Magnetically-driven selective synthesis of Au clusters on Fe_3O_4 Nanoparticles

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Electronic Supporting Information

Experimental

Chemicals

All reagents were commercially available and used as received without further purification. Iron (II) sulphate heptahydrate ($FeSO_4 \bullet 7\ H_2O$), Gold (III) chloride hydrate ($AuCl_3$, Aldrich), sodium hydroxide (NaOH), potassium nitrate (KNO_3), sulfuric acid (H_2SO_4) and polyethylenimine (PEI, branched, $M_W \approx 25$ kDa) were obtained from Sigma Aldrich.

Synthesis of PEI-Fe_3O_4 MNPs

The nanoparticles were synthesized by a modified oxidative hydrolysis method, which consist of the precipitation of an iron salt ($FeSO_4$) in a basic media (NaOH) and in the presence of a mild oxidant.[1] In a typical synthesis, a mixture of 1.364 g of KNO_3 and 0.486 g of NaOH was dissolved in 135 ml of distilled water in a three-necked flask bubbled with N_2. Then 15 ml of 0.01 M H_2SO_4 solution containing 0.308 g of $FeSO_4 \cdot 7H_2O$ (previously flowed with N_2 for 2 h) and varying amounts of PEI (0.3 or 0.15 g) were added dropwise under constant stirring. When the precipitation was completed and additional 5 min of N_2 flow was allowed to pass and the suspension with the black precipitate was held at 90ºC for 24 h under N_2. Afterward, the solution was cooled at room temperature with an ice bath, and the solid was separated by magnetic decantation and washed several times with distilled water[2].

Characterization of PEI-Fe_3O_4 MNPs

Transmission Electron Microscopy (TEM): MNPs average size, distribution and morphology were studied by transmission electron microscopy (TEM) using a FEI Tecnai T20 microscope and operating at acceleration voltage of 200 KV. STEM-HAADF images were obtained in a FEI Tecnai F30 microscope operated at an acceleration voltage of 300 KV. The microscope was equipped with a HAADF (high angle annular dark field) detector for STEM mode and EDX (X-ray energy disperse spectrometry). Samples were prepared by placing one drop of a dilute suspension of nanoparticles in ethanol on a carbon-coated copper grid and allowing the solvents to evaporate at room temperature. The average particle size and distribution were evaluated by measuring 200 particles.

ATR infrared Spectroscopy (ATR-IR): The ATR-IR spectrum was used to analyze functional groups of PEI-Fe_3O_4 nanoparticles and verify PEI presence on Fe_3O_4-MNPs surface. The spectrum was taken from 4000 to 400 cm^{-1} on a Nicolet Impact 410 spectrometer. From Fig S1 it can be observed that the IR spectra of PEI-Fe_3O_4 nanoparticles have the characteristics bands of PEI polymer.

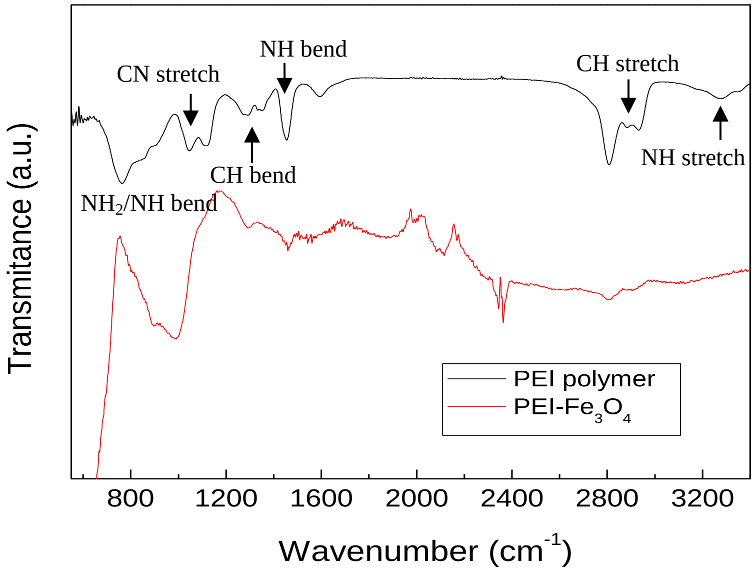

Fig S1. ATR-IR spectra of PEI polymer and PEI-Fe_3O_4.

