Method Article

Synthesis, transfer, and characterization of core-shell gold-coated magnetic nanoparticles

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Abstract

Magnetic separation has gained new popularity as a versatile partitioning method with the recent growth in nanotechnology and related biotechnology applications. In this study, iron oxide magnetic nanoparticles were synthesized via solvothermal methods and directly coated with gold to form core-shell gold-coated magnetic nanoparticles (Fe\textsubscript{3}O\textsubscript{4}-AuNPs). High-resolution transmission electron microscopy with Energy dispersive X-ray spectroscopy results suggest that temperature and reaction time play an important role in the formation of small, monodisperse Fe\textsubscript{3}O\textsubscript{4}-AuNPs. We also demonstrate that increased 4- dimethyl(amo)pyridine (DMAP) concentrations and vigorous stirring were required to successfully transfer Fe\textsubscript{3}O\textsubscript{4}-AuNPs into aqueous solution. The structure and morphology of the synthesized and transferred Fe\textsubscript{3}O\textsubscript{4}-AuNPs was further confirmed by UV–vis absorption spectroscopy and solubility experiments.

- Direct coating of Fe\textsubscript{3}O\textsubscript{4} with Au: Slowly heating by (10 °C/ min) until 180–190 °C without exceeding this reaction temperature and increasing the reaction time to 3 h from 1.5 h
- High yield transfer of Fe\textsubscript{3}O\textsubscript{4}-AuNPs was achieved using 4- dimethyl(amo)pyridine (DMAP) as phase transfer catalyst

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Article Info

Method name: Solvothermal synthesis of iron oxide nanoparticles with direct gold coating to form core-shell gold-coated magnetic nanoparticles. Phase transfer of core-shell gold-coated magnetic nanoparticles from organic to aqueous using 4- (dimethyl)amino pyridine (DMAP) as a phase transfer agent

Abbreviations: Fe\textsubscript{3}O\textsubscript{4}-AuNPs, core-shell gold-coated magnetic nanoparticles; HR-TEM, high-resolution transmission electron microscopy; (HR-TEM/EDS), high-resolution transmission electron microscopy with energy-dispersive X-ray spectroscopy; TMAOH, tetramethylammonium hydroxide; DMAP, 4-dimethyl(amo)pyridine.

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https://doi.org/10.1016/j.mex.2019.02.006
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Keywords: Iron oxide, Gold-coated, Core-shell, Core-shell gold-coated magnetic nanoparticles, Magnetic separation, Fe3O4-AuNPs, 4-Dimethyl(amo)pyridine, DMAP, Nanoparticle phase transfer, Aqueous phase transfer, Solvothermal, Thin gold coating, Nanoparticle, Synthesis

Article history: Received 29 August 2017; Accepted 5 February 2019; Available online 8 February 2019

Specifications Table

| Subject area       | Chemistry |
|--------------------|-----------|
| More specific subject area | Core-shell nanoparticle synthesis and phase transfer |
| Method name        | Solvothermal synthesis of iron oxide nanoparticles with direct gold coating to form core-shell gold-coated magnetic nanoparticles, Phase transfer of core-shell gold-coated magnetic nanoparticles from organic to aqueous using 4-(dimethyl)amino pyridine (DMAP) as a phase transfer agent |
| Name and reference of original method | Monodispersed Core-Shell Fe3O4-Au Nanoparticles, Synthesis of core-shell gold coated magnetic nanoparticles and their interaction with thiolated DNA, Spontaneous phase transfer of nanoparticulate metals from organic to aqueous media |
| Resource availability | 10.1021/jp0543429, 10.1039/c0nr00621a, 10.1002/1521-3773 |

Method details

Overview

Nanoparticles provide an increased surface area to volume ratio and unique physicochemical properties that are useful in a wide range of applications [1–3]. Core-shell nanoparticles are a class of nanoparticles consisting of an inner core nanoparticle that is coated with a different material as an outer shell. Various core-shell nanoparticles ranging in size, shape, surface coverage and morphology have been synthesized and reported. However, the most common core-shell nanoparticle shape is the concentric spherical which consists of a complete covering of a spherical nanoparticle with another material. This system is advantageous because the chemical or physical properties of a nanoparticle surface can be altered without losing the properties provided by the core material [4]. As a result of the increased functionality within a single system, core-shell nanoparticles have great potential in a wide range of applications including biomedical [5,6] and pharmaceutical [7] applications, catalysis [8], electronics [9], and optics [10].

