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Size-dependent catalytic effect of magnetite nanoparticles in the synthesis of tunable magnetic polyaniline nanocomposites

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(Article begins on next page)

1 **Size-dependent catalytic effect of magnetite nanoparticles in the synthesis of**  
2 **tunable magnetic polyaniline nanocomposites**

3  
4 **Ermelinda Falletta<sup>1\*</sup>, Anna M. Ferretti<sup>2</sup>, Sara Mondini<sup>2</sup>, Claudio Evangelisti<sup>2†</sup>, Elena**  
5 **Capetti<sup>2</sup>, Elena Sonia Olivetti<sup>3</sup>, Luca Martino<sup>3</sup>, Cinzia Beatrice<sup>3</sup>, Gabriel Soares<sup>3</sup>,**  
6 **Massimo Pasquale<sup>3</sup>, Cristina Della Pina<sup>1</sup>, Alessandro Ponti<sup>2\*</sup>**

7 <sup>1</sup> *Department of Chemistry, University of Milan, via C. Golgi, 19, 20133, Milan (Italy)*

8 <sup>2</sup> *Istituto di Scienze e Tecnologie Chimiche “Giulio Natta” (SCITEC), Consiglio Nazionale*  
9 *delle Ricerche, via G. Fantoli 16/15, 20138, Milan (Italy)*

10 <sup>3</sup> *Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce 91, 10135, Torino*  
11 *(Italy)*

12  
13 \* Corresponding author, e-mail: [alessandro.ponti@scitec.cnr.it](mailto:alessandro.ponti@scitec.cnr.it), [ermelinda.falletta@unimi.it](mailto:ermelinda.falletta@unimi.it)

14  
15 † Present address: Istituto di Chimica dei Composti Organometallici (ICCOM), Consiglio  
16 Nazionale delle Ricerche, Via G. Moruzzi 1, 56124, Pisa (Italy)

17  
18 **Abstract**

19 Nanocomposites comprising magnetic nanoparticles (NPs) embedded in an organic conducting  
20 polymer are promising materials that may allow one to exploit synergic effects between the  
21 electrically conducting and the magnetically permeable components. Having already shown  
22 that magnetite NPs can be conveniently used as a catalyst for the oxidative polymerization of  
23 the aniline dimer resulting in NPs embedded in the final composite and how to modulate the  
24 magnetic coercivity of the composites, we now turn to investigate how the size of magnetite  
25 NPs affects the polymerization and the properties of the final composite. Magnetite NPs of  
26 diameter 2.3, 10, and 27 nm turned out to be effective catalysts with cheap oxidants such as  
27 H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>. Yield data show that the rate-determining step occurs on the NP surface.  
28 Extensive characterization shows that the NPs are well-dispersed in the composite with no  
29 significant morphological change. The static magnetic properties of the composites are widely  
30 different, e. g, the magnetic blocking temperature shifts from 290 K for 27 nm NPs to 54 K for  
31 10 nm NPs while composites with 2.3 nm NPs are virtually unblocked down to 5 K. The  
32 dynamic electromagnetic behavior studied up to the microwave range only shows energy  
33 absorptions associated to the ferromagnetic resonance, at frequencies around 1 GHz.

34

35 **Keywords:** Fe<sub>3</sub>O<sub>4</sub>, PANI, magnetic nanoparticles, catalysis, electromagnetic absorption.

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38

## Introduction

39 Since their discovery, intrinsically conducting polymers (CPs) have emerged as outstanding  
40 materials for numerous applications in many sectors, ranging from sensors (Wang *et al.*, 2020)  
41 to biomedicine (Kaur *et al.*, 2015) passing from organic solar cells (Dong *et al.*, 2012),  
42 environmental remediation (Ibanez *et al.*, 2018) and so on (Yang *et al.*, 2019; Li *et al.*, 2020).

43 Among CPs, polyaniline (PANI) is unique for its ease of synthesis, low cost, biocompatibility,  
44 environmental stability, and extraordinary tunable properties (Badra *et al.*, 2009).

45 In recent years, materials combining characteristics and properties of two or more components  
46 have been sought and required in many sectors. Among them, PANI/Fe<sub>3</sub>O<sub>4</sub> nanocomposites  
47 have been recently investigated as advanced materials being both electrically conducting and  
48 magnetically permeable and having potential application in fields such as batteries (Wang *et al.*,  
49 2017), electromagnetic interference shielding (Movassagh-Alanagh *et al.*, 2017),  
50 environmental remediation (Muhammad *et al.*, 2019), cancer therapy (Ahmadkhani *et al.*,  
51 2019),.

52 Several approaches have been developed to prepare these composites: mixing of PANI with  
53 Fe<sub>3</sub>O<sub>4</sub>, self-assembly method, *in situ* polymerization, ultrasonic irradiation (Qiu *et al.*, 2006).

54 The ability of magnetite (and cobalt ferrite) nanoparticles (NPs) to act as catalysts in the PANI  
55 synthesis was explored for the first time by us in the catalytic polymerization of *N*-4-  
56 (aminophenyl)aniline (Della Pina *et al.*, 2012; Della Pina *et al.*, 2014; Della Pina *et al.*, 2015;  
57 Falletta *et al.*, 2015). Most recently, Mišurović and coworkers applied Fe<sub>3</sub>O<sub>4</sub> NPs as the catalyst  
58 in the aniline polymerization (Mišurović *et al.*, 2019).

59 Exploiting magnetite NPs of different size to catalyze the polymerization of AD and prepare  
60 PANI/Fe<sub>3</sub>O<sub>4</sub> nanocomposites would allow one to tune the magnetic properties of the  
61 composites provided that the NPs are size monodisperse and effective as a catalyst. The first  
62 requirement can be met thanks to the well-established methods of size-controlled colloidal  
63 nanochemistry (Ferretti *et al.*, 2021). As to the second one, the activity of a heterogeneous  
64 catalysts is strongly related to its particle size since it is intrinsically dependent on the surface-  
65 to-volume ratio, which dramatically grows passing from bulk to nano-dimensions. Moreover,  
66 compared to bulk materials, NPs have a larger surface density of atoms in sites, such as corner  
67 or edge sites, that maximize their reactivity because NPs are synthesized under kinetic control

68 and have spherical shape without the well-defined facets or crystals grown near thermodynamic  
69 equilibrium. However, because of the small dimensions, the outstanding activity of  
70 nanostructured materials is sometimes compromised by their strong interaction with  
71 intermediates and by aggregation phenomena. To the best of our knowledge, the size-dependent  
72 catalytic activity of Fe<sub>3</sub>O<sub>4</sub> NPs in the oxidative polymerization of *N*-4-(aminophenyl)aniline  
73 has not yet been investigated. Here, we report our recent results in the production and  
74 characterization of conducting and magnetic PANI/Fe<sub>3</sub>O<sub>4</sub> composites exploring at the same  
75 time the effect of the Fe<sub>3</sub>O<sub>4</sub> NP size on their catalytic activity and the variation of the  
76 electromagnetic properties of the materials as function of the NP size.

77

78

79

## Experimental

### 80 *Materials*

#### 81 *Chemicals*

82 All chemicals were bought from Merck and used without any purification process. Acetone  
83 (Aldrich) was distilled over KMnO<sub>4</sub> and stored under argon before use in the synthesis of 2.3  
84 nm NPs.

85

#### 86 *Synthesis of 2.3 nm magnetite NPs coated with oleic acid and derived from iron solvated metal* 87 *ions (SMA).*

88 The synthesis of Fe-SMA was carried out in a static metal vapor synthesis reactor described  
89 elsewhere (Evangelisti *et al.*, 2015) and equipped with an alumina-coated tungsten crucible  
90 heated by Joule effect with a generator with a maximum power of 2 kW. Fe-solvated metal  
91 atoms (SMA) were prepared according to a previously described procedure (Barbaro *et al.*,  
92 2015; Campisi *et al.*, 2019). Briefly, Fe vapors generated in high vacuum ( $1 \cdot 10^{-5}$  mbar) by  
93 resistive heating of an alumina-coated tungsten crucible, filled with approximately 300 mg of  
94 iron, were co-condensed at  $-196$  °C with acetone vapor (100 mL) in the glass reactor chamber  
95 for 1 h. The reactor chamber was then warmed to the melting point of the solid matrix (ca.  $-95$   
96 °C), and the resulting brown Fe-solvated metal atoms (SMA) solution (95 mL) was siphoned  
97 at a low temperature into a Schlenk tube under argon atmosphere. Oleic acid (1 mL) was added  
98 to the Fe-SMA at low temperature ( $-40$ °C) under gentle stirring, and then was left overnight at  
99 room temperature to the open air. In these conditions, a red-brown precipitate was formed,  
100 which was collected by centrifugation. The precipitate was dissolved in *n*-hexane (50 mL),  
101 precipitated with acetone (50 mL) and collected by centrifugation. This latter procedure was

102 repeated three times to remove the excess of oleic acid. The solid was then dispersed in toluene  
103 (75 mL). The iron content of the toluene dispersion, measured by the ICP-OES procedure  
104 described below, resulted 2.60 g/L.

