

A Facile and Green Synthetic Route for Preparation of Heterostructure Fe₃O₄@Au Nanocomposites

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Abstract. Magnetic nanoparticles offer many exciting opportunities in biology and biomedicine, such as magnetic resonance imaging, magnetic hyperthermia therapy, biomedical diagnosis. The synthesis of multifunctional magnetic nanocomposites that possess water-solubility, magnetic properties and optical stability by a green method at room temperature in aqueous phase is still an unmet need. Here, we developed a simple and green method for preparing Fe₃O₄@Au integrated the super-paramagnetic and optical properties by seed-mediated growth at mild condition in aqueous phase. The amphiphilic, non-ionic and nontoxic polymer poly(vinylpyrrolidone) (PVP) was used as a coupling agent for synthesis of Fe₃O₄@Au nanocomposites, which avoided the direct connection of Au and Fe₃O₄, and improved the saturation magnetization values of Fe₃O₄@Au to 40 emu/g at room temperature. We anticipate that the multifunctional Fe₃O₄@Au nanocomposites with high magnetic and good optical properties will provide a platform for potential diagnostic and therapeutic biomedical applications.

1 Introduction

Magnetic iron oxide nanoparticles (MNPs) have attracted considerable interest due to its superparamagnetism, and offered many exciting opportunities in biology and biomedicine, including magnetic resonance imaging, magnetic hyperthermia therapy, biosensor, separation and purification of protein and cell [1-5]. Meanwhile, the gold NPs have been extensively used in biosensor, surface enhanced Raman spectroscopy, and therapy applications, due to its well-known catalytic activity, optical properties, chemical functionality, and biocompatibility [6-8]. Bifunctional nanomaterial integrates gold and iron oxides into a single nano-platform, and by combining the advantages of gold and iron oxides, it shows enhanced physical and chemical properties [9]. Au shell layers provide stability and easy functionalization to the nanocomposites in solution, and render the magnetic NPs with plasmonic properties.

There are a number of literatures about the synthesis of MNPs@Au nanocomposites. Various nanocomposites with high shape regularity and a narrow size distribution were prepared by the thermolysis of organometallic precursors in hot organic solutions (180–190 °C) [10,11], or via thermally activated hetero-interparticle coalescence between gold and magnetic NPs under an

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encapsulating environment at temperature elevation (140–160 °C) [12]. All these methods involve hot organic solutions, resulting in the NPs capped with organic surfactants, which render them unsuitable for biomedical applications. Sun et al. synthesized the oleylamine and oleic acid capped Fe_3O_4 NPs via thermal decomposition of iron(III) leate in a mixture of oleylamine and oleic acid, and then, they synthesized the $\text{Fe}_3\text{O}_4/\text{Au}$ NPs in a chloroform solution in the presence of the Fe_3O_4 NPs. Core/shell $\text{Fe}_3\text{O}_4/\text{Au}$ NPs could be used as seeds for continued growth of Au shell or Ag shell in aqueous solution. [13] Lyon et al. provided a rapid and effective route for synthesis of magnetic core/shell particles that were soluble in aqueous media [14]. However, this method can't form Au shell on Fe_3O_4 NPs directly. The Fe_3O_4 NPs need to be exposed to air for extended periods (~1 week), or oxidized to form $\gamma\text{-Fe}_2\text{O}_3$, which decreases the saturation magnetization and elongates the synthesis time. Liu et al prepared ultra-small dimensional PVP-coated $\text{Fe}_3\text{O}_4/\text{Au}$ nanocomposites in octyl ether by nanoemulsion polyol process [15]. However, it also needs high temperature (280 °C) to form the $\text{Fe}_3\text{O}_4/\text{Au}$ nanocomposites, and the transfer of the NPs from organic phase to aqueous phase. Miao et al provided a facile route at room temperature in aqueous phase [16], through 11-mercaptoundecanoic acid used as a linker, for preparation of magnetically responsive $\text{Fe}_3\text{O}_4@\text{Au}$. Unfortunately, this method requires tedious washing and sonicating processes as well as long preparation time (over one day). Consequently, routine synthesis often involves high temperature, several separate and time-consuming processes in order to obtain such heterostructure nanocomposites. Thus, the synthesis of a uniform and monodisperse multifunctional nanocomposite that suitably integrates Fe_3O_4 NPs and gold nanoshells, and possesses water-solubility, magnetic properties and optical stability by a rapid simple methodology at room temperature in aqueous phase is still a great challenge.

