Electronic Supplementary Information

Assembling magneto-plasmonic microcapsules by using a micro-fluidic device

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1. **Synthesis of Fe_2O_3 magnetic nanoparticles:** Hydrophobic Fe_2O_3 nanoparticles with an average diameter of 6 nm were synthesized following a modified procedure developed by Sun et al.[19] All chemical reagents were purchased from Aldrich and used as received, iron (III) acetylacetonate ($Fe(acac)_3$), 1,2-hexadecanediol, oleic acid, oleylamine, benzyl ether, absolute ethanol and cyclohexane. Initially Fe_2O_3 were synthesized by mixing ($Fe(acac)_3$) (2 mmol), 1,2-hexadecanediol (10 mmol), oleic acid (6 mmol) and benzyl ether (20 mL) under nitrogen atmosphere and heating the system to 200°C for 2 hours while stirring under a slow flow of nitrogen. The nitrogen flow was stopped and the mixture was further heated to reflux (~250°C) for 1 hour. The black-brown colored mixture was cooled to room temperature, and stirring was maintained for an additional 4 hours. Fe_2O_3 nanoparticles (6 nm ± 1.2) were isolated by precipitating the particles with ethanol (40 mL), followed by centrifugation at 10 000 rpm for 30 min. The black-brown precipitate was dissolved in 10 mL of cyclohexane in the presence of 50 μL of oleic acid and 50 μL of oleylamine forming a non-transparent black-brown colloid. Any particulate residue was removed by centrifugation at 6000 rpm for 10 min. The particles were again precipitated from the supernatant with ethanol (20 mL), centrifuged at 10000 rpm for 20 min, and re-dispersed in 10 mL of cyclohexane.

   The surface of MNps covered with oleic acid was modified with 11-mercaptoundecanoic acid (MUA) according to a modified method of Sun et al. (Sun,

X. Journal of Applied Physics 2005, 97, 10Q901-1; Sperling, R.A. *Phil. Trans. R. Soc. A* (2010) **368**, 1333–1383). 10mM of MUA acid was added to the stock solution of MNps and was stirring overnight. After was centrifuged, washed and re-dispersed in cyclohexane.

The particles had a narrow size distribution, as confirmed by TEM (Fig. S1). Final concentration: 1.8×10^{16}Nps/L.

2. **Synthesis of 7nm gold nanoparticles:** An aqueous solution (20 mL) containing $HAuCl_4$ (0.25 mM) and trisodium citrate (0.25 mM) was prepared in a flask. Then, ice-cold, freshly prepared $NaBH_4$ (0.6 mL, 0.1 M) solution was added to the mixture while stirring vigorously. The solution was allowed to age for 3 hous, and then used as a seed solution. While stirring, 2.5 mL of this seed solution was mixed with 7.5 mL of an aqueous solution containing $HAuCl_4$ (0.25 mM) and polyvinylpyrrolidona (0.1% PVP, M_W ~10.000). Then freshly prepared ascorbic acid solution (0.05 mL, 0.1M) was added to the mixture and allowed to react for 20 min while stirring.

   The average diameter of the gold nanoparticles was determined by TEM (9 nm ±1.5 nm) (Fig. S2). Final concentration: 1.9×10^{15}Nps/L.

3. **Layer-by layer method (LBL):** The deposition of a two-layer of polymer film onto the negatively charged γ-Fe_2O_3-AuNps microcapsules was completed as follow: The precursor polyelectrolyte layer was a cationic polymer poly(diallyldymethylammonium chloride) (PDADMAC)) with a concentration of 1 mg mL^{-1} where was deposited onto the negatively charged γ-Fe_2O_3-AuNps microcapsule (adsorption time of 20 min). The second layer of polyelectrolyte was the 1 mg mL^{-1} anionic polymer poly(styrenesulfonate) (PSS) that was added to the microcapsules solution. In each step the samples were centrifuged at 5000 rpm for 5

min in order to extract the excess of polyelectrolyte and to wash and the subsequent redispersion in water.

4. **Microreactor:** The Y-shape glass microreactors (µR) were purchased from Micronit Microfluidics BV. The dimensions provided by Micronit are: width = 150 µm, height = 150 µm, length = 0.83 m. Outlet tube (inner diameter 150 µm, length = 14 cm) were purchased from Polymicro.