105

106 *Synthesis of 10.9 nm magnetite NPs coated with oleic acid.*

107 The NPs were synthesized by a modification of a published procedure (Hyeon *et al.*, 2001).  
108 Oleic acid (2.68 mL, 8.51 mmol) was dissolved in dioctyl ether (12 mL) in a 100 mL three-  
109 neck round-bottom flask, equipped with condenser and thermometer, under magnetic stirring  
110 and N<sub>2</sub> atmosphere. The solution was subjected to three vacuum–N<sub>2</sub> cycles at RT and then  
111 heated to 105 °C. Three vacuum–N<sub>2</sub> cycles were carried out at 105 °C. Next, iron pentacarbonyl  
112 (280 µL, 2.13 mmol) was injected into the solution and the reaction mixture was heated to reflux  
113 (*ca.* 285 °C) at a rate of 3 °C/min using a programmable heating unit. The solution turned black  
114 after 50 min at reflux and was aged for an additional hour before cooling to RT. The NPs were  
115 precipitated from the reaction mixture by adding acetone (60 mL), separated by centrifugation,  
116 and dispersed in petroleum ether (45 mL). To further purify the NPs, acetone (60 mL) was  
117 added to the NP dispersion and the NPs were collected by centrifugation and dispersed in  
118 toluene (23 mL). The iron content of the toluene dispersion, measured by the UV-Vis procedure  
119 described below, was 9.7 g/L.

120

121 *Synthesis of 26.0 nm magnetite NPs coated with oleic acid.*

122 The NPs were synthesized by a modification of a published procedure (Park *et al.*, 2004). The  
123 metal precursor Fe(III) trioleate (FeOl<sub>3</sub>) was synthesized as follows. Potassium oleate (5.77 g.,  
124 18 mmol) and FeCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in a mixture of H<sub>2</sub>O (10 mL) and EtOH (12 mL) in  
125 a 100 mL round-bottom flask under magnetic stirring and N<sub>2</sub> atmosphere. Hexane (21 mL) was  
126 added to the reaction mixture, which was then heated to 70 °C for 4 h. After cooling to RT, the  
127 mixture was transferred to a 100 mL separatory funnel and the aqueous phase discarded. The  
128 red-brown organic phase was washed with deionized water (2 x 10 mL) and with saturated  
129 aqueous NaCl solution (2 x 40 mL). The organic phase was evaporated under reduced pressure  
130 and the waxy red-brown FeOl<sub>3</sub> dried under vacuum (rotary pump) at 50 °C (oil bath) for a few  
131 hours. To synthesize the NPs, FeOl<sub>3</sub> (1.27 g, 1.52 mmol) and oleic acid (240 µL, 0.76 mmol)  
132 were dissolved in trioctylamine (13 mL) in a 50-mL three-neck round-bottom flask, equipped  
133 with condenser and thermometer, under magnetic stirring and N<sub>2</sub> atmosphere. The reaction  
134 mixture was heated to reflux (*ca.* 360 °C) at a rate of 10 °C/3 min and aged for 30 min using a  
135 programmable heating unit. After cooling to RT, the NPs were precipitated from the reaction

136 mixture by adding acetone (60 mL), separated by centrifugation, and dispersed in toluene (15  
137 mL). To purify the NPs, this procedure was repeated two more times. The iron content of the  
138 toluene dispersion, measured by the UV-Vis procedure described below, was 0.68 g/L. Such  
139 low concentration was required to ensure colloidal stability of these NPs.

140

#### 141 *Determination of the iron content of NP dispersions*

142 ICP-OES procedure. The Fe content in SMA-derived NPs was determined by inductively  
143 coupled plasma-optical emission spectroscopy (ICP-OES) (ICAP 6300 Duo, Thermo Fisher  
144 Scientific) and an external calibration methodology. The limit of detection (LOD) calculated  
145 for iron as 5 ppb. For the analysis, the toluene dispersion of SMA-derived NPs (0.5 mL) was  
146 heated in a porcelain crucible over a heating plate and the solvent was evaporated. The solid  
147 residue was dissolved in aqua regia (2 mL), heated until complete evaporation and the solid  
148 residue was then dissolved in 0.5 M aqueous HCl. The iron content was then measured by ICP-  
149 OES.

150 UV-Vis procedure. This procedure is described in detail in (Mondini *et al.*, 2015) and is here  
151 briefly outlined. About 0.1 mL of toluene NP dispersion is dissolved in aqua regia and  
152 evaporated. The residue is re-dissolved in 0.1 M HCl and the solution is buffered with PBS (pH  
153 7). The solution is then treated with tiron in excess to form the red iron complex  $[\text{Fe}(\text{tiron})_3]^{3-}$   
154 that is spectrophotometrically determined by a calibration method.

155

#### 156 *PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites preparation using H<sub>2</sub>O<sub>2</sub> as the oxidant*

157 500 mg of *N*-4-(aminophenyl)aniline (aniline dimer, AD) were dispersed in 30 mL of water  
158 acidified with 2.7 mL of HCl 1 M (AD/HCl = 1, molar ratio). The mixture was stirred for 30  
159 minutes. Then, 1.2 mL of an aqueous of H<sub>2</sub>O<sub>2</sub> 35% was added (H<sub>2</sub>O<sub>2</sub>/AD = 5, molar ratio,  
160 followed by different amounts of Fe<sub>3</sub>O<sub>4</sub> NPs. After 24 h, a dark green solid was recovered by  
161 filtration, washed with water and acetone abundantly until clearness of the mother liquors and  
162 dried in an oven at 60°C until it reached a constant weight.

163

#### 164 *PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites preparation using O<sub>2</sub> as the oxidant*

165 500 mg of *N*-4-(aminophenyl)aniline (aniline dimer, AD) were dispersed in 30 mL of water  
166 acidified with 2.7 mL of HCl 1 M (AD/HCl = 1, molar ratio). The mixture was stirred for 30  
167 minutes and then different amounts of Fe<sub>3</sub>O<sub>4</sub> NPs were added. The reaction mixture was stirred  
168 under pressure of molecular oxygen (3 bar) for 72 h at 80°C. Finally, a dark green solid was

169 recovered by filtration, washed with water and acetone abundantly until clearness of the mother  
170 liquors and dried in an oven at 60°C until it reached a constant weight.

171

### 172 *Materials Characterization*

173 The TEM images, electron diffraction (ED) patterns, Electron Energy Loss Spectroscopy  
174 (EELS) data, and Energy Filtered (EF-TEM) TEM images were recorded by a ZEISS LIBRA  
175 200FE TEM that operates at 200kV and is equipped with a second generation in-column  $\Omega$   
176 filter and a HAADF detector for STEM imaging. The samples were prepared by dropping 7  $\mu$ l  
177 of NP dispersion on a copper grid coated with a 1-3 nm carbon film and letting it dry overnight.  
178 The magnetite NPs were colloiddally dispersed in toluene, whereas the composite samples were  
179 suspended in isopropanol. TEM and EF-TEM Images were processed by means of the iTEM  
180 TEM Imaging Platform software (Olympus) and the NP size distribution was measured by the  
181 software PEBBLES (Mondini, *et al.*, 2012).

182 FT-IR spectra of composites were recorded in the transmittance mode in the range 500-4000  
183  $\text{cm}^{-1}$  at 64 scans per spectrum and a 2  $\text{cm}^{-1}$  resolution by JASCO FT/IR-410 spectrophotometer  
184 (JASCO Corporation, Tokyo, Japan). A small amount of each sample was dispersed in KBr and  
185 compressed in 13 mm diameter pellets with a 10-ton hydrostatic press for 15 min.

186 X-ray powder diffraction (XRPD) analyses were carried out in a  $2\theta$  range between 10° and  
187 80° on a Philips PW 3710 Bragg-Brentano goniometer (Philips, Amsterdam, Netherlands)  
188 equipped with a scintillation counter, a slit with 1° divergence, a receiving slit of 0.2 mm and a  
189 0.04° Soller slit system. A graphite-monochromatic Cu  $K\alpha$  radiation was adopted at a nominal  
190 X-ray power of 40 kV  $\times$  40 mA.

191 The metal loss in the  $\text{Fe}_3\text{O}_4/\text{PANI}$  composites was determined by atomic absorption  
192 spectroscopy on a AAAnalyst 100 PerkinElmer instrument.

193 Magnetization measurements of composites synthesized using  $\text{H}_2\text{O}_2$  were carried out by a  
194 Quantum Design MPMS XL-5 SQUID magnetometer. Weighted amounts of composite were  
195 sealed in Teflon tape. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves  
196 were recorded in the 5-300 K range. After cooling the sample from 300 to 5 K in zero field, the  
197 ZFC magnetization was recorded on heating to 300 K using a measuring field  $H_{\text{meas}} = 10$  Oe.  
198 Next, the FC magnetization was measured ( $H_{\text{meas}} = 10$  Oe) while cooling the sample from 300  
199 to 5 K under  $H_{\text{cool}} = 10$  Oe. In the case of the sample with the largest NPs (PANI/NP27), the  
200 highest temperature was set to 350 K. Magnetization isotherms (hysteresis loops) were recorded  
201 between +50 kOe and -50 kOe at 5 K after cooling in zero magnetic field. All data were  
202 corrected for the diamagnetism of the sample holder and PANI and then scaled to the NP mass.

