Colloidal Preparation of γ-Fe_2O_3@Au [core@shell] Nanoparticles

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ABSTRACT

γ-Fe_2O_3@Au core-shell nanoparticles were prepared through a combined route, in which high temperature organic solution synthesis and colloidal microemulsion techniques were successively applied. High magnification of TEM reveals the core-shell structure. The presence of Au on the surface of as-prepared particles is also confirmed by UV-Vis absorption. The magnetic core-shell nanoparticles offer a promising application in bio- and medical systems.

INTRODUCTION

To date development of (magnetic-core)@(gold-shell) structured nanocomposites has attracted more attention due to the requirement of advanced manipulation in bio-systems such as MRI agents. Previously, we have successfully developed an approach for preparing Fe@Au nanoparticles through a reverse microemulsion route [1], and demonstrated that we were able to fabricate gold-coated iron (Fe@Au) superparamagnetic nanoparticles with ~10 nm in size. Notwithstanding this achievement, we currently realize that it would be more useful if the magnetic properties of such core-shell nanoparticles could be further enhanced and stabilized. One of the possibilities of improving this is to increase the crystallinity of the "core" material. Another issue is to avoid a possible oxidation on those metal-containing nanoparticles if they are exposed to the atmosphere for a long term, say several days. In order to improve the magnetic quality and to solve the existing problems, we therefore alternatively proposed a new design using γ-Fe_2O_3 nanocrystals as the "core" material instead of Fe nanoparticles, and conducted the preparation of (γ-Fe_2O_3-core)@(Au-shell) nanoparticles through a colloidal microemulsion technique. The motivation of this work is to establish a new approach for developing desirable magnetic (core-shell) nanoparticles, in which the "core" possesses enhanced and stabilized magnetic behaviors, whereas the "shell" must be "swallowable" in aqueous bio-system through special coordination bond such as Au----S-protein. This paper only focuses on the preparation of novel core-shell nanoparticles and structural analysis. The section of magnetic characterization and potential bio-application will be discussed in an additional report.

EXPERIMENTAL

The experimental section is described in two parts: fabrication of γ-Fe_2O_3 core nanocrystals through a high temperature organic solution approach and processing of Au-shell nanocomposites via a microemulsion route.

Reagents

All the solvents and starting materials including toluene (99.8%), hexadecane (99%), ethanol (99.9%), dioctylether (99%), iron pentacarbonyl (99.999%), lauric acid (99.5%), trimethylamine N-oxide (98%), hydrogen tetrachloroaurate (III) trihydrate (ACS reagent), sodium borohydride (99%), tetraoctylammonium bromide (98%), Brij 97 (surfactant) and 1-dodecanethiol (98+%) were purchased from Aldrich and used without further purification.

Fabrication of γ-Fe_2O_3 core nanocrystals

Synthesis of γ-Fe_2O_3 core nanocrystals was conducted through a high temperature processing approach in organic solution [2] using a setup that is similar to our previous one [3]. A typical experiment is described as the follows. Under a flowing argon, 0.57g of dehydrated $(CH_3)_3NO$ (~7.60 mmol) and 0.95g of lauric acid (~4.65 mmol) were added into a degassed dioctylether (~18ml) and the mixture was heated to at 120 ^{o}C in a three-neck flask. 0.2 ml of $Fe(CO)_5$ (~1.50 mmol) was subsequently injected into this hot solution with a syringe while stirring under argon atmosphere. The resulting mixture was maintained at 120 ^{o}C for 1 hour with vigorous stirring and then refluxed under argon for an additional 2 hours. When the suspension was cooled to 40 ^{o}C, the resulting black precipitate was collected by adding excessive ethanol and centrifugation. The precipitate was re-dispersed into toluene, and monodisperse iron oxide nanocrystals of ~14 nm in diameter were collected by employing a size-selection technique [4] in which a solvent pair containing toluene-ethanol was used.

