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2 **Identification of a Fe(OH)₂-like phase in the core–shell structure of nano-zero-valent Fe and its**
3 **evolution when interacting with Pd²⁺_{aq} ions by Mössbauer spectroscopy, XPS, and TEM**

4
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16
17 **Abstract**

18 Synthesized Fe@FeOx nanoparticles (NPs) were fully characterized by spectroscopic techniques and
19 (scanning) transmission electron microscopy to resolve the presence of a Fe(OH)₂-like phase. The
20 different phases detected in the core–shell nanostructure of these NPs were corroborated by
21 Mössbauer and X-ray photoelectron spectroscopies. Metallic iron (Fe⁰), ferrous (Fe^{II}) hydroxide,
22 magnetite (Fe^{III}₂Fe^{II}O₄), and a top layer of ferric (Fe^{III}) oxide were identified. Interestingly, ferrous
23 hydroxide reacted with Pd²⁺_{aq} upon coating of the supporting core–shell material when Pd was added
24 to produce Fe@FeOx/Pd NPs.

25 **Keywords:** Iron, Superparamagnetism, TEM, XPS, TMS, Core–shell

26 **1. Introduction**

27 Zero-valent iron nanoparticles (Fe-NPs) have been synthesized using various methods including (i)
28 ball milling of bulk Fe particles, (ii) reduction of Fe oxides to Fe⁰ with hydrogen gas and (iii) aqueous
29 reduction of ferric (Fe^{III}_{aq}) or ferrous (Fe^{II}_{aq}) species [1,2]. In aqueous solution, the most commonly
30 used method is the reduction of ferric species by sodium borohydride (NaBH₄) as initially proposed
31 by Wang et al. [3]. In comparison with the classical micrometric-sized Fe⁰ granular materials, Fe-NPs
32 present generally higher chemical reactivity due to their higher surface to volume ratio. Fe-NPs have
33 been used to eliminate organic and inorganic pollutants and their efficiency when directly injected in
34 groundwater [4,5]. Furthermore, when the surface of these NPs is modified by organic stabilizers,
35 their agglomeration decreases and their dispersion into the reactive media increases [6].
36 Additionally, Fe-NPs were used as a substrate to stabilize metallic clusters such as Cu⁰ or Pd⁰ on their
37 surface [3,7,8]. The preparation of NPs with such modified surfaces was performed relatively easily
38 by reducing Cu^{II} or Pd^{II} salt at the NP–water interface. In addition, metal-coated Fe-NPs were shown
39 to be effective catalyzers to oxidize formate and reduce carbon dioxide to formate [8] or to catalyze
40 the reaction between iodobenzene with benzene boronic acid to form a biphenyl product
41 (Suzuki–Miyaura cross-coupling reactions) [7]. Many core–shell structures containing metals and
42 oxides have been studied for their original magnetic properties (e.g. Fe_(1-x)O/Fe₃O₄ [9] and Ni/Au [10])
43 or their electrocatalytic properties (e.g. Pd/Pt [11]). Zero-valent NPs have the advantage of being
44 relatively cheap and ecofriendly NPs with Fe⁰ or Fe^{II} redox active species present in their structure.
45 Another important potential application of Fe-NPs free of metallic Fe⁰ and containing Fe₃O₄ or
46 maghemite γ-Fe₂O₃, is as materials for the treatment of cancers by magnetic hyperthermia [12–15].
47 The numerous implications of Fe-based materials in various technological applications make the full
48 characterization of these materials very important.

49 The nanostructure and physicochemical properties of the Fe-NPs synthesized in the presence of
50 NaBH₄ have been studied using several techniques, including X-ray diffraction (XRD) [3,7,8,16–19],
51 scanning electron microscopy (SEM) [16,19,20], high-resolution transmission electron microscopy

52 (HR-TEM) coupled with energy dispersive X-ray spectroscopy (EDX) or electron energy loss
53 spectroscopy (EELS) [7,8,16–18], atomic force microscopy (AFM) [13], X-ray photoelectron
54 spectroscopy (XPS) [8,17,20], X-ray absorption near edge structure (XANES) [7,17], Raman [18] and
55 Mössbauer spectroscopies [19–21] and finally electrochemically using cycling voltammetry or
56 chronoamperometry [8]. In all these studies the NPs were constituted by a metallic Fe⁰ core and a Fe
57 oxide shell. The chemical composition and the phase partition in the core–shell were shown to
58 depend on the synthesis conditions such as the nature of the Fe salt containing either Fe^{II} or Fe^{III}
59 species and the contact time between the Fe salt and the reducing agent NaBH₄ [18]. The XRD
60 analyses provide essential information about the structure of the core constituted by metallic bcc Fe
61 [3,7,16–18]. In some studies, very low intensity or broad diffraction peaks attributed to Fe oxides
62 were observed [17]. Nevertheless, XRD is certainly not the most suitable technique to characterize
63 more or less crystallized thin Fe oxide coatings present at the surface of Fe-NPs. The presence of a
64 mixture of Fe^{II} and Fe^{III} species in the shell was clearly shown in XANES and XPS studies [7,8,17]. Using
65 a series of reference samples, Yao et al. [7] estimated the relative proportion of Fe⁰, Fe^{II}, and Fe^{III}
66 species in Fe-NPs. The determination of such a speciation was also possible using XPS [8,17], which
67 probes the extreme surface of the analyzed materials (maximal analysis depth < 10 nm). Since the
68 average sizes of the synthesized Fe-NPs were 10–50 nm [7,8,17,18,20], XPS provided a good picture
69 of the chemical composition of the NPs. In addition, such results should be carefully analyzed by
70 considering the various fitting procedures used [22,23]. The unique technique ⁵⁷Fe Mössbauer
71 spectroscopy is used to determine the mineralogical nature of the Fe-rich phases as well as their
72 relative proportions. Relatively complex Mössbauer spectra of Fe-NPs were recorded at room
73 temperature (RT, 298 K) [19,21]. The complexity of the spectra is directly related to the reduced size
74 of the grains and then their superparamagnetic behavior [24–27]. In all the Mössbauer spectra
75 previously shown, Fe⁰ was clearly identified but the exact chemical nature of the Fe oxides present in
76 the shell was not. Moreover, some of the Mössbauer spectra at 298 K exhibited a paramagnetic
77 ferrous doublet that was not fully interpreted [19–21]. Indeed, recording the Mössbauer spectra in a

78 full range of temperatures of 4–298 K is generally required to obtain full characterization of a sample.
79 This characterization has never been done for Fe/FeO_x NPs. In our study, a combination of
80 microscopic and spectroscopic techniques – TEM/scanning TEM (STEM) coupled with EELS/X-ray
81 chemical imaging and electron diffraction, XPS and Mössbauer spectroscopy – were used to highlight
82 the nanostructure of Fe-NPs and their evolution when interacting with Pd^{II}_{aq} ions.

83

84 **2. Materials and methods**

85 *2.1. Preparation methods*

86 Iron(II) sulfate heptahydrate (FeSO₄·7H₂O, 99%), palladium(II) chloride (PdCl₂, 99%),
87 polyvinylpyrrolidone (PVP, average molecular weight = 55 000), NaBH₄, and glacial acetic acid were
88 purchased from Sigma Aldrich. Hydrochloric acid (HCl, 36.5%) was purchased from J.T. Baker.

89 The Fe@FeO_x NPs were prepared by mixing 8.0 mL of 0.625 M FeSO₄·7H₂O aqueous solution and 10
90 mL of 2 M PVP methanol solution. The solution was then manually stirred with a glass rod for 1 min.
91 The starting reagents were immediately reduced by adding dropwise 2.0 mL of a 1.82 M NaBH₄
92 aqueous solution. The mixture turned into a thick black liquid that was stirred for 3 min. Finally, 0.15
93 mL of 0.5 M H₂SO₄ was added, followed by 0.05 mL of 1 M glacial acetic acid to neutralize the
94 remaining NaBH₄. The final solution was centrifuged at 3400 rpm and washed with methanol. During
95 the synthesis, solution pH increased from 4.1 to 6.8 and reached a final value of 6.1 at the end of the
96 synthesis.

97 The Fe@FeO_x/Pd NPs were obtained by dispersing the Fe@FeO_x NPs into methanol and adding 133
98 μL of 0.5 M H₂PdCl₄. The solution was then shaken for 30 s and sonicated for 30 min to facilitate the
99 galvanic displacement process. The solution was centrifuged at 3400 rpm, rinsed with methanol, and
100 dried in a vacuum desiccator.

101

102 *2.2. Methods employed for solid characterization*

103 *2.2.1. TEM*

104 The TEM and STEM investigations were carried out using a JEM - ARM 200F Cold FEG TEM/STEM
105 (JEOL, Japan) operating at 200 kV, coupled with a GIF Quantum 965 ER (Gatan-Ametek, USA), and
106 equipped with a spherical aberration (Cs) probe and image correctors (CEOS GmbH, Germany). For
107 TEM/STEM observations, one drop of a dispersed solution of NPs was deposited on a carbon-coated
108 copper grid.

