

Synthesis and properties of Au–Fe₃O₄ heterostructured nanoparticles

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ABSTRACT

Au–Fe₃O₄ composite nanoparticles have received much research interest due to their promising biomedical applications. In this work, Au–Fe₃O₄ composites with well-defined dimer-like nanostructure were synthesized via thermal decomposition route. The surfactant 1,2-hexandiol has proved to be critical for the formation of the Au–Fe₃O₄ hetero-dimers. The hetero-dimers production yield could be significantly improved to be 90% when the 1,2-hexandiol concentration was optimized at 0.6 M. The obtained Au–Fe₃O₄ hetero-dimers possess dual-functionalities of plasmon resonance and magnetization. Moreover, the Fe₃O₄ domain of the hetero-dimers can be tuned readily by adjusting the molar ratio between Fe and Au sources. Furthermore, it was demonstrated that these Au–Fe₃O₄ hetero-dimers could be further developed into star-like Au–Fe₃O₄ nanoparticles which showed plasmon absorption at NIR region.

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1. Introduction

Magnetic Fe₃O₄ nanoparticles have been well recognized for many specific biomedical applications including T₂ magnetic resonance imaging (MRI) contrast agent, bioseparation/biomarkers, drug delivery, and hyperthermia for cancer therapy, etc. [1–4]. Meanwhile, Au nanoparticles have also been widely applied to optical coherence tomography (OCT), colorimetric detection and photothermal therapy because of their high scattering cross section and plasmonic absorption [5–7]. By integrating these two nanomaterials into a single platform, more versatile multifunctional properties for various biomedical applications can be achieved. Thus, many research efforts have been made to develop nanocomposites between Au and Fe₃O₄ [8–10]. Au–Fe₃O₄ hetero-dimer is one of the typical Au–Fe₃O₄ composite nanostructures, of which one Fe₃O₄ nanoparticle grows epitaxially onto another Au nanoparticle. Due to the lattice mismatch induced strain and electrons interaction/transfer across the interface between two components, the properties of the Au and Fe₃O₄ can be modulated and some new properties might be introduced [11–14].

The key to achieving the Au–Fe₃O₄ hetero-dimers is to suppress homogenous nucleation and promote heterogeneous growth of Fe₃O₄ on Au seeds. To realize this, the lattice spacings of the two components, Au and Fe₃O₄, should be generally matched to lower the energy required for epitaxial growth. As reported, the lattice spacing of Fe₃O₄ (1 1 1) plane is 0.485 nm, which is almost twice of that of the Au (1 1 1) plane. This provides a good opportunity to grow Fe₃O₄ on Au nanoseeds epitaxially. To date, the most promising

method for synthesizing Au–Fe₃O₄ hetero-dimers is based on a thermal decomposition approach [15,16]. In brief, Au seed nanoparticles were formed and dispersed in an organic solvent first. Fe precursor was then injected and decomposed at an elevated temperature. Eventually Fe₃O₄ nanoparticles nucleated and grew epitaxially on the Au seed nanoparticles. In this approach, the synthesis conditions including surfactant amount, reaction temperature and the ratio of Au seed to Fe precursor must be optimized in order to prevent homogeneous nucleation of Fe₃O₄ and make sure the concentration of the Fe precursor is below the homogeneous nucleation threshold throughout the synthesis [17,18]. Although the synthesis of Au–Fe₃O₄ heterostructures by using this method has been reported, these critical synthesis conditions have not yet been well studied [11,13–17]. As a consequence, the success rate of synthesizing the well-defined Au–Fe₃O₄ hetero-dimers is usually quite low.

In the present work, we study the effects of surfactant 1, 2-hexandiol (HDD) on the formation of Au–Fe₃O₄ hetero-dimers by using the thermal decomposition method. For the first time, we find that the amount of HDD played an important role in the successful formation of Au–Fe₃O₄ hetero-dimers. By tuning the Au seeds-to-Fe precursor ratio, we have also been able to adjust the size of Fe₃O₄ domain and then tune the magnetic property as well as the plasmonic property of the nanocomposites. Therefore we have a good chance to reveal the dependence of plasmonic and magnetic properties of the hetero-dimers on the single Fe₃O₄ domain sizes, which was rarely well investigated in the previous reported work [11,15,16]. Moreover, we have demonstrated that these hetero-dimers could be further developed into star-like structure with near infrared (NIR) absorption, which is useful in various bio-applications including optical coherence tomography (OCT) and photothermal therapy [19].