Characterization: Optical spectra were obtained on Avaspec-USB2 UV-VIS-NIR Spectrometer. Fluorescence microscopy images were observed by using a Zeiss Axiovert 200 microscope (X 40, NA 0.65, HBO 100) and rhodamine filter set with pictures taken by a CCD camera and digitalized on a computer. All Transmission Electron Microscopy (TEM) images were obtained by using a JEOL 10 CX instrument (100kV). Scanning Electron Microscopy (SEM) images were observed on a SEM-FEG ZEISS ULTRA 55 apparatus. Energy-dispersive X-ray Spectra (EDS) and elemental maps were obtained using the apparatus in mode EDS at an accelerating voltage of 15kV. The magnetization curves of the maghemite particles suspension were determined using a vibrating magnetometer. The shape of the magnetization curves was fitted according to Langevin's law, which gives the relationship between the magnetization M of the magnetic particles per unit volume as a function of their volume fraction.

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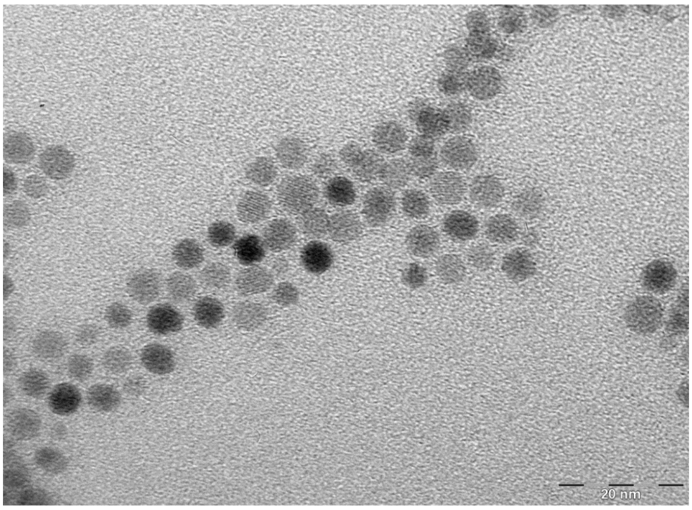

Fig. S.1: TEM images of 6.5 ± 1.1 nm Fe_2O_3 Nanoparticles.

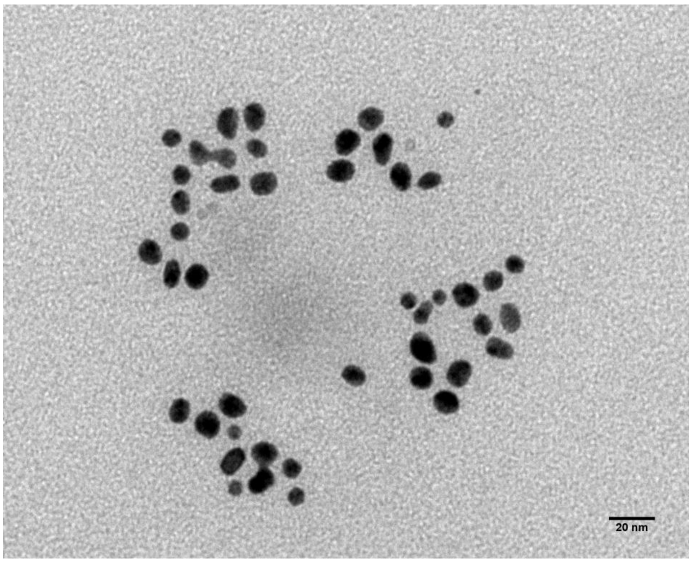

Fig. S.2: TEM images of Au Nanoparticles.