Formation of Au-shelled nanoparticles

The core-shell structured γ-Fe_2O_3@Au nanoparticles were prepared from a normal microemulsion system containing Brij 97 (surfactant), non-polar organic phase and aqueous phase [5]. In a typical experiment, Brij 97 (30 g) was dissolved in 140 ml of deionized water. This solution was equally split into two portions in two conical flasks, designated as A and B. 10 ml of additional deionized water and 0.4g of hexadecane/toluene suspension containing 0.05 mmol of γ-Fe_2O_3 nanocrystals and 0.03 mmol of Au^{3+} pre-prepared using Brust's method [6] were added into the first portion (Part A). The system was then heated with stirring to 65 ^{o}C for 15 min to form a microemulsion. Simultaneously, 0.35 g of hexadecane and 10 ml of aqueous solution consisting of deionized water and 0.05g of $NaBH_4$ was added into the second portion of surfactant solution (Part B) with agitation, respectively. The conical flask (Part B) was then moved into an ultrasonic water bath at 65 ^{o}C to eliminate the gas bubbles possibly generated from a decomposition of $NaBH_4$.

The microemulsion composition consisting of Brij 97, water, γ-Fe_2O_3 nanocrystals and Au^{3+} in hexadecane (Part A) was mixed with the other microemulsion system (Part B) containing Brij 97, $NaBH_4$ in water and hexadecane under ultrasonication and mechanical stirring, allowing the reduction to take place. One drop of 1-dodecanethiol was also introduced into the system and the mixture was allowed to stir for 15 min. Equal amount of ethanol was subsequently added into this resulting black solution. Solid particles were flocculated by a centrifugation. The sample was "washed" by using ethanol and centrifugation repeatedly at least for 4 times to remove the residue of surfactant and reagent before its characterization. The core-shell particles are soluble in water.

RESULTS AND DISSCUSION

One of the key issues for ensuring the success of core-shell nanoparticle preparation is the high crystallinity of the core materials, which is also important in our case to enhance the magnetic properties when the core-shell particles are applied to the bio-system in next stage. Therefore, we employed a high temperature organic solution approach to generate γ-Fe_2O_3, the core material.

Figure 1(a) shows an XRD pattern of γ-Fe_2O_3, the core nanocrystals prepared from the high temperature organic solution process. Figure 1(b) depicts a TEM diffraction pattern on these nanocrystals, being in agreement with the XRD pattern. As indexed in Figure 1(a), all the detectable peaks are attributed to the phase of γ-Fe_2O_3 (single phase). Average crystalline size was estimated as ~12 nm by applying the Scherrer Equation [7] to the line broadening of the (311), (400) and (440) peaks. The procedure of preparing γ-Fe_2O_3 nanoparticles in this paper was directly adopted form T. Hyeon's work [2]. T. Hyeon and co-workers have carefully characterized their oxide nanoparticles by investigating XPS/Raman spectra and by comparing their XRD d-spacing values with those from the standard γ-Fe_2O_3 and Fe_3O_4 JCPDS cards (supporting information of [2]), confirming the existence of γ-Fe_2O_3 rather than Fe_3O_4. In our work, the XRD d-spacing values are also close to those of γ-Fe_2O_3, instead of Fe_3O_4. We therefore assume that the oxide we produced possesses a phase of γ-Fe_2O_3, in place of Fe_3O_4, although we have not further investigated these nanoparticles using other techniques such as mössbauer spectroscopy. The TEM image of these bare core particles is also showed in Figure 2. We have further analyzed the particle size distribution of these core materials by using the light scattering technique. As illustrated in Figure 3, the size distribution was calculated as $\delta < 8\%$. The mean hydrodynamic particle size was therefore calculated as ~34 nm. As expected, the particle size measured by the light scattering technique is larger that either observed by TEM or estimated from XRD data due to the different instrumental nature of working function.

