Supplementary Information

Spectral drifts in surface textured Fe_3O_4-Au, core-shell nanoparticles enhance spectra-selective photothermal heating and scatter imaging.

Grace Brennan [a], Nanasaheb Thorat [a,b], Martina Pescio [a], Silvia Bergamino [a], Joanna Bauer [b], Ning Liu [a], Syed A. M. Tofail [a], Christophe Silien [a].

[a] Modelling Simulation and Innovative Characterisation (MOSAIC), Department of Physics, School of Natural Sciences and Bernal Institute, University of Limerick, Limerick, V94 T9PX, Ireland.
[b] Department of Biomedical Engineering, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, Wybrzeże Stanisława Wyspiańskiego 27, Wrocław 50-370, Poland.

SI.1 Materials, detailed synthesis procedure, and characterisation techniques

Materials

Iron Oxide Nanoparticles in Chloroform, 20 nm from Ocean NanoTech, (3-Aminopropyl) triethoxysilane (APTES), Hexane anhydrous 95%, Sodium hydroxide reagent grade, ≥98%, pellets (anhydrous), Tetrakis(hydroxymethyl) phosphonium chloride (THPC) solution 80% in H_2O, Hydrogen tetrachloroaurate(III) ($HAuCl_4$) ≥99.9% trace metals basis, Acetic acid ≥99%, Potassium carbonate ≥99%, Formaldehyde 36.5-38% in H_2O, Ethanol anhydrous, were all purchased from Sigma Aldrich and used without further purification. Milli-Q® ultrapure water with a resistivity of 18.2 MΩ.cm was used throughout this work.

Synthesis procedure

Ligand Exchange of Oleic acid to Amine termination. To replace the Oleic acid (OA)-capping on the surface of the core iron oxide nanoparticle with a functional silane layer, a protocol reported by Davis et al. [1] was modified. To a dry vessel, 5 mg of the hydrophobic OA-capped nanoparticles were separated and suspended in 30 mL of hexane and 3 µL of acetic acid, APTES was added in excess and then sealed. The solution was sonicated at 40˚C for two hours and then agitated using a shaking incubator at room temperature for three days followed by another sonication at 40˚C for two hours. At this stage, a black precipitate should be visible with a clear organic solution, indicative of a successful phase transfer. If this precipitation does not occur, the nanoparticles should be separated magnetically, and the steps should be repeated. The precipitate was washed through magnetic separation and supernatant removal followed by bath sonication to resuspend in fresh solvent. These functionalised iron oxide nanoparticles were washed twice in hexane then twice in ethanol to remove excess ligands. The precipitate was resuspended into 5ml of ethanol, showing a dark black solution. This nanoparticle stage is denoted “O” throughout this paper.

Core-satellite iron oxide-seeded gold Nanoparticles. The Duff et al. [2] method for obtaining sub-5 nm gold nanoparticle seeds was followed. 10 mL of 0.1 M sodium hydroxide was added to 90 mL of MilliQ water under vigorous stirring. To this, 24 µL of 80% THPC was added. After ten minutes of stirring, 4 mL of 1% $HAuCl_4$ was quickly injected into the solution. A dark yellow-brown solution was obtained. This solution was aged for at least one week in the dark at 4˚C and then used without further purification. To coat the amine functionalised iron oxide core nanoparticles with gold seeds, the following procedure was followed. 3.5 mg of the previously functionalised iron oxide nanoparticles was suspended in 7 mL of ethanol and bath sonicated for 30 minutes. This was added to 7 ml of seed solution and was shaken until the supernatant was colourless after magnetic separation. This indicated the successful adherence of gold seeds onto the magnetic nanoparticle. The precipitate was then combined with 5 mL of seed solution and 5 mL of ethanol, bath sonicated for thirty minutes, and the solution was subsequently stirred overnight. The resulting solution was magnetically separated and redispersed in water using a bath sonicator several times to a final volume of 10 mL. This nanoparticle stage is denoted "Os" throughout this paper.

