Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

TEM for gold nuclei deposition at different pHs

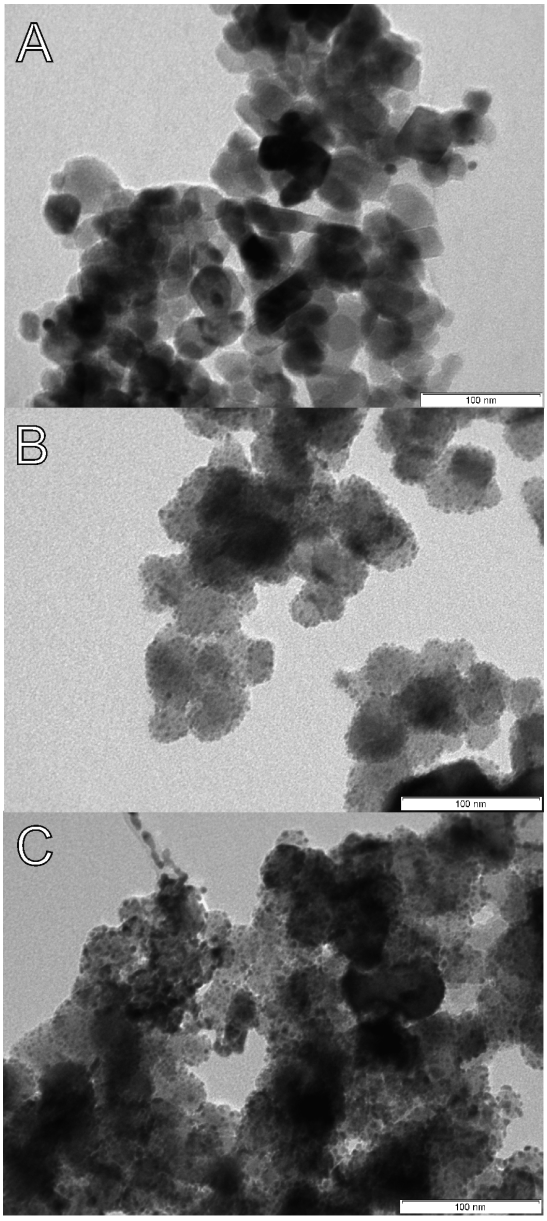

Figure S1 – TEM images of magnetite NPs after gold deposition procedure performed at different pHs: A –pH – 5; B- pH 8; C- pH 10

XPS after gold nuclei deposition

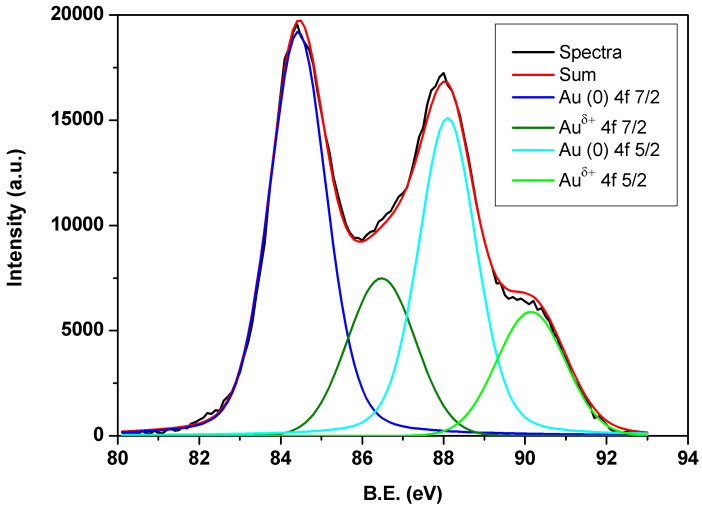

Figure S2 –XPS spectra and main deconvoluted contributions of Au 4f peaks for Au$^{\delta+}$ and Au (0) duplets after gold nuclei deposition

