

## Experimental Supporting Information (ESI)

### XPS measurements

XPS measurements allowed us to monitor the changes of surface states of the magnetic nanoparticles (NPs) during the entire synthesis and functionalization pathway and to determine the thickness of the resulting polymer coating.

The XPS survey spectrum of the **bare NPs** presents characteristic peaks at 710, 783, 285 and 530 eV corresponding to Fe 2p<sub>3/2</sub>, Co 2p<sub>3/2</sub>, C 1s and O 1s. Carbon and oxygen peaks correspond essentially to organic residues adsorbed on the surface (DEG and cobalt acetate used for the polyol process). The relative intensities of iron and cobalt peaks allowed us to calculate the thickness of cobalt oxide shell.

We synthesized core-shell NPs composed of an iron oxide core and a cobalt oxide shell. The ratio of iron and cobalt peaks can be written in the Equation 1. <sup>1</sup>

$$\frac{I(\text{Co})}{I(\text{Fe})} = \frac{\sigma(\text{Co}) \times T_s(\text{Co}) \times \lambda[\text{Co}(\text{CoO})] \times C(\text{Co}) \times \left[ 1 - \exp\left(\frac{-d(\text{CoO})}{\lambda[\text{Co}(\text{CoO})] \times \cos\theta}\right) \right]}{\sigma(\text{Fe}) \times T_s(\text{Fe}) \times \lambda[\text{Fe}(\text{Fe}_3\text{O}_4)] \times C(\text{Fe}) \times \exp\left(\frac{-d(\text{CoO})}{\lambda[\text{Fe}(\text{CoO})] \times \cos\theta}\right)} \quad (\text{Eq. 1})$$

where  $\sigma(\text{Fe})$  and  $\sigma(\text{Co})$  are the photo-ionization cross section for Fe(2p<sub>3/2</sub>) and Co(2p<sub>3/2</sub>) signals respectively;  $T_s(\text{Fe})$  and  $T_s(\text{Co})$  are the analyser transmission functions of the spectrometer for iron and cobalt.

$\lambda[\text{Fe}(\text{Fe}_3\text{O}_4)]$ ,  $\lambda[\text{Fe}(\text{CoO})]$  and  $\lambda[\text{Co}(\text{CoO})]$  are the free paths of Fe(2p<sub>3/2</sub>) and Co(2p<sub>3/2</sub>) photoelectrons in Fe<sub>3</sub>O<sub>4</sub> and CoO oxide matrices respectively.

$C(\text{Fe})$  and  $C(\text{Co})$  are the number of Fe and Co atoms per unit oxide volume;  $\theta$  is the electron take-off angle (as a common approximation,  $\cos\theta$  is usually fixed to 0.5) and  $d(\text{CoO})$  is the thickness of the cobalt oxide shell. Considering R parameter equal to:

$$R = \frac{I(\text{Co})}{I(\text{Fe})} \times \frac{\sigma(\text{Fe})}{\sigma(\text{Co})} \times \frac{T_s(\text{Fe})}{T_s(\text{Co})} \times \frac{\lambda[\text{Fe}(\text{Fe}_3\text{O}_4)]}{\lambda[\text{Co}(\text{CoO})]} \times \frac{C(\text{Fe})}{C(\text{Co})} \quad (\text{Eq. 2})$$

One can write that:

$$R = \frac{1 - \exp\left(\frac{-2d(\text{CoO})}{\lambda[\text{Co}(\text{CoO})]}\right)}{\exp\left(\frac{-2d(\text{CoO})}{\lambda[\text{Fe}(\text{CoO})]}\right)} \quad (\text{Eq. 3})$$

All the ratio listed in Eq. (2) were inferred from the analysis of the high resolution Fe 2p and Co 2p XPS spectra.  $\lambda$  values (in nm) were calculated using the Dench and Seah equation specifically established for oxides<sup>15</sup>

$$\lambda(k) = 0.55E_k^{0.5} \times a_k^{1.5} \quad (\text{Eq. 4})$$

<sup>1</sup> D. Briggs, M. P. Seah. Practical surface analysis in Auger and X-ray photoelectron spectroscopy, Vol 1, 1990.

Where  $E_k$  and  $a_k$  are the kinetic energy (eV) of the ejected core electron and the  $k$  atom size, respectively.  $E_k$  values are tabulated while  $a_k$  ones are calculated using the following Equation (Eq 5):

$$a_k = \frac{A \times 10^{24}}{\rho \times n \times Na} \quad (\text{Eq. 5})$$

Where  $A$  is the molecular weight ( $\text{g mol}^{-1}$ ) of the  $k$  based oxide phase,  $\rho$  its density ( $\text{kg m}^{-3}$ ) and  $n$  the number of atoms per molecular formula unit.  $Na$  is the Avogadro number.