Complete Core/Shell Nanoparticles. The protocol for obtaining gold/iron oxide nanoparticles was based on the Oldenburg et al. protocol [3] for gold coating silica microspheres. Gold hydroxide ($AuCl_4$- to $Au(OH)_3$) plating solution for completing the gold shell was prepared as follows. 100 mg of potassium carbonate was dissolved by stirring in 400 mL of water. After ten minutes of stirring, 0.5 mL of 0.5 M $HAuCl_4$ was added and stirred until the solution was colourless. This solution was kept in the dark at 4˚C until needed. 2.5 mg of the previously synthesised core-satellite nanoparticles were bath sonicated and added to 250 ml of the gold hydroxide solution. The solution was sonicated for one hour and then under stirring, 100 µL of 0.05 M $HAuCl_4$ and five minutes later 100 µL formaldehyde were added dropwise into the solution. An aliquot of 50 ml was taken. This process may be repeated to obtain more complete gold shells. The solution was magnetically washed at least twice in water to prevent retention of gold nanoparticles. The magnetic separation takes significantly more time than without the gold shell; the solutions were magnetically separated for ~6 hours with a permanent magnet at the side of the vessel. After the first gold reduction, this nanoparticle aliquot is denoted "R1" throughout this paper. The nanoparticles after the second reduction were referred to as "R2" and the third as "R3". See Fig. S1 for camera pictures of iron oxide-gold particle solutions Os, R1, R2, and R3 with and without a magnet applied to the side of the vessel demonstrating unambiguously that the solutions only contains magnetic materials as expected for clean core-shell nanoparticle solutions.

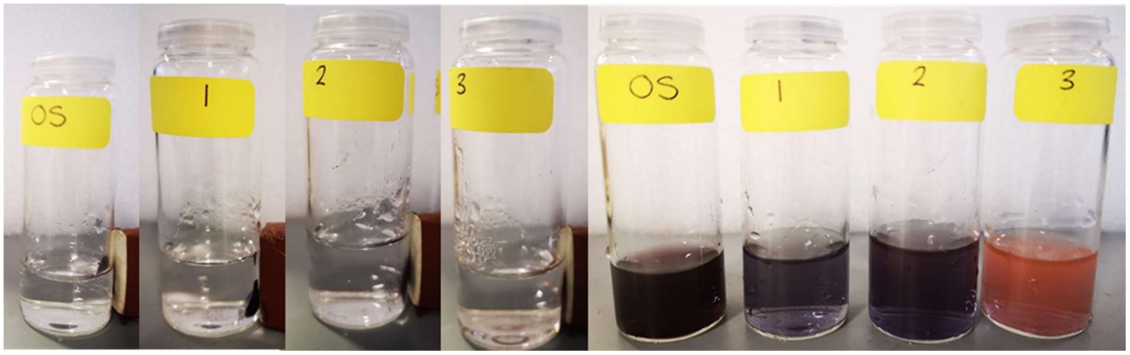

Fig. S1: Solutions of magnetic-plasmonic nanoparticles Os, R1, R2, and R3 with (left) and without (right) permanent magnet at the right-hand side of the vessel.

Characterisation. *Extinction and Scattering Measurements.* Extinction measurements were carried out on a homebuilt setup using a deuterium-halogen UV-Vis-NIR light source (DH2000-BAL, Ocean Optics) using only halogen as the light source, quartz cuvettes (CV10Q3500, Thorlabs) and Flame Spectrometer (Ocean Optics) paired with OceanView software. Scattering measurements were obtained on a homebuilt dark-field microspectroscope. A 150 W halogen light source was used (OSL2, ThorLabs), an Olympus 1.2-1.4 NA dark-field condenser using type-F immersion oil and a 0.9 NA 100× Olympus objective (MPLFLN100×) in collection, a Princeton instruments Acton series SP2300, with a 600/mm grating blazed at 750 nm onto a cooled PIXIS 256 CCD camera. The grating is moved to collect the spectrum in 100 nm increments with 50 nm overlap, each section acquiring for 15 seconds with two accumulations. Aqueous nanoparticle suspensions were sonicated for 30 minutes and a very low concentration was dropcast on a glass slide (ITO-coated for SEM correlation). Under dark-field illumination, aggregates of nanoparticles could be distinguished by increased scattering intensity and these were discarded. The dark-field spectrum was corrected by subtracting the spectrum of a nearby area (clean and free of particles) and dividing by the white light spectrum. Laser dark-field imaging was conducted with a Coherent Libra Ti:Saphire regenerative amplifier combined with a TOPAS optical parametric amplifier generating a 1 kHz high pulse energy tunable coherent beam. It should be noted that this laser is unsuitable for photothermal measurements due to the lower average powers focused on the samples (ca. 2 μW). A long working distance Leitz objective with NA 0.6 was used in illumination with a dark field NA 0.8 Olympus objective as collection. A homemade mask was placed to block the centre of the back aperture so that only high angle scattering was detected by the photomultiplier tube detector. Images were recorded by scanning the samples position in the focus using a Physics Instruments piezo-electric scanner.

