Synthesis and Characterization of Gold-Silver Alloy Nanoshells on Gd-doped Iron Oxide Nanoparticle Cores

Jose M. Penaloza, Dana. E. Gheorghe, Malavosklish Bikram

Department of Pharmacological & Pharmaceutical Sciences, College of Pharmacy, University of Houston Houston, Texas, 77030

RICE-HOUSTON AGEP Alliances for Graduate Education and the Professoriate

Introduction

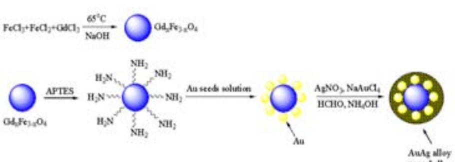
Relevance on the development of a composite system, which consists of a reproducible and consistent synthesis method is the key to unlocking the potential applications nanoparticles may have in the scientific community. Interest in semiconductor core materials and an outer metal shell, is currently being motivated by their promising potential in the biomedical field. Core size and shell thickness are the two variables of magnetic nanoparticles that can be manipulated in order to tune their magnetic and optical properties.

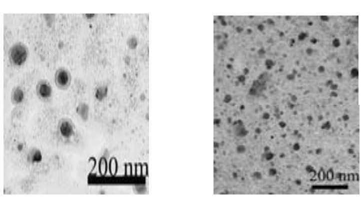
Motivation

In the biomedical field there is an urgent need to develop diagnostic contrast agents for magnetic resonance imaging (MRI), which will help with the early detection of different types of cancer. Currently, clinically approved contrast agents do exist but these lack the ability to target specific tissues. Iron oxide nanoparticles have the unique characteristic of magnetic strength held within the core that could lead to the development of specific target site therapies, therefore replacing chemotherapy. A challenge with nanoparticles is to improve their magnetic properties, which in turn would lead to higher imaging sensitivity. This hurdle can be overcome by doping the core with a transition metal, in particular lanthanides which hold distinctive magnetic and optical properties associated with electronic configuration. Also two drawbacks of nanoparticles is their high sensitivity to light and air, as well as their tendency to form aggregates. Inert metals, in particular gold nanoshells have been a topic of interest due to the ability to tune their optical properties; moreover, they can be stabilized in an efficient manner in corrosive biological conditions.

Synthesis

Preparation of $Gd_xFe_{3-x}O_4$: aqueous solutions of $FeCl_2$, $FeCl_3$ and $GdCl_3$ were allowed to react with NaOH, under an inert atmosphere. Functionalization of the resulted nanoparticles was performed using APTES (aminopropyltriethoxy silane) and it was confirmed by IR spectroscopy. Gold-silver alloy nanoshells on gold-seeded Gd-doped iron oxide nanoparticles were successfully prepared via solution-phase reduction of a mixture of gold (III) and silver (I) salts. Influence of time on the formation of the nanoshells was studied by using different reaction times (30 min, 1 day, and 7 days).





(A) (B)

Figure 1. TEM images of 1 layer AuAg alloy on $Gd_xFe_{3-x}O_4$ (A) average diameter of core 52.8 nm, average thickness of nanoshell 9.8 nm; (B) average diameter of core 68.8 nm

Results

1. X-ray Diffraction

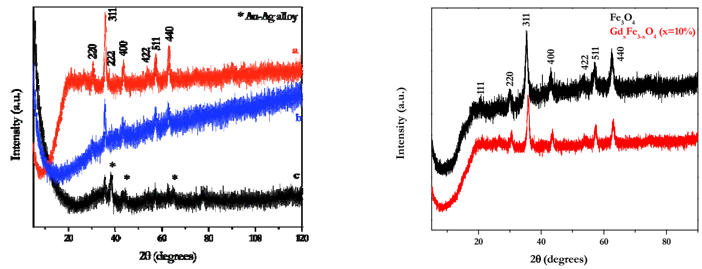


Figure 2. X-ray powder pattern of a-$Gd_xFe_{3-x}O_4$, b-$Gd_xFe_{3-x}O_4$/Au, c-$Gd_xFe_{3-x}O_4$/Au/AuAg ; XRD analysis of Fe_3O_4 and $Gd_xFe_{3-x}O_4$ (X=10%) indicating the incorporation of Gd(III) ions within the magnetite structure.