Using Eqs (4) and (5), we calculated  $\lambda[\text{Fe}(\text{CoO})] = 1.51 \text{ nm}$ ,  $\lambda[\text{Co}(\text{CoO})] = 1.44 \text{ nm}$  and  $\lambda[\text{Fe}(\text{Fe}_3\text{O}_4)] = 1.58 \text{ nm}$ . Replacing these parameters by their calculated values in Eq. (3), we obtain an average thickness of 1.7 nm for the CoO shell with a standard deviation of ca. 20 % (mainly due to the lake of precision of the electron mean free paths).

In order to determine the PMMA thickness, we need to consider a 3 layer based system:  $\text{Fe}_3\text{O}_4$  core, CoO shell and PMMA coating. The previous equations are modified as following:

For  $\text{Fe}_3\text{O}_4$  core:

$$I(\text{Fe}) \propto \sigma(\text{Fe}) \times \lambda_{\text{Fe}}(\text{Fe}_3\text{O}_4) \times T_s(\text{Fe}) \times C(\text{Fe}) \times \left[ \exp\left(\frac{-d_{\text{CoO}}}{\lambda_{\text{Fe}}(\text{CoO}) \cos \theta}\right) \times \exp\left(\frac{-d_{\text{PMMA}}}{\lambda_{\text{Fe}}(\text{PMMA}) \cos \theta}\right) \right] \quad (\text{Eq. 6})$$

For CoO shell:

$$I(\text{Co}) \propto \sigma(\text{Co}) \times \lambda_{\text{Co}}(\text{CoO}) \times T_s(\text{Co}) \times C(\text{Co}) \times \left[ \exp\left(\frac{-d_{\text{PMMA}}}{\lambda_{\text{Co}}(\text{PMMA}) \cos \theta}\right) \times \left( \exp\left(\frac{-d_{\text{CoO}}}{\lambda_{\text{Co}}(\text{CoO}) \cos \theta}\right) \right) \right] \quad (\text{Eq. 7})$$

For PMMA layer (made of carbon element):

$$I(\text{C1s}) \propto \sigma(\text{C1s}) \times \lambda_{\text{C1s}}(\text{PMMA}) \times T_s(\text{C1s}) \times C(\text{PMMA}) \times \left[ 1 - \exp\left(\frac{-d_{\text{PMMA}}}{\lambda_{\text{C1s}}(\text{PMMA}) \cos \theta}\right) \right] \quad (\text{Eq. 8})$$

To subtract the instrumental factor and calculate PMMA thickness, we used the  $I(\text{C1s})/I(\text{Fe})$  ratio:

$$\frac{I(\text{C1s})}{I(\text{Co})} = \frac{\sigma(\text{C1s}) \times T_s(\text{C1s}) \times \lambda_{\text{C1s}}(\text{PMMA}) \times C(\text{C1s}) \times \left[ 1 - \exp\left(\frac{-d(\text{PMMA})}{\lambda_{\text{C1s}}(\text{PMMA}) \times \cos \theta}\right) \right]}{\sigma(\text{Co}) \times T_s(\text{Co}) \times \lambda_{\text{Co}}(\text{CoO}) \times C(\text{Co}) \times \left[ \exp\left(\frac{-d(\text{CoO})}{\lambda_{\text{Co}}(\text{CoO}) \cos \theta}\right) \times \exp\left(\frac{-d(\text{PMMA})}{\lambda_{\text{Co}}(\text{PMMA}) \cos \theta}\right) \right]} \quad (\text{Eq. 9})$$

where  $\sigma(\text{Co})$  and  $\sigma(\text{C1s})$  are the photoionization cross section for Co  $2p_{3/2}$  and C1s signals, respectively;  $T_s(\text{Co})$  and  $T_s(\text{C1s})$  are the analyzer transmission functions of the spectrometer for each element;  $\lambda_{\text{C1s}}(\text{PMMA})$ ,  $\lambda_{\text{Co}}(\text{CoO})$  and  $\lambda_{\text{Co}}(\text{PMMA})$ ,  $\lambda_{\text{Co}}(\text{CoO})$  are the free path of C1s and Co  $2p_{3/2}$  photoelectrons in CoO oxide or PMMA matrices, respectively;  $C(\text{Co})$  and  $C(\text{C1s})$  are the number of Co and C atoms per unit oxide volume;  $\theta$  is the electron take-off angle (as a common approximation,  $\cos \theta$  is usually fixed to 0.5) and  $d(\text{CoO})$  and  $d(\text{PMMA})$  are the thickness of the cobalt oxide shell and PMMA layers respectively. Finally, we obtained Eq. 10.

