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Formation of Swiss-cheese Nanostructure of α-Fe_2O_3 by Reduction

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Swiss-cheese nanostructures have unique properties and a wide range of applications due to their large surface-to-volume ratios compared to traditional nanostructures, and have attracted intense research focus [1]. By understanding the formation mechanism of the Swiss-cheese structure, researchers can develop biological strategies to tune the properties of single-crystals extrinsically. However, there are technical difficulties in preparing this complicated Swiss-cheese nanostructured metal oxides. The limited understanding of the microstructural evolution makes the fabrication even more challenging. Here we introduce a new approach to prepare these nanostructures of metal oxides and articulate the development mechanism of the structures at atomic resolution.

α-Fe_2O_3 nanowires samples were prepared by thermal oxidation of pure iron foils [2]. As-prepared α-Fe_2O_3 nanowires were transferred onto a Si_3N_4 membrane TEM window and then loaded into an environmental transmission electron microscope (ETEM). Pure dry hydrogen (99.999%) was flowed into the ETEM column to achieve a partial pressure of 0.5 Pa. The sample was then heated up to 500 °C. The *in situ* observations of the oxide reduction were conducted under these conditions by time-resolved (video rate), high-resolution transmission electron microscopy (HRTEM) imaging and nano-beam electron diffraction.

In situ observations, at both low and high (atomic-scale) magnifications, were conducted for the reduction of α-Fe_2O_3 nanowires. The low-magnification morphology evolution is shown in Fig. 1. After heating for 57 min in H_2 at 500 °C, oxygen vacancies formed and coalesced together to form the Swiss-cheese structure with tiny craters (Fig. 1(b-f)). As the reduction proceeded, the craters coalesced with each other and developed into nano trenches. The sizes of the nanowires shrank, and finally the nanowires disintegrated into nanoparticles within the skeleton of the original nanowires. Nano-beam electron diffraction of the area of the nanowire, marked by red circle in fig. 1(f) shows that it is Fe_3O_4 <111>. Fig. 1(h) is the nano-beam diffraction of the nanoparticle (square in fig. 1(f)), that can be indexed as γ-Fe <111> structure, indicating the coexistence of Fe_3O_4 and metal Fe, and possibly FeO as well, which we confirmed using atomic-resolution imaging (see below).

Fig. 2(a-f) shows a set of HRTEM images extracted from an *in situ* video showing the evolution of a crater to form the Swiss-cheese structure at atomic scale. From the diffractograms (fig. 2(a, b)), we confirm that the formation of craters is concomitant with the phase transformation from Fe_3O_4 to FeO, with the crystallographic orientation of Fe_3O_4 <111> || FeO <111>, respectively. The crater is also faceted in the shape of an irregular triangle. The facets of the crater are parallel to FeO{111}. This is expected as the {111} planes are the close-packed planes in the cubic structure of both Fe_3O_4 and FeO. Phase transformation from Fe_3O_4 to FeO, is accompanied by volume shrinkage, which causes the crater formation [3, 4].

Fig. 3 is an HRTEM image extracted from another video, showing the transformation from Fe_3O_4<111> to FeO<111> and from Fe_3O_4 to Fe nanoparticle. Figs. 3(b, c) are the diffractograms from square "B" and "C" marked in fig. 3(a), belonging to the Fe_3O_4 <111> and FeO <111> structures, respectively, which agree with results obtained from data shown in Fig. 2. The Fe atoms rearranged to form a nanoparticle of Fe {111}, independent from the crystal orientation of the skeleton of Fe_3O_4. This agrees with the low magnification observation shown in Fig. 1. In addition, it also confirmed the coexistence of FeO and Fe in the matrix of Fe_3O_4 in the Swiss-cheese nanostructure.

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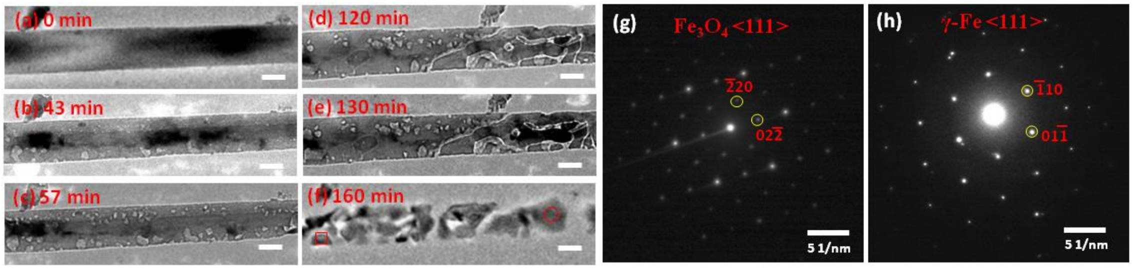

Figure 1. (a-f) The morphology evoluation of Fe_2O_3 nanowire prepared by thermal oxidation of pure Fe foil. (g, h) Nano-beam electron diffraction of the marked circle and square regions of the nanowire in (f), respectively.

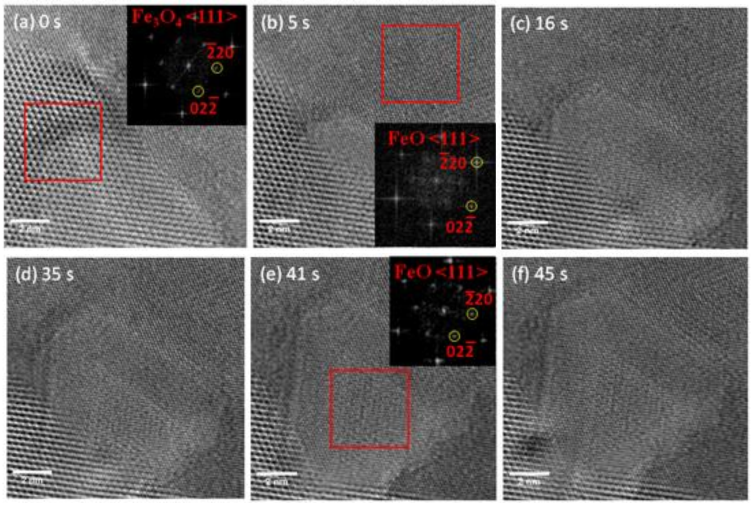

Figure 2. (a-f) The HRTEM frames extracted from a video taken during the *in situ* reduction, showing the development of a crater on the swiss-cheese-like structure of Fe_3O_4 from the initial stage. The insets in (a, b, e) are the diffractograms from the marked squares, respectively, indicating that the structure is a combination of Fe_3O_4, FeO and Fe.

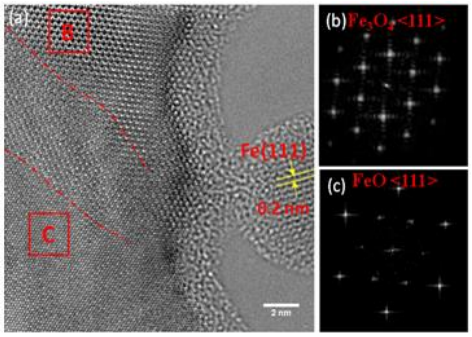

Figure 3. (a) HRTEM image extracted from a video showing the reorganization of the atoms during the transformation from Fe_3O_4 to FeO then to Fe. (b) The diffractograms of region B and C marked in (a), respectively. The dash-dot lines mark the boundary between Fe_3O_4 and FeO. Both phases coexist in the region between the two lines. (The image was averaged and filtered to reduce noise).