

Supporting Information for
Dendritic Oxide Growth in Zero-Valent Iron Nanofilms Revealed by Atom Probe
Tomography

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Focused Ion Beam Milling. We used focused ion beam (FIB) milling to fabricate conical shaped ZVI “tips”. The local electrode APT analytical method requires the use of conical shaped tips with end radius of curvature of ~50 nm and 100 μm height. The FIB process has two main stages. The first stage shown in Fig.1 involves making a wedge-shaped lift-out from a region of interest of the ZVI film with a protective capping (see Fig S1.A.). The wedge is then lifted out with a micromanipulator and a section (“blank”) of it is mounted onto a ~150 μm tall silicon post on a micropost array (see Figs. S1.B and S1.C) by depositing platinum patches as seen in Fig.S1.D. The next stage of the FIB process (Fig. 2) involves sharpening of the blank into a conically-shaped sharp tip. The sharpening is done by first trimming (Figs. S2.A and S2.B) the broad sides of the blank into a pyramidal shape, followed by annular milling (Fig. S2.C) to achieve the desired conical shape and sharpness (Fig S2.D).

Atom Probe Tomography Procedure. A sample tip is mounted onto a nano-positioning stage and pointed towards a funnel-shaped local electrode. With the help of two optical microscopes, the specimen tip is aligned roughly opposite to center of the local electrode's aperture. An electric field is then introduced on the specimen tip by applying a direct voltage which results in the initiation of ion-emission by field evaporation. Using initial ion events from the inert chromium cap, a 30 pJ laser beam spot (pulse rate 250 kHz) is aligned on the specimen tip. The laser beam spot is centered on the apex of the specimen's tip and scanned continuously in the xy direction of a small scanning area during the evaporation process to allow for drift compensation. Once a sufficient signal is achieved and the xy scan is reproducible after three consecutive scans, a focus scan is performed. The detection rate is gradually increased in addition to voltage ramping as the tip is aligned. The aim is to obtain a steady rate of detected ion events. The species that are emitted are ionized and projected radially onto a position sensitive 2D micro-channel plate (MCP) detector. The time-of-flight mass spectrometer allows for the detection of the mass-to-charge ratio of each ion based on the time it takes to reach the detector.

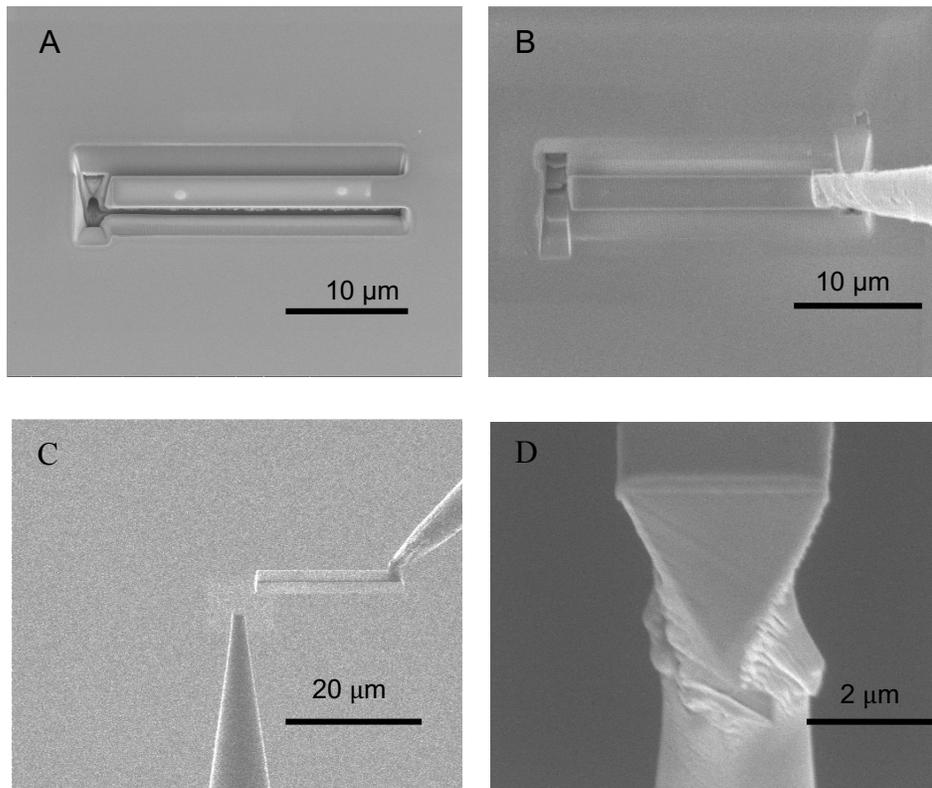
Figures and Captions.

