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## **Novel Synthetic Routes to Formation of Magnetic Nanocomposites**

Anindya Pradhan  
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# Novel Synthetic Routes to Formation of Magnetic Nanocomposites

A Thesis

Submitted to the Graduate Faculty of the  
University of New Orleans  
in partial fulfillment of the  
requirements of the degree of

Master of Science  
in  
Chemistry

by

**Anindya Pradhan**

B.S. Calcutta University, 1998  
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December, 2006

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## Table of Contents

1. List of Figures .....	vi
2. List of Tables .....	vii
3. Abstract .....	viii
4. Introduction .....	1
5. Experimental Procedure .....	8
6. Results and Discussion .....	10
7. Silver Magnetite Nanocomposites.....	21
8. Titanium Gold and Titanium Magnetite Nanoparticles.....	22
9. Conclusion .....	25
10. Future Research .....	26
11. References .....	28
12. Vita .....	31

## List of Figures

Fig 1.	Schematic of Sonochemical Process.....	6
Fig 2.	Magnetic separation of gold-magnetite nanocomposites.....	10
Fig 3.	TEM image of gold-magnetite nanocomposite in methanol.....	11
Fig 4.	EDS spectrum of composite particles .....	11
Fig 5.	Magnetization vs. temperature for nanoparticles .....	12
Fig 6.	Hysteresis loop for magnetic nanocomposites .....	13
Fig 7.	TEM image of Au-magnetite nanocomposite in DEG .....	16
Fig 8.	TEM of Au-magnetite in oleic acid additive .....	16
Fig 9.	Absorbance spectra of three Au-magnetite particles .....	17
Fig 10.	EDS Spectra for the Au-magnetite nanocomposites in DEG .....	17
Fig 11.	EDS Spectra for the Au-magnetite in Oleic Acid .....	18
Fig 12.	Magnetization vs. temperature for gold magnetite in DEG .....	19
Fig 13.	Magnetization vs. temp. for gold magnetite in oleic acid .....	19
Fig14.	Hysteresis loop for Au-magnetite nanoparticle in DEG .....	20
Fig 15.	Hysteresis loop for Au-magnetite material in oleic acid .....	20
Fig 16.	TEM image of silver-magnetite nanocomposite .....	21
Fig 17.	TEM image of silver-magnetite nanocomposite .....	21
Fig 18.	TEM image of gold-titanium dioxide nanocomposite .....	22
Fig 19.	TEM image of gold-titanium dioxide nanocomposite .....	22
Fig 20.	TEM image of titanium dioxide-magnetite nanocomposite .....	23
Fig 21.	TEM image of titanium dioxide-magnetite nanocomposite .....	23
Fig 22.	EDS spectrum of titanium dioxide-magnetite nanocomposite ...	24

## List of Tables

Table 1. The ratios of the Au and Fe in the samples with MeOH, DEG and Oleic acid by ICP measurements .....	15
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## **Abstract**

Novel synthetic routes to formation of gold-magnetite nanoparticles have been designed by sonochemistry. Treatment of preformed magnetite nanoparticles with ultrasound in aqueous media with dissolved tetrachloroauric acid resulted in the formation of gold-magnetite nanocomposite materials. These materials maintained the morphology of the original magnetite particles. The morphology of the gold particles could be controlled by adjusting experimental parameters, including the addition of small amounts of solvent modifiers such as methanol, diethylene glycol, and oleic acid. Further experiments were conducted with silver and titanium. Morphology and properties of nanocomposites were analyzed by transmission electron microscope (TEM), energy dispersive spectra (EDS), superconducting quantum interference device (SQUID) and inductively coupled plasma (ICP). The nanocomposite materials were magnetic and exhibited optical properties similar to gold nanoparticles. Magnetic nanoparticles have a wide range of potential applications including uses as medical diagnostic tools, drug delivery systems, and biosensors.



## Introduction

Nanoparticles are small crystalline particles with characteristic size smaller than 100 nm, located in the transition region between molecules and microscopic (micron-size) structures. There are various types of nanoparticles synthesized, like, insulating (ceramics), metallic and semiconductor. Recently hollow nanocrystals have also been synthesized which are spherical shells on the nanoscale<sup>1</sup>.

Surface modification of nanometer sized inorganic core with different inorganic shell to form core/shell type nanostructures has become an important route to functional nanomaterials. Such modification has brought about interesting physical and chemical properties of the nanostructured materials that have shown important technological applications<sup>2-4</sup>.

Monodisperse particles, i.e. particles of uniform size dispersed in a fluid are achievable and this is one of the reasons for the increased interest in nanoparticles in recent times<sup>6</sup>. Nanosize particles have a tendency to stick to surfaces and in some cases to each other, forming clusters of particles. This is caused by the relatively large electromagnetic forces, i.e., when particles carry a net charge there is a strong electrostatic repulsion between them, by Coulomb's law, and they stick strongly to oppositely charged particles, or uncharged polarizable surfaces. Nanoparticles of ferroelectric or ferromagnetic materials demonstrate a strong dipole-dipole interaction while nonpolar particles polarize

and interact through the van der Waals forces. Nanoparticles can be self-assembled, which is another reason for interest in them.

Nanoparticles have been produced and used for a very long time. They are usually used as pigments in inks, paints and glazes<sup>7</sup>. They are also an essential ingredient in sun protection lotions, and in other cosmetics. Nanoparticle applications can be separated into different categories according to the role played by the particles. The simplest case is where their size, shape, surface chemistry, or other physical properties, affect their immediate environment. They have also been recognized to function as catalysts for carbon nanotube growth. Another application is where the particles communicate information on the local environment or modify some local physical property in a way that can be detected in real-time.