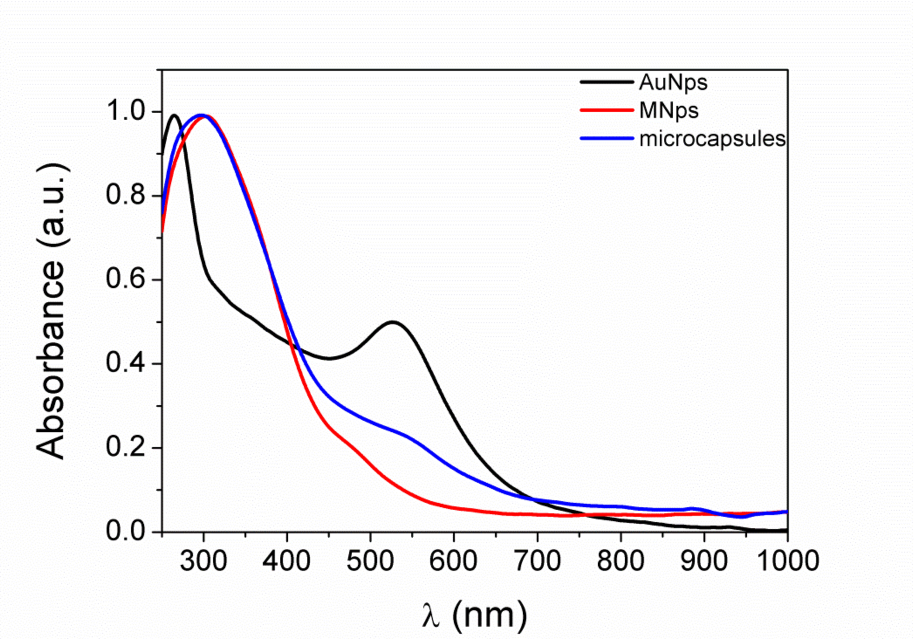

Fig. S.3: Normalized UV-Vis absorption spectrum of the free Au and MNps and of the obtained microcapsules.

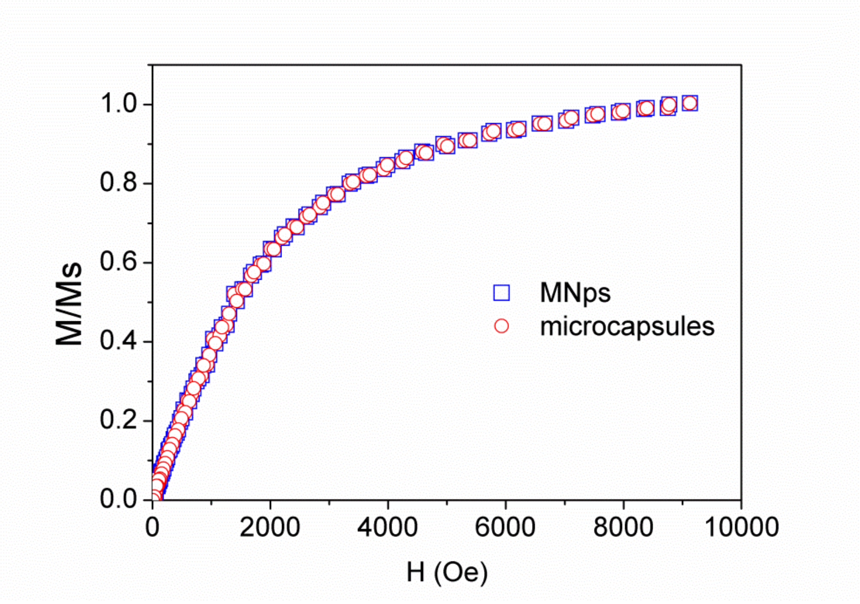

Fig. S.4: The variation of the magnetization (M) of the magnetic nanoparticles normalized to the saturation magnetization (Ms) as a function of applied magnetic field (H) recorded from free (open squares) and assembled MNps in the shell of the capsules (open circles) revealed superparamagnetic behavior without hysteresis. Both curves presented the same shape, which was well fitted by Langevin's law for a log-normal distribution of magnetic grains of 6.3 nm mean diameter and 0.2 standard deviation.

