

Microstructure of Core-Shell Structured Iron-Iron Oxide Nanoparticles

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Metallic iron exposed to air even at room temperature is instantly passivized by a thin layer of oxide, as what happens on the surface of metallic utensils we use daily. This layer of oxide has a thickness of 2 - 3 nm, and the formation process of this thin oxide layer is normally referred to as initial oxidation. Relative to the abundant experimental observation and theoretical derivation on the growth of thick oxidation layer on metal surface at high temperature, atomic level understanding of the initial oxidation is rather limited. This is related to the fact that the initial oxide layer normally forms at an uncontrollable manner. The kinetic theory for the initial oxidation has been established by Cabrera and Mott more than half a century ago [1]. In this theory, they made two assumptions: (1) tunneling of electrons from the metal to the surface adsorbed oxygen, leading to the ionization of the surface adsorbed oxygen, thus inducing an electrical field, and (2) the electric field drives outward transport of metal ions to combine with the surface chemically adsorbed oxygen ions. No experimental observation has ever been made to demonstrate that the cations outwards transport indeed happens. We report in this letter our observation of injection of vacancies into single crystal α -Fe nanoparticle during the initial oxidation of the iron at room temperature and condensation of those vacancies leads to the formation of void which is subsequently enclosed in the Fe-core/oxide-shell structured nanoparticles. These observations provide direct evidence that, during the initial oxidation of iron at room temperature, the outward diffusion of iron is indeed the dominant process. There exists a critical size of ~ 8 nm for which the iron has been fully oxidized, leading to a hollow iron oxide nanoparticle. For particle larger than the critical size, an iron/iron oxide core-shell structure was formed and voids reside at the interface between the oxide shell and the iron core. The present observation also adds new dimensions for designing of metal/metal-oxide/quantum antidotes (vacancy cluster) nanoclusters for applications related to optical, magnetic, and electrical properties of the core-shell structured nanoparticles.

Contrasted with the understanding of high temperature growth of thick oxide layer, less is known about the initial oxidation process of iron and the structural nature of their product. The initial oxidation process has two features: the formed oxide layer is normally just a few nanometer; and the growth rate is pretty fast. Depending on the type of migrating lattice defects, the reaction of oxide either can be at the metal-oxide interface (oxygen ions inward transport) or at the oxide-gas interface (metal ions outward transport). Under the frame of the Cabrera-Mott theory of oxidation of metal [1], the oxidation process of iron can be described as the following: upon initial attachment of oxygen onto the surface of metal and formation of a thin layer of oxide, electron tunnels through the thin oxide layer and ionizes the oxygen, leading to an electrical field between the metal and the surface of the oxide layer. The electrical field will subsequently drive the outwards diffusion of the ionized Fe. With the Cabrera-Mott model, estimation has given that at room temperature, it takes about 0.2 femto second to form an initial 1 nm

thickness of oxide layer on a freshly exposed iron surface, and 40 seconds for a film of 2 nm, 40 weeks for a film of 3 nm, and 600 years for a film of 4 nm [2].

A general feature for the air exposed iron particle is a core-shell structure. However, depending on the size of the particle, it possesses fine structural features. This is illustrated in the high resolution transmission electron microscopy (HRTEM) image of Fig. 1. For particles with a size of larger than ~ 10 nm, it shows a core-shell structure with the thickness of the oxidized layer being around 3.2 nm, as typically shown Fig. 1(a). Electron diffraction and HRTEM imaging have revealed that although the core Fe is a single crystal, the oxide layer is not single crystal. It is composed of small crystallites which were oriented differently. This feature was clearly demonstrated by the HRTEM image showing in Fig. 1(b), for which a single crystal Fe core was surrounded by several crystallite of oxides. The oxide layer is composed of either Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ based on

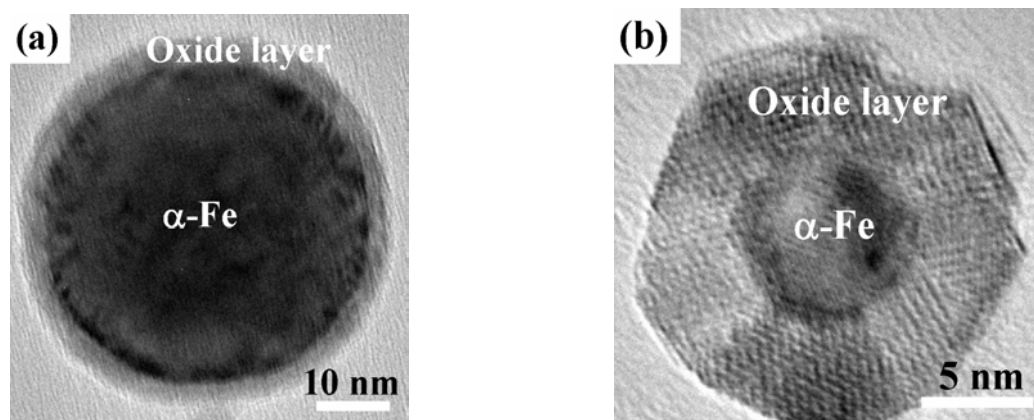


Fig. 1 Core-shell structured Fe-iron oxide nanoparticles

the lattice fringe space measurement. However, a complete differentiation of these two phases based on HRTEM imaging is not possible. Multidomain orientations of the oxide layer indicate that the nucleation and growth of the oxide shell on the single crystal surface of Fe follows a homogenous nucleation process. The specific orientation relationship between the oxide shell and the Fe core will be further investigated. No other structural features such as pore or void can be imaged on this large particle, as similarly in the case of following the oxidation of bulk iron specimen.

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