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Fe$_2$O$_3$-Au Hybrid Nanoparticles for Sensing Applications via SERS Analysis

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Abstract: Nanoparticles with large amounts of surface area and unique characteristics that are distinct from their bulk material provide an interesting application in the enhancement of inelastic scattering signal. Surface Enhanced Raman Spectroscopy (SERS) strives to increase the Raman scattering effect when chemical species of interest are in the close proximity of metallic nnaostructures. Gold nanoparticles of various shapes have been used for sensing applications via SERS as they demonstrate the greatest effect of plasmonic behavior in the visible-near IR region of the spectrum. When coupled with other nanoparticles, namely iron oxide nanoparticles, hybrid structures with increased functionality were produced. Multifunctional iron oxide-gold hybrid nanostructures have been created via solution chemistries and investigated for analyte detection of a model analyte. By exploiting their magnetic properties, nanogaps or "hot spots" were rationally created and evaluated for SERS enhancement studies.

Introduction:

Incident light scatters as it transmits through a chemical species. The extent to which the electric field is distorted, the degree to which the light is scattered, is a measure of the polarizability of the species of interest. (1) By analyzing the extent to which the species scatters light a unique fingerprint of the species can be observed. This fingerprint is derived from the distinctive inelastic collision scattering signal, Raman scattering. Through employing the fingerprint capabilities of Raman scattering an advantageous spectroscopy technique can be derived to provide data on the identity of the analyte. The main obstacle facing this form of analysis is the intensity of the Raman scattering signal. (2). Due to the low intensity scattering signal of the not forbidden but rare occurrence of inelastic collisions during the introduction of incident light, a technique needs to be established to enhance the spectra.

Surface Enhanced Raman Spectroscopy (SERS) strives to increase the Raman scattering effect to allow this spectroscopic technique to provide fingerprint characterization of chemical species allowing for broader applications. SERS is an analytical technique that is based on increasing the vibrational motions created as a result of the inelastic collisions of nanoparticles through the addition of a supplemental source to enhance the interactions of the incident light with the analyte of interest and strengthen the scattering signal (1).

The Raman enhancement technique was first observed by Fleischmann's group when on the surface of a silver electrode (2). This enhancement was due to the interaction of the rough metal surface leading to the increase of the inelastic collision signal (2). The presence of the metal surface roughness increased the scattering effect and led to better sensitivity (2). SERS has been a growing chemical field, since the recent advances in the nanoscience and nanotechnology fields, leading to extraordinary results to increase the Raman signal. Enhancements of 10^6 are often claimed, and higher values are seen in specific instances (3). Even single molecule detection was reported by several groups when employing nanoscale materials (3).

Nanoparticles with large amounts of surface area and unique characteristics that are distinct from their bulk material provide an interesting application in the enhancement of inelastic scattering signal. (3) SERS has been explored through using nanoparticles to increase the Raman signal for sensing, bioanalysis, catalytic analysis, and environmental applications.

Figure 2: Nanoparticle Localized Surface Plasmon Resonance

Nanoparticles have plasmonic characteristics with oscillating electrons on the large surface area of the chemical species (3). There are two types of surface plasmons, propagating surface plasmons and localized surface plasmon resonance (3). Propagating surface plasmons are composed of electrons that oscillate as a longitudinal wave at a metal surface and can be used for some

forms of enhancement (3). Localized surface plasmon resonance (LSPR) has the greatest contribution to SERS as electrons oscillate around nanoparticle surfaces (3). Hot spots represent the surface plasmon resonance localization creating points on the metal nanoparticles that lead to increased Raman scattering, these hot spots can be increased by changing the size and shape of the nanoparticle to alter the amount and location of hot spots on the surface of the particle (17). The nanoparticles are smaller than those that experience propagating surface plasmons (4). Nanoparticles are smaller than the wavelength of the incident light as illustrated in Figure 2 allowing the electric field to propagate around the surface of the particle. The LSPR can be used for SERS by matching the nanoparticle's size, shape or composition to compliment the incident wavelength of light (4). Lasers can therefore match the plasmon band of the nanoparticles increasing the interaction of the plasmon band with the incident light, because lasers can be fabricated in the same wavelength of light as these particles. The LSPR of the nanoparticle can contribute additionally to SERS through ground state interactions, resonant process, photon-driven electron-transfer, and transient electron enriched states (3).

