

Facile and Green Approach To Fabricate Gold and Silver Coated Superparamagnetic Nanoparticles

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ABSTRACT: Superparamagnetic magnetite nanoparticles are coated with homogeneous gold and silver shells using a simple aqueous based seed mediated method at room temperature with dopamine as a surfactant. Nanoparticles of Au in the range 2–3 nm are attached to amine functionalized Fe₃O₄ nanoparticles, acting as seed for the growth of ultrathin Au or Ag shells. The monodispersed core–shell nanoparticles Fe₃O₄@Au and Fe₃O₄@Ag have a particle size range of 10–13 nm with a shell thickness of approximately 2–3 nm. They are magnetically purified and are superparamagnetic at 300 K with saturated magnetization values of 41 and 35 emu g⁻¹, respectively.

Introduction

Superparamagnetic iron oxide nanoparticles (SPIONs) consisting of maghemite (γ -Fe₂O₃) or magnetite (Fe₃O₄) have attracted much interest due to their potential applications in magnetic guided drug delivery,¹ specific targeting and imaging of cancer cells,² hyperthermia treatment of solid tumors,³ and contrast enhancement agents in magnetic resonance imaging (MRI).⁴ However, the extent of biomedical applications of SPIONs strongly depends upon their stability in physiological solutions and the extent to which their surfaces can be chemically functionalized. Techniques for coating magnetic nanoparticles with biocompatible layers have been widely studied. Coating SPIONs with organic shell such as macrocyclic surfactants⁵ and polymers⁶ or inorganic shell⁷ can enhance their stability, dispersibility, and functionality of the otherwise naked magnetic nanoparticles. While coating of magnetic nanoparticles with polymers and silica shell has been extensively studied, there are limited reports on the coating of SPIONs with metallic shells. For biomedical applications, elemental gold and silver are ideal coating targets due to their low reactivity, high chemical stability, and biocompatibility, as well as their affinity for binding to amine (–NH₂) or thiol (–SH) terminal groups of organic molecules.⁸ Moreover, Au and Ag shells also render plasmonic properties to SPIONs,⁹ with gold coated particles imparting a 6-fold enhancement in trapping efficiency and detection sensitivity as compared to similar-sized polystyrene particles. In addition, the absorption of irradiation by gold at the most common trapping wavelength (1064 nm) imparts a dramatic heating of the particles (266 °C/W),¹⁰ with Au or Ag coated SPIONs serving as excellent heating source following magnetically targeting a tumor.^{11,12}

The synthesis of Fe₃O₄@Au/Ag core–shell nanoparticles is challenging given the difference in surface energies of the two materials.¹³ Consequently, gold and silver metals tend to nucleate rapidly forming discrete nanoparticles in solution without coating the surface of magnetite. γ -Fe₂O₃@Au or partially oxidized Fe₃O₄@Au core–shell nanoparticles (~60 nm) have been reported by depositing Au onto the surfaces of 9 nm particles involving the use of aqueous hydroxylamine.¹⁴ Core–shell nanoparticles of Fe₃O₄@Au and Fe₃O₄@Ag ranging

from 18 to 30 nm in size have also been prepared, using a reverse micelle method,¹⁵ but are capped with organic surfactants which renders them unsuitable for biomedical applications as they disperse in organic solvents. Recently, hydrophobic Fe₃O₄@Au and Fe₃O₄@Au@Ag core–shell nanoparticles have been prepared by reducing HAuCl₄ and AgNO₃ in a chloroform solution of oleylamine as a surfactant. Following this they can be transferred to the aqueous phase by mixing them with an aqueous cetyltrimethylammonium bromide (CTAB).¹⁶ Overall it is evident that a simple aqueous based synthetic method to coat Fe₃O₄ nanoparticles with uniform and relatively thin layers of noble metal (Au, Ag) shells that have minimal perturbations on the magnetic properties for applications in biomedical field is an important objective. Herein, we report a strategic route to coat SPIONs with 2–3 nm thick homogeneous Au and Ag shells in aqueous solution at room temperature. This straightforward approach affords core–shell nanoparticles with superparamagnetic properties, at the same time rendering plasmonic properties to the nanoparticles. Refluxing nanoparticles of Fe₃O₄ with (3-aminopropyl)triethoxysilane (APTES) for a few hours results in functionalizing the surface of the particles with –NH₂ groups. However, these nanoparticles are unstable in aqueous solution, and the synthetic procedure is time-consuming and requires high temperatures.¹⁷ We recently used sulfonated calixarenes to template and stabilize nanoparticles of Fe₃O₄ where the phenolic groups at the base of the calixarenes bind to surface metal centers.⁵ Dopamine, Scheme 1(a), also has phenolic groups which can behave similarly, albeit with now two adjacent –OH groups on the same aromatic ring which form a chelate ring to a metal center, as expected in the deprotonated form, with their terminal primary amine groups poised to bind to other metal centers.^{18,19} The utility of dopamine as such a surfactant features in the present study, as a linker molecule for metal centers on the surface of Fe₃O₄ and Au or Ag, Scheme 1. We find that the dopamine can be easily attached to the iron oxide nanoparticles in a single-step process by sonicating the nanoparticles with dopamine in aqueous solution at room temperature at pH ~ 9. The resulting amine functionalized Fe₃O₄ nanoparticles are stable in aqueous solutions for months, with no evidence of precipitation, thereby circumventing the need for using other surfactants. The presence of dopamine on the nanoparticles was established using FTIR as evidenced by the peaks characteristic of –NH₂ at 1617, 1600, and 1585 cm⁻¹ (see Figure S1 in the Supporting Information). The Fe₃O₄ nanoparticles were prepared

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