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Electronic Supporting information

Self-assembly of a superparamagnetic raspberry-like silica/iron oxide nanocomposite using epoxy-amine coupling chemistry

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1. Reagents and instrumentation

1.1. Reagents

With the exception of oleic acid (>90%) and N,N-dimethylformamide (DMF), which were obtained from Alfa-Aesar, all reagents were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification. All aqueous solutions were prepared using ultrapure water from a Milli-Q system (Millipore, resistivity 18.2 MΩm at 25ºC).

1.2. Instrumentation

Fourier-transform infrared (FT-IR) spectroscopy was carried out in a JASCO FT/IR-4100 spectrometer. **Zeta-potential** was measured using a Malvern Zetasizer Nano-ZS90. **Scanning electron microscopy (SEM)** was performed using a FEI Quanta 250 FEG microscope. **Transmission electron microscopy (TEM)** was carried out using a FEI Tecnai G2 20 TWIN TEM microscope, operated at an accelerating voltage of 100 kV. Samples were prepared on 200 mesh copper grids with a carbon sputter coated Formvar substrate. **X-ray energy dispersion (EDX)** spectroscopy was conducted with an EDAX DPP-II analyzer installed on TEM. **Thermogravimetric analysis (TGA)** was carried out using a TA Instruments METTLER TOLEDO (TGA/DSC1 model). All samples were conditioned using a N_2 flow of 50 ml/min at 30 ºC for 15 min before measurement, and then heated from 30 to 1000 ºC at 10ºC/min under an air atmosphere of 50 mL/min. **X-Ray Diffraction (XRD)** was performed using a PANalytical X´Pert PRO MPD diffractometer with Cu kα_1 radiation (λ = 1.540598 Å). XRD patterns were assigned using the JCPDS database. **Magnetization measurements** were obtained in an EV9 Vibrating Sample Magnetometer (MicroSense). Samples were measured at 2 T under nitrogen atmosphere at both 300 K and 77 K.

2. Experimental methods.

Synthesis of monodisperse SPION-OA.

10 nm diameter monodisperse SPION-OA nanoparticles were prepared as described in *Park et al.*[1] The iron(III) oleate complex precursor required for this was characterized

by FT-IR, which revealed its characteristic C=O stretching peak at 1717 cm^{-1} (Fig. S1a), and also by TGA (Fig. S1b).

To produce SPION-OA the iron(III)–oleate precursor was decomposed at high temperature in octadecene.[1] SPION-OA displayed characteristics FT-IR spectra (Fig. S2a) and X-ray diffraction (XRD) pattern (Fig. S2b). The reflection 2θ peaks obtained by XRD coincided with the JCPDS database for inverse spinel magnetite (JCPDS file 19629; Joint Committee on Powder Diffraction: Swarthmore, PA), and also indicated that our material was crystalline. Confirming the latter, we verified the superparamagnetic character of these particles (Fig. S3a). We also carried out TGA analyses of our SPION-OA preparations (Fig. S3b), which showed a total weight loss of 83.4 % and provided an explanation for the apparently low saturation magnetization values observed in Fig. S3a.

Synthesis of SPION-APTES.

SPION-APTES were prepared following the silane ligand exchange method described by De Palma et al.[2] These particles were analyzed by FT-IR, which revealed the characteristic bands for the Si-O-Si vibrations in the silane layer (1000-1150 cm^{-1}) and the two N-H bendings at 1631 and 1550 cm^{-1}, typical of amine groups (Fig. S4, black line).

Synthesis of SPION-APTES/SA.

The SPION-APTES/SA nanoparticles were prepared according the procedure described in *An et al*[3], with modifications. Briefly, 40 mg of SPION–APTES were dissolved in 20 mL DMF, and mixed with 20 ml of 0.2 M succinic anhydride, also in DMF. This mixture was stirred for 2h at room temperature to produce SPION-APTES/SA particles, which were subsequently purified by centrifugation and resuspension in DMF. The FT-IR spectrum of these particles displayed two vibrations at 1555 and 1410 cm^{-1}, assigned to the asymmetric and symmetric COO$^-$ stretchings, respectively, which were not observed in their SPION-APTES precursor (Fig. S4, red line).

Ninhydrin method.

