Coexistence of plasmonic and magnetic properties in Au₈₉Fe₁₁ nanoalloys

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Abstract

We show that Au₈₉Fe₁₁ nanoparticles are the first example of a new class of multifunctional nanoalloys with potential applications in nanomedicine, photonics, spintronics and magneto-plasmonic devices. Au₈₉Fe₁₁ nanoparticles are synthesized by laser ablation of a bulk Au-Fe alloy target in liquid solution. The plasmonic response of the gold moiety and the magnetism of the iron moiety coexist in the nanoalloy with strong modification compared to single element nanoparticles, revealing a non linear surface plasmon resonance dependence on the iron fraction and a transition from paramagnetic to a spin glass state at low temperature. The nanoalloy retains the surface chemistry of gold and can be coated in one pot with thiolated molecules. Moreover, they are promising as contrast agents for magnetic resonance imaging.

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Extraordinary physical-chemical properties are found in nanoscale gold^{1, 2} and iron.³⁻⁵ Gold nanoparticles (AuNPs) have surface plasmon resonances in the visible,^{2, 6} are biocompatible,⁷ chemically inert¹ and easily functionalizable through the formation of sulfur-gold bonds.^{1, 8} Iron nanoparticles (FeNPs) have high saturation magnetization⁹ and are biocompatible,¹⁰ although they easily undergo to oxidation in absence of an efficient passivation coating³ and their surface functionalization can be complex.¹⁰

Combining the physical-chemical properties of gold and iron in a single nanostructure would be of striking interest for various applications,¹¹ such as in nanomedicine,^{12, 13} in information technology¹⁴⁻¹⁷ and in catalysis.¹⁸⁻²⁰ In particular for what concern Au-Fe alloys, the high spin-orbit coupling characteristic of Au may induce appealing properties for spintronic applications, like high magnetic anisotropy,²¹ large magneto-optical responses,²² high magneto-resistance²³⁻²⁵ and spin Hall effects.^{26, 27}

Au-Fe alloys with a Fe content exceeding 2.5% are not thermodynamically stable at room temperature,²⁸ although kinetically stable bulk AuFe alloys can be obtained by quick cooling of the melted metals^{29, 30} and thin alloy films can be obtained by radiofrequency sputtering.²² At the nanoscale, the attempts to synthesize gold - iron alloy nanoparticles on substrates or in solution are limited in number. AuFe alloy nanoparticles (AuFeNPs) were previously obtained by sequential ion implantation of iron in Au NPs embedded in silica matrix,^{15, 31, 32} by simultaneous reduction of Au salts and decomposition of Fe compounds in the presence of capping molecules dissolved in liquid solutions,³³⁻⁴² by electrodeposition on amorphous carbon electrodes from aqueous solution of electrolytes,⁴³ in high-vacuum chambers by pulsed laser deposition^{44, 45} or by evaporation of a bulk alloy on a liquid hydrocarbon substrate.⁴⁶

The reports on structure – properties relationship of these nanoparticles are sometimes conflicting, especially regarding plasmonic and magnetic responses, and deserve further investigations. For instance, both blue^{31, 45} and red shifted^{34, 35, 39, 40} plasmon resonances, compared to that of pure gold nanoparticles, were assigned to AuFe alloys with same stoichiometry. Indeed, the characterization of products was not accurate enough to exclude phase segregation and to confirm homogeneous alloying at the single nanoparticle level. This is a relevant point, since bottom up synthetic approaches often yield byproducts such as clustered iron atoms in the gold matrix,^{36-40, 47} iron-gold core-shell structures^{11, 34, 35} or iron oxide-gold heterostructures and agglomerates,^{39-41, 44} owing to the unfavorable thermodynamics for the formation of Au-Fe alloys.²⁸ Moreover, all previous methods have problems related to surface accessibility,^{15, 31-46} which is important for catalytic applications¹⁸⁻²⁰ and for conjugation with functional molecules.¹¹⁻¹³ Thus, new synthetic methods

are desired, that allow the synthesis of large amounts of well dispersed nanoparticles, requiring low-cost non-toxic precursors and bypassing the thermodynamic limitations to alloy formation.

Here we report a new environmentally friendly top-down approach for the synthesis of AuFeNPs whose surface is highly available to conjugation with thiolated molecules. These AuFeNPs are composed by 89% of Au and 11% of Fe and show the coexistence of plasmonic and magnetic properties, although with important differences compared to the single element Au or Fe nanoparticles.

