TAILORING THE SUPERPARAMAGNETIC BLOCKING TEMPERATURE OF γ-FE$_2$O$_3$ NANOPARTICLES BY ADSORPTION OF COBALT (II) IONS.

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The influence of the adsorption of Co(II) ions on the structural and magnetic properties of γ-Fe$_2$O$_3$ nanoparticles has been studied. The γ-Fe$_2$O$_3$ nanoparticles were prepared by co-precipitation of Fe(II) and Fe(III) from an aqueous solution of iron (III) and iron (II) chlorides with a molar ratio Fe(III)/Fe(II) of 2 to form Fe$_3$O$_4$ and subsequently oxidized with HNO$_3$ to form γ-Fe$_2$O$_3$. The Co(II) ions were adsorbed, in a post-synthesis process, by contacting an aqueous suspension of particles with an aqueous solution of Co(II) ions, with a given concentration, in nitrate media. Transmission electron microscopy (TEM) studies show that the particle size (D_{TEM} ~ 10 nm) and its distribution are kept unmodified by the Co adsorption. Fig. 1 shows high resolution TEM micrographs of both, the pristine particles and particles with ~1000 mg of Co(II) adsorbed per kg of iron oxide. The TEM micrographs did not show the presence of a shell or a pronounced crystal growth. However, due to the nature of the preparation process by adsorption from aqueous solution, it is expected that the cobalt (II) will diffuse across the particles following a concentration gradient that extends from the surface towards the core. Analysis of the selected-area electron diffractograms, as well as the generated fast Fourier transform (FFT) of the high resolution images, yielded lattice spacings which were identified with those of inverse spinel structure. Despite the small