

## Single-Source Magnetic Nanorattles

### By Using Convenient Emulsion Polymerization Protocols

*Daniel Scheid<sup>1</sup>, Gennady Cherkashinin<sup>2</sup>, Emanuel Ionescu<sup>2</sup> and Markus Gallei<sup>1,\*</sup>*

<sup>1</sup>Ernst-Berl Institut für Technische und Makromolekulare Chemie, Technische Universität Darmstadt,  
Alarich-Weiss-Str. 4, D-64287 Darmstadt, Germany

<sup>2</sup>Materials Science Department, Technische Universität Darmstadt, Jovanka-Bontschits-Str. 2, D-64287  
Darmstadt, Germany

Corresponding author: [m.gallei@mc.tu-darmstadt.de](mailto:m.gallei@mc.tu-darmstadt.de)



## Experimental

**Instrumentation.** Transmission electron microscopy (TEM) was performed on a Zeiss EM10 with an operating voltage of 60 kV. For investigation of the single particles, the diluted dispersions were drop-casted on carbon-coated copper grids (Plano GmbH, Germany) and dried at room temperature. For the preparation of ultrathin sections, the magnetic core/shell particles were embedded in an epoxy resin (UHU endfest) and cut into slices of 50-70 nm using an ultramicrotome Ultracut UTC (Leica) equipped with a diamond knife. TEM images were recorded with a slow-scan CCD camera TRS (Tröndle). For TGA analyses TA Instruments TGA Q-500 were used from 35 °C to 800°C with a heating rate of 10 K min<sup>-1</sup> under oxygen atmosphere. Dynamic light scattering (DLS) measurements of the beads were performed on a Nanophox photon cross-correlation spectrometer (Sympatec). The experiments on diluted dispersions of the beads after each step of the particle synthesis were carried out at an angle of 90° at 20 °C. For ceramization, particles were treated in a Carbolite CWF 11/13 high temperature oven. WAXS measurements were conducted using a Siemens D500 diffractometer in the reflection mode with the same incident X-ray wavelength of 1.54 Å at a step width of 0.04°. For a qualitative analysis the programm Match! from Crystal Impact was used. The corresponding structures were taken from Crystallography Open Database. A quantitative analysis was partially performed by the program FullProf using the Rietveld refinement algorithm. Centrifugation was performed with an Avanti J-30I from Beckman Coulter for half an hour with a speed of 17000 rpm. For the XPS measurements, dried iron oxide particles and silica were pressed in a separate indium foils. XPS studies were carried out on a PHI 5000 spectrometer with the monochromatic Al-K<sub>α</sub> radiation ( $h\nu = 1486.6$  eV). The diameter of the X-ray beam spot was 200 μm. High resolution photoelectron spectra were collected at a pass energy of  $E_{pas} = 23.5$  eV and an electron escape angle of  $\theta = 45^\circ$ . The binding energies were calibrated with respect to the Ag3d<sub>5/2</sub> photoelectron line and the Fermi level of a sputtered Ag foil. Micro-Raman spectra (10 scans, each lasting 3 s) were recorded in backscattering mode with a Horiba LabRam HR 800 micro-Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany) equipped with an air-cooled Ar<sup>+</sup> ion



laser (emission line 514.5 nm). The excitation line has its own interference filter (to filter out the plasma emission) and a Raman notch filter (for laser light rejection). The measurements were performed with a spectrometer grating of  $1800\text{ gmm}^{-1}$  and a confocal microscope (long working distance objective, magnification 50 $\times$ ; numerical aperture (NA) 0.5; focused laser spot diameter ca. 2  $\mu\text{m}$ ). The laser power (ca. 20 mW) was attenuated on the sample in the range of 2 mW–20  $\mu\text{W}$  by using neutral density (ND) filters in order to avoid phase transformations of the iron oxides upon laser irradiation. Spectral resolution at the conditions was about  $1\text{ cm}^{-1}$  and the spatial resolution ca. 1  $\mu\text{m}$ .

**Reagents.** All chemicals and solvents were purchased from Fisher Scientific, Sigma-Aldrich and Alfa Aesar and used as received if not otherwise stated. 2-(methacryloyloxy)-ethyl ferrocenecarboxylate (FcMA) was synthesized according to literature.<sup>1</sup> The removal of methyl methacrylate (MMA) stabilizer was achieved by extraction with 1 N sodium hydroxide solution. Afterwards, MMA was washed with water until neutrality, followed by drying with sodium sulfate.

