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Synthesis of CoFe₂O₄ nanocubes

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Declarations of interest : none

ABSTRACT

Nanocubes of cobalt ferrite with stoichiometric composition, 20 nm in size, were obtained by a solvothermal route, with acetylacetonates precursors and benzyl alcohol as a solvent, in presence of oleylamine and a mixture oleic acid/oleylamine. The cobalt ferrites were characterized by X-ray diffraction and transmission electron microscopy coupled with energy dispersive spectroscopy. Synthesis parameters such as temperature, duration of the thermal treatment, concentration of precursors, were optimized.

keywords: cobalt ferrite, nanocubes, solvothermal, surfactant

29 INTRODUCTION

30 Ferrites are known for a long time for their magnetic properties along with good chemical
31 stability under harsh environment. MFe_2O_4 compounds (M = metal 3d) are often biocompatible [1-
32 3] and currently literature about ferrites nanoparticles is abundant, because of their potential in
33 drugs delivery , in cancer curing through magnetic heating, or in medical imaging [4-8]. As
34 nanoparticles, cobalt ferrite $Co_xFe_{3-x}O_4$ are superparamagnetic, or ferrimagnetic, depending on
35 temperature of use and particle size [9-11]. In addition, these materials also have interesting
36 catalytic and photocatalytic activity in various reactions, for applications in the field of water
37 treatment [12-13] and gas sensing [14-15]. Creating composite materials based on $CoFe_2O_4$
38 nanoparticles can lead to new functional membranes; $CoFe_2O_4$ magnetostrictive nanoparticles
39 were included in piezoelectric polymers or dispersed in self-assembly of cellulose nanowhiskers in
40 order to obtain magnetoelectric membranes [16-17]. Tuning the size, shape and composition of
41 ferrite nanoparticles allows to tune their properties. Modifying the shape of magnetic nanocrystals
42 modifies the surface anisotropy, hence is a key factor for tuning their magnetic properties, so
43 attempts were done to synthesize various shape such as nanoplatelets [18], nanocubes [19],
44 nanotubes and nanorods [20], and recently nanohexagons [21]. But it is in the domain of catalysis
45 and gas sensing that many studies were conducted about the link between shapes and properties,
46 leading to review papers [14,22].

47 Recently cobalt ferrites were investigated for their catalytic efficiency in various gas
48 conversion [23-28]. The nanoparticles had no specific morphology, and the different behaviors
49 were explained in terms of cation composition and particle sizes. The reactivity to gas of one given
50 compound depends indeed on the surface/volume ratio, the porosity, the cation composition, but
51 also on the exposed crystallographic facets [26]. Moreover, the shape of nanoparticles can be as
52 fundamental as their size in determining the uniqueness and novelty of material properties [19,30].

53 In order to tailor the reactivity and catalytic properties of cobalt ferrites and to decorrelate
54 the different influence on these properties, nano ferrites with different shapes, ie nanooctahedron
55 [31,32] and nanocubes (this work) were synthesized. Cobalt ferrites are mixed ferrites, with an
56 inversion degree that varies with the cobalt amount, particle size, and the synthesis method [33-

36], so the cation distribution, about the tetrahedral and octahedral sites, should also be taken into account when discussing cobalt ferrites properties [21].

Depending on the synthesis methods, the shape of nanoparticles is governed by the differences in surface energy, or by the differences in growth velocity of specific crystallographic facets. Surface energy considerations concern processes at thermal equilibrium, as facets growth velocity is linked to out of equilibrium processes [37]. For a face centered cubic structure (FCC), the surface energies of low Miller indices are ranked in the following order $\gamma\{1\ 1\ 1\} < \gamma\{1\ 0\ 0\} < \gamma\{1\ 1\ 0\}$. Thus, an octahedron, which is built by 8 $\{111\}$ facets, is the equilibrium shape of a particle with an FCC structure. Out of equilibrium process synthesis can lead to out equilibrium crystals shapes, such as nanocubes, when the growth velocity of $\{111\}$ outrank the one of $\{100\}$ facets [37]. The growth velocity of facets, and thus the size and shape of particles, can be tailored by the use of specific surfactants[38-40].

The shape variation of cuboctahedron nanoparticles, limited by $\{111\}$ and $\{100\}$ facets, can be characterized by the ratio $r = \gamma\{1\ 0\ 0\} / \gamma\{1\ 1\ 1\}$, with $r = \sqrt{3}$ for an octahedron and $r = \sqrt{3}/2$ for a cube. Intermediate values correspond to cuboctahedron. The r ratio can be directly measured on images of $[110]$ projected particles by measuring the h_{100}/h_{111} , h_{100} and h_{111} are the distances between two parallel $\{100\}$ and $\{111\}$ faces [41].

Many attempts were done to tailor the shape of nanoparticles, but mostly on noble metal particles [42-46]. Concerning cobalt ferrites, few CoFe_2O_4 particles with specific shapes such as nanooctahedron [31-32,47], core shell cubic shapes [48], mesoporous nanospheres [49], or nanocubes [50] are reported.

Recently, nanocubes of $\text{Co}_{0.6}\text{Fe}_{1.4}\text{O}_4$ have been synthesized from thermal decomposition of cobalt and iron organometallic precursors in long chain and high melting organic solvents in the presence of reducing agent and Oleic acid (OAc) and/or oleylamine (OAm) as surfactant [19,48,51-53]. However, either the obtained cobalt ferrite nanoparticles were cobalt deficient, or the composition of the nanoparticles was not controlled. This cobalt deficiency leads to the occurrence of Fe^{2+} in the cobalt ferrite, which in turn modify the catalytic and electrical properties compared to CoFe_2O_4 stoichiometric particles.

85 In this paper, for the first time, stoichiometric nanocubes of CoFe_2O_4 were synthesized from
86 a single step solvothermal method, the benzyl alcohol route [54]. The benzyl alcohol route was
87 already successfully used to obtain faceted cobalt ferrite with controlled composition, but with
88 irregular shape [10,23]. OAm and/or OAc were added to the reaction medium and their effects on
89 the composition and shape of the nanoparticles were investigated. In addition, for the
90 nanoparticles produced with only OAm as surfactant, the synthesis parameters (temperature,
91 reaction time, concentration of the precursors and concentration of OAm) on the nanoparticles
92 shape were optimized.

94 MATERIALS AND METHODS

96 Materials

97 Iron (III) Acetylacetonate ($\text{Fe}(\text{acac})_3$ 97%), Cobalt (II) Acetylacetonate ($\text{Co}(\text{acac})_2$ 98%),
98 benzyl alcohol (99,8 %), OAc (90%), OAm (70%), absolute ethanol (99,8%), acetone (99.5%) and
99 dichloromethane (99.5%) were purchased from Alfa Aesar or Sigma-Aldrich and used in the
100 synthesis reaction as received.