The AuFeNPs are obtained by laser ablation synthesis in solution (LASiS), focusing 1064nm laser pulses (9 ns, 10 Hz, 30mJ/pulse) on a bulk Au₇₃Fe₂₇ alloy target dipped in a solution of pure ethanol (Figure 1A). This is a top-down approach⁴⁸⁻⁵¹ which can bypass the thermodynamic limitations to the room temperature formation of Au-Fe alloys.^{48, 52} The formation of nanoparticles is immediately visible through the reddish color of the solution, which becomes purple after a few hours due to particles aggregation. After LASiS, an aqueous solution containing disodium ethylenediaminetetraacetic acid (EDTA) and thiolated polyethyleneglycol (PEG) is added to the AuFeNPs dispersion in ethanol and the solution is kept at 60°C for 1 hour (Figure 1B). In few minutes after the addition of EDTA/PEG, the color of the solution changes back from purple to reddish. The AuFeNPs solution is then purified by dialysis and washed multiple times with deionized water. The final solution of PEG-AuFeNPs is indefinitely stable in water and air over time.

The crystalline phase of PEG-AuFeNPs is identified by X-ray diffraction analysis. The diffraction pattern shows a face centered cubic structure (fcc) analogous to pure gold (Figure 1C). In the diffraction pattern of PEG-AuFeNPs there are no peaks of other iron compounds like iron oxides or metal iron. The refined lattice parameter of the fcc unit cell is 0.4041 nm, smaller than the value of pure gold (0.4079 nm – pdf file 00-004-0784). This is compatible with an alloy of Fe and Au where iron atoms are present in the Au crystal lattice as random substitutional impurities,^{28, 30} therefore the PEG-AuFeNPs are a solid solution of Au and Fe. To determine the iron content in the AuFe alloy, we compared the experimentally measured refined lattice parameter with those reported for bulk AuFe in literature (for details see Methods), and we found that it corresponds to an alloy with Au 89% and Fe 11% elemental composition. Exactly the same elemental composition of Au₈₉Fe₁₁ was found independently by inductively coupled plasma-mass spectrometry (ICP-MS).

Figure 1. Synthesis and Characterization of PEG-AuFeNPs. (A) Water soluble PEG-AuFeNPs were obtained in two steps: in the first step AuFeNPs were produced in ethanol from a $\text{Au}_{72}\text{Fe}_{28}$ bulk target by LASiS; (B) in the second step, they were treated with EDTA and conjugated with thiolated PEG, to obtain PEG-AuFeNPs stable in water. (C) Powder XRD analysis of PEG-AuFeNPs (black line) and Rietveld fitting (red line). (D-E) TEM images of AuFeNPs as obtained by LASiS in EtOH (D) and after treatment with EDTA and coating with PEG (E). (F) FTIR spectrum collected on powder PEG-AuFeNPs, showing the vibrational fingerprint of PEG.

The iron content in PEG-AuFeNPs is lower than in the bulk $\text{Au}_{73}\text{Fe}_{27}$ alloy target used for LASiS, meaning that iron is lost during the laser ablation process. In LASiS, the difference between the stoichiometry of alloy nanoparticles and the original alloy target is observed when the two elements in the alloy have different reactivity or different heat of vaporization.^{48, 52, 53} In the present case, the heat of vaporization of gold and iron are similar (324 and 340 kJ mol^{-1} respectively), but iron can react with oxygen dissolved in non deaerated solvents, as reported for instance during LASiS of NiFe NPs.⁵⁴ Transmission electron microscopy (TEM) images collected on AuFeNPs solution just after the LASiS, namely prior to the addition of EDTA/PEG, show the presence of iron oxide and amorphous phases (Figure 1D), likely due to the reaction of ablated Fe atoms with the liquid solution. A similar result was reported for laser ablation of bulk iron in various solvents like ethanol and water.⁵⁵⁻⁵⁷ The addition of EDTA and the subsequent dialysis are required for selective removal of iron oxides and hydroxides,^{55, 56} without affecting AuFeNPs. TEM images collected on PEG-AuFeNPs solution show that all the iron oxide and amorphous phases are effectively removed by this procedure (Figure 1E), in agreement with the results of XRD. Indeed, the surface of AuFeNPs obtained following this procedure is free from other stabilizing molecules and highly available to

conjugation with thiolated molecule, exploiting the formation of stable Au-S bonds with surface gold atoms. Hence, we added thiolated PEG simultaneously with EDTA in order to coat AuFeNPs with a shell of hydrophilic polymer. The successful coating of AuFeNPs with PEG, after the purification/washing stages, is confirmed by Fourier transform infrared (FTIR) spectroscopy on dried sample (Figure 1F). The one-pot surface conjugation of AuFe alloy nanoparticles with the desired thiolated molecules is highly important for most technological applications¹¹⁻¹³ and for accurate characterization of magnetic and plasmonic properties on well dispersed (i.e. not agglomerated) alloy nanoparticles.