109 2.2.2. XPS

110 The XPS spectra were recorded on an AXIS Ultra DLD (Kratos Analytical, Ltd) equipped with a
111 monochromatized AlK α X-ray anode at 1486.6 eV (spot size 700 μm \times 300 μm). High-resolution
112 spectra were acquired at a pass energy of 20 eV (core level spectra). Charging effects were
113 compensated through low-energy electron flooding. In order to decrease any surface contamination
114 and characterize the chemical composition underneath the surface, sputtering was done using an Ar⁺
115 ion beam energy of 5.05 kV. Data analysis and curve fitting were performed using Casa XPS software.
116 A Gaussian/Lorentzian (70/30) product function and a nonlinear Shirley background were used.
117 Binding energies were calibrated by assigning the adventitious carbon C 1s peak to 284.6 eV. The
118 high-resolution spectra were deconvoluted into the components corresponding to bond types. The
119 chemical state information from the Fe2p core level was obtained following the procedure of
120 Grosvenor et al. [22] to describe the multiplet structure of Fe oxides. Thus, four and three
121 components were used to account for the multiplet structure of Fe^{III} and Fe^{II} bound to O₂,
122 respectively. Additionally, broad peaks at around ~715 and ~720 eV were added to account for the
123 Fe^{II} and Fe^{III} satellites.

124

125 2.2.3. Transmission Mössbauer spectroscopy (TMS)

126 Mössbauer spectroscopy was performed at 297, 130, 77, 38, 16, 10, 7, and 4 K with a constant
127 acceleration Mössbauer spectrometer, 512 multichannel analyzer (Halder Electronic GmbH), and a 50
128 mCi source of ⁵⁷Co embedded in a Rh matrix maintained at RT. Samples were prepared under N₂
129 atmosphere in an anoxic glove box (Jacomex) using appropriate amounts (10 mg of powder per cm²)

130 of solid samples to get optimal experimental conditions. Measurements were recorded in the
131 velocity range of $\pm 11 \text{ mm s}^{-1}$. Analyses were first carried out between ambient temperature and 10 K
132 on the ARS cryostat (Advanced Research Systems, Macungie USA) equipped with a vibration isolation
133 stand developed at LCPME and then for the lowest temperatures of 7.8 and 4 K on a Janis cryostat
134 (SHI-850, Janis Research Co., Wilmington, MA, USA). Mössbauer spectra were collected in
135 transmission mode. The 50 mCi source of ^{57}Co in the Rh matrix was maintained at RT and mounted at
136 the end of a Mössbauer velocity transducer. Both spectrometers were calibrated with a 25- μm foil of
137 $\alpha\text{-Fe}$ at RT. Spectra were computer-fitted with the Voigt-based fitting model for paramagnetic sites
138 corresponding to a doublet with a distribution of quadrupole splittings and magnetic sites
139 corresponding to a sextet with a distribution of magnetic hyperfine fields (HFDs), as implemented in
140 Recoil software [28]. Nevertheless, an exception was adopted for the spectra recorded below 10 K
141 where the appearance of a magnetic order for phases containing Fe^{II} species required the full static
142 Hamiltonian site model to solve the mixed hyperfine interactions.

143

144 **3. Results and discussion**

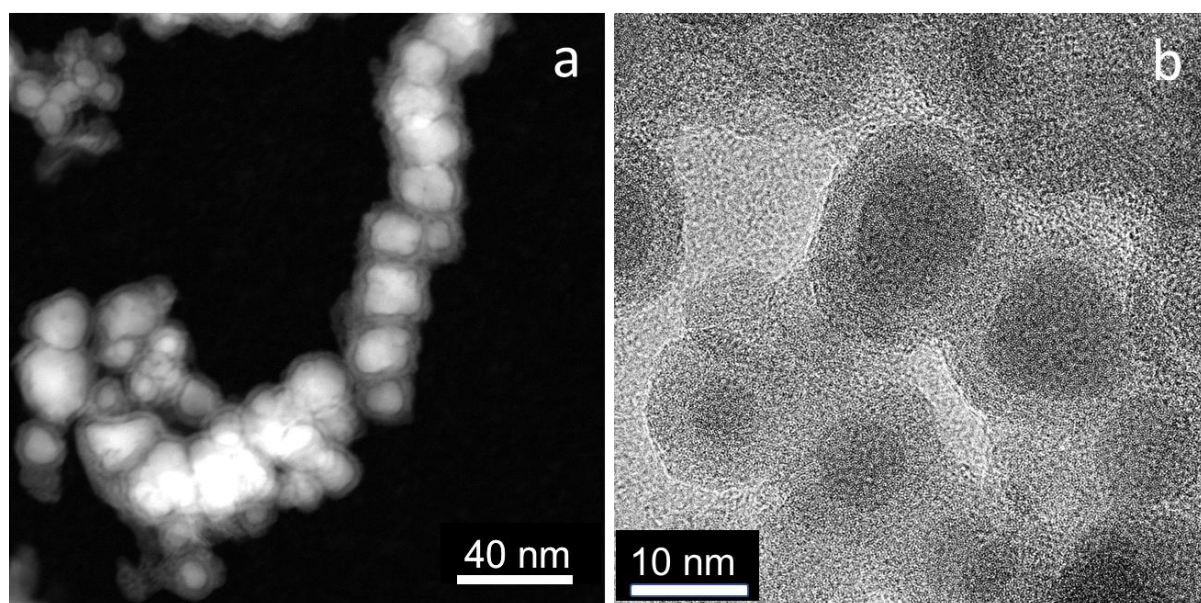
145 *3.1. TEM/STEM-EELS analysis*

146 *3.1.1. Characterization of Fe@FeOx NPs*

147 High-angle annular dark field (HAADF) (Z contrast; Z, atomic number) micrographs showed the of the
148 Fe@FeOx NP structure (Fig. 1a). The NPs were mostly spherical in shape, with a core (very bright) and
149 shell (less bright) as previously observed [7]. They also appeared in a chain-like aggregate
150 conformation (Fig. 2). The diameter range of these NPs was $\sim 13\text{--}20 \text{ nm}$ with a shell thickness of $\sim 3\text{--}5$
151 nm (Fig. 1a and b). The bright field (BF)-TEM micrographs and the corresponding selected area
152 electron diffraction (SAED) pattern were also recorded (Fig. SI-1). Very diffuse diffraction rings were
153 obtained, showing that the phase present in the NPs was very poorly crystallized. The TEM results
154 were in very good agreement with the complementary XRD pattern obtained for the Fe@FeOx
155 sample (Fig. SI-2), in which only two very broad diffraction peaks, attributed to the most intense

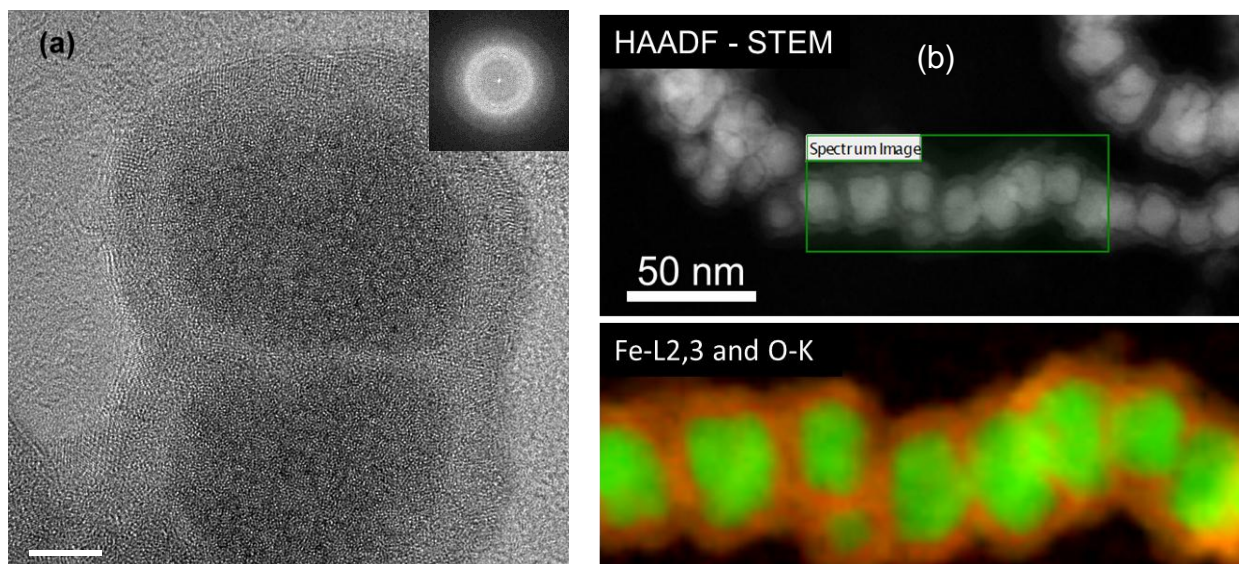
156 (110) crystallographic plane of Fe^0 and the (311) crystallographic plane of magnetite, were measured.
157 Fig. 2a exhibits HR-TEM micrographs and a high-resolution micrograph with its corresponding Fast
158 Fourier Transform (FFT). The d-spacings measured on the FFT were 2.60 and 2.06 Å. These values can
159 be attributed to the (311) and (400) crystallographic planes of magnetite. The d-spacing of 2.06 Å
160 could also be attributed to the (110) diffraction plane of $\alpha\text{-Fe}$, meaning that a superposition of the
161 diffraction rings due to the (110) plane of $\alpha\text{-Fe}$ and the (400) plane of Fe_3O_4 is also possible.
162 Moreover, HR-TEM micrographs confirmed the layered nanostructure of the shell (Fig. 1b). The
163 STEM-EELS experiments, performed to simultaneously acquire HAADF micrographs for the O-K and
164 Fe- $L_{2,3}$ edges (Appendix A), showed that the core of the NPs contained contributions of both metallic
165 Fe (Fe^0) and Fe oxide (Fe^{II} and Fe^{III}), making the separation between the different phases difficult. The
166 EDX elemental mapping removed this difficulty and the combined elemental mapping for the Fe- $L_{2,3}$
167 and O-K edges revealed a metallic Fe^0 core (green) and a Fe oxide shell (orange) (Fig. 2). This result
168 was also confirmed by the STEM-EDX line profile on an individual NP (Fig. SI-3).

