

ESI FOR:

**Controlled Formation of Porous Magnetic Nanorods via a
Liquid/Liquid Solvothermal Method**

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Experimental Section

Preparation of 1D β -FeOOH nanocrystals. All chemicals reactants (purity >99.9%) were purchased from Sigma Aldrich and used without additional purification. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was used as precursor of the akaganeite nanocrystals. Igepal CO-520 and cyclohexane dehydrated with zeolites were used as the surfactant and the continuous oil phase, respectively. Water-in-oil microemulsions were prepared at room temperature by mixing and strong stirring a mixture of Igepal CO-520 (0.2 M referred to the total volume of the organic layer) and concentrated ammonium hydroxide aqueous solution (NH_4OH , 7.5M) with cyclohexane. Deionized water was used in all experiments. Ethanol was used for washing. The synthesis of uniform akaganeite nanocrystals was performed by solvothermal destabilization of reverse microemulsions. In this procedure, 4 mL of an aqueous solution of Fe (III) chloride with the required concentration were placed in the bottom of 25 mL cylindrical tubes ($r = 0.9$ cm and $h = 17$ cm and thermal resistance until 180°C) and subsequently slowly covered with 10 mL of cyclohexane. Cyclohexane has a lower density than water and thus remains at the top of this biphasic solution. Next, 10 mL of a transparent reverse microemulsion (10 mL of cyclohexane containing 1.756 g of Igepal CO-520 and a fixed volume of aqueous NH_4OH) were placed on the top of the cyclohexane layer. This protocol was carried out to minimize the contact of the reverse microemulsion with the bottom aqueous layer. Lastly, the cylindrical tubes were sealed, and both Fe (III) aqueous solution and NH_4OH microemulsion were allowed to react by heating at different temperatures for 24 hours. Under these conditions, the controlled destabilization of the reverse micelles on the top organic layer with temperature produces a phase separation (water containing NH_4OH separates from cyclohexane). The gravity induces the aqueous phase containing NH_4OH to migrate downwards the bottom of the tube, where it comes into contact with the bottom aqueous layer. There diffusion and thermal mixing are the mechanisms responsible to put the ammonium hydroxide into contact with FeCl_3 to form the nanorods. After then, the nanocrystals were decanted by centrifugation at 9.000 rpm during 1 hour, and washed with ethanol and then with water. Finally, samples were dried at 45°C . Dried samples were analyzed without further treatment.

Preparation of porous magnetic nanorods. Nanorods were obtained by heating the β -FeOOH nanocrystals at 275 °C in a H_2 stream of 20 L h^{-1} for 60 min. After then, the powders were cooled down to room temperature under the hydrogen atmosphere. Finally, a N_2 gas wetted with ethanol was passed through the sample (~ 1 h) to prevent rapid oxidation in case metallic iron was formed.

Sample Characterization. Phase identification was performed by X-ray analysis. X-ray diffraction (XRD) patterns were collected from 10 to 70° (2 θ) by using a Siemens D5000 instrument with CuK α radiation ($\lambda=0.15406$ nm) operating at 40 kV and 20 mA. The crystal domain size (DXRD) was determined from the X-ray profiles following the Scherrer equation by using the DIFRACPLUS EVA software (BRUKER AXS). Morphology and particle size of the obtained samples were studied with a TEM JEOL Jem1010 microscope working at 100 KeV. The mean length (L) and width (W) were evaluated from the electron micrographs by counting around one hundred particles. Images of the lattice planes fringes present in the samples were determined by using a TEM Phillips CM200FEG Supertwin microscope working at 200 KeV. The analysis of the HRTEM micrograph was carried out by using the Digital Micrograph software package (GATAN, INC). Magnetic properties of the samples were recorded in a vibrating sample magnetometer (MLVSM9 MagLab 9 T, Oxford Instrument). The saturation magnetization (M_s) and coercivity field values (H_c) were obtained from the magnetization curves registered up to a field of 5T. The M_s values were obtained from 1/H extrapolation at high fields. Dynamic light experiments (DLS) were carried out in a Nanosizer ZS (Malvern Instrument) to determine the hydrodynamic size. The hydrodynamic size (expressed in number of particles) was obtained for a water suspension with content in nanomagnets about 5 mg mL^{-1} .

