**Electronic Supplementary Information**

Efficient functionalization of magnetite nanoparticles with phosphonate using a one-step continuous hydrothermal process
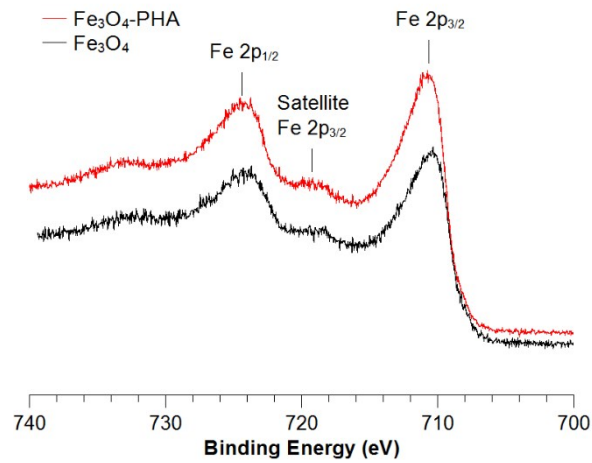
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[a] *Laboratoire Interdisciplinaire Carnot de Bourgogne UMR 6303 CNRS-Université Bourgogne Franche-Comté, 9 Av. A. Savary, BP 47870 F-21078 DIJON Cedex, France.*

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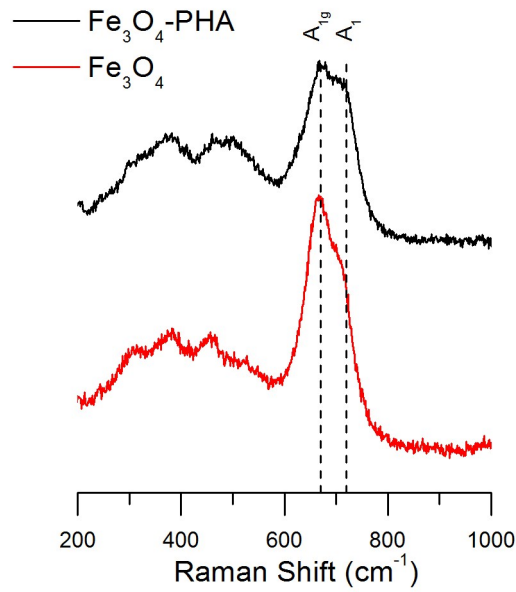
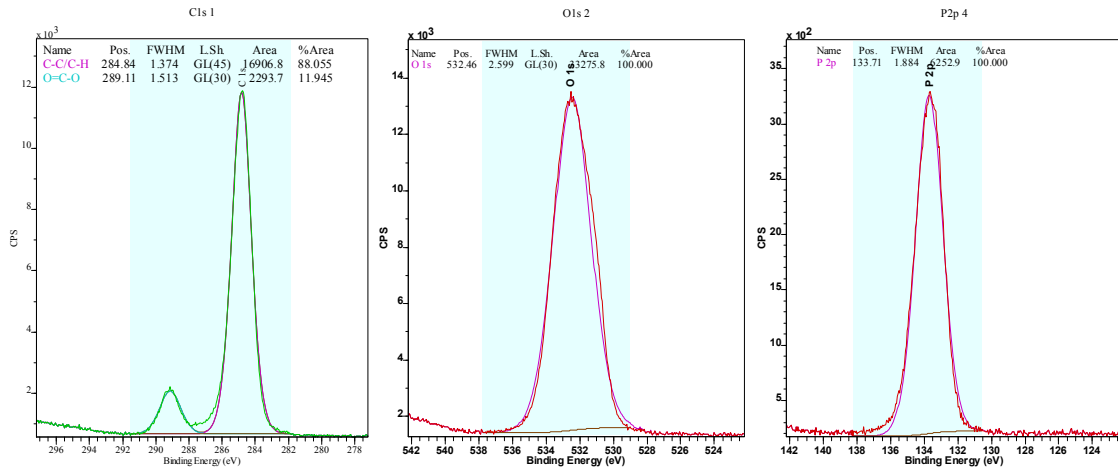**Fig. S1:** Raman spectra in the range of 200-1000 cm^{-1} on Fe_3O_4 and Fe_3O_4-PHA NPs

Fig. S2: Normalized XPS spectra of Fe2p collected on Fe_3O_4 and Fe_3O_4-PHA NPs

Table S1. Satellites peaks positions of Fe_3O_4 and Fe_3O_4-PHA NPs

	Fe 2p$_{1/2}$ (eV)	Satellite Fe 2p$_{3/2}$ (eV)	Fe 2p$_{3/2}$ (eV)	Δ(Satellite- Fe 2p$_{3/2}$) (eV)
Fe_3O_4	724.0	718.6	710.4	8.2
Fe_3O_4-PHA	724.0	718.7	710.5	8.2

Fig. S3: Normalized XPS spectra of C1s, O1s and P2p collected on PHA molecule

ICP-AES measurements

The sample mass was 10, 07 mg dissolved in a total volume of 10 mL.

