# Synthesis and Property Investigation of Fe₃O₄ Core and Ag, Au Bimetallic Shell Nanocomposites

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Novel nanocomposite with $Fe_3O_4$ core and Ag/Au bimetallic shell were fabricated by galvanic replacement reaction. The $Fe_3O_4$ core has good magnetism and Ag/Au shell shows characteristic surface plasmon resonance peaks of Ag and Au, as indicated by UV-visible absorption spectra. Surface-enhanced Raman scattering investigation reveals $Fe_3O_4$/Ag, Au presents much stronger surface-enhanced Raman scattering enhancement than $Fe_3O_4$/Ag, which is ascribed to the formation of holes during the replacement reaction.

**Keywords: Fe₃O₄, Bimetallic, Surface plasmon resonance, Surface-enhanced Raman scattering.**

## INTRODUCTION

Recently, preparation of $Fe_3O_4$ nanoparticles has been studied extensively due to their unique magnetic properties, good biocompatibility and potential applications in areas such as cancer diagnosis, drug delivery, biological separation and detection[1-3]. Unfortunately, magnetic $Fe_3O_4$ nanoparticles are easy to aggregate and due to the lack of functional groups, the magnetic nanoparticles are difficult to couple with biomolecules directly, which limits the application of magnetic nanomaterials[4]. In order to overcome these disadvantages, coating magnetic nanomaterials with metal or metal oxide shell to form composite magnetic nanoparticles has attracted much attention[5]. By virtue of its exceptional good stability and facility of surface functionality, gold was generally verified to be an excellent material to coat $Fe_3O_4$ nanoparticles[6]. The most important is Au shell provides the magnetic core with surface plasmonic properties, which makes the composite particle a special surface-enhanced Raman scattering (SERS) substrate. Surface-enhanced Raman scattering is widely used as a powerful analytical tool to study structures of adsorbed molecular systems and the physical chemistry of a surface[7]. Obviously, such versatile core-shell structured particles, which could provide real-time biomolecular information, are extremely attractive for biomedical applications.

With respect to surface-enhanced Raman scattering signal intensity, Ag is generally considered to provide larger enhancement than Au, despite the fact that Ag is not preferred for *in vivo* studies of biological system[8]. Therefore, Ag, Au bimetallic nanostructures, combining the benefits of the surface properties of Au with the optical enhancing properties of Ag, are fascinating target materials. In this paper, nanocom-posites with magnetic $Fe_3O_4$ as cores and novel bimetallic Ag, Au as shells were fabricated, which showed good magnetic properties and exhibited stronger Raman intensity than nanocomposites with pure Ag shells.

## EXPERIMENTAL

Hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot 4H_2O$), silver nitrate ($AgNO_3$), sodium citrate ($NaC_6H_5O_7 \cdot 2H_2O$), ammonia ($NH_4OH$), ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and crystal violet ($C_{25}H_{30}N_3Cl \cdot 9H_2O$) were purchased from Shanghai Reagents Co. and used as received. Ultrapure water (18 MΩ cm⁻¹) was used in all experiments.

**Preparation of Fe₃O₄ nanoparticles:** Naked $Fe_3O_4$ nanoparticles were prepared by chemical coprecipitation of $Fe^{3+}$ and $Fe^{2+}$ ions with a molar ratio of 2:1. Briefly, 4.46 g of $FeCl_3 \cdot 6H_2O$ and 2.3912 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 250 mL of $N_2$ purged ultrapure water under vigorous stirring. 19 mL sodium citrate solution (1 mol/L) and 100 mL ammonium hydroxide solution (1 mol/L) were mixed uniformly and then dropped into above-mentioned $Fe^{2+}$ and $Fe^{3+}$ mixed solution at a rate of 4 mL/min under nitrogen gas protection and vigorous stirring at 50 °C.

