Nanopores in hematite (α-Fe₂O₃) nanocrystals observed by electron tomography

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ABSTRACT

We report the first characterization of the internal structural features within rhombohedral nanocrystals of hematite (α-Fe₂O₃), specifically nanoscale pores (nanopores) within these crystals observed by high-angle annular dark-field scanning transmission electron microscopy tomography. Three-dimensional observations of the internal structure of hematite nanocrystals suggest that the nanopores are formed due to a large reduction in solid volume during the transformation of a poorly crystalline precursor [aggregates of ferrihydrite: Fe₅₋ₓO₄₋ₓ(OH)ₓ₋₃H₂O], which results in the formation of pores between grain boundaries. This formation mechanism is different from those previously reported, such as hollow cores originating from screw dislocations. We also discuss dissolution experiments of the hematite nanocrystals in ascorbic acid solution, in which we demonstrated that the nanopores are reactive sites for dissolution and enlarged by preferential etching. Our findings are of fundamental importance to understanding how certain crystal morphologies, internal structures, defects, and reactive sites occur in nanocrystals formed from a poorly crystalline precursor.

Keywords: Iron oxide nanoparticle, hematite, nanopore, scanning transmission electron microscopy, electron tomography, Kirkendall effect

INTRODUCTION

Iron oxide and iron (oxy)hydroxide minerals, hereafter iron oxides, are present in almost all of the various compartments of the Earth’s surface global system—the atmosphere, hydrosphere, crustal lithosphere, pedosphere, and biosphere—and take part in the manifold interactions between these compartments. Much of the iron oxide in nature is found as nano-sized particles (nanoparticles) in, for example, soil (e.g., Waychunas et al. 2005), river water (e.g., Hochella et al. 2005), airborne mineral dust (e.g., Utsunomiya and Ewing 2003), living organisms (e.g., Banfield et al. 2000), and even martian environments (e.g., Christensen et al. 2001). The pattern of occurrence and distribution of different iron oxides in nature are affected by particle size (Navrotsky et al. 2008, 2010) as well as other extrinsic parameters such as pH, temperature, and pressure. The biogeochemical and ecological impacts of nano-sized iron oxides and other nonminerals and mineral nanoparticles are some of the fastest growing areas of research today (Wigginton et al. 2007; Hochella et al. 2008; Echigo et al. 2012).

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