Here, we developed a simple and green method for preparing $\text{Fe}_3\text{O}_4@\text{Au}$ by the seed-mediated growth. The Fe_3O_4 particles were prepared by coprecipitation of an Fe(II) and Fe(III) salt in alkaline medium at room temperature. The amphiphilic, nonionic, nontoxic, polymer poly(vinylpyrrolidone) (PVP) was used as a mediator to stabilize Fe_3O_4 NPs. It provided sufficient steric stabilization for the colloids to avoid aggregation. On the other hand, it was small enough to form a relatively homogeneous and slightly negative charge layer onto Fe_3O_4 NPs colloids. The number of NPs decorated with PVP could be controlled by changing the molecular weight of PVP [17]. Gold seeds (~4 nm) with positive charge were absorbed on the PVP modified Fe_3O_4 NPs. Au shells were formed by reduction of Au^{3+} onto the surfaces of Fe_3O_4 NPs by the hydroxylamine hydrochloride. To the best of our knowledge, the rapid synthesis of three-layer nanocomposites with Fe_3O_4 as the core, PVP coating as a media and Au shell by room temperature in aqueous solution with high yield have not been reported before. Such $\text{Fe}_3\text{O}_4@\text{Au}$ nanocomposites show excellent monodispersity in particle size, outstanding magnetic response, well-defined optical properties and long-term stability, which has made it promising for biomedical applications.

2 Experiment

2.1 Materials

Poly(vinylpyrrolidone) (PVP, Mw 58,000), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron(III) chloridehexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}_3\text{HCl}$) were purchased from Aladdin[®](Shanghai, China). Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%) and cetyltrimethyl ammonium bromide (CTAB) were purchased from Sigma-Aldrich (New Jersey, USA). Deionized water (DI, 18 $\text{M}\Omega \text{ cm}^{-1}$) was used in all experimental processes as needed. All materials were used as received without further processing.

2.2 Synthesis of Fe_3O_4 NPs

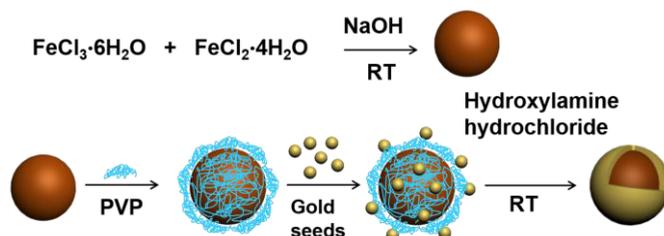
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.825 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.895 g) were dissolved in 15 ml of degased DI water. 5 ml of NaOH solution (5.8 M) was added into the iron chloride mixture dropwise by a syringe. The reaction was continues for 30 minutes with continuous stirring at room temperature under nitrogen protection. Then, washed the black precipitate with magnetic separation twice. The black Fe_3O_4 NPs were re-dispersed in PVP solution with weight ratio of 1:5 to form a stable suspension.

2.3 Synthesis of Fe_3O_4 @Au nanocomposites

Firstly, 4 nm gold seeds were prepared through borohydride reduction of gold salt in the presence of CTAB, which also made the gold seeds positively charged. The fresh sodium borohydride solution (0.01 M) was added to the mixture of 0.1 M of CTAB and 0.2 mM gold chloride acid solution. The color of the mixture turned from yellow to light brown, indicating gold seeds were formed. 2.8 ml of diluted Fe_3O_4 NPs solution (2mg/ml) was stirred with 0.5 ml gold seeds for 1 hours. The mixture was isolated by magnet, and the precipitates were re-dispersed in the mixture of 4 ml DI water, 0.4 ml (1% wt.) citric acid and 0.2 ml 0.025M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. The pH of the mixture was adjusted to pH=9 by NaOH, then, 0.2 ml of hydroxylamine hydrochloride was added. The color of the reaction solution changed from black to red wine, indicating Fe_3O_4 @ Au nanocomposites were successfully synthesized.

3 Results and discussions

The approach for the synthesis of the Fe_3O_4 @Au nanocomposites was illustrated in scheme 1. A “seed-mediated growth” strategy was used to synthesize the Fe_3O_4 @Au nanocomposites [18]. We chose a two-step method for preparation of Fe_3O_4 @Au nanocomposites. As shown in scheme 1, the Fe_3O_4 NPs were fabricated firstly by coprecipitating of Fe^{2+} and Fe^{3+} ions (in the molar ratio of 2:3) by alkaline solution. After 30 mins’ reaction, the Fe_3O_4 NPs were precipitated by magnet, and then washed and re-dispersed in DI water. After that, the amphiphilic, nonionic, nontoxic PVP was used as a mediator to stabilize Fe_3O_4 NPs. It provided sufficient steric stabilization of the colloids to ensure well-dispersed magnetic particles NPs. On the other hand, it formed relatively homogeneous and slightly negative charge layer onto Fe_3O_4 . Gold seeds were synthesized by borohydride reduction of gold salt in the presence of CTAB. The surfactants CTAB not only used as stabilizer for the Gold seeds, but also made the gold seeds negatively charged. The gold seeds were absorbed on the Fe_3O_4 NPs by the electrostatic interactions between the slightly negatively charged PVP on Fe_3O_4 NPs and positively charged gold seeds. The water-soluble core/ shell Fe_3O_4 /PVP/ gold seeds serve as seeds for the formation of Fe_3O_4 @Au nanocomposites with thicker Au coating. Hydroxylamine hydrochloride was used as a mild reducing agent to form thicker Au coating on Fe_3O_4 by simply adding more HAuCl_4 in alkaline condition. The processure involved herein was perform at room temperature and in aqueous phase. The mild and simple synthetic conditions reported here avoided the tedious procedure to transfer nanocomposites from organic phase to aqueous phase, and avoided the usage of toxic solvents.



