Development of core/shell superparamagnetic iron oxide/silica nanorods Daniel Carmona, Nuria Miguel, Alejandro G. Roca, Francisco Balas and Jesús Santamaría

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Aqueous suspensions of iron oxide nanoparticles (MNPs) have been shown to be promising materials for diagnose and treatment of several illnesses^{1,2}. Drug delivery carriers, NMR contrast agents and nano heat power sources are typical apical application where MNPs has gained attention due to their magnetic properties or low toxicity. However, one of the best problems of these suspensions is the lack nof colloidal stability at physiological pH because magnetic particles tend to agglomerate and coagulate causing thrombus in blood vessels and veins. An accurate surface treatment that involves the hydrolysis and condensation of silica alcohoxide precursors onto the particle surface provides several advantages over other surface treatments³. Silica not only provides an electrostatic repulsion between particles at pH 7 but also chemical stability, low toxicity and a very reactive surface composed by silanol groups for further amine, carboxylic or thiol functionalization. Moreover, silica matrix has shown to present a great potential for their adsorption capacity and integration of other type of particles or fluorescent probes⁴. Final properties of silica-coated iron oxide nanoparticles will depend on the type of aggregate that they form apart from their intrinsic properties.

In this work, we have studied the particle structure that is synthesized between the magnetic iron oxide nanoparticles and silica using magnetite/maghemite particles with different size, aggregation degree and surface nature. The final properties of these particles will be strongly depending on the particle shape and encapsulation degree. Magnetic nanoparticles were synthesized by thermal decomposition of iron acetylacetonate in triethyleneglycol (TREG). Using this strategy, high-quality one-step biocompatible particles could be obtained. TREG acts as solvent, redactor and capping agent providing hydroxyl groups to the surface⁵. Carboxylic moiety was easily incorporated to the particles by adding DMSA (dimercaptosuccinic acid) to the suspension. Naked nanoparticles of maghemite were obtained by classical coprecipitation from iron salts. Silica coating was performed to the three suspensions using well known Stöber method⁶ in very dilute concentrations at different hydrolysis times.

Transmission Electron Microscopy studies are used for description of the real structure of silica/iron oxide nanoparticles. When maghemite nanoparticles synthesized by coprecipitation were used for silica coating, spherical silica particles with spherical aggregates of iron oxide nanoparticles inside were formed. Particle size increases from 20 n to 300 nm when the hydrolysis time goes from 1 to 6 hours. For suspensions that consist on maghemite nanoparticles coated by TREG, unexpected rod shape maghemite aggregates embbebed in silica rods of around 700 nm were obtained. When TREG molecules were exchanged by DMSA from the maghemite nanoparticles, individual particles or clusters formed by less that 5 were coated by a thin silica layer that growth with the hydrolysis time leading to spherical particles of 50-200 nm of average size. Aggregate size of the starting suspension, medium ionic strength and pH, hydrolysis time but specially particle surface functional groups seems to be responsible for the final particle structure.

These results indicate that by selection of the synthesis condistions, the morphology of iron oxide/silica nanocomposites can be tailored from nanoparticles to nanorods. Also, the relative positions of silica and iron oxide nanoparticles can be determined at will. This is of particular relevance for the design of drug magnetic carriers or magnetic separation devices because magnetic properties of the material can be tuned by changing particle density and aggregate shape inside the silica particle and adsorption/release capacity can be tuned by changing the silica matrix size and their shape.

References

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Figures

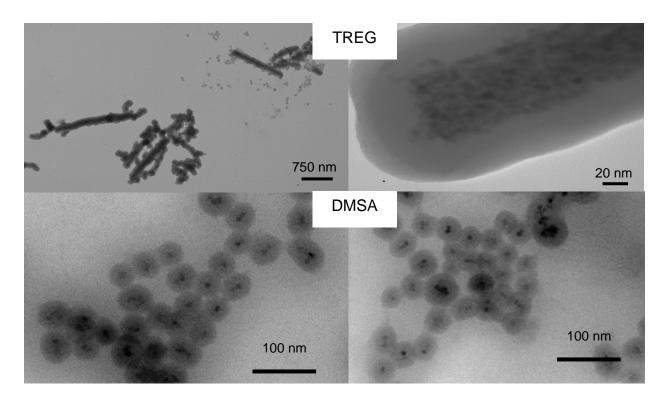


Fig 1.TEM mages of different silica-iron oxide composite nanoparticles obtained using different preparation procedures.