Table S1. Experimental conditions for the controlled synthesis of one-dimensional β -FeOOH nanocrystals. The table also lists the sizes deduced from TEM analysis and XRD for (002) and (200) planes. As we describe in the experimental section the surfactant concentration and reaction time were fixed in all experiments to 0.2 M (referred to the total volume of organic content) and 24 hours, respectively.

Sample	[Fe] (M)	NH ₄ OH (μ L)	T (°C)	TEM _{SIZE} (nm)			XRD _{SIZE} (nm)	
				Long	Short	Axial Ratio	(002)	(200)
AK-1	0.1	320	100	45 $\pm$ 5	8 $\pm$ 1	5.6	34	9
AK-2	0.1	256	50	70 $\pm$ 10	12 $\pm$ 2	5.8	67	15
AK-3	0.1	128	100	110 $\pm$ 28	20 $\pm$ 5	5.5	114	23
AK-4	0.25	128	100	150 $\pm$ 30	22 $\pm$ 4	6.8	177	30
AK-5	0.5	128	100	245 $\pm$ 45	24 $\pm$ 6	10	220	36
AK-6	1	128	100	425 $\pm$ 120	30 $\pm$ 8	14	340	41

Figure S1: X-Ray diffraction patterns of the samples prepared by a ternary water-in-oil/water liquid method. All peaks corresponds to β -FeOOH. Table S1 lists the experimental conditions to obtain these particles.

