Supporting Information

Huge Specific Absorption Rate and Transverse Relaxivity Effects in Manganese Ferrite Nanoparticles Obtained by Electrochemical Route

Eva Mazarío,[¤] *Jorge Sánchez-Marcos,*[¤] *Nieves Menéndez,*[¤] *Magdalena Cañete,*[φ] *Alvaro Mayoral,*[§,†] *Sara Rivera-Fernández,*[†] *Jesús M. de la Fuente,*[†,‡,◊] *Pilar Herrasti*[¤*]

[¤] Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid. C/ Francisco Tomás y Valiente, 7. 28049, Madrid, Spain.

[φ] Departamento de Biología, Facultad de Ciencias, Universidad Autónoma de Madrid, C/ Darwin 2, 28049 Madrid, Spain.

[§] Laboratorio de Microscopias Avanzadas (LMA), Zaragoza, Spain.

[†] Instituto de Nanociencia de Aragón, Universidad de Zaragoza, Mariano Esquillor s/n, 50018 Zaragoza. Spain.

[‡] Instituto de Ciencia de Materiales de Aragón, CSIC/Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009, Zaragoza. Spain

[◊] Institute of Nano Biomedicine and Engineering, Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, Research Institute of Translation Medicine, Shanghai Jiao Tong University, Dongchuan Road 800, 200240 Shanghai, People's Republic of China.

Figure S1

Experimental

The infrared spectra were recorded in the range 4000 - 550 cm^{-1} on a Fourier transform infrared spectrometer (FTIR, Bruker model IFS66V). Powder MNPs were dispersed in KBr at 1 wt% and pressed in a pellet.

Results

The conjugation of citric acid onto the $MnFe_2O_4$ surface was established from FTIR spectroscopy. Figure S1 shows the FTIR spectra of pure CA (black), pure MNPs (red) and MNPs capped CA (blue). The absorption bands for the pure CA are well resolved, the 1708 cm^{-1} peak (asymmetric stretching) assignable to the C=O vibration from the COOH group in neat CA is present as a broad band. This peak shifts to a lower value (1616 cm^{-1}) when the carboxylate groups of CA binding with de nanoparticle surface by chemisorption of carboxylate ions rendering partial single bond character to the C=O bond [1]. Furthermore, the vibrational modes appearing at 1388, 1250 and 1065 cm^{-1} in MNPs – CA correspond to the symmetric stretching of COO, symmetric stretching of C–O, and OH group of CA [2]. The strong IR absorption band at 575 cm^{-1} in the low frequency region can be associated to the Fe–O stretching vibrational mode of manganese ferrite skeleton.

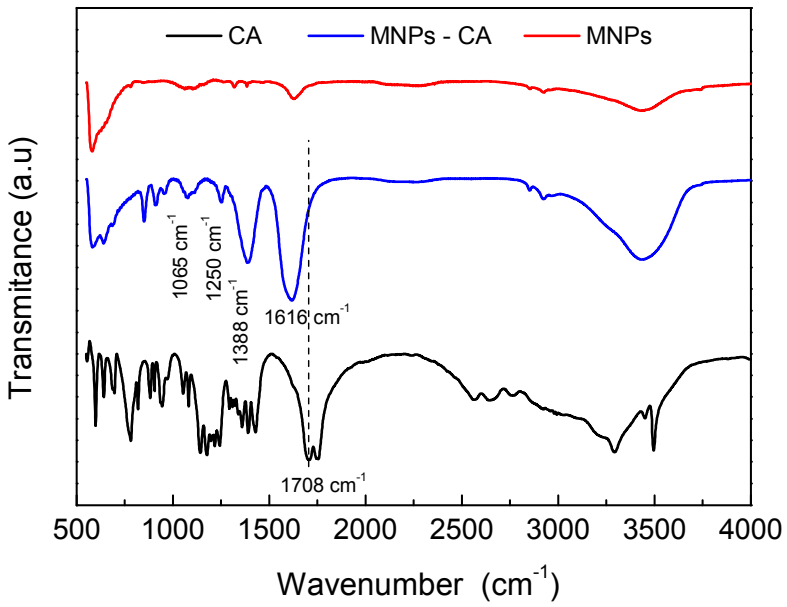

Figure S1. Infrared spectra of manganese ferrite functionalize with citric acid (blue line), pure citric acid (black line) and pure manganese ferrite (red line).

