Electronic Supplementary Material (ESI) for Nanoscale.

Tuning coercivity and exchange bias by controlling the interface coupling in bimagnetic core/shell nanoparticles

Gabriel C. Lavorato, Enio Lima Jr., Horacio E. Troiani, Roberto D. Zysler and Elin L. Winkler*

Centro Atómico Bariloche, CNEA-CONICET, Av. Bustillo 9500, Bariloche, Río Negro, Argentina. Tel: +54 294 4445158; E-mail: winkler@cab.cnea.gov.ar

Figure S1 shows TEM micrographs and electron diffraction pattern of $CoO/Co_{1-x}Zn_xFe_2O_4$ nanoparticles for x=0, 0.5 and 1. The core/shell morphology and the spinel structure of the shell were confirmed by dark-field images recorded by collecting the electron reflections with the objective aperture positioned on a section of the inner diffraction ring of the electron diffraction pattern indexed as the 022 of the spinel structure. The brighter contrast of the reconstructed image corresponds to the spinel phase.

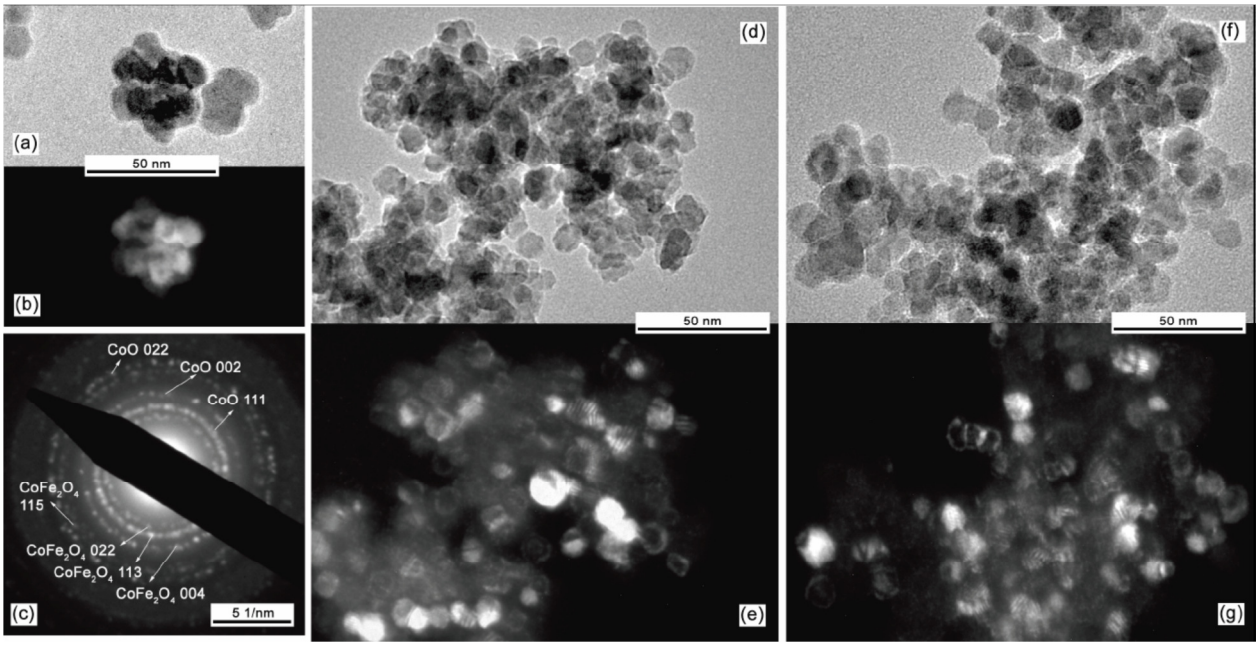

Figure S1: (a,d,f) Bright-field images, (b,e,g) dark-field images and (c) electron diffraction pattern for $CoO/Co_{1-x}Zn_xFe_2O_4$ nanoparticles (samples Zn-0, Zn-0.5 and Zn-1 from left to right). The dark-field images were constructed by positioning the objective aperture on the position of the 022 diffraction ring of the ferrite and reflect the core/shell structure of the samples.