At the beginning of the coprecipitation process, the colour of the solution turned from light yellow to dark brown, which further turned into black. After the complete addition of sodium citrate and ammonium hydroxide solution, the reaction was kept for another 45 min. Then the black precipitate was collected on a magnet and washed with ultrapure water three times, which finally dispersed in 100 mL ultrapure water for further use.

**Preparation of Fe₃O₄/Ag nanoparticles:** The core/shell structured Fe₃O₄/Ag nanocomposites were prepared by reduction of $Ag^+$ onto the Fe oxide surfaces. 0.35 mL sodium citrate (0.155 mol/L) and 3 mL as-prepared Fe₃O₄ solution were dissolved in 100 mL ultrapure water, which were heated up to boil under vigorous stirring. Then 5 mL AgNO₃ (0.01 mol/L) solution was added quickly. After boiling for 15 min, the heater was turned off and the resultant was washed with ultrapure water and collected by magnetic separation. 5 mL of HCl (2 mol/L) was added to remove the uncoated Fe₃O₄. After washed twice with H₂O, the resultant was dispersed in 100 mL ultrapure water.

**Preparation of Fe₃O₄/Ag, Au nanoparticles:** The obtained Fe₃O₄/Ag nanoparticles served as seeds for the formation of Fe₃O₄/Ag, Au nanoparticles. 6 mL HAuCl₄ solution (0.1wt. %) was added into 20 mL as-prepared Fe₃O₄/Ag solution under stirring. Galvanic replacement reaction took place between surface Ag and HAuCl₄ and the colour of the solution changed with the increase of reaction time. After 40 min, the colour of the solution changed from light yellow to chartreuse and after 90 min, the colour turned into brown. After 120 min, the solution was dark red, which kept unchanged for longer time, indicating the completion of the replacement reaction. The products obtained with these three different reaction times were washed with ultrapure water respectively.

## RESULTS AND DISCUSSION

Fe₃O₄ particles are prepared by coprecipitation of a Fe(II) and Fe(III) salt in alkaline medium and the reaction was as follows:

$$Fe^{2+} + 2Fe^{3+} + 8NH_3 \cdot H_2O \rightarrow Fe_3O_4 + 8NH_4^+ + 4H_2O \qquad (1)$$
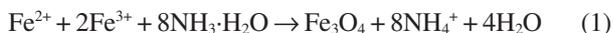
The obtained Fe₃O₄ nanoparticles were well dispersed by electrostatic and repulsive interactions between counter ions in solution. Fig. 1 displays the aggregation of Fe₃O₄ nanoparticles in external magnetic field. It is obvious that the father away from the magnet, the more shallow of the solution, which indicated the movement of Fe₃O₄ nanoparticles along the magnetic field, demonstrating its potential applications in magnetic separation and targeted delivery.



Fig. 1. Photo of aqueous solution of Fe₃O₄ under external magnetic field

Silver was deposited on the surface of magnetic Fe₃O₄ nanoparticles by reduction of AgNO₃ (Fig. 2). The UV-visible absorption spectrum of the Fe₃O₄/Ag nanoparticles is shown in Fig. 3(a). The absorption band around 310 nm is the characteristic surface plasmon resonance (SPR) absorption peak of Ag. It has been verified that no absorption appears in UV-visible spectra of bare Fe₃O₄ nanoparticles[9]. In addition, the Fe₃O₄/Ag nanoparticles were collected by magnetic separation, so the nonmagnetic Ag nanoparticles would be removed. In view of the above two points, it could be concluded the Fe₃O₄ nanoparticles had been successfully coated by Ag shells.