203 The ac magnetic properties were determined using an Agilent 4395A impedance analyzer using  
204 a coaxial short 16454A magnetic material test fixture, and a test of the dielectric properties was  
205 performed using a parallel plate method with the 16453A dielectric material test fixture.

206

207

208

## Results and discussion

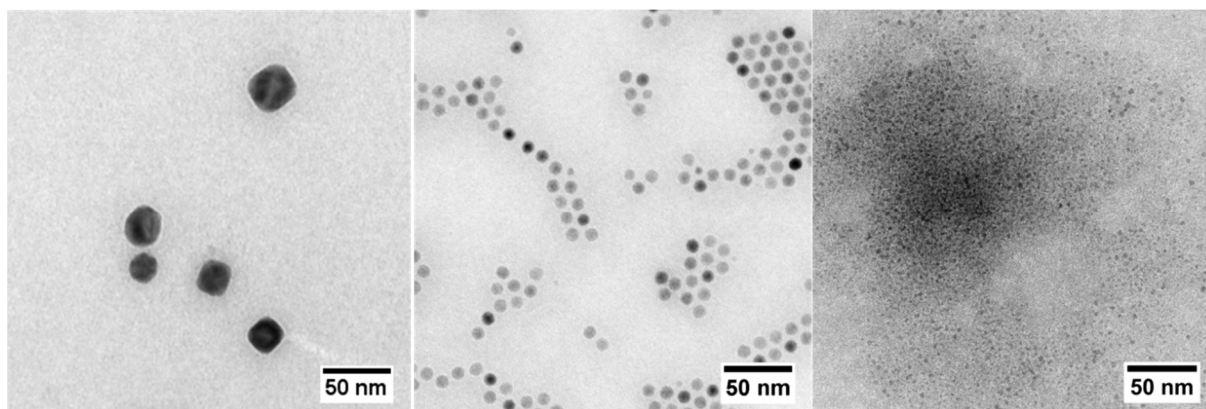
### 209 *Magnetite nanoparticles*

210 To study how the NP size affects the catalytic polymerization of AD and the properties of the  
211 resulting nanocomposite, we prepared magnetite NPs of different size by different procedures,  
212 each yielding NPs with good size dispersity and uniform shape. We used thermal decomposition  
213 to prepare medium and large NPs (Hyeon *et al.*, 2001; Park *et al.*, 2004), whereas very small  
214 NPs were synthesized by metal vapor synthesis technique (Barbaro *et al.*, 2015; Campisi *et al.*,  
215 2019). TEM images of the NP samples are reported in Figure 1. We obtained the NP  
216 morphological parameters by analyzing the TEM images using the Pebbles software  
217 (Mondini, *et al.*, 2012) and collected them in Table 1 (The histograms of the NP diameter can  
218 be found in the ESI) The three NP samples have largely different size: the diameters span more  
219 than an order of magnitude (2.3 to 27 nm) while the surface (related to the catalytic activity)  
220 and the volume (related to the magnetic properties of the composite) span more than two and  
221 three orders of magnitude, respectively. The size dispersion is good to excellent. The 28%  
222 dispersion of NP2 may seem large but one should note that the standard deviation of 0.64 nm  
223 is smaller than the magnetite cell size (0.84 nm). All NPs have spherical shape, except for the  
224 largest nanoparticles in NP27 that display cuboidal shape (see ESI for further TEM images of  
225 NP27). The crystal phase of the NP27 and NP10 samples was confirmed to be spinel (cubic  
226 ferrite) by ED (see ESI). No diffraction ring can be seen in the ED pattern of NP2 NPs. As  
227 already reported (Barbaro *et al.*, 2015), such small NPs are crystalline, and the absence of  
228 diffraction rings can then be ascribed to the very wide breadth of the rings. Finally, we note that  
229 in this paper, for the sake of clarity, we use the term “magnetite” or “Fe<sub>3</sub>O<sub>4</sub>” NPs to indicate  
230 iron oxide NPs with cubic ferrite crystal structure and composition Fe<sub>3-x</sub>O<sub>4-x</sub> ( $0 \leq x \leq 1$ ), varying  
231 between magnetite and maghemite.

232

233





234

235 **Figure 1.** TEM images of as synthesized NPs. a) NP27, b) NP10 c) NP2.

236

237 **Table 1.** Parameters of the distribution of the diameter of as-synthesized magnetite NPs. The  
 238 number of measured NPs  $N$  is reported along with the mean, standard deviation, and variation  
 239 coefficient of the diameter distribution.

Sample	$N$	Mean (nm)	Standard deviation (nm)	Variation coefficient (%)
NP2	463	2.3	0.64	28
NP10	1417	10.0	0.43	4.3
NP27	181	27.1	4.3	16

240

241

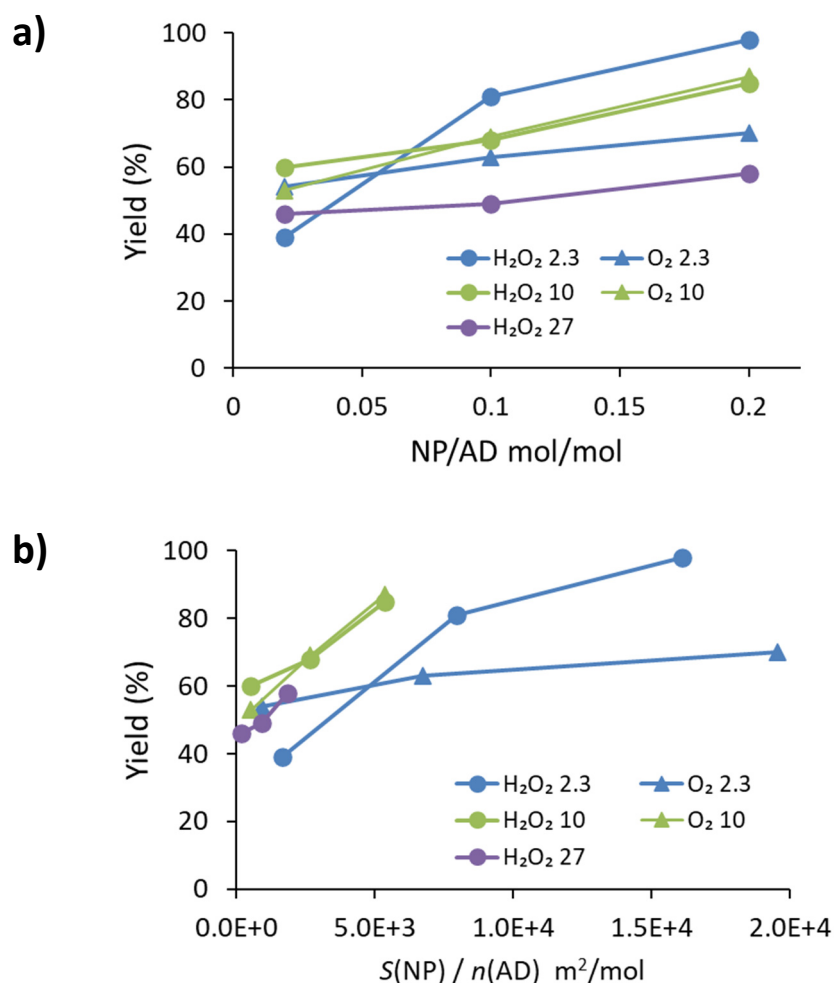
#### 242 *Polymerization of AD in the presence of $Fe_3O_4$ nanoparticles*

243 The dependence of the catalytic activity of  $Fe_3O_4$  NPs on their size was evaluated in the AD  
 244 oxidative polymerization. The catalytic performance of the NPs is assessed keeping in mind  
 245 that the NPs are both the catalyst and the magnetic load.

246 In Figure 2 the yield (mass %) of composites PANI/ $Fe_3O_4$ NPs is plotted versus the NP/AD  
 247 molar ratio, where the numerator is the amount of  $Fe_3O_4$  contained in the NPs.

248

249



250 **Figure 2.** Yield (mass %) of composite from the AD polymerization in the presence of  
 251 magnetite NPs. The yield is plotted as a function of (a) the NP/AD molar ratio and (b) the ratio  
 252 of the NP surface area  $S$  to the molar amount  $n$  of AD.

253

254 The NP/AD molar ratio was chosen so to explore a NP/AD range that would reasonably yield  
 255 composites with the desired electrical and magnetic properties. As previously reported, the  
 256 oxidant used for the polymerization reaction (H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub>) does not significantly affect the  
 257 properties of the PANI/Fe<sub>3</sub>O<sub>4</sub> composites (Della Pina *et al.*, 2012). Because H<sub>2</sub>O<sub>2</sub> is especially  
 258 attractive for the liquid-phase oxidation, due to the high percentage of active oxygen and the  
 259 production of water as only by-product, we here focused on composites obtained using H<sub>2</sub>O<sub>2</sub>.  
 260 Polymerizations carried out using O<sub>2</sub> as the oxidant are included for comparison.