The reduction (yet availability) of amine groups on the surface of SPION-APTES produced as described above was confirmed by a colorimetric reaction using ninhydrin.[4] Briefly, 1 mL of SPION-APTES or SPION-APTES/SA in water (at a concentration of 2.5 µg/mL) were mixed with 1 mL of ninhydrin solution[4] in glass tubes, heated until boiling, and then chilled on ice. 5 mL of 50% ethanol were added to each tube and mixed thoroughly, and the absorbance of the resulting mixture at 570 nm was determined using a spectrophotometer.

Synthesis of silica NPs.

Silica NPs were produced using a modified Stöber method described in *English et at.*[5] The resulting particles were analysed by XRD, which revealed the characteristic 2θ reflection peak of amorphous silica (Figure S5a). Further analysis of these particles by FT-IR revealed the absorption peak at 1064 cm^{-1}, corresponding to the Si-O-Si asymmetric stretching vibration, and the peaks (950 cm^{-1} and 800 cm^{-1}) ascribed to the asymmetric bending and stretching vibration of Si-OH (Figure S5b).

Synthesis of epoxy-silane modified silica NPs.

Silica NPs (0.5 g) were suspended in toluene (100 mL) by sonication for 15 min. 5 mL of 3-(3-Glycidyloxypropyl)trimethoxysilane (GPES) were slowly added to the suspension of NPs and the mixture was heated to 90 ºC for 48 h under an inert gas saturated atmosphere, and then cooled down to room temperature. The resulting epoxy-silane coated silica NPs were collected by centrifugation (9780 xg; 10 min at 4 ºC) and resuspended in toluene, and subsequently purified through several cycles of centrifugation and re-dispersion in absolute ethanol.

Further characterization of raspberry-like nanocomposites.

Additional TEM images of the superparamagnetic nanocomposites are showed in Figure S6. The zeta-potential analysis reveals a surface charge change from +41 mV of epoxylated silica NPs to -32 mV of the nanocomposites (Fig. S7a). The FT-IR shows that after the SPION coating new bands appeared in low frequency region (~600 cm^{-1}) characteristic of the Fe-O skeleton, the N-H bendings (~1600 cm^{-1}) of amine and the COO^{-} stretchings (1400-1500 cm^{-1}) of carboxylic acid groups (Fig. S7b). Fig. S8 shows an energy dispersion X-ray analysis (EDX) performed in situ during TEM image capture of empty copper grids (blank control), a SPION-APTES/SA, an epoxylated silica particles and a raspberry-like nanocomposite. The appearance of the chemical signal of Fe in the EDX spectra for the hybrid material confirms the presence of SPION shell.

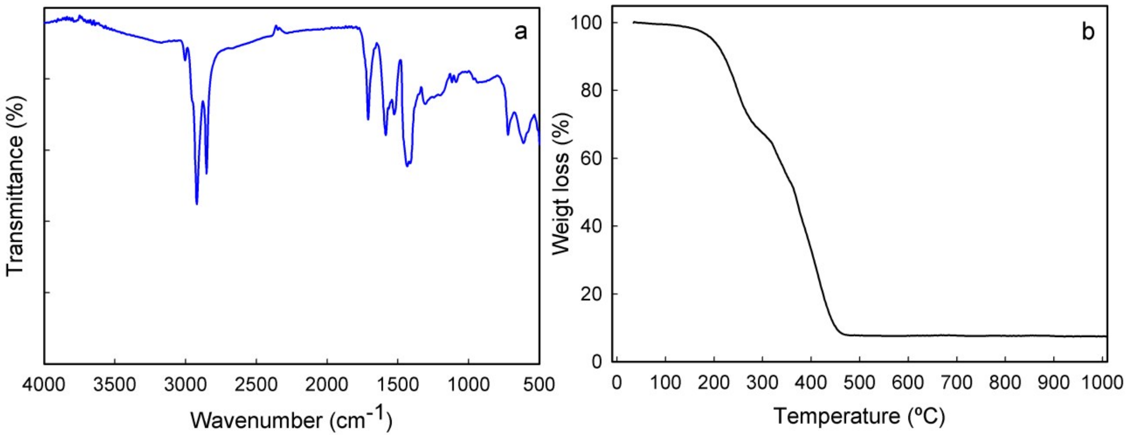

Fig. S1: FT-IR spectrum (a) and TGA curve (b) of iron (III) oleate complex.