Photothermal Measurements. A 532 nm 80 MHz, ca. 6 ps Spark Lasers Antares fibre laser was used to irradiate nanoparticle solutions with a collimated beam of diameter 5 mm. To generate other wavelengths from 690 – 2300 nm, a tuneable near infrared synchronously pumped optical parametric oscillator (Levante Emerald, APE, Berlin) was used, using the 532 nm 80MHz as pump. A constant nanoparticle count of 10 μg/ml Fe_3O_4 was dispersed in 1 ml

of water in an Eppendorf tube and the solutions were maintained at room temperature before exposure to the laser beam and measurements. The temperature of the Eppendorf tube was monitored noncontact using a calibrated FLIR A655sc infrared camera with ResearchIR software.

Electron Microscopy. 2 µL of a low concentration, sonicated nanoparticle suspension was drop cast onto a holey carbon filmed copper TEM grid (AGS147, Agar Scientific). The excess solution was removed after one minute to obtain isolated nanoparticles. A JEOL JEM-2100F field emission transmission electron microscope with an acceleration voltage of 200 kV was used to image the nanoparticles.

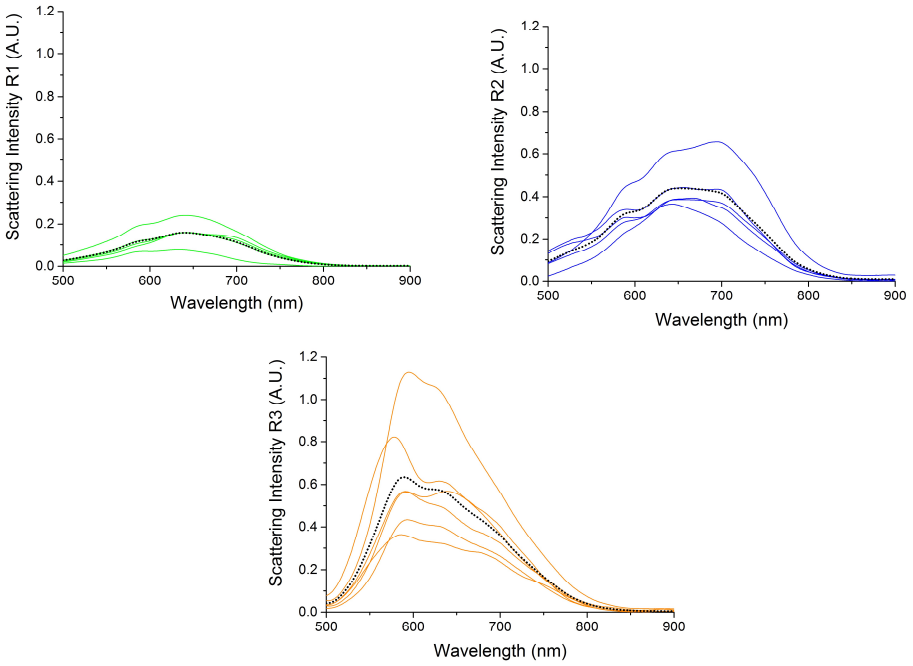

Fig. S2: Scattering of individual particle series for each of the detectable magnetic-plasmonic stage, R1 top left, R2 top right and R3 bottom. The black dotted line in each plot represents the average spectra.