The finite size and surface effects gives rise to some noteworthy phenomenon to magnetic nanoparticles including superparamagnetism, high field irreversibility, high saturation field, shifted loop after field cooling<sup>8</sup>. The fact that particles of a ferromagnetic material below a critical size (<15 nm) would consist of a single magnetic domain was evident from the work of Frenkel and Dorfman. The particle shows an atomic paramagnetic behavior (superparamagnetism) except an extremely large moment above a certain temperature called the blocking temperature.

The particles need to show superparamagnetic behavior at room temperature<sup>9</sup>. The other application like medical diagnosis and curative therapy

require these particles to be stable in physiological pH and salinity conditions. The particle size is a key issue since the precipitation due to gravity can be avoided with smaller particles. On the other hand steric and coulombic repulsions can also be of importance with respect to charge and surface chemistry.

It is necessary to coat these magnetic nanoparticles with a biocompatible polymer during or after synthesis to prevent formation of large aggregation, charges from the original structure and biodegradation in systems for in vivo applications<sup>10</sup>. Among the range of magnetically responsive components (from magnetite to samarium-cobalt systems) magnetite and its oxidized form ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) are most commonly employed. Nickel and cobalt are susceptible towards oxidation and have alarming toxicity. So they are of little or no interest. Thus for in vivo biological applications the magnetic particles must be synthesized from non-toxic, non-immunogenic material with small particle size to maintain circulation after injection through the capillary systems of organs and tissues. Further more it is also necessary to have a higher magnetization for the particles so that their movement can be controlled by an external magnetic field and can be immobilized to the targeted pathogenic tissue<sup>11</sup>.

For in vitro applications restrictions are a bit relaxed with respect to sizes. Superparamagnetic nanocrystals dispersed in submicrometric diamagnetic particles with long sedimentation times can be used. The advantage appears in the functionality of the nanoparticles. In nut shell for all applications the size,

shape, the size distribution and surface chemistry of the particles as well as their magnetic properties are always of prime importance.

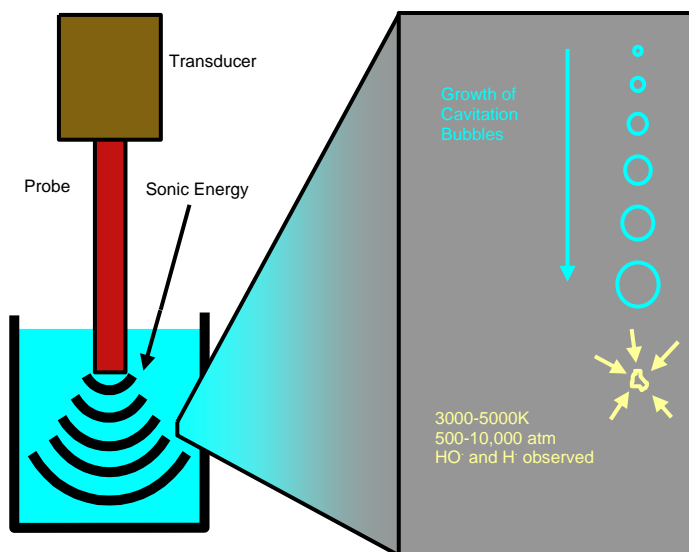
Recently many attempts have been made to develop processes and techniques that would yield core shell uniform nanoparticles with controlled size and shape. Developments in nanotechnology demand building blocks with increasing structural and compositional complexity, which can be reproducibly self-assembled into functional materials. In this regard, nanoparticles with core-shell morphologies represent a new type of constructional unit consisting of two dissimilar compositional and structural domains. Such materials should have enhanced physical and chemical properties and a broader range of applications than their single-component counterparts.

During the last several years, interest in the study of nanostructured materials has been increasing at an accelerating rate, stimulated by recent advances in materials synthesis and characterization techniques and the realization that these materials exhibit many unique and interesting physical and chemical properties with a number of potential technological applications. As never before, magnetic materials are the key to the future of the storage industry.

Preparation of gold-magnetite nanocomposites, especially those with a core-shell structure<sup>12</sup>, has been a topic of much interest. Magnetic nanoparticles have a wide range of potential applications<sup>13</sup>, including uses as medical diagnostic tools<sup>13</sup>, drug delivery systems<sup>13-15</sup>, and biosensors<sup>13,14</sup> as well as

molecular sensors<sup>16</sup>. Effective use of magnetic nanoparticles for these purposes requires several characteristics such as uniform and controllable particle size, shape, and morphology, substantial and reliable magnetic properties<sup>17,18</sup>, low toxicity, stability in biological or environmental systems<sup>13,14</sup>, and readily functionalizable surfaces to allow chemical and biological selectivity<sup>19</sup>. Gold coated magnetite has been proposed as an effective material that would meet these requirements. It has been well established that gold can be functionalized with thiolated organic molecules<sup>20</sup> and via amide coupling chemistry<sup>21</sup>. Researchers have successfully bound thiol modified DNA and various other enzymes to gold particles<sup>22</sup>.

Obtaining novel materials with controlled size or shape<sup>23,24</sup> under mild conditions and with safe precursors is an issue that has engaged many researchers. Sonic energy has been routinely used in the field of materials science for many years. Its chemical effects have recently come under investigation for the acceleration of chemical reactions<sup>25,26</sup> and for the synthesis of new materials<sup>25</sup>, as well as for the generation of novel materials with unusual properties<sup>26</sup>. Many reactions which are normally sluggish can be accelerated by application of ultrasound. The acceleration is due to either physical or chemical effects of cavitation. Physical effects can enhance the reactivity of a catalyst by enlarging the surface area or by improving mass transport<sup>26</sup>. Chemical effects of ultrasound enhancements of reaction rates occurs through high temperature, high pressure, and highly reactive radical species formed during cavitation<sup>26</sup>.



