doi:10.1017/S1431927615005772 Paper No. 0498 Microsc. Microanal. 21 (Suppl 3), 2015

Atomic-Scale Characterization of the Reduction of α-Fe_2O_3 Nanowires

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Reduction of metal oxides is a reaction of removing lattice oxygen and plays an role in producing active materials for a variety of applications ranging from catalysis to electronic devices [1]. The reduction of iron oxides has been investigated intensively because of its vital role in heterogeneous catalysis. The variable valence states of Fe cause a rather complicated Fe-O phase diagram, leading to the possibility of multiple phases being formed during redox reactions. It has, therefore, been a longstanding challenge in understanding the reduction mechanism of Fe_2O_3. Here, we present observations of an iron oxide superlattice structure resulting from oxygen vacancy ordering and stacking fault formation as well as the phase transformation pathway during the reduction of α-Fe_2O_3 nanowires

The α-Fe_2O_3 nanowires were prepared by the thermal oxidation of pure iron [2]. The reduction was conducted in a vacuum chamber at T = 500 ℃ with the pressure of H_2 gas (99.999% purity) at 270 Pa. The morphologies of the nanowires both before and after the H_2 reduction were examined using a scanning electron microscope (SEM). The crystal structure and valence state of the nanowires were characterized by TEM imaging, diffraction, and electron energy-loss spectroscopy using an aberration-corrected TEM operated at 300 kV.

Fig. 1 shows SEM images of the nanowires before and after the reduction reaction. It can be seen that the as-prepared nanowires have a smooth surface morphology while the reduced nanowires show the formation of bulges on the surface. Fig. 2 (a) illustrates a bright-field TEM image of a single reduced nanowire with the presence of bulges on the surface. Fig. 2 (b) presents a HRTEM image at relative low magnification of the parent nanowire as marked with the red square in Fig. 2 (a).The upper-right inset in Fig. 2 (b) is an optical diffractogram of the HRTEM image, which shows the presence of superlattice diffraction spots in addition of the fundamental reflections associated with the α-Fe_2O_3 structure of the parent nanowire. The lower-right inset in Fig. 2 (b) is simulated diffraction pattern using the α-Fe_2O_3 structure with the removal of oxygen atoms (i.e., the ordering of oxygen vacancies) of every 10^{th} $\{3\bar{3}00\}$ plane. Fig. 2 (c) illustrates the formation of another type of defects, i.e., stacking faults, with the shifting of atomic planes, forming the banded structure in the parent region of the reduced nanowire. There have been several reports suggesting that the formation of the modulated structure in α-Fe_2O_3 is caused either by oxygen-vacancy ordering [3] or by stacking fault formation [4]. Here we find that both oxygen-vacancy ordering and stacking faults appear during the reduction process.

In addition to the formation of the modulated structure by ordering of oxygen vacancies or stacking faults, phase transitions are also observed in the reduced nanowires. Fig. 3 (a) shows a TEM image of a reduced nanowire. The diffraction pattern (inset in Fig. 3(a)) shows that both the parent and the bulge area have a cubic structure, which can be indexed either as γ-Fe_2O_3 (space group: $P4_132$; nearly cubic with a small tetragonal distortion) or Fe_3O_4 (space group: $Fd\bar{3}m$) due to their close lattice constants. Electron energy loss spectroscopy (EELS) was used to further distinguish the two structures. Fig. 3 (b)

shows the Fe L edge. The L_3/L_2 ratio of the parent nanowire is ~ 5.0, higher than that of the bulge area (~ 4.5), indicating their different oxidation states, i.e., the parent nanowire is γ-Fe_2O_3 while the bulge area is Fe_3O_4. Due to the similar lattice constants of the two phases, their interface is coherent and the Fe_3O_4 bulge forms epitaxially with the γ-Fe_2O_3 nanowire (Fig. 3 (c)), where the γ-Fe_2O_3 phase is formed by the conversion reaction of the initial α-Fe_2O_3 nanowire. Fig. 3(d) is a simulated HRTEM image of the γ-Fe_2O_3/Fe_3O_4 interface, which matches well with the experimental one shown in Fig. 3(c). In conclusion, TEM analysis indicates the reduction process involves the formation of a superlattice caused by both oxygen-vacancy ordering and stacking faults and a topotactic reaction from γ-Fe_2O_3 to Fe_3O_4.

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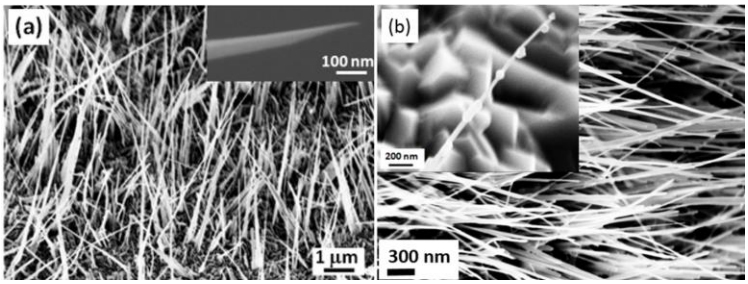

Figure 1. (a) SEM image of the as-prepared α-Fe_2O_3 nanowires, with the inset showing the smooth surface and tapered tip of the nanowires [2], (b) SEM image of the reduced nanowires with the inset showing bulge formation on the parent nanowires.

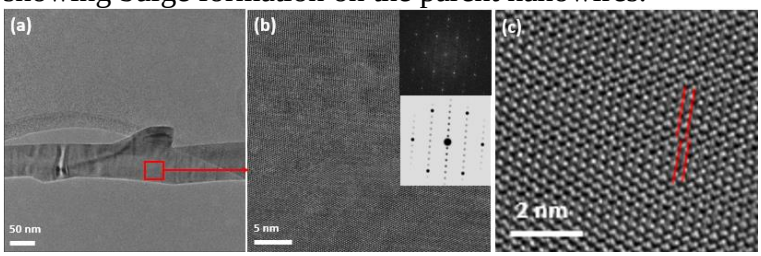

Figure 2. (a) a single α-Fe_2O_3 nanowire after the H_2 reduction, (b) HRTEM image showing the presence of superlattice due to oxygen-vacancy ordering , the insets are the experimental and simulated diffractograms, and (c) HRTEM showing the presence of stacking faults (image filtered to reduce noise).

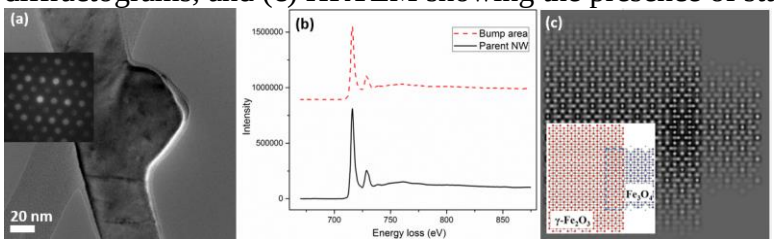

Figure 3. (a) Iron oxide Nanowires with bump along the parent nanowire, the inset shows the [110] zone-axis diffraction pattern from both the parent nanowire and bulge area , (b) EELS of the two areas with different L_3/L_2 ratios of Fe L edge, indicating that the parent nanowire is γ-Fe_2O_3 and the bump area is Fe_3O_4, (c) HRTEM image showing the γ-Fe_2O_3/Fe_3O_4 interface area, (d) The simulated HRTEM of γ-Fe_2O_3 and Fe_3O_4, with the inset of the structure model, showing a coherent interface.