2. Infrared Spectroscopy

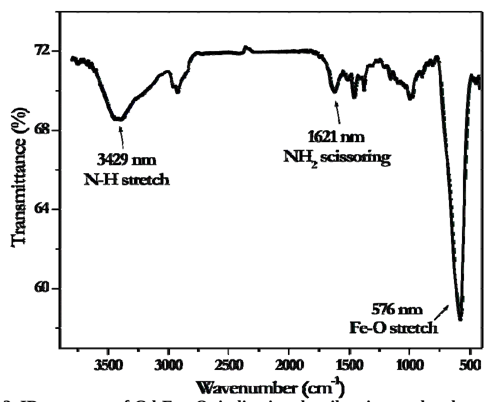


Figure 3. IR spectrum of $Gd_xFe_{x-3}O_4$ indicating the vibration modes characteristic of the functionalized nanoparticles.

3. Scanning Electron Microscopy Analysis

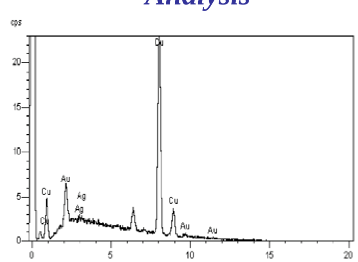


Figure 4. SEM/EDX analysis indicating the formation of the AuAg alloy.

4. Dynamic Light Scattering

Table 1. Growth in the diameter of nanoparticles is seen after each step of synthesis.

Compound	Mean Diameter (nm)
Fe_3O_4	64.0
Fe_3O_4-Gd-NH_2	140.5
Fe_3O_4-Gd-NH_2Au	256.0

Results

5. UV-Vis spectroscopy

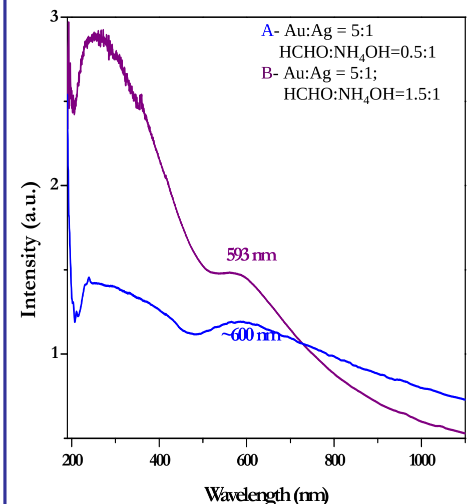


Figure 5. UV-Vis spectra of deposited AgAu alloy on the Gd-doped magnetite cores (reaction time 7 days).

Conclusions

- A new procedure was developed for the preparation of gold-silver alloy nanoshells on Gd-doped iron oxide nanoparticles which exhibit strong absorption at ~600 nm.
- The incorporation of Gd (III) ions in the structure of Fe_3O_4 was confirmed by XRD.
- The functionalization of the nanoparticles was confirmed by IR spectroscopy, as well as by TEM analysis, which indicated the dispersion of the nanoparticles.
- DLS analysis indicated, as expected, an increase of the size of the nanoparticles due to the functionalization and the gold seeding steps.
- Formation of the AuAg nanoshells is confirmed by SEM/EDX analysis as well as X-ray powder diffraction.
- Develop a new procedure with nanoparticle core exhibiting a strong absorption at ~700 nm.

Acknowledgments

*UH AGEP Program-Dr. Christina Chan
*Dr. Malavosklish Bikram
*Dr. Irene Rusakova
*Office of Undergraduate Research-The Honors College