169



170

171 **Fig. 1.** (a) HAADF-STEM and (b) HR-TEM micrographs of Fe@FeOx nanoparticles.



172

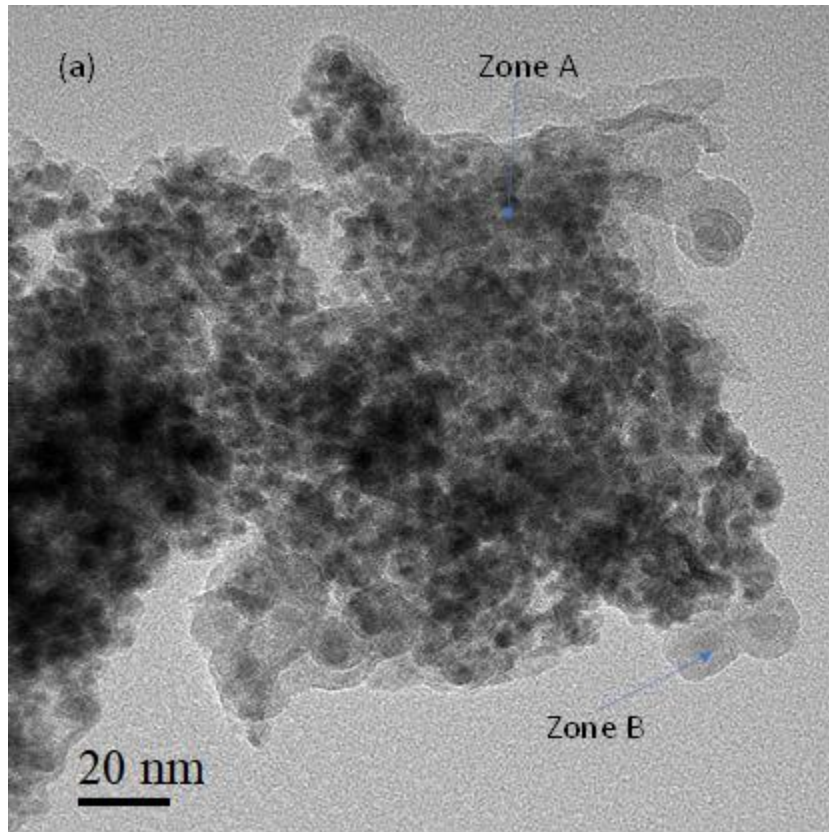
173 **Fig. 2.** (a) HR-TEM micrographs of Fe@FeOx sample and its FFT in the inset. (b) HAADF image of
 174 Fe@FeOx nanoparticles and corresponding elemental mapping. The zones highlighted in green and
 175 orange correspond to Fe-rich and O-rich areas, respectively. The figure was adapted from data of a
 176 previous work [8].

177

178 3.1.2. Characterization of Fe@FeOx/Pd NPs

179 The nanostructure of Fe@FeOx NPs exposed to H₂PdCl₄ was studied using TEM and STEM (Fig. 3). The
 180 images displayed a heterogeneous distribution of dense NPs forming aggregates of several hundreds
 181 of nanometers constituted by grains of about 5 nm (see the dense dark NPs in Zone A in Fig. 3a). A
 182 few uncovered core-shell Fe@FeOx NPs were visible (Zone B in Fig. 3a). On one hand, the zones
 183 corresponding to the dense NP aggregates were analyzed more specifically and the corresponding
 184 FFT pattern displayed rings with *d*-spacings typical of fcc metallic Pd⁰ (Fig. 3b). Additionally, STEM-X-
 185 ray mapping was performed (Fig. 4). The analysis showed that both Pd and Fe were present in the
 186 aggregates of zone A (~80 at.% of Pd and ~20 at.% of Fe). On the other hand, analysis of the
 187 diffraction pattern for areas containing uncoated core-shell Fe@FeOx NPs (Zone B) revealed the
 188 presence of magnetite (FFT similar to that recorded in Fig. 2a).

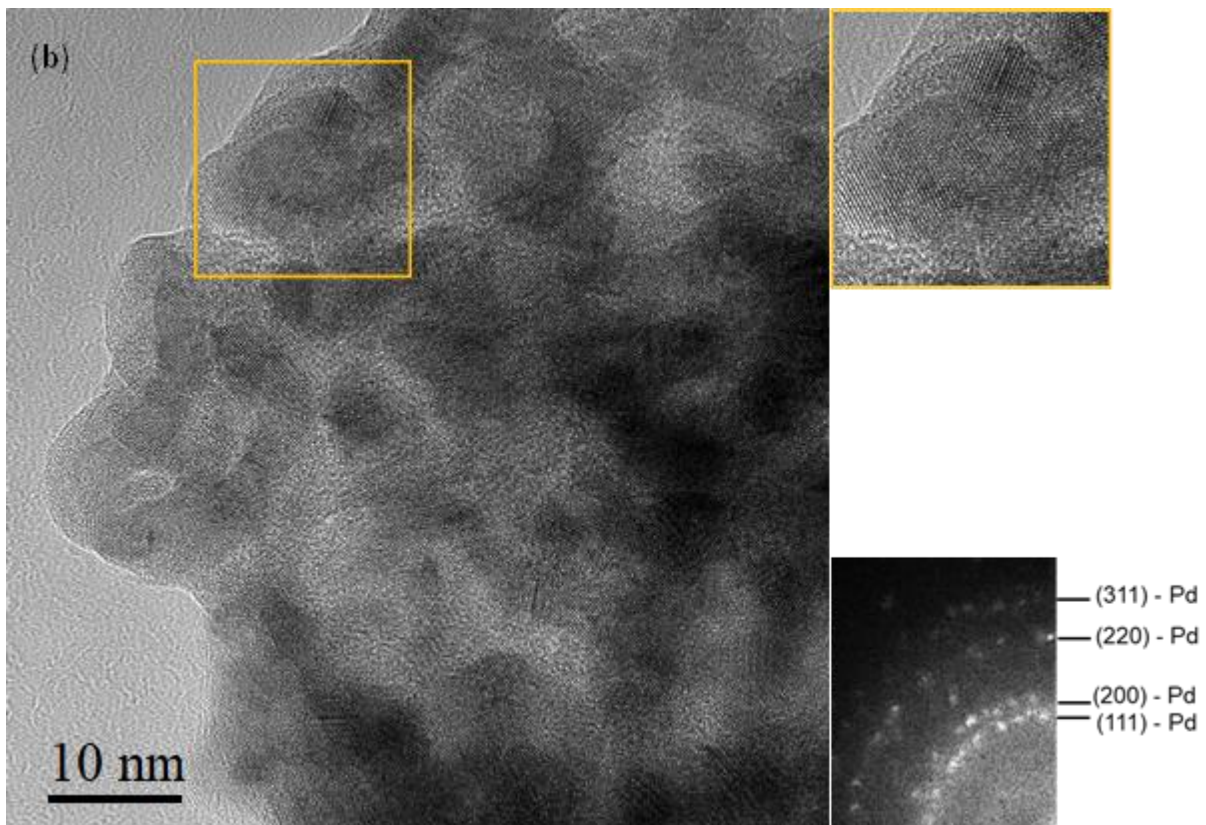
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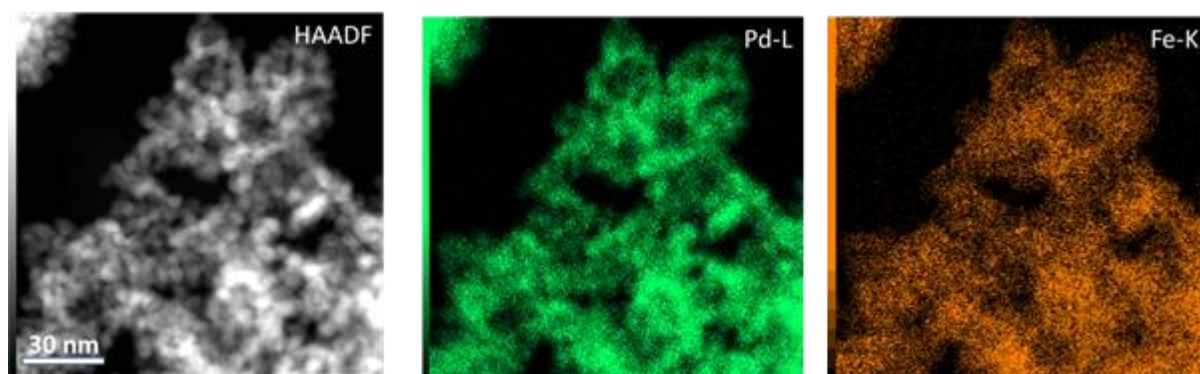


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194

195 **Fig. 3.** (a) Typical BF-TEM micrograph showing Pd-rich zones (Zone A) and uncovered core-shell
196 Fe@FeOx NPs (Zone B). (b) HR-TEM micrograph and corresponding FFT recorded in a Pd-rich zone
197 (Zone A). The indexation of the Pd⁰ diffraction rings is also given.