The interesting and various applications of nanoparticles for enhancement of signal for inelastic collisions has lead the way for increased research on the composition, size, shape and other properties of the particles to provide the greatest magnitude of enhancement for real world applications. (2,3)

Gold and silver nanoparticles have been widely used for applications in SERS because they demonstrate the greatest effect of plasmonic behavior when compared to other nanoparticles. They are highly stable and their plasmonic properties occur in the visible-near IR range allowing the optical properties to be easily monitored (16). These characteristics of gold and silver have even lead to their use in art such as stained glassed windows and other dyes (16).

Additional improvements can be found by using laser frequencies which are resonant with electronic and vibrational transitions of the analyte, thereby increasing the efficiency of the Raman process. In previous research it has been found bimetallic silver-gold nanowire provides the greatest enhancement when compared to silver nanowires and gold nanotubes (5). This enhancement was attributed to the unique shape of the nanoparticle which allowed a higher tunability to match the wavelength of incident light (5).

Continuing to explore hybrid structures and their impact on the enhancement of Raman scattering signal has led to research using core-shell nanoparticles for SERS. The advantages of the core-shell nanoparticles include the versatility of design, inexpensive nature of the materials with less use of precious metals, tunability of wavelength of excitation, greater stability, and biocompatibility for application and size and shape controllability (3). Through the investigation of core-shell nanoparticles researchers have found a dependency of the enhancement factor with regard to the nanogap on the surface of the interface (3). Large enhancement factors are expected for molecules at junctions between aggregated nanopaticles. This is a result of localized surface plasmon (LSP) coupling between nanoparticles and enhanced electromagnetic field intensity localized at nanoparticle junctions, known as "hot spots"; it is not due to electron tunneling (6). The problem that arises in the design of such nano-architectures is the ability to produce the particles in a uniform, reproducible way for large scale application. Physical vapor deposition techniques have been used to fabricate uniform nanogaps that lead to high enhancement

responses (3). The use of physical vapor deposition is an interesting development in SERS research; however, this form of synthesis limits the scale of production inhibiting large scale industrial applications. Furthermore, new fabrication techniques are sought that allow one to create the particles on a large scale, uniformly, with reproducible responses. One way of addressing these limitations is by developing scalable wet chemical approaches that can allow the creation of reproducible, rationally designed nanogaps leading to additional enhancements effects needed for ultra-low detection of analytes.

Multifunctional hybrid nanostructures can be synthesized by wet chemistry techniques and provide promising characteristics for usage in SERS. The characteristics of hybrid nanoparticles differ from the characteristics of simple metallic structures with the hybrid structures having increased functionality.

Iron oxide-gold hybrid nanostructures have been investigated due to their dual plasmonic behavior of gold and the magnetic properties of iron. Several studies investigated the hybrid Au–Fe_2O_3 for various applications. For example, Tian's group synthesized gold nanorods with an iron oxide core for cancer cell separation and detection applications (14). The gold to iron ratio was determined to be at an optimal ratio of 15:1 gold and iron oxide (14). Once the core-shell nanoparticles were synthesized, detection of 4-aminothiopehnol via SERS analysis was investigated (14). The SERS enhancement data showed that the increase in signal intensity was a result of the electromagnetic interactions, not direct chemical enhancement as a result of the iron oxide shell (14). These core-shell nanoparticles were used for biological applications utilizing the magnetic properties for proper in vivo positioning and the plasmonic characteristics for enhancement of Raman signal (14). Further investigation of the analysis of core-shell nanoparticles with iron oxide cores and gold shells may yield even higher SERS applications with similar applications.

Additionally, iron oxide-gold hybrid nanostructures were also investigated for sensing applications. (7). Gao and coworkers shows that, when exposed to a magnetic field, nanostructures can be rationally assembled in unique structures that allow formation of nanogaps. Enhancement Raman responses resulted recorded were attributed to the presence of nanogaps . The study showed that Au–Fe_3O_4 hybrid nanostructures with a 0.2 gold-iron oxide ratio produced the highest enhancement responses (7). This enhancement effect was attributed to the creation of "hot spots" between neighboring Au nanoparticles (7).

Similar structures have been synthesized by others and explored for SERS applications. For example, hybrid structures comprised of an iron oxide sphere decorated with gold nanoparticles were produced through a citrate reduction protocol (8). These hybrid structures contained nanogaps as a result of the loading of the gold on the iron oxide the interaction between gold particles may create interesting characteristics for SERS (8). One could rationally assemble the iron oxide based multifunctional nanostructures by employing their magnetic properties and concentrate the particles over a smaller area and test them for SERS enhancement studies. Nanogaps have previously been controlled through wet chemical synthesis using linkers to control the size of the gap and regulate the plasmonic hot spots created between the sites (11). To control the size of the nanogaps without the use of linkers the size and shape of the constitute nanoparticles can be monitored to determine the loading capacity of gold on the substrate.