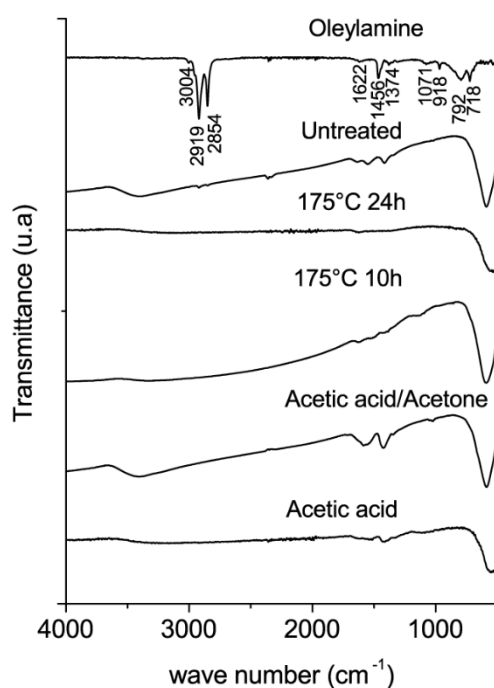
102 Synthesis of CoFe_2O_4 nanoparticles

103 Nanoparticles of cobalt ferrite were produced by the non-aqueous synthesis benzyl alcohol
104 route [54] in the presence of different surfactants. In a typical synthesis, the surfactant was
105 dissolved in 20 mL benzyl alcohol and then 1mmol of cobalt (II) acetylacetonate was added to the
106 solution. The mixture was left under stirring for 2h for homogenization and, subsequently, 2 mmols
107 of Iron (III) acetylacetonate were added. This corresponds to an acetylacetonate concentration of
108 0.15 M. The molar concentration of precursors was varied in this work between 0.08 M and 0.31M.
109 As surfactant, OAc, OAm as well as an equimolar mixture of OAc/OAm, were used, with a molar
110 concentration of 0.6 M, corresponding to a molar concentration ratio ($[\text{surfactant}] : [\text{Fe}(\text{acac})_3]$) of 6.
111 With OAm as surfactant, at an acetylacetonate molar concentration of 0.15M, the molar
112 concentration of surfactant was varied from 0.4M to 0.75M. The mixture was then stirred for

113 another 2 h, transferred to a 45 ml teflon beaker, which was sealed in a steel autoclave and
114 heated in an oven at 175 °C for 48 h. After the thermal treatment, in order to remove excess of
115 solvent and surfactant, the suspension was diluted in absolute ethanol and centrifugated 3 times.
116 Each time the supernatant was taken away, and alcohol was added. A final cycle of washing was
117 done using dichloromethane and acetone in a 1:1 ratio. After washing, the powder was dried at 80
118 °C for 2 h. This way, one gram of powder was produced in one synthesis.

119 Thermal and chemical methods were applied to remove the residues of surfactants [55] and
120 their efficiency tested using Fourier Transform InfraRed spectroscopy (FTIR). For thermal
121 annealing two different treatment times were studied, namely 10h and 24h in air at 175 °C.
122 Concerning the chemical washing the nanoparticle powders were purified using a mixture of acetic
123 acid and acetone or using pure acetic acid. When the mixture was used, the nanoparticles were
124 washed with 100 mL of solution acetic acid/acetone with volumetric ratio of 1:3, then centrifugated
125 and washed with absolute ethanol. When pure acetic was used, the nanoparticles were dispersed
126 in pure acetic acid by vigorous stirring at 80 °C for 10h, and then collected by adding ethanol
127 followed by centrifugation.

128 Figure 1 shows the FTIR spectra obtained on a CoFe_2O_4 powder synthesized with OAm,
129 before and after different purification treatments.



131 Figure 1: FTIR spectra of CoFe₂O₄ powders synthesized with OAm, before and after different
132 purification methods. The FTIR spectrum of pure oleylamine is reported as a reference.
133

134 The FTIR spectrum of the CoFe₂O₄ nanoparticles without purification presents absorption
135 bands around 1330-1650 cm⁻¹, 2919 cm⁻¹ and 2854 cm⁻¹, which correspond respectively to the
136 flexion modes of the -NH₂ group, methyl groups and to the stretching modes of CH bonds. The
137 presence of these bands confirms the existence of OAm at the surface of the nanoparticles [56],
138 so from Fig.1 on can conclude that chemical washing was not efficient. None of the energy bands
139 related to the OAm molecule is observed in the IR spectrum of the heated nanoparticles at 175°C
140 for 24h, which proves the removal of the surfactant from the nanoparticles. On the other hand, the
141 IR spectra of the nanoparticles heated at 175 °C for 10 h or submitted to chemical washing reveal
142 residual peaks around 1330-1650 cm⁻¹. The presence of these bands and absence of energy
143 bands around 2919 cm⁻¹ and 2854 cm⁻¹ indicates the breakage of the OAm molecule and its
144 transformation into a smaller amine. Therefore, among the methodologies used, the heat
145 treatment at 175 °C for 24 hours is the most effective treatment for obtaining OAm-free
146 nanoparticles.
147
148

149 **Characterization**

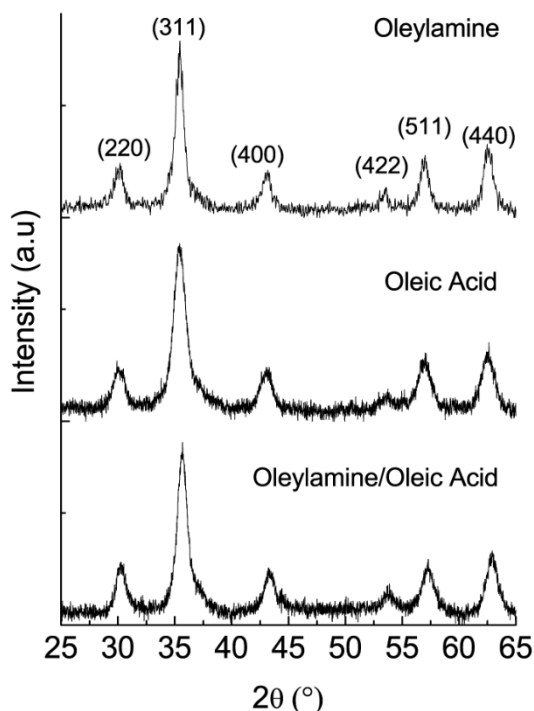
150
151 X-ray diffraction (XRD) patterns of the powders were recorded on an Empyrean
152 diffractometer (Panalytical) equipped with a CuK_α radiation source ($\lambda = 0.15406$ nm). Each sample
153 was continuously scanned in a θ -2 θ mode from 25 to 65° with a step of 0.007° and a scan speed
154 of 0.002°/s. Morphologies, crystal sizes and chemical composition of the nanoparticles were
155 determined by transmission electron microscopy (TEM), coupled with energy dispersive
156 spectroscopy (EDS), using a Tecnai G2 200 kV with a LaB₆ source. The statistical study on
157 particle size was carried on over 200 particles for each powder. For each sample, at least 20 EDS

158 analyses were performed at different scales to insure reliable statistical results. FTIR spectra were
159 recorded in the wave number range 4000-500 cm^{-1} using a Bruker-Tensor 27 spectrometer.