Scheme 1. Schematic synthetic route for preparation of heterostructured Fe_3O_4 @Au nanocomposites at room temperature in the aqueous phase.

We further characterized the optical and magnetic properties of synthesized magnetic nanocomposites. The product of $\text{Fe}_3\text{O}_4@\text{Au}$ was dispersed in aqueous solution with a well monodispersity. The nanocomposites exhibited red wine color, which indicating the formation of Au shell on the magnetic nanocomposites (Figure 1a). The nanocomposites were effectively separated from the solution in the presence of a magnetic field by a magnet, leaving the bulk solution clear and transparent (Fig. 1b), which demonstrated the effective magnetic separation characteristics of $\text{Fe}_3\text{O}_4@\text{Au}$ nanocomposites. After the removal of the external magnet and with slightly shaking, the transparent solution turned to red wine color again as shown in Figure 1a. The respective absorption spectra measured for Fe_3O_4 NPs, Au seeds and $\text{Fe}_3\text{O}_4@\text{Au}$ were shown in Figure 2. The solution of Fe_3O_4 NPs and Au seeds did not show any obvious measurable surface plasmon resonance (SPR) peak in the visible region. However, the $\text{Fe}_3\text{O}_4@\text{Au}$ NPs showed a clear SPR peak at 540 nm, indicating the formation of Au shell on Fe_3O_4 NPs. Measurements of the SPR band of the NPs provided complementary evidence of the $\text{Fe}_3\text{O}_4@\text{Au}$ nanocomposites.

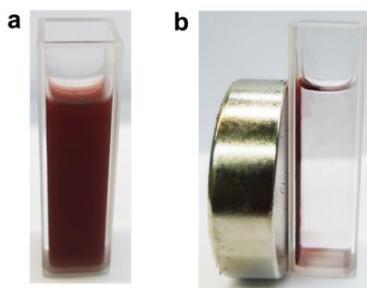


Figure 1. Photo images of $\text{Fe}_3\text{O}_4@\text{Au}$ with absence (a) and presence (b) of an external magnet.

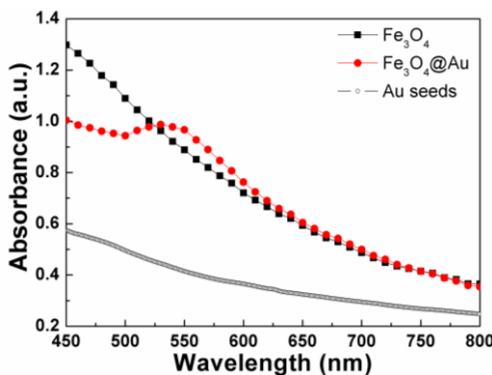


Figure 2. Absorption spectra for Fe_3O_4 NPs, Au seeds and $\text{Fe}_3\text{O}_4@\text{Au}$ nanocomposites.

In order to further determine the crystallinity and structure of the nanocomposites, powder X-ray diffraction (XRD) spectrum was utilized. Figure 3 showed the XRD of $\text{Fe}_3\text{O}_4@\text{Au}$ and the corresponding standard cards, JCPDS 88-0315 for Fe_3O_4 and 04-0784 for cubic gold. The line broadening observed in the XRD spectra is indicative of the small size of the NPs. All the patterns of the $\text{Fe}_3\text{O}_4@\text{Au}$ nanocomposites are in agreement with the spectral peak of gold standard XRD diffraction spectrum (JCPDS # 4-0784), as well as the standard of Fe_3O_4 diffraction spectrum (JCPDS # 88-0315). XRD patterns for $\text{Fe}_3\text{O}_4@\text{Au}$ NPs show characteristic peaks (at $2\theta=30.157^\circ$, 35.521° , 43.172° , 53.561° , 57.098° , 62.703°), are in corresponding with their indices (220), (311), (400), (422), (511) and (440) of Fe_3O_4 with cubic phase (JCPDS 88-0315), indicating that the NPs are pure Fe_3O_4 . Besides the XRD patterns belonging to Fe_3O_4 (JCPDS 88-0315), all the other diffraction peaks at $2\theta=38.184^\circ$, 44.392° , 64.576° , and 77.547° , are identified as characteristic (111), (200), (220) and (311) planes of cubic Au (JCPDS 04-0784).