Several research groups have investigated hybrid magnetic nanoparticles for detection via SERS concentrating on the collection of nanoparticles in a centralized area. (9) Concentrated and non-concentrated sample were evaluated using 4-mercaptopyridine and bacteria as SERS reporters (9). The Raman scattering signal was greatly enhanced when the concentrated nanoparticle assemblies were used for detection; the authors proposed that this was due to the high density of "hot spots" formed as a result of the concentration of particles (9). Additionally, Li and coworkers explored the use of hybrid nanostructures, specifically with magnetic-plasmonic functionalities, as biomarkers for cancer detection applications (15). The team used NiFe cores with Au shelling and found that the nanoparticles were magnetically responsive allowing for aggregation and the creation of dimers and trimers hot spots for SERS observation (15).

By exploring the nanogap of the hybrid iron oxide-gold nanoparticles a greater understanding of the SERS capability can be established. The magnetic properties of the iron oxide add an additional characteristic to achieve a higher density of reproducible nanoparticles for SERS capability. Synthesis of the iron oxide-gold nanoparticles will be performed by a citrate reduction method. SERS analysis will be obtained by using 4-mercaptobenzoic acid (4-MBA). SERS analyte must be electron rich allowing a change in the polarizability, such as benzene. Additionally, this compound will be used as the ideal analyte for Raman detection because of its large packing density. (12). The 4-MBA binds through the sulfide group to the gold nanoparticle on the hybrid composite structures (5). The ring-breathing modes of the 4-MBA display changes in the polarizability and can be observed in Raman scattering signals at approximately 1070 and $1575 cm^{-1}$ (5,13). By using 4-MBA Raman enhancement can be monitored while maintaining a controlled environment of the analyte of interest.

Objectives:

1. Synthesize Fe_2O_3-Au hybrid nanocrystals

2. Prepare a SERS colloidal solution for analysis

3. Employ the magnetic properties of the iron oxide to concentrate the nanoparticles into a dot while controlling with one sample that is not concentrated

4. Attempt to control the size of the nanogap by changing the composition of the iron oxide to the gold and controlling the size of the particles

5. Analyze each sample using various characterization techniques including SEM, Dynamic Light Scattering, UV-VIS spectroscopy, Vibrating Sample Magnetometer, EDS and EDS mapping, and Raman Spectrometer

6. Interpret the UV-vis spectroscopy data to determine the wavelength of excitation best to match the laser beam with

7. Use the laser that is closest to that range and determine if there is enhancement of the Raman signal

8. Analyze results and determine if the result and procedure are reproducible

9. Apply the nanoparticles for industry including sensing and waste analysis techniques

Materials:

- Stock Solution of Fe_2O_3
- Conical flask (25mL)
- Heating mantel
- Sodium citrate
- Chloroauric acid
- Deionized water
- 4-MBA
- Silicon Chips

Methods:
Nanomaterials Synthesis Protocol:

Synthesis of Fe₂O₃-Au hybrid nanoparticles: (10)

Synthesis of Fe_2O_3-Au hybrid nanoparticles: (10)

1. Prepare a stock solution of Fe_2O_3 of 25 mM.
   Note: All stock solutions are prepared using deionized water unless stated otherwise.
2. Take a 25 ml conical flask.
3. Add 10 ml deionized (DI) water and a stir bar, and place it on a heating block.
4. Add 100 µl of Fe_2O_3 stock solution (25 mM) to this flask.
5. Heat the solution while stirring for approximately 5 min.
6. Prepare 10 ml 1% sodium citrate by dissolving 0.1 g of sodium citrate to 10 ml of water.
7. Add 1 ml of the 1% sodium citrate solution to the 25 ml flask containing the Fe_2O_3 aqueous solution.
8. Bring the solution to a boil (100 °C).
9. Add 250 µl of 0.01 M chloroauric acid.
10. Continue heating the solution at 100 °C for 10 min. After several minutes (2-3 min), the solution turns red/brownish indicating that Au nanoparticles are being produced.
11. Remove the solution from the heating block and allow it to cool off at RT (approximately 20 °C) (1-2 hr).
12. Purify the samples by centrifugation for 7 min at 4,700 × g.
13. Remove the supernatant from the centrifuged samples.
14. Re-disperse the centrifuged nanoparticles in DI water, up to 10 ml.
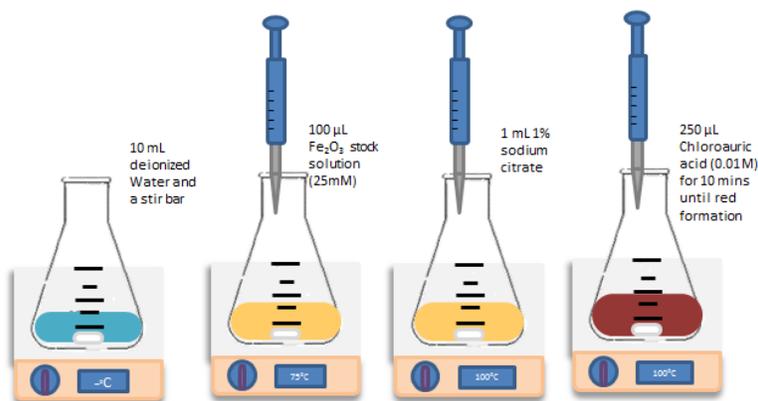
Synthesis of Fe_2O_3 nanoparticles: (10)