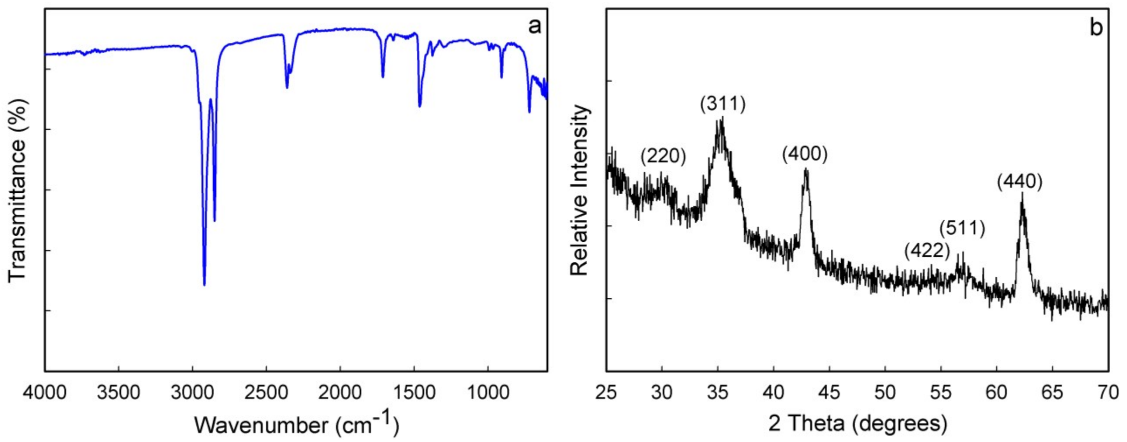

Fig. S2: FT-IR spectrum (a) and XRD plot (b) of SPION-OA.

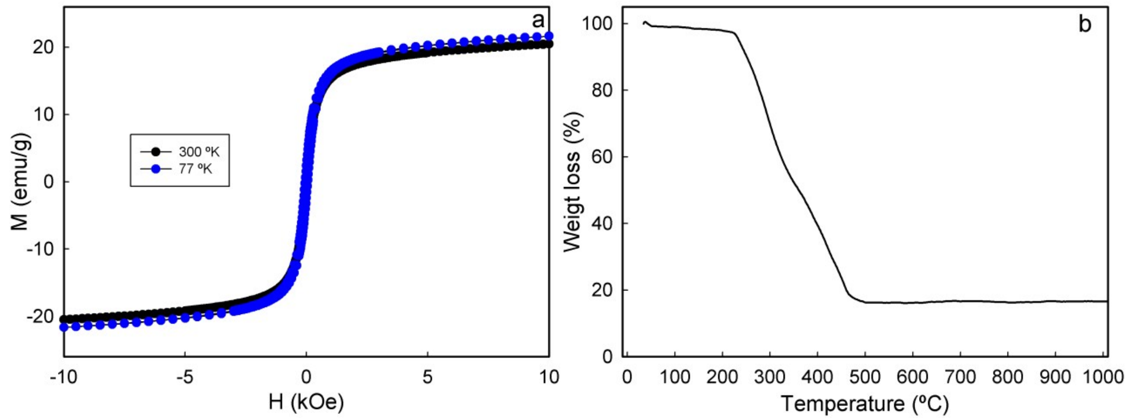

Fig. S3: Magnetization (a) and TGA (b) plots of SPION-OA.

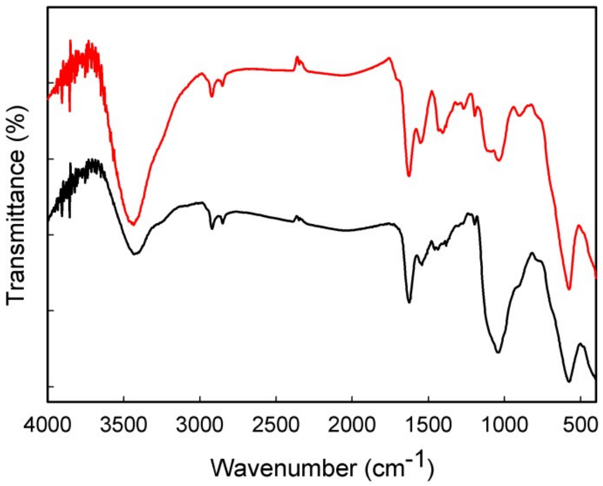

Fig. S4: FT-IR spectrum of SPION-APTES (black line) and SPION-APTES/SA (red line).

