

Controlled formation of porous magnetic nanorods *via* a liquid/liquid solvothermal method†

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Porous magnetic nanorods with sizes readily modulated and high water affinity are prepared *via* a water-in-oil/water solvothermal method.

Uniaxial nanoparticles have attracted much attention due to their particular properties as a consequence of their low dimensionality, size effects and high surface area.¹ Particularly, those based on iron oxide are highly attractive. Magnetite (Fe₃O₄) can be used for spintronics devices because of its high spin polarization at the Fermi level and high Curie temperature.² Recently, iron oxide nanorods have been shown to have potential for biomedical applications.³ Methods have been developed to synthesize nanorods (NRs) with high crystallinity and narrow size distribution by thermal decomposition or sol–gel reactions in reverse micelles.⁴ However, as-synthesized NRs are not directly suited to most applications since the core is covered with a chemically-inert shell comprising hydrophobic long-chain alkyl surfactants. Two phase and/or interface liquid–liquid methods have been recently shown to be adequate for the controlled synthesis of equiaxial nanomaterials.⁵ Li and co-workers have used a liquid–solid–solution phase transfer for the controlled synthesis of nanoparticles (including nanorods) but the materials are capped with long-chain alkyl surfactants.⁶

We have recently reported a new ternary water-in-oil/water liquid solvothermal method for the controlled synthesis of equiaxial ZrO₂ nanoparticles.⁷ The method combines the advantages of the *in situ* controlled release methods (controlled addition) with the advantages of solvothermal methods (highly crystallinity). Here, we show that this new method can also be applied for the controlled synthesis of iron oxide-based magnetic NRs. We demonstrate, as a proof-of-concept, that these 1D nanostructures can be easily provided with magnetic functionality, and then grafted with carboxylate moieties to produce water suspensions with solid concentrations as high as 5 mg mL⁻¹. A schematic representation of the method is displayed in Fig. 1. The method involves a bottom aqueous layer containing a low cost inorganic salt (FeCl₃) and a top organic layer containing the precipitating agent. The top organic layer is a water-in-oil microemulsion (two liquid phases forming a homogenous dispersion), in

which the precipitation agent (NH₄OH) is located in the water nanocontainers formed by the reverse micelles. Controlled destabilization of the reverse micelles on the top organic layer with temperature produces a phase separation (water containing NH₄OH separates from cyclohexane). Gravity induces the aqueous phase containing NH₄OH to migrate down towards the bottom of the tube, where it comes into contact with the bottom aqueous layer. There diffusion and thermal mixing are the mechanisms responsible for putting the ammonium hydroxide into contact with FeCl₃ to form the nanorods.⁸ Non-ionic surfactants are used to form the microemulsions in the top organic solvent and the absence of stirring during the synthesis assure that these surfactants mainly remain in the top organic layer. Further thermal reduction in a H₂ atmosphere produces porous magnetic NRs, and grafting with carboxylate moieties produces water suspensions with solid concentrations as high as 5 mg mL⁻¹. Destabilization of microemulsions with temperature assures a broad range of conditions for the *in situ* controlled supply of precipitating agents in contrast to methods using urea (> 80 °C to generate hydroxyl anions or, using the urease enzyme, low temperatures where the enzyme is active).

Fig. 2 clearly shows that nanorods from 45 to 430 nm in long axial length can be prepared by this method (for details, see ESI†). Tuning of the particle size was achieved by judicious variation of the experimental conditions assuming in a first approach that the system followed a nucleation–growth mechanism. In the framework of a nucleation theory, smaller nuclei and nanocrystals will be more stable if the reaction occurs faster. This can be achieved by increasing the reaction temperature while fixing all the other experimental conditions (70 to 45 nm in long axial length when increasing the temperature from 50 to 100 °C, Fig. 2 AK-1, AK-2, Table S1 in ESI†). A size reduction in long axial length can also be achieved by increasing the volume of NH₄OH (7.5 M) in the microemulsions while fixing all the other experimental

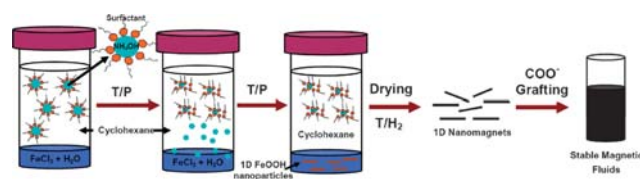


Fig. 1 Schematic representation of the methodology used to prepare porous magnetic nanorods. The vessels where the reaction takes place are kept closed.

