

Supporting Information

for

Iron quantification of iron at sub femtogram level in magnetite hybrid silica methacrylate core-shell nanocomposite particles by sp-ICP-MS.

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Materials.

3-(trimethoxysilyl)propyl methacrylate (TPM, Sigma-Aldrich), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, >99%), iron(II) sulfate heptahydrate ($\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$, Sigma-Aldrich, 99.0%), ammonium hydroxide (NH_4OH , Sigma-Aldrich, 28-30%), tetramethylammonium hydroxide (TMAH, Sigma-Aldrich, 25%), potassium persulfate (KPS, Sigma-Aldrich, 99%).

Synthesis of Fe_3O_4 nanoparticles

First, Fe_3O_4 nanoparticles (NPs) were synthesized through the Massart coprecipitation method.¹ Briefly, 30 ml of iron precursor solution ($\text{Fe(III)/Fe(II)} = 2$) was prepared by mixing 24 ml of a 1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in Milli-Q water solution with 6 ml of 2 M $\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$ in HCl 1 M solution. The iron solution was then added drop by drop and under intense magnetic stirring to a 300 ml of 0.7 M ammonia solution, prepared with NH_4OH 28-30 %. After 15 minutes of stirring, magnetic decantation was performed and the pellet was either resuspended in 50 ml of a 1 M TMAH solution for the stabilization of colloid magnetic sol or washed five times through magnetic decantation and washing steps in water before resuspended in 20 ml of Milli-Q water (pH = 6.5).

Synthesis of magnetic HySi@Fe and Fe@HySi hybrid nanocomposites.

The HySi@Fe nanocomposites composed of Fe_3O_4 NPs decorating hybrid silica/metacrylate nanospheres were synthesized using a protocol developed by Sacanna et al.² and adapted to our case. Briefly, the pH of 80 ml aqueous Fe_3O_4 NPs (0.4 mg/ml) stabilized by TMAH was first adjusted between 8.5 and 9.5. Then, 465, 200 or 100 μl of TPM were added and the mixture was gently stirred by hand and left for 48 hours for the emulsion formation. The amount of TPM was varied in order to tune the final nanocomposite sizes. In the next step, after 20 minutes N_2 purge of the solution, KPS was added to have a final concentration at 8.5 mM. The N_2 purge

was continued for 10 minutes and finally the polymerization was initiated by heating the solution to 70°C for 5 hours.

The Fe@HySi nanocomposites composed of Fe₃O₄ NPs encapsulated in hybrid silica/methacrylate nanospheres were synthesized by a simple modification of the above procedure. Typically, 465 µl of TPM were added in 80 ml of ligand free Fe₃O₄ NPs solution (0.4 mg/ml). Then 1.6 ml NH₄OH (28-30%) were added to allow hydrolysis and condensation of TPM. After 15 minutes the solution became turbid indicating the formation of TPM particles. Finally, N₂ purge and methacrylate polymerization were carried out using the same conditions as for HySi@Fe. All the prepared particles were washed by magnetic decantation and resuspension in Milli-Q water 3 times.

Characterization.

Scanning Electron Microscopy (SEM) and Scanning Auger Mapping (SAM)

A JEOL JAMP 9500 F Auger spectrometer (JEOL Ltd., Tokyo, Japan) working under UHV conditions (pressure 2×10^{-7} Pa) was used for both SEM and SAM characterization. For the SEM observation, a droplet of moderate concentrated washed particles solution was deposited onto an aluminum foil and dried at 120°C. SEM analyses were performed at 30 kV with an electron beam current at 1 nA. SAM experiments were carried out using 20 kV and a beam current at 5 nA.

Cross-section polishing of Fe@hySi nanocomposites.

A JEOL Cross-Polisher (JEOL Ltd., Tokyo, Japan) was used for the cross-cut polishing of the Fe@HySi nanocomposites before the Auger SAM mapping. The particles were first filtered with 0.22 µm Millipore filters, washed with Milli-Q water and dried. A small amount of particles in powder were mixed with colloidal graphite glue, diluted with acetone, and a droplet of this mixture was quickly deposited onto a silicon wafer, which was fixed on a cross-section polisher sample holder. The droplet was left to dry at room temperature. This procedure was repeated several times before SAM analyses.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) images were taken with a Philips CM 200 (200 kV) instrument equipped with a LaB6 source. The samples dispersed in ethanol or water were dropped onto a carbon copper grid and dried at room temperature before analysis. Basic size distributions of nanocomposites were evaluated systematically by statistical counting using ImageJ software on several tenth of particles.

