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Ordered Interstitial Fe Introduced New Phase In $Fe_{2+x}O_3$ Nanowires

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Iron oxides nanowires are of significant scientific and technological importance. For example, Fe_3O_4 magnetite nanowires are expected to play an essential role as materials for high-density magnetic storage and magnetoresistive devices due to their unique magnetic properties [1]. The stability and semiconductor (n-type) properties of Fe_2O_3 allow it to be used as photocatalyst [2]. By controlling solid vapor deposition process, we have successfully synthesized Fe_3O_4 magnetite and Fe_2O_3 Hematite nanowires. Besides these two phases, a new intermediate phased ion oxide ($Fe_{2+x}O_3$) has been characterized by transmission electron microscopy (TEM), which has not been reported in bulk materials from our knowledge.

Figure 1(a) and (b) are the bright-field and dark-field TEM images of the as-synthesized $Fe_{2+x}O_3$ nanowires, the different contrast in Fig. 1(b) indicates the existence of domain structures. The select-area electron diffraction (SAED) pattern shown in Fig. 1(c) cannot be indexed using the parameter of hematite, magnetite or maghemite. The existence of domain structure and the high-resolution transmission electron microscopy (HRTEM) images indicate that this diffraction pattern contains three overlapped patterns with 120º among them. The diffraction spots with stronger intensity can be indexed using hematite structure. After titling the sample, we got a set of diffraction patterns, using which the reciprocal lattice of the new phased iron oxide has been reconstructed. If we consider the hexagonal hematite lattice parameter as a and c, the superstructure belongs to orthorhombic system with $a' = a$, $b' = \sqrt{3}\, a$ and $c' = 2c$.

The HRTEM image recorded from the nanowire is shown in Fig. 2, which can be understood as interstitial Fe introduced superstructure. The structure model has been built up in Fig. 3(b). Figure 3(a) is the perfect hematite structure. Compared with hematite structure where each Fe occupies in one oxygen octahedron, one of these oxygen octahedra in the super-cell of the new phase contains two Fe ions. The simulated image inserted in Fig. 2 fits well to the experimental observed one.

[1] A. Fert, L. Piraux, J. Magn. Magn. Mater. **200**, 338 (1999).
[2] Harolad H. Kung, Transition Metal Oxides: Surface Chemistry and Catalysis, Elsevier, New York, 1989.

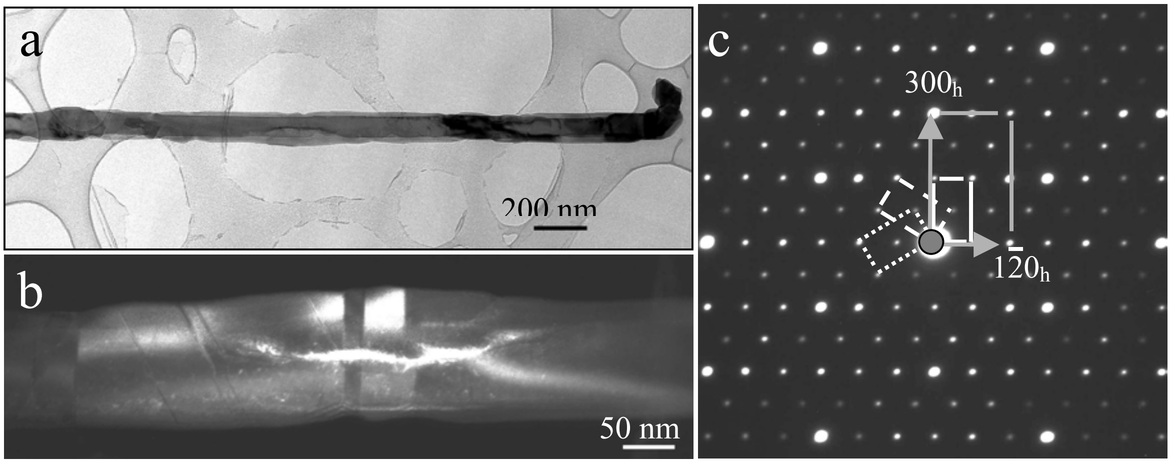

Figure 1. Bright-field (a) and dark-field (b) TEM images of the $Fe_{2+x}O_3$ nanowires. The diffraction pattern in (c) includes three overlapped patterns with 120º rotation relationship among them along c axis.

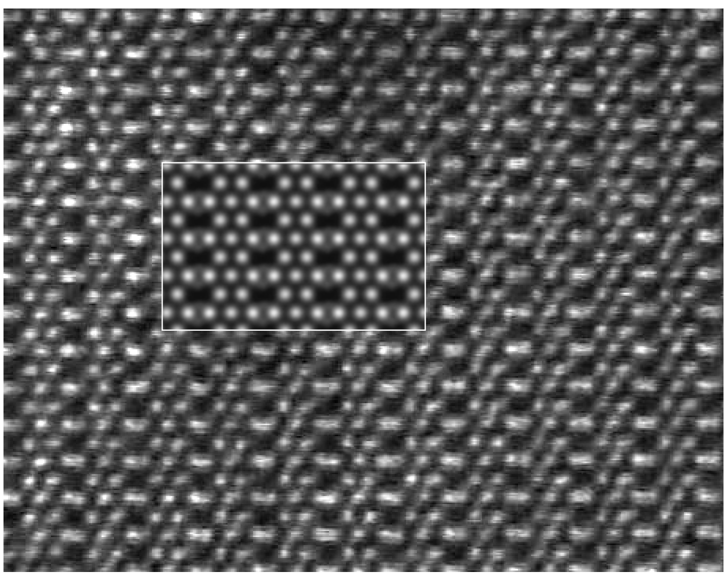

Figure 2. HRTEM image from the new phase $Fe_{2+x}O_3$ superstructure. The insert is simulated image based on the model shown in figure 3(b).

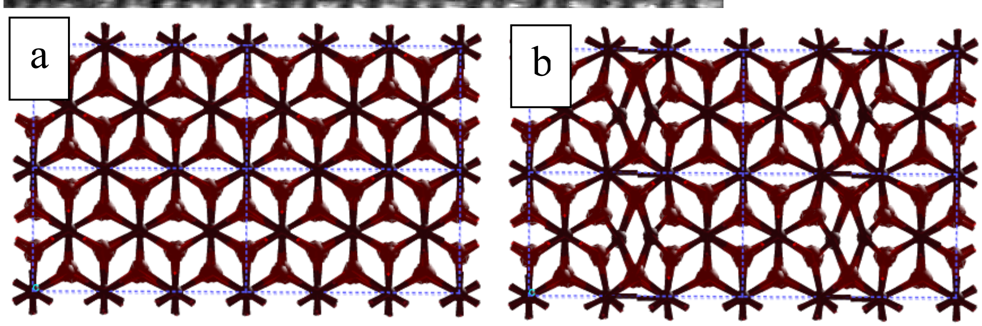

Figure 3. The model of hematite (a) and the new phase $Fe_{2+x}O_3$ superstructure (b) based on the existence of interstitial Fe. In the superstructure, one octahedral site is occupied by two Fe ions.