Nanostructured spinel cobalt ferrites: Fe and Co chemical state, cation distribution and size effects by X-ray Photoelectron Spectroscopy

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Figures

Figure S1: XRD patterns of the $CoFe_2O_4$ samples

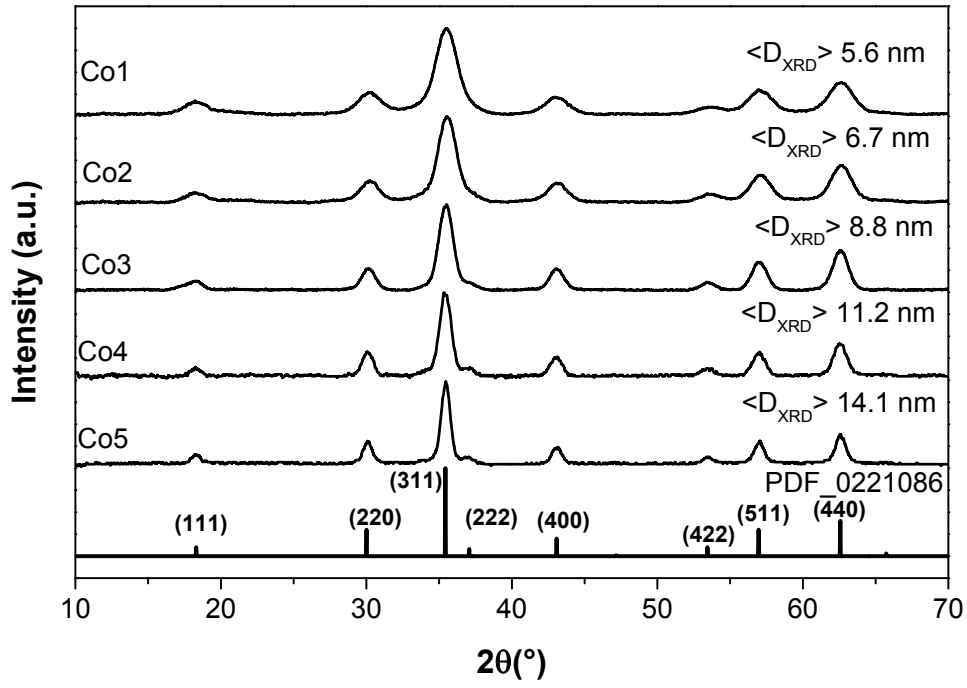
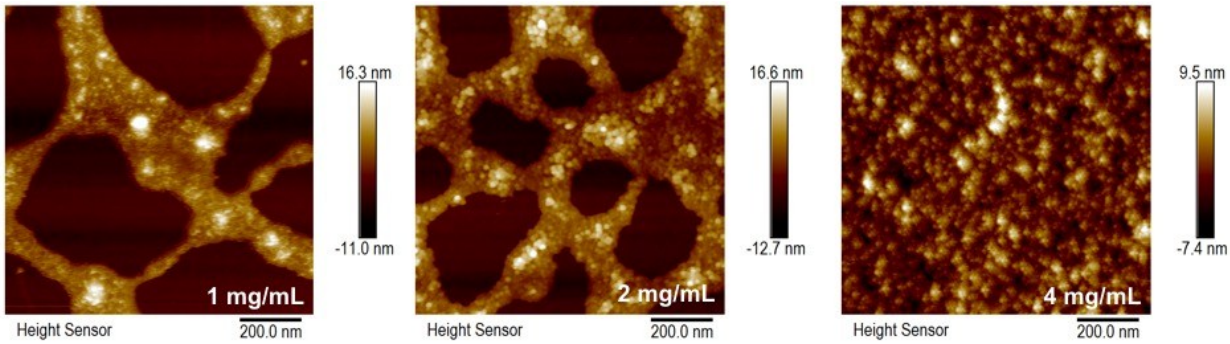
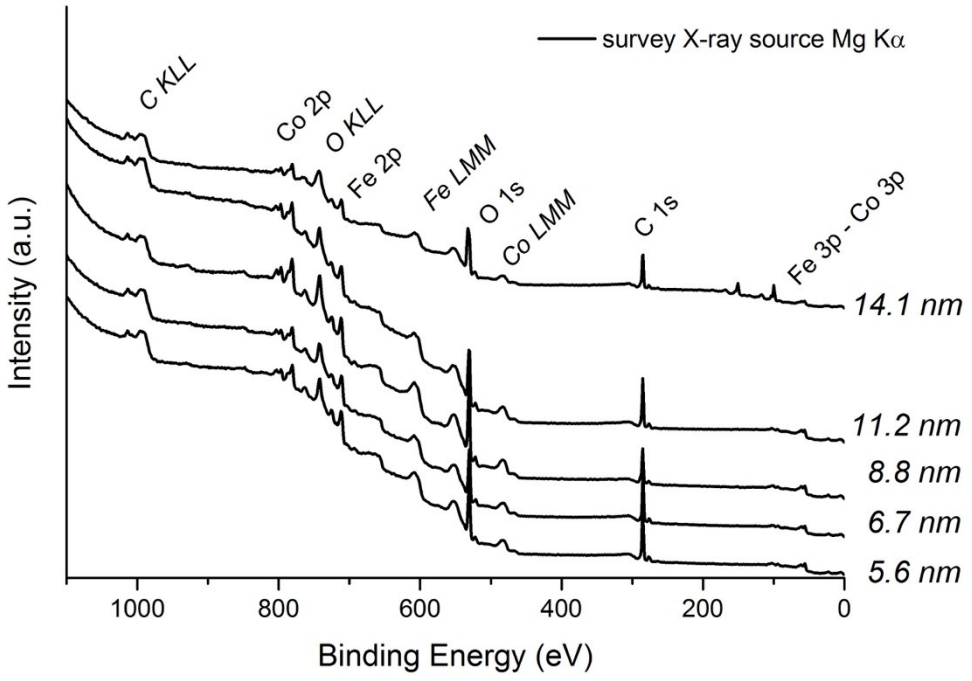