Microemulsion is a powerful approach to synthesize nanometer-sized particles, not only because the method gives narrow size distribution, but also because the method can geometrically control the particle growth, offering a new chance of nanocoating. A microemulsion is a thermodynamically stable, isotropic dispersion of oil droplets (5-50 nm indiameter) in a water continuous phase. These nanodroplets are stabilized by surfactant molecules adsorbed at the oil-water interfaces, acting as "nano-reactors" ---- if an inorganic reaction takes place within them. Our design is to introduce the "core" nanoparticles into these "nano-reactors" and to subsequently perform the second reaction (shell-formation) within them as well. Since these "nano-reactors" are surrounded by a surfactant layer (droplet wall), the growth of as-formed particles would be efficiently restricted and prevented from their further connection, possibly forming the "shell". Using this approach we can manipulate our γ-Fe_2O_3 nanocrystals which are hydrophobic (being capped with organic species) into the oil droplets in microemulsions, and obtain gold shell if Au^{3+} could be presented into the same droplets as well. This idea was introduced, for the first time, into our current investigation.

Figure 4 exhibits the TEM images of γ-Fe_2O_3@Au nanoparticles. As expected, the Au layer can be observed on the surface of γ-Fe_2O_3 nanocrystals (see the insets). In Figure 4, the contrast between the core (the central dark part) and shell (the relatively light part in the edge) of the nanoparticles is easily distinguishable in the inserted HTEM images. Although the electron density of Au is greater than γ-Fe_2O_3, it is not surprising to have observed that the central part is darker than the edge if one keeps the 3D nature of this spherical particle in mind. This structural observation is also in agreement with that of a Fe@Au nanoparticle system reported previously [8]. It is also worth mentioning that there may be more than one core in a particle unit according to the TEM observation. Since the shell component grew within microemulsion droplets, it is possible to contain more than one γ-Fe_2O_3 core nanocrystal in a droplet. EDS (energy dispersive x-ray spectroscopy) analysis on this sample (Figure 5) reveals that the Au component as the coating shell occupies ~30.2 at.% based on 100% of Au and Fe, whereas the rest contribution is considered being from the core material. The presence of gold on the surface of core-shell particles has also been confirmed by an UV–Vis photospectrum as shown in Figure 6. The UV-Vis absorption peak can be determined at ~572 nm, shifted from the absorption wavelength of 525nm of 10 nm Au nanoparticles. According to previous reports, such shift of absorption wavelength can be attributed to several factors that affect the gold plasmon resonance, such as the variation in size, change of shape and even agglomeration degree of gold particles [9]. Actually, we have also prepared additional core-shell samples with lower Au-composition. When the content of Au coating layer was reduced to ~18 at% [10], for instance, the corresponding plasmon resonance peak was observed at around 552 nm.

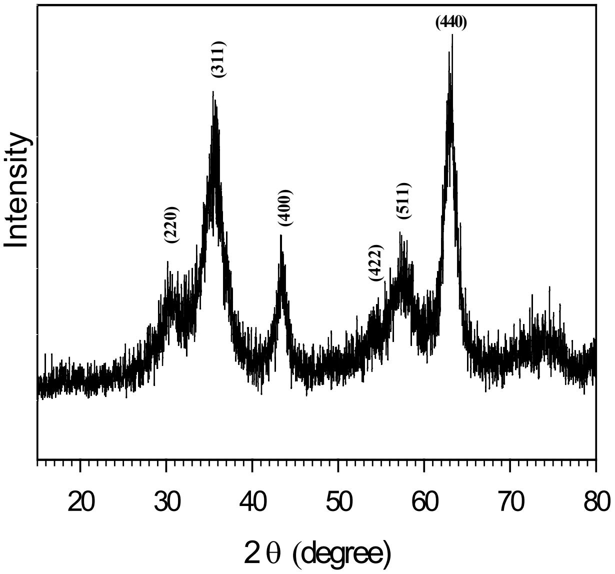


Figure 1(a): XRD pattern of γ-Fe_2O_3 nano-crystals (core material).