198



199

200 **Fig. 4.** STEM X-ray mapping of the Fe@FeOx/Pd NPs in a Pd-rich zone (Zone A).

201

202 3.2. XPS analysis

203 3.2.1. Characterization of Fe@FeOx NPs

204 An XPS analysis provides valuable information about the chemical composition of a sample and
205 chemical bonding of atoms from the surface of a material. The surface quantitative elemental
206 composition determined by XPS before and after Ar⁺ sputtering is reported in Table 1. As expected,
207 Fe, oxygen (O), and carbon (C) were present in Fe@FeOx NPs. The Ar⁺ sputtering decreased the C
208 contribution and increased that of Fe, while the amount of O was not significantly affected. Due to
209 the spin-orbit j-j coupling, the Fe 2p core levels split into 2p_{1/2} and 2p_{3/2} components, situated at
210 ~710.2 and ~723 eV, respectively (Fig. 5a). In addition, there was a relatively strong satellite peak in
211 the 718–720 eV region, which is characteristic of a Fe^{III}-rich surface (Fig. 5a). The deconvolution of
212 the Fe 2p_{3/2} region was performed with contributions from Fe⁰ (706.7 eV), Fe^{II} (708.5–710.5 eV), and
213 Fe^{III} (710.1–713.5 eV) [22,23]. This fitting procedure allowed the determination of the relative
214 proportion of Fe⁰, Fe^{II}, and Fe^{III} species present on the surface of Fe@FeOx NPs (Table 1). A relative
215 proportion as high as ~85% of Fe^{III} species was found, with much lower proportions of Fe^{II} and Fe⁰ of

216 around 11% and 4%, respectively. The relatively low concentration of Fe⁰ can be easily understood
 217 since the Fe⁰ core is covered by a relatively thick oxide layer (3–5 nm) of magnetite (Fig. 6a), as
 218 previously observed using TEM (Fig. 1b). The magnetite top layer showed a Fe^{III}/Fe^{II} ratio of 7.7 and
 219 then appeared to be partially oxidized into a very thin layer of Fe^{III}-rich oxides, most likely an epitaxial
 220 layer of maghemite γ -Fe₂O₃. The Ar⁺ sputtering partially removed both the C contamination and the
 221 γ -Fe₂O₃ top layer (Fig. 6b). Fig. 5b displays a Fe 2p spectrum with characteristics much closer than the
 222 reference spectra of magnetite synthesized under ultra-vacuum [29,30]. In particular, the detection
 223 of a much higher concentration of Fe^{II} species (~48%, Table 1) correlates well with the presence of a
 224 strong satellite peak around 716 eV in the Fe 2p spectrum (Fig. 6b). Note that the ratio Fe^{III}/Fe^{II} of 1
 225 measured after Ar⁺ sputtering was significantly lower than the expected value of 2 corresponding to
 226 stoichiometric magnetite Fe^{III}₂Fe^{II}O₄. This result may be attributed to the coexistence of a Fe^{II}-rich
 227 extra-phase beside magnetite, which is in good agreement with the Mössbauer results presented
 228 later in section 3.3.

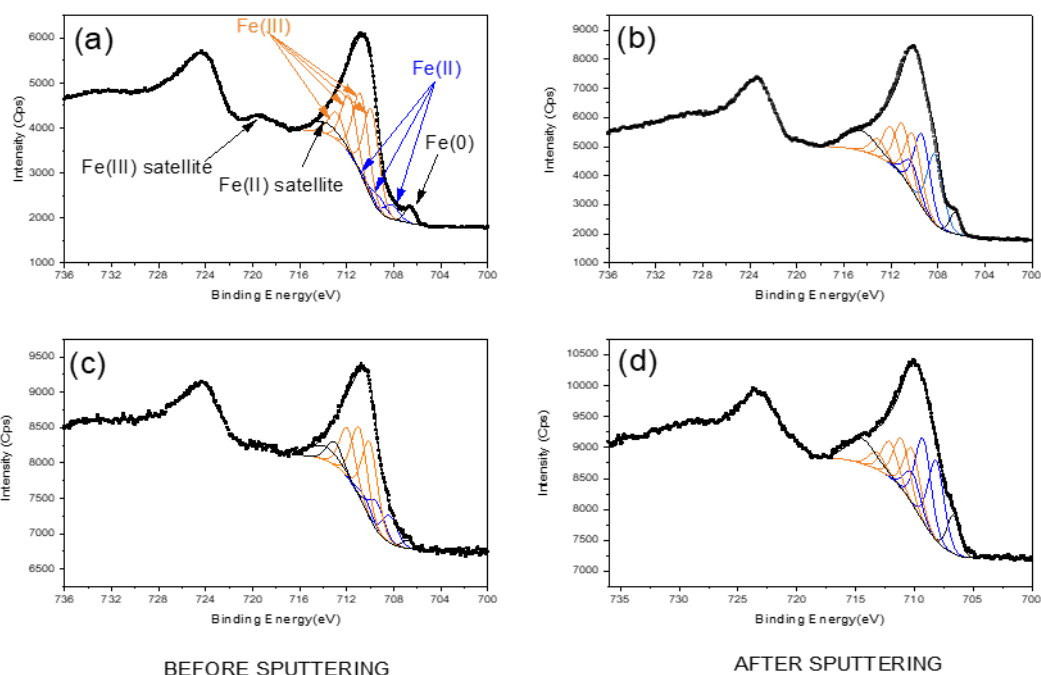
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Sample	Elemental composition (at.%)					Proportion of iron species (at.%)		
	Fe	O	Pd	C	Fe/O	Fe(0)	Fe(II)	Fe(III)
Fe@FeOx	9.4	44.3	-	46.3	0.21	3.6	11.1	85.3
Fe@FeOx after 4 min Ar ⁺ sputtering	18.1	45.9	-	36.0	0.39	4.0	48.2	47.8
Fe@FeOx/Pd	3.2	41.1	7.0	48.7	0.08	1.8	22.6	75.6
Fe@FeOx/Pd after 4 min Ar ⁺ sputtering	8.0	39.6	11.9	40.5	0.2	7.6	47.0	45.4

230

231

232 **Table 1** Relative elemental composition (at.%) and iron speciation determined from XPS analysis.



BEFORE SPUTTERING

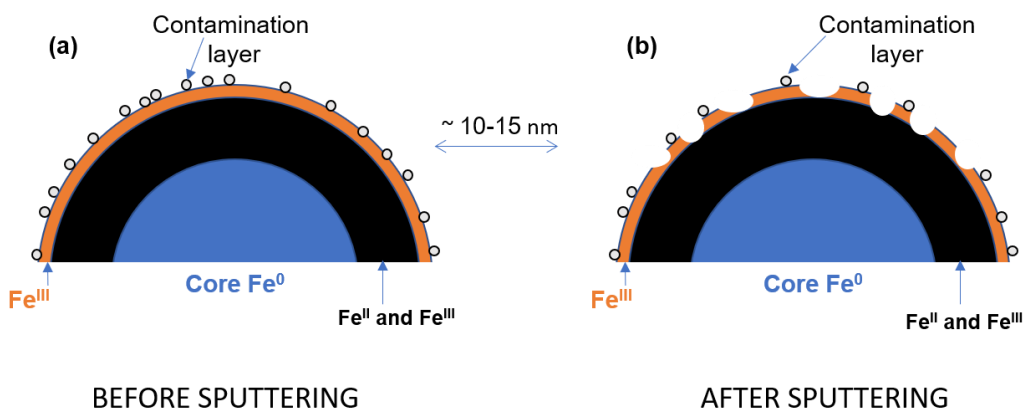
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235 **Figure 5:** Fe2p XPS spectra of various NPs: (a) Fe@FeOx as prepared (before sputtering), (b) Fe@FeOx
 236 after a short Ar⁺ sputtering, (c) Fe@FeOx/Pd as prepared and (d) Fe@FeOx/Pd after a short Ar⁺
 237 sputtering. The spectra were adjusted by a procedure using various multiplets as described
 238 previously [22-23].

