

Striking “Nano-onion” nanoparticles with core (γ -Fe) / double shell (α -Fe / Fe-oxide): synthesis, microstructure and magnetism.

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The large variety of magnetic scenarios displayed by nanoparticle (NP) systems is mainly governed by the reduced size and/or miscellaneous morphologies of the particles, because surface, interface or finite-size effects play an important role. Furthermore, the physical-chemical nature of the surrounding medium or matrix (amorphous or crystalline, insulating or conducting, magnetic or non-magnetic...) strongly influences the magnetic properties of the NPs. The complete understanding of the correlation between microstructure, morphology and magnetic behaviour is, at present, an interesting and novel issue that can lead to functionalize NPs for potential applications.

We have followed an inexpensive and easy-to-follow synthesis technique to fabricate massive (several grams) samples. The chemical process consists on a pyrolysis process taking place inside the restricted volume formed by the pores of an activated carbon and leads to the encapsulation of Fe-NPs on the nanoporous of the carbon matrix. The Fe-NPs present a broad particle-size distribution (5-40 nm) (Fig. 1). A combined structural and magnetic study seems to suggest that most of the nanoparticles of mean size ~ 15 nm have exotic “onion-like” core-shell morphology of γ -Fe nucleus surrounded by a concentric double shell of α -Fe and maghemite-like oxide (Fig. 2). The true nature of Fe-oxide was successfully evidenced through room temperature X-ray absorption spectroscopy. The whole system does not reach a fully superparamagnetic regime even at 750 K, probably due to higher blocking temperatures for the largest nanoparticles. Mössbauer spectrometry indicates that low temperature para-to-antiferromagnetic transition for the γ -Fe phase cannot be discarded. In addition, the external Fe-oxide shell exhibits spin-glass behaviour giving rise to the freezing of its magnetic moments at low-temperatures. Hence, we propose a competing double magnetic coupling: (i) the oxide shell / α -Fe interaction and, (ii) the possible antiferromagnetic coupling between γ -Fe nucleus and α -Fe layer; as being both responsible for the observed exchange bias effect at $T = 5$ K ($H_{\text{ex}} \approx 150$ Oe).

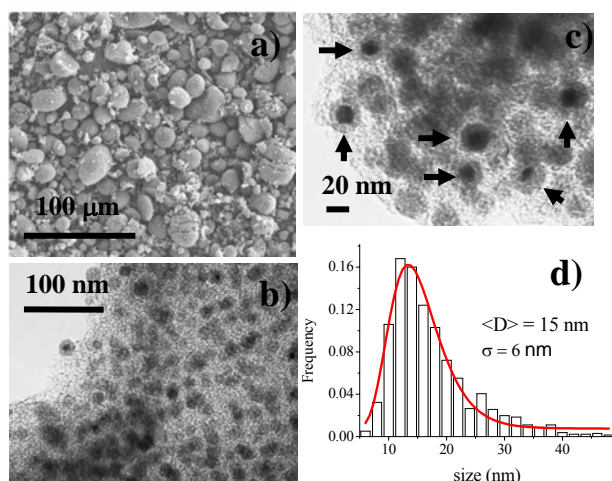
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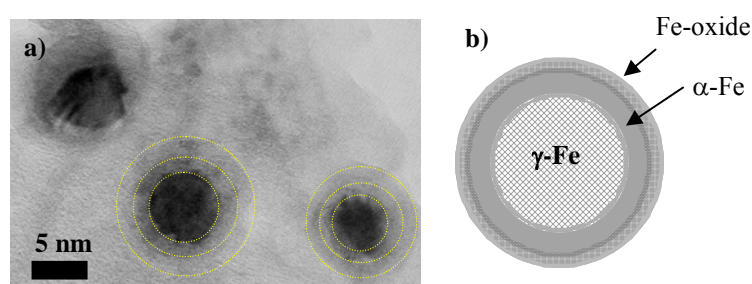
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Figures:



(a) SEM image showing almost spherical AC powders with a size in the 10 – 60 μm range. (b) and (c) Different details of TEM images for Fe-NPs. Arrows are pointing out Fe-NPs with different core/shell morphology. (d) Histogram of the NP diameter together with a fit (red solid line) to a log-normal function. The mean particle size obtained is $\langle \tau(\sigma) \rangle = 15(6)$ nm.



(a) TEM image showing in detail an Fe-NP with three different electronic densities and a well-defined “onion-like” morphology. In the figure, yellow lines are guides to the eye. (b) Schematic drawing of the morphology of Fe-NPs in Fe-AC sample.