By TEM, we find that PEG-AuFeNPs have average size of 30 nm, with a standard deviation of 6 nm, and well defined crystalline structure. Stacking faults and twinned crystallites are frequently observed in the nanoalloys (Figure S1 in Supplementary Information). Planar defects in fcc metals are usually associated to internal stresses due to the rapid cooling,⁵⁸ and are typical of LASiS.^{48, 52} The analysis in energy-filtered TEM (EFTEM) mode provides further information about the elemental distribution of Au and Fe in individual PEG-AuFeNPs. Elemental mapping is performed on 5 nanoparticles with sizes between 15 and 50 nm by selecting the Au N-edge (83 eV) and the Fe L-edge (708 eV) respectively (Figure 2A and Figure S2 in Supplementary Information). In all particles analyzed, a complete overlap of the distribution of gold and iron is observed, meaning that the particles have a homogeneous alloy structure. Moreover, we found that the Fe percentage in each single nanoparticle oscillates between 15% and 9%, with an average value of 11%, in fair agreement with the XRD and ICP-MS evaluations. Further confirmation of the homogeneous distribution of Fe in the nanoalloy is found by X-ray energy dispersive spectroscopy (XEDS) within one single nanoparticle with spatial resolution of 1 nm, performed in scanning transmission electron microscopy (STEM) configuration (Figure 2B).

Figure 2. Single nanoparticle elemental analysis. (A) EFTEM mapping of Au N-edge (83 eV) and Fe L-edge (708 eV), showing that both elements are well overlapped. Scale bars are 10 nm. (B) STEM analysis carried out within a single AuFeNPs assess the phase homogeneity and the Au₈₉Fe₁₁ stoichiometry of the nanoalloy. Scale bar is 10nm.

Remarkably, all structural characterizations, even when carried out on different PEG-AuFeNPs batches, show no modification of the results on different times after the synthesis, which proves the reproducibility of the synthesis and the stability in time of our nanoalloys in air and in water.

The UV-visible absorption spectra of AuFeNPs in ethanol (as obtained from LASiS) and of PEG-AuFeNPs in water both showed the presence of a surface plasmon resonance (Figure 3A). Surface plasmon bands are originated by the collective excitation of conduction electrons in nanoscale metals by annihilation of the incident photons,⁵⁹ and their resonance energy depends on NPs composition, shape, aggregation and chemical-physical environment.⁵⁹⁻⁶¹ In the case of AuFeNPs in ethanol, the plasmon band extends from 500 nm to 700 nm due to aggregation of particles and consequent plasmon hybridization (red line in Figure 3A),^{61, 62} while the spectrum of PEG-AuFeNPs in water shows a narrower plasmon resonance centered at 510 nm (black line in Figure 3A), suggesting that NPs are well dispersed and isolated in the liquid.⁶² For the sake of comparison, the plasmon band of pure PEG-Au NPs with same average size dispersed in H₂O is

also shown in Figure 3A. The plasmon band of PEG-AuFeNPs is less intense and blue shifted by 10 nm compared to the plasmon band of PEG-AuNPs. The Mie model can provide a good description of the optical properties of nanospheres, when the appropriate optical constant is used.^{59, 62} Therefore, we adapted the optical constant measured by ellipsometry on bulk Au₈₄Fe₁₆ alloy²² (for details see Methods) and we calculated the extinction spectrum of a 30 nm metal sphere by the Mie model. As shown in Figure 3B, the calculated spectrum (black line) agrees well with the experimental one, reproducing both damping and blue shift of the surface plasmon resonance. This result also suggests that previous reports on the observation of red shifted plasmon resonance in Au-Fe alloy nanoparticles^{34, 35, 39, 40, 63} are likely due to samples with heterogeneous composition or to particles aggregation.

Figure 3. Optical properties of AuFeNPs. (A) UV-vis spectra of AuFeNPs as obtained by LASiS in ethanol (red line), of PEG-AuFeNPs in water (black line) and of PEG coated AuNPs (green line). Inset: PEG-AuFeNPs in water have reddish colour (left), different from the purple colour of pure Au NPs (shown on the right for comparison). (B) Extinction cross section (σ_{ext}) calculated by the Mie model for a 30nm Au₈₉Fe₁₁ (black line) and Au (green line) nanospheres in water. The dashed blue line is the σ_{ext} calculated by the Mie model for a 30nm nanosphere with optical constant obtained by the linear average of pure Au and Fe metals (for details, see text).