Figure S1. Scanning Electron Microscopy (SEM) Images of Part I of FIB fabrication of APT tips from ZVI films. **(A)** Cutting a wedge-shaped blank into the ZVI film deposited on silicon wafer [SEM conditions: 1.4nA, 5kV]. **(B)** Lifting out the blank with a micromanipulator [1.4nA, 5kV]. **(C)** Attaching the blank to a silicon micropost located on a micropost array [Ion-beam image, 28pA, 30kV] **(D)** Section of blank attached by platinum deposition to a silicon micropost on a micropost array [1.4nA, 5kV].

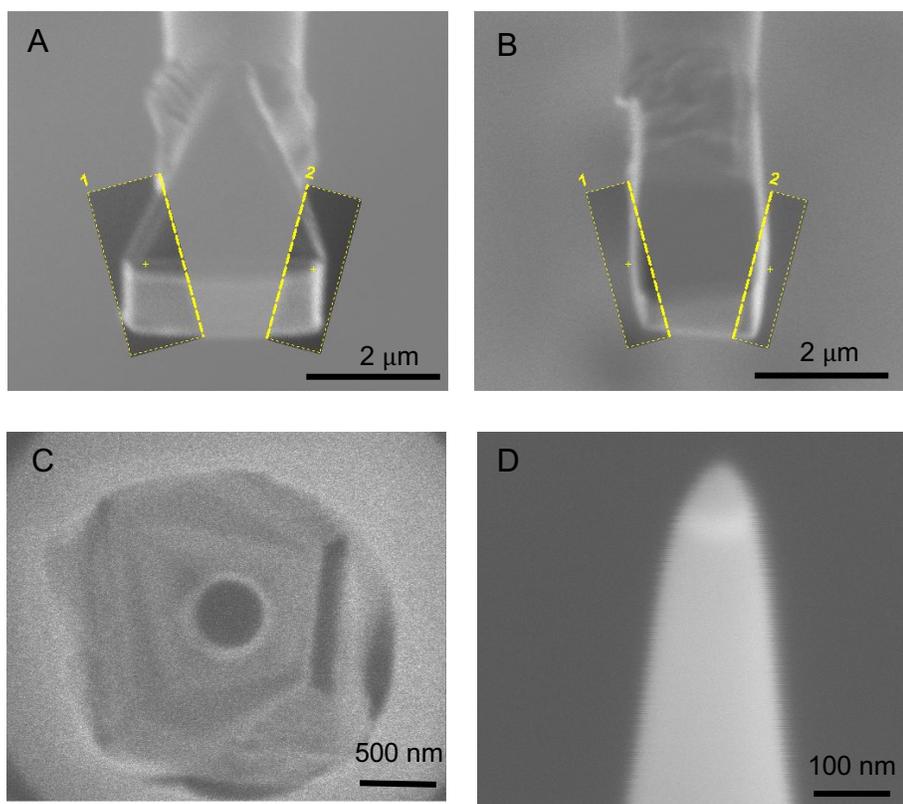


Figure S2. SEM Images of Part II of FIB fabrication of APT tips from ZVI films. (**A** and **B**) Triangular milling of the broad sides of the blank to obtain a pyramidal shape [0.28nA, 30kV] (**C**). Annular milling of the blank [28pA, 30kV] to shape a tip and (**D**) Low voltage circular milling to achieve the final shape of a needle-shaped ZVI tip ready for APT analysis [1.4nA, 5kV].

