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Research articles

Tuning dipolar magnetic interactions by controlling individual silica coating of iron oxide nanoparticles

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ABSTRACT

Single and fixed size core, core–shell nanoparticles of iron oxides coated with a silica layer of tunable thickness were prepared by chemical routes, aiming to generate a frame of study of magnetic nanoparticles with controlled dipolar interactions. The batch of iron oxides nanoparticles of 4.5 nm radii, were employed as cores for all the coated samples. The latter was obtained via thermal decomposition of organic precursors, resulting on nanoparticles covered with an organic layer that was subsequently used to promote the ligand exchange in the inverse microemulsion process, employed to coat each nanoparticle with silica. The amount of precursor and times of reaction was varied to obtain different silica shell thicknesses, ranging from 0.5 nm to 19 nm. The formation of the desired structures was corroborated by TEM and SAXS measurements, the core single-phase spinel structure was confirmed by XRD, and superparamagnetic features with gradual change related to dipolar interaction effects were obtained by the study of the applied field and temperature dependence of the magnetization. To illustrate that dipolar interactions are consistently controlled, the main magnetic properties are presented and analyzed as a function of center to center minimum distance between the magnetic cores.

1. Introduction

Magnetic nanoparticles have been a very active field of study for several decades owing to their multiple applications in several technologies. Since the initial formulations from the fundamental point of view [1], the physics beneath magnetism at the nanoscale still remains an incomplete puzzle [2].

Studies of superparamagnetic nanoparticles generally report the magnetic behavior either as a "weakly interacting system" or a "strongly interacting system", yet many attempts are being made to obtain in the laboratory an ideal enough system to be used as a tool to quantify and fully understand the role of dipolar interactions between nanoparticles and to test some of the existing models that describe them [2].

Being able to differentiate the effects of interactions from the effects of size, shape and anisotropy easy axis distributions in real samples is not an easy task, and represents a big challenge from the very moment of the synthesis route selection. In this regard, chemical synthesis routes have become a good way to obtain uniform and nearly monodisperse samples with good crystallinity, with phases and size control. Among them, thermal decomposition of organic precursors has become a popular route, since it yields some of the best reported samples, providing an easy control of the parameters, and the advantage of an organic coating on the nanoparticles surface that facilitates further functionalization.

Beyond good quality magnetic nanoparticles, a framework to unravel the interplay between their intrinsic properties and the interactions between them can be provided by a non-magnetic isolating media like polymers or proteins [3–9], with limitations on concentration and homogeneity control. In order to overcome this constraint, the coating of each nanoparticle has been a good approach, and amorphous silica provides a chemically and mechanically resistant shell with several advantages for applications related to the widely studied chemistry of the SiO_2 and its intrinsic properties like biocompatibility [10–18].

Several advantages for morphologically controlled homogenous core-shell systems have been addressed from the applications point of view [11,12,19], but from the magnetism fundamental point of view, only a few establish a direct relationship between the geometrically generated interparticle distance and the

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magnetic features [7,14], potentially useful to clarify the interspacing that defines the nature and magnitude of interactions in a given system. To this aim a profound structural characterization is indispensable and techniques like SAXS arises as a statistically strong characterization method. No reports of systematic SAXS studies were found by the authors for this synthetic route, as the one presented here.

In this work iron oxides nanoparticles (IONPs) were synthesized via thermal decomposition and systematically coated with silica (SiO_2) via the inverse microemulsion method, increasing the thickness of the shell with the amounts of silica precursor. A detailed structural and morphological characterization is presented here and related to the main magnetic features.

2. Experimental

As schematized in Fig. 1, IONPs were prepared by thermal decomposition of an iron organometallic precursor [20], and then coated with SiO_2 via a reverse microemulsion method, following a procedure to obtain nanoparticles with a single iron oxide core and different silica shell thicknesses [21].