### **Synthesis of Cross-Linked PMMA-*co*-FcMA Particles**

2-(methacryloyloxy)-ethyl ferrocenecarboxylate (FcMA) containing particles were synthesized by starved feed emulsion polymerization. A 250 mL vessel equipped with stirrer, reflux condenser and nitrogen feeding was heated to 75°C and then filled with monomer emulsion containing 18.8 mg sodium dodecylsulfate (SDS), 110 g deionized water, 0.9 g destabilized methyl methacrylate (MMA) and 0.1 g Allyl methacrylate (ALMA). The polymerization was initiated by adding 12.5 mg sodium disulfite (NaDS), 43.8 mg sodium persulfate (NaPS) and 12.5 mg NaDS in this order (each component is dissolved in 1.25 mL water). 10 min after the reaction mixture turned milky, a monomer emulsion containing 100 mg SDS, 100 mg potassium hydroxide (KOH), 125 mg Dowfax2A1, 45 g water, 22.8 g MMA, 11.2 g FcMA and 3.5 g ALMA was added with a constant flow rate of  $0.2\text{ mL min}^{-1}$ . After complete addition of monomer emulsion, the reaction was finished by holding the temperature for an additional hour.



## Synthesis of SiO<sub>2</sub>@FcMA-*co*-MMA Particles

In a typical procedure, 89 g of the FcMA-containing dispersion (22 wt%) was filled in a 250 mL vessel with stirrer, reflux condenser and nitrogen feeding. The mixture was stirred at 75 °C and buffered at pH 7 – 7.5 using 0.75 mL sodium dihydrogen phosphate (2% aqueous, SDP) and 1 mL sodium bicarbonate (2% aqueous, SBC). After adding 20 mg NaPS, a monomer emulsion with 0.25 g ALMA, 2.5 g MMA, 4.75 g 3-(trimethoxysilyl)propyl methacrylate (MEMO), 18.8 mg SDS, 5 g water, 0.125 mL SDP and 0.25 mL SBC was fed with a constant flow rate of 0.2 mL min<sup>-1</sup>. After complete addition of monomer emulsion, the reaction was finished by holding the temperature for another hour. In a subsequent step, the particles were transferred in a Stöber process. Typically, 29 g of the latex was mixed with 840 mL ethanol and 48 mL ammonia solution (25 vol%). Then 30 g TEOS diluted in 30 g ethanol were added and the dispersion was gently stirred at ambient temperature for 16h.

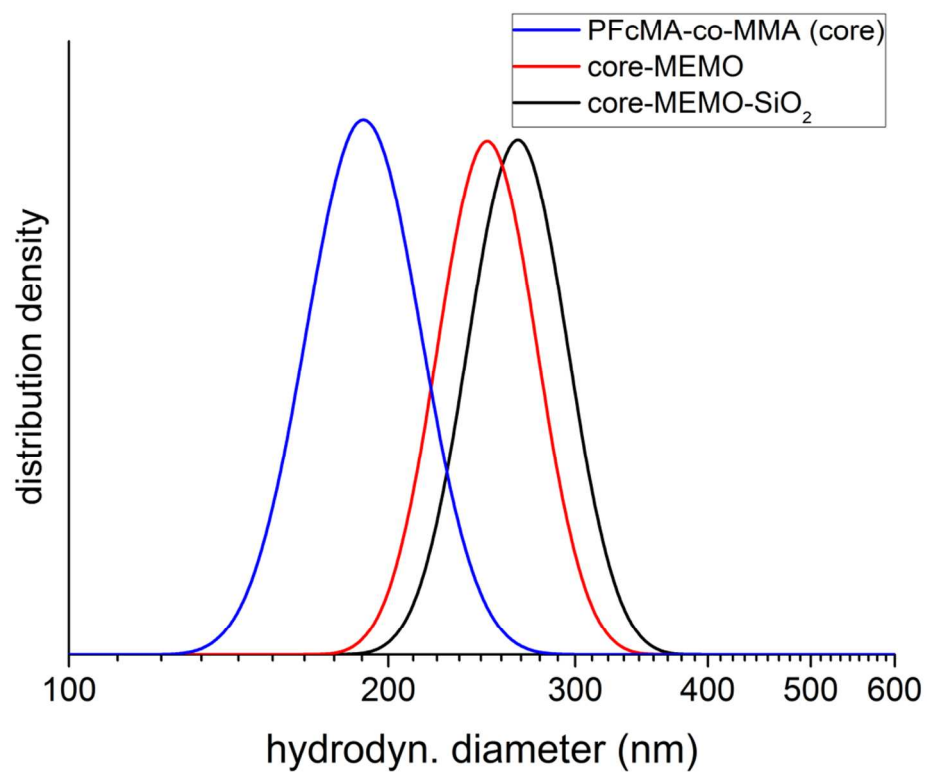
## Preparation of magnetic SiO<sub>2</sub> hollow spheres