The presence of an organic coating after the thermal treatment of the nanoparticles was analyzed by TEM and FT-IR. From the HRTEM images obtained for different samples (presented in figure S2) an amorphous layer of ≈2 nm can be identified, which is presumably avoiding the coalescence of the nanoparticles during the annealing, and

prevents its agglomeration. In fact the annealed nanoparticles can be redispersed in hexane or toluene after sonication for 1 h.

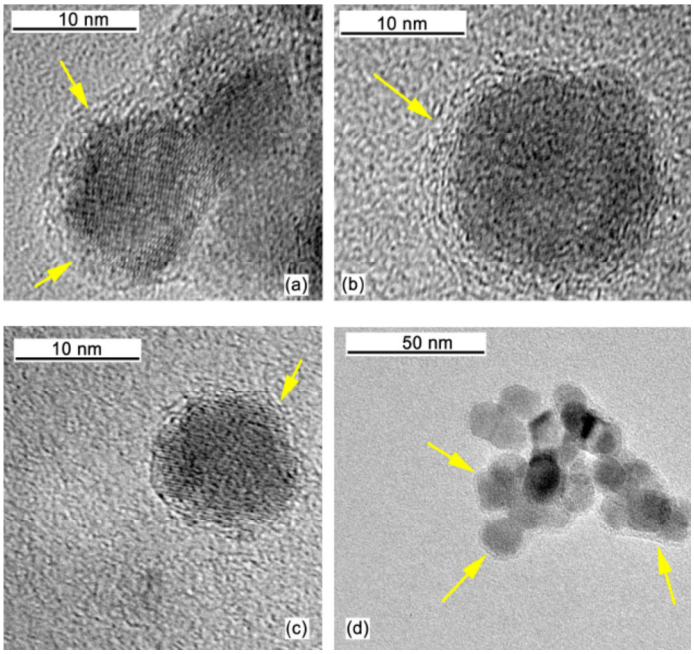

Figure S2. HRTEM images of annealed (a,b) $CoO/Zn_{0.5}Co_{0.5}Fe_2O_4$ (sample Zn-0.5) (c) $CoO/Zn_{0.25}Co_{0.75}Fe_2O_4$ (sample Zn-0.25) and (d) $CoO/ZnFe_2O_4$ (sample Zn-1) nanoparticles. The arrows indicate the presence of an organic coating.

FT-IR spectroscopy experiments have been performed for the particles before and after the thermal treatment, and the obtained spectra were also compared with uncoated nanoparticles (naked nanoparticles, obtained by annealing the nanoparticles at 900 ºC). As can be observed from figure S3, the characteristic bands corresponding to CH_2 stretching (2852 cm^{-1} and 2922 cm^{-1}), the –COO- stretching vibrations (1454 cm^{-1}, 1562 cm^{-1}) and CH_3 stretching (1409 cm^{-1}) are still present in the sample annealed at 300 ºC [1-3], in agreement with the presence of an organic coating revealed by TEM measurements. In addition, the absence of the 1750-1700 cm^{-1} band, characteristic of the C=O stretching vibration of the oleic acid, indicates that the bond with the particle is through the COO group of the oleic acid [2,4].

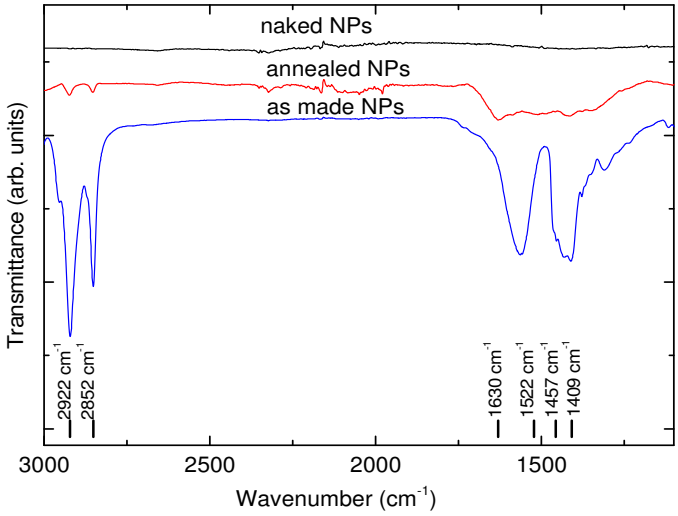

Figure S3: FT-IR spectra of as-made, annealed and naked nanoparticles of $CoO/Zn_{0.25}Co_{0.25}Fe_2O_4$

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