261 In all experimental conditions explored, the yield increases with the amount of NPs, confirming  
 262 the catalytic role of the NPs. More insight can be gained when the yield is plotted as a function  
 263 of the ratio  $S/n(AD)$ , where  $S$  is the total core surface area of the NPs and  $n(AD)$  is the molar  
 264 amount of AD (Figure 2b). The area  $S$  is estimated from the total mass of Fe<sub>3</sub>O<sub>4</sub> in the composite

265  $m$  and their mean surface area  $\langle s \rangle$  and volume  $\langle v \rangle$  measured from TEM images as  $S = m \langle s \rangle$   
266 /  $\rho \langle v \rangle$ , where  $\rho = 5.17 \text{ g/cm}^3$  is the density of magnetite. When small NP2 are used, a  
267 significant fraction of the NPs is not embedded in the final composite (see ESI). We corrected  
268 the data for NP2 in Figure 2b by considering the surface of embedded NPs only. The lack of  
269 smallest NPs can be attributed to their very high surface area that makes them more sensitive  
270 to the environment. The stability of such small particles is difficult to study and aggregation  
271 and dissolution phenomena have to be considered.

272 The yield vs.  $S/n(\text{AD})$  data for the larger NPs (NP10 and NP27) is scarcely affected by the NP  
273 size or oxidant. They cluster along a straight line, indicating that the slow initial steps of the  
274 polymerization (Tzou and Gregory, 1992) occur on the surface of the NP inorganic core. This  
275 linear behavior extends to high conversion, suggesting that the NPs are stable against  
276 aggregation in the reaction conditions.

277 The yield of NP2 is always lower than that of the larger NPs. When  $\text{H}_2\text{O}_2$  is used as an oxidant,  
278 the yield data of NP2 is parallel to that of the larger NPs but shifted to the right (Figure 2b).  
279 This suggests that partial NPs aggregation occurs during the polymerization, as confirmed by  
280 TEM (see Figure 4 below), thus decreasing the available active sites for the AD oligomerization  
281 and hindering transport of AD to them. When  $\text{NP/AD} = 0.2 \text{ mol/mol}$ , parallelism is lost as the  
282 yield levels off because most of the AD has undergone polymerization. When NP2 are used  
283 with  $\text{O}_2$ , the yield at  $\text{NP/AD} = 0.02 \text{ mol/mol}$  is comparable to that of the larger NPs showing  
284 that the NP surface is as active as in the other cases. However, the yield increases very slowly  
285 with the  $S/n(\text{AD})$  ratio. We admit that we could not find a better explanation for this behavior  
286 than invoking extensive NP aggregation when the NP/AD ratio is larger than 0.02 and  $\text{O}_2$  is  
287 used as an oxidant.

288 In summary, magnetite NPs with size from 2.3 to 27 nm are able to catalyze the polymerization  
289 of AD, using either  $\text{H}_2\text{O}_2$  or  $\text{O}_2$  as oxidant, and with yield ranging from 39% to 98%. It is  
290 therefore feasible to produce magnetic PANI composites with magnetite NPs spanning a size  
291 range wider than an order of magnitude.

292

### 293 *PANI/Fe<sub>3</sub>O<sub>4</sub>NPs characterization*

294 All composites were characterized by different techniques in order to investigate the effect of  
295 the presence of the magnetic NPs in the final materials. Here, we report the results obtained for  
296 the composites synthesized in the presence of  $\text{H}_2\text{O}_2$  as the oxidant and using a NP/AD molar  
297 ratio of 0.2, because they are the most representative. These three composites are named  
298 PANI/NP2, PANI/NP10, and PANI/NP27.

299 The amount of magnetic NPs inside the composites was indirectly evaluated by the analysis of  
300 iron in the mother liquors obtained after the filtration of the materials. The results show that  
301 only for the composite PANI/NP2 the content of NPs within the polymeric matrix is not  
302 quantitative (16% of Fe<sub>3</sub>O<sub>4</sub>, cfr. ESI). In all other cases, during the polymerization reaction the  
303 inorganic component is completely embedded in the polymeric matrix (33% of Fe<sub>3</sub>O<sub>4</sub> in  
304 PANI/NP10, 31% of Fe<sub>3</sub>O<sub>4</sub> in PANI/NP27).

305

#### 306 *Fourier-transform infrared (FT-IR) spectroscopy*

307 All composites comprise a polymeric matrix consisting of PANI in the form of conducting  
308 emeraldine, as shown by characteristic infrared bands (see ESI). In particular, the broad band  
309 between 3400-1800 cm<sup>-1</sup> confirms that the polymer was obtained in highly conjugated form  
310 (Šeděnková *et al.*, 2008), the band at 1570 and 1490 cm<sup>-1</sup> are assigned to the C=C stretching  
311 vibration of quinoid and benzenoid rings respectively, whereas C-N stretching vibration is  
312 responsible of the band at 1304 cm<sup>-1</sup> (Cionti *et al.*, 2020). The band at 1240 cm<sup>-1</sup> is due to C-  
313 N<sup>+•</sup> stretching vibration (Šeděnková *et al.*, 2008) and that to 1146 cm<sup>-1</sup> derives from Q=NH<sup>+</sup>-  
314 B, B-NH<sup>+</sup>-B stretching (Mišurović *et al.*, 2019). C-H out-of-plane bending vibrations of 1,4-  
315 disubstituted aromatic rings lead to the bands in the 820-800 cm<sup>-1</sup> range (Socrates, 2004).  
316 Finally, the two bands at 800 and 759 cm<sup>-1</sup> suggest the presence of C-H vibrations of 1,2,4-  
317 trisubstituted and 1,2-disubstituted rings (Socrates, 2004).