162 RESULTS AND DISCUSSIONS

164 Influence of the nature of the surfactant on the chemical purity and shape of CoFe_2O_4 165 particles

166 Figure 2 shows the XRD patterns of the cobalt ferrite nanoparticles synthesized with OAm,
167 OAc or a mixture OAc/OAm as surfactants. The XRD patterns of the nanoparticles confirm the
168 formation of the cubic spinel structure with the space group Fd-3m , in accordance with the
169 standard ICDD 22-1086, for the different powders. No additional peaks were present in the XRD
170 patterns, indicating single phased powders.



171
172 Figure 2 – XRD patterns of CoFe_2O_4 synthesized with different surfactants.

173
174 The TEM analysis coupled with EDS confirmed that the powders were single phased, each
175 particle being monocrystalline, and showed the homogeneity of their chemical composition (Table

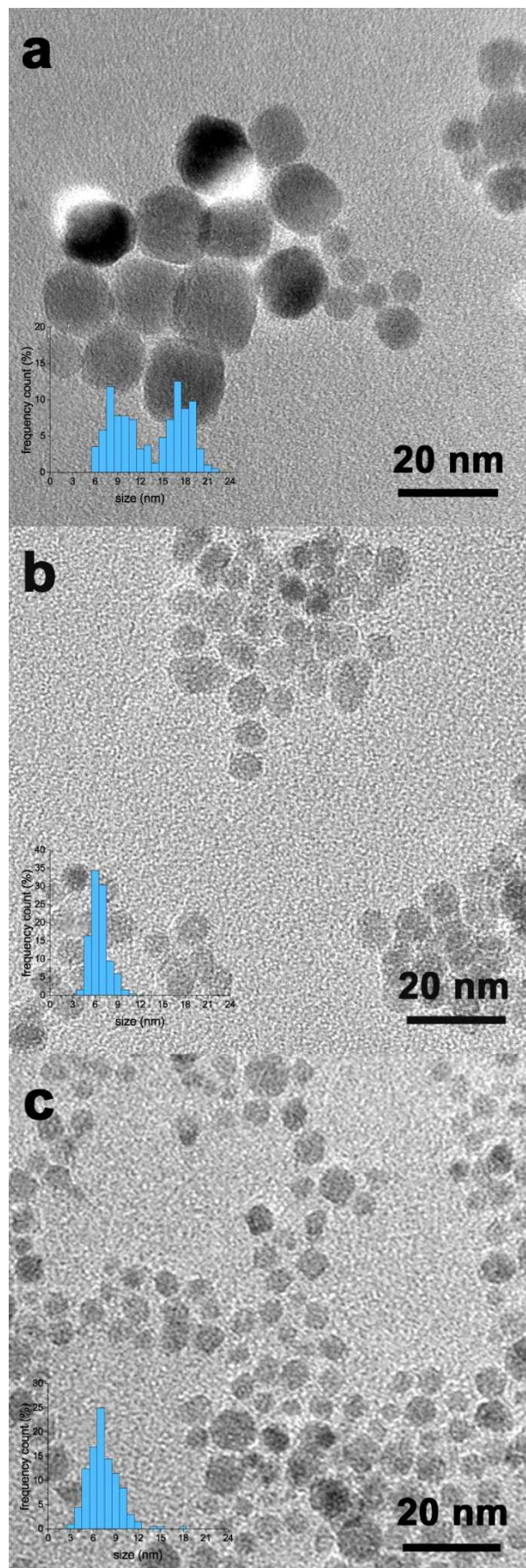
176 1). The nanoparticles synthesized only with OAm and OAc as surfactant have an atomic
 177 percentage of iron and cobalt corresponding to the stoichiometric composition CoFe_2O_4 . On the
 178 other hand, the powder prepared with the OAc/ OAm mixture has a chemical composition of
 179 $\text{Co}_{0.6}\text{Fe}_{2.4}\text{O}_4$, thus is deficient in cobalt. Co-deficient cobalt ferrite are synthesized in reducing
 180 reaction medium where the Fe (III) ions are partially reduced to Fe (II) replacing Co(II) in the
 181 formation of ferrites [57].

182
 183 Table 1 - Mean composition with the standard deviation σ , obtained by EDS analyses.

Surfactant	at.% Co	at. %Fe	Co/Fe	σ	Chemical formula
OAm	33	67	0.49	0.01	CoFe_2O_4
OAc	35	65	0.54	0.02	$\text{Co}_{1.05}\text{Fe}_{1.95}\text{O}_4$
OAc/ OAm	22	78	0.28	0.01	$\text{Co}_{0.6}\text{Fe}_{2.4}\text{O}_4$

184
 185 The amine and carboxylic acid functional groups present in OAm and OAc may act as
 186 reducing agents, and they are more reductive when used together in an mixture than when they
 187 are used separately [58]. Cobalt-deficient cobalt ferrite nanoparticles have also been obtained by
 188 thermal decomposition of acetylacetonates with an OAc/ OAm mixture [57,59]. Thus, one can
 189 conclude that the cobalt deficiency in the ferrite is due to a too reductive reaction medium, leading
 190 to the formation of ferrous ions.

191 Figure 3 shows the TEM images and particle size distributions of the nanoparticles
 192 produced with OAm (Fig.3a), OAc (Fig.3b) and OAc/ OAm (Fig.3c) as surfactants. Monodisperse
 193 nanoparticles were obtained in the presence of the different surfactants, but the type of surfactant
 194 influences the morphology and the size distribution of the nanoparticles. A powder consisting of
 195 two populations with distinct sizes was obtained in the presence of OAm. We observe clearly in
 196 the TEM image (Fig.3a) the presence of nanocubes around 20nm in size and smaller faceted
 197 particles, some of them having also a cubic shape.



198

199 Figure 3 –TEM images of CoFe_2O_4 nanoparticles along with the size distribution obtained with

200 OAm (a), OAc (b), OAc/ OAm (c)

201

202 The crystallite size distribution histogram exhibits a bimodal profile in which each of the
203 curves fits into a lognormal distribution profile. The nanocubes have an average size of 18 nm,
204 while the smaller particles have a size of about 8 nm. The nanoparticles obtained with OAc have
205 not well-defined shapes, (Fig.3b), while the ones produced with OAc/ OAm (Fig.3c) have shown
206 heterogeneous morphology, some of the particles being also cubic in shape. In both cases, the
207 size distribution is adjusted to the lognormal distribution and the mean crystallite is 7 nm (Fig.3b
208 and 3c). The powder synthesized with OAc has a narrower size distribution than the two other
209 powders, indicating a greater homogeneity in crystallite size.