**Figure 1.** Schematic of Sonochemical Process

Cavitation in a liquid occurs due to the stresses induced in the liquid by the passing of a sound wave through the liquid<sup>25</sup>. A sound wave consists of compression and decompression/rarefaction cycles. If the pressure during the decompression cycle is low enough, the liquid can be torn apart to leave small bubbles<sup>25,26</sup>. These cavitation bubbles grow during subsequent decompression phases, and contract during compression phase. Because of an imbalance between growth and contraction, the bubbles increase in size until they are no longer stable. At this point the bubbles implode violently during the next compression. During implosion temperatures can reach an estimated 5000°C, pressures can reach several hundreds of atmospheres, and solvent molecules can be homolytically cleaved to form species such as hydroxyl radical and hydrogen atoms<sup>26</sup>. Formation of gold nanoparticles during sonication has been

previously reported, and the mechanism was proposed to occur through hydrogen atom reduction of dissolved gold<sup>27</sup>.

## Experimental Procedures

In our study we have introduced two new approaches of synthesizing magnetic nanoparticles. They are

1. Sonochemical synthesis of gold magnetite nanoparticles with various surfactants.
2. Synthesis of gold titanium dioxide nanoparticles, magnetite-titanium dioxide core/shell nanoparticles and magnetite-titanium-gold core shell nanoparticles.

We have been able to achieve interesting results in the first part of the experimental section. They are reproducible and these particles show higher magnetization than magnetite particles. Magnetic properties of the nanocomposites can be tuned by changing the amount of gold particles in the sample. With proper choice of surfactants these properties can be controlled. It has been well established that gold can be functionalized with thiolated organic molecules and via amide coupling chemistry. Researchers have successfully bound thiol modified DNA and various other enzymes to gold particles.

In the first part of the study, sonochemical methods were utilized to produce gold-magnetite nanocomposite materials<sup>28</sup>. 0.1 mM H<sub>2</sub>AuCl<sub>4</sub> solution was prepared in nanopure water. 50 ml of the prepared solution was sparged in argon for 20 min. 100 μL methanol was added and was sparged with argon for another 5 min. 100 μL of preformed magnetite<sup>29,30</sup> suspended in methanol was added to the above solution and sparged for another 10 min. Then it was

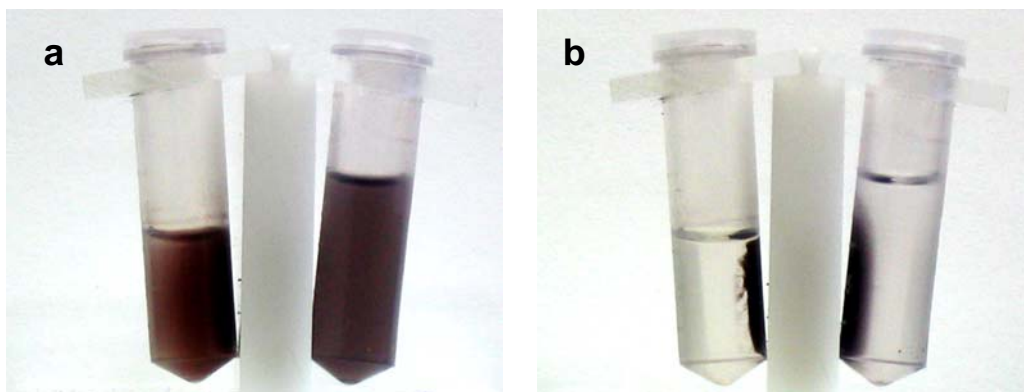


sonicated under argon atmosphere for 10 min at 50% amplitude using an ultrasonic processor. The solution then turned pink/purple depending on the size of the gold nanoparticles. The whole solution was then transferred into a test-tube and kept in front of a strong magnet for at least one day until the whole solution became clear as the gold-magnetite nanocomposites stuck to the wall of the test-tubes. Then the transparent solution was carefully taken out of the test-tube in front of the magnet so that the particles remained against the test-tube walls. After washing, the nanocomposite particles were dispersed in 2 ml of ethanol and stored in capped tubes. These were then used for TEM studies.

In the other sets of experiments 100  $\mu\text{L}$  of each of diethylene glycol (DEG) and oleic acid were used as surfactants in addition to 100  $\mu\text{L}$  of methanol during the sparging processes. The remaining of the experimental procedure remained the same and the extraction process was also the same.

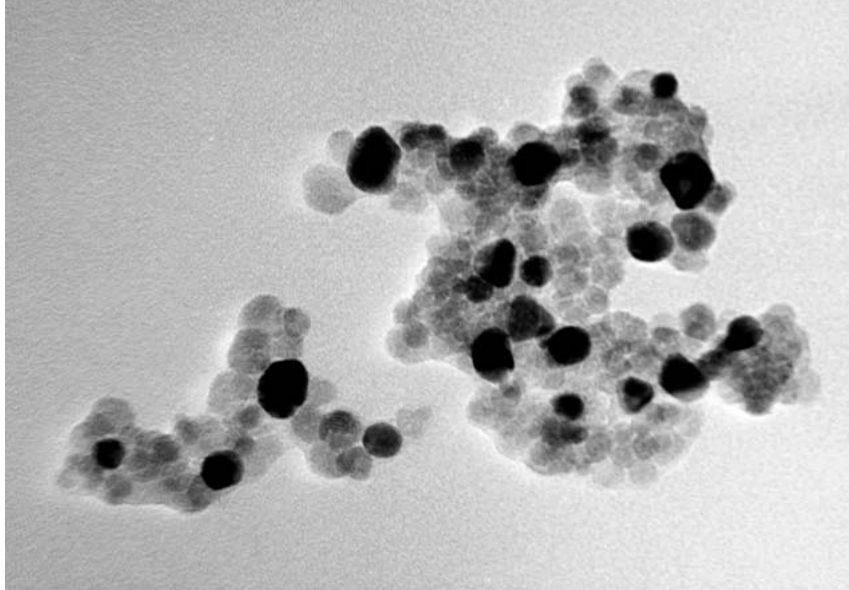
## Results and Discussion

Sonication of magnetite nanoparticles in the absence of  $\text{HAuCl}_4$  did not cause any observable changes in the TEM images of the magnetite particles. In the presence of  $\text{HAuCl}_4$ , sonication resulted in the appearance of a red or purple coloration of the particles, as depicted in Figure 2.