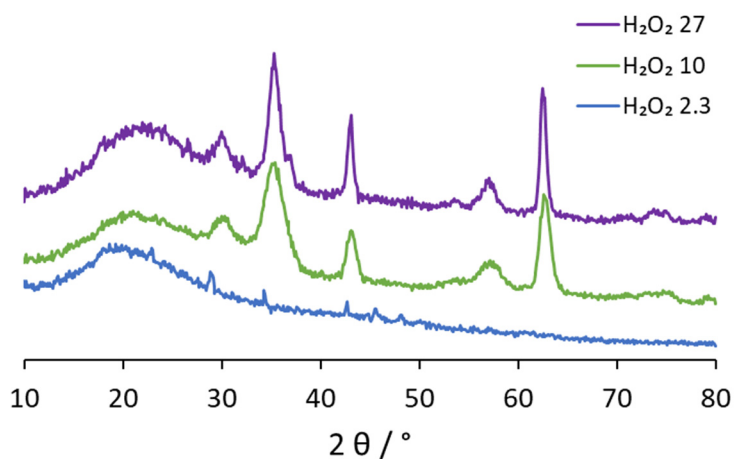
318

#### 319 *X-ray powder diffraction (XRPD)*

320 The XRPD patterns of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites are reported in Figure 3.

321

322



323

**Figure 3.** XRPD patterns of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites.

324

325

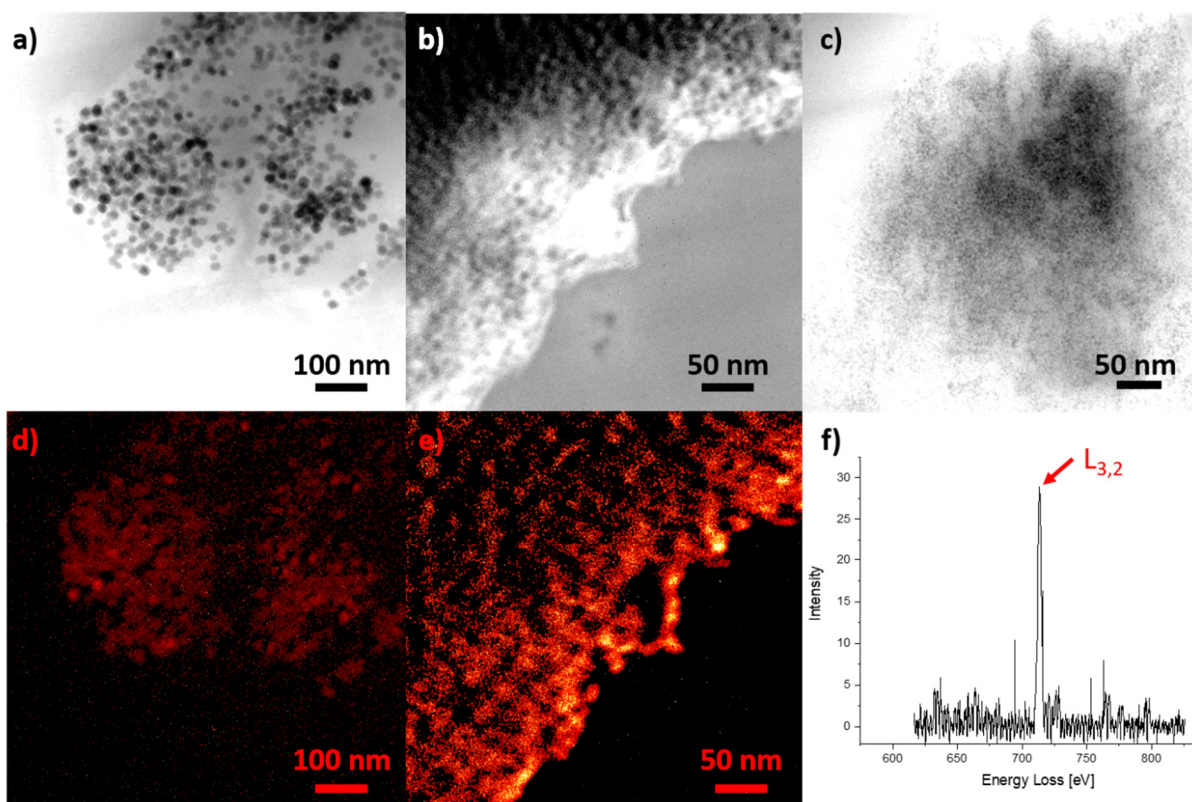
326 The XRPD patterns of the composites show the typical Bragg diffraction peak at  $2\theta \approx 20^\circ$  for  
327 the polymer. Peaks at  $2\theta = 30.1, 35.6, 43.2, 53.8, 57.2,$  and  $63.0^\circ$  are prominent in the patterns  
328 of composites including NP10 and NP27. They can be assigned to cubic ferrite (spinel) NPs,  
329 showing that during the synthesis of the composites the magnetic NPs were embedded into the  
330 polymer. The XRPD pattern of PANI/NP2 composites only shows the peak of PANI. Since the  
331 presence of small NP2 in the composite is established by TEM techniques (see the net section),  
332 the absence of the peaks typical of the spinel structure could be due to the amorphousness of  
333 the NPs. However, NP2 were already shown to be crystalline (Barbaro *et al.*, 2015). Therefore,  
334 the inability to detect the spinel peaks is ascribed to combined effect of the larger peak width  
335 expected for smaller NPs (about fourfold wider than for PANI/NP10) and the lower magnetite  
336 content in PANI/NP2.

337

### 338 *TEM microscopy*

339 The TEM investigation of the composites has two goals: to establish the presence of magnetite  
340 NPs within the composites and to ascertain whether the NPs underwent morphological changes  
341 during the polymerization reaction. The investigation could not rely on conventional TEM  
342 imaging only because the composite granules are thick enough to be opaque to the electron  
343 beam except for the very edges of the granules (see ESI).

344



345

346 **Figure 4.** TEM of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites. EF-TEM images filtered at 30 eV of a)  
 347 PANI/NP27, b) PANI/NP10, and c) PANI/NP2. False-color EF-TEM images filtered at 713 eV  
 348 providing Fe maps of d) PANI/NP27 and e) PANI/NP10. The sample regions imaged are the  
 349 same as in a) and b). f) Background-subtracted EELS spectrum of PANI/NP2 showing the iron  
 350 *L*<sub>3,2</sub> peak.

351

352 We thus resorted to energy-filtered TEM (EF-TEM) techniques by which the image is formed  
 353 by detecting electrons that lost energy during the interaction with sample (Figure 4). In images  
 354 filtered at 30 eV loss, the contrast between NPs and polymer is enhanced since electrons can  
 355 lose 30 eV only by interacting with nearly-free aromatic  $\pi$  electrons, the so-called plasmonic  
 356 mode, so that the polymer matrix appears light gray whereas the NPs appear dark. The enhanced  
 357 contrast between NPs and polyaniline allowed us to identify the NPs inside the composite  
 358 (Figure 4a-c). The NPs are well dispersed within the composites. Some NP agglomeration was  
 359 observed in the case of the PANI/NP2 (dark region in Figure 4c). NP measurement was  
 360 unfortunately reliable only for PANI/NP10 and PANI/NP27. The results are collected in Table  
 361 2. Comparing this data with those in Table 1, one can see that the NP10 are unchanged while  
 362 the NP27 decreased in size by about 2 nm during the polymerization. In both cases, the size

363 dispersion is unchanged. We can therefore expect that the properties of the magnetic NPs are  
 364 unaffected by the polymerization, except for what relates to the interparticle distance.

365

366 **Table 2.** Parameters of the distribution of the diameter of magnetite NPs present in  
 367 PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites. The number of measured NPs  $N$  is reported along with the  
 368 mean, standard deviation, and variation coefficient of the diameter distribution.

Composite	$N$	Mean (nm)	Standard deviation (nm)	Variation coefficient (%)
PANI/NP10	335	10.2	0.63	6.2%
PANI/NP27	207	25.0	4.6	18%

369

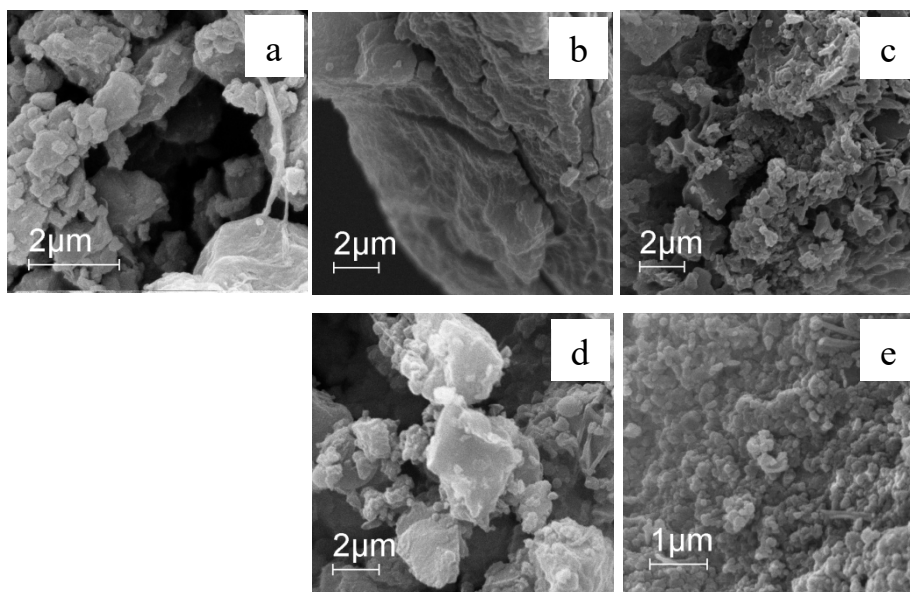
370

371 We also confirmed the presence of iron in the embedded NPs detecting electrons with energy  
 372 loss of 713 eV, typical of iron ( $L_{2,3}$  peak). The EF-TEM iron maps of PANI/NP27 and  
 373 PANI/NP10 (Figure 4d,e) show that the iron signal coincides with the NPs as seen in the  
 374 corresponding 30 eV loss images (Figure 4a,b). In the case of PANI/NP2, the intensity of the  
 375 EF-TEM iron map was too low to reliably identify the NPs within the composite. The presence  
 376 of iron in PANI/NP2 was established thanks to the EELS spectrum that displays the iron  $L_{3,2}$ ,  
 377 peak at 713 eV (Figure 4f). The crystal structure of the embedded NPs was analyzed by ED  
 378 (see ESI): the ED patterns confirmed that PANI/NP27 and PANI/NP10 comprise cubic ferrite  
 379 NPs. PANI/NP2 gave no detectable diffraction rings.

380

381 *SEM microscopy*

382 In Figure 5, SEM images of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites are displayed.



383

384 **Figure 5.** SEM images of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites (a: PANI/NP27, b: PANI/NP10, c:  
385 PANI/NP2) or O<sub>2</sub> as oxidant (d: PANI/NP10, e: PANI/NP2).