210 More details about the morphology of the particles were obtained by high-resolution
211 transmission electron microscopy (HREM). Information about the crystalline planes coupled with
212 the different projected shapes in the Figure 4 makes it possible to identify a cube seen along
213 different directions. Fig.4a.b.c show the HRTEM images of CoFe_2O_4 particles synthesized with
214 OAm as surfactant, respectively viewed along the $[100]$, $[10\bar{1}]$ and $[111]$ directions. The
215 projected shape of the grain oriented along the $[100]$ is a square (Fig.4a) and the Fourier
216 transform (FFT) (inset of Fig.4a) corresponds to the diffraction pattern along a $[100]$ zone axis of
217 a cubic spinel structure, with the $\{022\}$ and $\{004\}$ planes imaged. The structure factor associated to
218 the $\{200\}$ planes is null for the spinel structure, which explains why they do not appear in the
219 HREM image. The crystalline planes $\{022\}$ and $\{004\}$ are respectively at 45° and parallel to the
220 faces (Fig. 4a), we can therefore conclude that this particle is indeed a nanocube, and not an
221 octahedron.

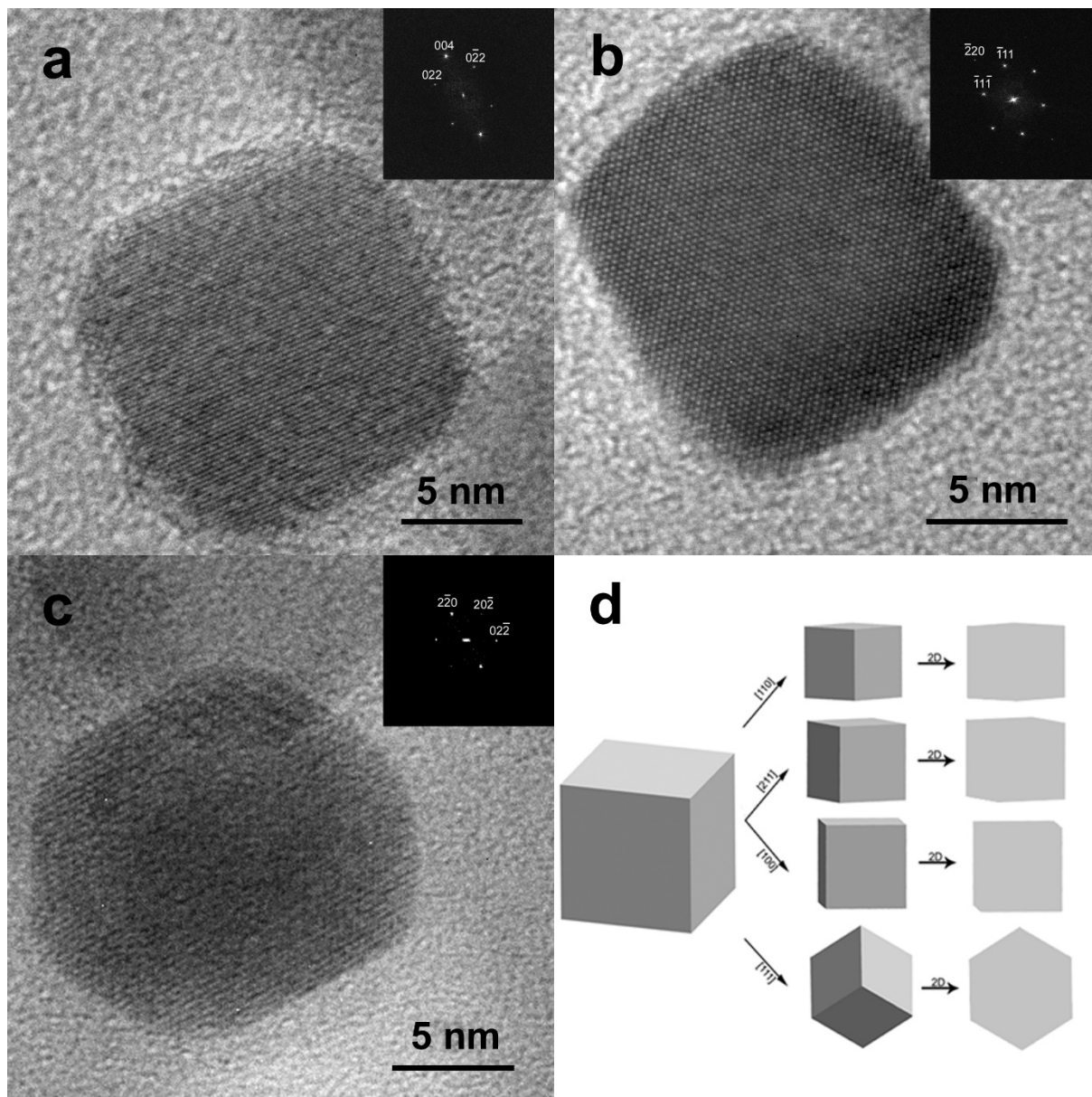
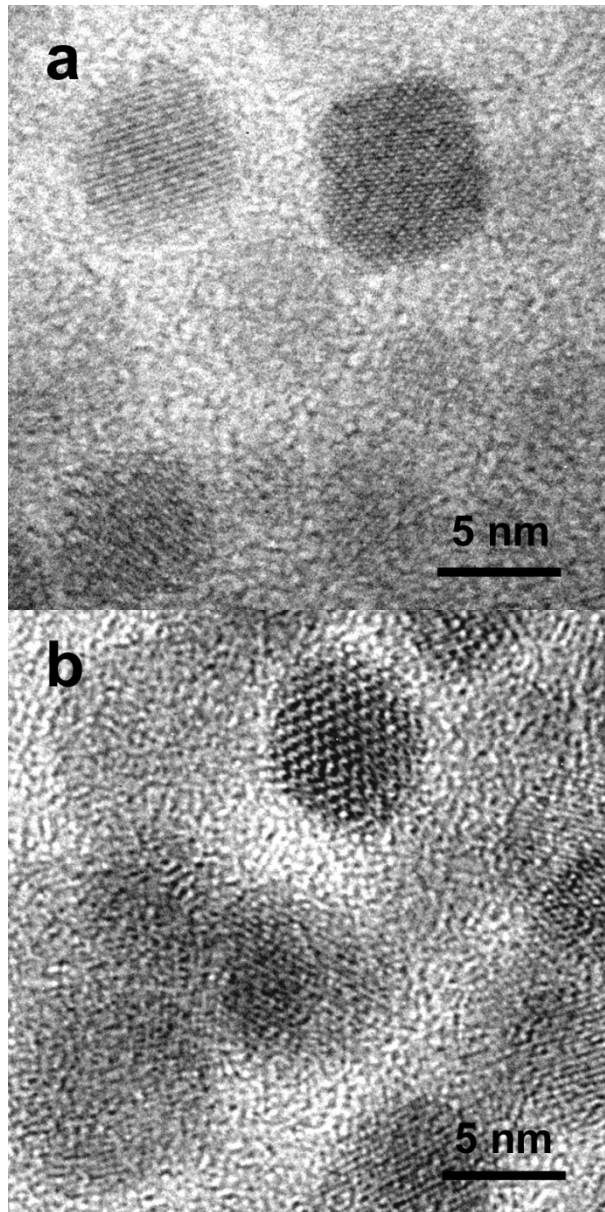


Figure 4 – HRTEM images of nanocubes of CoFe_2O_4 (a) oriented along $[100]$ (b) oriented along $[110]$ (c) oriented along $[111]$, (d) 2D projected forms of a cube along different axes.