**Figure 2.** Gold magnetite nanocomposite materials suspended in ethanol prior to (a) and after (b) magnetic separation. The brown/purple color is from gold nanoparticles. Note that all the color is removed after separation, indicating that the gold was attached to magnetite

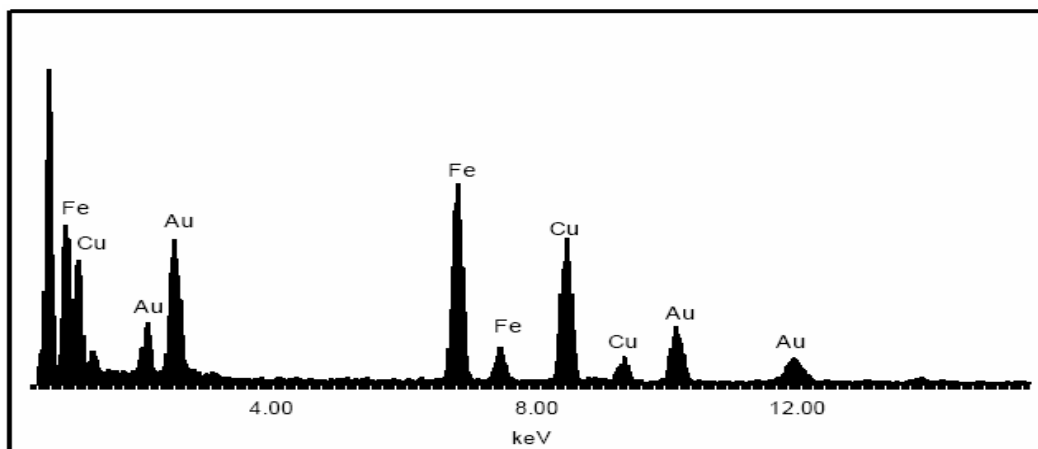
Exposing these materials to a magnetic field resulted in removal of all colored material from the liquid. This result indicates that the gold particles must be physically or chemically attached to the magnetite. This attachment is at least strong enough to cause the suspended gold particles to migrate with the magnetite in a magnetic field. TEM images of these particles revealed the presence of both gold and magnetite forming a nanocomposite material (see Figure 3).



**Figure 3.** TEM image of gold-magnetite nanocomposite material formed by sonication of magnetite in aqueous  $\text{HAuCl}_4$  with added methanol. Dark particles are gold, grey particles are magnetite.

Observation of the particles in Figure 3 suggests a high degree of agglomeration between magnetite particles. This degree of agglomeration is likely due to the removal of the initially present capping ligand during the sonication process.

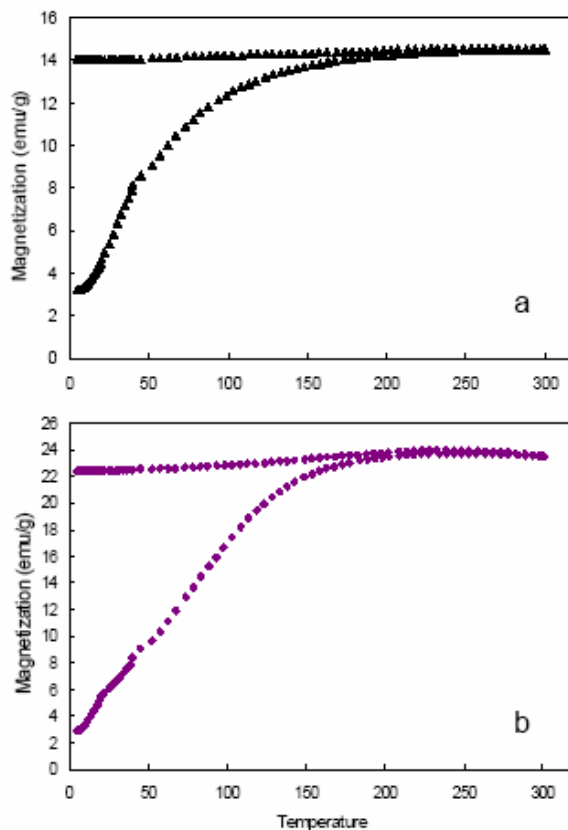
EDS analysis of the particles indicated the presence of both iron and gold,



**Figure 4.** EDS spectrum of composite particles depicted in Figure 3. Cu and C peaks are from TEM grid

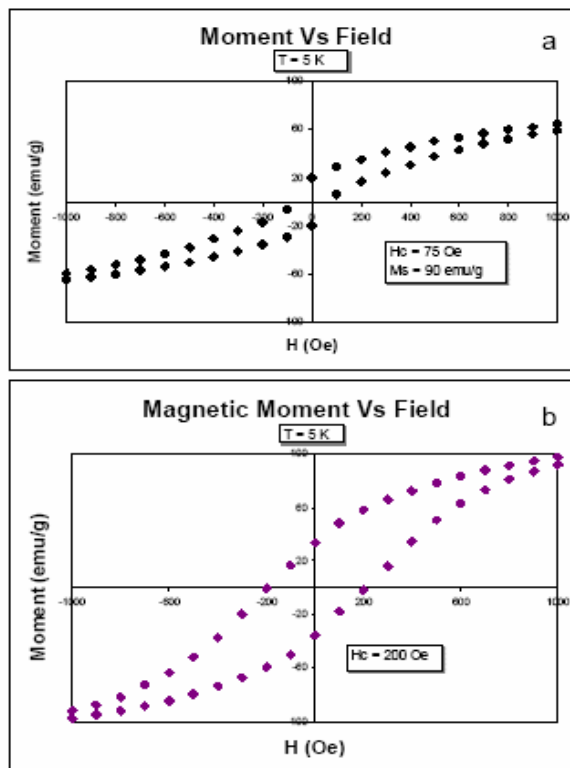
as illustrated in Figure 4. The data presented in this EDS spectrum were collected from multiple particles, and is therefore representative of the composite material. Additional EDS spectra collected on single particles verified that the dark particles in the TEM image (Figure 4) are in fact gold and the grey particles contain iron as the only metal.