Obtained core shell particles were purified by two centrifugation-redispersion-steps. After drying the particles in vacuum, they were tempered at 500°C for 5h.

## Uniform SiO<sub>2</sub> Nanorattles with Magnetic Core

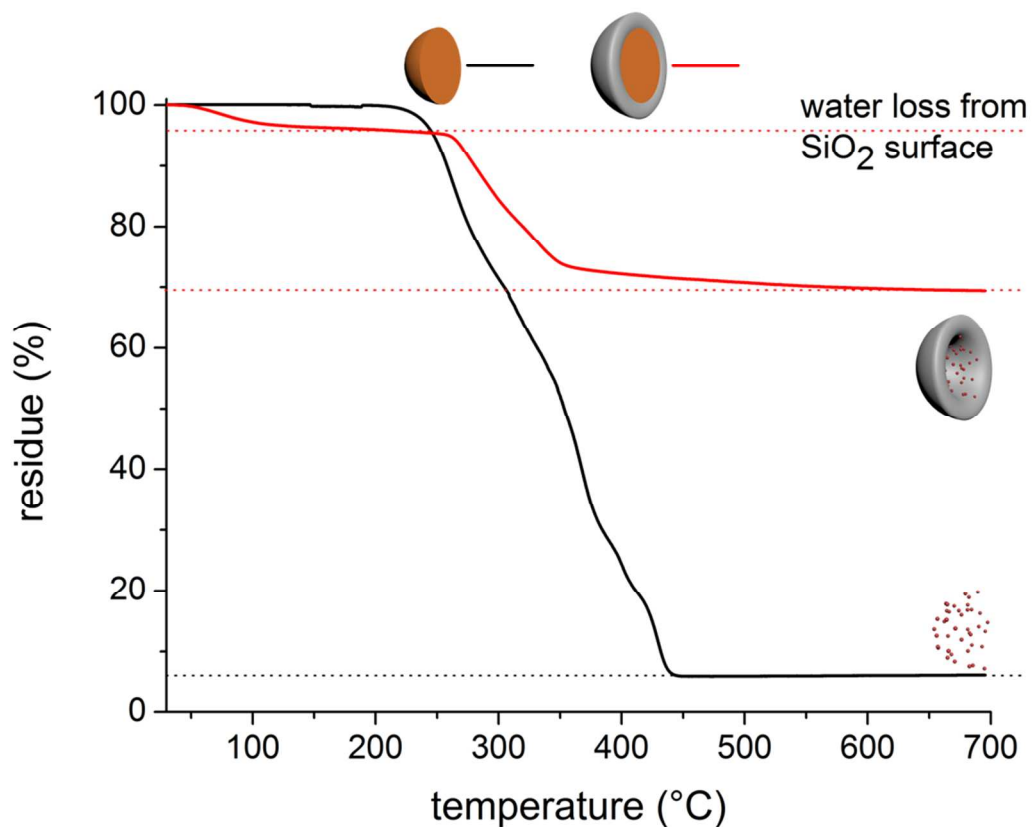
Magnetic SiO<sub>2</sub> hollow spheres (4.8 g) were dispersed in 390 mL ethanol with 15 mL ammonia solution by sonication. Then, 0.47 mL MEMO was added and the mixture was gently stirred at ambient temperature for 1h, and one more hour at 60°C. Afterwards, the solvent was replaced with 40 mg SDS in 200 mL water by distillation. Total volume was reduced to 120 mL before filling the dispersion in a 250 mL vessel at 75°C equipped with reflux condenser, stirrer and nitrogen feeding. After the addition of 100 mg NaPS, a monomer emulsion containing 17 mg SDS, 52 mg Dowfax2A1, 8.7 g MMA, 50 mg KOH and 13 g water was added with 0.2 mL min<sup>-1</sup>. MEMO functionalization and Stöber process were conducted analogous to the description above.