While iron oxide nanoparticles (Fe3O4 NPs) have been successfully used as platforms for rapid and versatile partitioning methods, they are limited in their widespread application. Fe3O4 NPs have a large surface area to volume ratio with a low surface charge at neutral pH which typically leads to aggregation. In addition, Fe3O4 NPs have low electrical conductivity and poor optical properties [11–15]. One solution is to coat magnetic nanoparticles with another material, such as gold. The gold coating has the additional benefit of enhancing the surface biocompatibility [16,17], bioaffinity [18], optical properties [19], chemical stability [20] and conductivity [21] of the nanoparticle with that of gold, while maintaining the magnetic properties of iron oxide. Therefore, methods for the efficient preparation of Fe3O4-AuNPs are of interest in order to facilitate their use in a wide range of applications, including bioseparation [16], electrochemical sensors [22], targeted delivery [23] and bioimaging [24]. In particular, these bionanotechnology applications would require the nanoparticle to be dispersed in water.

Synthesis methods play an important role in the successful production of small, mono-disperse core-shell nanoparticles. Furthermore, for each application, the size, coating, and composition must
be tunable, yet reliable. Therefore, many synthesis methods have been developed in an attempt to produce nano-sized core-shell particles. \( \text{Fe}_3\text{O}_4\)-AuNPs have been synthesized using hydroxylamine seeding [18], reverse micelles [25], Y-ray radiation [26], laser ablation [27], sonochemical [28] and wet chemical reactions [29], layer-by-layer electrostatic deposition [30], and photochemical reduction [31]. However, many of these synthesis methods either require costly, specialized equipment or are known to produce larger nanoparticles (>60 nm). Notably, \( \text{Fe}_3\text{O}_4\)-AuNPs have been formed through a sequential synthesis process where iron oxide nanoparticles were synthesized and, subsequently, directly coated with gold through nucleation of gold on the surface. This simple synthetic method has been reported to easily produce small core-shell gold-coated magnetic nanoparticles (Illustration 1) [32]. However, this method served as the foundation for this work as certain reaction conditions and modifications described herein were found to be essential to achieve the monodispersity and quality required for our application [33].

Iron oxide (\( \text{Fe}_3\text{O}_4 \)) nanoparticles are commonly synthesized through solvothermal methods. Reducing \( \text{Fe} (\text{acac})_3 \) with 1,2-hexadecanediol in the presence of oleic acid and oleylamine successfully produces \( \text{Fe}_3\text{O}_4 \) seeds. This synthesis method is advantageous as it a simple procedure capable of producing small, monodisperse and stable iron oxide nanoparticles [34]. In addition, using oleylamine and oleic acid as stabilizing agents allows the previously synthesized iron oxide nanoparticles to be easily and directly coated with gold through a thermally active process [35].

As for most synthetic procedures, many factors must be controlled for the successful synthesis of core-shell nanoparticles. The rate at which the reaction temperature is increased, the reaction time and the precise control of the reaction temperature not only improved the synthesis of the iron oxide nanoparticle core, but also improved the stability, uniform coating, and composition of the final core-shell nanoparticle product. Small monodisperse gold-coated magnetic nanoparticles were required for our aqueous separation applications. Following procedures described by Robinson et al., it was found that we could not achieve a monodisperse iron oxide sample [32]. In addition, we found that this procedure was unable to successfully produce uniform coverage of the particles, resulting in mixtures of uncoated and coated particles. Thus, by following Wang et al. and further optimizing the reaction conditions, we were able to synthesize small, monodisperse \( \text{Fe}_3\text{O}_4\)-AuNPs with a consistent, thin gold coating [33]. In this work, core-shell gold-coated magnetic nanoparticles were synthesized with various reaction parameters to determine the importance of reaction time and temperature for this synthetic process. To characterize the final \( \text{Fe}_3\text{O}_4\)-AuNPs product, high-resolution transmission electron microscopy (HRTEM) with Energy dispersive spectroscopy (EDS), and UV–vis absorption