The gold-magnetite nanocomposite material was also characterized to determine its magnetic properties using a SQUID magnetometer. Substantial changes in the magnetic properties of these materials were observed compared to the untreated magnetite precursor material. Figure 5 compares the



**Figure 5.** Magnetization vs. temperature for magnetite nanoparticles (a) and gold-magnetite nanocomposite material (b). In each panel, the top curve is for the field cooled sample and the bottom curve is for the zero field cooled sample.

magnetization vs. temperature behavior of the untreated magnetite and the gold-magnetite nanocomposite material. While the general shape of these curves is similar, the gold-magnetite nanocomposite material exhibited a substantially higher magnetization of about 23 emu/g compared to 14 emu/g for the untreated magnetite. In both cases, the magnetization was normalized to total mass of magnetite in the sample. In addition to the differences in magnetization, the coercivity of the sample changed upon formation of the nanocomposite material. The untreated magnetite had an observed coercivity of 75 Oe, while the gold-magnetite nanocomposite material exhibited a substantially increased coercivity of 200 Oe. These data are depicted in Figure 6.



**Figure 6.** Hysteresis loops for untreated magnetite (a) and gold-magnetite nanocomposite material (b).

Also apparent in this figure, is the significantly larger saturation magnetization ( $M_s$ ) for the nanocomposite material ( $M_s \sim 125$  emu/g) compared to that of the untreated magnetite ( $M_s \sim 90$  emu/g). The changes in magnetic properties are most likely due to changes in the surface characteristics of the magnetite. During sonication, the capping ligands initially present can be removed. Removal of these capping ligands could cause a change in the surface charge or magnetic domains. Surface modification of the magnetite is also possible under the reactive conditions that occur during sonication. In addition, interactions between magnetite particles could be enhanced by their direct contact, which is not possible with capping ligands present. Finally, interaction of the magnetite surface with gold could contribute to changes in the surface states, yielding altered magnetic properties. A control experiment was performed in which magnetite was sonicated under identical conditions but with no  $\text{HAuCl}_4$  present. The magnetic properties for these particles showed decreased saturation magnetization ( $M_s \sim 5$  emu/g) compared to untreated magnetite.

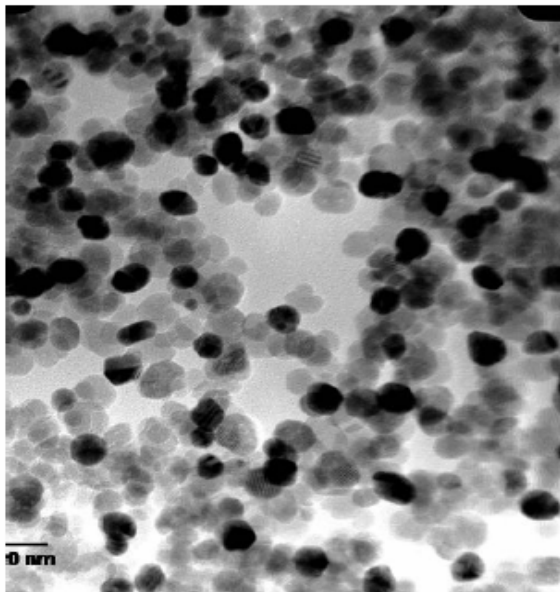
The fact that magnetite sonicated in the absence of gold exhibited decreased magnetization and magnetite sonicated in the presence of gold showed increased magnetization, indicates that interaction of gold with magnetite is a significant factor in controlling the magnetic properties of the composite material.

Additional investigations utilized diethylene glycol or oleic acid in place of methanol. These additives served two purposes: 1) they acted as hydroxyl radical scavengers, thereby promoting the reducing conditions needed for gold metal formation and 2) they acted as capping ligands for the particles. In addition to these functions, the additives were also found to change the gold particle size and the Fe/Au ratio in the composite materials (Table 1). Therefore, adjusting the identity and amounts of these additives may provide a mechanism for preparing gold-magnetite nanocomposite materials with a range of selected Fe/Au compositions and particle sizes.

**Table 1.** The ratios of the Au and Fe in the samples with MeOH, DEG and Oleic acid. Data obtained from the ICP.

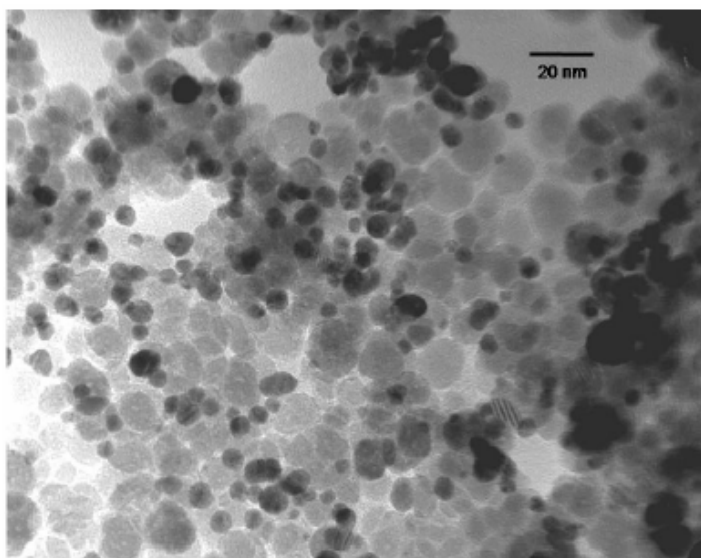
<b>Sample prepared with</b>	<b>Au weight %</b>	<b>Fe weight %</b>
Methanol	26	74
Diethylene Glycol	57	43
Oleic Acid	50.4	49.6