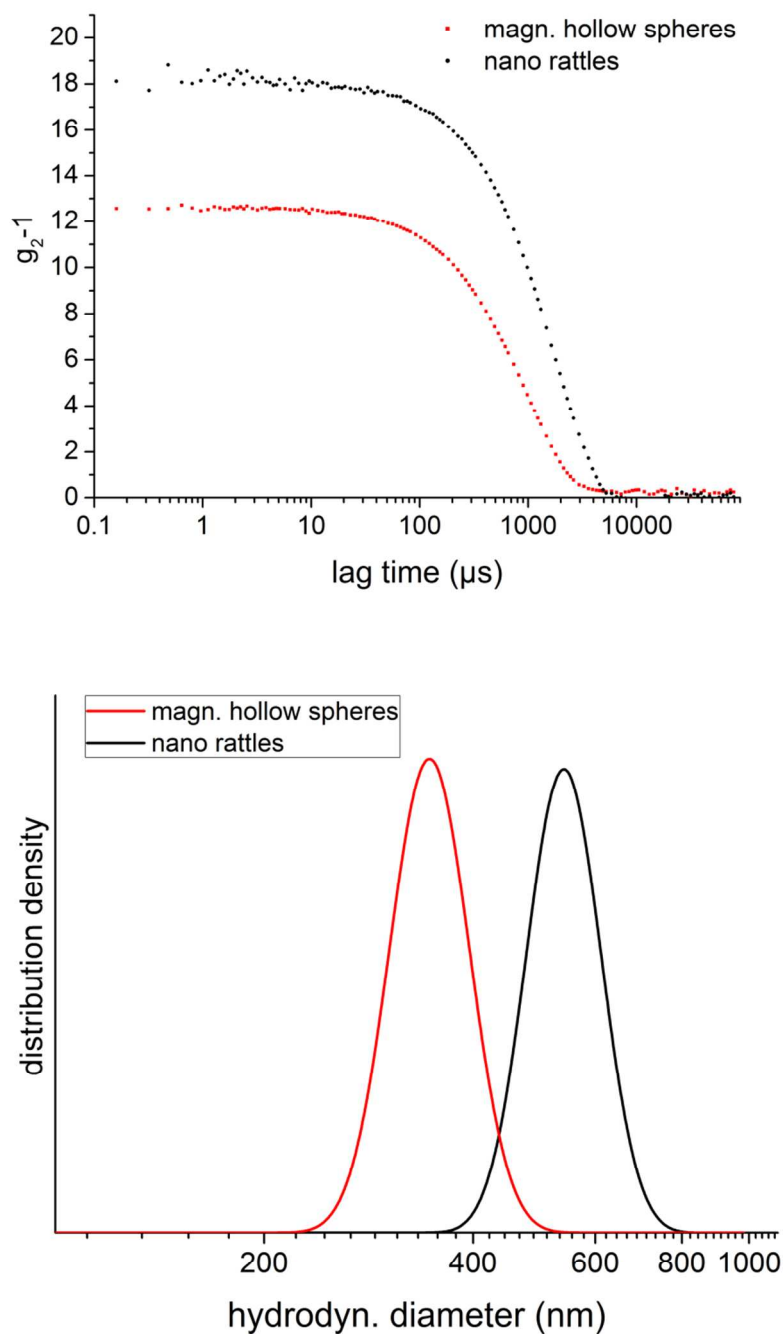
**Figure S1.** DLS measurements of the step-wise preparation of SiO<sub>2</sub>@PFCMA-*co*-PMMA particles.