Illustration 1. Illustration of the coating process: (A) \( \text{Au} (\text{CH}_3\text{COO})_3 \) is reduced by 1,2-hexadecanediol in the presence of oleic acid and oleylamine at a temperature of 180–190°C. (B) thermally active partial desorption of the capping layer occurs. (C) the reduction of \( \text{Au} (\text{CH}_3\text{COO})_3 \) results in deposition of Au on the surface of the exposed surface of the magnetic nanoparticles, and (D) the re-encapsulation of the Au shell with oleylamine and oleic acid.

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spectroscopy were employed. Finally, we needed to transfer the nanoparticles into water, requiring a phase transfer step. Phase transfer of the synthesized Fe₃O₄-AuNPs with tetramethylammonium hydroxide (TMAOH), a capping agent used by Robinson et al. and Wang et al., led to aggregation and reduced yield [32,33].

Therefore, we attempted to transfer the synthesized core-shell nanoparticles from hexanes to water using 4-dimethyl(aminopyridine (DMAP) as a phase transfer catalyst. Previously, Gittins and Caruso used DMAP to transfer tetraoctylammonium bromide (TOAB) capped gold nanoparticles from toluene to water through a proposed ligand exchange mechanism [36]. In this work, DMAP was used to transfer Fe₃O₄-AuNPs from hexanes to water. It is proposed that DMAP displaces oleylamine and oleic acid to transfer the nanoparticles across the solvent layer, providing solubility in water for bionanotechnology applications. The transferred DMAP-capped Fe₃O₄-AuNPs were characterized with HRTEM/EDS and through solubility experiments (Illustration 2).

**Experimental**

**Materials**

Iron (III) acetylacetonate (Fe(acac)₃), 99%, oleylamine (70%), oleic acid (99%), phenyl ether (99%), anhydrous sodium citrate (99%), 4-dimethyl(aminopyridine (99%) and other solvents (hexanes, toluene and absolute ethanol) were purchased from Sigma-Aldrich (Oakville, ON, Canada). 1,2-Hexadecanediol was purchased from VWR (Mississauga, ON, Canada). Gold (III) acetate (Au(ac)₃) was purchased from Alpha Aesar (Haverhill, Massachusetts, USA). 300 mesh × 83 µm pitch copper TEM grids were purchased from Ted Pella (Redding, CA, USA). All glassware used for the Fe₃O₄-AuNP synthesis was washed with aqua regia (3:1 mixture concentrated HCl/HNO₃) and rinsed thoroughly with deionized water. The glassware was then rinsed with acetone before being dried in an overnight or until used for synthesis.

Unless otherwise specified, all synthetic procedures were performed using standard Schlenk techniques under an argon (5.0, 99.999%) atmosphere.

**Synthesis of Fe₃O₄ nanoparticles**

0.71 g of Fe(acac)₃ was dissolved in 20 mL of phenyl ether with 2 mL of oleic acid and 2 mL of oleylamine (end volume of 24 mL) with vigorous stirring. Once dissolved, 2.58 g of 1,2-hexadecanediol was added. A water cooled condensing column was fitted to the flask. The solution was slowly heated to 210 °C as to ensure the temperature did not exceed 210 °C, and kept at reflux for 2 h at this temperature. After 2 h, the bright red suspension appeared dark brown in colour, and was allowed to cool to room temperature under argon overnight.