386

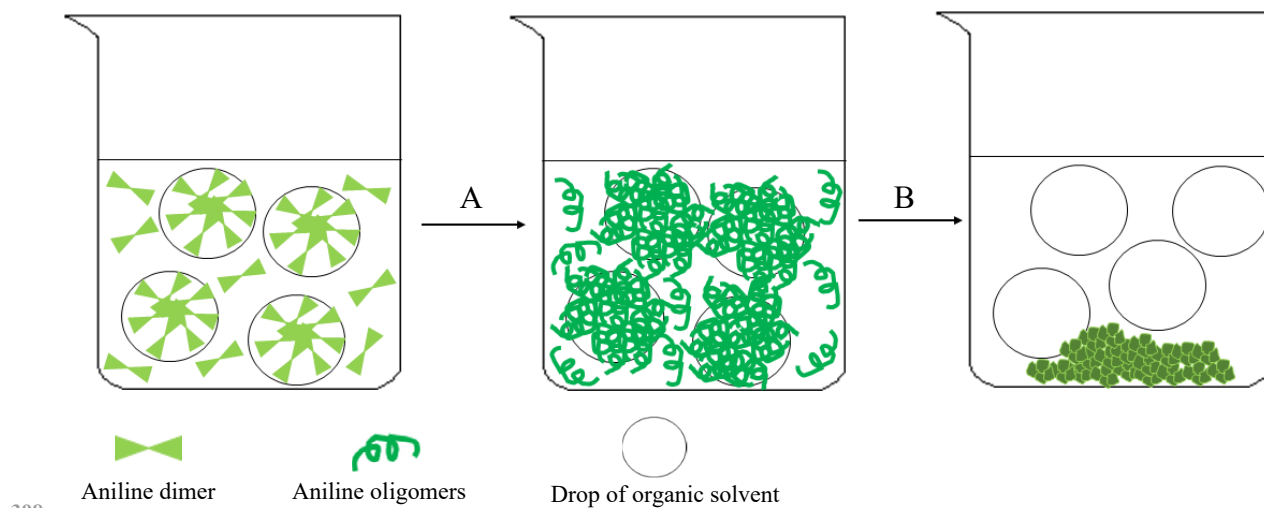
387 When compared to PANI obtained by the oxidative polymerization of AD in the presence of a  
388 homogeneous catalyst, e.g., Fe(III) (Della Pina *et al.*, 2018), PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites  
389 display a more globular morphology, sparsely intermixed with nanorods. As previously  
390 reported (Della Pina *et al.*, 2012), when AD hydrochloride is polymerized by H<sub>2</sub>O<sub>2</sub> in water in  
391 the presence of magnetite NPs dispersed in an organic phase as the catalyst, an interfacial  
392 polymerization occurs. Thanks to its solubility in organic solvents, AD hydrochloride can  
393 diffuse into the organic phase where Fe<sub>3</sub>O<sub>4</sub> NPs are present, and the oxidative polymerization  
394 can take place at the interface between the organic and aqueous phases (Scheme 1).

395

396

397





399 **Scheme 1.** Proposed mechanism of nanoglobules formation. A) oligomerization step, B)  
400 polymerization step.

401

402 During the first steps of the reaction, only PANI oligomers are produced that are soluble in  
403 organic solvents and, as a consequence, they can diffuse inside the toluene drops. When the  
404 polymeric chains grow longer, they become insoluble and precipitate from the reaction mixture  
405 leading to globular materials.

406 Even though this hypothesis of mechanism seems to be in contrast with that previously reported  
407 (Della Pina *et al.*, 2012), it has to be considered that the amount of organic phase was changed  
408 and the catalysts were obtained by a different synthetic approach (co-precipitation reaction in  
409 Della Pina *et al.*, 2012, thermal decomposition here).

410

#### 411 *Magnetic properties*

412 The thermal behavior of the magnetization  $M$  of the PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites (oxidant:  
413 H<sub>2</sub>O<sub>2</sub>; NP/AD = 0.02 mol/mol) was investigated by means of ZFC/FC experiments (Figure 6).  
414 The main magnetic parameters are collected in Table 3. The ZFC/FC curves of the composites  
415 are widely different. Reversible behavior is indicated by the identity of the ZFC and FC data,  
416 which is clearly visible in the high temperature range for all composites. The reversibility  
417 corresponds to the superparamagnetic (SPM) regime where thermal agitation quickly flips the  
418 NP magnetization. Upon cooling the two curves diverge as soon as thermal agitation is not able  
419 to overcome the barrier for magnetization reversal of some NPs and irreversibility sets in. The  
420 irreversibility temperature  $T_{irr}$ , defined as the temperature at which the difference between the  
421 FC and the ZFC magnetization  $(M_{FC} - M_{ZFC})/M_{FC} = 3\%$ , is larger than RT for PANI/NP27, as  
422 low as 110 K for PANI/NP10, and probably less than 80 K for PANI/NP2 (in the latter case,

423 the smallness of  $M_{FC}-M_{ZFC}$  prevents an accurate determination of  $T_{irr}$ ). Thus, PANI/NP27  
 424 contains NPs both in the SPM and blocked regime even at RT, in agreement with the ideal RT  
 425 blocking diameter of magnetite (26 nm) (Coey, 2010).

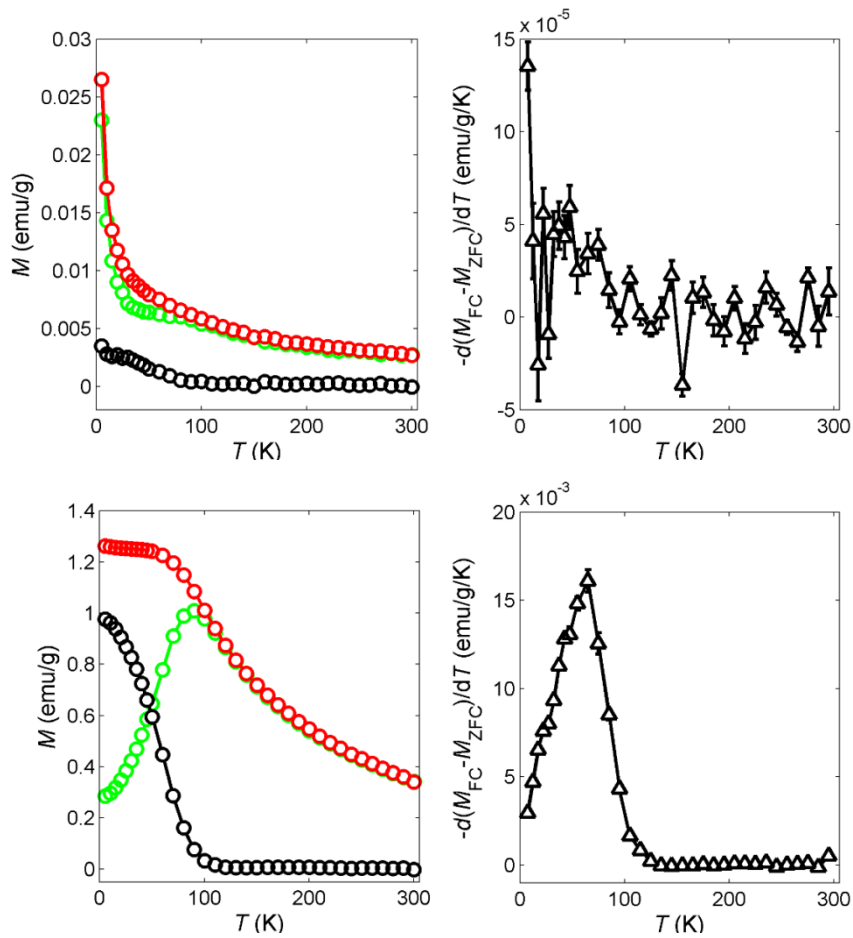
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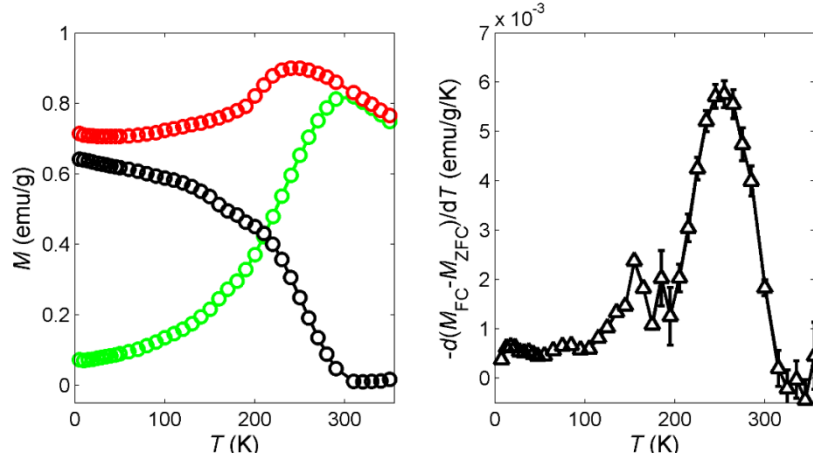
427 **Table 3.** Magnetic parameters of the ZFC/FC magnetization of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs composites.

Composite	$T_{irr}$ (K)	$T_{der}$ (K)	HWHH	
			(K)	$\langle T_b \rangle$ (K)
PANI/NP2	< 80 K	–	–	–
PANI/NP10	110	60	29	54
PANI/NP27	310	250	41	290

428

429





430 **Figure 6.** Thermal behavior of the low-field ( $H = 10$  Oe) magnetization of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs  
 431 composites. In the left panels, the ZFC (green) and FC (red) magnetizations are shown along  
 432 with their difference (black). In the right panels, the  $-d(M_{FC}-M_{ZFC})/dT$  derivative is plotted to  
 433 represent the distribution of the blocking temperatures. Top: PANI/NP2, middle: PANI/NP10,  
 434 bottom: PANI/NP27. The error bars represent 1 standard deviation; the error bars are not visible  
 435 when the standard deviation is smaller than the symbol size.