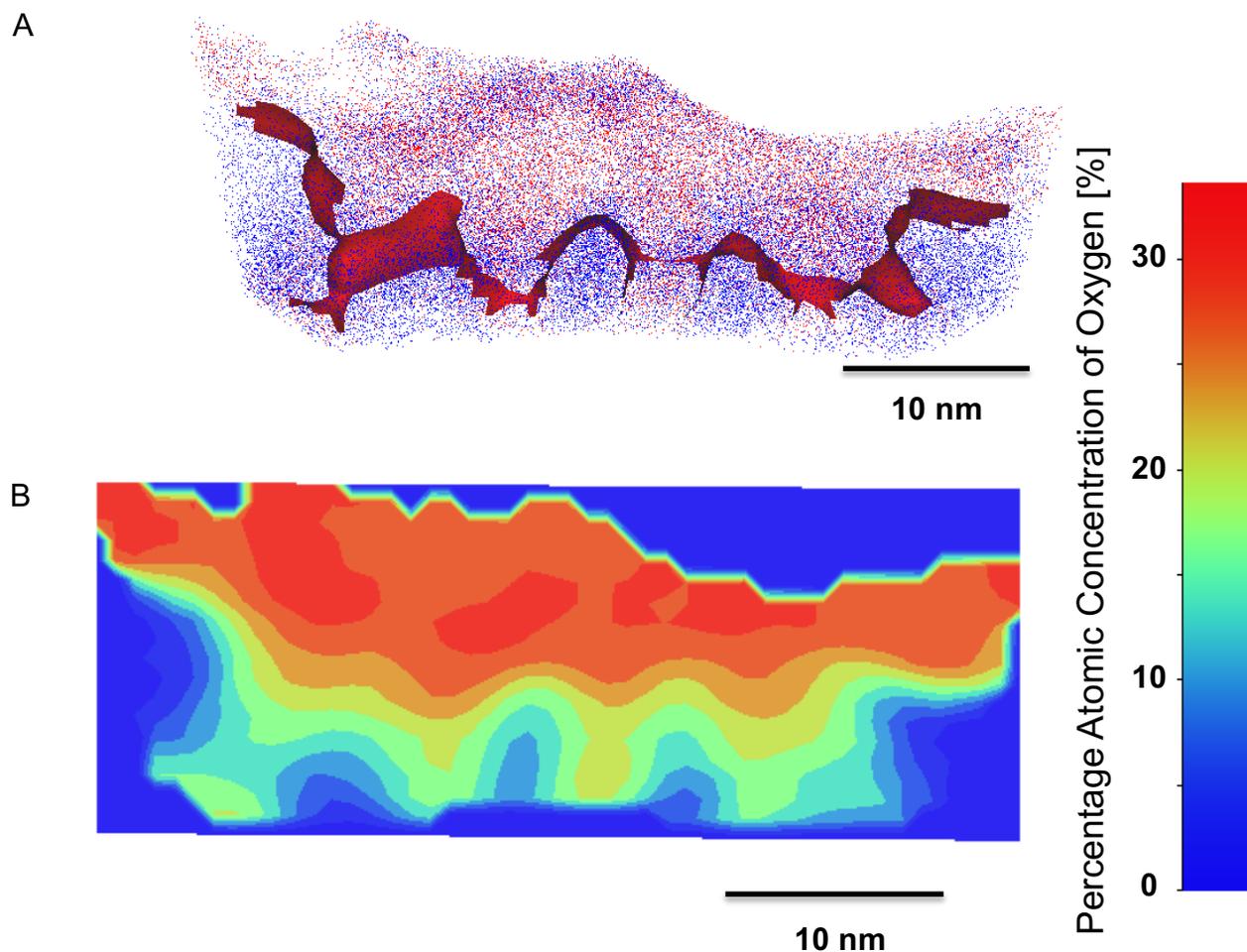


Figure S3. (A) 18 atomic % isoconcentration surface of $\text{FeO}^+ + \text{Fe}_2\text{O}_2^+ + \text{O}^+ + \text{O}_2^+$ (red) of a cut portion of a ZVI tip different from the one shown in Fig. 5 depicting dendritic features extending from the oxygen-rich overlayer into the bulk ZVI film at the bottom. Blue dots represent Fe^+ , Fe^{2+} and FeH^+ ions. Here, the ZVI tip is sliced 5 nm in the x-direction and the image is projected