1. Prepare a stock solution of Fe_2O_3 of 25 mM.
   Note: All stock solutions are prepared using deionized water unless stated otherwise.
2. Take a 25 ml conical flask.
3. Add 10 ml deionized (DI) water and a stir bar, and place it on a heating block.
4. Add 100 µl of Fe_2O_3 stock solution (25 mM) to this flask.
5. Heat the solution while stirring for approximately 5 min.
6. Prepare 10 ml 1% sodium citrate by dissolving 0.1 g of sodium citrate to 10 ml of water.

7. Add 1 ml of the 1% sodium citrate solution to the 25 ml flask containing the Fe_2O_3 aqueous solution.
8. Bring the solution to a boil (100 °C)..
9. Continue heating the solution at 100 °C for 10 min.
10. Remove the solution from the heating block and allow it to cool off at RT (approximately 20 °C) (1-2 hr).
11. Purify the samples by centrifugation for 7 min at 4,700 × g.
12. Remove the supernatant from the centrifuged samples.
13. Re-disperse the centrifuged nanoparticles in DI water, up to 10 ml.

Synthesis of Au nanoparticles: (10)
1. Take a 25 ml conical flask.
2. Add 10 ml deionized (DI) water and a stir bar, and place it on a heating block.
3. Prepare 10 ml 1% sodium citrate by dissolving 0.1 g of sodium citrate to 10 ml of water.
4. Add 1 ml of the 1% sodium citrate solution to the 25 ml flask
5. Bring the solution to a boil (100 °C).
6. Add 250 μl of 0.01 M chloroauric acid.
7. Continue heating the solution at 100 °C for 10 min. After several minutes (2-3 min), the solution turns red/brownish indicating that Au nanoparticles are being produced.
8. Remove the solution from the heating block and allow it to cool off at RT (approximately 20 °C) (1-2 hr).
9. Purify the samples by centrifugation for 7 min at 4,700 × g.
10. Remove the supernatant from the centrifuged samples.
11. Re-disperse the centrifuged nanoparticles in DI water, up to 10 ml.

Synthesis of SERS colloidal solution:
Method 1(5):
- 500 μL of 2 mM aqueous solutions of 4-MBA was added to 1 mL aliquots of purified samples
- Allow 1 hour before centrifugation
- Separate particles by using a magnet to separate the nanoparticles from the supernatant or use centrifugation purification for 10 minutes at 7000 rpm and re-dispersed in water
Method 2 (9):
- Clean and prepare silicon chips by rinsing with distilled water and acetone and drying under a stream of nitrogen (cleaned in UV/ozone cleaner for 20 minutes)
- 500 μL of 2 mM aqueous solutions of 4-MBA was added to 1 mL aliquots of purified samples
- Allow 1 hour incubation
- Drop 10 μL of iron oxide-gold hybrid nanoparticles with 4-MBA onto the chip
- Condense the particles by using a corner of a permanent magnet, 5 minutes, until a dot forms

Characterization Techniques:

1. SEM

   Characterize morphologies of the Fe_2O_3 and Fe_2O_3-Au nanoparticles to determine the decorating capacity of the gold nanoparticles and determine reproducibility of the crystals when concentrated in a nanodot.

2. Dynamic Light Scattering

   DLS will be used to determine the hydrodynamic size and zeta potential of the nanoparticles by analyzing the surface charge before and after 4MBA addition. This will provide information of the tendency of the particle to aggregate in solution helping to determine if the nanoparticles will remain uniform after formation.