X-Ray Photoelectron Spectroscopy (XPS)

A thermo K-alpha spectrometer with a hemispherical analyzer and a micro-focused monochromated Al K α radiation ($h \cdot \nu = 1486.6$ eV) at 72 W was used. The diameter of the analysis area was set at 400 µm and for evaluation of the repeatability, 3 different areas of each sample were systematically measured. The peaks were recorded with constant pass energy of 20 eV. The analysis was performed under pressure maintained below $1 \cdot 10^{-7}$ mbar and under charge compensation. The calibration of the binding energy scale was performed by fitting the hydrocarbon contamination C 1s core peak at 285.0 eV. To prepare the samples for analyses,

the particles were washed through 3 cycles of magnetic decantation/resuspension in Milli-Q water after finally being concentrated in a small volume of water. The solution was then dried at 60°C in an oven. The formed powder was deposited onto a double tape fixed on the sample holder before XPS analysis.

Results of Physicochemical Characterization

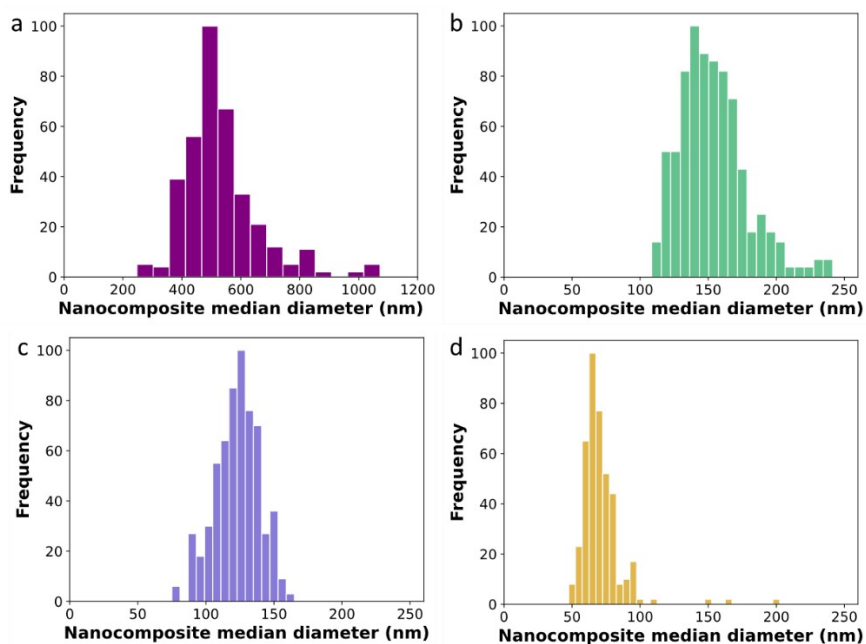


Figure S1. Nanocomposite size distributions measured by TEM of Fe@HySi (a) and HySi@Fe synthesized with TPM/Fe₃O₄ = 0.16 (b), TPM/Fe₃O₄ = 0.07 (c) and TPM/Fe₃O₄ = 0.03 (d).

Table S1. Characteristic data obtained from TEM particle size distribution for the two nanocomposites.

Nanocomposite type	Fe@HySi	HySi@Fe		
		0.03	0.07	0.16
TPM/Fe ₃ O ₄	0.16	0.03	0.07	0.16
Mean diameter (nm)	507	70	121	150
Median diameter (nm)	480	66	122	146
STDEV (nm)	127	21	17	25

The Fe2p_{3/2} high resolution XPS spectrum (Fig. S2 ESI†) presents a low intensity peak at 708.7 eV corresponding to Fe²⁺ species, while the wide peak with a maximum at 710.1 eV is associated to Fe³⁺ oxidation state. The area ratio between these two Fe species does not translate pure magnetite Fe₃O₄ NPs but highlights its partial oxidation into maghemite (Fe₂O₃) NPs.^{24–26}

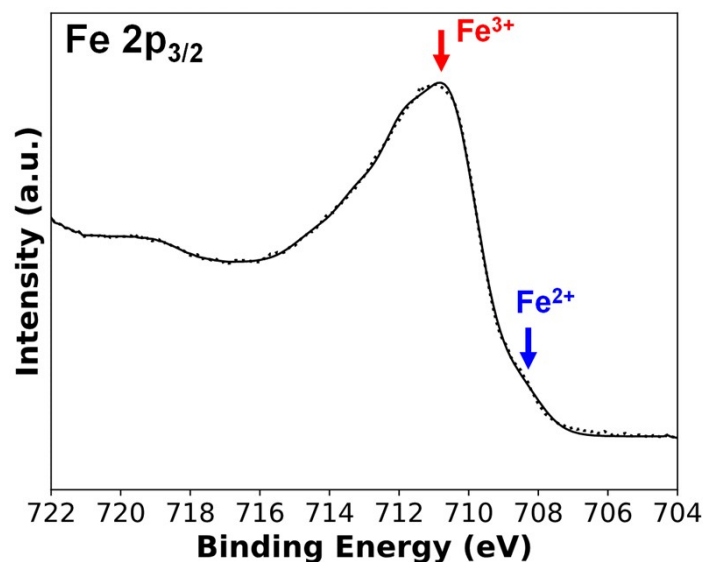


Figure S2. XPS Fe2p_{3/2} high resolution spectrum of as synthesized Fe₃O₄ nanoparticles

