Synthesis and characterization of monodisperse core-shell Fe\textsubscript{3}O\textsubscript{4}@Au nanostructures

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Abstract. This work reports a synthesis of monodisperse core-shell Fe\textsubscript{3}O\textsubscript{4}@Au nanostructures. Fe\textsubscript{3}O\textsubscript{4} (~4.9 nm) and core-shell Fe\textsubscript{3}O\textsubscript{4}@Au (5.0–5.6 nm) nanostructures were successfully synthesized via thermal decomposition method of iron compounds in the presence of oxygen-containing ligands. XRD analysis revealed the pure face-centered cubic (FCC) structure of Fe\textsubscript{3}O\textsubscript{4} with 2\texttheta/g peaks at 31°, 38°, 44° and 64°, 77° and 81° attributed to Fe-Au, which can be indexed to lattice planes of gold in a cubic phase. In addition, UV-Vis spectra showed a significant difference absorbance peak between Fe\textsubscript{3}O\textsubscript{4}NP and Fe\textsubscript{3}O\textsubscript{4}@AuNP.

Keywords: Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{3}O\textsubscript{4}@Au, core-shell nanostructures, thermal decomposition

1. Introduction

It is widely reported that nanoparticles can take a significant part in the improvement of sensor performance, due to the large specific surface area, outstanding conductivity and compatibility. Currently, various types of nanoparticles have been extensively used to fabricate a wide variety of electrochemical sensors [1]. In all sorts of nanoparticles, superparamagnetic iron oxide nanoparticles, especially Fe\textsubscript{3}O\textsubscript{4} nanoparticles (Fe\textsubscript{3}O\textsubscript{4} NP) have gained much attention because of their particular magnetic properties and their ability to be easily chemically altered to increase biocompatibility and dispersibility [2]. Furthermore, the synthesis of noble metal nanostructures has attracted many attentions because of its unique chemical properties, physical properties, and interesting catalytic properties [3]. In addition, bimetallic nanostructures also exhibit greatly increased optical, catalytic and electrical properties of each monometallic constituent [4]. It was reported that gold-coated Fe\textsubscript{3}O\textsubscript{4}NP (Au-Fe\textsubscript{3}O\textsubscript{4}NP) is more active than the single component gold nanoparticles (AuNP) or Fe\textsubscript{3}O\textsubscript{4} NP [5]. The increased activity comes from the partial charge transfer between Au and Fe\textsubscript{3}O\textsubscript{4} at the nanoscale particle interface. Furthermore, with Au coating, the Fe\textsubscript{3}O\textsubscript{4}NP can be more efficiently stabilized in corrosive biological conditions and immediately functionalized through the well-developed Au-S chemistry; the coating also renders the Fe\textsubscript{3}O\textsubscript{4}NP with plasmonic properties [6].

In this study, Fe\textsubscript{3}O\textsubscript{4}@AuNP with high mono dispersity was synthesized. The synthesis started from Fe\textsubscript{3}O\textsubscript{4}NP, synthesized by high thermal decomposition methods of iron compounds in the presence of oxygen-containing ligands. The use of acetylacetonates [7] and acetates [8] were normally reported as the ligands. However, oleic acid was used in this method. Together with oleic acid, oleyl amine was also
used as surfactants to react with the metallic organic precursor to form an intermediate Fe\textsuperscript{3+} complex, which further decomposed to form Fe\textsubscript{3}O\textsubscript{4}NP. Then, the coating of Au on the surface of Fe\textsubscript{3}O\textsubscript{4}NP was conducted by reducing gold ions in chloroform solution containing of oleyl amine at room temperature. The results showed that monodisperse Fe\textsubscript{3}O\textsubscript{4}@AuNP could be synthesized with an average size of 5.0 nm. This nanoparticle is ready for many applications, such as sensors or drug delivery.

