# Analysis of Oxidation State in Iron Oxide Nanoparticles with Various Size by Fe L-edge

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Magnetic nanoparticles have attracted much attention due to the potential application in biomaterials, ferrofluids, medical imaging, drug targeting, magnetic resonance image and catalysis. It is well-known that inverse spinel structure consisting of $Fe^{3+}$ in tetrahedral (A) and $Fe^{2+}$ and $Fe^{3+}$ in octahedral sites (B) in one unit cell. The magnetite nanoparticles transform from ferrimagnetic to superparamagnetic property in the room temperature, as the particle size decrease to the below of critical size. Hence, the reduction of particle size to nano scale can products a special superparamagnetic property, indicating a rapid response to given magnetic field, so that it is used as a negative contrast reagent in magnetic resonance image technique. The structure of iron oxide materials exist in froms of α-$Fe_2O_3$,γ-$Fe_2O_3$ and $Fe_3O_4$, but the structure between γ-$Fe_2O_3$ and $Fe_3O_4$ are difficultly distinguished by determining by X ray powder diffraction. The oxidation state of iron ion on the surface of nanoparticle with high specific surface area is sensitive to surrounding, because of exposure to the surfactant. As the specific area increase with the decrease of nanoparticles, the iron ions on the surface of nanoparticles gradually play an important role to control the magnetic properties. Hence, the chemical structure of iron oxide material is determined well by the characterization of iron oxidation, rather than the X-ray powder diffraction owing to similar structure. The analysis of oxidation state of iron ion can identify the structure and chemical environment of iron oxide nanoparticles. In recent decade, much efforts have been focused on the development of new method to fabricate nanocrystals with high monodispersity and uniformity size, such as chemical coprecipitation, hydrothermal, thermal decomposition and so forth. Among then, the thermal decomposition method provides a good growth environment for formation of monodisperse iron oxide nanoparticles, which display uniform chemical information from each nanoparticle. Herein, we focus on the synthesis of monodisperse magnetite particles and analysize the chemical environment of iron ion to identify the structure of iron oxide nanoparticles.

XAS is a powerful technique which measures the difference in the core-level X-ray absorption spectrum. It provides information on the electronic and chemical structure of the material. It has been applied extensively to study the chemical structure of iron oxide nanoparticles with different specific area ratio. In this work, we use XAS to investigate the contribution of $Fe^{2+}$ and $Fe^{3+}$ site in iron oxide nanoparticles. The samples are prepared by mixture of $Fe(acac)_3$, oleic acid, oleylamine, 1,2-tetradecanediol, and phenyl ether and magnetically stirred in a Schlenk flask under a flow of nitrogen. The mixture is slowly heated to reflux for 30 min and then removed heat source to cool down under room temperature. Using as-prepared nanoparticle as seed, mixtures of different concentration growth solution with seed are heated to reflux for 90 min to let seed grow completely..

In Fig. 1, the XAS spectra of iron oxide nanoparticles with different particle sizes show a deep at around 707 eV, which is a characteristic of magnetite. However, the shape of absorption peak is changed with the size of iron oxide nanoparticles, which is apparently contributed to the difference in the ratio between $Fe^{2+}$ and $Fe^{3+}$ ions in each site of inverse spinel structure. The results indicate the reduction of nanoparticle size induce $Fe^{3+}$ ion, it may be caused by surfactant as oleic acid. In Fig. 2, the first derivative of XAS provide clear change among various size of iron oxide nanoparticles.

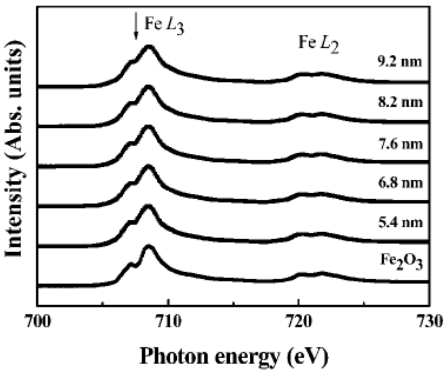


**Fig. 1:** XAS spectra for iron oxide nanocrystals with varying particle size.

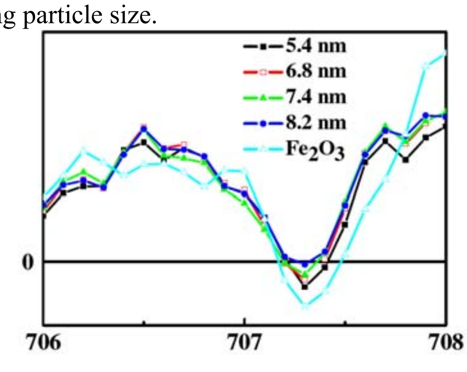


**Fig. 2:** The first derivative of XAS in the range of 706 ~ 708 eV photon energy.