When the particle is oriented along $[10\bar{1}]$, the projected shape is a rectangle, and the crystalline planes imaged are $\{111\}$ and $\{202\}$, the latter being parallel to one of the sides of the rectangle (Fig. 4b). For a particle oriented along a $[111]$ direction (Fig.4c), the observed shape is hexagonal and the $\{220\}$ planes of the spinel structure are parallel to the hexagon faces. For a cubic form, the projected shapes along different low index directions are shown in Fig. 4d. These projected shapes, associated with the imaging of the planes parallel to the faces, allow to conclude that Fig.4b and 4c correspond to nanocubes. The nanocubes are not always $[100]$ oriented on the carbon grid, thus do not always exhibit a square shape. This HREM study, which

233 images the crystallographic planes, makes it possible to conclude that we succeeded in
234 synthesizing nanocubes using OLA as surfactant.

235
236 Nanocubes could also be produced with the mixture of OAc/ OAm, an a typical HREM
237 image is shown in Fig. 5a. As expected for a cube oriented along a [100] direction, the imaged
238 crystalline planes {022} of the spinel structure are at 45° of the faces of the particles. However,
239 these nanocubes are cobalt deficient with regards to the expected CoFe_2O_4 composition. Finally,
240 using only OA as surfactant led to faceted particles (Fig.5b) with different shapes. The interaction
241 of OAc and OAm with iron oxide nanoparticles was studied through molecular mechanics
242 modeling [56]. It was shown that the binding energy of surfactants to the nanoparticle surfaces
243 with OAc solely was always lower than in the case of OAc/ OAm mixtures. This may explain our
244 results concerning the use of OAc and OAc/ OAm.



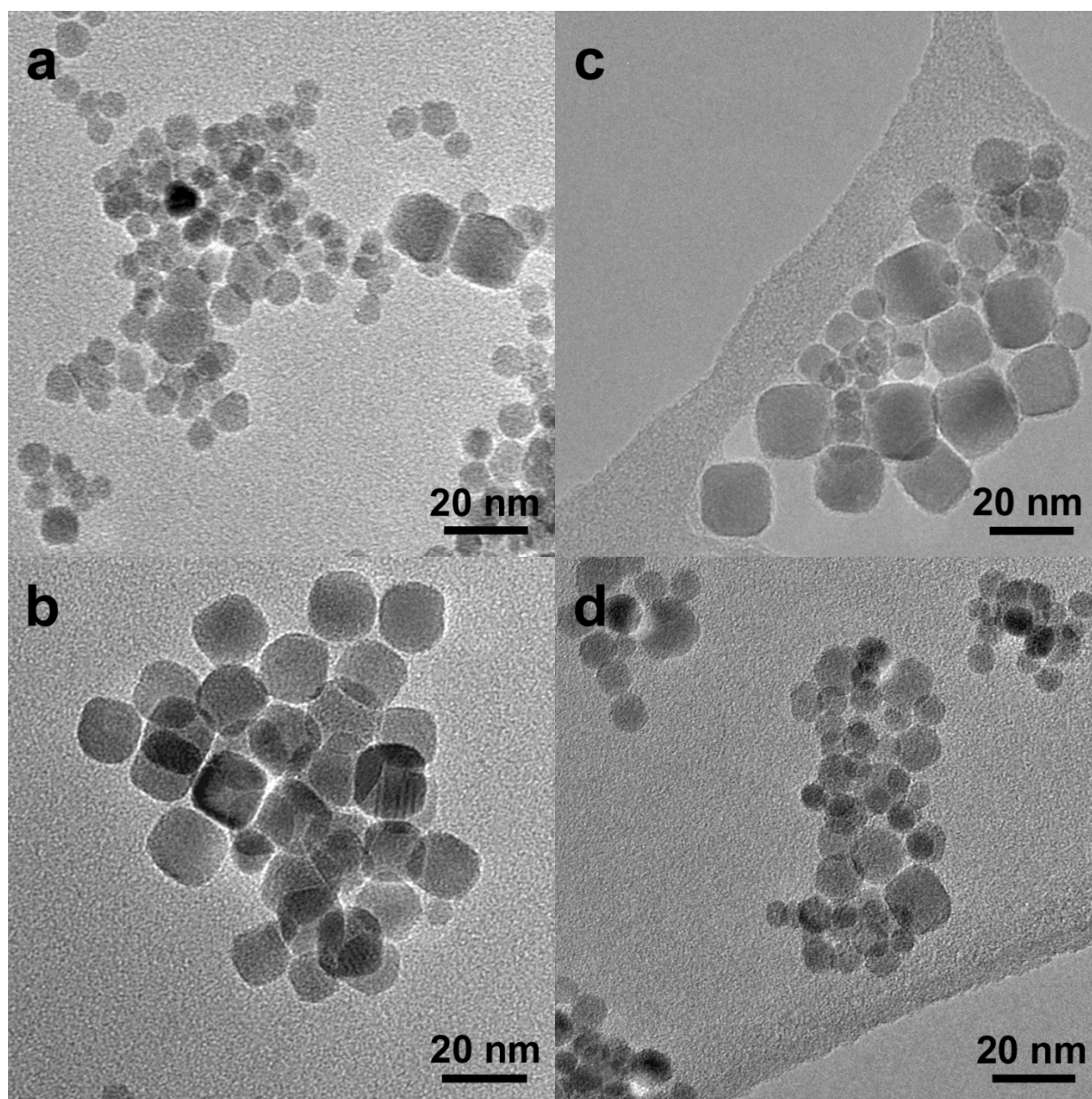
245
246 Figure 5 : a) HRTEM image of a [100] oriented $\text{Co}_{0,6}\text{Fe}_{2,4}\text{O}_4$ nanocube obtained with OAc/ OAm as
247 surfactants, with the {220} planes imaged b) HRTEM image of a faceted CoFe_2O_4 particle
248 obtained with OAc as surfactant, the {111} and {311} planes are imaged.
249

250 **Influence of the amount of oleylamine on the shape and size of CoFe_2O_4 particles**