**Direct coating of Fe₃O₄ nanoparticles to form Fe₃O₄-AuNPs**

10 mL of previously prepared Fe₃O₄ in phenyl ether (above reaction product) was added to 30 mL of phenyl ether with vigorous stirring. To this solution, 0.83 g of Au(ac)₃, 3.1 g of 1,2-hexadecanediol, 0.5 mL of oleic acid and 3 mL of oleylamine were added quickly. This suspension was heated slowly (10 °C/min) until 180–190 °C and maintained at this temperature under reflux for 3 h. The solution was allowed to cool to room temperature under argon overnight. 5 mL of the solution was transferred to a 125 mL Erlenmeyer flask and 15 mL of ethanol was added to it. The solution was agitated gently resulting in a visible aggregation of the nanoparticles and a colour change from dark purple to dark blue/black. The flask was then placed on a magnet for 5–10 min to magnetically separate the particles from the supernatant solution. The supernatant solution was decanted as waste and the precipitated nanoparticles were washed three times with 15 mL of absolute ethanol. The nanoparticles were then redispersed in a solution of 10 mL of hexanes, 0.25 mL of oleic acid and 0.25 mL of oleylamine. This procedure was repeated multiple times to obtain purified Fe₃O₄-AuNPs in hexanes. Solutions appeared dark red-purple in colour, and were stored in glass covered by foil at room temperature.
Illustration 2. Illustration of the proposed ligand exchange phase transfer of AuNPs from hexanes (capped with oleylamine and oleic acid) into aqueous solution using DMAP.
Transfer of Fe$_3$O$_4$-AuNPs with 4-dimethyl(amin0)pyridine

The following methods were not performed under Argon. 0.5 M DMAP solution was prepared by adding 0.68 g of DMAP into 1 mL of Milli-Q 18.2Ω water. 1 mL of Fe$_3$O$_4$-AuNPs was added to a 1 mL aliquot of 0.5 M aqueous DMAP solution in a glass vial. Two phases were observed, a dark purple hexane layer (top) and a clear aqueous layer (bottom). The phases were thoroughly mixed with vigorous stirring (via a magnetic stir rod and plate) for 1 h. At this time, the top hexane layer appeared light purple to clear and the bottom aqueous layer appeared dark purple suggesting that the nanoparticles were successfully transferred into aqueous solution. The bottom layer was transferred with a Pasteur pipette to a new glass vial and purified by washing the nanoparticles with a 0.5 M DMAP solution via magnetic separation.

Characterization of synthesized Fe$_3$O$_4$-AuNPs

The UV–vis absorption characterization of the Fe$_3$O$_4$-AuNPs was performed using a Cary 300 Bio UV–vis spectrophotometer (Varian, Santa Clara CA). Fe$_3$O$_4$-AuNPs were prepared as described and analyzed at each step during synthesis. Transmission electron micrographs were taken with a FEI Technai G2 F20 TEM at the Carleton University Nano-imaging Facility, with a field emission source at a voltage of 200 kV using Gatan Microscopy Suite 2 V. All images were taken on dry 300 mesh x 83 μm pitch carbon coated copper TEM grids at room temperature. Grids were prepared by placing 4 μL of Fe$_3$O$_4$-AuNP (in various solvents) on a TEM grid. The TEM grids were allowed to dry for 4–24 h depending on the solvent. Images were taken at 1–2 μm, 100–200 nm and 5–10 nm for each grid. EDS of each Fe$_3$O$_4$-AuNPs sample was taken at a 20° take off angle with an Oxford X-ma x 80 mm EDS detector using Aztec software. Transmission electron micrograph images were analyzed for nanoparticle size distribution using ImageJ software. The scale of the image was reset from metres to pixels.

Bandpass filter and threshold were used to improve the resolution of the image for analysis. The area of each nanoparticle was determined with the nanoparticle analysis function. A histogram was assembled for the frequency of each nanoparticle diameter, assuming perfect sphericity. The average nanoparticle diameter with standard deviation for a number of nanoparticles was calculated.