As shown in Figure 3A, the plasmon band is damped by the presence of Fe atoms in the gold lattice, that was somewhat expected since metal Fe NPs do not have a plasmon resonance in the visible range.⁵⁹ However, it is worth emphasizing that a much lower plasmon damping is found in the extinction spectra of 30nm Au₈₉Fe₁₁NPs calculated by considering as optical constant (ϵ_{Alloy}) the linear average of the optical constants of pure Au (ϵ_{Au}) and Fe (ϵ_{Fe}), i.e. $\epsilon_{\text{Alloy}} = 0.89 \epsilon_{\text{Au}} + 0.11 \epsilon_{\text{Fe}}$ (dashed line in Figure 3B), instead of using the experimental optical constant for the bulk AuFe alloy. Such result proves that plasmon damping in Au-Fe nanoalloy has a non linear dependence on the iron fraction. Indeed, the nanoalloy extinction spectrum shows changes compared to pure Au

NPs in the range below 450 nm (Figure 3A,B). According to previous reports on thin AuFe alloy films,²² such changes are due to single electron transitions from iron d states lying below the Fermi surface of the Au₈₉Fe₁₁ nanoalloy. Low frequency interband transitions are frequently observed in alloys of noble metals and transition metals with partially occupied d states⁶⁴⁻⁶⁶ and they are known to strongly affect the intensity of the plasmon resonance, because plasmon excitations can rapidly decay into electron hole pairs.⁶⁴ Therefore, the nonlinear dependence of the plasmon damping versus the concentration of Fe can be related to the effect of iron d states on the relaxation frequency of conduction electrons^{22, 64, 66, 67} and this finding further supports the formation of an alloy where Fe is homogeneously dispersed in the crystal lattice.

The magnetic properties of the Au₈₉Fe₁₁ nanoalloy retain the main features of Au-Fe solid solutions. The magnetic field dependence of the magnetization (M) of PEG-AuFeNPs is measured at two different temperatures. At 300 K, M linearly increases with the applied field, (blue curve in Figure 4A) as expected for a system made of paramagnetic impurities (Fe) dispersed in a diamagnetic host (gold).⁶⁸ Conversely, at low temperature (3 K), the signature of collective magnetic correlations appears, as suggested by the magnetic irreversibility we observe on cycling the magnetic field between ± 5 T (blue line, Figure 4A): the hysteresis loop is open with a coercive field, $\mu_0 H_C = 121$ mT and reduced remnant magnetization, $M_{0T}/M_{5T} = 0.30$; at the highest measuring field of 5 T, M reaches 9.9 Am²/kg, a value 5 times larger than at 300 K, although being still far from saturation.

The temperature dependence of M is measured also using a smaller probe field (5 mT) after Zero Field Cooled (ZFC) and Field Cooled (FC) procedures (Figure 4B), and displays the thermal irreversibility typical of a spin freezing process. ZFC magnetization exhibits a broad maximum centred at 75K, while the FC magnetization decreases from 3 K to 15 K and then follows the same trend of the ZFC curve, that is approached for $T > 100$ K. The nature of this spin “blocking” is further investigated by measuring the temperature dependence of the AC magnetic susceptibility $\chi = \chi' + i\chi''$ in the 1 Hz - 1 kHz frequency range. Below ca. 130 K, the in-phase component, χ' , exhibits a frequency dependent signal with a broad maximum, which shifts from 70.6 K to 74.6 K when frequency is increased by three order of magnitude (Figure 4C). The development of the frequency dependence is accompanied by a non zero out-of-phase component, χ'' , which increases on decreasing temperature down to ca. 50 K (See Figure S3 in Supplementary Information). A rough indication on the nature of the observed magnetic dynamics can be obtained by considering the frequency shift with decade change in frequency and applying the empirical formula proposed by Mydosh.⁶⁹ In this way, we find $\Delta T_{\max}/[T_{\max} \Delta \log(2\pi\nu)] \sim 0.01-0.02$, that is within the range expected for canonical spin-glass systems ($10^{-3}-10^{-2}$).⁶⁹