Figure S2: Atomic force microscopy images of spin coating deposited cobalt ferrites.



Cobalt ferrite samples were dispersed in hexane with different ferrite/hexane ratios and deposited on silicon wafer by spin coating before XPS. To check the homogeneity of the covering of the silicon wafer atomic force microscopy was used and the optimum condition for a proper covering of the silicon wafer was found to be 4 mg ferrites in 1 cm^3 of hexane.

Figure S3: survey spectra of the cobalt ferrite samples acquired using Mg Kα X-ray source.



Tables

Table S1**.** Synthesis conditions adopted for tuning the size of the cobalt ferrite nanoparticles

Sample	<D_{XRD}> (nm)*	n $CoFe_2$-Oleate (mmol)	Seed $CoFe_2O_4$ (mmol)	1-pentanol (mL)	Octanol (mL)	Toluene (mL)	Distilled water (mL)	Temperature	Reaction time
Co1	5.6(2)	3	-	20	-	-	10	180 °C	10h
Co2	6.7(1)	6	-	10	10	-	5	180 °C	10h
Co3	8.8(2)	6	-	10	10	-	5	220 °C	10h
Co4	11.2(6)	2.5	-	10	-	10	5	230 °C	10h
Co5	14.1(8)	1	0.1	10	-	10	5	220 °C	10h

* standard deviations are given in parentheses and the uncertainty is on the last digit.

Table S2: curve fitting parameters of the Fe $2p_{3/2}$ according to multiplet splitting approach.

Sample	Fe $2p_{3/2}$ I	Fe $2p_{3/2}$ II	Fe $2p_{3/2}$ III	Fe $2p_{3/2}$ IV
Line shape	GL(70)	GL(70)	GL(70)	GL(70)
Binding Energy	BE (I): ranging 710.0-710.3 eV	Peak 1 + 1.0	Peak 1 + 2.2	Peak 1 + 3.6
FWHM (eV)	2.2	Peak I *1	Peak I*1	Peak I*1
Area	Area Peak I	Peak I * 1	Peak I *0.7	Peak I * 0.33

Table S3: curve fitting parameters of Co $2p_{3/2}$ signal according to multiplet splitting approach.

Sample	Co $2p_{3/2}$ I	Co $2p_{3/2}$ II	Co $2p_{3/2}$ III	Co $2p_{3/2}$ IV
Binding Energy	780.5	710.9	711.9	713.1
FWHM (eV)	2.3	Peak I *1.5	Peak I*1.02	Peak I*2
Area	Area Peak I	Peak I * 0.81	Peak I *0.03	Peak I * 0.68

Fe/Co ratio

Fe/Co ratios were calculated taking into account the Tougaard's background-subtracted Fe 2p and Co 2p (both $2p_{3/2}$ and $2p_{1/2}$ components) peaks' areas.
The experimental areas were corrected according to the first principle method,[1] assuming the sample homogeneity, for the Scofield's photoionization cross sections (σ),[2] and the intensity/energy response function (IERF). The inelastic mean free path (λ) was calculated according to Seah and Dench.[3]
In the following table the values of these parameters are reported for Co 2p and Fe 2p peaks.
The angular asymmetry factor LA(γ) was not taken into account, because for the Sigma 2 spectrometer the instrument's source to analyzer angle of 54° is operating at the magic angle.

	σ	IERF	λ
Co 2p	18.48	0.053	2.56
Fe 2p	15.97	0.040	2.68

References

1. M.P. Seah in *Surface analysis by auger and X-ray photoelectron spectroscopy*, D. Briggs and J.Y. Grant Eds, IM Publication Surface Science Spectra, Manchester, 2003, Chapter 13, 345 - 375
2. J.H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.*, 1976, **8**, 129 – 137
3. M. P. Seah, and W. A. Dench, *Surf. Interface Anal.*, 1979, **1**, 2 – 11