XPS spectra for star shaped gold coated magnetic NPs

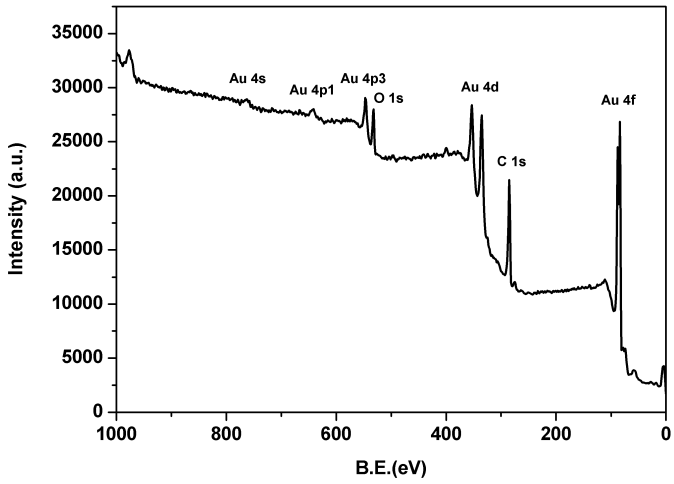

Figure S3 - XPS survey spectra for the star shaped gold coated magnetite NPs

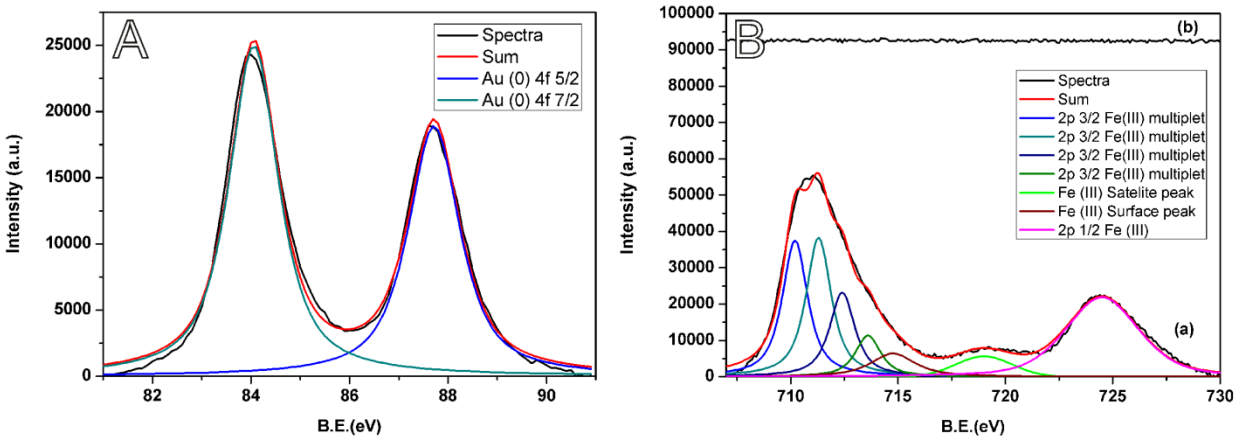

Figure S4 – A- XPS spectra of Au 4f zone for the star shaped gold coated NPs; B –XPS spectra of the Fe 2p zone for: (a) Magnetic NPs after deposition precipitation and (b) star shaped gold coated NPs.

EDX spectra for star shaped gold coated NPs:

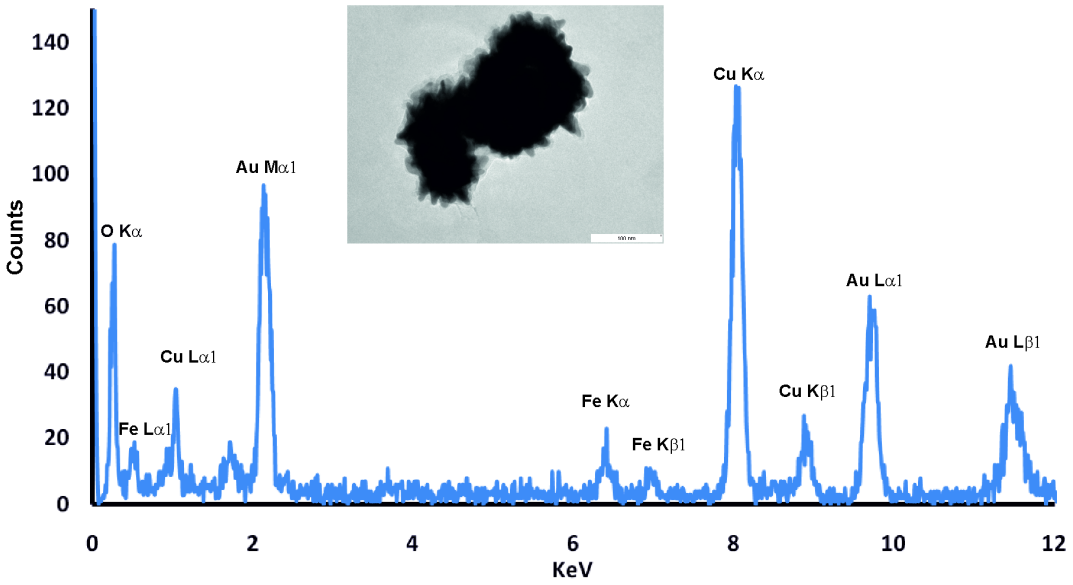

Figure S5 - EDS spectra of the nanoparticles showed in the inset, showing the presence of gold and iron in the NPs (Cu peaks originate from the TEM grid).

Structure of NTA ligand used:

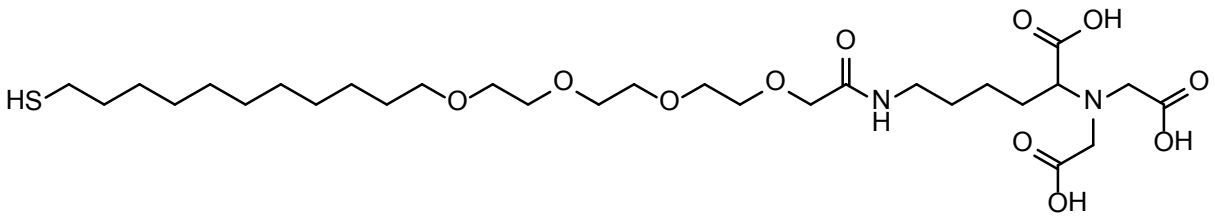

Figure S6 – Chemical structure of the NTA ligand used for the functionalization of the NPs for capture of histidine tagged MBP.

ICP results and calculation of approximate Ni^{2+} per nanoparticle.

Table 1 – Concentrations of elements Au, Fe and Ni determined by ICP atomic absorption for star shaped gold coated NPs before and after functionalization

	Au	Fe	Ni
C (mM) before funcionalization	5.55	0.93	-
C (mM) after funcionalization	2.18	0.5	0.007

For the calculation of the approximate number of nickel ions per NP we first calculated the moles of iron per NP. For that purpose we used the diameter of the magnetite NPs as determined by TEM (~33nm) together with the density and molar mass of magnetite:

$$mol\ {}^{Fe}/_{NP} = \left(\frac{4}{3}\pi\left(\frac{d_{NP}}{2}\right)^3\right) \times \left(\frac{1}{\rho_{Fe_3O_4}}\right) \times \left(\frac{2}{MM_{Fe_3O_4}}\right)$$

Assuming that all the iron present in the sample comes from the magnetite NPs we can then calculate the number of NPs using the concentration of iron determined by ICP and the calculated amount of iron per NP:

$$NPs/_L = \frac{mol\ Fe\ (ICP)}{mol\ Fe/_{NP}}$$

The amount of nickel ions per magnetic NP can then be determined by simply dividing the amount of Ni obtained by ICP by the total number of NPs (this assumes that all NPs are core shell and that the amount of gold only and uncoated NPs are negligible)

$$Ni/_{NP} = \frac{mol\ Ni\ (ICP)}{NPs/_L}$$

This calculation when applied to the values obtained by ICP yields an approximate number of 1000 Ni ions per NP.

Magnetic characterization.

Both uncoated and Au coated magnetite NPs, at 300 K and 5 K displayed magnetic hysteresis on the M(H) curves, with a similar magnitude in their coercive fields (Hc) at the same temperature, showing a ferromagnetic behavior in the range of temperatures studied. This is confirmed by the normalized ZFC/FC (Fig.5) curves where both curves are always bifurcated (from the starting point T=370K) in the range of temperatures measured typical of a multi-

domain character. The multi-domain nature of the MNPs is also evident in the ZFC curve by the small increase on the M(T) curve at T*, probably resulting from reorientation of the multi-domains inside the nanoparticle.