3. UV-VIS spectroscopy

   Analyze the changing of morphology as the iron oxide nanoparticles are decorated with gold nanoparticles to verify synthesis of a nanocomposite material by observing a shift in the absorption of UV-Vis light.

4. Vibrating Sample Magnetometer

   Analyze the magnetic properties of the iron oxide present in the hybrid multi-functional nanoparticle to determine the extent of the ferromagnetic behavior if the compositions of the particles are altered in the pursuit of higher enhancement of a Raman scattering signal.

5. EDS and EDS mapping

   Determine the concentration of individual elements: gold, iron and oxygen by mapping each atom to determine the composition of the hybrid nanoparticles to analyze the presence of plasmonic and magnetic properties with respect to localized area.

6. Raman Spectrometer

   Analyze if the presence of the Fe_2O_3 –gold hybrid nanoparticle enhances the Raman signal using comparison to iron oxide particles and gold nanoparticles.

Results

The scattering of light as a result of the transmittance of an applied electric field through the electron cloud occurs via inelastic and elastic collisions. Rayleigh scattering represents the elastic collision of light where the scattered photon has the same energy as the incident photon. Elastic collisions are the most abundant form of light scattering from the introduction of incident photons. They represent changes in direction of photons not changes in vibrational energy (1). The energy is conserved in the collision as illustrated in Figure 1. The dipole changes during elastic collisions, however the species has no change in polarizability. Inelastic collisions experience a change in polarizability, producing a unique fingerprint scattering signal that can be matched to a specific element of interest. Raman scattering can be used for analysis of
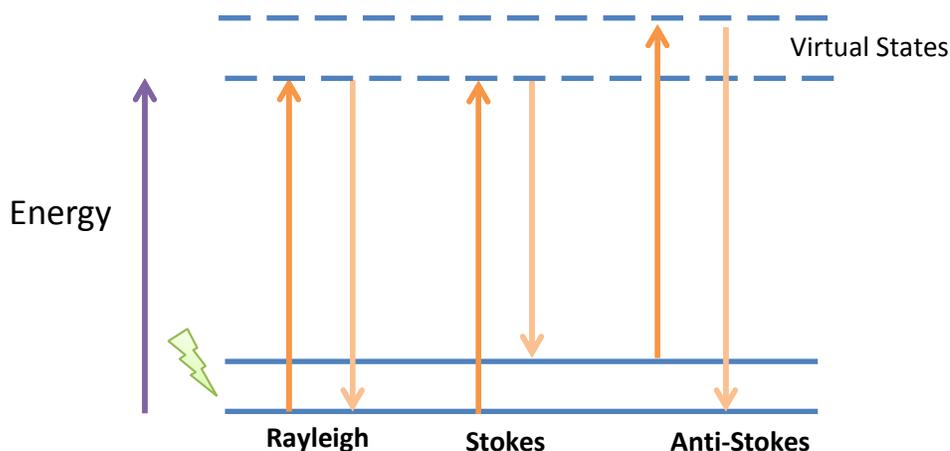

Figure 1: Virtual State Energy Diagram representing Rayleigh elastic collisions and Raman inelastic Stokes and Anti-Stokes collisions

composition and trace analysis of species within complex matrices using the vibrational information (2). However, the Raman signal is weak when compared to Rayleigh scattering. Raman scattering is less likely to occur and when it does it occurs in both Stokes and anti-Stokes forms as illustrated in Figure 1. Stokes scattering occurs when the scattered photon of light is of a lower energy than the incident light. Anti-stokes scattering is observed when the incident photon of light gains energy. The loss and gain of energy is a result of the excitation of the electron to virtual states, non-quantized short lived energy states, without the conservation of energy from the incident photon.