The XPS high resolution spectra (Fig. S3 ESI†) show the same environments of Fe for HySi@Fe (Fig. S3d) as for Fe₃O₄ NPs (Fig. S1). The C1s (Fig. S3a) spectra confirm the presence of the methacrylate functional group in all nanocomposites with typical CH₂-CH₂ (285.0 eV), C-(CO) (286.1 eV), C-O (286.9 eV) and O-C=O (289.0 eV) bonds. Moreover, the O1s spectra (Fig. S3b) also show the methacrylate signature with C-O (533.6 eV) and C=O (532.4 eV) bonds, the latest including the signal of the oxygen atoms from Si-O bonds as well (see all quantification data in Table S2).

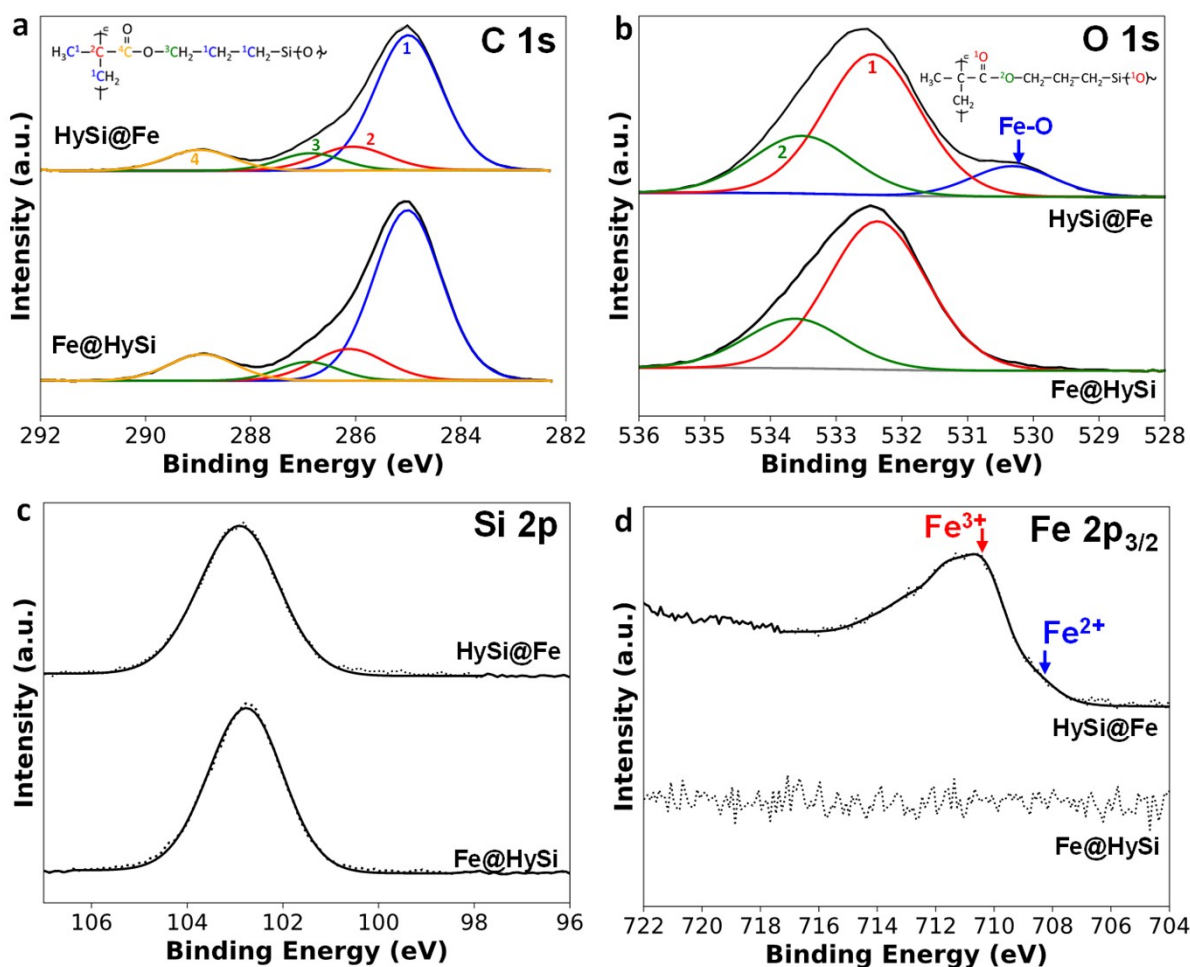


Figure S3. XPS high resolution spectra of (a) C 1s (b) O 1s (c) Si 2p and (d) Fe 2p_{3/2} for HySi@Fe (up) and Fe@HySi (down) nanocomposites.