251

252 Powders were synthesized with different amounts of OAm, characterized by a
253 $[\text{OAm}]/[\text{Fe}(\text{acac})_3]$ ratio of 4, 5, 6, 6.5, and 7.5. Figure 6 shows the corresponding TEM images of
254 the different powders. For $[\text{OAm}]:[\text{Fe}(\text{acac})_3] = 5$ (Fig.6b) and 6.5 (Fig.6c), the results in terms of
255 size and distribution are similar to those obtained with an initial ratio of 6 (Fig. 3). The CoFe_2O_4
256 nanoparticles are nanocubes of 18 nm in size and small faceted nanoparticles. For

257 [OAm]:[Fe(acac)₃] = 4 (Fig. 6a) or 7.5 (Fig.6d), there is a significant decrease in the population of
258 nanocubes, the powders consist mainly of faceted nanoparticles without well-defined shape. This
259 indicates that for a [OAm]: [Fe(acac)₃] = 4, the amount of surfactant is insufficient to influence the
260 morphology of the particles. On the other hand, for [OAm]: [Fe(acac)₃] =7.5, the excess of
261 surfactant limits the growth of the nanoparticles and leads to a powder composed mainly of small
262 polyhedral particles [35]. Therefore, in the current study, the formation of nanocubes was
263 observed for a ratio of [OAm] surfactant to the [Fe(acac)₃] precursor in the range of 5 to 6.5.
264



265
266

267 Figure 6 Effect of the concentration of oleylamine on the CoFe_2O_4 particle shape a)
268 $[\text{OAm}]:[\text{Fe}(\text{acac})_3] = 4.0$ b) $[\text{OAm}]:[\text{Fe}(\text{acac})_3] = 5$ c) $[\text{OAm}]:[\text{Fe}(\text{acac})_3] = 6.5$ d) $[\text{OAm}]:[\text{Fe}(\text{acac})_3]$
269 $= 7.5$

271 **Effect of the synthesis parameters**

272
273 The effect of other synthesis parameters such as the time and temperature of the
274 solvothermal synthesis and the concentration of the precursor was also investigated. For each
275 condition of synthesis analyzed only one of the parameters was modified.

276 Figure 7 shows TEM images of CoFe_2O_4 powders synthesized at 175 °C for different
277 synthesis times 12h (Fig. 7a), 24h (Fig. 7b) 48h (Fig. 7c) and 96h (Fig. 7d). The size distribution
278 for each powder is indicated. The reaction time clearly influences the size distribution of the
279 particles. A short time of solvothermal synthesis (12h) gives a majority of faceted and small
280 nanoparticles (8-10 nm). Some nanoparticles have a size in the range of 14 nm to 18 nm.
281 However, despite the size approaching the size of the cubes obtained in the synthesis performed
282 during 48h (Fig. 7c), these nanoparticles are not clearly cubes. The bimodal distribution of
283 nanocubes and faceted nanoparticles appears for a reaction time of 24 hours. A reaction time of
284 48h seems to widen the size distribution of the smaller particles, and a time of 96h tends to
285 remove the bimodal nature of the size distribution.

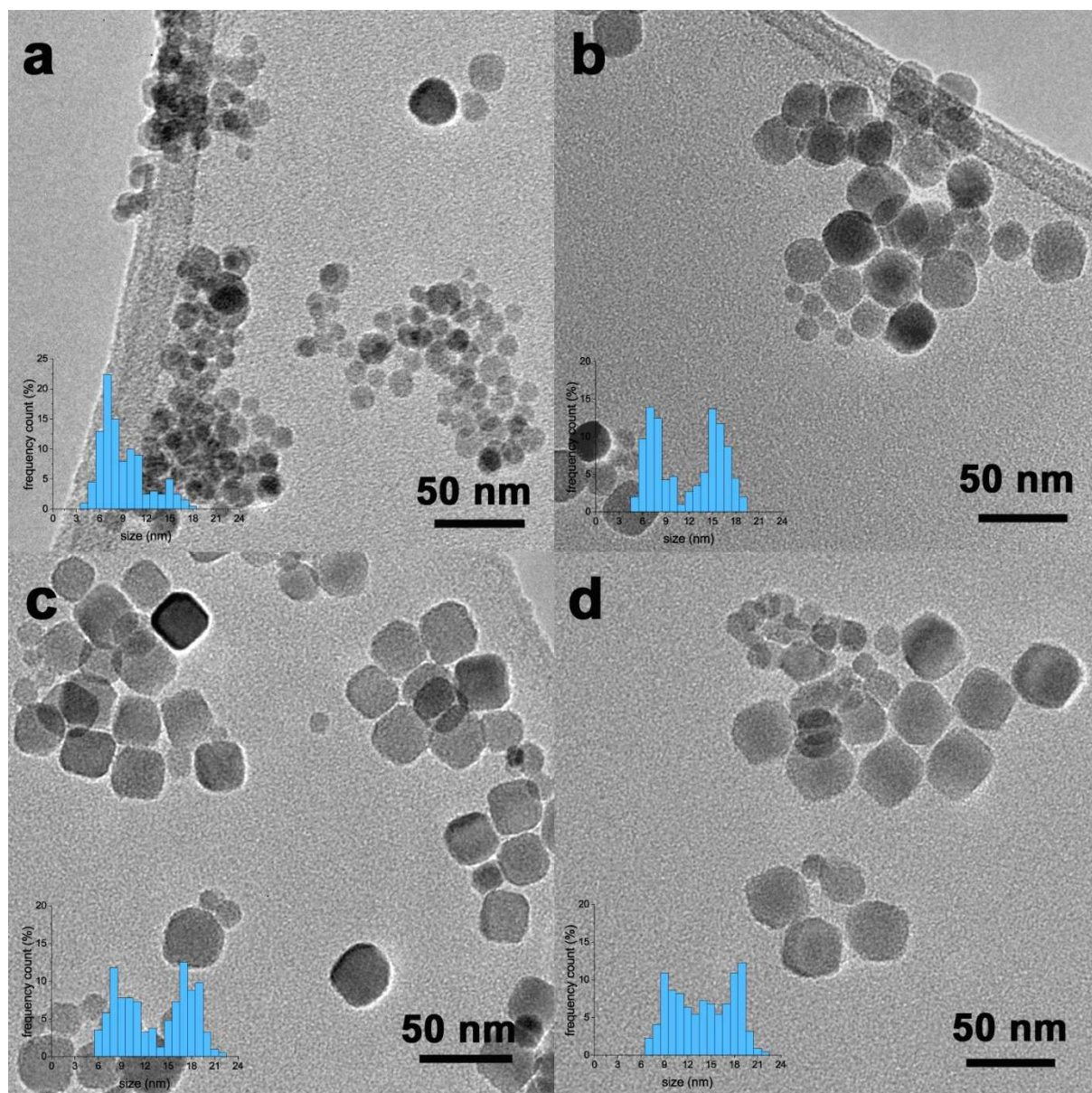


Figure 7 – CoFe₂O₄ nanoparticles produced at 175°C and [OAm]:[Fe(acac)₃] = 6 for a) 12h, b) 24h, c) 48h, d) 96h.