Figure S2

Experimental

Thermogravimetric analysis, (TGA) was conducted using a Mettler Toledo Instrument (TG/SDTA851e model) under air flow, with a heating rate of 10 ºC min^{-1} from room temperature to 800 ºC.

Results

Thermal analysis operating in the temperature range of 25-700 ºC was performed to confirm the organic coating on the surface of the manganese ferrite. Figure S2 displays the TGA curve of $MnFe_2O_4$- CA, showing that about 33% of the weight of the material was lost in this temperature range. The initial weight loss in the range of 80-200 ºC may correspond to the evaporation of water

physically absorbed on the nanoparticles. The second one, between 200 and 600 ºC may be attributed to the elimination of citrate covering the nanoparticles. This suggests that around 67% (wt) of the nanoparticles were composed of magnetic core and the rest consisted of organic compounds and water.

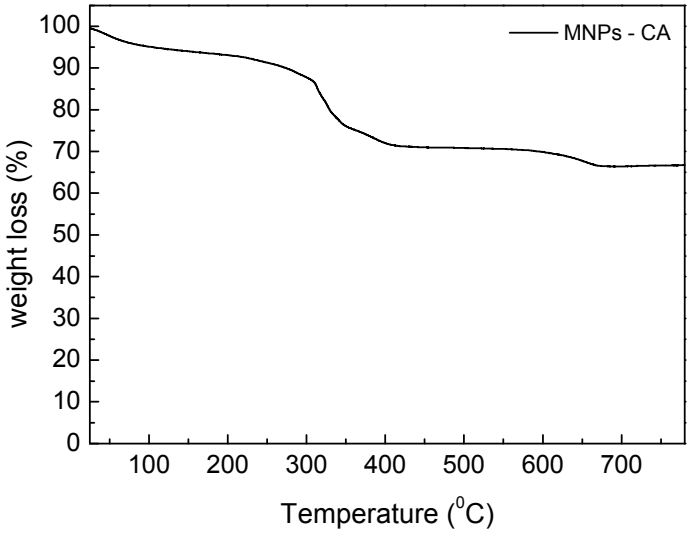

Figure S2. Thermal decomposition traces of citric acid functionalized manganese ferrite.

Figure S3

Experimental

Colloidal properties of the samples were studied in a Zetasizer Nano S, from Malvern Instruments. The hydrodynamic size of the particles in suspensions was measured by dynamic light scattering (DLS Brookhaven Instruments Corportion. 90 plus), and the zeta potential was measured as a function of pH at 25 °C, using 10^{-2} M KNO_3 as background electrolyte and HNO_3 and KOH to change the pH of the suspensions.

Results

The hydrodynamic size and Zeta Potential of $MnFe_2O_4$– CA were measured against the pH. Citric acid conjugated particles at pH 7 have a hydrodynamic size of 95 nm, with a polidispersity index (PDI) less than 0.2, this low value resulting in a monodispersed colloid. In addition, changes of pH on the medium did not significantly vary the hydrodynamic size of the sample. Figure S3 shows the zeta potential measurements at different pH values between 3 and 12. The ferrofluid at pH 7 exhibits a negative surface potential of around – 25 mV, which confirms the presence of carboxylate groups on the nanoparticles surface assuring a longer term stability of the ferrofluid at pH above 4. The isoelectric point (IOP) is not observed in measured pH range of 3–12(IOP of bare manganese ferrite is 6.2).

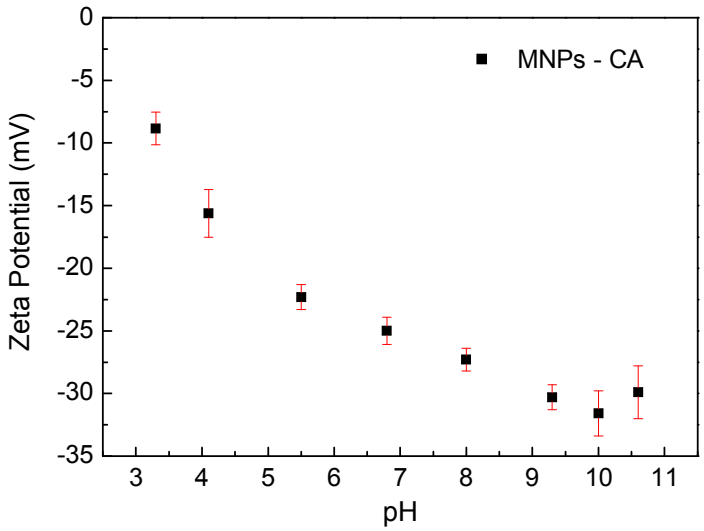

Figure S3. Zeta potential versus pH of citric acid functionalized manganese ferrite. Each data point represents the mean of triplicate experiments and error bars correspond to standard deviation.