Results and discussion

Iron oxide nanoparticles synthesis

Robinson et al. and, originally, Sun and Zeng report the synthesis of size-controlled magnetite nanoparticles through a solvothermal method where Fe(acac)$_3$ is reduced by 1,2-hexadecanediol in the presence of two capping agents (oleylamine and oleic acid) [31,33]. Fe(acac)$_3$ was mixed with 1,2-hexadecanediol, oleylamine, and oleic acid in phenyl ether under nitrogen and heated to reflux [31]. However, when the solution was heated to the boiling point of phenyl ether (258 °C) for 2 h, the size distribution of the synthesized magnetite nanoparticles was quite extensive (Fig. S1). Alternatively, when the temperature of the solution was heated to 210 °C, as was suggested by Wang et al, the size distribution of the synthesized magnetite nanoparticles was narrowed producing more mono-disperse Fe$_3$O$_4$ NPs [32]. HRTEM characterization displays the size-controlled synthesis of small, mono-disperse Fe$_3$O$_4$ NPs (Fig. 1) with an average diameter of 5.96 nm (σ = 0.23 nm, n = 7) (Fig. S9). Furthermore, HRTEM/EDS confirms that the nanoparticles are composed of iron oxide (Fig. 2).

Gold coating to form Fe$_3$O$_4$-AuNPs

Following Robinson et al., the synthesized Fe$_3$O$_4$ were cooled to room temperature and used without any further separation [32]. Fe$_3$O$_4$ NPs were coated with gold by reducing gold acetate with 1,2-hexadecanediol in the presence of the previous formed Fe$_3$O$_4$ NPs, oleylamine and oleic acid in phenyl ether. Under inert atmosphere, the solution was heated to 180–190 °C and maintained at this temperature with vigorous stirring for 1.5 h. Unexpectedly, the HRTEM images suggested that the
Complete coating of the Fe₃O₄ NPs with gold was unsuccessful, and instead the synthesis produced two distinct sizes of nanoparticles (Fig. S3). HRTEM with EDS confirmed that the smaller particles were uncoated iron oxide, and the larger particles were AuNPs or Fe₃O₄ NPs coated with gold (Fig. S4).

It is suggested that temperature plays an important role in the partial desorption of the Fe₃O₄ NP capping agents and is required for the reduced gold acetate to directly coat the exposed Fe₃O₄ NPs. The partial desorption of the Fe₃O₄ NPs capping agents occurs at a specific temperature as it is a thermally active process. Therefore, if the temperature is increased suddenly, AuNPs may begin to form separately since the Fe₃O₄ NP surface is unavailable as a nucleation site. Wang et al. report a precise, incremental increase in temperature by 10 °C/min until a temperature of 180–190 °C was achieved [33]. Again, this temperature was maintained for 1.5 h. In addition to incorporating this incremental increase in reaction temperature, the solution was maintained at this temperature for a longer period of time (3 h). These changes were found to greatly improve the final Fe₃O₄-AuNP product.

The synthesized Fe₃O₄-AuNPs were characterized by HRTEM/EDS and UV–vis absorption spectroscopy. Fig. 3 displays the small, mono-disperse Fe₃O₄-AuNPs and HRTEM/EDS confirms the presence of both iron oxide and gold (Fig. 4). The {111} lattice spacing on the surface of the synthesized core-shell nanoparticles was found to be approximately 0.243 Å which is characteristic of gold (Fig. S8).
Fig. 2. HRTEM image with corresponding EDS spectrum of synthesized Fe$_3$O$_4$ NPs in diphenyl ether. A strong EDS peak is observed for carbon due to carbon-coated TEM grid. Peaks for both Fe and O depict the presence of iron oxide nanoparticles.
Fig. 3. HRTEM images of synthesized Fe$_3$O$_4$-AuNPs with 500, 100, 10 and 5 nm scale bars.
While no uncoated Fe₃O₄ NPs were observed on the TEM grids, it was important to ensure that the particles imaged were of a core-shell structure with the expected composition, not just AuNPs without a magnetic core. First, it was noted that the average size of the imaged nanoparticles increased from 5.96 nm ($\sigma = 0.23$ nm, $n = 7$) to 6.53 nm ($\sigma = 1.18$ nm, $n = 71$), which is attributed to the addition of a gold shell (Figs. S5 and S6). Furthermore, the samples imaged were separated by magnetic separation prior to deposition onto the TEM grids, which should preclude the deposition of any AuNPs lacking a magnetic core. This was further confirmed by imaging a mixture of separately synthesized AuNPs and Fe₃O₄ nanoparticles before and after magnetic separation and comparing these TEM/EDS results with the TEM/EDS results of our synthesized Fe₃O₄-AuNP product (Figs. S11 and S12).