Preliminary Results:
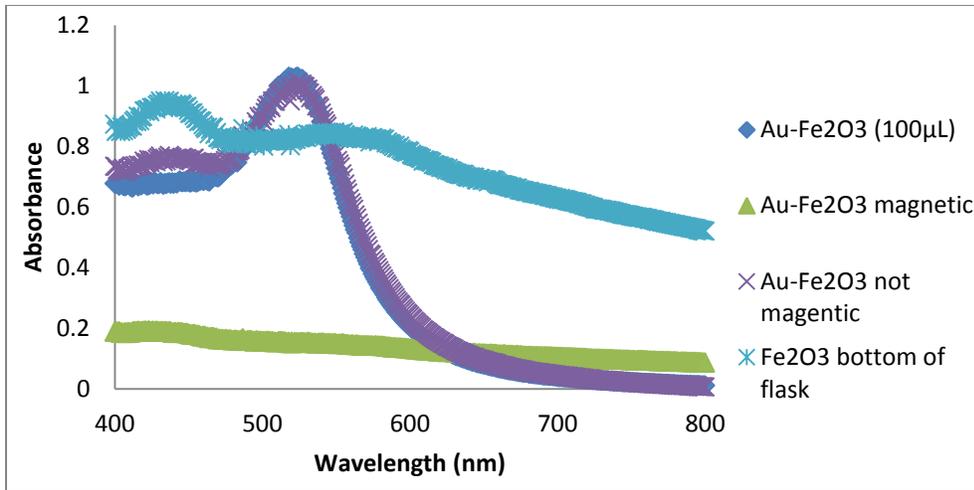
- 100µL of Fe_2O_3 produced a UV-Vis peak with only gold properties showing that the amount of Fe_2O_3 must be increased

- The Fe_2O_3 was increased to 1mL using a stir bar and the stir bar was found to interfere with the formation of the particles due to the magnetic iron oxide not interacting as much with the gold
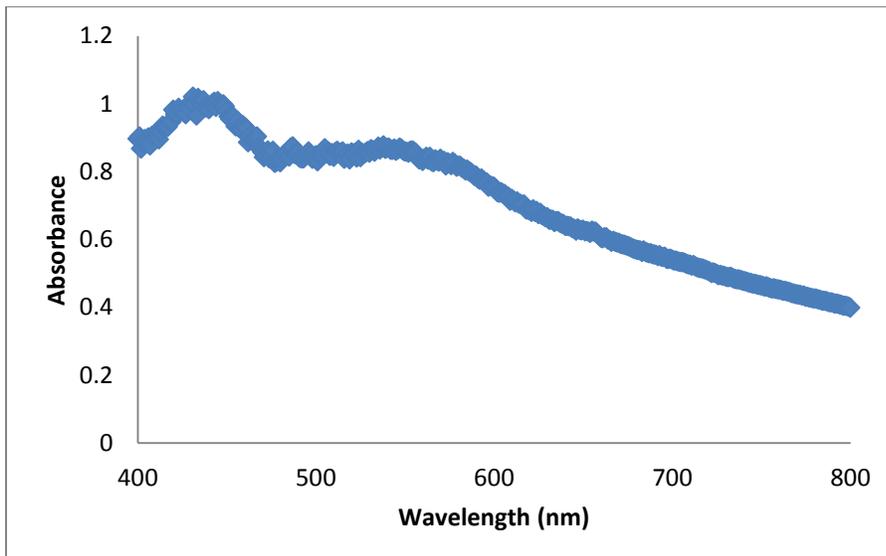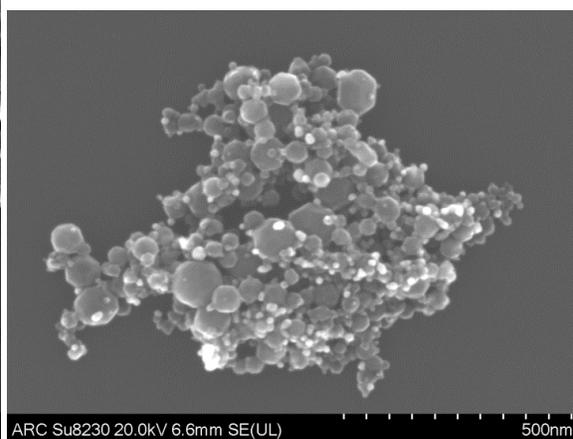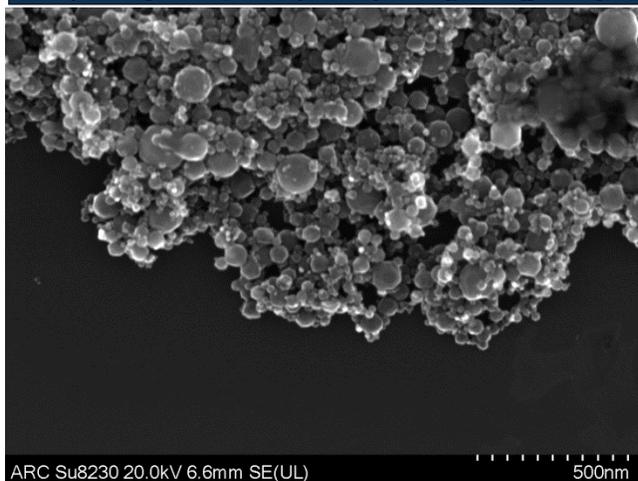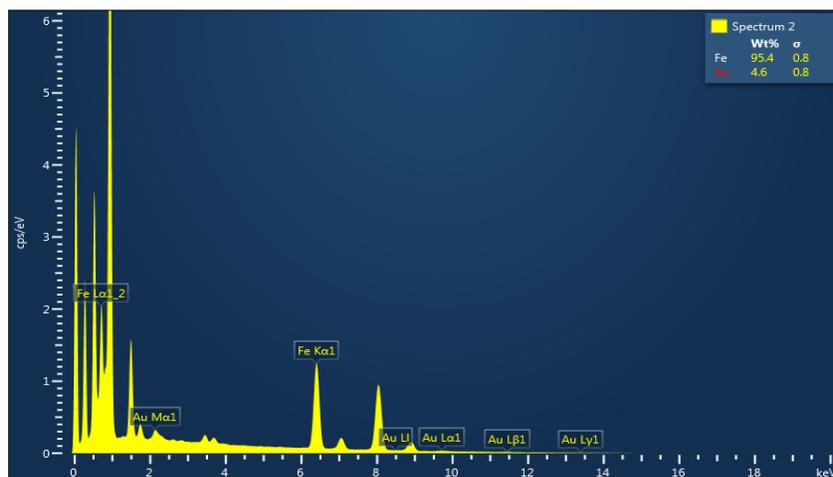
- 1 mL of iron oxide was used and the product was collected with UV-vis results that suggested hybrid multifunctional formation