Thus, the FTIR, TGA and Zeta potential results confirmed that manganese ferrite nanoparticles have been functionalized with citric acid.

Figure S4

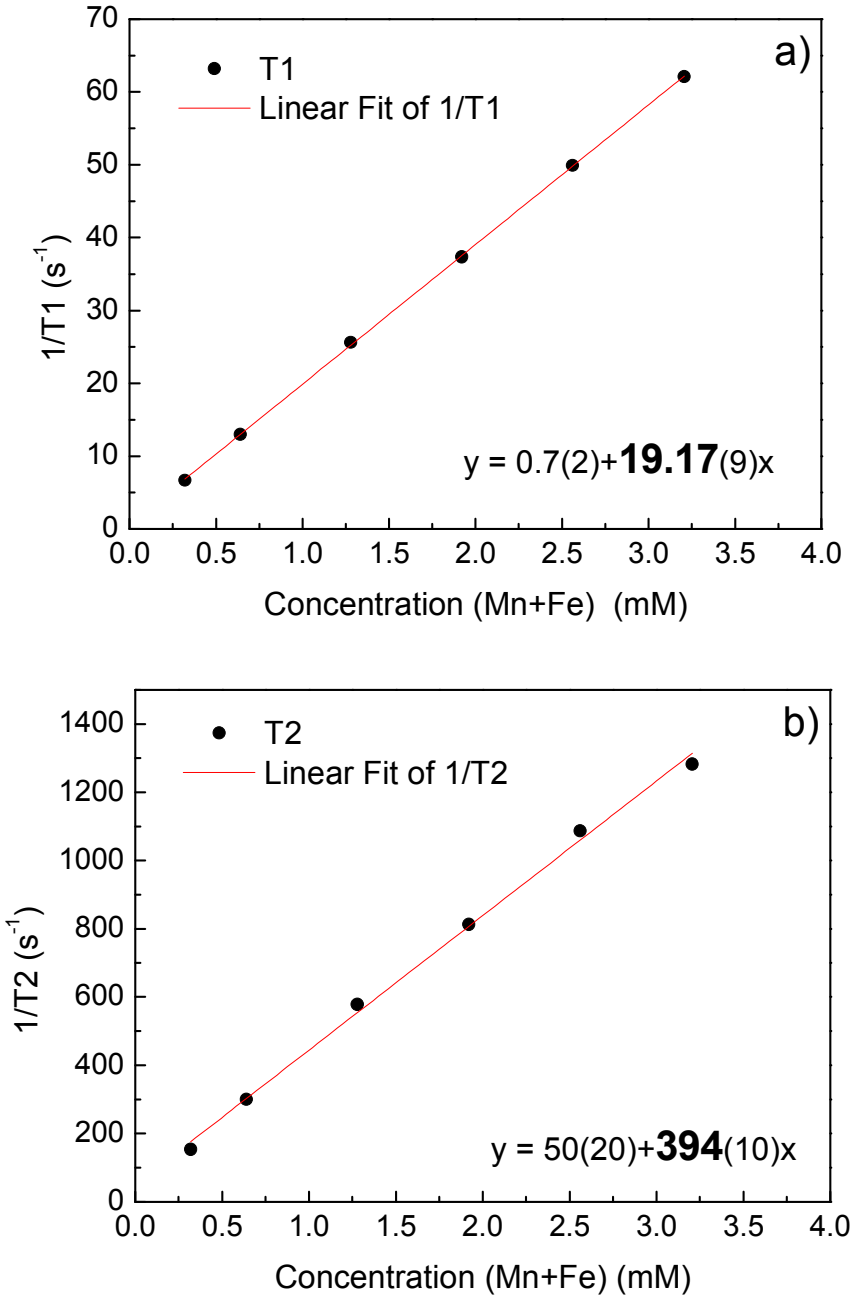

Figure S4. T1 and T2 inverse measurements vs manganese and iron milimolar concentration. The slope of these curves corresponds to r1 and r2 relaxivities.

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