2. Materials and method

2.1. Materials and instruments

Iron-oleate complex, synthesized from Iron (III) hexahydrate (FeCl\textsubscript{3}.6H\textsubscript{2}O, 98 \%) and oleic acid (C\textsubscript{8}H\textsubscript{3}2O\textsubscript{2}, OLA, 90). These chemicals as well as Gold (III) chloride trihydrate (HAuCl\textsubscript{4}.3H\textsubscript{2}O, 99) and oleyl amine (C\textsubscript{18}H\textsubscript{37}N, OAm, 70 \%) were supplied by Sigma-Aldrich, while sodium oleate (C\textsubscript{13}H\textsubscript{33}NaO\textsubscript{2}, 97 \%) was from Tokyo Chemical Industry, Ltd). All chemicals were reagent grades. The distilled water with a resistivity greater than 18.2 M\(\Omega\)cm was used.

2.2. Synthesis of Fe\textsubscript{3}O\textsubscript{4}@AuNP

Fe\textsubscript{3}O\textsubscript{4}NP was synthesized according to thermal decomposition method reported by Kim et al. with some modifications using an Fe-oleate complex as a precursor [9]. Fe-oleate complex (3.0 g) and oleic acid (0.593 mL) were dissolved in 1-octadecene (21.32 mL) in a three-neck bottom round reaction flask under stirring conditions. To initiate the reaction, the temperature was raised to 60 °C for 15 min, then to 320 °C with a speed of 3.3 °C min\textsuperscript{-1} under atmospheric nitrogen. After cooling to the room temperature, the product was washed to produce dark-brown particles (Fe\textsubscript{3}O\textsubscript{4}NP), which can be drawn by an external magnet. Fe\textsubscript{3}O\textsubscript{4}@AuNP was synthesized based on the procedure carried out by Xu et al., with some modifications [6]. Fe\textsubscript{3}O\textsubscript{4}NP acted as the core, while Au was coated as the shell at the surface of Fe\textsubscript{3}O\textsubscript{4}NP by reducing gold ions in chloroform contained in oleyl amine.

Briefly, chloroform (10 mL) containing of 2 mg Fe\textsubscript{3}O\textsubscript{4}NP and oleyl amine (2 mmol) were mixed with a dropwise addition of 2.5 mL 10 mM gold solution. The mixture was stirred at 500 rpm to make homogeneous and monodispersed nanoparticles. After 20 h, two layers of brown (bottom) and murky white (top) were formed, then ethanol (10 mL) was added. After centrifuged at 10,000 rpm at 10 °C for 30 min, two separated phases, dark brown (bottom) and clear (top) were formed with precipitate (Fe\textsubscript{3}O\textsubscript{4}@AuNP). The precipitate was then washed and was dried under vacuum overnight. To make water-soluble Fe\textsubscript{3}O\textsubscript{4}@AuNP, dried Fe\textsubscript{3}O\textsubscript{4}@AuNP was dissolved in aqueous solution consists of 0.1 M CTAB and 0.1 mM sodium citrate.

2.3. Characterizations

Transmission Electron Microscope (TEM) images were recorded by using JEOL JEM-2100F. The Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) measurements were performed with a Spectro blue-ICP-OES (Ametek). The X-Ray Diffraction (XRD) measurements were conducted in Rigaku D/MAX2500V/PC scanning 2\(\theta\) at 30 to 90 degree, while the Scanning Electron Microscope (SEM) was Zeiss EVO M10.

