetic properties, eminent biochemical characteristics and potential for technological applications. To date, five crystalline polymorphs of Fe_2O_3 are known: (1) α-Fe_2O_3 (i.e., hematite), (2) β-Fe_2O_3, (3) γ-Fe_2O_3 (i.e., maghemite), (4) ε-Fe_2O_3 (i.e., luogufengite),and (5) ζ-Fe_2O_3, all of which have different morphologies, various size and magnetic properties. Among the iron-oxides, ε-Fe_2O_3 is considered as a remarkable phase due to its giant coercive field at room temperature and ferromagnetic resonance capability. The natural ε-Fe_2O_3 (luogufengite) is discovered from vesicles' surfaces of basaltic scoria. Here we present the first size-dependent phase map for ε-Fe_2O_3 via a γ→ε→α pathway together with the activation energies for the phase transformations based on X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). HRTEM images of ε-Fe_2O_3 nanocrystals show the inversion and pseudo-hexagonal twins, which are fundamentally important for understanding the correlation between its nanostructure and magnetic properties. Two activation energies for γ-Fe_2O_3→α-Fe_2O_3 phase transformations are 186.37±9.89 kJ mol^{-1} and 174.58±2.24 kJ mol^{-1}, respectively. The results provide useful information about the size, crystal structure and transformation of the nanometric iron-oxide polymorphs for applications in areas such as designing engineered materials. Combining the phase map with their kinetic properties predicts that stability regime of the nanosized Fe_2O_3 polymorphs as the function of crystal size, temperature and annealing times. The proposed size-dependent phase map will help to improve controlled synthesis of ε-Fe_2O_3 nanocrystal, a promising material for many future applications.

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