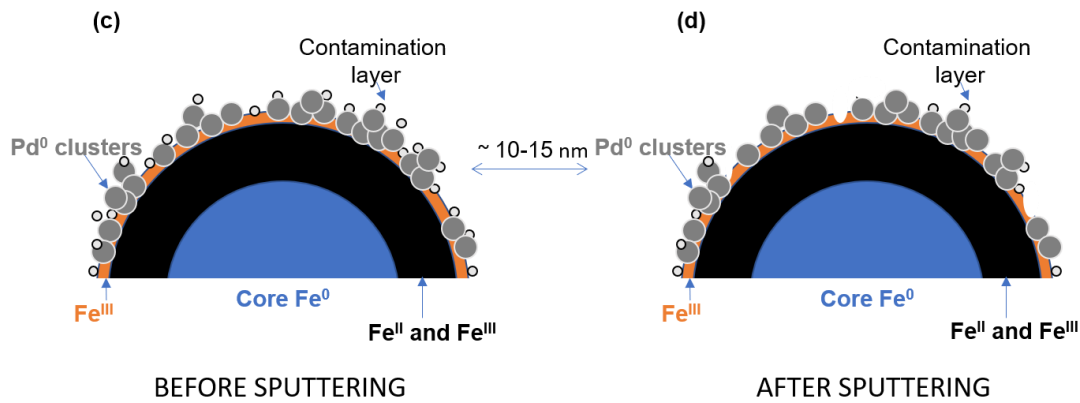
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BEFORE SPUTTERING

AFTER SPUTTERING

240



241

242 **Fig. 6.** Schematic view of the NP surface. Fe@FeOx NPs (a) before and (b) after Ar⁺ sputtering.

243 Fe@FeOx/Pd NPs (c) before and (d) after Ar⁺ sputtering.

244

245 3.2.2. Characterization of Fe@FeOx/Pd NPs

246 Consistent with the TEM results, XPS measurements indicated that Fe@FeOx NPs showed Pd in
 247 addition to C, O, and Fe atoms (Table 1). The Pd 3d_{5/2} peak position was at a binding energy of 335.5
 248 eV, confirming the presence of metallic Pd⁰. The presence of Pd⁰ aggregates also induced a significant
 249 decrease in the relative abundance of Fe by a factor of ~3 (from 9.4% to 3.2%, Table 1). Such a
 250 decrease was used to estimate the thickness (T_{Pd}) of the Pd coating according to the following
 251 equation:

$$252 \quad T_{Pd} = -\lambda \times \ln \left(\frac{I[Fe]_c}{I[Fe]_0} \right) \quad \text{Eq. 1}$$

253 where λ is the inelastic mean free path of the Fe 2p electrons ($\lambda \sim 1$ nm [31]), $I[Fe]_c$ is the relative
 254 abundance of Fe recorded for the substrate coated with a top layer of Pd⁰ of thickness (T_{Pd}), and
 255 $I[Fe2p]_0$ is the relative abundance of Fe 2p recorded for the uncovered substrate ($T_{Pd} = 0$ nm).

256 An estimated thickness of Pd⁰ of ~1 nm was computed using Eq. (1), derived for a uniform coating on
 257 a flat surface. The obtained value should therefore be considered a very rough estimation of the Pd⁰
 258 coating thickness (within an order of magnitude). The TEM showed that the deposited Pd⁰ did not
 259 form a uniform coating but rather clusters (Fig. 3a), therefore the actual Pd⁰ thickness was certainly

260 higher or lower than ~ 1 nm. A schematic representation of these Pd⁰ clusters before and after Ar⁺
261 sputtering is given in Fig. 6c and d. The sputtered Fe@FeOx/Pd NPs was characterized by a higher
262 concentration of Fe^{II} species in comparison with the as-prepared Fe@FeOx NPs (before sputtering).
263 As observed for Fe@FeOx NPs, the Ar⁺ sputtering led to a significant decrease of the C and Fe^{III}
264 contents and a Fe^{II}/Fe^{III} ratio of ~ 1 was determined.

265

266 3.3. TMS analysis

267 3.3.1. Relaxation phenomena and characterization of Fe@FeOx NPs

268 In a first step, the Mössbauer spectra were recorded in a temperature range from RT to 10 K (Fig. 7).
269 A general feature was the shape of Mössbauer spectra characterizing the presence of magnetic
270 relaxation with two regimes: one above and one below 77 K. The term relaxation covers different
271 phenomena subject to various terms, i.e. time-dependent and (or) also temperature-dependent
272 phenomena. Two characteristic times are generally considered in Mössbauer spectroscopy: (i) the
273 mean life time of the excited nuclear level (100 ns), which determines the resolution of the spectra,
274 and (ii) the inverse of the nuclear Larmor precession frequency, which is the frequency at which the
275 magnetic moment of the nucleus precesses (~ 34 MHz) in the HFD. When an isolated magnetic
276 particle is small enough, its magnetic moment (the macro spin) fluctuates between the easy
277 directions of magnetization. The characteristic time of such a fluctuation is designated as the “flip”
278 time and corresponds to the inverse of the transition rate. The Mössbauer spectrum of such a
279 particle strongly depends on the ratio between the transition rate and the Larmor frequency. If the
280 “flip” time of the magnetic moment of the particle is much longer than the nuclear Larmor
281 precession period, then the nucleus feels the magnetic field due to the electronic cloud (particle
282 magnetic moment) and interacts with it through its nuclear magnetic moment (Zeeman splitting). In
283 this situation, the obtained Mössbauer spectrum present a magnetic structure. On the contrary, if
284 the “flip” time of the magnetic moment of the particle is much shorter than the nuclear Larmor
285 precession period, the nucleus perceives a zero (time-average) particle magnetic moment. The latter

286 situation prevents the observation of a magnetic structure in the Mössbauer spectrum, which
287 corresponds to superparamagnetic relaxation. Among principal types of relaxation,
288 superparamagnetism in small magnetic particles became the subject of several publications [23–27].
289 In particular, Mössbauer spectroscopy was shown to be extremely sensitive to some of the size-
290 dependent properties of very small particles.

291 In the first temperature range from RT to 77 K, spectra were fitted with two (or three) quadrupole
292 doublets D1, D2 (or D3), and two (or three) sextets. The detailed values of the hyperfine parameters
293 of the components used to fit the Mössbauer spectra recorded for Fe@FeOx NPs were provided (see
294 Appendix B, Table B-1). Doublet D1 was characterized by large CS and Δ values of 1.28 and 2.10 mm
295 s^{-1} , respectively. The value of Δ and its increase with lowering temperature is typical of a Fe^{II} state in
296 an octahedral site.

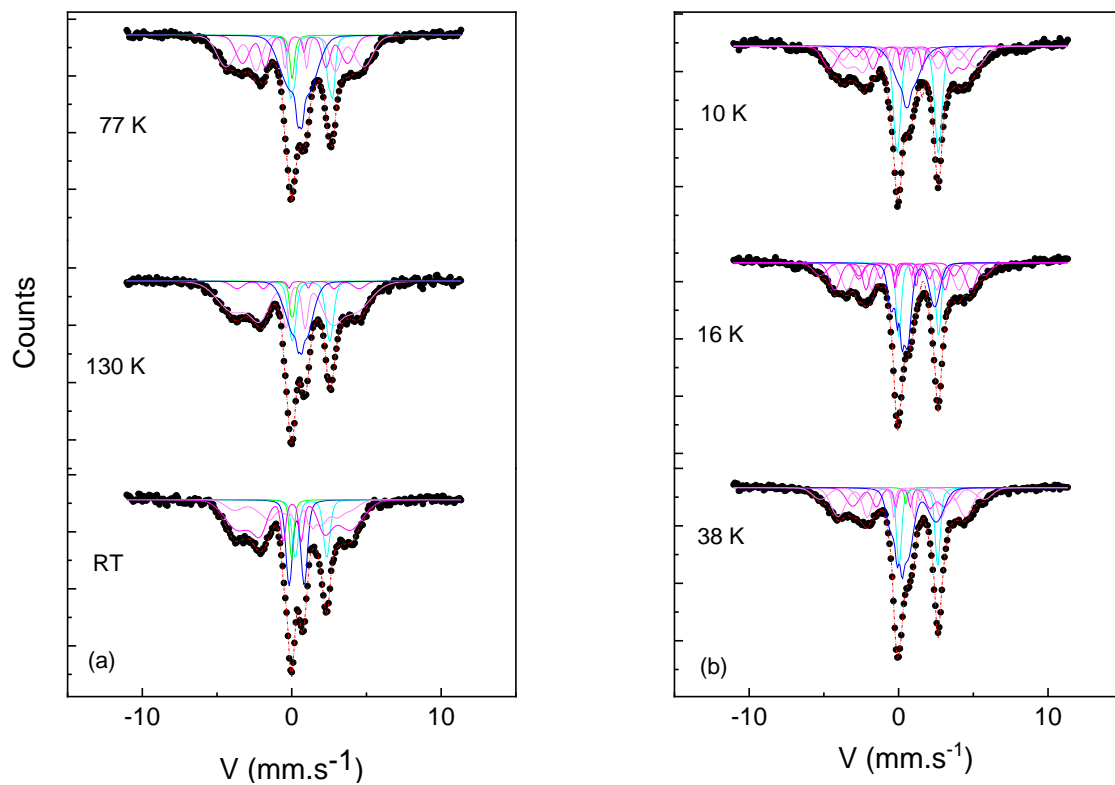
297 At RT, another paramagnetic component was reasonably described as a superimposition of
298 elemental sub-spectra D2 and D3 whose hyperfine parameters differed from those of the ferrous
299 doublet. The spectrum of a magnetic component constituted by two sextets (S1 and S2) was also
300 observed. Sextets S1 and S2 could be ascribed to the components of a superparamagnetic magnetite
301 whose HFDs are reduced with respect to bulk magnetite. Superparamagnetic relaxation was the most
302 important determining factor for the temperature dependence of spectra due to the range of
303 particles size as measured by TEM. Indeed, the Morup model [23] developed for studying the
304 Mössbauer spectra of NPs explained the reduction of the HFDs with asymmetric and broad lines.