Determination of PEI-Fe_3O_4-MNPs content in the magnetic colloids

Measurement of the PEI-Fe_3O_4 concentration of each colloid was made through UV spectrophotometry after complete dissolution of the MNPs in acid media. Ferrous ions present in the solution were oxidized to ferric ions by HNO_3 prior to reacting with thiocyanate salt to form the iron- thiocyanate complex ($[Fe(SCN)_6]^{3-}{}_{(aq)}$). PEI-MNPs were completely dissolved in 1:1 v/v HCl 6M-HNO_3 (65%) for 2 h at elevated temperatures (50-60 ºC). Potassium thiocyanate was added to the Fe^{3+} solution and then the iron concentration was determined by spectrophotometric measurements at 478 nm using a CARY-50 Probe UV-visible recording spectrophotometer.

Magnetic Hyperthermia Experiments

Magnetic hyperthermia device: The alternating magnetic field (AMF) experiments were performed at a frequency *f* = 580 kHz and amplitude H = 24.8 kAm^{-1} , using a commercial applicator device (model DM100 device, nB Nanoscale Biomagnetics, Spain). To determine the SPA values of pure colloids (PEI-Fe_3O_4 MNPs of 40 and 25 nm), the temperature increase of 1 mL of each suspension (at concentration of 1.5 mg⁄mL) was measured using an optical fiber system dipped into the sample. The SPA values (measured in W per gram of MNPs) for each colloid were calculated from the initial slope of the ΔT versus time data and using the equation:

$$SPA = \frac{\rho_c C_c}{\Phi}\left(\frac{\Delta T}{\Delta t}\right)$$

where C_c and ρ_c are the specific heat capacity and density of the colloid, respectively, Φ the weight concentration of the MNPs in the colloid and ΔT/Δt represents the increase of temperature in the time interval considered.

Synthesis of Au-Fe_3O_4-PEI: 100 µl of the PEI-Fe_3O_4 suspension (0.23 mg Fe_3O_4 NPs/ml) were mixed with 250 µl of $HAuCl_4$ (1.3 mM) and 750 µl of absolute ethanol. The resulting solution was exposed to alternating magnetic field (580 kHz, H = 24.8 kA/m) for different application times, 15 and 60 minutes.

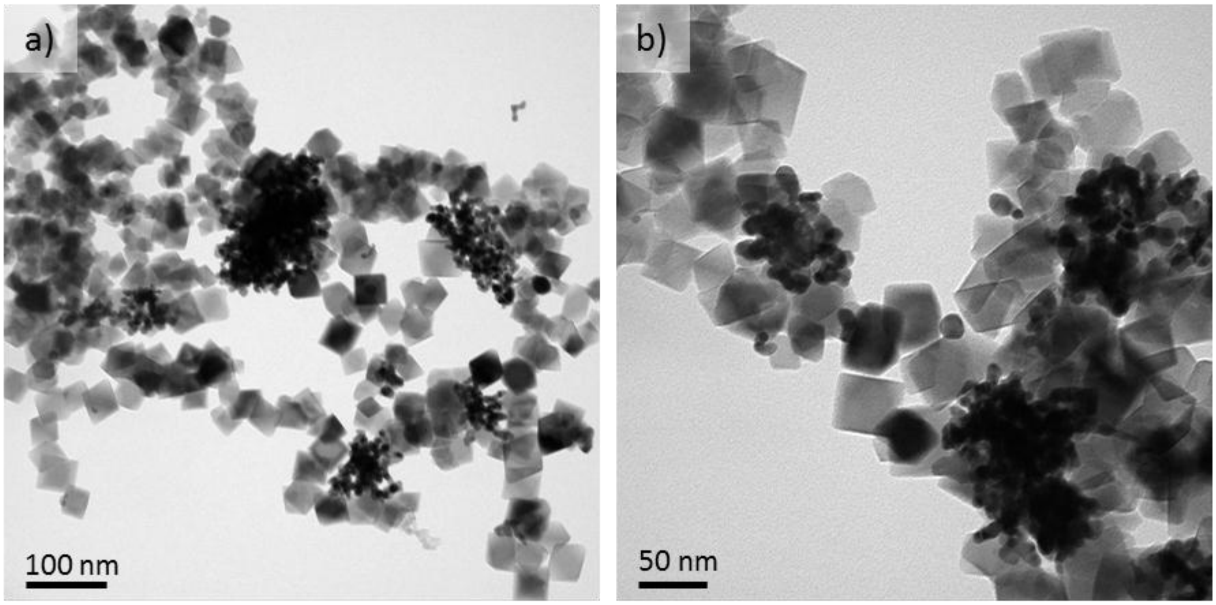

Fig. S2: TEM images of Au aggregates, appearing around 40 nm MNPs, obtained at 75ºC-15 minutes without IH.