Figure 4. Magnetic properties of AuFeNPs. (A) Hysteresis loops measured at 3 K and 300 K. (B) Temperature dependence of the ZFC and FC magnetizations. (C) In-phase component χ' of the AC magnetic susceptibility recorded at frequencies between 1 Hz and 1000 Hz. Disordered bulk $\text{Au}_{1-x}\text{Fe}_x$ alloys with an iron content below the percolation threshold ($x = 0.155$) exhibit a paramagnetic to spin-glass transition at a freezing temperature, T_g , which increases with x up to ca. 50 K.⁷⁰ The spin – glass behavior originates from the random distribution of the Fe atoms within the gold lattice and competing ferromagnetic (FM) – antiferromagnetic (AFM) exchange interactions between Fe through the conduction band of Au (Ruderman-Kittle-Kasuya-Yosida mechanism).⁷¹⁻⁷³ Contrariwise, by increasing the concentration above the percolation threshold, Fe atoms start to cluster, and the nearest-neighbor direct exchange leads to long range ferromagnetic order. For iron content exceeding 24%, a transition to a ferromagnetic ordered state occurs, while in the intermediate composition range (from 16% to 24%) an additional transition below the critical temperature from the ferromagnetic to a spin-glass state is observed (re-entrant spin-glass).⁷⁰ Noteworthy is the value of the density of magnetization ($9.9 \text{ Am}^2/\text{kg}$) measured at 5 T which corresponds to a magnetic moment of $0.32 \mu_B/\text{atom}$. Assuming that only Fe atoms contributes to the total magnetization, the net magnetization of Fe is $292 \pm 30 \text{ Am}^2/\text{kg}$, which corresponds to a magnetic moment of $2.92 \pm 0.3 \mu_B/\text{Fe atom}$. This value is remarkably high if compared to bulk Fe *bcc* ($2.2 \mu_B/\text{Fe atom}$),³ especially if one considers that the system is still far from saturation. However, it is in good agreement with experimental values⁷⁴ and theoretical predictions⁷⁵ reported for bulk Au-Fe alloy, where the Fe atoms in the *fcc* crystalline structure are in the high spin state due to the stabilizing effect conferred by the lattice expansion.⁷⁶ On the other hand, also the magnetic polarization of Au atoms by the nearest-neighbor Fe atoms provides an additional contribution to the total magnetic moment,⁷⁴ but it is usually found to be lower than $0.03 \mu_B/\text{Au atom}$ and, therefore, it does not produce a significant variation of M .⁷⁷ Both the low temperature spin-glass behaviour and the large net magnetization of Fe fully supports the homogenous random distribution of iron atoms within each nanoalloy particle and excludes the presence of clustered Fe centres.

Being PEG-AuFeNPs paramagnetic at room temperature, we evaluated their ability to act as contrast agents for magnetic resonance imaging. The ^1H NMR Dispersion profile has been performed at room temperature by measuring the longitudinal and the transverse nuclear relaxation times (T_1 and T_2 , respectively) in the frequency range $10 \text{ kHz} \leq \nu \leq 60 \text{ MHz}$.⁷⁸ The range was chosen in order to cover the typical fields for MRI tomographs, used both in clinics ($H = 0.2, 0.5$ and 1.5T) and research laboratories. The relaxivities r_1 and r_2 weighted by the magnetic center concentration (i.e. the inverse of T_1 and T_2 respectively, see Methods for details) as the function of frequency are reported in Figures 5A. The $r_1(\nu)$ behavior gives information on the physical mechanisms affording the shortening of ^1H nuclear relaxation times. In general, two different relaxation mechanisms contribute to the $r_1(\nu)$ curve.⁷⁹⁻⁸¹ At low frequencies ($\leq 1\div 5 \text{ MHz}$), the mechanism driving the nuclear relaxation is the Néel relaxation of the particle magnetization, giving a correlation time related to the magnetic anisotropy barrier;⁷⁹⁻⁸¹ at high frequencies ($\geq 1\div 10 \text{ MHz}$) the dominant mechanism is the Curie relaxation, which takes into account the diffusion of water molecules (with diffusion correlation time $\tau_D = r^2/D$, where r is the distance of closest approach and D the diffusion coefficient of water molecules) in the presence of magnetic centres.⁷⁹⁻⁸¹ While the first mechanism gives a flattening of $r_1(\nu)$ at frequencies $\nu < 1\div 5 \text{ MHz}$, the second mechanism is responsible of the maximum in $r_1(\nu)$ at higher frequencies. In addition, for particles characterized by a distance $< 5 \text{ nm}$ between the magnetic core and the hydrogen nuclei of the bulk water, a dispersion at intermediate frequencies occurs.⁷⁹⁻⁸¹ In the case of PEG-AuFeNPs the absence of the high-frequency maximum and of the low-frequency dispersion are observed in the $r_1(\nu)$ of Figure 5A. This can be attributed to the dominant contribution coming from the high magnetic anisotropy due to the diameter $\sim 30\text{nm}$ of PEG-AuFeNPs and to the PEG shell, whose thickness in water can be estimated in $10\text{-}15\text{nm}$,⁸² which shields all the other contributions.^{83, 84}