305 At 130 K, doublet D2 disappeared and an additional broad sextet appeared with lower HFD than
306 those of S1 and S2. The superposition of D2 and D3 at RT with the transformation from D2 to S3 at
307 130 K corresponded to metallic Fe-NPs that present superparamagnetic behavior. Doublets D2 and
308 D3 (or D3 and S3 with a low HFD) were obtained to the detriment of the classical α -Fe sextet
309 characterized by a HFD of 329 kOe. The presence of paramagnetic doublets was observed in a
310 previous study of ultrathin pure ⁵⁷Fe (thickness lower than one monolayer) prepared under ultrahigh

311 vacuum [32]. In the temperature range of 38 to 10 K, the line shapes were poorly evolved compared
312 to those obtained between ambient temperature and 77 K. One should note that the CS value of 0.78
313 mm s^{-1} obtained for the Fe^0 sextet at 38 K was much higher than the expected value of 0.12 mm s^{-1} .
314 Such a discrepancy could be due to the complexity of our fitting procedure using multiple
315 components.

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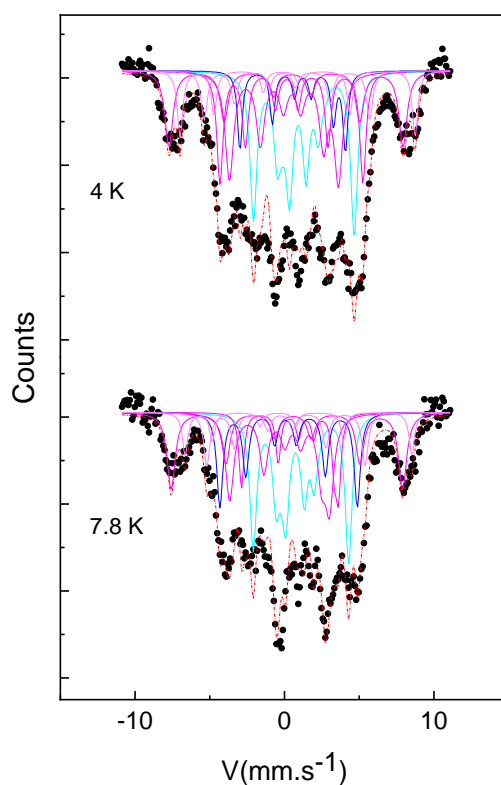
320 **Fig. 7.** Mössbauer spectra for Fe@FeOx NPs recorded between room temperature and 10 K. (a) Solid
321 black circles, experimental curve; dash dot line in red, global computed curve; solid line, sub-
322 components of the spectra; cyan, D1 associated with Fe(II) in $\text{Fe}(\text{OH})_2$; green and blue, D3 and D2 (or
323 sextet) associated with $\text{Fe}(0)$, respectively; magenta, sextets S1 and S2 associated with magnetite.

324 (b) Solid black circles, experimental curve; dash dot line in red, global computed curve; solid line, sub-
325 components of the spectra; cyan, D1 associated with Fe(II) in Fe(OH)₂; blue, sextet associated with
326 Fe(0); magenta, sextets S1 and S2 associated with magnetite.

327

328 The global shape of the spectra recorded at temperatures of 7.8 and 4 K (Fig. 8) completely differed
329 from those recorded above 10 K. The adjustment of such spectra was relatively complex and may not
330 be unique. Here, seven components were used to properly fit the experimental spectra. Six sextets
331 were necessary to reproduce the magnetite contribution. Metallic Fe (Fe⁰) NPs gave rise to one
332 sextet (green line). Moreover, according to literature [33], at low temperature, microcrystalline
333 magnetite requires five sextets – attributed to one Fe^{III} located in tetrahedral sites, two Fe^{III} in
334 octahedral sites, and two Fe^{II} in octahedral sites. In addition, the calculated HFDs were much lower
335 than expected for microcrystalline magnetite. The effects of apparent reduction of the HFD as a
336 function of temperature or volume of the crystallites were widely debated in various theoretical
337 models [23–27,34]. These effects were combined and explained by two phenomena: (i) the
338 proportion of surface atoms and (ii) the fluctuation of the magnetization due to the interactions
339 between particles. Finally, the Fe^{II} species observed in a paramagnetic state between 300 and 10 K
340 were described with an octet (cyan line) corresponding to a magnetically-ordered Fe^{II} phase below 10
341 K. The electric quadrupole interaction cannot be treated as a perturbation of the Zeeman splitting
342 [35,36], and it was not possible to analyze the spectra in terms of six-line patterns (sextets) as in the
343 case of the magnetism of ferric components. Therefore, the sub-spectrum comprising eight lines was
344 fully computed by solving the eigenvalues of the Hamiltonian (but only four lines were observable
345 due to the overlap of some transitions). The hyperfine parameters of this octet (Table B-2) were in
346 agreement with some of the features of ferrous hydroxide [Fe(OH)₂] [37]. In particular, the HFD of
347 this octet characterized by a value of 160 kOe was comparable to that measured previously for
348 microcrystalline Fe(OH)₂ (220 kOe), which underwent a magnetic phase transition from paramagnetic
349 to an antiferromagnetic state below the Néel temperature of 34 K. However, the quadrupole splitting

350 values reported for the Fe^{II} doublet in the temperature range of 300 to 12 K were significantly lower
351 than that previously reported for bulk Fe(OH)₂ at 90 K (QS = 3 mm s⁻¹ [36]). The origin of this
352 difference between the nanosized “Fe(OH)₂-like” phase and bulk Fe(OH)₂ is still unclear and needs
353 further investigation.
354



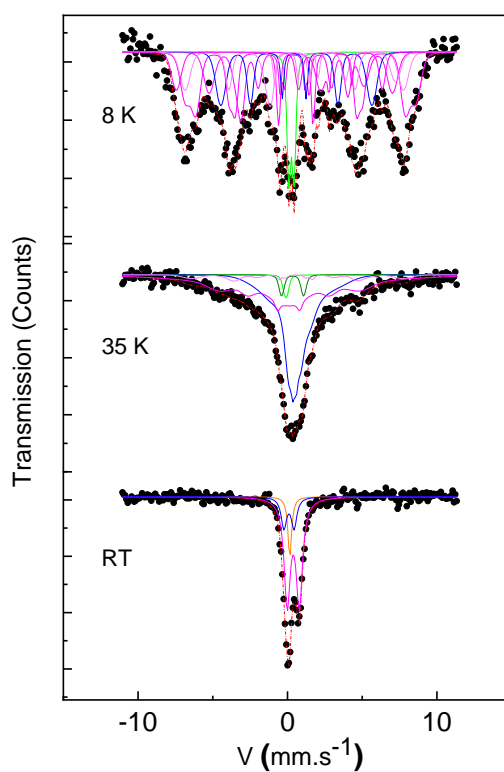
355
356
357 **Fig. 8.** Mössbauer spectra for Fe@FeOx NPs recorded at 7.8 and 4 K. Solid black circles, experimental
358 curve; dash dot line in red, global computed curve; solid line, sub-components of the spectra; cyan,
359 octet associated with Fe(II) in Fe(OH)₂ magnetically ordered; blue, sextet associated with Fe(0);
360 magenta, sextets S1–S5 associated with magnetite.

361 362 3.3.2. Characterization of Fe@FeOx/Pd NPs

363 The Mössbauer spectra at RT, 35 K, and 4 K for the Pd-coated NPs were measured (Fig. 9). The RT
364 spectrum was easily fitted with two doublets and one singlet. In contrast to the sample without Pd, a

365 doublet corresponding to a pure ferrous site was not observed. At 35 K, there was a significant
366 change from a sharp quadrupole doublet to a central broad line. This central line was deconvoluted
367 by three sextets with weak magnetic fields and two small remaining paramagnetic doublets. This
368 transition can be attributed to the dynamic effect resulting from the fluctuations in the local
369 environment of the probe nucleus (^{57}Fe), such as those arising from superparamagnetism. This was
370 confirmed by the line shapes of the spectrum recorded at 8 K, which evolved gradually to a six-line
371 spectrum. At this last temperature, the spectrum exhibited complex magnetic interactions due to the
372 presence of multiple components. The fitting displayed one residual doublet (8% of relative
373 abundance) and six sextets, among which one corresponded to α -Fe (15% of relative abundance) and
374 five components assigned to magnetite (77%). As specified above, the center shift and the hyperfine
375 magnetic fields (Table B-3) deviated from those tabulated for α -Fe components and magnetite. These
376 results confirmed the superparamagnetism behavior as expected for NPs.

377
378



379

380

381 **Fig. 9.** Mössbauer spectra of Fe@FeOx/Pd NPs at various temperatures. Solid black circles,
382 experimental curve; dash dot line in red, global computed curve; solid line, sub-components of the
383 spectra. Spectrum recorded at room temperature (RT); orange, singlet associated with
384 superparamagnetic phase; blue, doublet associated with Fe(0); magenta, doublet associated with
385 superparamagnetic phase. Spectrum recorded at 35 K; green, doublet associated with
386 superparamagnetic phase; blue, broad sextet associated with Fe(0); magenta, sextets associated with
387 magnetite. Spectrum recorded at 8 K; green, doublet associated with superparamagnetic phase;
388 blue, sextet associated with Fe(0); magenta, sextets S1–S5 associated with magnetite.