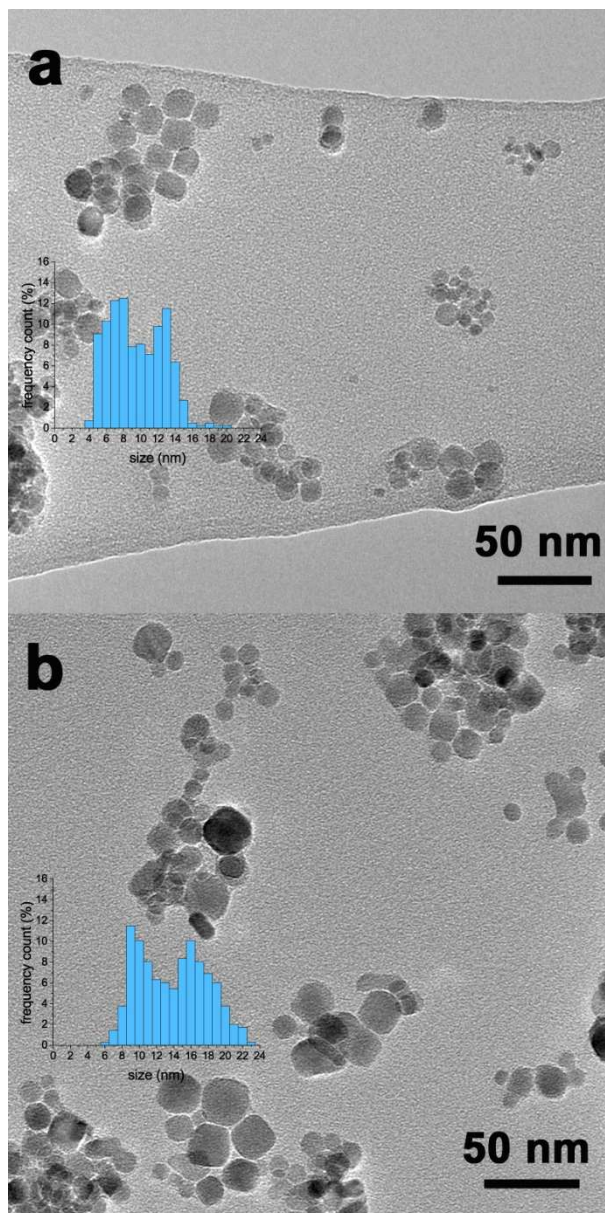
The temperature of the solvothermal treatment influences also the morphology of the CoFe₂O₄ nanoparticles. Figure 8 shows TEM images of CoFe₂O₄ nanoparticles along with the particle size distribution for thermal treatments at 150°C and 200 °C, during 24h. Due to the teflon nature of the vessel, temperatures above 200°C could not be tested.

The powder synthesized at 200 ° C has a bimodal size distribution (Fig. 8b) but this bimodality is less marked than in the case of the powder obtained at 175 °C for 24 hours (Fig.7b). There is an increase of both populations and a size overlap. The increase of temperature from 175°C to 200°C, therefore, has a similar effect to an increase of the reaction time from 48 to 96

298 hours (Fig.7). The small particles have intermediate forms between cubes and spheres and an
299 average size of 9-10 nm. The largest nanocubes (16-18 nm) obtained at 200 °C appear with more
300 rounded corners and faces than those obtained at 175 °C, indicating that an increase in
301 temperature favors the appearance of micro facets {111} or {110}.

302 The powder obtained at 150 °C for 24 hours (Fig. 8a) also has two populations of particles
303 with a weak bimodal size distribution, as in the case of the powder obtained at 200 °C. The size of
304 the nanoparticles is smaller than in the case of other powders: the average value of the smallest
305 particles is 7 nm and the larger ones have an average size of 12-13 nm. As in the previous cases
306 (175 °C and 200 °C), the larger particles have a shape close to the cube whereas for the small
307 ones the shape is not so well defined. So, a small temperature variation of $\pm 15\%$ around 175°C
308 gives a more or less bimodal distribution.

309 Similar results were obtained on the synthesis of FePt nanocubes from the thermal
310 decomposition of organometallic precursors. The formation of cubic or spherical nanoparticles is
311 then linked to the reaction temperature, and the increase in temperature favors the production of
312 spherical nanoparticle [44].