Instead, $r_2(\nu)$ rapidly increases up to $64 \text{ s}^{-1}\text{mM}^{-1}$ for $\nu > 7\text{MHz}$ (Figure 5A), i.e. up to a relaxivity comparable to commercial superparamagnetic contrast agents like Endorem^(TM) ($99 \text{ s}^{-1}\text{mM}^{-1}$) for the typical clinical field $H = 1.5\text{T}$. Therefore, AuFe nanoalloys are promising negative contrast agents, as confirmed also by the efficiency parameter r_2/r_1 , reported in Figure 5B, that is greater than 5 in all the frequency range and reaches values above 10^2 at high fields, whereas the threshold value is ca.2 for most negative contrast agents.^{81, 83, 84} An example of the contrast ability of the PEG-AuFeNPs is obtained by comparing a phantom containing the aqueous suspension of PEG-AuFeNPs with a phantom containing pure water. The T_2 -weighted image, reported in Figure 5C, is obtained with a Spin Echo sequence (see Methods for details) and it is in agreement with the measured r_2 relaxivities at 8.5MHz (operating field of 0.2T). As can be seen from the image, the

solution containing the nanoalloy is darker than water, confirming the efficacy of our material in contrasting images.

Figure 5. Relaxivity properties of AuFeNPs solutions. (A) Longitudinal (r_1) and transversal (r_2) relaxation rates for PEG-AuFeNPs (respectively red squares and black circles). (B) r_2/r_1 ratio vs frequency. (C) Even at low frequency (8.5MHz), the phantom containing a solution of the nanoalloy is darker than pure water, showing the contrast ability of the PEG-AuFeNPs solution.

In summary, we showed that plasmonic and magnetic properties coexist in $\text{Au}_{89}\text{Fe}_{11}$ nanoalloys obtained by laser ablation synthesis in solution. LASiS is a top down “green” technique capable of bypassing the thermodynamic limitations for the synthesis of Au-Fe alloys and generating nanoparticles that can be coated in one pot with thiolated ligands. So obtained PEG coated AuFe nanoalloys have homogeneous $\text{Au}_{89}\text{Fe}_{11}$ composition and excellent stability in air and in aqueous solution. The ability of PEG-AuFeNPs to act as negative contrast agents for magnetic resonance imaging is also demonstrated. The investigation of plasmonic properties revealed a nonlinear dependence on the composition. Most importantly, plasmonic and magnetic properties coexist in the nanoalloy disclosing the possibility to observe novel spin-dependent plasmonic phenomena at the nanoscale. Therefore, our results mark a step forward in the development of a new class of multifunctional nanoalloys with potential applications in nanomedicine, photonics, spintronics and magneto-plasmonic devices.

Methods.

AuFeNPs synthesis and PEGylation. AuFeNPs were obtained by laser ablation synthesis in solution (LASiS). Laser ablation was carried out with Nd:YAG Quantel YG981E laser pulses at 1064 nm (9 ns) focused with a f 10cm lens on a metal plate placed at the bottom of a cell containing pure ethanol (HPLC grade, Fluka). Pulses of 30 J/cm^2 at a 10 Hz repetition rate and a plate of AuFe alloy (Au 73% atomic, Fe 27% atomic, 99.9% purity, purchased from MaTecK GmbH) were used for LASiS of AuFeNPs. Scanning Electron Microscopy - Energy Dispersive Spectroscopy analysis

with a FEI Quanta 200 was performed on the target prior to LASiS to assess the uniformity of the alloy plate.

After the LASiS, the ethanol solutions of AuFeNPs (0.05 mg/ml) was diluted 1:2 with an aqueous solution of disodium ethylenediaminetetraacetate (EDTA >98%, Sigma Aldrich) 5.0 mM and thiolated polyethylene glycol (PEG-SH, 5000 Mw, from Lysan Bio) 0.05 mM. The solution was kept at 60°C for 1 hour, then it was washed with dialysis membranes (10000 Da, from Sartorius) and resuspended in deionized water.

AuFeNPs structural characterization. UV–vis absorption spectra were recorded with a Varian Cary 5 spectrometer using 2 mm optical path quartz cells. FTIR measurements were recorded on a dried PEG-AuFeNPs powder on a KBr window with a Nicolet 5700 spectrophotometer.

The inductively coupled plasma-mass spectrometry (ICP-MS) measurements were carried out with a Thermo Elemental X7 Series instrument equipped with the PlasmaLab software package. For instrument calibration, a standard Au and Fe solutions were purchased from Spectrascan.