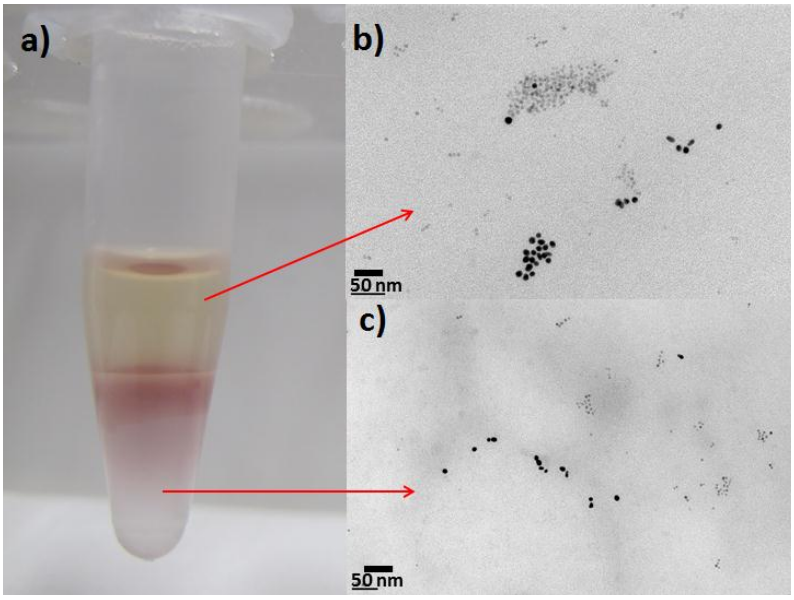

Fig. S.5: a) three different phases obtained in the outlet of the microreactor, b) TEM image of organic phase, c) TEM image of aqueous phase.

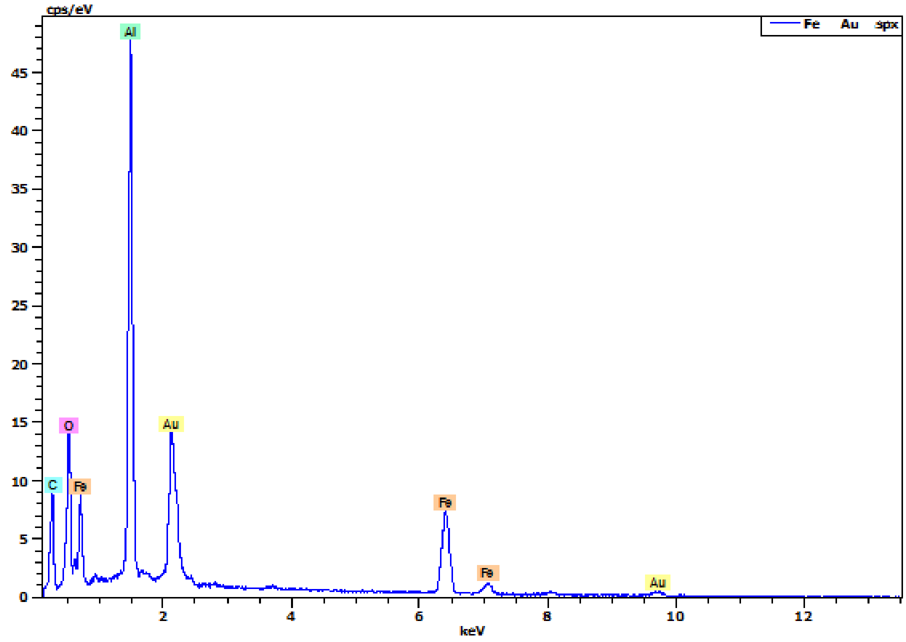

Fig. S.6: EDS Analysis of γ-Fe_2O_3-AuNps assembly in a microcapsule.

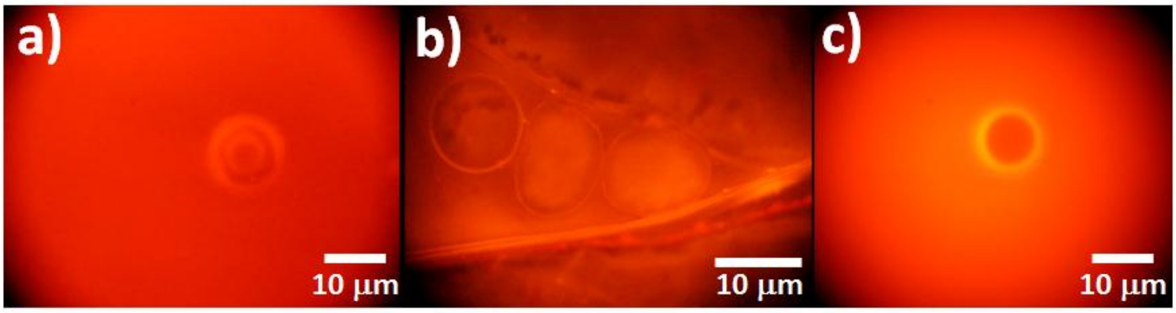

Fig.S.7: Fluorescence microscopy images of γ-Fe_2O_3-AuNps microcapsules after addition of a) Rhodamine B isothiocyanate in the core b) additional image of a), c) Rhodamine B isothiocyanate in the external aqueous phase.