Magnetically-driven selective synthesis of Au clusters on Fe₃O₄ 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 (FeSO₄ · 7 H₂O), Gold (III) chloride hydrate (AuCl₃, Aldrich), sodium hydroxide (NaOH), potassium nitrate (KNO₃), sulfuric acid (H₂SO₄) and polyethylenimine (PEI, branched, M₇₈ ≈ 25 kDa) were obtained from Sigma Aldrich.

Synthesis of PEI-Fe₃O₄ MNPs

The nanoparticles were synthesized by a modified oxidative hydrolysis method, which consist of the precipitation of an iron salt (FeSO₄) 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 KNO₃ and 0.486 g of NaOH was dissolved in 135 ml of distilled water in a three-necked flask bubbled with N₂. Then 15 ml of 0.01 M H₂SO₄ solution containing 0.308 g of FeSO₄-7H₂O (previously flowed with N₂ 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 N₂ flow was allowed to pass and the suspension with the black precipitate was held at 90°C for 24 h under N₂. 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 water².

Characterization of PEI-Fe₃O₄ 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-Fe₃O₄ nanoparticles and verify PEI presence on Fe₃O₄-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-Fe₃O₄ nanoparticles have the characteristics bands of PEI polymer.

![IR Spectra](image)

**Fig S1.** ATR-IR spectra of PEI polymer and PEI-Fe₃O₄.

**Determination of PEI-Fe₃O₄-MNPs content in the magnetic colloids**

Measurement of the PEI-Fe₃O₄ 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 HNO₃ 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-HNO₃ (65%) for 2 h at elevated temperatures (50-60 °C). Potassium thiocyanate was added to the Fe³⁺ 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 \( f = 580 \text{ kHz} \) and amplitude \( H = 24.8 \text{ kA/m} \), using a commercial applicator device (model DM100 device, nB Nanoscale Biomagnetics, Spain). To determine the SPA values of pure colloids (PEI-Fe\(_3\)O\(_4\) 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 \( \Delta T \) versus time data and using the equation:

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SPA = \frac{\rho_c c_c}{\Phi} \left( \frac{\Delta T}{\Delta t} \right)
\]

where \( C_c \) and \( \rho_c \) are the specific heat capacity and density of the colloid, respectively, \( \Phi \) the weight concentration of the MNPs in the colloid and \( \Delta T/\Delta t \) represents the increase of temperature in the time interval considered.

*Synthesis of Au-Fe\(_3\)O\(_4\)-PEI:* 100 µl of the PEI-Fe\(_3\)O\(_4\) suspension (0.23 mg Fe\(_3\)O\(_4\) 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, \( H = 24.8 \text{ kA/m} \)) 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$_3$O$_4$ nanocrystal facets of 40 nm Au-Fe$_3$O$_4$ 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 Fe₃O₄ NPs after 60 min reaction in the absence of MIH