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† Electronic supplementary information (ESI) available: Details of the experimental method. A table listing the experimental conditions. XRD patterns and HR-TEM micrographs. See DOI: 10.1039/b805239e

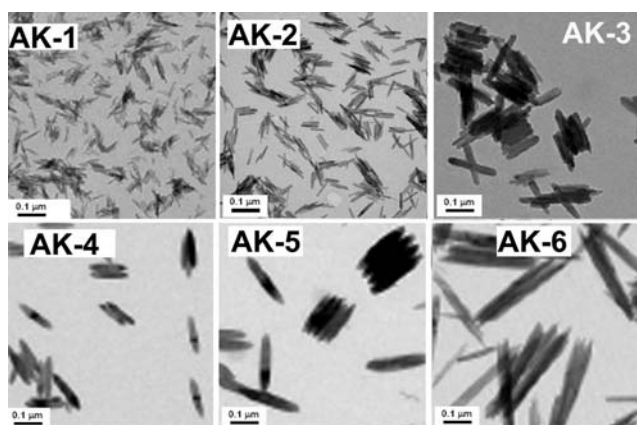


Fig. 2 TEM micrographs of the nanorods (45 to 450 nm).

conditions (110 to 45 nm when increasing the NH_4OH volume in the microemulsion from 128 to 256 μL , Fig. 2 AK-1, AK-3, Table S1 in ESI†). A size reduction in long axial length can also be made by changing the Fe(III) concentration in the bottom aqueous layer from 1 to 0.1 M while fixing all the other experimental conditions (425 to 110 nm, Fig. 2 AK-3, AK-4, AK-5 and AK-6, Table S1 in ESI†). The precipitation pH for the more concentrated preparations is more acidic (the amount of NH_4OH added is the same in all preparations), which results in lower precipitation rates and the increase in particle size with respect to Fe(III) diluted suspensions. We have no clear explanation for the increase in axial ratio at sizes with lengths bigger than 150 nm but it seems that preferential growth is favored when increasing the size above this limit. XRD clearly confirms the formation of $\beta\text{-FeOOH}$ crystals (Fig. S1 in ESI†). The similarity of the sizes by TEM and those estimated by XRD (Table S1 in ESI†) for the (002) and its perpendicular (200) lattice planes indicate that particles preferentially grow in the [002] direction. Finally, it is worth noting that monodisperse $\beta\text{-FeOOH}$ nanocrystals of $45 \pm 5 \times 8 \pm 1$ nm can be produced for a concentration of FeCl_3 of 0.1 M. This concentration is five times higher (0.02 M) than that reported for the synthesis of monodisperse $\beta\text{-FeOOH}$ particles ($65 \pm 8 \times 14 \pm 2$ nm).³

$\beta\text{-FeOOH}$ 1D nanostructures can be transformed into 1D porous ferrimagnetic materials by thermal reduction in a H_2 atmosphere.³ We have restricted our study to four samples with long axial lengths smaller than 200 nm (45 to 150 nm). A practical route for sterilization involves filtering through 200 nm pore membranes. A temperature of 275 °C was selected for reduction in a H_2 atmosphere (for details, see ESI†). Fig. 3 clearly shows that the resulting particles preserve their morphology and have incipient porosity that could be exploited for drug-delivery applications. Porosity comes from dehydroxylation of $\beta\text{-FeOOH}$ particles during the thermal reduction treatment. In fact, it has been recently reported by Hyeon and co-workers that a silica coating carried out in 1D $\beta\text{-FeOOH}$ nanocrystals by a simple methodology is sufficient to increase the temperature of reduction (to preserve the morphology at higher reduction temperatures), and to be able to produce magnetic capsules of applicability in biosciences.³ XRD (Fig. S2 in ESI†) and HR-TEM (Fig. S3 in ESI†) show the presence of a porous