The X rays diffraction pattern was collected by a Philips diffractometer constituted by an X'Pert vertical goniometer with Bragg–Brentano geometry, a focusing graphite monochromator and a proportional counter with a pulse-height discriminator. Nickel-filtered Cu K α radiation and a step-by-step technique are employed (steps of $2\theta = 0.05^\circ$), with collection times of 30 s per step. A previously published method was used for line broadening analysis (LBA). The quantitative phase analysis by X-ray diffraction was performed using the Rietveld method (DBWS9600 computer program written by Sakthivel and Young and modified by Riello et al.).⁸⁵ According to the following files for Au_{1-x}Fe_x alloys we obtained the calibration curve to evaluate the Fe loading of the alloy:

x	pdf file	structure	cell parameter Å
0	pdf 00-004-0784	fcc	4.079
0.01	pdf 00-040-1295	fcc	4.073
0.4	pdf-04-005-6758	fcc	3.946
0.5	pdf 03-065-9857	fcc	3.885
0.5	pdf 04-001-2773	fcc	3.89
0.9	pdf 03-065-9856	fcc	3.68
0.92	pdf 04-001-2774	fcc	3.68
0.95	pdf 01-072-5264	bcc	2.892
0.96	pdf 04-004-4296	bcc	2.888
1	pdf-00-006-0696	bcc	2.886
1	pdf-04-007-9753	bcc	2.865
1	pdf-04-014-0360	bcc	2.868

In order to take into account Au_{1-x}Fe_x solid solutions with different structure (bcc and fcc) the calibration is obtained by fitting the average volume per atom in the cell. The calibration curve and the equation of the polynomial interpolation is reported in Figure S4 of Supplementary Information.

Transmission electron microscopy analysis was performed with a JEOL JEM 3010 microscope operating at 300 kV and equipped with a Gatan Multiscan CCD Camera model 794. The samples for TEM analysis were prepared by evaporating NPs suspensions on a copper grid coated with an amorphous carbon holey film.

Additional TEM analysis was carried out with a TitanTM TEM (FEI Company, Hillsboro, OR 97124) operating at 300 keV beam energy and equipped with a TridiemTM post-column energy filter (Gatan, Inc., Pleasanton, CA 94588) and an X-ray energy dispersive spectroscopy (XEDS) system (EDAX Inc., Mahwah, NJ 07430). The samples were imaged at a magnification of 500 kX in energy-filtered TEM (EFTEM) mode with 14 eV energy slit inserted around the zero energy-loss electrons for acquiring the high resolution TEM micrographs (HRTEM-Micrographs). The presence of peaks in the processed Fast Fourier Transforms (FFT) of each HRTEM image shows that all of the nanoparticles investigated for the analysis were having a crystalline structure. HRTEM images were acquired close to 1-2 Scherzer defocus. Elemental mapping for Au and Fe was performed by selecting their N-edge (83 eV) and L-edge (708 eV) respectively for the 3 window mapping method (1 post edge of 15 eV and 2 pre-edge with 15 eV width). Each elemental map was then line profiled across the diameter of each nanoparticle to show the amount of elemental signal across the whole of nanoparticle. Au and Fe signal counts were then summed and corrected with cross-sections using the experimental collection angle and energy windows adapted for EFTEM mapping of each element. Scanning transmission electron microscopy (STEM) was performed with the electron beam at 300 keV for acquiring the X-ray energy dispersive spectra (XEDS) from different locations on a same nanoparticle with about one nanometer spatial resolution. An annular dark-field (HAADF) STEM detector from Fischione Inc. was employed to generate the STEM micrographs. Au and Fe elemental compositions were determined under standardless and Cliff-Lorimer approximations.

The sample for analysis with the Titan TEM was obtained by mixing 10 µl of PEG-AuFeNPs solution with 100 µl of a 10 mg/ml polyvinyl alcohol solution in water (PVA, average 200000 Mw, from Fluka) and depositing one drop on a copper grid coated with an holey carbon film. PVA prevented particles agglomeration after drying of the drop.

Mie model calculations.