436

437 Upon further cooling below  $T_{irr}$ , more NPs enter the blocked regime. In this temperature region,  
 438 the three samples display largely different behavior.  $M_{FC}$  and  $M_{ZFC}$  of PANI/NP2 are similar  
 439 down to 5 K, showing that the NPs in this composite are subject to low barriers for  
 440 magnetization rotation, as expected for very small NPs. PANI/NP10 displays a strong decrease  
 441 of  $M_{ZFC}$  and a flattening of  $M_{FC}$  at low temperature. The larger difference between  $M_{FC}$  and  
 442  $M_{ZFC}$  corresponds to larger barriers. The  $M_{FC}$  and  $M_{ZFC}$  of PANI/NP10 and PANI/NP2 are  
 443 typical of weakly interacting NPs. In the case of PANI/NP27, both  $M_{FC}$  and  $M_{ZFC}$  decrease from  
 444 250 K down to 5 K, showing strong interparticle interactions and the onset of a frozen spin-  
 445 glass-like state where the magnetization is frozen in one of the many minima of a complex free-  
 446 energy landscape created by the magnetostatic interaction among the NPs. The presence and  
 447 freezing temperature of the spin-glass-like state agree with an estimate of the relative strength  
 448 of the magnetostatic interaction among the NPs (see ESI).

449 A representation of the magnetization rotation barriers of a composite (in terms of blocking  
 450 temperature  $T_b$ ) can be obtained as the derivative of the difference between the FC and ZFC  
 451 magnetization  $-d(M_{FC}-M_{ZFC})/dT$  (Figure 6, right panels) (Bruvera *et al.*, 2015). This  
 452 representation faithfully displays the distribution of  $T_b$  in the case of weakly-interacting NPs.  
 453 When a spin-glass-like state sets in, the concept of  $T_b$  of individual NPs is not appropriate but  
 454  $-d(M_{FC}-M_{ZFC})/dT$  however provides useful information about the barriers, (Woińska *et al.*,

455 2013) though they are a property of the whole sample and cannot be tied to individual NPs. The  
 456 mode  $T_{\text{der}}$  and half-width-half-height (HWHH) of the  $T_b$  distribution can be found in Table 3  
 457 along with the mean barrier  $\langle T_b \rangle$ . PANI/NP2 has barriers with  $T_b < 80$  K but  $T_{\text{der}}$  and  $\langle T_b \rangle$   
 458 could not be reliably determined. These barriers, which are related to a small part of the total  
 459 magnetization, as shown by the  $M_{\text{FC}} - M_{\text{ZFC}}$  difference, can be attributed to a few NP aggregates.  
 460 The barriers in PANI/NP10 are distributed about  $T_{\text{der}} = 60$  K ( $\langle T_b \rangle = 54$  K) and extend down  
 461 from 100 K (HWHH 29 K). A similar peak is observed in the PANI/NP27  $T_b$  distribution, but  
 462 it occurs at higher  $T_{\text{der}} = 250$  K ( $\langle T_b \rangle = 290$  K) with HWHH = 41 K. The barrier distribution  
 463 has a broad tail extending down to 5 K, which is related to collective barriers in the frozen state.  
 464 The  $T_b$  of our composites agree with the  $T_b$  measured for magnetite NPs in the  $d = 10$ -20 nm  
 465 range (Yun *et al.*, 2014) (see ESI for a detailed comparison).

466 To gain more insight into the magnetic properties of the composites, magnetization isotherms  
 467 were measured between  $-50$  and  $+50$  kOe at 5 K. The shape of these hysteresis loops (see ESI)  
 468 and the magnetic parameters collected in Table 4 confirm the almost complete magnetic  
 469 reversibility of PANI/NP2 at low temperature and the irreversible behavior of PANI/NP10 and  
 470 PANI/NP27.

471 In summary, these composite materials display a variety of magnetic behavior that can be  
 472 selected by choosing the NP size, e.g., the SPM regime can be shifted from RT to  $T \approx 5$  K.

473

474 **Table 4.** Magnetic parameters from the magnetization isotherm of PANI/Fe<sub>3</sub>O<sub>4</sub>NPs  
 475 composites. The isotherms were measured between  $-50$  and  $+50$  kOe at 5 K.

Composite	$M_{50}$ (emu/g) <sup>a,b</sup>	$M_{\text{rem}}$ (emu/g) <sup>a</sup>	$M_{\text{rem}} / M_{50}$	$H_c$ (kOe)
PANI/NP2	$55.2 \pm 0.8$	–	–	–
PANI/NP10	$53.4 \pm 0.7$	$12.8 \pm 0.2$	$0.24 \pm 0.02$	0.45
PANI/NP27	$42 \pm 1$	$6.2 \pm 2$	$0.15 \pm 0.04$	0.61

476 <sup>a</sup> Mass magnetization referred to the NP mass. <sup>b</sup> The magnetization at 50 kOe  
 477 ( $M_{50}$ ) is far from the saturation value.

478

479

#### 480 *Dynamic electromagnetic absorption and Ferromagnetic resonance*

481 Magnetic materials subjected to an external applied field may show losses attributed to different  
 482 phenomena, also frequency dependent. In quasi static conditions, losses are dominated by the  
 483 hysteresis loss associated to the reversal of the magnetization direction which occurs whenever  
 484 a portion of a domain wall moves between different pinning sites corresponding to two local

485 energy minima and some energy is dissipated to the crystal lattice. Dynamic losses due to the  
 486 flow of eddy currents and joule heating within the material under ac excitations are associated  
 487 to the magnetic flux variations. At higher frequencies, when flux penetration may be reduced  
 488 due to the skin effect, energy dissipation is caused by ferromagnetic resonance, occurring  
 489 whenever the frequency of the external ac magnetic field coincides to the Larmor precession  
 490 frequency of the magnetization vector. These effects tend to limit the useful frequency range of  
 491 magnetic materials in practical devices.

492 Due to their extremely small size, nanosized objects such as NPs do not exhibit large hysteresis  
 493 or dynamic losses and can thus be suitable as inductors even above the MHz frequency range.  
 494 In fact, NPs with diameters of the order of 10 nm are single domain and magnetization reversals  
 495 occur only through rotations, which produce very small dissipation with respect to hysteresis.  
 496 Dynamic losses due to large scale eddy currents are also suppressed in NPs, because inter-  
 497 particle conduction is hindered by the organic shell and losses arise at frequencies above 1 GHz  
 498 only due to the resonant magnetic behavior, and to verify this hypothesis dielectric  
 499 characterization was also performed up to the GHz range.

500 The real and imaginary part of the magnetic permeability using the following relations (Fiorillo,  
 501 2010):

502

$$503 \quad \mu' = 1 + \frac{Im\{\Delta Z_{in}^*\}}{f\mu_0 h \ln \frac{R_m}{r_m}} \quad (1)$$

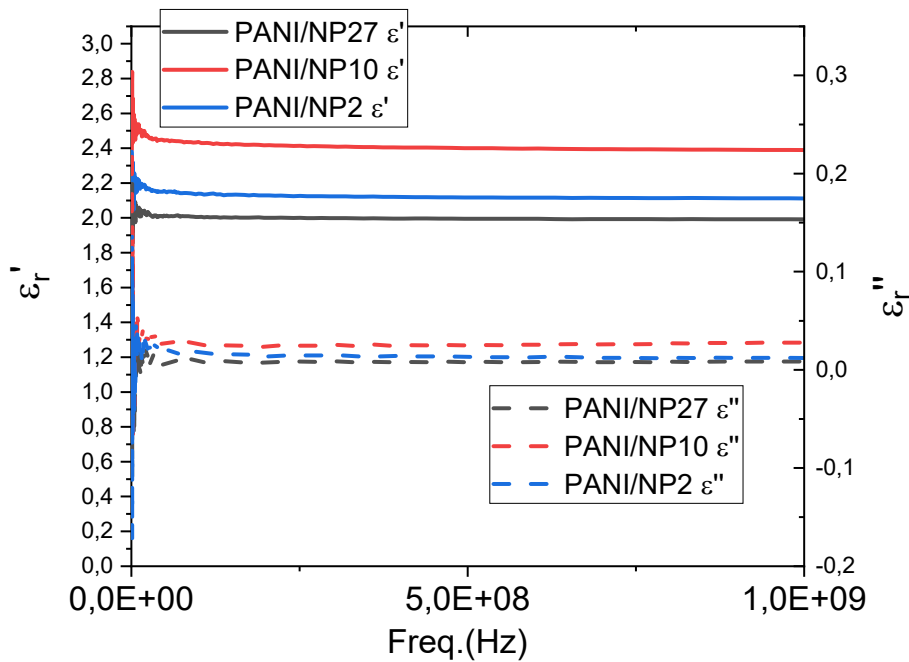
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$$505 \quad \mu'' = \frac{Re\{\Delta Z_{in}^*\}}{f\mu_0 h \ln \frac{R_m}{r_m}} \quad (2)$$

506

507 where  $h$ ,  $R_m$  and  $r_m$  are the thickness, the outside diameter, and the inside diameter of the ring  
 508 sample, respectively,  $\Delta Z_{in}^* = Z_{in,sample}^* - Z_{in,air}^*$ , where  $Z_{in,sample}^*$  and  $Z_{in,air}^*$  are the circuit  
 509 impedances in the the presence or absence of the toroidal sample and  $f$  is the frequency.  
 510 Capacitance and dielectric properties were determined directly and calibrated through a Teflon  
 511 reference, and show that the dielectric properties are constant across the spectrum observed up  
 512 to above 1 GHz, without any visible resonant absorption (Figure 7).

