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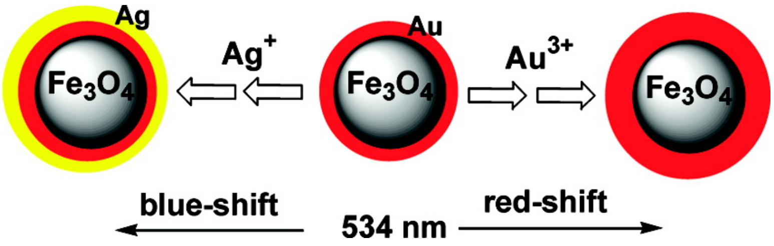

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Magnetic Core/Shell Fe_3O_4/Au and Fe_3O_4/Au/Ag Nanoparticles with Tunable Plasmonic Properties

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Synthesis of magnetic nanoparticles has long been of scientific and technological interest due to their potential applications in tissue imaging,[1] drug delivery,[2] and information storage.[3] Important progress has been made in chemical synthesis of monodisperse magnetic nanoparticles of metals,[4] alloys,[3b] and oxides.[5] Recently, incorporation of optically active components onto magnetic nanoparticles has attracted much attention. Dumbbell-like Au−Fe_3O_4[6] or CdS−FePt[7] nanoparticles have been synthesized and shown interesting optical properties in Au or CdS and magnetic properties in Fe_3O_4 or FePt. Au coating over magnetic nanoparticles is an even more attractive composite system:[8,9] with Au coating, the magnetic nanoparticles, especially high moment metallic magnetic nanoparticles, can be stabilized more efficiently in corrosive biological conditions and readily functionalized through the well-developed Au−S chemistry; the coating also renders the magnetic nanoparticles with plasmonic properties. This makes the core/shell composite nanoparticles extremely interesting for magnetic, optical, and biomedical applications.

Here we present a facile synthesis of Au- and Ag-coated Fe_3O_4 nanoparticles with controlled plasmonic and magnetic properties. The synthesis starts with room temperature coating of Au on the surface of Fe_3O_4 nanoparticles by reducing $HAuCl_4$ in a chloroform solution of oleylamine. The Au-coated Fe_3O_4 nanoparticles are then transferred into water by mixing them with sodium citrate and cetyltrimethylammonium bromide (CTAB). The water-soluble core/shell Fe_3O_4/Au nanoparticles serve as seeds for the formation of Fe_3O_4/Au nanoparticles with thicker Au coating by simply adding more $HAuCl_4$ in the reducing condition or for the preparation of Fe_3O_4/Au/Ag nanoparticles by adding $AgNO_3$ to the reaction mixture. The plasmonic properties of these core/shell nanoparticles can be tuned by controlling the coating thickness and coating materials. Our synthesis is fundamentally different from the previous methods in synthesizing Au- and Ag-coated magnetic nanoparticles in aqueous[8] and organic solutions[9] and achieves the uniform coating of Au and Ag on monodisperse Fe_3O_4 nanoparticles. The mild synthetic conditions reported here will also allow the synthesis of core/shell Fe_3O_4/Au with different shapes, facilitating the tuning of plasmonic properties in a wide range of spectrum.[10]

The oleylamine and oleic acid capped 10 nm Fe_3O_4 nanoparticles were synthesized via thermal decomposition of iron(III) oleate in a mixture of oleylamine and oleic acid[11,12] and were used for the synthesis of Fe_3O_4/Au nanoparticles. Figure 1A outlines the synthesis: 10 nm Fe_3O_4 nanoparticles (i) were first coated with a thin layer of Au to make Fe_3O_4/Au (ii). The coating experiment was carried out by gently reducing hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot 3H_2O$) in a chloroform solution of oleylamine in the presence of (i).[12] Oleylamine was used as a mild reducing agent as well as a surfactant. The as-prepared core/shell nanoparticles (ii) dispersed well in nonpolar solvent. To make water-soluble core/shell nanoparticles (iii), the dry hydrophobic nanoparticles (ii) were dissolved in an aqueous solution containing 0.1 M CTAB and 0.1 mM sodium citrate. It is well-known that sodium citrate can attach to Au and provides a negatively charged surface for Au nanoparticle stabilization.[13] However, our test showed that sodium citrate alone could not stabilize Fe_3O_4/Au nanoparticles in water. Combined CTAB, a cationic surfactant, with citrate, and the Fe_3O_4/Au nanoparticles were well-stabilized due to the formation of a CTAB double layer on the nanoparticle surface.[10a,b] The core/shell Fe_3O_4/Au nanoparticles (iii) capped with citrate−CTAB were readily dispersed in water, forming a light pink colloidal solution.[12] The same CTAB/citrate method could be applied to dissolve oleylamine capped Au nanoparticles into water, but not Fe_3O_4 nanoparticles, indicating that the as-prepared core/shell nanoparticles are coated with Au.