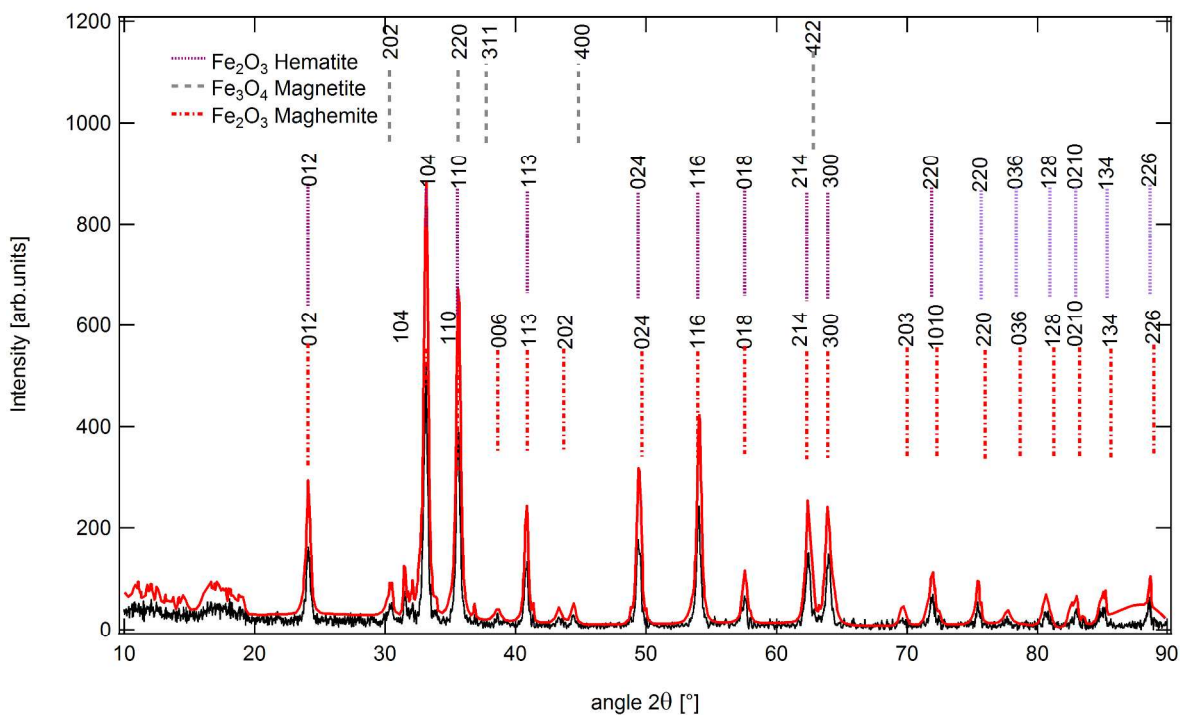
**Figure S2.** Thermogravimetric analysis of the PFcMA-containing core particles (black line). The final residue could be assigned to the three different types of iron oxides with 6.2 wt% ceramic yield (see main text). The red line corresponds to the TGA for silica-shell magnetic core particles. The weight loss of about 4.3 wt% beginning at 100°C could be assigned to a water loss, while the second step beginning at 250°C could be assigned to stem from the ceramization process yielding 69.4 wt% of the final silica-shell magnetic core ceramic.