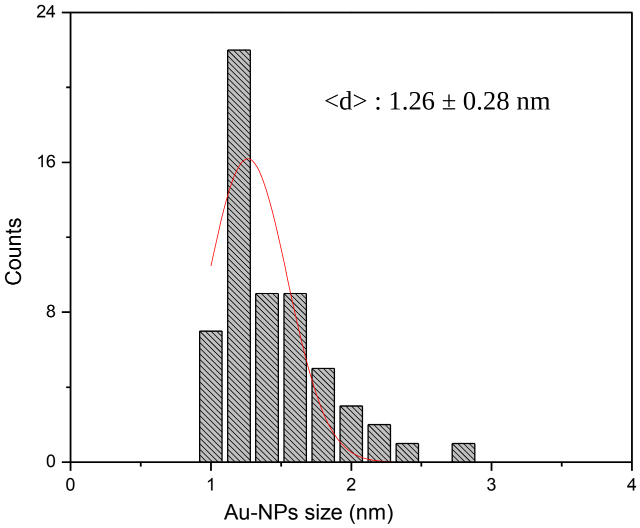

Fig. S3: Histogram of Au-NPs diameter grown onto 25 nm MNPs after 1h incubation without IH.

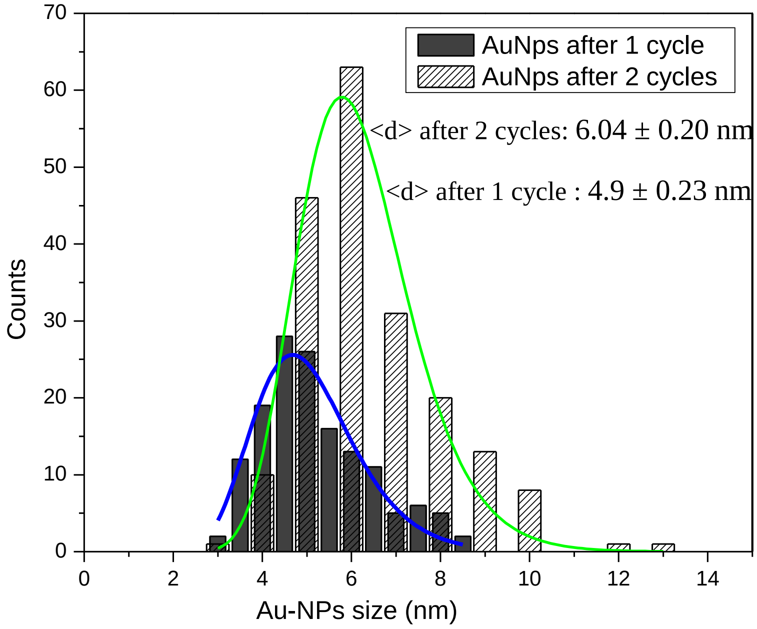

Fig. S4: Histogram of Au-NPs diameter grown onto 25 nm MNPs after 1 and 2 cycles of IH at *f* = 580 kHz and H = 24.8 kAm^{-1}.