- SEM images and EDS confirmed these results as the iron oxide was shown to be decorated with gold nanoparticles.
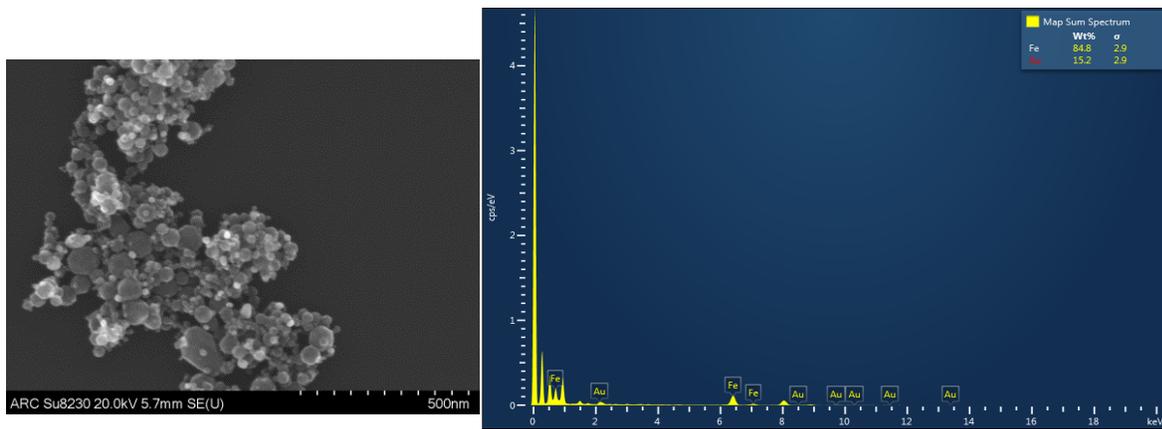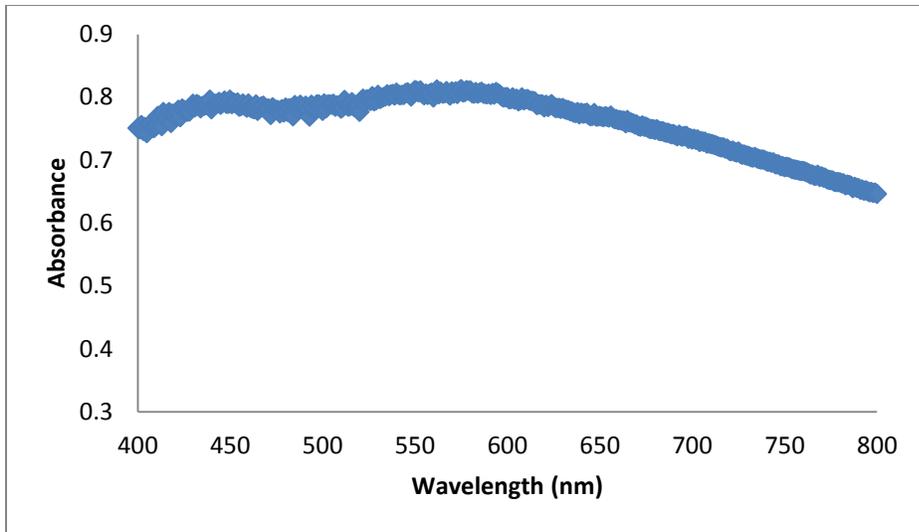
EDS Layered Image 1
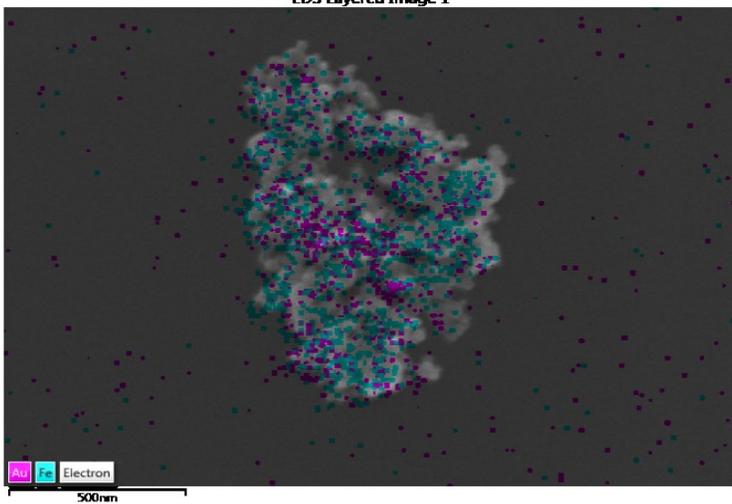
- Au-Iron oxide hybrid structures used as a seeded method to increase gold loading