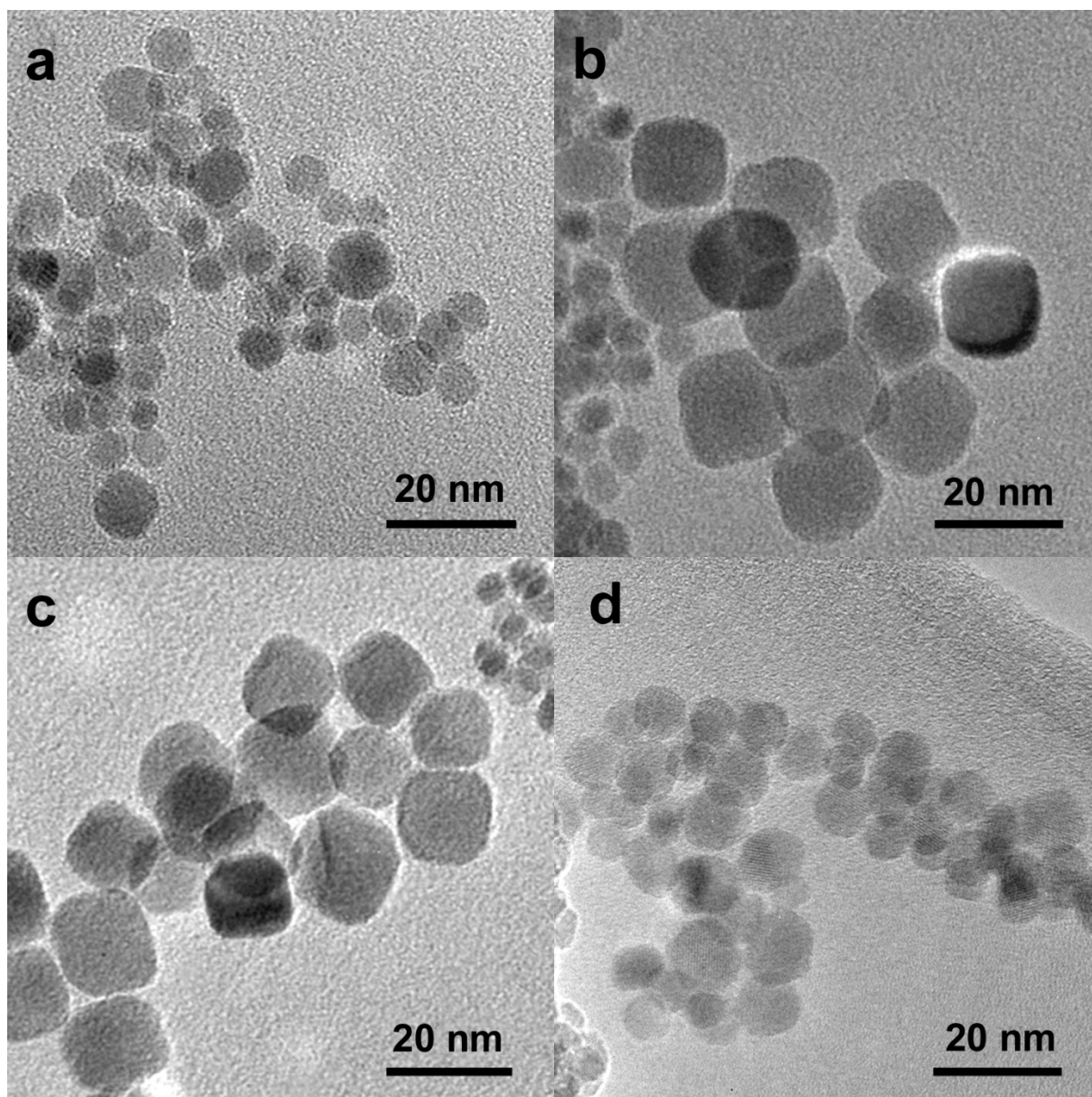


313

314 Figure 8 : CoFe₂O₄ nanoparticles and size distribution obtained at different temperature (a) 150°C
 315 for 24h (b) 200°C for 24h.

316

317 Figure 9 shows the influence of the concentration of Fe (III) and Co (II) acetylacetonates on
 318 the CoFe₂O₄ nanoparticles shape, in the 0.08M to 0.6M range. For precursors concentration of
 319 0.15 M and 0.31 M, nanocubes were produced. (Fig. 9b and 9c). However, for low (0.08M) or high
 320 concentration (0.6M) only small nanoparticles without well-defined shape with average size of 7.5
 321 and 9 nm, respectively, were obtained (Fig.9a and 9d).



322

323

324 Figure 9 – CoFe_2O_4 nanoparticles synthesized at 175°C with different acetylacetonates
325 concentration (a) 0.08M (b) 0.15M (c) 0.31M (d) 0.6M

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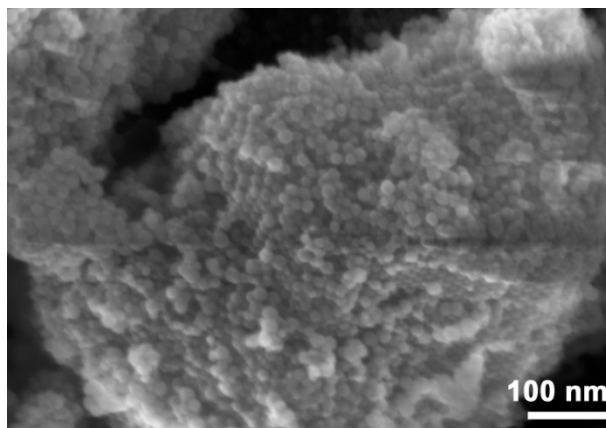
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333

A high concentration of precursors increases the rate of germs and promotes the formation of a large number of small particles, followed by their coalescence due to a proximity effect of germs. This promotes rapid particle growth, and thus comparable kinetics of the different facets leading to spherical shapes or to not well-defined shapes [61]. A too low concentration of precursors limits nuclei growth due to lack of material in their vicinity, which results in a lower rate of diffusion and collisions, favoring the formation of small particles. Hence, small particles are observed.

334 According to the results shown in this paper, it appears that the synthesis of nanocubes can
335 be obtained under very specific conditions of temperature, time, nature of surfactant, as well as
336 concentration of precursors and surfactant .

337 Figure 10 shows a
338 nanocubes.



339 typical population of

340
341
342
343
344
345 Figure 10 SEM image of CoFe₂O₄ nanoparticles synthesized at 175°C, with an
346 acetylacetonate concentration of 0.15 M, and an OAm concentration of 0.6M.

347
348 Well defined nanocubes were obtained with OAm, not with OAc or a mixture of OAc/ OAm. In
349 literature, solely OAm led to spherical nanoparticles and this was attributed to weak bonding of
350 OAm on the surfaces of the particles [62-64]. On the contrary, the strong binding of OAc on the
351 particles surfaces was considered to be responsible of the shape control [50,65]. But then, the
352 most used synthesis method in these papers was the thermal decomposition one. In case of a
353 solvothermal route using benzyl alcohol and OAm, as in this work, nanocubes of Pt were
354 successfully grown [66]. This indicates that the shape control is not only linked to the nature of
355 surfactant, but also to the synthesis method in which the surfactant are used. A nanocube is an
356 out of equilibrium form, so can be obtained in out of equilibrium process when the growth velocity
357 of {100} facets is limited, or the growth of {111} and {110} facets is increased. A possible
358 explanation for the formation of nanocubes would be that, in the presence of OAm, during the
359 growth process, the smaller nanoparticles coalesce preferably on a specific facet of the larger
360 nanoparticles, ie {111} [67] and/or that the OAm molecules are adsorbed onto the cobalt ferrite
361 facets {100}, limiting the growth of these faces. In this work, the nanocubes powders exhibit a

bimodal size distribution, with nanocubes around 20 nm and smaller particles around 8 nm, a mixture of cubes and faceted particles. A bimodal size distribution is often explained by the Ostwald ripening process, in which larger particles grow at the expense of smaller ones [68,69]. The fact that increasing time of synthesis from 12h to 96 h diminish the amount of small particles points to this ripening process. Bimodal nanoparticles size distribution has been already observed by other researchers in the synthesis of nanoparticles using OAm as surfactant and in the production of nanoparticles by solvothermal method [43,68,70-71].

Conclusion

Cobalt ferrite nanoparticles were obtained from the non-aqueous route of benzyl alcohol with the addition of different surfactants. The nanoparticles synthesized with OAm have a cubic shape, with the stoichiometric composition CoFe_2O_4 , and exhibit a bimodal size distribution. The nanoparticles synthesized with OAc solely have no specific shape, and those obtained with an equimolar mixture of OAc and OAm are cobalt deficient with a $\text{Co}_{0.6}\text{Fe}_{2.4}\text{O}_4$ composition.

The synthesis parameters (surfactant concentration, precursor concentration, temperature and reaction time) influence the shape of the nanoparticles synthesized in the presence of OAm. The different analyzed parameters did not allow to obtain one sized nanocubes, however, for the first time, stoichiometric CoFe_2O_4 nanocubes were obtained, using a solvothermal route with benzyl alcohol and oleylamine.

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