389

390 *3.4. Identification and proportion of the phases present in Fe@FeOx and Fe@FeOx@Pd NPs*

391

The characterization techniques used in this study gave us valuable complementary information
392 about the nature of the phases present in our NPs. The TEM electron diffraction patterns showed
393 that the shell of the Fe@FeOx NPs was mainly constituted by magnetite and the coating of
394 Fe@FeOx/Pd NPs was Pd⁰. Metallic Fe⁰ was identified in both Fe@FeOx and Fe@FeOx/Pd NPs by XPS,
395 confirming that the shell was mainly composed of a mixture of Fe^{II} and Fe^{III} species. Moreover, the
396 extreme surface of magnetite was constituted by a Fe^{III}-rich phase, most probably a very thin layer of
397 γ -Fe₂O₃. The ⁵⁷Fe TMS is a unique technique that can determine the nature and relative proportion of
398 the phases. Our measurements identified magnetite, metallic Fe⁰, and a Fe(OH)₂-like phase Fe@FeOx
399 NPs. Compared to the much more stable γ -Fe₂O₃ or Fe₃O₄ phases, Fe(OH)₂ is an air-sensitive phase
400 and is unstable at the surface of the shell. It is most likely that this Fe(OH)₂-like phase could be
401 stabilized at the Fe⁰–Fe₃O₄ interface if protected from air; its disappearance as measured by TMS
402 confirmed the very high reactivity of the Fe(OH)₂ phase. One may hypothesize that the reduction of
403 Pd^{II}_{aq} ions to Pd⁰ was due to an electron transfer between Fe(OH)₂-like phase and Pd^{II}_{aq} via the
404 conductive external layer of Fe₃O₄. Interestingly, the radius of the spherical NPs was on average two
405 times that of the core, meaning that the dimension of the core radius was close to the thickness of

406 the shell. As detailed in Appendix C, the volume of the shell was about seven times the volume
407 occupied by the atoms in the core. Note that this ratio of seven is independent of the size of the NPs.
408 Knowing the atomic density of the Fe atoms in magnetite ($0.041 \text{ At. } \text{\AA}^{-3}$) and Fe^0 ($0.085 \text{ At. } \text{\AA}^{-3}$), a
409 ratio Fe shell/Fe core of ~ 3.4 was computed. This means that the core contained $\sim 22\%$ of the Fe
410 atoms, a value comparable to the relative proportion of Fe^0 ($\sim 15\%$) derived from Mössbauer
411 spectroscopy at very low temperature (4 K). Therefore, phase proportions derived from TEM or TMS
412 measurements on Fe@FeOx were quantitatively consistent. Note also that the relative proportion of
413 Fe^0 determined in this study ($\sim 15\%$) is in good agreement with that measured by Kanel et al. ($\sim 19\%$)
414 [20] and this relative proportion did not vary significantly after contact with $\text{Pd}^{\text{II}}_{\text{aq}}$ (Appendix B). In
415 fact, the quantity of Fe atoms present in the Fe-NPs ($\sim 5 \times 10^{-3}$ moles) was in significant excess
416 compared to the quantity of $\text{Pd}^{\text{II}}_{\text{aq}}$ introduced in the medium ($\sim 0.067 \times 10^{-3}$ moles). Therefore, only
417 the specific reactive Fe species, in our case the Fe^{II} species present in $\text{Fe}(\text{OH})_2$ -like phase, was
418 oxidized. However, note that the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratio measured by XPS did not increase significantly after
419 covering the NPs with Pd^0 (Table 1) as would be expected from the interpretation of the Mössbauer
420 data. This observation could be related to the difference in analysis depth between both techniques
421 or to an eventual preferential Ar^+ -sputtering effect. Moreover, by assuming that only the $\text{Fe}(\text{OH})_2$ -like
422 phase was involved in the reduction of the $\text{Pd}^{\text{II}}_{\text{aq}}$ to Pd^0 , the thickness of the Pd^0 coating can be
423 estimated (Appendix C). The values obtained for Pd^0 coating were quasi-linearly dependent on the
424 radius (R_c) of the Fe^0 core. The R_c values of 5–30 nm yielded Pd^0 thicknesses of ~ 0.1 – 0.53 nm (Eq. C-1
425 in Appendix C), consistent with the mean thickness of Pd^0 of ~ 1 nm estimated using XPS.

426

427 **4. Conclusion**

428

429 Mössbauer spectroscopy and XPS were used to determine the nature of the phases present in the
430 core–shell nanostructure of Fe@FeOx NPs. Metallic Fe^0 , a $\text{Fe}(\text{OH})_2$ -like phase, magnetite, and a top
431 layer of ferric oxides were identified. Interestingly, the $\text{Fe}(\text{OH})_2$ -like phase was fully transformed

432 when the Fe@FeO_x NPs reacted with Pd^{II}_{aq} and concomitantly the proportion of Fe⁰ did not vary
433 significantly. The relative proportion of Fe species present in the core and the shell was revealed by
434 TEM images and determined quantitatively by Mössbauer spectroscopy using the full temperature
435 range of 4–298 K.

436

437 **Declaration of Competing Interest**

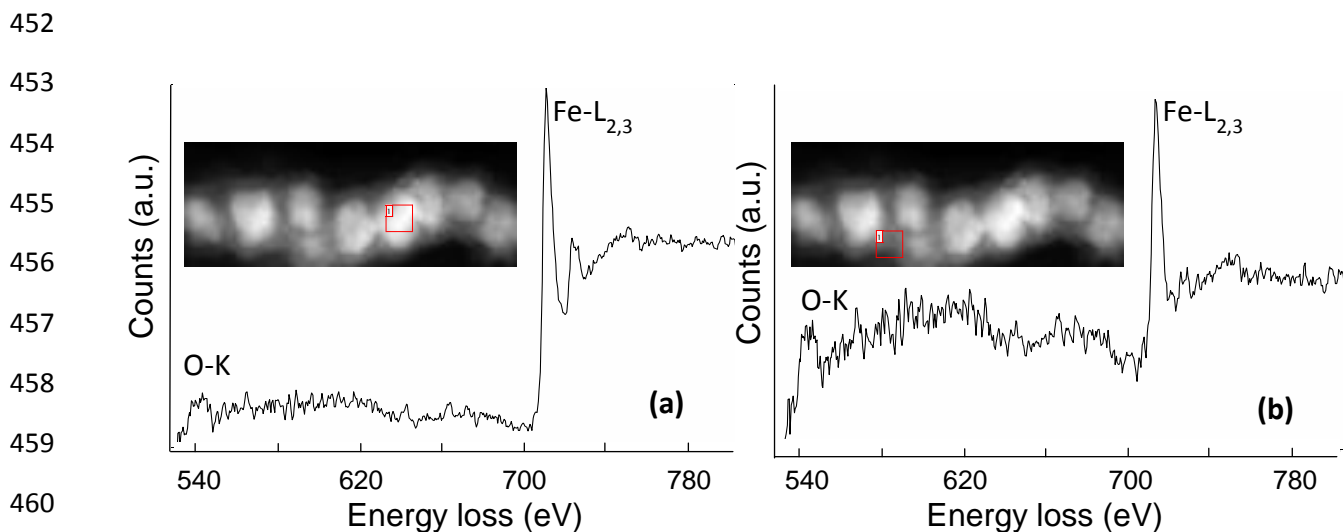
438 The authors declare that they have no known competing financial interests or personal relationships
439 that could have appeared to influence the work reported in this paper.

440

441 **Acknowledgments**

442

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444 measuring the pH values at each step of the synthesis of the NPs. Aurélien Renard (Université de
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446 XPS experiments were supported by means of the Spectroscopy and Microscopy Core Facility of SMI
447 LCPME (Université de Lorraine, CNRS, LCPME- <http://www.lcpme.cnrs-nancy.fr>), which is gratefully
448 acknowledged.

451 **Fig. A-1.** EELS analysis of the (a) core and (b) shell of Fe@FeOx NPs.

464 **Table B-1** Hyperfine parameters of the Mössbauer spectra of Fe@FeOx NPs at different
 465 temperatures recorded on the ARS instrument (see experimental section 2.2.3). CS, Δ , ϵ , H, and RA
 466 are the center shift, quadrupole shift, quadrupole splitting, hyperfine field, and relative abundance of
 467 components, respectively.