Table S2. XPS binding energies (eV) and relative atomic percentages for the two nanocomposites types for TPM/Fe₃O₄ = 0.16 (in parenthesis : the full width at half maximum).

Nanocomposite type	C 1s	O 1s	Si 2p _{3/2}	Fe 2p _{3/2}
Fe@HySi	285 (1.5) 47 % 286.1 (1.6) 9 % 286.9 (1.4) 5 % 289.0 (1.5) 7 %	532.4 (1.8) 17 % 533.6 (1.8) 6 %	102.6 (1.7) 6 %	-
Total at. %	68 %	23 %	6 %	
HySi@Fe	285 (1.5) 41 % 286.1 (1.6) 8 % 286.9 (1.4) 5 % 289.0 (1.5) 6 %	530.3 (1.5) 3 % 532.4 (1.7) 18 % 533.5 (1.8) 8 %	102.7 (1.8) 7 %	Fe ²⁺ 708.7 Fe ³⁺ 710.1
Total at. %	60%	29 %	7 %	1 %

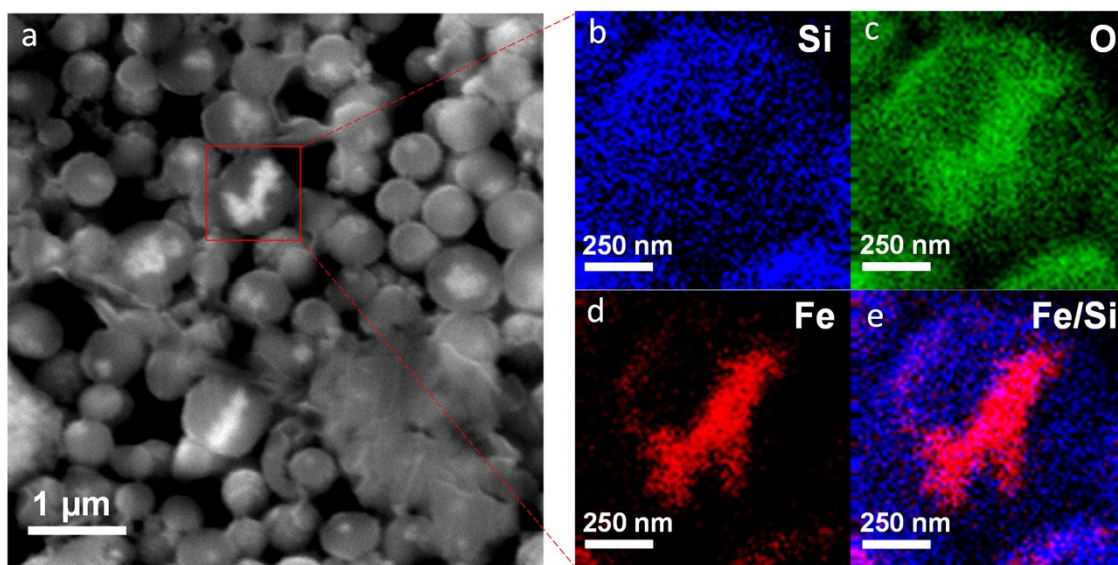


Figure S4. Scanning Auger Mapping of cross-cut Fe@HySi nanocomposites with (a) the SEM image of the selected particle and the different elemental maps of (b) Silicon, (c) Oxygen, (d) Iron and (e) Iron/Silicon overlay.

Resume of sp-ICP-MS results

Table S3 : Sum-up of sp-ICP-MS/MS data of the as synthesized nanocomposites

Nanocomposite type	Fe@HySi	HySi@Fe		
TPM/Fe ₃ O ₄	0.16	0.03	0.06	0.16
Mean Fe mass (fg)	16.80	0.12	0.12	0.92
Median Fe mass (fg)	9.31	0.05	0.09	0.49
STDEV Fe mass (fg)	20.85	0.30	0.11	1.98
Polydispersity index (PDI)	1.5	6.7	0.8	4.6
AVG nanocomposite number concentration (10 ¹⁴ /L)	0.53	0.48	2.77	2.00
STDEV nanocomposite number concentration (10 ¹⁴ /L)	0.01	0.05	1.17	0.18
Number of events	1170	918	969	670
Fe mass (fg) threshold	0.07	0.02	0.02	0.01
Equivalent Fe particle size (nm) threshold	29.7	19.9	18.2	15.8

References

- 1 R. Massart, *IEEE Trans. Magn.*, 1981, **17**, 1247–1248.
- 2 S. Sacanna, W. K. Kegel and A. P. Philipse, *Langmuir*, 2007, **23**, 10486–10492.