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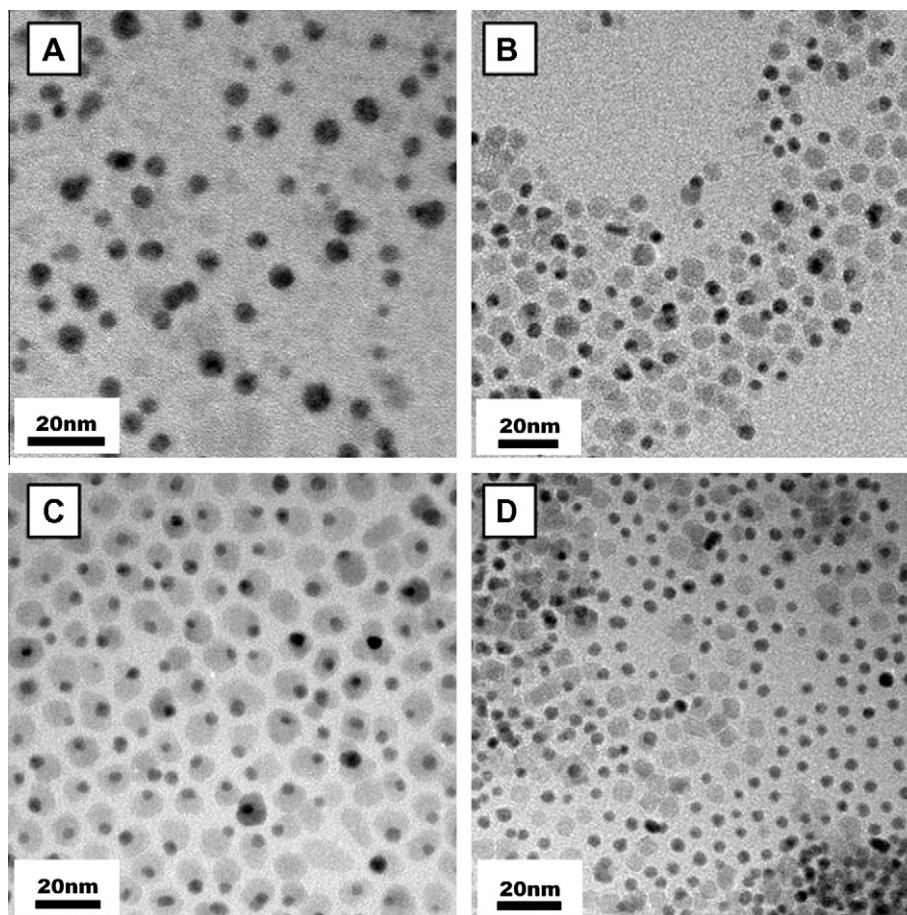


Fig. 1. TEM images of samples synthesized with different concentration of 1,2-hexadecanediol (HDD). (A) 0 M; (B) 0.3 M; (C) 0.6 M; (D) 1.2 M.

2. Experimental part

2.1. Materials

Iron(0) pentacarbonyl ($\text{Fe}(\text{CO})_5$), oleylamine (OAM), oleic acid (OA), 1,2-hexadecanediol (HDD), 1-octadecene (ODE), hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), cetyltrimethylammonium bromide (CTAB), silver nitrite, L-ascorbic acid. All chemicals are purchased from Sigma–Aldrich.

2.2. Synthesis of Au– Fe_3O_4 hetero-dimers

Au– Fe_3O_4 hetero-dimers were synthesized via hot injection technique [11]. Typically, 3.39 g OA, 3.21 g OAM and 3.43 g HDD were mixed with 10 ml ODE. The mixture was heated to 140 °C and maintained at that temperature for 20 min. Then 0.3 ml (2 mmol) $\text{Fe}(\text{CO})_5$ was quickly injected to the solution. After 3 min, an ODE solution containing 40 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 0.6 ml OAM was quickly added to the solution, leading to an immediate color change from transparent yellow to deep violet, indicating the formation of gold nanoparticles. The solution was then heated to 310 °C and refluxed at that temperature for 1 h. After cooling down, the particles were precipitated by adding iso-propanol and the supernatant was decanted. The precipitation was dissolved in hexane. Insoluble substance was separated by centrifugation at 4000 rpm for 10 min. The remained solution was washed with iso-propanol for 3–4 times and was suspended in hexane.

2.3. Synthesis of star-like Au– Fe_3O_4 nanoparticles

The obtained Au– Fe_3O_4 hetero-dimers were applied to phase transfer using CTAB before seeded growth [20]. In general, 1 mL solution of chloroform containing 10 mg of Au– Fe_3O_4 nanoparticles were added into 5 mL 0.2 M CTAB solution. After vigorous vortex and sonification for 30 min, the opaque solution became semi-transparent gel. The gel was then heated to 70 °C to evaporate the chloroform, leaving a transparent clear solution. Seeded growth in aqueous solution was carried out by adopting the widely used method for synthesizing Au nanorods, [21] except that the seeds were replaced by phase transferred Au– Fe_3O_4 nanoparticles and HCl was not used. The typical growth solution was composed of 10 ml CTAB (0.1 M), 500 μl HAuCl_4 (0.01 M), 100 μl AgNO_3 (0.01 M) and 80 μl L-ascorbic acid (0.1 M). After the fresh prepared seeds were injected, the solution was quickly mixed for a few seconds and left undisturbed overnight.

2.4. Characterization techniques

X-ray diffractometry (XRD) was carried out using an Advanced Diffractometer System (D8 Advanced Diffractometer System, Bruker, Karlsruhe, Germany). All transmission electron microscopy (TEM) images were obtained using JEOL 100CX instrument (200 kV). Samples were prepared by dipping carbon-coated copper grids into the sample solution followed by drying at room temperature. UV–Vis absorption spectra were carried out using Shimadzu UV-1601 UV–Vis spectrophotometer. The Baselines were collected

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