Figure 7 depicts the TEM for gold-magnetite nanocomposite material formed with diethylene glycol as additive, and Figure 8 presents the TEM image when oleic acid was used. When diethylene glycol was used, more uniform gold particles were observed. In addition, the Fe/Au ratio decreased compared to the material prepared using methanol as an additive. With oleic acid added, substantially smaller gold particles were observed, and the Fe/Au ratio decreased even further. EDS data collected for these particles verified the presence of both gold and iron in the nanocomposite material. As for the samples prepared with



**Figure 7.** TEM image of gold-magnetite nanocomposite formed with diethylene glycol additive

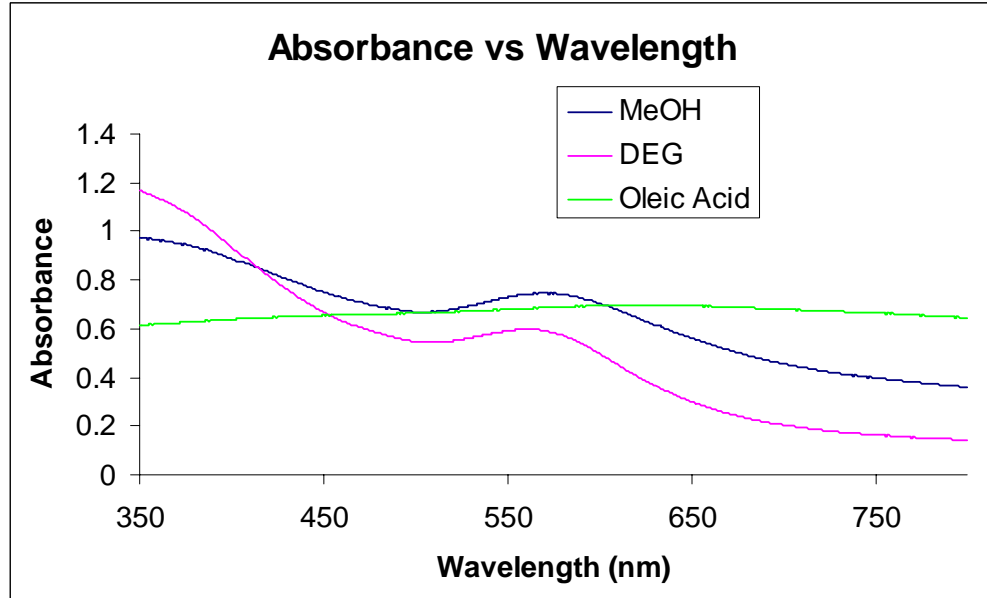
methanol, these particles were collected by magnetic separation, indicating that the gold and magnetite were bound together strongly enough to remain attached and migrate together in the magnetic field.



**Figure 8.** TEM image of gold-magnetite nanocomposite formed with oleic acid additive

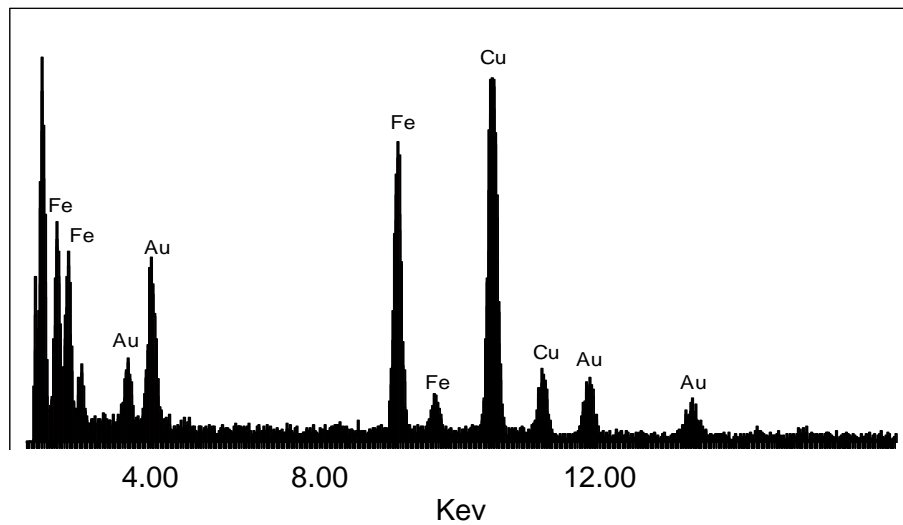


Figure 9 shows the absorbance spectra of the three types of gold magnetite nanocomposites suspended in ethanol. The Au-magnetite nanoparticle