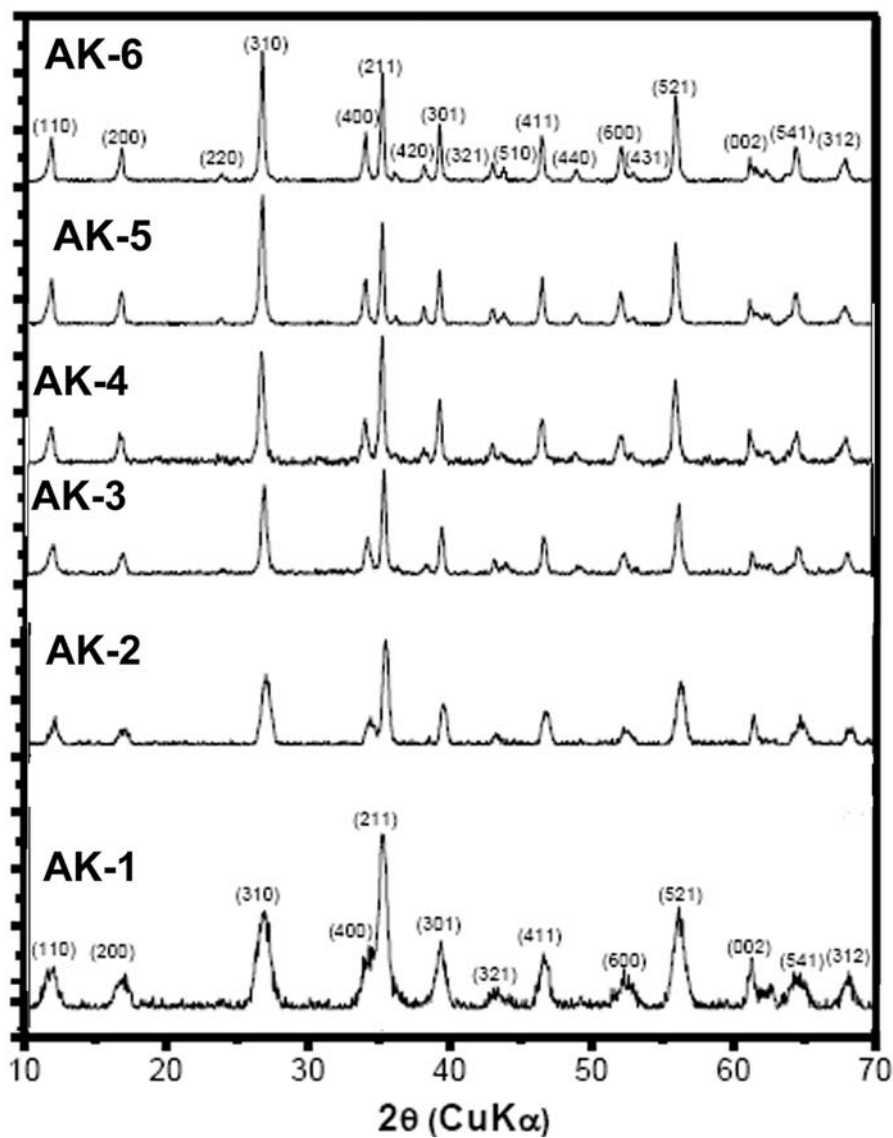


Figure S2: X-Ray diffraction patterns of samples AK-1, AK-2, AK-3 and AK-4 after reduction. The main diffraction peaks for iron oxide spinel (M, magnetite/maghemite) and hematite are marked (H).

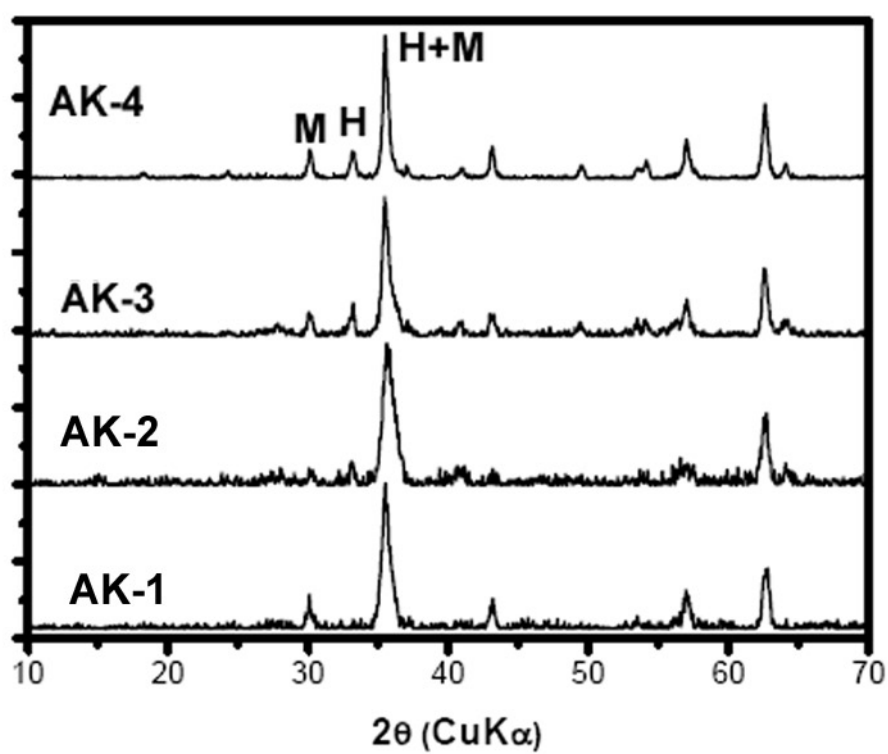


Figure S3: HRTEM image of a selected β -FeOOH samples heated at 275°C in a dynamic atmosphere of H_2 during 60 min: The image shows lattice fringes associated with hematite and an iron oxide spinel (maghemite or magnetite).