morphological changes, the magnetic properties are strongly affected by the cobalt adsorption. As can be seen in fig. 2, the coercivity, H_C, for the pure γ-Fe$_2$O$_3$ is much lower than the one for the cobalt-adsorbed γ-Fe$_2$O$_3$ in the whole temperature range. The temperature at which H_C becomes zero, i.e., the superparamagnetic blocking temperature, T_B, increases for the cobalt-adsorbed γ-Fe$_2$O$_3$ nanoparticles. Actually, at T = 250 K while the pristine nanoparticle is already superparamagnetic, the Co-adsorbed one still exhibits a H_C = 20 Oe. The results indicate that the magnetic properties of superparamagnetic iron oxide nanoparticles can be modified by using a simple metal adsorption *post-synthesis* route, without modifying their particle size or size distribution. The improvement of the magnetic properties is probably linked to an increase of anisotropy when going from γ-Fe$_2$O$_3$ towards CoFe$_2$O$_4$, since $K_{\text{CoFe2O4}}/K_{\text{γ-Fe2O3}}$ is about 10.

Figures:
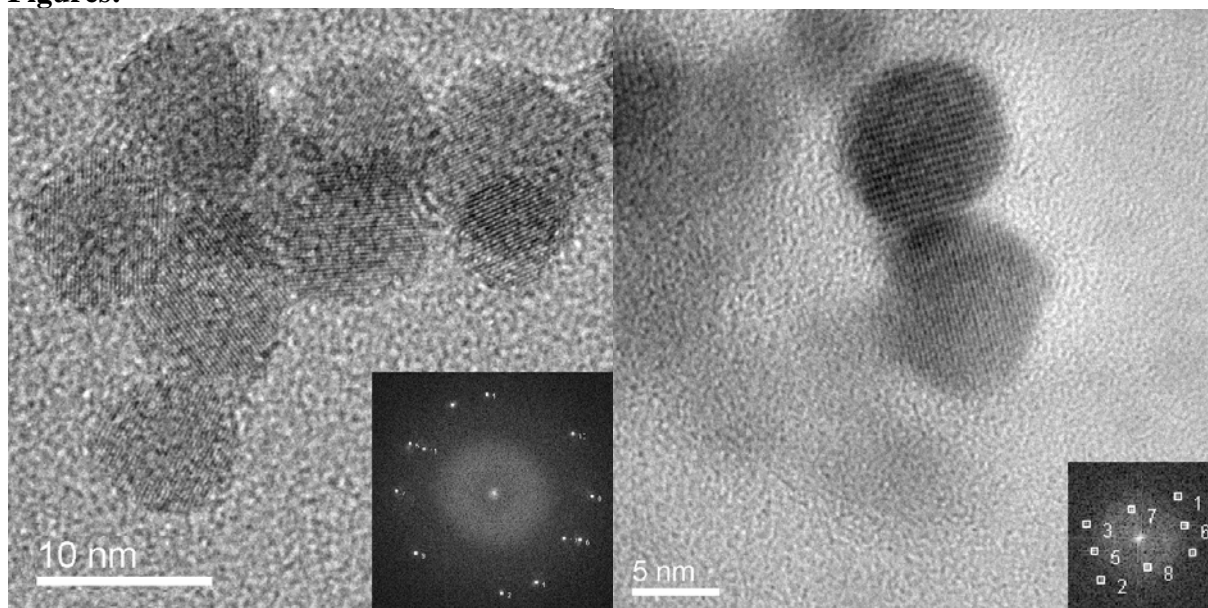
Figure 1 HRTEM of the pristine iron oxide particles (left) and the Co(II)-modified particles (right). The insets show the generated FFT of the images.
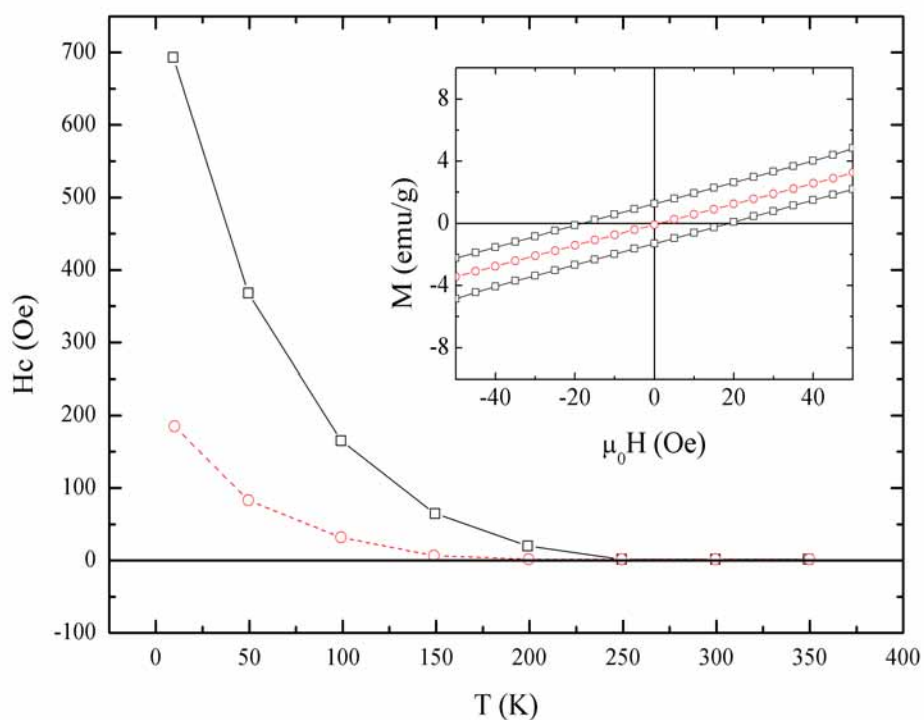
Figure 2 Temperature dependence of the coercivity, Hc, for pristine particles (circles) and for particles with Co(II) adsorbed (squares). The inset shows absence of hysteresis for the prisitine particles (circles) and the coercivity of about 20 Oe for the particles with Co(II) (squares), the loops were measured at 200 K. The modified particles have a Co(II) concentration of ~1000 mg of Co(II) per kg of iron oxide.