**Figure 9.** The absorbance spectra of the three types of gold magnetite nanocomposites suspended in ethanol.

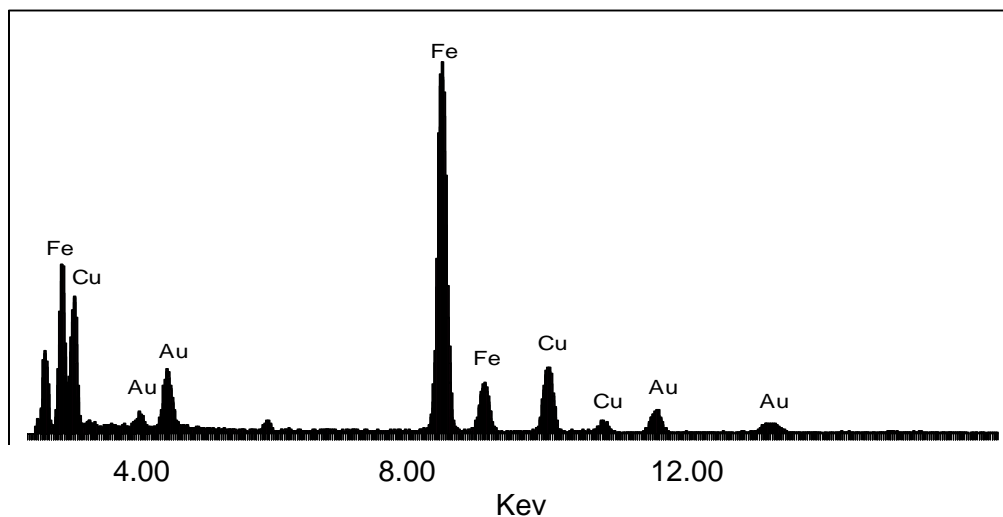
with MeOH shows an absorbance peak at 569 nm while that with DEG showed a maximum at 557 nm. The Au-magnetite nanocomposites prepared with oleic



**Figure 10.** EDS Spectra for the Au-magnetite nanocomposites in DEG

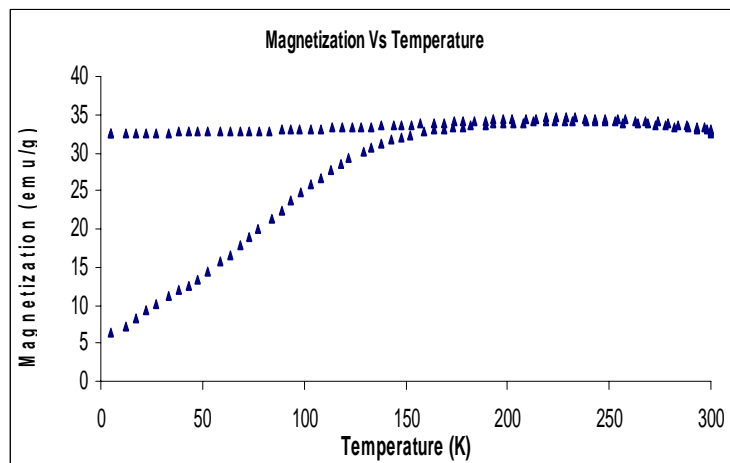
acid did not yield a clear absorbance maximum, possibly due to excessive scattering by the particles.

The EDS spectra for the gold magnetite nanoparticles also show the presence of both Au and Fe. This can be seen in Figures 10 and 11.

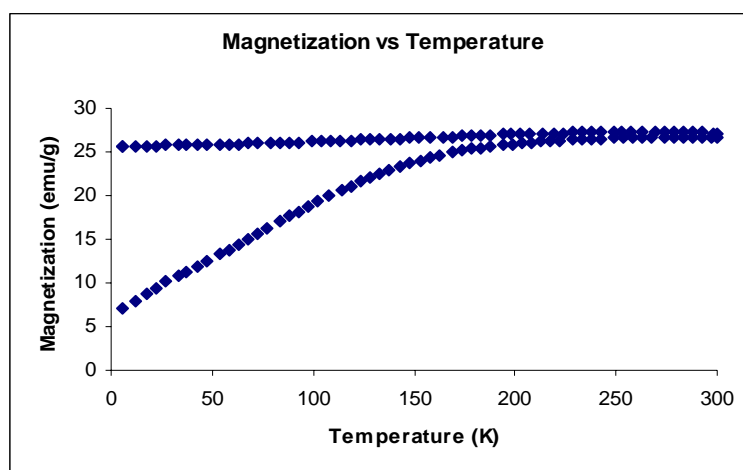


**Figure 11.** EDS Spectra for the Au-magnetite nanocomposites in Oleic Acid

The gold-magnetite nanocomposite material was also characterized to determine its magnetic properties using a SQUID magnetometer. Substantial changes in the magnetic properties of these materials were observed compared to the untreated magnetite precursor material. Figure 12 and 13 shows the magnetization versus temperature plot of the gold-magnetite nanocomposites with DEG and Oleic acid. The general shape of the graphs remained almost similar but the nanocomposites with DEG and oleic acid showed higher magnetization value of  $\sim 33$  emu/g and 27 emu/g respectively. In both cases, the magnetization was normalized to total mass of magnetite in the sample. In addition to the differences in magnetization, the coercivity of the sample



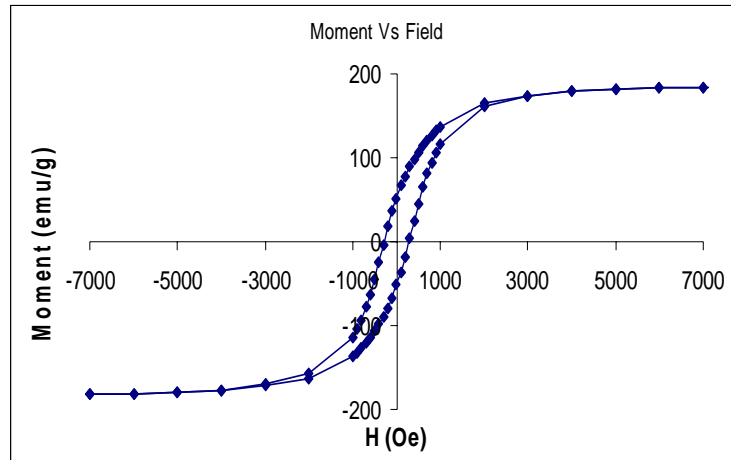
**Figure 12.** Magnetization vs. temperature for gold magnetite nanocomposite material with DEG in 100 Oe