As shown in Fig. 2, the Ag coated Fe₃O₄ nanoparticles served as seeds for the synthesis of Fe₃O₄/Ag, Au nanoparticles through galvanic replacement reaction between Ag and HAuCl₄. Since the standard reduction potential of $AuCl_4^-$/Au pair (0.99 V *vs* standard hydrogen electrode, SHE) is higher than that of the $Ag^+$/Ag pair (0.8 V *vs* SHE), silver would be oxidized into $Ag^+$ while Au(III) be reduced into gold[10]:
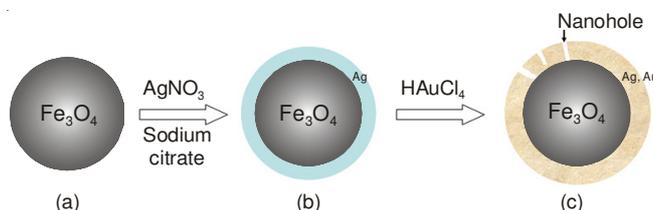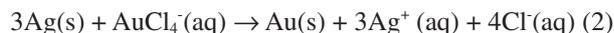


Fig. 2. Schematic illustration of surface coating of Fe₃O₄ nanoparticles

$$3Ag(s) + AuCl_4^-(aq) \rightarrow Au(s) + 3Ag^+ (aq) + 4Cl^-(aq) \quad (2)$$

Consequently, partial Ag in the shell was substituted by Au and Ag/Au bimetallic shell was formed. The UV-visible absorption spectrum of the Fe₃O₄/Ag, Au nanoparticles is displayed in Fig. 3(b). Fig. 3(c) is the UV-visible absorption spectrum of Fe₃O₄/Au and the band around 527 nm is contributed to the surface plasmon resonance of Au. Compared with the absorption spectra of both Fe₃O₄/Ag and Fe₃O₄/Au, it is concluded from Fig. 3(b) that Ag/Au bimetallic shell was obtained. In Fe₃O₄/Ag, Au exist separately in the shell instead of forming alloy, which would present only one surface plasmon resonance band locating between that of Ag and Au[11].
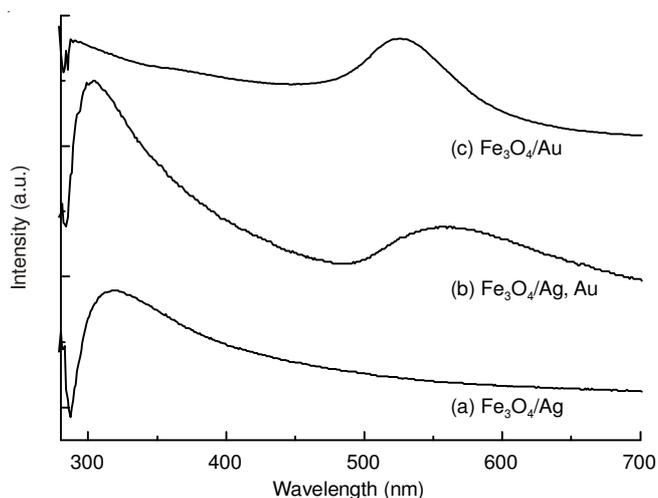


Fig. 3.  UV-visible absorption spectra of (a) Fe₃O₄/Ag, (b) Fe₃O₄/Ag, Au and (c) Fe₃O₄/Au

Fig. 4 reveals the UV-visible absorption spectra of $Fe_3O_4$/Ag, Au prepared with replacement reaction time of 40 min, 90 min and 120 min, respectively. With the increase of reaction time, more and more Au atoms deposited onto the $Fe_3O_4$ surface at the expense of Ag atoms and as a result the surface plasmon resonance band of Au grows stronger compared with that of Ag.
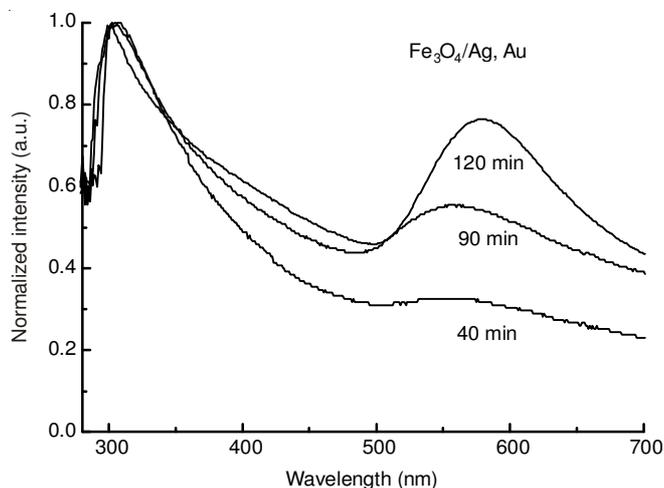


