Highlights

Advanced materials and techniques for organic electronics, biomedical and sensing applications - 2019

Vacancy-Driven Noncubic Local Structure and Magnetic Anisotropy Tailoring in Fe_xO-$Fe_{3-\delta}O_4$ Nanocrystals

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Here, we combine nano-chemistry, detailed characterization, and theoretical considerations to explore the relation of structural defects on the size and shape of iron-oxide nanocrystals and to determine how these couple to magnetic properties relevant to nanobiotechnology. In fact, we have found, by total x-ray scattering experiments coupled to atomic pair distribution function (x-PDF) analysis, the unexpected experimental observation that metal atoms pulled out from the crystal lattice, during the oxidative conversion of antiferromagnetic wüstite (Fe_xO) into a ferrimagnetic spinel magnetite ($Fe_{3-\delta}O_4$), create vacant sites in the magnetite. These sites are correlated to each other via local tetragonal distortions, especially for spherical nanocrystals (single-crystalline nanoparticles) compared to cubic ones and for the smaller sizes. The emerging local symmetry breaking due to defect, change the nanocrystal's magnetic anisotropy in the favorable direction. The vacancies act as pinning centers impeding the coherent reversal and easy relaxation of the spins. This allows surprisingly a nonzero exchange bias even in the fully oxidized, $Fe_{3-\delta}O_4$-like derivative of wüstite, and a remarkable ten-fold rise of the nanomaterial's thermo-responsive performance, as compared to that obtained by defect-free nanocrystals, based on Monte Carlo simulations.

The investigation suggests the broader implications of atomic-scale defect control as a design parameter that favors anisotropic properties for optimized nanomaterials, with simultaneous diagnostic and therapeutic capabilities, such as thermosensitive cellular processes guided by magnetic images, sought in the field of theranostics.

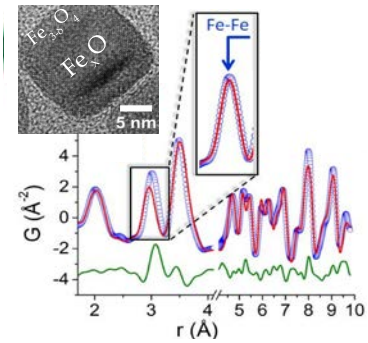

Fig. 1 x-PDF fit (red solid line) in the "low-r" region of a core-shell cubic nanoparticle sample assuming a single phase inverse cubic spinel atomic configuration (Fd-3m symmetry), showing that this model fails to fit the peak at about 3Å (blue circles), and in the top right insert there is the result obtained by a two-phase model of the cubic rock-salt and tetragonal ($P4_32_12$ symmetry) crystallographic configurations, showing an improved quality of the fit and indicating a possible localized tetragonal distortion. A typical core-shell cubic nanocrystal of the sample used is in the top left.

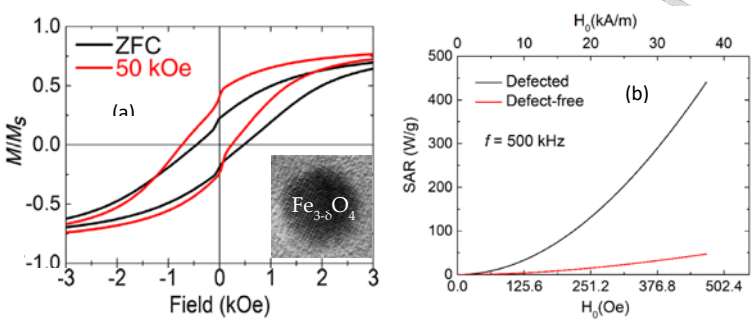

Fig. 2: (a) Normalized hysteresis loops at 5 K for the single-phase spherical nanoparticles taken under zero- and field- cooled (H_{cool} = 50 kOe) protocols, (b) Monte Carlo calculation of SAR (specific adsorption rate) values as a function of the AC field amplitude, H_0, at a field frequency f = 500 KHz.