Therefore, it is concluded that using stable, mono-disperse Fe₃O₄ NPs, increasing the reaction temperature at precisely 10 °C/minute and heating the solution for 3 h instead of 1.5 h greatly influenced the success of the Fe₃O₄-AuNP synthesis.

**DMAP transferred Fe₃O₄-AuNPs**

Aqueous nanoparticle dispersibility is essential for many applications, in particular for biological purposes. Since the aforementioned synthesis is conducted in organic solvent (phenyl ether), the capping agents (oleylamine and oleic acid) allow the nanoparticles to be dispersed in non-polar solvents such as hexanes. Therefore, ligand exchange must be accomplished to achieve dispersibility in water.

Tetramethylammonium hydroxide (TMAOH) has been reported to replace capping agents on the surface of synthesized Fe₃O₄-AuNPs. In doing so, the capping agents present during synthesis can be replaced through a ligand exchange with a water-soluble capping agent such as citrate. Robinson et al. and Tintore et al. reported that the original oleylamine/oleic acid capping agents could be replaced with citrate when the synthesized Fe₃O₄-AuNPs were first washed with 1 M TMAOH [32,37].

When the phase transfer was attempted, although it was successful, the yield was insufficient for our future separation-based applications (Fig. S10). Visible by HRTEM, the transferred citrate capped Fe₃O₄-AuNPs were so dilute as to be colorless solutions. This may not be concerning for applications such as bio-imaging, however this is problematic for applications that require a visible indication that the Fe₃O₄-AuNPs are being separated from solution via magnetic separation. Therefore, reducing aggregation and loss of product during transfer was of interest. Previously, Gittins and Caruso reported transfer of AuNPs from organic solvent to aqueous solution using 4-dimethyl(amo)pyridine (DMAP) as a phase transfer catalyst [36]. It was reported that tetraoctylammonium bromide (TOAB) was replaced by DMAP.
on the AuNP surface resulting in a spontaneous transfer of the AuNPs from toluene to water within 1 h. Adsorption of the endocyclic nitrogen of DMAP, is proposed to displace of the primary amine of oleylamine on the AuNP surface through a ligand exchange. Compared to the primary amine of oleylamine, DMAP creates a stronger bond with the gold atoms on the nanoparticle surface. This is attributed to the charge localization of the DMAP conjugate acid, which raises the energy of the lone pair on the nitrogen atom [37]. The position of the ligand’s HOMO and LUMO orbitals in relation to the Fermi level of Au determines the strength of the Au–ligand interaction. This is further explained by the Hard-Soft Acid-Base theory [38]. When metals (including Au) are in a 0 oxidation state, they are considered a soft acid [39,40]. HSAB classifies DMAP as a borderline to soft base, while the primary amine of oleylamine is a relatively hard base. Therefore, a soft base, like DMAP, interacts more strongly with the gold nanoparticle surface in comparison and will likely replace oleylamine via phase transfer. In our study, the Fe3O4-AuNPs were capped with oleylamine/oleic acid and were dispersed in hexanes. These differences were noted and accounted for by increasing the concentration of DMAP (0.1 M–0.5 M) and vigorously stirring the solution during transfer. The synthesized Fe3O4-AuNPs were successfully transferred into water through a proposed ligand exchange mechanism. It is suggested that, according to Hard-Soft Acid-Base (HSAB) theory, the endocyclic nitrogen of DMAP interacts more strongly with the gold nanoparticle surface in comparison to oleylamine/oleic acid [36,40–44]. Fig. 5 displays the location of the Fe3O4-AuNPs over time during transfer. Before transfer, the Fe3O4-AuNPs capped with oleylamine/oleic acid are soluble in hexanes (top layer). Adding a 0.5 M solution of DMAP in water results in the Fe3O4-AuNPs spontaneously transferring across the phase boundary into the water layer. After 1 h with vigorous stirring, it was found that most of the Fe3O4-AuNPs were transferred and soluble in water. The transferred DMAP-capped Fe3O4-AuNPs were characterized by HRTEM/EDS and UV–vis absorption spectroscopy. Although there still remained a notable decrease in yield, transfer of the Fe3O4-AuNPs with DMAP was found to be successful. Fig. 6 displays HRTEM images of mono-disperse Fe3O4-AuNPs. HRTEM/EDS confirms the expected core–shell gold-coated magnetic nanoparticle morphology (Fig. 7). The size distribution is estimated to be consistent with the oleylamine/oleic acid capped Fe3O4-AuNPs in hexanes, with the DMAP capped Fe3O4-AuNPs having an approximate average diameter of 6.45 nm ($\sigma = 1.07\text{ nm}$, $n = 73$) (Fig. 7). Furthermore, although the concentration decreases, UV–vis absorption spectroscopy displays an absorption peak at approximately 535 nm corresponding to mono-disperse Fe3O4-AuNPs (Fig. 9).