Fig. 4.　Normalized UV-visible absorption spectra of $Fe_3O_4$/Ag, Au prepared with different replacement reaction time

Coating $Fe_3O_4$ cores with noble metals imparts the nanocomposites specific surface plasmon resonance property and could be utilized as surface-enhanced Raman scattering substrates. The surface-enhanced Raman scattering activity of both $Fe_3O_4$/Ag and $Fe_3O_4$/Ag, Au prepared with different time was investigated by using crystal violet as probe molecule and the results are revealed in Fig. 5. Apparently, the Ag/Au bimetal coated nanoparticles show much stronger enhancement than the pure Ag coated ones. According to eqn. 2, only one gold atom can be generated at the expense of three silver atoms, so the oxidation of Ag by the Au(III) solution would require Ag atoms migrate to the surface and generate holes, as illustrated in Fig. 2 (c). Ag/Au bimetal synthesized by galvanic replacement has been studied by other researchers and hole
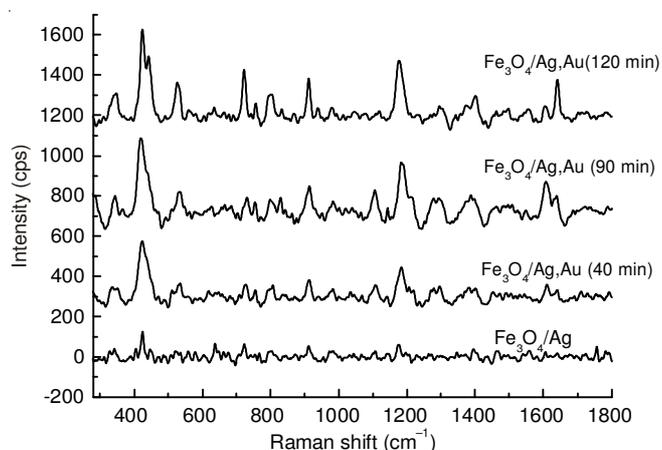


Fig. 5.　Surface-enhanced Raman scattering (SERS) spectra of crystal violet using $Fe_3O_4$/Ag and $Fe_3O_4$/Ag, Au prepared with different time as substrates

structures were clearly observed[12]. These holes have been proved to be efficient surface-enhanced Raman scattering "hot spots" and would provide huge electromagnetic enhancement for the molecules in their vicinity[13]. It is also shown in Fig. 5 that with the increase of replacement reaction time, the surface-enhanced Raman scattering intensity increases slightly, resulting from the generation of more and more holes.

## Conclusion

Novel core-shell structured $Fe_3O_4$/Ag, Au bimetallic nanocomposites were fabricated by directly deposition of Ag on magnetic $Fe_3O_4$ and subsequent galvanic replacement reaction between Ag and $HAuCl_4$. UV-visible spectra indicate the successful forming of Ag/Au bimetallic shell and the composition ratio of Ag and Au decreases with the elongation of replacement reaction time. surface-enhanced Raman scattering investigation reveals $Fe_3O_4$/Ag, Au presents much stronger enhancement than $Fe_3O_4$/Ag due to the generation of holes in the shell. Thus, the $Fe_3O_4$/Ag, Au nanocomposites, integrating the good magnetic property of $Fe_3O_4$ and excellent surface-enhanced Raman scattering activity of Ag/Au bimetal, would be an attractive material in practical application.

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