513



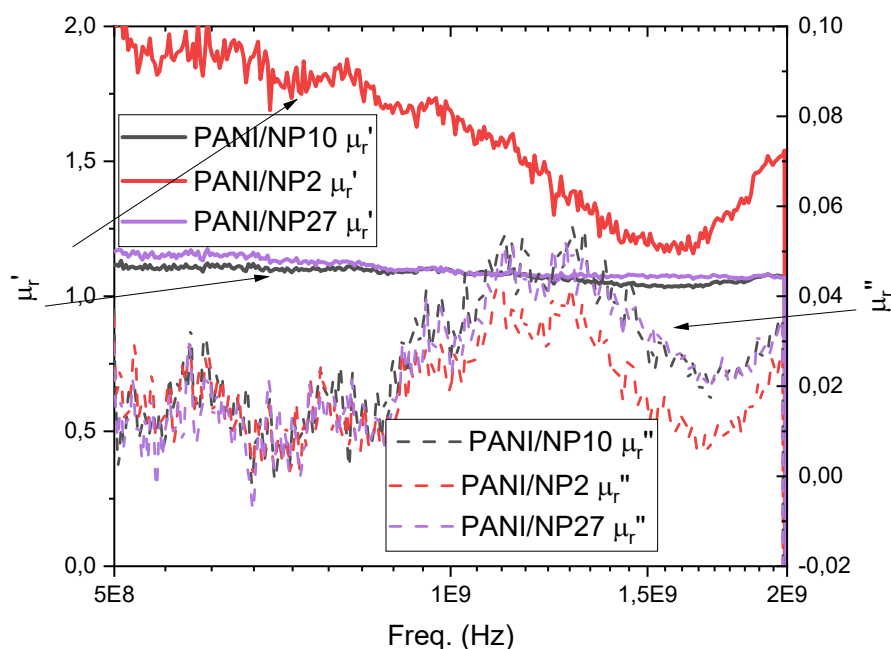
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515 **Figure 7.** Real ( $\epsilon_r'$ ) and imaginary ( $\epsilon_r''$ ) part of the relative permittivity of the PANI/Fe<sub>3</sub>O<sub>4</sub>NPs  
 516 composites. The data exhibits a rather flat behavior up to 1 GHz.

517

518 The ac permeability results (Figure 8) show that PANI/NP2, the composite with 2.3 nm single  
 519 domain NPs, with vanishing  $M_{rem}$  (Table 4) and higher static initial permeability, has the highest  
 520 real part of permeability also in ac. The other samples show relative permeabilities just slightly  
 521 above 1. All composites display a wide frequency peak of the imaginary part of the  
 522 permeability, which starts below 1 GHz and has a peak at 1.1-1.2 GHz, depending on the  
 523 composite, clearly showing that ac losses are only associated to the ferromagnetic resonance.  
 524 The large peak width reflects the distribution of particle dimensions and magnetic properties  
 525 (also due to exact size, chemical composition, etc.). These results, while compatible with  
 526 previous literature (Yun *et al.*, 2014), extend the experimental frequency range explored and  
 527 prove that PANI composites with very small Fe oxide particles are instrumental to the  
 528 successful use of these materials as energy absorbers in the GHz range.

529



530

531 **Figure 8.** Real ( $\mu_r'$ ) and imaginary ( $\mu_r''$ ) part of the relative permeability of the samples.  $\mu_r''$   
 532 shows an absorption behavior, due to the ferromagnetic resonance, at frequencies slightly above  
 533 1 GHz.

534

535

536

### Conclusions

537 We have shown that magnetite NPs spanning the size range from 2.3 to 27 nm are able to  
 538 catalyze the oxidative polymerization of the aniline dimer and remain within the polymer so to  
 539 form PANI/Fe<sub>3</sub>O<sub>4</sub> composites. The yields are in all cases high enough to be of practical  
 540 importance. Their dependence on the NP surface area shows that i) the NPs are stable against  
 541 aggregation in the reaction conditions, ii) the catalytic effect is due to the NPs (and not to Fe<sup>3+</sup>  
 542 ions leached into the aqueous phase), and iii) the NPs are a main factor affecting the  
 543 polymerization yield. The smallest NPs seem to be not completely stable in the reaction  
 544 conditions probably because of their very high surface area that makes them more sensitive to  
 545 surface effects such as aggregation and degradation. The embedded NPs retain the shape and  
 546 size of the pristine NPs and are well-dispersed in the PANI matrix.

547 The NPs in the composite do not interact by direct exchange, *i.e.*, they retain their magnetic  
 548 individuality thanks to the oleic acid coating that prevents direct contact between the NPs. This  
 549 enables easy modulation of the composite magnetic properties based on the NP size. Occurrence  
 550 of NP direct contact in the composite would have led to unpredictable magnetic properties

551 depending on the details of the polymerization. For the dynamic electromagnetic behavior, the  
552 imaginary part of the permeability only shows an absorption, not associated with any dielectric  
553 loss, but rather due to the ferromagnetic resonance, at frequencies slightly above 1 GHz. Our  
554 synthetic method thus provides a pathway to prepare composites with tailored magnetic  
555 properties by customizing the size of the magnetite NPs. It would also be conceivable to prepare  
556 composites containing NPs with different size in controlled proportion.

557

558

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562

563 **Conflict of interest.** The authors declare no conflict of interest.

564

565

### Supplementary data

566

567 Electronic Supplementary Material associated with this article can be found in the online  
568 version of this paper (DOI: xxxxxxxxxx).

569

570

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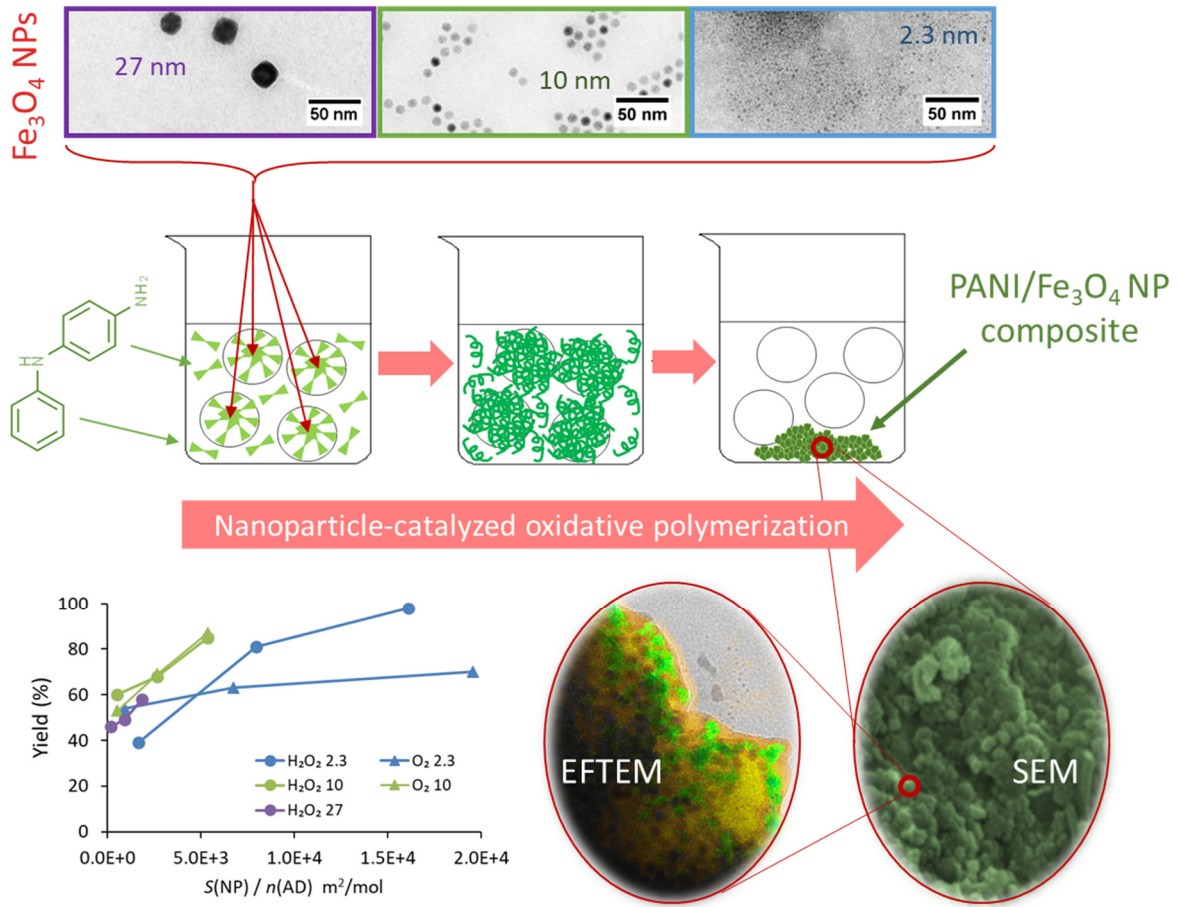
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681 **Graphical Abstract**

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