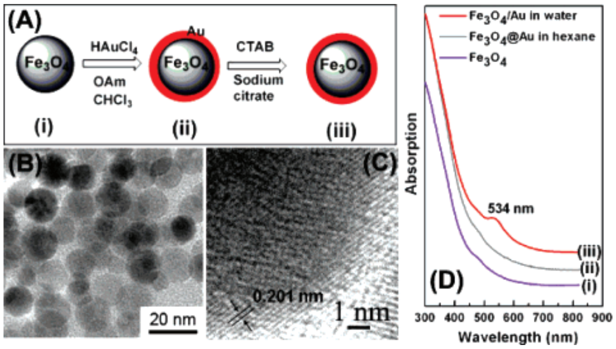

Figure 1. (A) Schematic illustration of surface coating of Fe_3O_4 nanoparticles (i) with Au to form hydrophobic Fe_3O_4/Au nanoparticles (ii) and hydrophilic Fe_3O_4/Au nanoparticles (iii). (B) TEM image of the nanoparticles (iii); (C) HRTEM image of part of a single Fe_3O_4/Au nanoparticle from (B). (D) UV−vis absorption spectra of the nanoparticles (i) in hexane, (ii) in hexane, and (iii) in water.

Transmission electron microscope (TEM) analysis on both Fe_3O_4 and Fe_3O_4/Au nanoparticles reveals that the overall inorganic diameter is increased from 10 nm of the as-synthesized Fe_3O_4 nanoparticles to ∼12 nm of the Fe_3O_4/Au (iii) nanoparticles. Figure 1B is the TEM image of core/shell nanoparticles (iii), and Figure 1C shows the high-resolution TEM (HRTEM) of a single Fe_3O_4/Au nanoparticle. The lattice fringes in the Au shell are clearly seen in the HRTEM, and the interfringe spacing is 0.201 nm, close to the interplane distance of the (200) planes in the face centered cubic (fcc) Au, indicating the Fe_3O_4 nanoparticles are coated with a layer (∼1 nm) of crystalline Au.[12] UV−vis absorption of the as-synthesized Fe_3O_4 nanoparticles (i) and the core/shell nanoparticles [(ii) and (iii)] shows different absorption properties as shown in Figure 1D. The core/shell nanoparticles (ii) dispersed in hexane have a similar spectrum to that from (i). Once capped with citrate and CTAB, the nanoparticles (iii) show an absorption band at 534 nm. Clearly, this optical property change is caused by the change of surface charge. It is known that the surface plasmon for the small Au nanoparticles has a strong absorption when the surface of the particles is charged, while no surface plasmon is observed when

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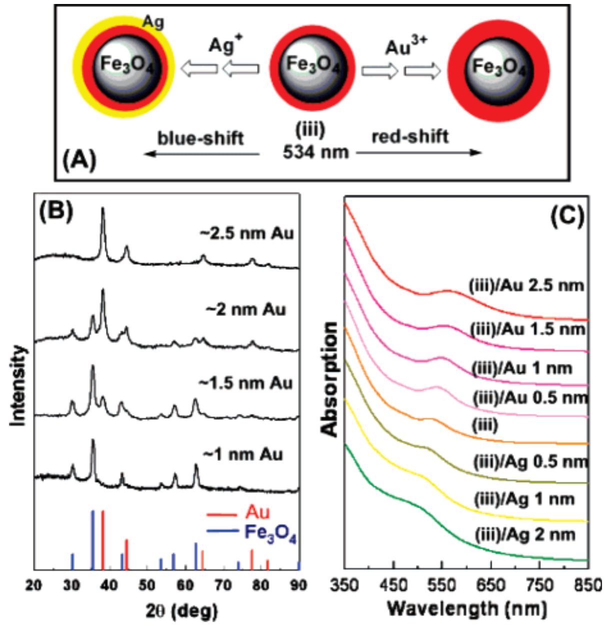