The iron and phosphorus contents were determined (after dissolution in HNO_3 and ultrasound treatment) by ICP-AES and led to the following results:

Table S2. Mass concentrations of Fe and P determined by ICP

Iron concentration Fe_{ICP}	Phosphorus concentration P_{ICP}
57.64 %	1.14 %
580.43 mg/mL	11.48 mg/mL

Note that ratio of iron over phosphorus is $R_{Fe/P}$ = Fe_{ICP}/P_{ICP} = 57.6% / 1.14% = 50.6

> Calculation of PHA molecule number:

P_{ICP} is the phosphorus concentration in our sample, 1 mole of PHA (M(PHA) = 6 × 12.011 + 13 × 1.0079 + 5 × 15.9994 + 1 × 30.973761 = 196.14 g/mol) contains 1 mole of phosphorus (M(P) = 30.973761 g/mol).

$$\text{Number(PHA)} = \frac{P_{ICP} \times N_A}{M(P)} = 2.23 \times 10^{20} \text{ PHA}$$

With P_{ICP} the phosphorus concentration 11.48 × 10^{-3} g (considering 1 L), N_A the Avogadro number 6.022×10^{23} mol^{-1}, $M(P)$ the atomic weight of phosphorus 30.973761 g.mol^{-1}

> Calculation of the $Fe_{3(1-\delta)}O_4$ (δ = 0.065) surface available for PHA grafting:

Fe_{ICP} is the concentration of iron in our sample made of oxidized magnetite $Fe_{3(1-\delta)}O_4$ (δ = 0.065) ↔ $Fe_{2.805}O_4$ (M($Fe_{2.805}O_4$) = 2.805 × 55.845 + 4 × 15.9994 = 220.64 g/mol) in which there are 2.805

moles of iron. The specific surface area of $Fe_{2.805}O_4$ was determined by BET measurement to be 147 m²/g. As a consequence, the surface developed by our sample is given by the following equation:

$$\text{Surface}\left(Fe_{3(1-\delta)}O_4\right) = \frac{Fe_{ICP} \times M\left(Fe_{2.805}O_4\right) \times SSA}{2.805 \times M(Fe) \times 10^{-18}} = 12.01 \times 10^{19} \text{ nm}^2$$

With Fe_{ICP} the iron concentration 580.4×10^{-3} g (considering 1 L), $M\left(Fe_{3(1-\delta)}O_4\right)$ the molecular weight of oxidized magnetite 220.64 g/mol, SSA the specific surface area of $Fe_{3(1-\delta)}O_4$ NPs 147 m².g^{-1}, $M(Fe)$ the atomic weight of iron 55.845 g/mol

> ➤ Calculation of PHA coverage on oxidized magnetite:

Subsequently of previous calculations, the coverage of PHA molecules on $Fe_{3(1-\delta)}O_4$ corresponds to the ratio of the number of PHA molecules by the available surface of $Fe_{3(1-\delta)}O_4$.

$$\text{Coverage} = \frac{\text{Number(PHA)}}{\text{Surface}\left(Fe_{3(1-\delta)}O_4\right)} = 1.86 \text{ PHA/nm}^2$$

> ➤ In short, the PHA coverage can be calculated as follows:

$$\text{Coverage (PHA/nm}^2) = \frac{2.805 \times P_{ICP} \times M(Fe) \times N_A \times 10^{-18}}{Fe_{ICP} \times M(P) \times M\left(Fe_{2.805}O_4\right) \times SSA}$$

Finally, assuming spherical-shaped NPs with a diameter of ϕ_{TEM} = 7 nm, one NP surface is $\pi\phi_{TEM}^2$ = 153.94 nm². Hence 1.86 × 153.94 = **286 PHA/NP**. This result is in the same order of magnitude[i] than other stabilized iron oxide nanoparticles and about half the theoretical maximum number of phosphonate groups (the footprint of which is determined to be 18.5 Å² by Miles *et al.* or 24 Å² by Daou *et al.*)[ii,iii] which is estimated to be 153.94 × 100 / (18.5 or 24) = [641-832] phosphonate max. on 7-nm NPs.

> ➤ Calculation of the proportion of each phase:

Fe_{ICP} = 57.64%, so the **proportion of $Fe_{2.805}O_4$** = 57.64/(2.805 × 55.845/220.64) = **81.2%** (weight)

P_{ICP} = 1.14%, so the **proportion of PHA** = 1.14/(30.974/196.14) = **7.2%** (weight)

And so **remaining compounds** such as physisorbed, chemisorbed water *etc.* represent **11.6%** (weight), in good agreement with TGA results (7.9% of physisorbed and chemisorbed water).

With $M(Fe)$ = 55.845 g/mol, $M\left(Fe_{2.805}O_4\right)$ = 220.64 g/mol, $M(P)$ = 30.974 g.mol^{-1} and M(PHA) = 196.14 g/mol.

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[i] Y. Lalatonne, C. Paris, J. M. Serfaty, P. Weinmann, M. Lecouvey and L. Motte, *Chem. Commun.*, **2008**, 2553-2555

[ii] W. C. Miles, P. P. Huffstetler, J. D. Goff, A. Y. Chen, J. S. Riffle and R. M. Davis, *Langmuir*, 2011, **27**, 5456-5463

[iii] T. J. Daou, S. Begin-Colin, J. M. Grenèche, F. Thomas, A. Derory, P. Bernhardt, P. Legaré and G. Pourroy, *Chem. Mater.*, 2007, **19**, 4494-4505