

In situ XANES/EXAFS study of the formation of doped and undoped hollow γ -Fe₂O₃ nanoparticles

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Abstract: Hollow iron oxide nanoparticles are of great interest in a broad range of applications, such as cancer treatment, drug delivery, Li and Na ion batteries, etc. Though doping has been used for a long time to tailor optical, electronic and mechanical properties of nanoparticles, the mechanism of doping especially in nanometer sized systems is still not very well understood.

We have been successful in studying the schlenk line synthesis of un-doped and doped hollow iron oxide nanoparticles (NPs) by *in situ* synchrotron quick-scanning X-ray absorption spectroscopy. The γ -Fe₂O₃ nanoparticles were synthesized by thermal decomposition of iron pentacarbonyl (Fe(CO)₅). This experiment enabled us to probe in real-time the changes in the oxidation state and the chemical environment of Fe atoms and atoms of the dopants (Mo and Co) during the synthesis.

From the analysis of our XANES, EXAFS and TEM (transmission electron microscope) data, we observed that the doping process in this system is extremely different from previously known doping mechanisms of trapping and diffusion. We observed a few important phenomena in the kinetics of synthesis of iron oxide nanoparticles. We found that the presence of dopant precursor results in the accelerated decomposition of iron precursor and nucleation of Fe NPs. The atoms of the dopants are located at the surface of iron nanoparticles. The incorporation of the dopant atoms into iron oxide matrix occurred as a result of Kirkendall effect by which the inverse mass transport of Fe and O atoms internalizes dopant cations. Our results indicate a new mechanism of the doping process in metal oxide NPs.

In-situ studies of chemical reactions will enable scientists and engineers to synthesize nanoparticles with tailor-made properties.