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## Reductant-free synthesis of magnetoplasmonic iron oxide-gold nanoparticles

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### ABSTRACT

Stable suspensions of spherical 10–15 nm superparamagnetic iron oxide nanoparticles (SPIONs) have been synthesized by co-precipitation, stabilized with citric acid, surface functionalized with aminopropyltriethoxysilane (APTES) and finally decorated with ultra-small gold nanoparticles (GNPs) by in situ reduction of a soluble gold salt (HAuCl<sub>4</sub>), obtaining well dispersed SPIONs-GNPs colloids.

The morphology, size and stability of the SPIONs-GNPs suspensions have been controlled by adjusting the molar ratio of the reagents (Fe/HAuCl<sub>4</sub> and Fe/APTES). The synthesis route differs from that typically found in literature, using tunable chelating layer modifications (such as citric acid and –NH<sub>2</sub> groups) of the magnetic core, depositing GNPs on the amine-functionalized iron oxide surface without the use of a specific reducing agent, and tuning the process pH and temperature. An explanation of how the different chemical species involved in the synthesis route could be responsible for the reducing action has been provided. The SPIONs-GNPs colloids have been characterized after each synthesis step by Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM), energy-dispersive X-ray spectroscopy (EDXS), Fourier transform infrared spectroscopy (FTIR), ζ Potential measurements, magnetic measurements with a vibrating-sample magnetometer (VSM) and UV–VIS spectroscopy. The SPIONs-GNPs colloids showed magnetoplasmonic behaviors since they maintained the plasmonic properties of GNPs and the superparamagnetic response of iron oxide NPs.

### 1. Introduction

A huge amount of literature has recently been published about the synthesis and characterization of nanoparticles (NPs) for biomedical applications [1–6]. In particular, several authors have intensively investigated various synthesis methods for iron oxide NPs, such as magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) NPs, which are of interest because of their use for many purposes, such as drug delivery, magnetic resonance imaging (MRI), hyperthermia, cell labelling and separation. For these applications, the NPs should combine biocompatibility with superparamagnetic properties and specific surface functionalities [7,8].

Superparamagnetic NPs are of particular interest since they do not retain any magnetism after the removal of the magnetic field [9]. This property provides the opportunity to induce their magnetization, direct them to a specific target site and, finally, allows them to be heated in the presence of an externally applied alternating current (AC) magnetic field [10].

According to their diameter, they are generally classified as SPIONs (Superparamagnetic Iron Oxide Nanoparticles, several dozen of nm in diameter) or USPIO (Ultrasmall Superparamagnetic Iron Oxide Nanoparticle, less than 20 nm in size) which offer the advantages of longer circulation and less clearance [11]. SPIONs with tailored surface properties have a high potential for use in both in vitro and in vivo applications. Surface functionalities could be created by coating the nanoparticles with organic polymer (e.g. Polyethylene glycol, dextran, chitosan) metals (e.g. gold, silver) or oxides (e.g. silica or alumina), which are also being suitable for functionalization with various bioactive molecules [12–14].

Apart from SPIONs, gold nanoparticles (GNPs) have also been developed and utilized for a variety of biomedical applications, such as drug delivery, as a contrast agent for imaging and as a photosensitizer for phototherapy (PTT) [15,16]. PTT involves the use of light and a photosensitizer to generate heat for therapeutic purposes. As a photosensitizer, GNPs have received increasing attention due to their unique

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surface plasmon resonance (SPR) absorption at visible (VIS) or near-infrared (NIR) wavelengths [17], so they can be externally triggered and remote-controlled by using an external stimulus, such as light, with a typical “switchable” behavior. Depending on their size and geometry, the plasmon peak can be tailored from VIS towards NIR, which is desirable due to its deep penetrating capacity and minimal interference with water and biomolecules in tissues. PTT mediated by stimuli responsive GNPs could be particularly useful for the treatment of cancer. In fact, the intracellular uptake of GNPs, which upon irradiation convert absorbed light into thermal energy, produces intracellular heating and disrupts cancer cells. This is due to their increased heat sensitivity, as well as to the tumor’s inability to efficiently dissipate heat owing to its poor vascular networks [16].

NPs composed of a magnetic core (for example magnetite -  $\text{Fe}_3\text{O}_4$ ) and an external gold shell layer are of great interest because they simultaneously possess both magnetic and plasmonic properties [18,19]: the gold shell layer provides a plasmon resonant response to the magnetic NPs [20]. The combination of magnetic and plasmonic properties of different nanoscaled particles, acting in synergy in hybrid nanostructures (magnetoplasmonic nanoparticles), represents an innovative approach with potential application in a variety of biomedicine fields. One of this is the magneto-photothermal therapy of cancer, where guiding and imaging can be achieved due to the magnetic properties of SPIONs and the thermal action can be activated by SPR absorption.