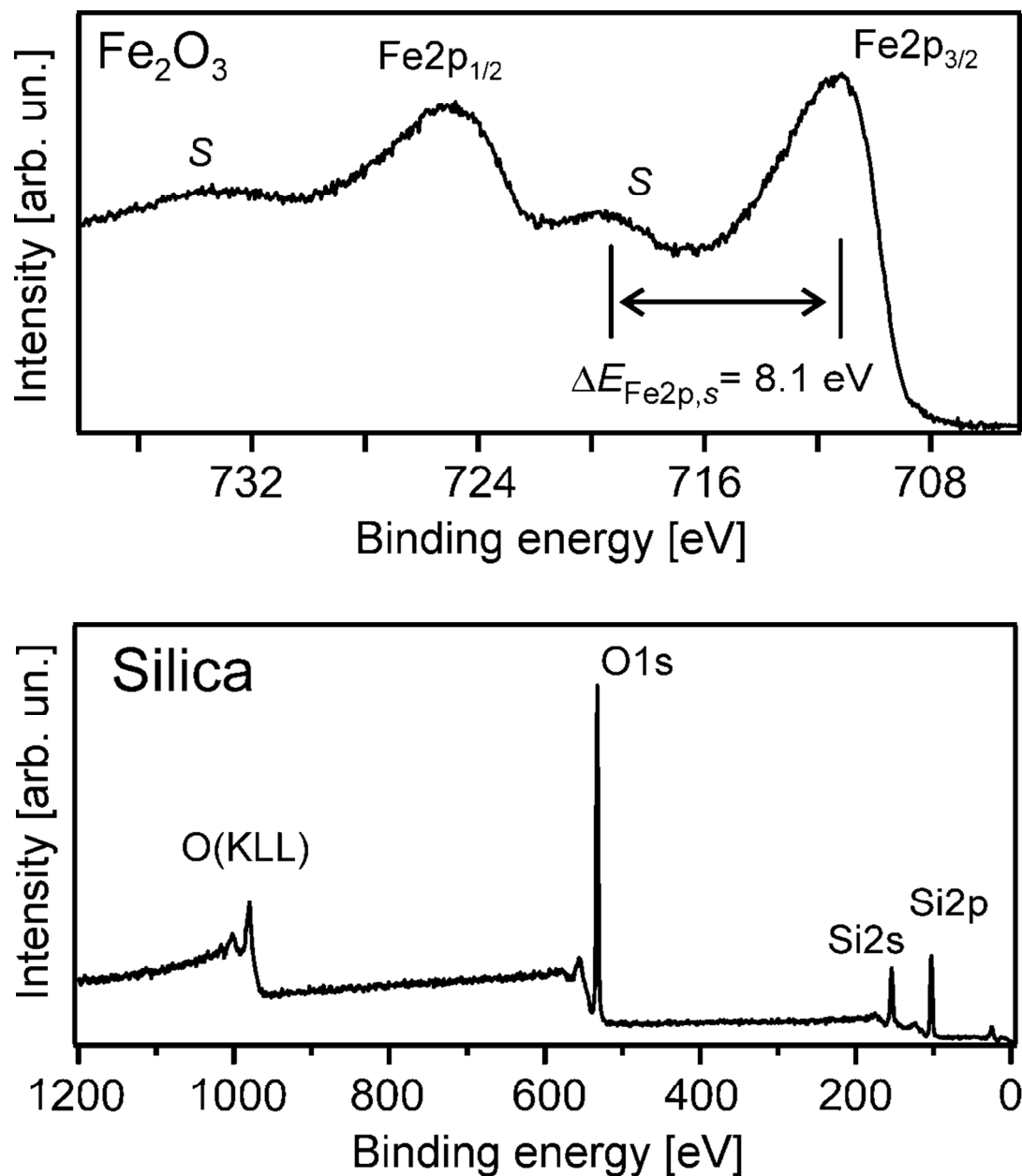
**Figure S3.** Top: Autocorrelation functions obtained by using dynamic light scattering measurements of the magnetic hollow spheres and the final ceramic nanorattles as dispersion in water. Bottom: Corresponding hydrodynamic radii for the ceramized core hollow spheres and the nanorattles.