Figure 2. (A) Schematic illustration of the formation of Fe_3O_4/Au and Fe_3O_4/Au/Ag and the control on the plasmonic properties; (B) XRD of the Fe_3O_4/Au nanoparticles with various Au coating thickness; (C) UV−vis absorption spectra of the core/shell Fe_3O_4/Au and Fe_3O_4/Au/Ag nanoparticles with various Au and Ag coating thickness.

the surface of these nanoparticles is protected by a long alkyl chain ligand in nonpolar solvent.[14] The charge density on the surface of the core/shell nanoparticles (iii) and the amplitude of the free electron oscillation within the particles are significantly increased due to the coating with citrate and CTAB, leading to enhanced plasmonic absorption.

Core/shell Fe_3O_4/Au nanoparticles (iii) can be used as seeds for continued growth of Au shell or Ag shell, as illustrated in Figure 2A. The deposition of Au or Ag was carried out by reducing $HAuCl_4$ or $AgNO_3$ using ascorbic acid in the presence of CTAB.[12] This reduction chemistry has been found to be effective in making a uniform coating layer on gold nanorods.[10] The coating thickness was controlled by the amount of $HAuCl_4$ or $AgNO_3$ present in the reaction mixture. Figure 2B gives a series of X-ray diffraction (XRD) patterns of the Fe_3O_4/Au nanoparticles with various Au coating thickness. The evolution of the diffraction peaks from fcc Au is clearly seen in the patterns. As Au coating thickness increases, the diffraction from Au dominates the pattern—at 2.5 nm coating, the diffraction from Fe_3O_4 is too weak to be detected due to the heavy atom effect of Au. TEM image analyses on both Fe_3O_4/Au and Fe_3O_4/Au/Ag nanoparticles indicate the increase of the overall diameter of the particles compared to the as-synthesized Fe_3O_4 nanoparticles,[12] proving the coating control in the synthesis.

The controlled coating of either Au or Ag on the Fe_3O_4/Au nanoparticles (iii) facilitates the tuning of plasmonic properties of these core/shell nanoparticles. Figure 2C lists a series of UV−vis spectra from Fe_3O_4/Au and Fe_3O_4/Au/Ag nanoparticles in aqueous dispersions. The starting Fe_3O_4/Au nanoparticles (iii) have an absorption peak at 534 nm. Depositing more Au on the nanoparticles leads to a red-shift of the absorption peak, while coating Ag on (iii) results in a blue-shift of the spectrum. The absorption band can be red-shifted to 561 nm by increasing the thickness of the Au shell to ∼3 nm or blue-shifted to 501 nm by coating 2 nm Ag on (iii). The deposition of Ag on Au changes the effective dielectric function of the Au/Ag shell toward Ag[15] and thus the shift of the absorption peak from 534 to 501 nm. Note that the thickness increase in the Au or Ag shell results in the decrease in magnetic moment of the core/shell nanoparticles due to the weight contribution from the nonmagnetic Au and Ag.[12]

We have shown that the core/shell structured Fe_3O_4/Au and Fe_3O_4/Au/Ag nanoparticles can be readily synthesized in aqueous solution and room temperature reaction conditions. The control on shell thickness allows the tuning of plasmonic properties of the core/shell nanoparticles to be either red-shifted (to 560 nm) or blue-shifted (to 501 nm). The significant contribution of the synthesis is that it offers not only a composite nanoparticle system with controlled magnetic and plasmonic properties but also a noble metal-coated surface for long-term stabilization of the magnetic core and nanoparticle functionalization. Such multifunctional nanoparticles should have great potentials for nanoparticle-based diagnostic and therapeutic applications.

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Supporting Information Available: Experimental and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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