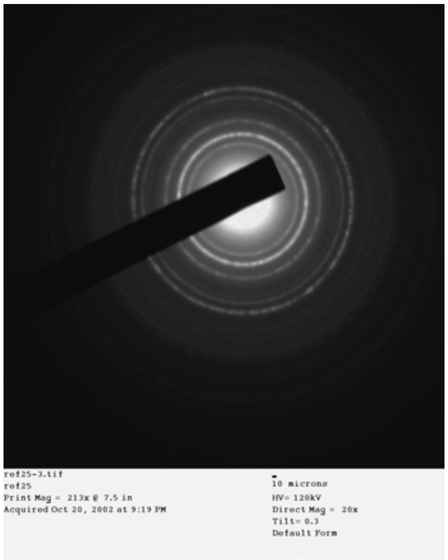
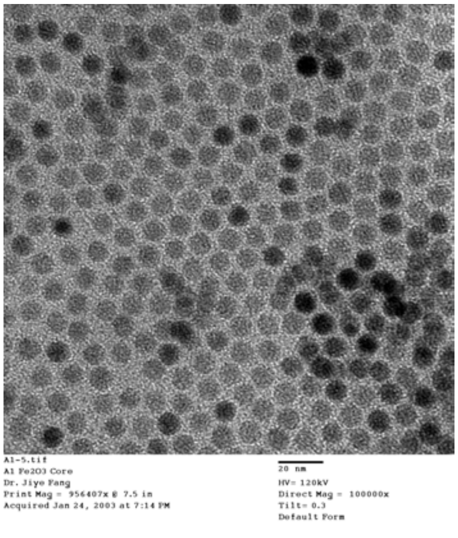


Figure 1 (b): TEM diffraction pattern of γ-Fe_2O_3 nanocrystals (core material).



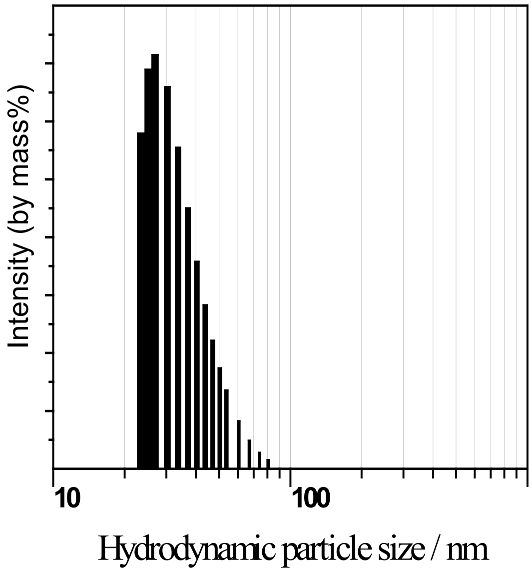


Figure 2: TEM image of γ-Fe_2O_3 nanocrystals (the bar represents 20 nm).

Figure 3. Size distribution of γ-Fe_2O_3 nano-crystals from light scattering measurement.

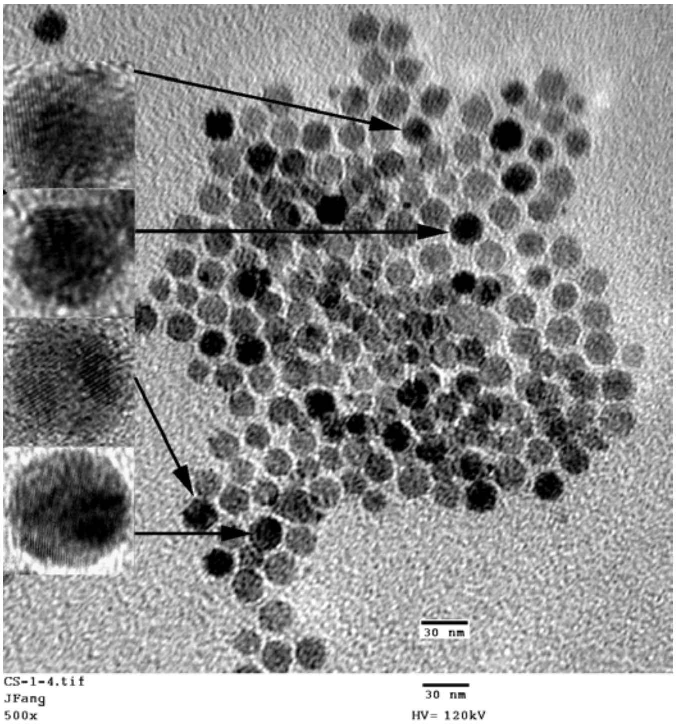


Figure 4. TEM image of γ-Fe_2O_3@Au (core-shell) nanoparticles (the bar indicates 30 nm). The insets show a high magnification of core-shell structures.