The extinction cross section of spherical nanoparticles was calculated using the Mie model for compact spheres.⁵⁹

$$\sigma = \frac{2\pi}{|k|^2} \sum_{L=1}^{\infty} (2L+1) \text{Re}[a_L + b_L] \quad (1.a)$$

$$a_L = \frac{m \cdot \psi_L(mx) \cdot \psi_L'(x) - \psi_L'(mx) \cdot \psi_L(x)}{m \cdot \psi_L(mx) \cdot \eta_L'(x) - \psi_L'(mx) \cdot \eta_L(x)} \quad (1.b)$$

$$b_L = \frac{\psi_L(mx) \cdot \psi_L'(x) - m \psi_L'(mx) \cdot \psi_L(x)}{\psi_L(mx) \cdot \eta_L'(x) - m \psi_L'(mx) \cdot \eta_L(x)} \quad (1.c)$$

$$m = \frac{n(R)}{n_m} \quad (1.d)$$

$$x = |\vec{k}|R \quad (1.e)$$

where σ is the extinction cross section of a sphere of radius R , k is the incident photon wavevector, Ψ_L and η_L are the spherical Riccati-Bessel functions, n_m is the real refraction index of the nonabsorbing surrounding medium, and $n(R)$ is the complex refraction index of the sphere of radius R . For all calculations we set the multipolar order $L = 3$ and $n_m = 1.334$ (for water matrix).

Since the optical constants of $\text{Au}_{89}\text{Fe}_{11}$ alloy are not available in literature, we used the linear averaging of the optical constants of pure Au from ref.⁸⁶ and for $\text{Au}_{84}\text{Fe}_{16}$ from ref.²². The optical constants were corrected for the size, as reported previously,^{59, 62} although the correction has negligible effects on 30 nm nanoparticles, that falls in between the intrinsic and extrinsic size effect regimes.⁵⁹

Magnetic characterization.

Magnetic measurements were performed using a Quantum Design MPMS SQUID magnetometer operating in the 1.8 - 350 K temperature range with applied field up to 5.0 T. Measurements were carried out on aqueous solution placed into a gel-cap and on dried powder obtained by gentle evaporation of few drops of the solution on a Teflon ribbon. The temperature dependence of the in-phase (χ') and out-of-phase (χ'') components of the AC susceptibility was measured with the same apparatus on a powder samples in the 1-1000 Hz frequency range with a field amplitude of 240 A/m. All data were corrected for the diamagnetic contribution of the sample holder and, when present, of the solvent, which were measured separately. After subtraction of the diamagnetic contribution, no noticeable differences among the magnetic behavior of the NPs in solution and in dried powder were observed.

Relaxivity measurements.

NMR data were collected by using two different pulsed FT-NMR spectrometers: *i*) a Smartracer Stellar relaxometer (with the use of Fast-Field-Cycling technique) for frequencies in the range $10 \text{ kHz} \leq \nu \leq 10 \text{ MHz}$, and *ii*) a Stellar Spinmaster for $\nu > 10 \text{ MHz}$.

Standard radio frequency excitation pulse sequences CPMG- (T2) and saturation-recovery (T1) were used. The contrast ability of PEG-AuFeNPs was investigated by measuring the longitudinal (r_1) and transversal (r_2) relaxation rates (Figure 5A) of protons (^1H) defined as:⁸¹

$$r_i = [(1/T_i)_{\text{meas}} - (1/T_i)_{\text{dia}}] / c \quad i=1,2$$

where $(1/T_i)_{\text{meas}}$ is the value measured for a concentration c of the magnetic center (in mM^{-1}) and $(1/T_i)_{\text{dia}}$ is the nuclear relaxation rate of the diamagnetic solvent (i.e. ultrapure H_2O), that is of the order of few seconds.

MRI experiments were performed at 8.5 MHz using an Artoscan Imager by Esaote SpA (Esaote, Genova, Italy). The used pulse sequence was an high resolution spin echo sequence with $\text{TR/TE/NEX} = 5000 \text{ ms}/120 \text{ ms}/2$, matrix = 256×192 , field of view = 180×180 . Here TE is the echo time, TR the repetition time, and NEX is the number of averages.

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Supplementary Information.

Coexistence of plasmonic and magnetic properties in Au₈₉Fe₁₁ nanoalloys

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Figure S1. HRTEM images of PEG-AuFeNP.

Figure S2. EFTEM mapping of Au N-edge (83 eV) and Fe L-edge (708 eV) on 4 NPs with size between 15 and 55 nm, showing that both elements are well overlapped. Scale bar is 10 nm.

Figure S3. Temperature dependence of the out-of-phase component of the AC magnetic susceptibility measured at five different log-spaced frequency between 1 and 1000 Hz. Although a frequency dependence is clearly observed, the large noise prevents any reliable quantitative data analysis.

Figure S4. The calibration curve used to evaluate the Fe loading of the alloy. In order to take into account $\text{Au}_{1-x}\text{Fe}_x$ solid solutions with different structure (bcc and fcc), the calibration is obtained by fitting the average volume per atom in the cell.