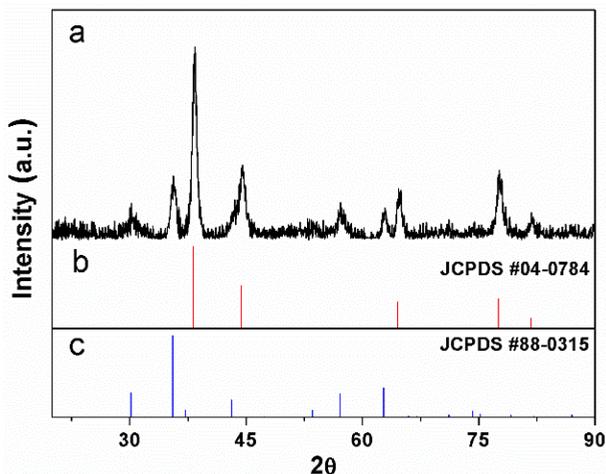


Figure 3. (a) XRD diffraction patterns of the as-prepared $\text{Fe}_3\text{O}_4@Au$, and the corresponding standard XRD diffraction spectrum (b) Au (JCPDS #04-0784) and (c) Fe_3O_4 (JCPDS #88-0315)

The magnetic properties of as-synthesized Fe_3O_4 and $\text{Fe}_3\text{O}_4 @ Au$ nanocomposites were measured by vibrating sample magnetometer at room temperature (300 K). The field-dependent magnetization curves shown in Figure 4 demonstrated that Fe_3O_4 and $\text{Fe}_3\text{O}_4 @ Au$ nanocomposites were superparamagnetic with a saturation magnetization values of 60 and 40 emu/g , respectively. A slight decline of the saturation magnetization value of $\text{Fe}_3\text{O}_4@Au$ after coating Au was due to the diamagnetic contribution of the Au. Fortunately, the saturation magnetization value of $\text{Fe}_3\text{O}_4@Au$ was relatively high compared with the literature reported previously [16]. The maximum magnetization value of the core/shell magnetic NPs was around 10-20 emu/g at room temperature [19]. The direct coating of Au onto magnetic NPs severely decreased the saturation magnetization of the magnetic core by 78% or more.[20,21]. In our method, PVP as a coupling agent, not only prevented the magnetic NPs from large-sized aggregated precipitates in solutions, but also decreased the effect of Au coating on the magnetic properties of $\text{Fe}_3\text{O}_4@Au$ nanocomposites. As a result, the PVP-processed $\text{Fe}_3\text{O}_4@Au$ nanocomposites with high saturation magnetisation improved the performance of operation and offer potential applications in different areas.

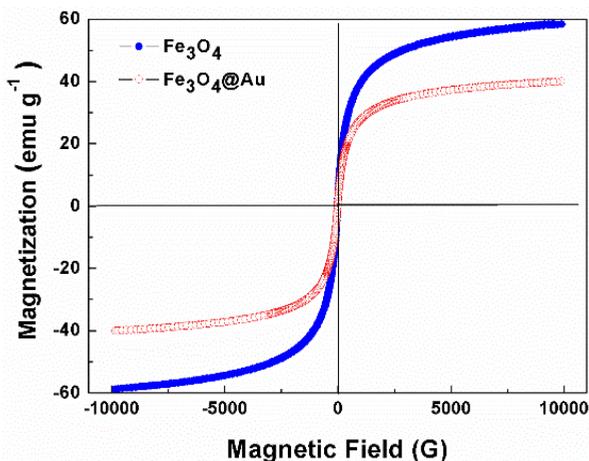


Figure 4. Hysteresis loops of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@Au$ (300 K)

4 Conclusions

In this research, we proposed a simple, rapid, non-toxic method for synthesis of water-soluble Fe₃O₄ @ Au nanocomposites in aqueous solution at room temperature. The synthesized multifunctional super-paramagnetic nanocomposites displayed interesting plasmonic properties and high saturation magnetization, which could be applied for various bio-applications. The significant contributions of the synthesis are listed as following. It offers a simple, fast and green method for preparing of multifunctional magnetic nanocomposites at room temperature in aqueous solution with large scale. It avoids tedious procedures to transfer the magnetic nanocomposites from organic phase to aqueous phase, and avoid the usage of toxic reagents (e.g. benzene). We anticipate that such multifunctional magnetic nanocomposites will have great potentials for nanoparticle-based diagnostic and therapeutic applications due to its magnetization and optical properties.

Acknowledgments

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