3. Results and discussion

3.1. Synthesis of Fe\textsubscript{3}O\textsubscript{4}NP

The synthesis of Fe\textsubscript{3}O\textsubscript{4} NO was conducted through two steps, including the iron oleate precursor and iron oxide nanoparticles synthesis (figure 1). In order to synthesize the nanoparticles with high-uniform size, complete separation of nucleation, and monodisperse, the iron-oleate complex was produced from the reaction between iron (III) chloride and oleic acid. The use of the iron-oleate complex as the precursor can control the amount of iron in the synthesis to form the monodisperse nanocrystals [10].
TEM image of the synthesized Fe$_3$O$_4$NP (figure 2) shows that the average size of Fe$_3$O$_4$NP was 4.9 ± 0.05 nm, while XRD pattern (figure 3a) shows a broadening peak, indicates the particle size was very small. The XRD profile of as-synthesized particles show a poor crystallinity in diffractogram; peaks are hardly visible above the noise as it may contain nanoparticles of various oxygen contents (multiple phases) [11]. However, the peaks related a spinel structure was obviously observed with a characteristic peaks for Fe$_3$O$_4$ (2θ) at 30°, 35°, 43°, 53°, 57° and 62° [12]. These peaks indicate the pure face-centered cubic structures of Fe$_3$O$_4$ [13]. Figure 3b shows the FTIR spectra of Fe$_3$O$_4$NP with oleic acid as the capping agent. A strong absorption of Fe-O stretching bond of bulk magnetite at a wavelength of 560 cm$^{-1}$ was observed [12], while the peaks at the wavelengths of 1400 cm$^{-1}$, 2850 cm$^{-1}$ and 3400 cm$^{-1}$ could be associated with the stretching modes of C=O, C-H and O-H bonds, respectively. The results indicated that the Fe$_3$O$_4$ was surrounded by the oleate with oxygen sites interact with iron.

3.2. Synthesis Fe$_3$O$_4$@AuNP
ICP-OES data was conducted to confirm the ratio of Fe and Au. Fe: Au mol ratio of 30:1 was observed. TEM image (Figure 4) observed for the two different Au (shell) and Fe$_3$O$_4$ (core) ratios showed a narrow particle size distribution (standard deviation below 10 %), indicated that the monodisperse particles were successfully synthesized. TEM images also shows that the average size of Fe$_3$O$_4$@Au nanostructures was around 5.0 nm.

Figure 1. Formation of Fe-oleate complex from sodium oleate [10].

Figure 2. (a) TEM Image of Fe$_3$O$_4$ nanoparticles and (b) its size distribution curve.
The XRD patterns in figure 5a show the Fe₃O₄NP before and after being coated with gold. The diffraction pattern of Fe₃O₄NP was too weak to be detected due to the heavy atom effect of Au. However, the peaks at 2θ of 31°, 38°, 44° and 64°, 77° and 81° were attributable to Fe-Au, and could be indexed to [111], [200], [311] and [222] lattice planes of gold in a cubic phase, respectively [14].

![Figure 3. (a) XRD pattern and (b) FTIR spectra of Fe₃O₄ nanoparticles.](image)

![Figure 4. (a) TEM images of Fe₃O₄@AuNP and (b) its size distribution curve.](image)

![Figure 5. (a) XRD pattern of Fe₃O₄NP and Fe₃O₄@AuNP, (b) SEM images oleyl amine-capped Fe₃O₄@AuNP and (c) UV-Vis spectra of Fe₃O₄NP and Fe₃O₄@AuNP.](image)
Figure 5 (continued). (a) XRD pattern of Fe₃O₄NP and Fe₃O₄@AuNP, (b) SEM images oleyl amine-capped Fe₃O₄@AuNP and (c) UV-Vis spectra of Fe₃O₄NP and Fe₃O₄@AuNP.

Figure 5b shows SEM images of Fe₃O₄@Au nanostructures. The morphology of oleyl amine-capped Fe₃O₄@Au nanostructures described spherical shapes as also shown by the TEM characterization in figure 4. Characterization using UV-Visible spectra (figure 5c) shows no absorbance peaks observed in visible region for Fe₃O₄NP, but Fe₃O₄@AuNP displays a broadening peak around 450–500 nm. A blue-shift in comparison to AuNP (520 nm) was observed due to the characteristic of Au. These results indicated that Au shell on the surface of Fe₃O₄NP was successfully formed.

4. Conclusion
Fe₃O₄NP was successfully synthesized by thermal decomposition method with Fe-oleate as the precursor. The nanoparticles have a spherical shape with a particle size of 4.9 nm. Fe₃O₄NP has been successfully coated with Au with Fe: Au ratio of 30:1. The Au coating increases the size of nanoparticles to be around 0.1 nm.

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