$$R_2 = \frac{I(\text{C1s})}{I(\text{Co})} \times \frac{\sigma(\text{Co})}{\sigma(\text{C1s})} \times \frac{T_s(\text{Co})}{T_s(\text{C1s})} \times \frac{\lambda_{\text{Co}}(\text{CoO})}{\lambda_{\text{C1s}}(\text{PMMA})} \times \frac{C(\text{Co})}{C(\text{C1s})} \quad (\text{Eq. 10})$$

Eq. 9 can be written as:

$$R2 = \frac{1 - \exp\left(\frac{-d(\text{PMMA})}{\lambda[\text{C1s}(\text{PMMA})\cos\theta]}\right)}{\exp\left(\frac{-d(\text{CoO})}{\lambda[\text{Co}(\text{CoO})\cos\theta]}\right) \times \exp\left(\frac{-d(\text{PMMA})}{\lambda\text{Co}(\text{PMMA})\cos\theta}\right)} \quad (\text{Eq. 11})$$

All the ratios listed in Equation 10 were inferred from the analysis of the high resolution Co 2p and C1s XPS spectra.  $\lambda\text{Co}(\text{CoO})$ , and  $d(\text{CoO})$  were calculated in the previous part and found to be equal to 1.44nm and 1.7 nm respectively.

We need to calculate  $\lambda\text{Co}(\text{PMMA})$ ,  $\lambda\text{C1s}(\text{PMMA})$  using the Dench and Seah equation established for polymers.<sup>2</sup>

$$\lambda_k(\text{polymer}) = \frac{0.11 \times E_k^{0.5}}{\rho(\text{polymer})} \quad (\text{Eq. 12})$$

Where  $E_k$  is the kinetic energy (eV) of the ejected core electron and  $\rho(\text{polymer})$  is the polymer density. Using Equation 12, we obtained  $\lambda\text{Co}(\text{PMMA}) = 2.50$  nm and  $\lambda\text{C1s}(\text{PMMA}) = 2.5$  nm. Replacing these parameters in Equation 12, we obtained an average thickness of 1.9 nm for the PMMA layer with a standard deviation of ca. 20 %.

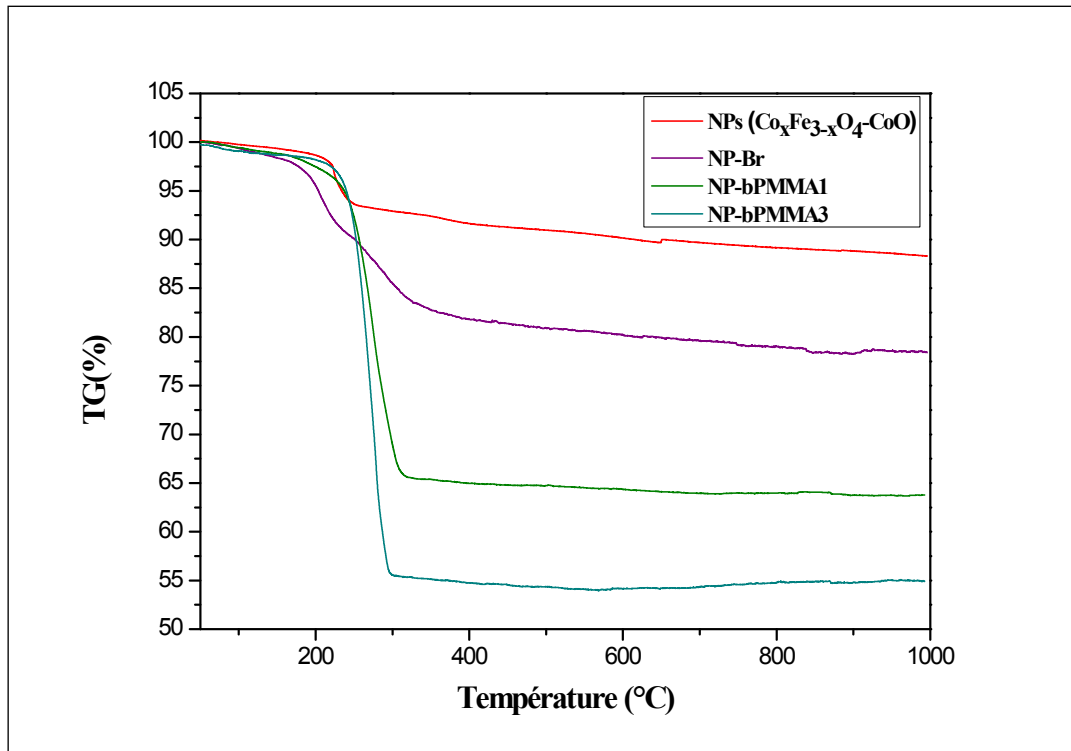
We could then calculate the thickness of PMMA layer but one has to be careful that the layer's thickness calculation is extrapolated from a model developed for flat and thin samples while we are considering nanoparticles. The surface irregularities can locally modify the photon incidence angle on the analysed substrate and increasing the crossed photon distance in the matter. C1s peaks used to calculate PMMA thickness can also be overestimated because of the unavoidable surface contamination.