SI.2 Comsol Multiphysics® Simulations

COMSOL Multiphysics® 5.3a, a finite element analysis (FEA) software was used with using the "Wave Optics" physics. A 3D cuboid model, similar to the "Scatterer on Substrate" example published by Comsol, was used to obtain the absorption, scattering and extinction cross-section of a single core-shell nanoparticle suspended in air (no substrate), see Fig. S3. The absorption cross-section was calculated by integrating the power loss density over the nanoparticle volume, which was then divided by the incident light intensity. The scattering intensity was obtained by integrating the dot product of the vector normal to the nanoparticle surface and the Poynting vector over the entire nanoparticle surface. Lastly, the extinction was computed as the sum of the absorption and scattering cross-section. The incident electromagnetic wave (linearly polarised plane wave with each plane wave being a solution to Helmholtz equation in the absence of nanoparticle) was defined as a background electric field which enters from one port with a specific area A and exits through the opposite cube face. The input power was defined as $P = I_0 \times A$, where I_0 is the incident field intensity in W/cm^2. Periodic Floquet boundary conditions were imposed and a perfectly matched layer (PML) was added to absorb any scattered field. Gold and iron oxide material properties were taken from the Comsol material library with optical properties for magnetite from Querry [4] and Johnston and Christy [5] for gold.

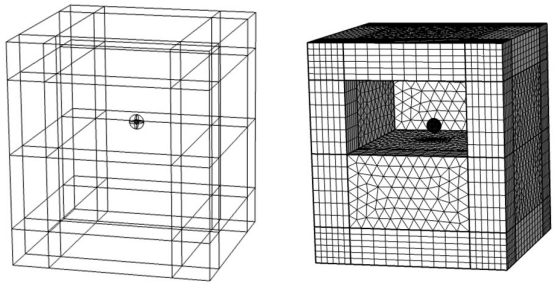

Fig. S3: Geometry and mesh of the Comsol Multiphysics ® Simulations model used in this research.

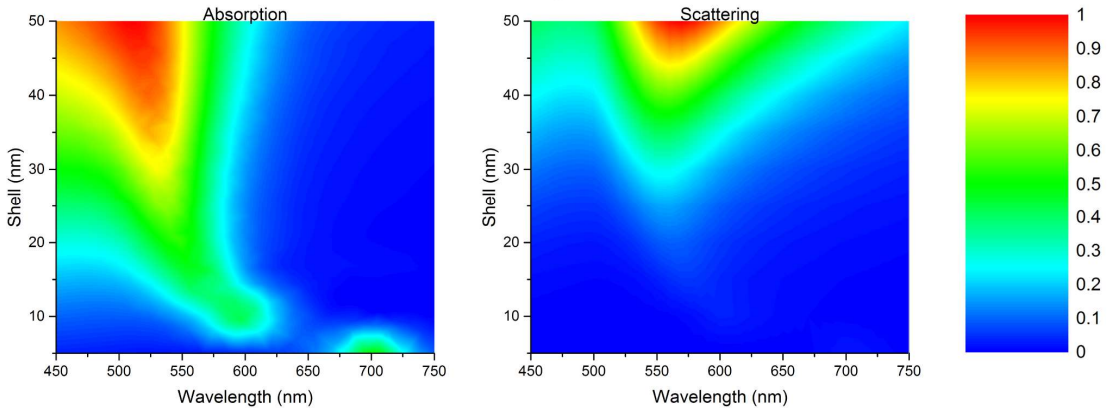

Fig. S4: Absorption (left) and scattering (right) for a 20 nm diameter Fe_3O_4 core with varied smooth gold shell thickness in a 3D plot with respect to wavelength, gold shell thickness and absorption/scattering intensity (colour scale). Spectral drifts between the optical absorption and scattering can be seen for thicker shells.

References

1 K. Davis, B. Cole, M. Ghelardini, B. A. Powell and O. T. Mefford, *Langmuir*, 2016, **32**, 13716–13727.

2 S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. Li, *J. Am. Chem. Soc.*, 2004, **126**, 273–279.

3 S. J. Oldenburg, R. D. Averitt, S. L. Westcott and N. J. Halas, *Chem. Phys. Lett.*, 1998, **288**, 243–247.

4 M. Querry, *US Army Chem. Res. Dev. Eng. Cent. (CRDC), Aberdeen Proving Ground, MD*.

5 S. Gupta, Q. Zhang, T. Emrick and T. P. Russell, *Nano Lett.*, 2006, **6**, 2066–2069.