Such hybrid nanoparticles offer a great advantage over existing pure magnetic or plasmonic nanoparticles due to the high degree of tailored optimization for diagnosis and therapeutic needs. Different approaches are available for the preparation of  $\text{Fe}_3\text{O}_4$ -Au NPs, such as the CTAB-based reverse micelle emulsion method [21,22], the oil-phase method [23–25], the gamma-ray irradiation method [26], thermal decomposition [19,27–29], and the aqueous-phase method, where Au NPs (GNPs) are formed on the surface of  $\text{Fe}_3\text{O}_4$  by using different reducing agents, such as: hydroxylamine [30], glucose [31], THPC (tetrakis-(hydroxymethyl)-phosphonium chloride) [32], sodium citrate [33,34] etc. Most of the reported synthesis routes are aimed at obtaining a continuous Au shell on a  $\text{Fe}_3\text{O}_4$  core. Moreover, despite the fact that several routes [35] have been developed for the fabrication of multifunctional  $\text{Fe}_3\text{O}_4$ /metal hybrid nanostructures, a niche offering easily achievable synthesis has still not been completely covered. The purpose of the present work is to obtain magnetoplasmonic stimuli responsive nanoparticles for magneto-phototherapy via a simple and non-conventional synthesis route. We propose a modified aqueous-phase method to produce GNPs which will attach themselves to the surface of the  $\text{Fe}_3\text{O}_4$  NPs (SPIONs) with a “raspberry-like” structure. The GNPs decoration has been performed without using any specific reducing agents, simplifying the synthesis steps while controlling the SPIONs-GNPs shape, size and distribution.

## 2. Methods

A co-precipitation method was used to prepare  $\text{Fe}_3\text{O}_4$  NPs (SPIONs). The SPIONs synthesis was followed by their surface functionalization and decoration with ultra-small GNPs, by using colloidal gold suspensions. Each step was optimized taking into account the SPIONs dispersion and the distribution of GNPs on the SPIONs surface. Two synthesis routes (A and B) have been developed, which differ one from each other for the stabilization step and the modalities of decoration of magnetite with colloidal gold:

### 2.1. Synthesis route A

- Synthesis of SPIONs by co-precipitation;
- Functionalization of SPIONs with by aminopropyltriethoxysilane (APTES) to introduce functional amino groups;
- Synthesis of colloidal gold solution (GNPs);

- Synthesis of Au - decorated SPIONs;

### 2.2. Synthesis route B

- Synthesis of SPIONs by co-precipitation;
- Stabilization of SPIONs in water with citric acid (CA) in order to obtain CA-capped SPIONs;
- Functionalization of CA-capped SPIONs by aminopropyltriethoxysilane (APTES) to introduce functional amino groups;
- Synthesis of colloidal gold solution (GNPs);
- Synthesis of Au - decorated SPIONs;

The experimental procedures of each step of the above mentioned synthesis methods are described in the following sections. All reactants were purchased from Sigma Aldrich®.

### 2.3. Synthesis of SPIONs

SPIONs were synthesized by the co-precipitation in aqueous media of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts in alkaline environment for ammonium hydroxide  $\text{NH}_4\text{OH}$  (Merck, 25% aqueous solution) [14]. This step was carried out in the same conditions both in the A and B synthesis routes. According to the literature, solutions of ferrous chloride  $\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$  (0.1 M, Sigma Aldrich, > 99%) and ferric chloride  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.1 M, Sigma Aldrich, > 99%) were used. The required amounts of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  have been dissolved in 100 ml of bi-distilled water and the two solutions have been magnetically stirred in separate beakers. The pH of the two solutions before mixing was around 3 for the first one (ferrous chloride) and around 2 for the second one (ferric chloride). When the complete dissolution of the salts was reached, 50 ml of 0.1 M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution and 37.5 ml of the 0.1 M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  one were mixed in a beaker, reaching a pH value around 1.9.  $\text{NH}_4\text{OH}$  was added drop by drop to the obtained solution, under continuous mechanical stirring, until the pH was around 10: the reaction mixture turned black, indicating the formation of a suspension of iron oxide NPs (SPIONs).

The resulted suspension was then sonicated for 20 min and washed several times with a solution of double distilled water and  $\text{NH}_4\text{OH}$  with a pH value of 10. Sedimentation of NPs was magnetically induced and three washing steps have been performed in order to remove all the unreacted compounds and the residual ammonia. The as obtained SPIONs have been finally re-suspended in 100 ml of distilled water at pH = 10.

### 2.4. Stabilization of the SPIONs suspensions with CA

The stability of iron oxide NPs in water is quite low, due to anisotropic dipolar attraction [36]. This could limit the nucleation of the Au nanoparticles [27]. In order to improve the suspension stability, achieving higher repulsive interactions between magnetite nanoparticles and prevent as much as possible both their aggregation and the formation of clusters of uncontrolled dimensions, in the synthesis B, CA (Sigma Aldrich, > 99.5%) was added as stabilizing agent. CA is a well-known surfactant, as reported in literature by several authors [37–39].

In this synthesis, 120 ml of a 0.05 M CA solution were added to the SPIONs, previously separated by sedimentation, and the pH was adjusted to a value of 5.2 by the addition, drop by drop, of a concentrated ammonia solution. The suspension was then heated to 80 °C and stirred (150 rpm) for a short time (90 min) in order to promote the CA adsorption on SPIONs [39] while minimizing the magnetite decomposition to maghemite. Subsequently, the stabilized NPs have been washed by means of an ultrafiltration device (Solvent Resistant Stirred Cells - Merck Millipore)(4 steps in 50 ml of bi-distilled water at pH = 10.2) and finally suspended in 120 ml of bi-distilled water. The pH of the final water suspension was further

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