doi:10.1017/S1431927611005605
Microsc. Microanal. 17 (Suppl 2), 2011

3D Characterization of Nano-Pipes and Nano-Pores in Hematite Particles

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Scanning transmission electron tomography was used to observe a 3D morphology of hematite nano-particles. In this work, 3D tomography of hematite particles, synthesized by forced hydrolysis of an acidic ferric nitrate solution, display nano-pipes and nano-pores which were not previously resolved by 2D HRTEM images. To study these nano-scale features, careful refinement of tomography tilt series acquisition parameters were carried out; thus, allowing higher STEM magnification to be used during a data set acquisition. Finally, a novel reconstruction algorithm called Interior Tomography (IT) is compared with Weighted Back Projection (WBP) and Serial Iterative Reconstruction Technique (SIRT) in studying the formation of nano-pipes and nano-pores in hematite particles.

Electron tomography was performed using a FEI Titan 80-300 electron microscope operated at 200 kV. Tilt-series were acquired in HAADF-STEM mode using a Fischione Model 3000 ADF detector at a beam convergence (half-angle) of 10.5 mrad and a Fischione 2020 ultrahigh-tilt single-axis tomography holder. Images were recorded every 1° in the tilt range of -65 to +65°. Hardware calibrations and software parameters were refined to improve tilt series acquisitions at high magnification. These parameters include: defocus, image shift, and specimen holder tilt shift. Once an acquisition of the tilt series was completed, images were spatially aligned by cross-correlation algorithm using FEI Inspect 3D Express software. 3D Visualization was performed using FEI Resolve RT.

Figure 1 a. is a representative HRTEM image of a 30 nm hematite particle showing nano-pipes propagating throughout its interior. These nano-pipes are not readily discerned in 2D images. Figure 1 b. shows a SIRT reconstructed rendering of a 30 nm hematite particle in which a nano-pipe opening is seen on the surface of the hematite particle. For this SIRT reconstruction, a STEM magnification of ≈ 1.8 Mx is used for observing nano-pipes and nano pores in hematite. In comparison, IT will be shown to use a lower magnification yet resolve these internal features.

In order to understand the formation of nano-pipes and nano-pores in hematite, an IT reconstruction algorithm is used and compared to WBP and SIRT. In contrast to WBP and SIRT, IT was developed as a means of accurately reconstructing a region of interest (ROI) within a field of view using X-ray tomography [1]. In this work, IT has been applied to electron tomography for the first time. Its application to electron tomography allows smaller particles (ROI) to be studied at lower magnifications; therefore, overcoming the limitations of particle shifts at high magnifications during sample tilting. Furthermore, with IT it is possible to use fewer projections without substantial image degradation [2]. This makes IT attractive for beam sensitive samples.

Currently, nano-structured hematite (α-Fe_2O_3) is considered an exciting and promising material for water-splitting [3], photo-catalyst [4] and solar-cell applications [5] because of the increasing band gap energy by quantum size effect. Also, hematite nano-particles are ubiquitous in natural environments and have many roles of absorbent, redox agent, transporter of heavy/toxic elements [6]. The presence of nano-pores and nano-pipes reported in this work will influence the properties of these particles. For example, nano-pipes and nano-pores will enhance hematite's performance as a catalyst by increasing its surface-area to volume ratio resulting in higher reaction rates. Hence, these nano-scale features are important from both an industrial and environmental aspects. [7]

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[7] This work has been supported by the NIH and the Institute for Critical Technology and Applied Science at Virginia Tech.

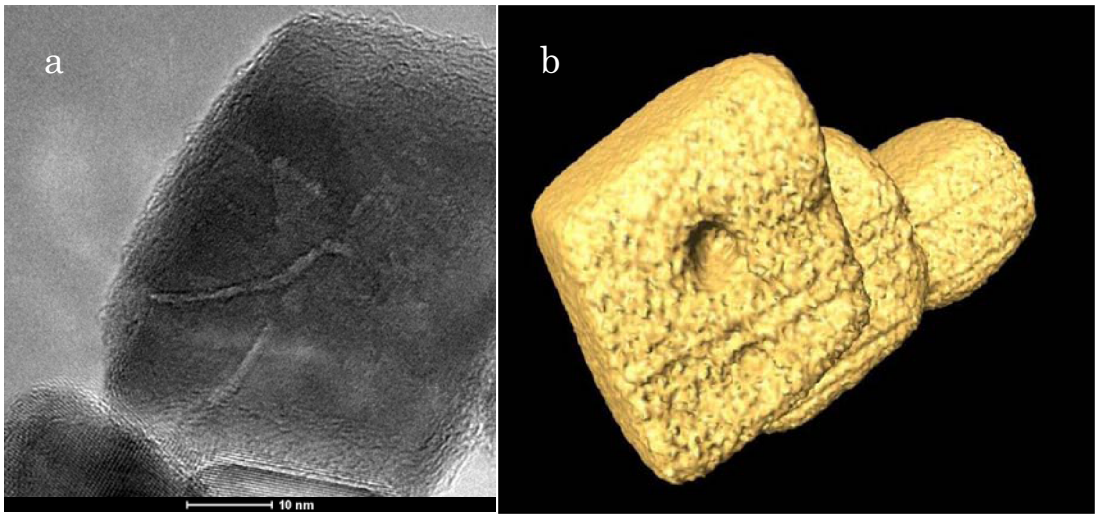

Figure 1 (a) HRTEM images of 30-nm hematite particles showing nano-pipes emerging from the particle's core to its surface. (b) 3-dimensioally reconstructed (SIRT) rendering of 30-nm hematite aggregate displaying a hole on the particle's surface formed by a nano-pipe.

https://doi.org/10.1017/S1431927611005605 Published online by Cambridge University Press