The main difference between the magnetic behavior of magnetite and core-shell nanoparticles is seen on the bifurcation of the normalized FC curves. An increase of the relative remnant magnetization (Mr/MS (T=300K) = 0.24 and 0.33 for uncoated and coated NPs, respectively) and a resulting increase of coercive field (HC; see table 1) is observed after Au-coating, a behavior commonly attributed to the increase of dipolar interactions, due to the possible existence of more than one magnetic core per gold-coated NP.[1, 2]

Table S2 - Magnetic characterization of uncoated and Au coated magnetite NPs

Sample	$\mathbf{M_S}^{\mathbf{T=5K}}$ **(emu/g)**	$\mathbf{H_C}^{\mathbf{T=300K}}$ **(Oe)**	$\mathbf{H_C}^{\mathbf{T=5K}}$ **(Oe)**	$\mathbf{M_r/M_S}$ **(T=300K)**	**Dl (nm)**
Fe_3O_4	78.97	66	224.5	0.24	**1.2**
Fe_3O_4@Au	7.47	83	310.0	0.33	

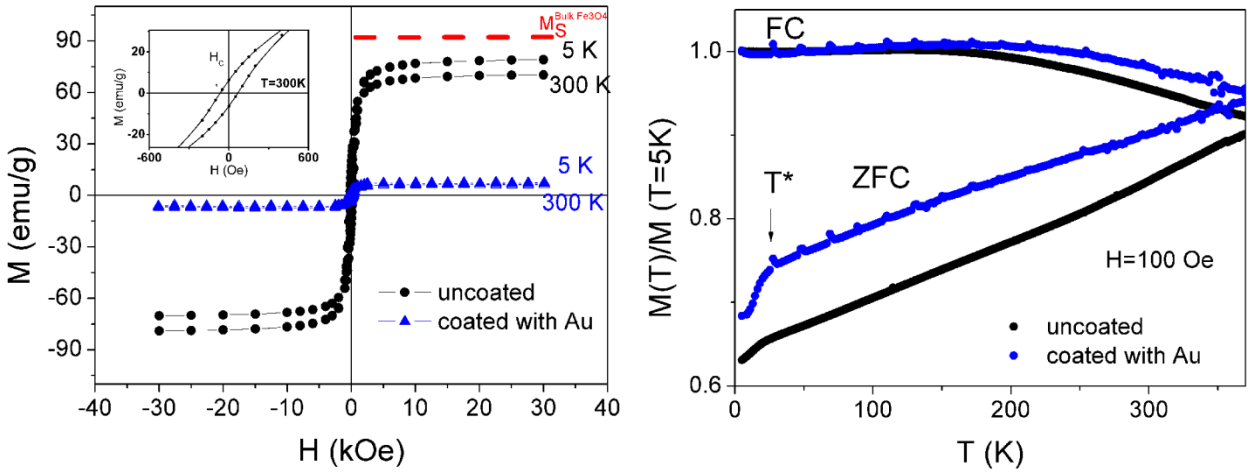

Figure S7 – Left: Magnetization vs. applied magnetic field at 5 K and 300 K with H up to 30 kOe for uncoated (black) and Au shell coated (blue) magnetite NPs. Inset shows magnification at low fields Right: Temperature dependence of the magnetization in ZFC and FC mode over a temperature range 5-370 K with H = 100 Oe. Curves were normalized at T = 5 K for the FC curve.

Bibliography

1. Demortiere, A.; Panissod, P.; Pichon, B. P.; Pourroy, G.; Guillon, D.; Donnio, B.; Begin-Colin, S., Size-dependent properties of magnetic iron oxide nanocrystals. *Nanoscale* 2011, 3, 225-232.

2. Papaefthymiou, G. C.; Devlin, E.; Simopoulos, A.; Yi, D. K.; Riduan, S. N.; Lee, S. S.; Ying, J. Y., Interparticle interactions in magnetic core/shell nanoarchitectures. *Physical Review B* 2009, 80, 024406.