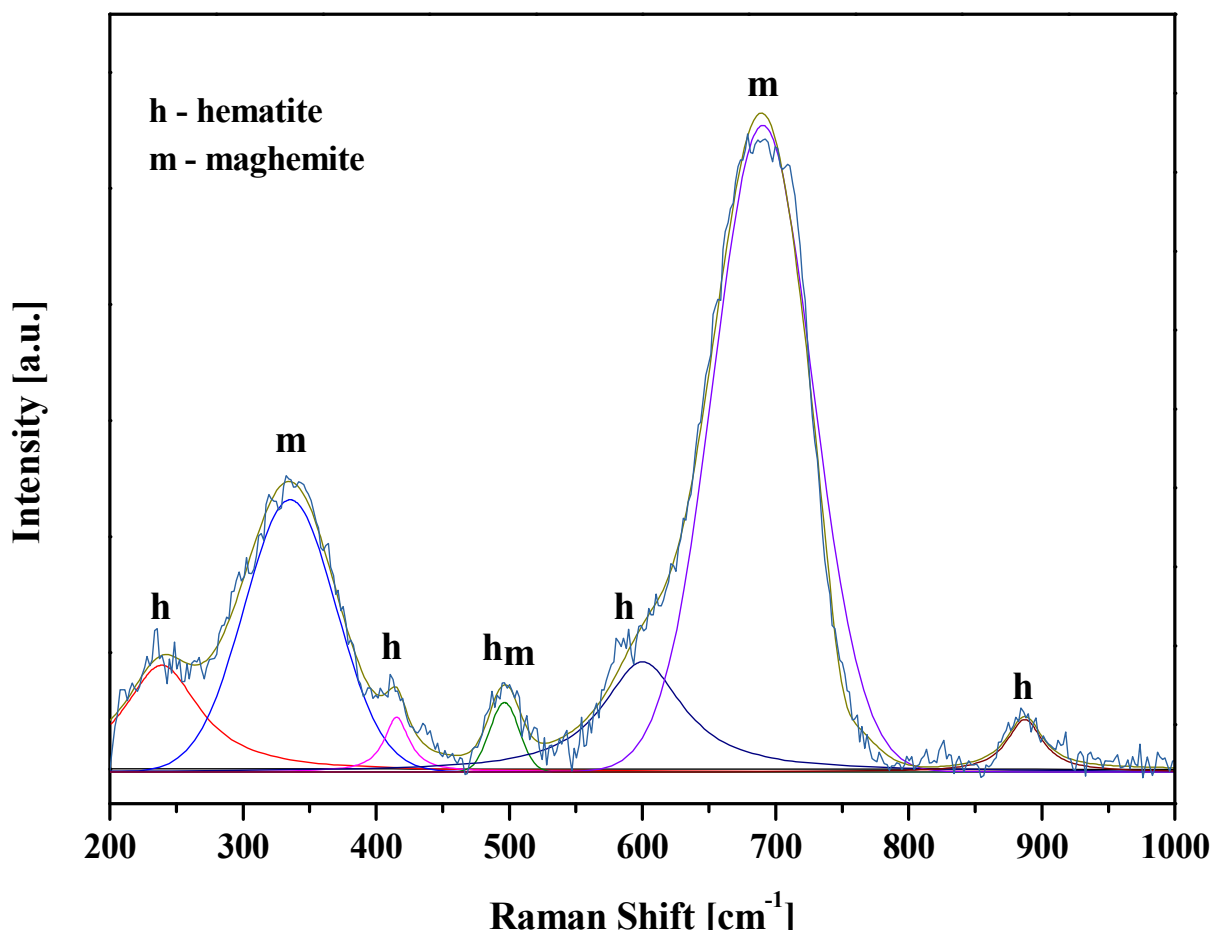
**Figure S4.** WAXS pattern of ceramized ferrocene-containing particles, which were treated thermally at 500°C for 5h yielding different types of iron oxides and signal assignment.





**Figure S5.** Top: The Fe2p photoelectron spectrum of the Fe<sub>2</sub>O<sub>3</sub>-powder obtained by annealing the PFcMA-containing particle core material. Bottom: XPS photoelectron spectrum of the nanorattle-type material featuring a thick silica shell ( $h\nu=1486.6 \text{ eV}$ ,  $E_{\text{pas}}=187.85 \text{ eV}$ ).





**Figure S6.** Raman spectrum of the Fe<sub>2</sub>O<sub>3</sub>-powder obtained upon thermal conversion of the PFcMA-containing particle core material showing the presence of hematite and maghemite.<sup>2,3</sup>

## References

1. Mazurowski, M.; Gallei, M.; Li, J.; Didzoleit, H.; Stühn, B.; Rehahn, M., Redox-Responsive Polymer Brushes Grafted from Polystyrene Nanoparticles by Means of Surface Initiated Atom Transfer Radical Polymerization. *Macromolecules* **2012**, 45, 8970-8981.
2. Hanesch, M., Raman spectroscopy of iron oxides and (oxy)hydroxides at low laser power and possible applications in environmental magnetic studies. *Geophys. J. Int.* **2009**, 177, 941-948.
3. Chamritski I.; Burns G., Infrared- and Raman-Active Phonons of Magnetite, Maghemite, and Hematite: A Computer Simulation and Spectroscopic Study. *J. Phys. Chem. B* **2005**, 109, 4965–4968.