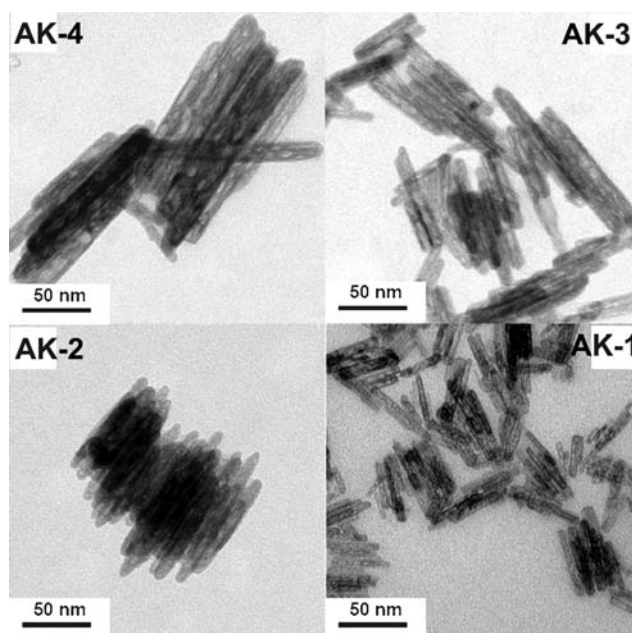


Fig. 3 TEM images of the reduced nanorods.

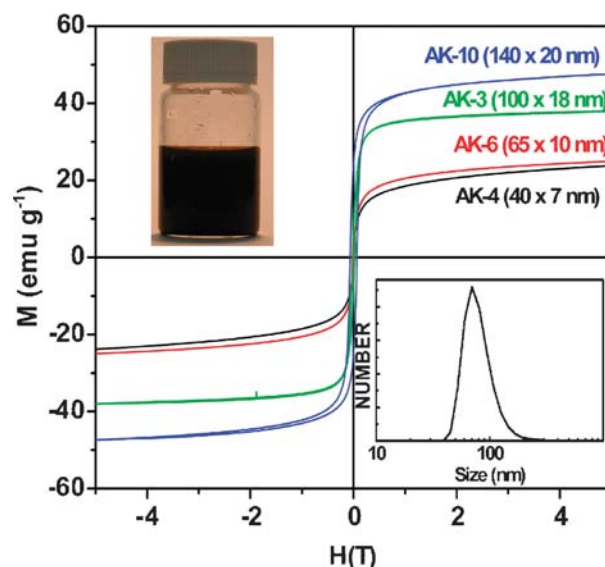


Fig. 4 Magnetization curves of the reduced samples. The figure also shows a nanorod suspension (5 mg mL^{-1}) and its hydrodynamic size (AK-2). Though DLS is not adequate to measure nanorods, the hydrodynamic size (75 nm) is similar to the long axial length of the nanorods (65 nm), which points to the absence of aggregates.

ferrimagnetic iron oxide spinel crystalline phase in all samples. Fig. 4 clearly shows that the particles are magnetic with values of saturation magnetization higher than 25 emu g^{-1} and values of the coercivity field changing from zero (as expected the smallest one presents superparamagnetic behavior) to 650 Oe for the particles with the highest axial ratio and high magnetic moment. In order to show that some of these preparations can be dispersed in water, we followed a standard protocol described by Lesieur *et al.*⁹ to graft carboxylates to the surface of the nanomagnets in sample AK-2. Fig. 4 (inset) shows that the hydrodynamic size of a

stable water suspension of 1D nanomagnets (5 mg mL^{-1}) is similar to the length of the long axis observed by TEM (no aggregation).

In summary, we have shown that a ternary water-in-oil/water solvothermal method can be used for the controlled synthesis of porous magnetic nanorods with sizes readily modulated. We have demonstrated that these nanostructures can produce porous magnetic nanorods that can be easily dispersed in water. The materials here prepared could be of interest to study fundamental phenomena associated with nanoparticle physics and nanobiology as well as to expand the capabilities of 1D iron oxide-based nanomagnets in different applications.

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