in the yz plane. (B) 2D Contour Plot of oxygen concentration for Fig. S3.A depicting the oxygen concentration gradient within the dendritic features. Color scale (see right) goes from blue to red with the red areas representing the highest concentration of FeO^+ , Fe_2O_2^+ , O^+ and O_2^+ .

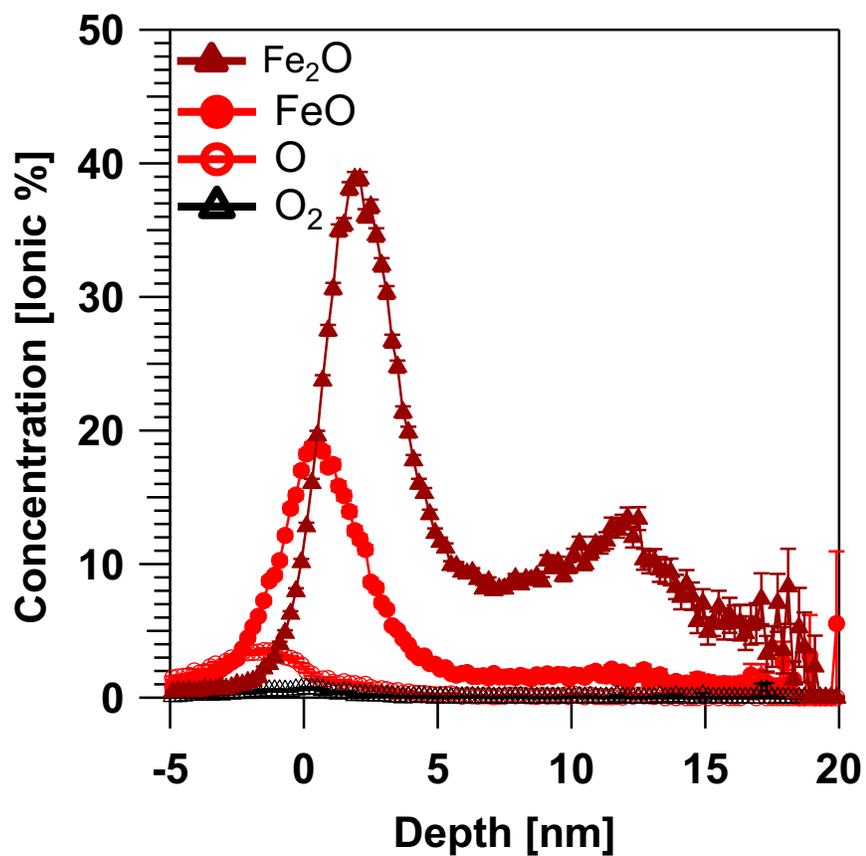


Figure S4. A proxigram profile of changes in ionic concentration (ionic %) of FeO⁺, Fe₂O²⁺, O₂⁺, and O⁺ for a typical ~ 20 nm ZVI film.