For the time being, we are not claiming that all the γ-Fe_2O_3 nanocrystals have been coated with gold. Based on the particle size and shell thickness observed from TEM and the percentage of gold component determined from EDS, however, we estimate that, at least, half of the particles should have been coated with considerable thickness of gold shell. It is possible to further refine the core-shell particles. For example, the γ-Fe_2O_3 containing nanoparticles can be separated from those particles that contained just gold using magnetic separation [8]. Of course, the thickness of the shell can also be controlled by optimizing the concentration of Au^{3+} and the percentage of oil-phase in the microemulsion system, and by further improving the reduction time. There is no trace of iron phase as determined from the core-shell samples based on our XRD results, indicating that the real "bare" γ-Fe_2O_3 nanoparticles do not exist in the composite samples although not all the core-shelled particles can be clearly observed according to the TEM image in Figure 4. Despite the fact that the γ-Fe_2O_3 may also be reduced because of the excess $NaBH_4$ when reducing the Au^{3+}, we believe that the reduction would occur on Au^{3+} first due to the considerably different voltage of redox potentials between the Au^{3+} (1.498V for $Au^{3+} + 3e \leftrightarrow Au$) and the Fe^{3+} (-0.037V for $Fe^{3+} + 3e \leftrightarrow Fe$). Once the metal gold forms within a droplet, it as a "shell" will protect the γ-Fe_2O_3 core from further reduction as the alkaline reducing agent is outside the droplet, i.e. in the water phase. Moreover, such a reaction in our work only lasts for 15 min. The excess reagent was removed by repeatedly washing after the reaction duration.

The magnetic properties of these core-shell nanoparticles were also studied using SQUID, and will be reported in additional publication. Currently, the further investigation of these magnetic core-shell nanoparticles for applying to a bio-system is in progress.

CONCLUSIONS

In this paper, we describe a preparation approach of γ-Fe_2O_3@Au core-shell nanoparticles through a combined processing of high temperature organic solution and colloidal microemulsion routes. These core-shell nanoparticles are magnetic, water-soluble and functional to special coordination of S-bond, making them very promising when applying to bio- and medical systems such as MRI agents. Unlike other metallic core-shell magnetic particles such as Fe@Au, in addition, these maghemite-containing particles are stable against their oxidation.

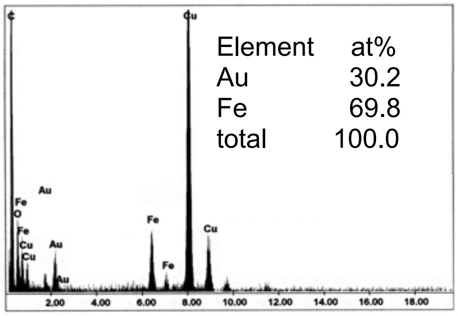


Figure 5. EDS spectrum of γ-Fe_2O_3@Au (core-shell) sample corresponding to Figure 4.

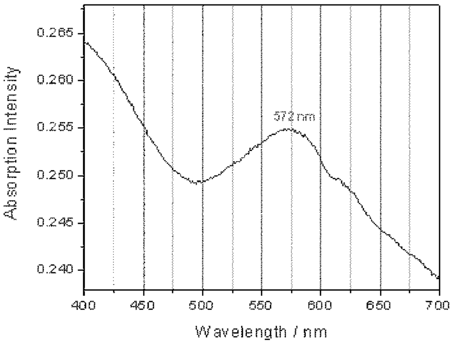


Figure 6. UV absorption spectrum of nano-meter-sized γ-Fe_2O_3@Au suspension in water solution.

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10. This molar percentage based on the determination from EDS is only for a relative comparison. It may not be the real composition value in core-shell particles as we assume that Au may partially self-aggregate intra-particles.