The PMMA thickness is probably over-evaluated, but it allows an estimation of NP-NP distance. Indeed, the thicker is the organic layer, the farer are the NPs.

---

<sup>2</sup> G. Beamson, D. Briggs. High-resolution monochromated X-ray photoelectron-spectroscopy of organic polymers – a comparison between solid-state data for organic polymers and gas-phase data for small molecules. *Mol. Phys.* 76, **1992**, 919-936.

## TGA measurements



The first weight loss is attributed to residual solvents and organic molecules. At 150 °C, the weight loss of 16 % can be due to the loss of polymerization initiators that allows determining the initiator grafting density: 2.8 initiators nm<sup>-2</sup>, in good agreement with previous results on similar systems (2.6 initiators nm<sup>-2</sup>).<sup>3</sup>

From the weight loss, we determined the monomer conversion (Eq. 13)

$$C_{(\%) } = \frac{m \times W_2}{d \times V} \quad (\text{Eq. 13})$$

With  $m$  the mass of the sample after polymerization,  $W_2$ , the weight loss (%) of organic matter of the polymerized sample,  $d$  the monomer density and  $V$  the volume of monomer introduced for the reaction.

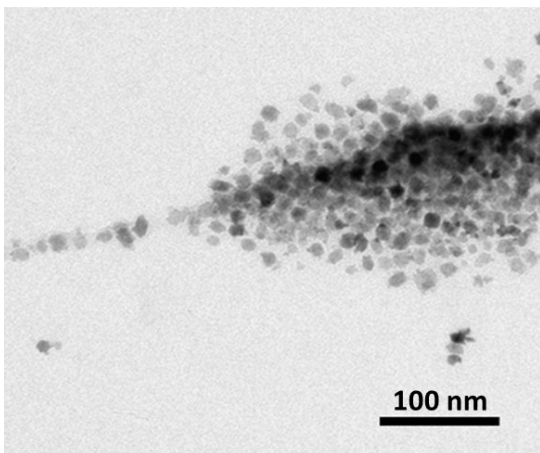
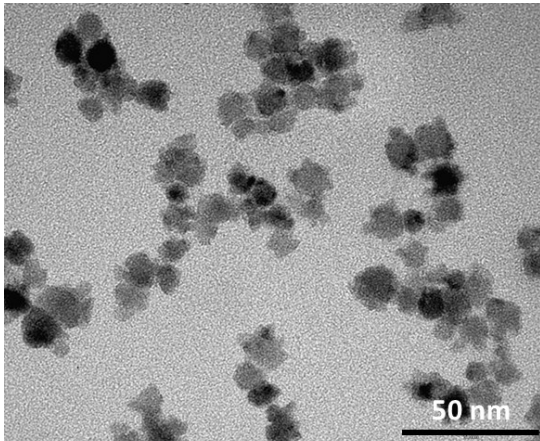
The conversion allowed determining the molecular weight ( $M_{w(\text{calc})}$ ) of the polymer (Eq. 14), assuming first that all Br extremities are initiating a polymer chain.

$$M_{w(\text{calc})} = \frac{\frac{[M]_0}{[I]_0} \times M_{mo} \times C}{100} \quad (\text{Eq. 14})$$

With  $[M]_0$  and  $[I]_0$  the amounts of monomer and initiator ( $4,6 \times 10^{-2}$ mol and  $4,3 \times 10^{-5}$ mol respectively).  $M_{mo}$  is the molecular weight of the monomer and  $C$  the conversion previously calculated (Eq. 13).

<sup>3</sup> Babu, K.; Dhamodharan, R. Grafting of Poly(methyl methacrylate) Brushes from Magnetite Nanoparticles Using a Phosphonic Acid Based Initiator by Ambient Temperature Atom Transfer Radical Polymerization (ATATRP). *Nanoscale Res. Lett.*, **2008**, *3*, 109–117.

## TEM pictures



On the top: *As prepared core-shell NPs.*  
On the bottom: *NPs after 1 h of polymerization.*