**Dispersion of Fe3O4-AuNPs with/without DMAP ligand exchange phase transfer**

To confirm that the original capping agents (oleylamine and oleic acid) of the synthesized Fe3O4-AuNPs were successfully replaced by DMAP, dispersibility of the original and ligand-exchanged Fe3O4-AuNPs was tested. Fig. 8A, displays oleylamine/oleic acid capped Fe3O4-AuNPs in water without replacing the capping agents with DMAP. The Fe3O4-AuNPs are not soluble in water when capped with oleylamine and oleic acid. This is confirmed by HRTEM characterization which displays extensive, irreversible solvent induced aggregation (Fig. 8). Similarly, the DMAP-capped Fe3O4-AuNPs were added to a solution of hexanes. Fig. 8B, displays the lack of colour in the top layer (hexanes) confirming the absence of the nanoparticles in that phase and suggesting that the ligands on the Fe3O4-AuNPs were replaced with water soluble DMAP.

**Magnetic separation DMAP coated Fe3O4-AuNPs**

When placed on the magnet, the DMAP transferred sample has clearer separation than the nanoparticles transferred with DMAP precipitation (Fig. 9). The precipitated Fe3O4-AuNPs could be precipitated and washed with magnetic separation, however this would only result in a decreased concentration of nanoparticles in solution. Therefore, ligand exchange of Fe3O4-AuNPs with DMAP is recommended for transfer and magnetic separation (Fig. 9B).