468 **T = 298 K**

Component	CS (mm s^{-1})	Δ or ϵ (mm s^{-1})	H (kOe)	RA (%)
D1: Doublet Fe(II)	1.28	2.1		12
D2: Doublet Fe(0)	0.33	1.01		18
D3: Doublet Fe(0)	-0.002	0.15		4
S1: sextet	0.41	-0.4	172	24
S2: sextet	0.08	0.05	237	42

469

470

471 **T = 130 K**

Component	CS (mm s^{-1})	Δ or ϵ (mm s^{-1})	H (kOe)	RA (%)
-----------	---------------------------	---	---------	--------

D1: Fe(II)	1.28	2.50		15
D3: Fe(0)	0.03	0.20		3
S1: Sextet 1	0.44	-0.02	253	5
S2: Sextet 2	0.20	-0.05	250	54
Sextet: Fe(0)	0.50	-0.04	47	22

472

473 **T = 77 K**

Component	CS (mm s ⁻¹)	Δ or ϵ (mm s ⁻¹)	H (kOe)	RA (%)
D1: Doublet Fe(II)	1.32	2.62		14
D3: most probably Fe(0)	0.03	0.19		4
Sextet	0.24	0.02	218	20
Sextet	0.24	-0.03	285	32
Sextet Fe(0)	0.55	-0.04	56	30

474

475 **T = 38 K**

Component	CS (mm s ⁻¹)	Δ or ϵ (mm s ⁻¹)	H (kOe)	RA (%)
D1: Doublet Fe(II)	1.32	2.58		14
D3: most probably Fe(0)	0.48	0.19		1
Sextet: magnetite	0.15	-0.14	190	15
Sextet: magnetite	0.29	-0.07	264	26
Sextet: Fe(0)	0.78	0.71	63	33
Sextet: magnetite	0.40	-0.16	339	11

476

477 **T = 16 K**

Component	CS (mm s ⁻¹)	Δ or ϵ (mm s ⁻¹)	H (kOe)	RA (%)
D1: Doublet Fe(II)	1.34	2.66		14
Sextet: magnetite	0.28	-0.14	174	9
Sextet: magnetite	0.34	-0.04	233	19
Sextet: most probably Fe(0)	0.74	0.68	61	29
Sextet: magnetite	0.37	-0.09	283	18
Sextet: magnetite	0.38	-0.14	341	11

478

479

480

481

482 **T = 10 K**

Component	CS (mm s ⁻¹)	Δ or ϵ (mm s ⁻¹)	H (kOe)	RA (%)
D1: Doublet Fe(II)	1.35	2.66		16

Sextet: magnetite	0.34	-0.02	197	12
Sextet: magnetite	0.27	0.11	249	13
Sextet: Fe(0)	0.80	0.89	56	30
Sextet: magnetite	0.21	-0.22	295	16
Sextet: magnetite	0.95	-0.13	300	12

483

484

485 **Table B-2** Hyperfine parameters of the Mössbauer spectra of Fe@FeOx NPs at different
486 temperatures recorded on the Janis instrument (see experimental section 2.2.3). CS, Δ , ε , H, and RA
487 are the center shift, quadrupole shift, quadrupole splitting, hyperfine field, and relative abundance of
488 components, respectively.

489 **T = 7.8 K**

Component	CS (mm s^{-1})	Δ or ε (mm s^{-1})	H (kOe)	RA (%)
Octet: Fe(II)	0.90	2.11	159	27
Sextet: magnetite	0.91	-1.09	201	9
Sextet: Fe(0)	0.17	0.21	285	15
Sextet: magnetite	0.36	-0.40	480	16
Sextet: magnetite	0.11	-0.88	207	19
Sextet: magnetite	0.25	1.38	470	6
Sextet: magnetite	0.09	0.38	328	8

490

491 **T = 4 K**

Component	CS (mm s^{-1})	Δ or ε (mm s^{-1})	H (kOe)	RA (%)
Octet: Fe(II)	1.10	2.40	162	27
Sextet: magnetite	0.89	-0.68	218	9
Sextet: Fe(0)	0.30	0.31	296	15
Sextet: magnetite	0.30	-0.40	486	14
Sextet: magnetite	0.23	-0.50	226	20
Sextet: magnetite	0.34	1.05	487	8
Sextet: magnetite	0.01	0.30	343	7

492

493

494 **Table B-3** Hyperfine parameters of the Mössbauer spectra of Fe@FeOx/Pd NPs at different
 495 temperatures. CS, Δ , ϵ , H, and RA are the center shift, quadrupole shift, quadrupole splitting,
 496 hyperfine field, and relative abundance of components, respectively.

497 **T = 298 K**

Component	CS (mm s^{-1})	Δ or ϵ (mm s^{-1})	H (kOe)	RA (%)
Singlet	0.15			12
Doublet: superparamagnetic magnetite	0.38	0.81		70
Doublet: superparamagnetic Fe(0)	0.10	0.69		18

498

499 **T = 35 K**

Component	CS (mm s^{-1})	Δ or ϵ (mm s^{-1})	H (kOe)	RA (%)
Doublet	-0.10	0.21		2
Doublet	0.33	1.47		3
Sextet	0.59	0.11	88	46
Sextet	0.10	0.02	206	43
Sextet	0.60	0.05	372	6

500

501 **T = 8 K**

Component	CS (mm s^{-1})	Δ or ϵ (mm s^{-1})	H (kOe)	RA(%)
	0.26	0.35		8
Sextet: magnetite	0.71	0.15	455	27
Sextet: magnetite	0.68	0.20	328	22
Sextet: Fe(0)	0.51	0.07	313	15
Sextet: magnetite	0.37	0.07	452	11
Sextet: magnetite	2.16	0.78	265	8
Sextet: magnetite	0.46	-3.07	299	10

502

503

504 **Appendix C**

505 Let us consider a spherical core–shell Fe⁰@FeO_x particle as schematized in Fig. C-1 with:

506 R_C , the radius of the core sphere (Fe⁰)

507 T_S , the thickness of the FeO_x shell

508 $V_C = \frac{4}{3} \cdot \pi \cdot R_C^3$, the volume of the core sphere

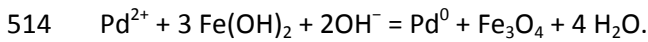
509 $V_S = \frac{4}{3} \cdot \pi \cdot [(R_C + T_S)^3 - R_C^3]$, the volume of the FeO_x shell

510 If $R_C = T_S$, then $V_S = 7 \cdot V_C$.

511

512 Let us consider the reaction of one core–shell Fe⁰@FeO_x particle with Pd²⁺. One can assume that:

513 (i) Fe(OH)₂ located in the shell is oxidized by Pd²⁺ ions to give Fe₃O₄ and Pd⁰ according to the reaction:



515 (ii) The obtained spherical particle present a Fe⁰ core and two shells made of Fe₃O₄ and Pd⁰ (Fig. C-1).

516 (iii) The densities of the various Fe oxides considered here are equal to that of Fe₃O₄.

517 From assumption (i), $N_{\text{Pd}^0} = \frac{1}{3} \cdot \%Fe^{II} \cdot N_{Fe}$, with N_{Fe} the number of Fe atoms into the particle,

518 $\%Fe^{II}$ the fraction of Fe atoms in the Fe(OH)₂ phase before reaction, and N_{Pd^0} the number of Pd

519 atoms into the obtained Pd⁰ phase after reaction. From assumptions (ii) and (iii), the thickness of the

520 Fe oxide shell remains unchanged (equal T_S) after reaction and N_{Fe} can be calculated as: $N_{Fe} =$

521 $C_{Fe} \cdot V_C + C_{Fe_3O_4} \cdot V_S$, with C_{Fe} (0.085 atom Å⁻³) and $C_{Fe_3O_4}$ (0.041 atom Å⁻³) the concentration of Fe

522 atoms into Fe⁰ and Fe₃O₄, respectively.

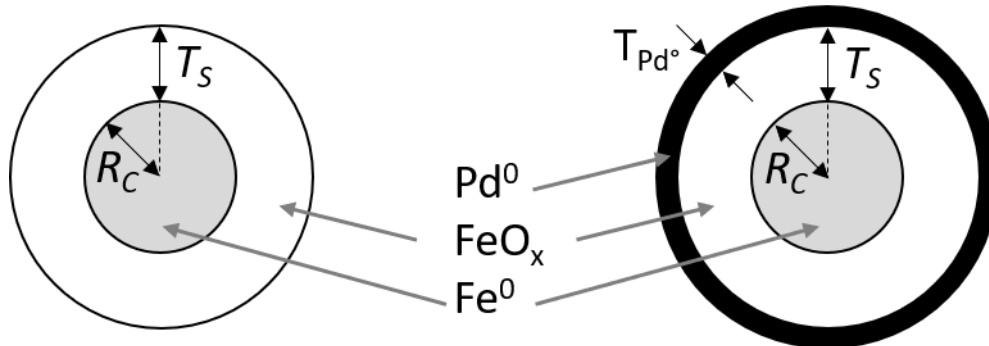
523 Therefore, the thickness (T_{Pd^0}) of the resulting Pd⁰ shell can be easily derived from the volume V_{Pd} of

524 the Pd⁰ shell given by: $V_{\text{Pd}} = \frac{M_{\text{Pd}}}{\rho_{\text{Pd}^0} \cdot \mathcal{N}_A} \cdot N_{\text{Pd}^0}$, with M_{Pd} the molar mass of Pd (106.4 g mol⁻¹), ρ_{Pd} the

525 density of Pd⁰ (12.02 g cm⁻³), and \mathcal{N}_A the Avogadro constant. It comes:

526 $T_{Pd^0} = [(A \cdot \%Fe^{II} + 8)^{1/3} - 2] \cdot R_C$ Eq (C-1)

527 With A a constant given by: $A = \frac{M_{Pd}}{3 \cdot \rho_{Pd^0} \cdot N_A} \cdot (C_{Fe} + C_{Fe3O4} \cdot 7)$



528

529 **Fig. C-1:** Schemes of Fe⁰@FeO_x (left) and Fe⁰@FeO_x/Pd⁰ (right) particles.

530

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