Supporting Information.

Monodisperse Magnetofluorescent Nanoplatforms for Local Heating and Temperature Sensing

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Nanoparticle characterizations: The size and morphology of the nanostructures as well as the crystal lattice were characterized using a JEOL 2010 (200 kV) transmission electron microscope (TEM). Samples for TEM analysis were prepared by drying a hexane dispersion of the particles on amorphous carbon coated copper grids (Ted Pella Inc). Powder X-ray diffraction patterns (XRD) of the NPs were recorded in Bragg-Brentano geometry using a Rigaku Ultima IV instrument with Cu(Kα) radiation (\(\lambda=1.5418 \text{ Å}\)). Magnetic measurements were performed using the Vibrating Sample Magnetometer of a Quantum Design Physical Property Measurement System model 6000 (PPMS) with a field of up to 90 kOe. The compositions were characterized by an Oxford energy-dispersive X-ray spectroscopy (EDS). UV-vis absorption spectra were collected using a Shimadzu model 3101PC UV vis NIR scanning spectrophotometer over a wavelength range from 300 to 800 nm. Photoluminescence spectra were obtained using a Fluorolog-3 spectrofluorometer. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 analyzer by heating the sample powders from room temperature to 650 °C at 20 °C min\(^{-1}\) in the sample pan under the protection of a gentle nitrogen flow.
Synthesis of 13-18nm Fe NPs: 0.3 ml oleylamine was dispersed in 20 ml ODE in a four-neck flask under a flow of nitrogen and heated to 120 °C. The solution was kept at 120 °C for 30 min before being heated to 180 °C. 0.7 ml Fe(CO)₅ was quickly injected into the mixture at 180 °C and the color of the solution changed from yellow brown to dark in about 1 min. The reaction was kept at that temperature for 20 min and then cooled down to room temperature. For 18 nm Fe NPs, the synthesis is the same except that at this point the solution was not cooled to room temperature but to 160 °C. Then, 0.15 ml Fe(CO)₅ was quickly injected and the solution was kept at 160 °C for another 15 min, followed by another injection and reaction for 15 min. Only then the solution was cooled to room temperature. From here on, the harvesting of the NPs was the same for all sizes. The light-brownish colored supernatant was decanted, and the NPs attracted on the magnet were collected by centrifugation, and then redispersed in hexane and stored under nitrogen.

Freshly prepared Fe NPs of 18 nm size have a higher initial saturation magnetization than that of MnFe₂O₄ NPs, reaching 130 emu g⁻¹ Fe. However, the magnetization of bare Fe NPs drops quickly due to surface oxidation when exposed to air. The oxidized surface layer of the NPs can be clearly observed in Figure S5. Figure S6 shows that the initial rate of magnetization reduction of Fe NPs is as high as -4.3% h⁻¹ in the first 4 hours, and then changes to -0.62% h⁻¹ in the next 20 hours (hollow spheres). After being exposed in air for 24 hours, the remaining magnetization is only about 71% of the initial magnetization. This indicates that further protection of the Fe NPs from oxidation is necessary for their practical applications. Therefore, silica shell was coated on Fe NPs to prevent the oxidation. Figure S7 shows that Fe/SiO₂ NPs with different
shell thickness were obtained by varying the amount of TEOS and ammonia. In contrast, silica coated Fe NPs show an initial rate of -0.43% h\(^{-1}\) within the first 10 hours, which then decreases to -0.15% h\(^{-1}\) between 10-72 hours. This suggests that the silica shell reduces the speed of Fe oxidation by orders of magnitude yet cannot prevent it completely. The incomplete protection is presumably due to the porous nature of the silica coating. Nevertheless, silica coated Fe NPs retain >90% of the magnetization within the first 24 hours, and may be advantageous in certain biomedical applications when the NP dosage needs to be minimized.

Figure S8 shows that embedding Rhodamine6G into the silica shell of the NPs extends the fluorophore’s lifetime. The fluorescence decay curve of the free Rhodamine6 at 30°C shows the instrument response time as very short lifetime and the Rhodamine6G decay time of 1.43 ±0.01 ns. The silica coated metal NPs show significant scatter broadening the instrument response time. The decay time of the embedded Rhodamine6G is of 1.64 ± 0.01 ns. After etching away the metal core and leaving only the silica shell with the Rhodamine6G, the scatter is reduced. The decay time of the embedded Rhodamine6G is now 1.47 ± 0.01 ns. At this point we cannot determine if the reduced Rhodamine6G lifetime in the empty shells versus the intact coated-NPs is a result of the etching process or of the absence of the metallic core.
Figure S1. The EDX analysis shows that the Fe to Mn molar ratio close to 2:1, the stoichiometry ratio of MnFe₂O₄.
Figure S2. The TEM image of SiO$_2$ coated MnFe$_2$O$_4$ NPs shows no free SiO$_2$ NPs formed in large area.
Figure S3. The low field (to 2000 Oe) hysteresis loops clearly show that before and after silica coating, the particles are superparamagnetic.
Figure S4. EDX analysis reveals that there is no heavy metal ions to the limit of the instrument resolution were detected after etching.
Figure S5. The TEM images of uncoated (a) 13 nm Fe/FeO$_x$, (b) 18 nm Fe/FeO$_x$ NPs.
Figure S6. The saturation magnetization of the NPs as a function of time of air exposure. Solid squares: Fe/silica NPs; circles: Fe NPs.
Figure S7. The TEM images of as-synthesized (a) 10 nm silica shell coated 13 nm Fe/FeO₅ NPs; (b) 2 nm silica shell coated 18 nm Fe/FeO₅ NPs.
**Figure S8.** Rhodamine6G fluorescence lifetime measured by TCSPC-FLIM at 30°C of free Rhodamine6G in aqueous solution (black symbols in (a)), embedded in the silica shell of silica coated NPs (black symbols in (a) and (b)), and embedded in the silica of empty shells after etching away the metal core (black symbols in (a) and (b)).
REFERENCES