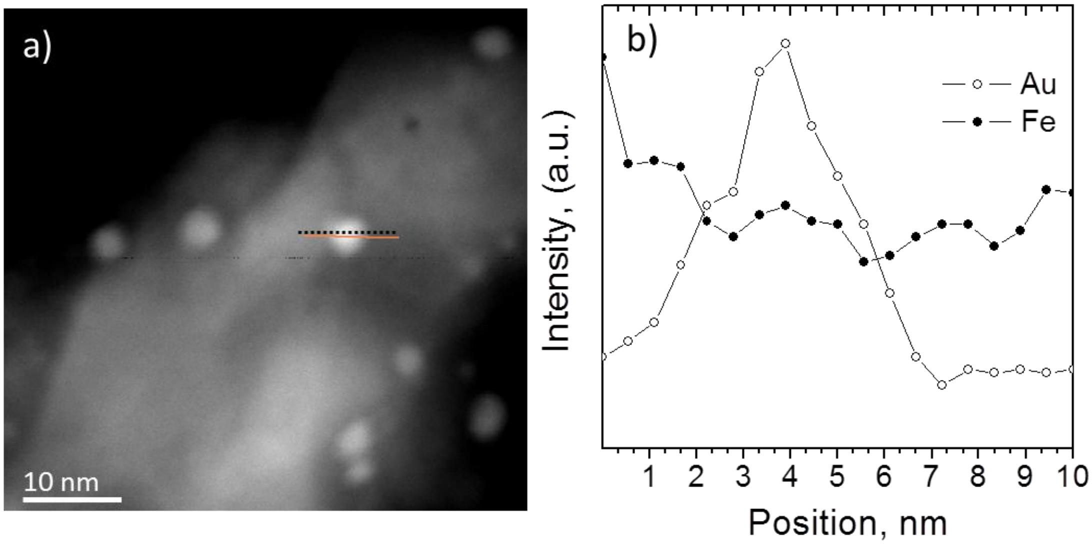

Fig. S5: a) STEM-HAADF image showing gold nanoparticles laid on the Fe_3O_4 nanocrystal facets of 40 nm Au-Fe3O4 NPs, obtained at 25ºC under MIH (580 kHz, 23.8 kAm-1 synthesis time = 60 min b) EDS-HAADF profile across a gold NPs located in a)

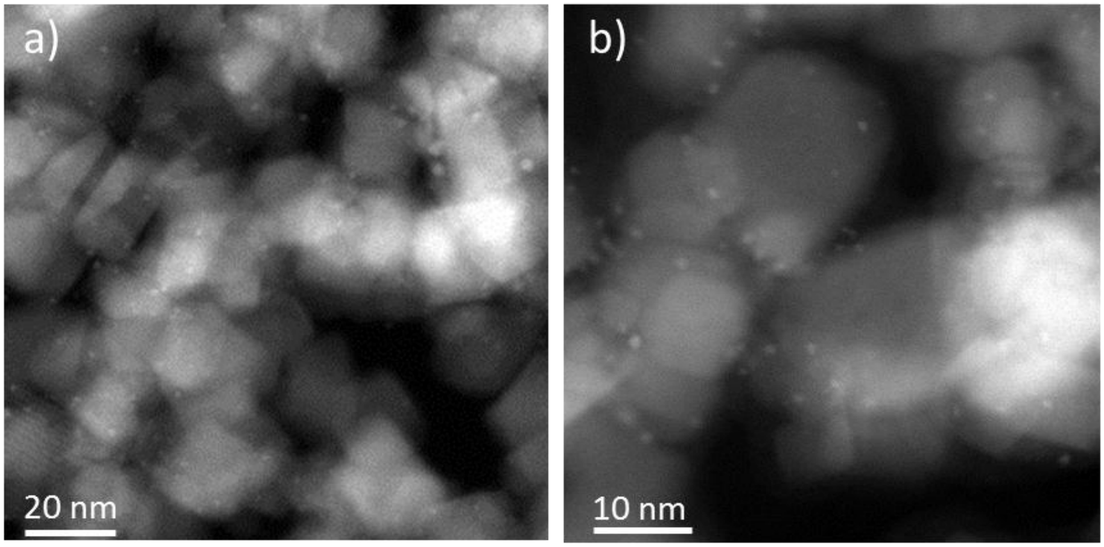

Fig. S6: STEM-HAADF images showing that gold nanoclusters are present on the surface of 25 nm Fe_3O_4 NPs after 60 min reaction in the absence of MIH

1. Riggio C, C. M., Hoskins C, Pinkernelle J, Sanz B, Torres TE, Ibarra MR, Wang L, Keilhoff G, Goya GF, Raffa V, Cuschieri A Poly-l-lysine-coated magnetic nanoparticles as intracellular actuators for neural guidance *International Journal of Nanomedicine* **2012,** *7* (1), 3155-3166.

2. M.P. Calatayud, V.Raffa, B. Sanz, T.E. Torres, M.R. Ibarra, C. Hoskins, A.Cuschieri, L.Y. Wang, J. Pinkernelle, G. Keilhoff and G. F. Goya. , To be published, 2012