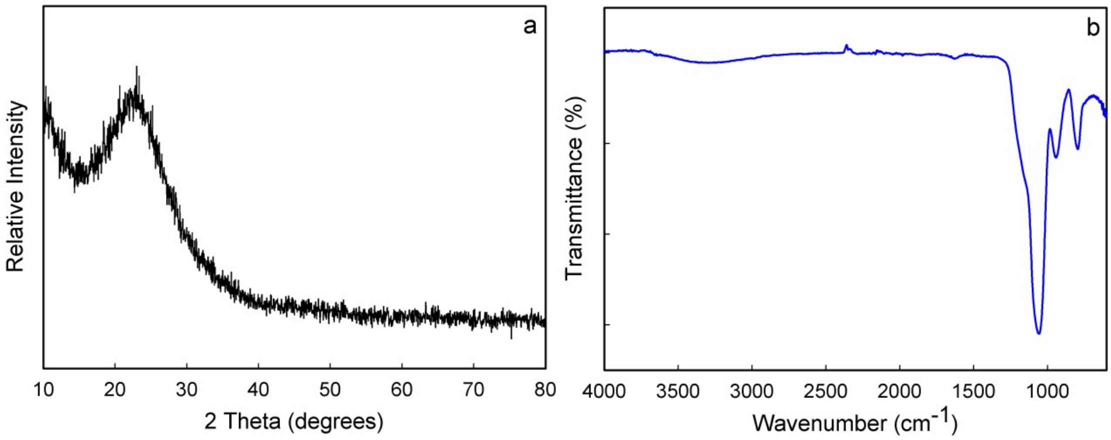

Fig. S5: DRX plot (a) and FT-IR spectrum (b) of bare silica NPs.

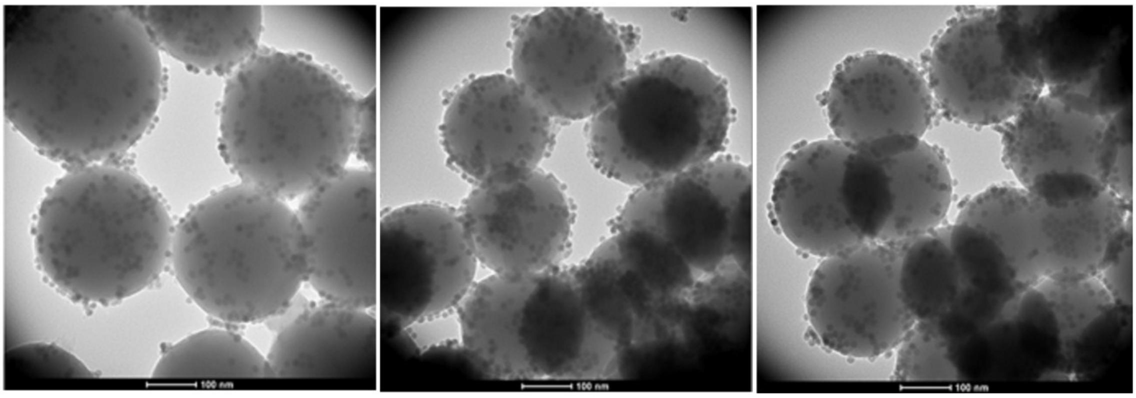

Fig. S6: Additional TEM images of the superparamagnetic nanocomposites.