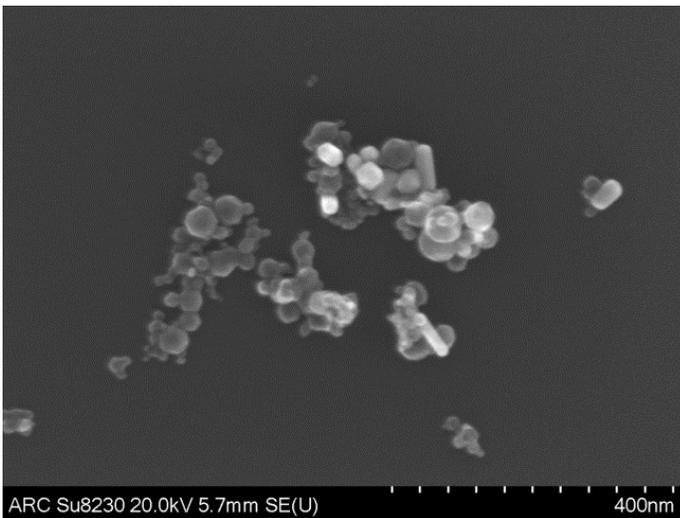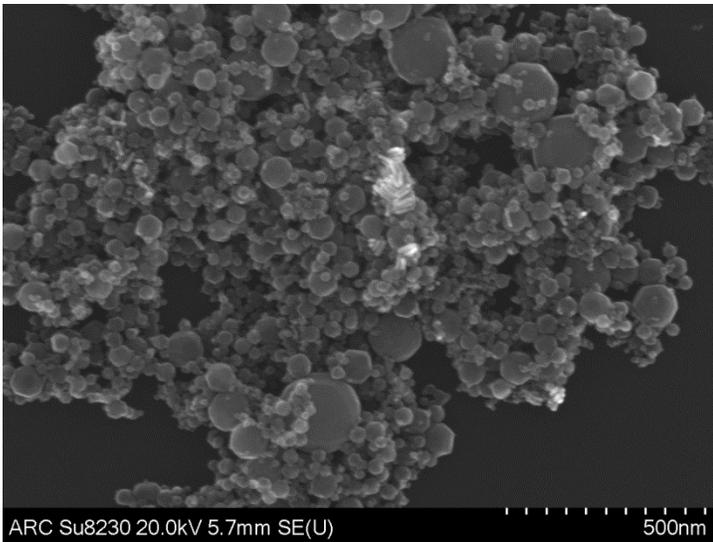
- Fe$_2$O$_3$-Au particles through electrostatic interactions with citrate

- Nanorods formed concentrated areas that were not uniformly decorated on the iron oxide

- The other shaped particles had better attachment but were non-uniform in shape

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