Chemicals: Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6\ H_2O$, 97%), Sodium hydroxide (NaOH) and ammonium hydroxide (28%) were purchased from Anedra. 1-octadecene, oleic acid, tetraethyl orthosilicate (TEOS) and Igepal CO-520 were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

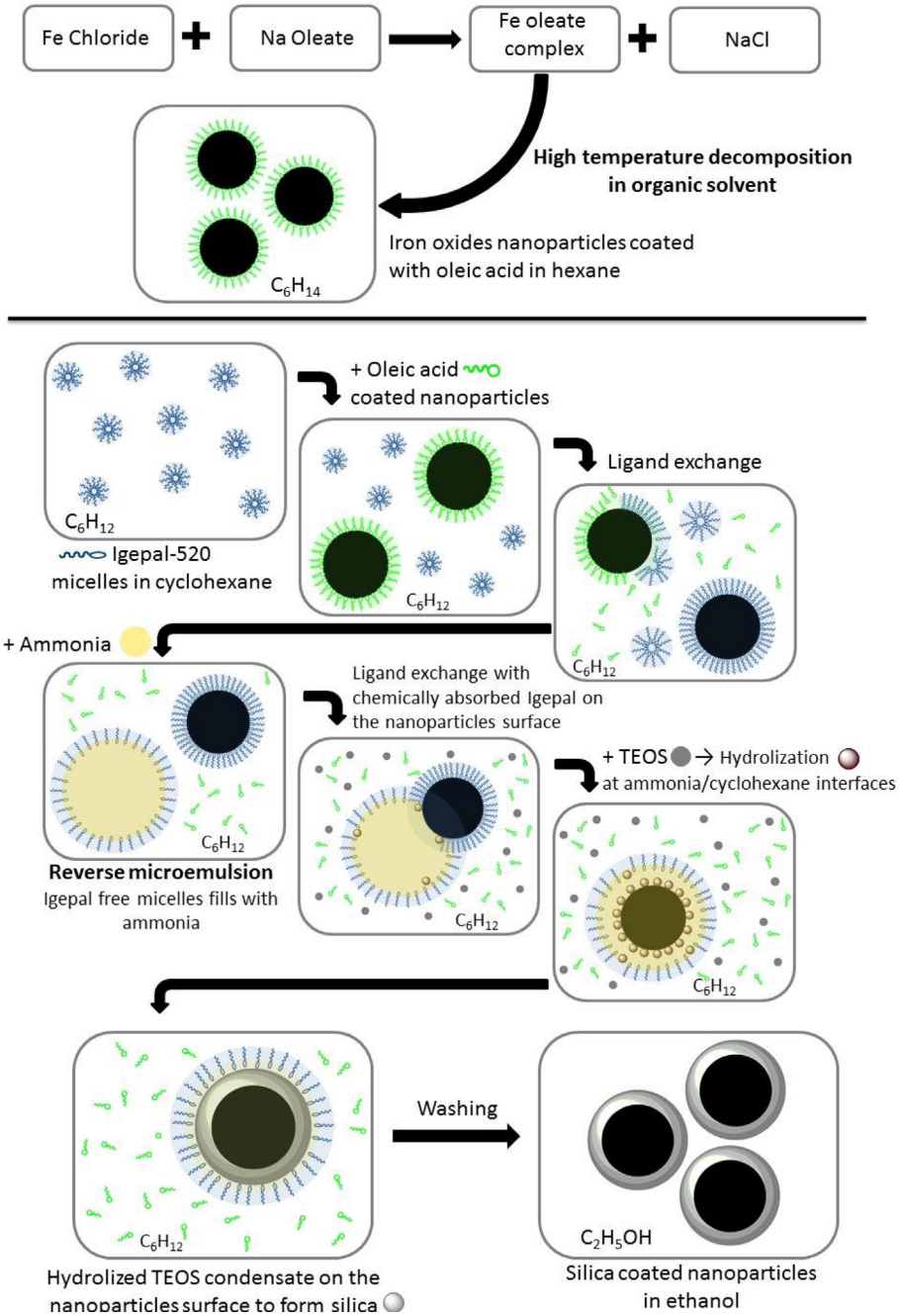

Fig. 1. (a) Schematized description of the nanoparticles formation and (b) posterior silica coating.