Nanopores in hematite (α-Fe₂O₃) nanocrystals observed by electron tomography TAKUYA ECHIGO,^{1,2,*} NIVEN MONSEGUE,^{3,4} DEBORAH M. ARUGUETE,^{1,3,†} MITSUHIRO MURAYAMA,^{3,4} AND MICHAEL F. HOCHELLA JR.^{1,3}

¹Center for NanoBioEarth, Department of Geosciences, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.
²Japan International Research Center for Agricultural Sciences, Ohwashi 1-1, Tsukuba 305-8686, Ibaraki, Japan
³Institute for Critical Technology and Applied Science, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.
⁴Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061, U.S.A.

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. Threedimensional 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: Fe_{8.2}O_{8.5}(OH)_{7.4}·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