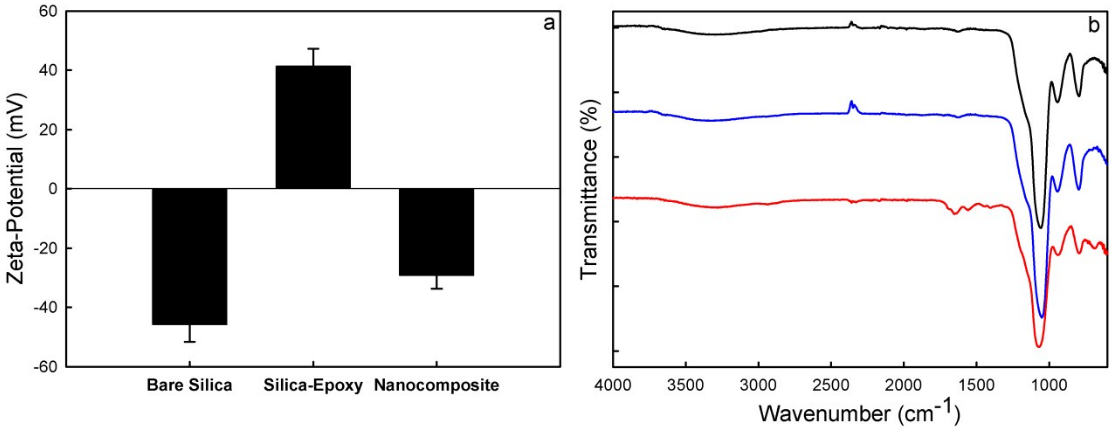

Fig. S7: Zeta-potential values (a) and FT-IR spectrum (b) of bare silica (black line), epoxy-modified silica (blue line) and superparamagnetic composite (red line) particles.

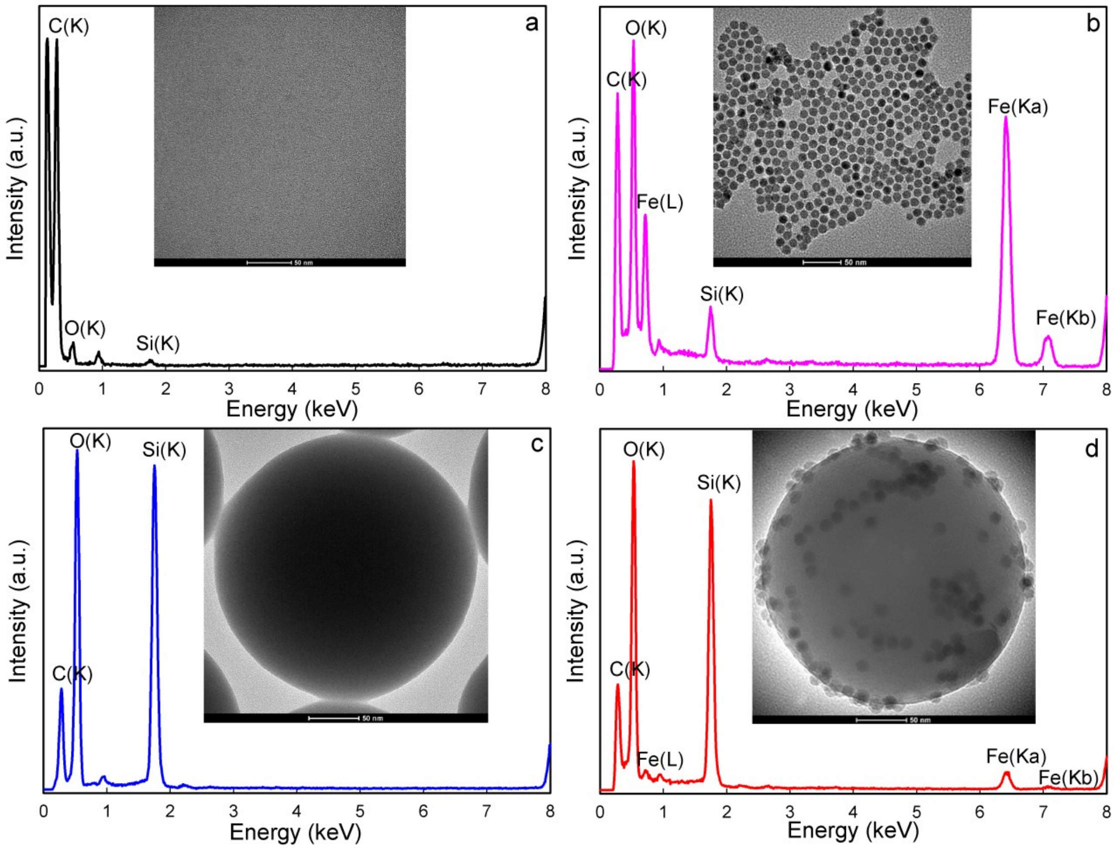

Fig. S8: EDX spectra with inset TEM image of an empty copper grid (a), a SPION-APTES/SA (b), an epoxy-modified silica (c) and a superparamagnetic nanocomposite (d).

References

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