**UV–vis absorption spectroscopy**

The unique physical and optical properties of AuNPs, specifically in comparison to magnetite nanoparticles, permits the use of UV–vis absorption spectroscopy to further confirm the presence of a
Fig. 5. Images of synthesized Fe₃O₄-AuNPs before (left), during (middle) and after (right) DMAP ligand exchange phase transfer.
Fig. 6. HRTEM image of transferred DMAP-capped Fe₃O₄-AuNPs in water with 100 and 20 nm scale bar.
Fig. 7. HRTEM image with corresponding EDS spectrum of transferred DMAP-capped Fe₃O₄-AuNPs in aqueous solution. Peaks for both Fe and Au depict the presence of Fe₃O₄-AuNPs.
Fig. 8. Images of oleylamine/oleic acid-capped Fe$_3$O$_4$-AuNPs in water (A), DMAP-capped Fe$_3$O$_4$-AuNPs in hexanes (B) and HRTEM image of image A with a 2 µm scale bar.
Fig. 9. Images of DMAP capped Fe₃O₄-AuNPs after precipitation with DMAP in hexanes without (A1) and with (A2) magnetic separation. and DMAP capped Fe₃O₄-AuNPs after ligand exchange transfer with DMAP in aqueous solution without magnetic separation (B1) and with magnetic separation (B2).
Fig. 10. UV-vis spectra of Fe3O4 NPs (100 times dilution factor of stock), Fe3O4-AuNPs (100 times dilution factor of stock) and transferred Fe3O4-AuNPs (20 times dilution factor of stock).
gold shell. UV–vis absorption spectrum of the core–shell nanoparticles can be insightful. Compared to AuNPs of the same size, a core Fe₃O₄ results in a slight red shift in the absorption, which can support other characterization methods. A thinner coating of Au on the Fe3O4 nanoparticles results in a spectrum that experiences a larger red-shift from that of AuNPs (525 nm). This shift results in absorption of approximately 530–540 nm for core–shell Fe₃O₄-AuNPs depending on the thickness of the Au shell [3]. In addition, the concentration of the Fe₃O₄-AuNP sample before and after phase transfer can be estimated to evaluate its efficiency. Fig. 10, displays the absorption spectra for Fe₃O₄ NPs, Fe₃O₄-AuNPs capped with oleylamine/oleic acid in hexanes and Fe₃O₄-AuNPs capped with DMAP in water. The localized surface plasmon resonance (LSPR) of AuNPs results in an absorption peak between approximately 520–550 nm depending on the diameter of the AuNP. The absorption peak at approximately 535 nm corresponds to the Fe₃O₄-AuNPs sample. In comparison to AuNPs, the absorption peak of the Fe₃O₄-AuNPs of the same size is red-shifted due to the core–shell structure [35,45]. It is noted that the concentration of DMAP capped Fe₃O₄-AuNPs is much lower than the synthesized Fe₃O₄-AuNPs in hexanes. However, the DMAP capped Fe₃O₄-AuNPs were less aggregated during transfer and, therefore, more concentrated in water than the TMAOH transferred citrate capped Fe₃O₄-AuNPs sample (Fig. S10).

Conclusions

This study highlights the importance of reaction temperature for the synthesis of small, mono– disperse magnetite nanoparticles and successful, direct coating of these nanoparticles with gold to form Fe₃O₄-AuNPs. Our work displays how a slight deviation in reaction temperature during the synthesis of Fe₃O₄ NPs results in a large size distribution and lack of core-shell formation in the subsequently prepared Fe₃O₄-AuNPs. Notably, we found that failing to precisely increase the reaction temperature led to the formation of separate AuNPs, or an inconsistent gold shell, in the presence of Fe₃O₄ NPs. In addition, a DMAP assisted ligand exchange was applied as a novel phase transfer method for the synthesized Fe₃O₄-AuNPs. We report that oleylamine and oleic acid can be replaced by DMAP on the Fe₃O₄-AuNP surface to achieve solubility in water and, more specifically, increase the concentration of Fe₃O₄-AuNPs transferred. Size distribution and consistent shell formation of Fe₃O₄-AuNPs has a number of implications in a wide range of applications. Therefore, it is of importance to understand the effects of slight temperature deviations on the structure, size and consistency of the synthesized Fe₃O₄-AuNPs product. In addition, some bionanotechnology applications require a high concentration of water soluble Fe₃O₄-AuNPs for separation-based techniques, which was accomplished using DMAP as a phase transfer catalyst.

Funding source

Natural Sciences and Engineering Research Council (NSERC) Discovery Grant 224070.

Acknowledgements

The authors thank Robinson et al., Wang et al. and Gittins et al. for the synthesis methods that were followed and modified in this work [31,32,35]. The authors would also like to thank Chris Mattice for assistance with laboratory glassware and assembly, Dr. Anatoli Ianoul and his research group for their assistance with nanoparticle synthesis and characterization techniques, Dr. Sean Barry and Matthew B.E. Griffiths for equipment and guidance in inert atmosphere synthesis techniques, and Jianqun Wang for his assistance with HR-TEM/EDS nanoparticle imaging and analysis.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mex.2019.02.006.
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