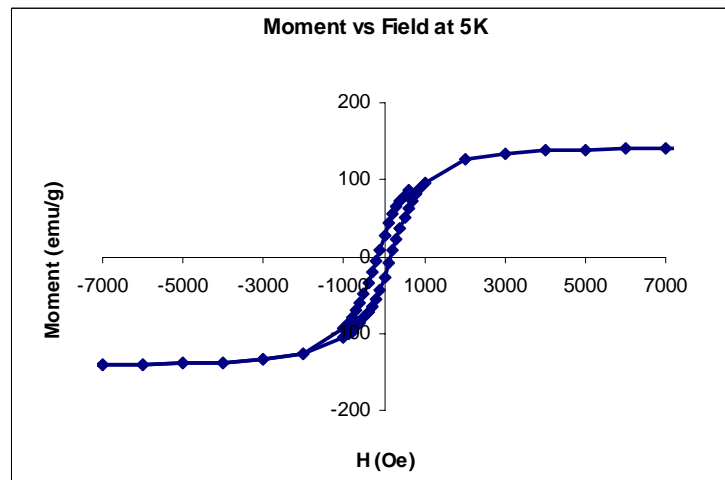
**Figure 13.** Magnetization vs. temperature for gold magnetite nanocomposite material with Oleic Acid in 100 Oe Field.

changed upon formation of the nanocomposite material. The gold-magnetite nanocomposite with DEG as the surfactant had an observed coercivity of 284 Oe, while the gold-magnetite nanocomposite material with Oleic Acid exhibited a coercivity of 155 Oe. These data are depicted in Figure 14 and 15 respectively. Also apparent from the figures, is the significantly

larger saturation magnetization ( $M_s$ ) for the nanocomposite materials ( $M_s \sim 186$  emu/g) and ( $M_s \sim 140$  emu/g) compared to the untreated magnetite ( $M_s \sim 90$  emu/g).



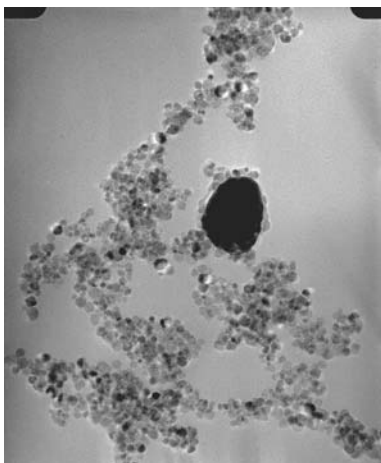
**Figure 14.** Hysteresis loop for gold-magnetite nanocomposite material in DEG at 5K.



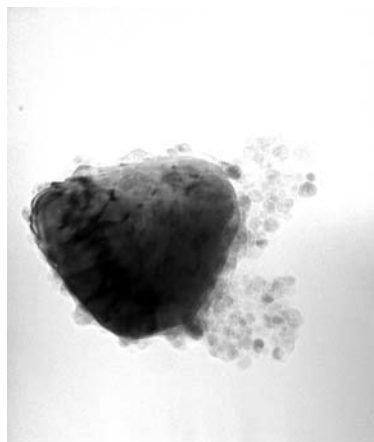
**Figure 15.** Hysteresis loop for gold-magnetite nanocomposite

## Silver Magnetite Nanoparticles

In addition to the studies utilizing gold, we have also investigated the ability to form silver-magnetite nanocomposite materials. Initial experiments met with limited success. While silver-magnetite nanocomposites were formed, there were few silver particles, and those that were formed were relatively large (~50-100 nm) as depicted in Figures 16 and 17. However, as with the gold-magnetite nanocomposite, the silver-magnetite material was magnetically separated, indicating that the silver and magnetite were bound tightly enough to cause the silver to move towards the magnet with the magnetite.



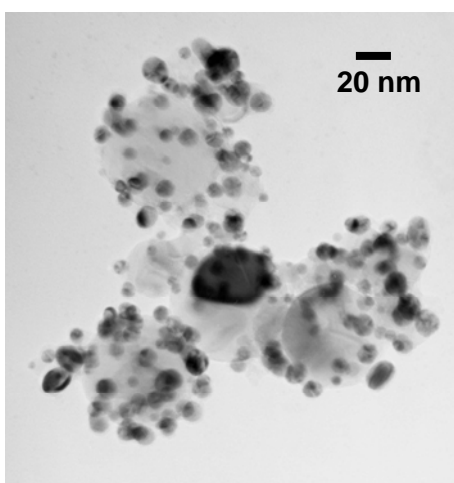
**Figure 16.** Silver magnetite nanocomposites.



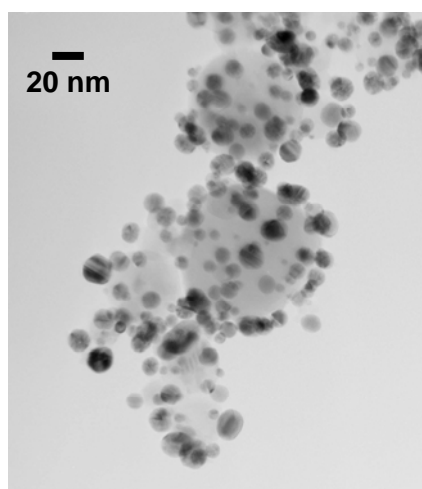
**Figure 17.** Silver nanoparticle with magnetite

## Titanium dioxide-Gold and Titanium dioxide-Magnetite Nanoparticles

Furthermore some preliminary work has been done with titanium. Firstly gold was tried to be coated on titanium by sonochemical process. But we saw no success in this method. So we tried a different approach by using UV light to coat titanium with gold. In this process we became successful and got good results which are shown in Figure 18 and 19.



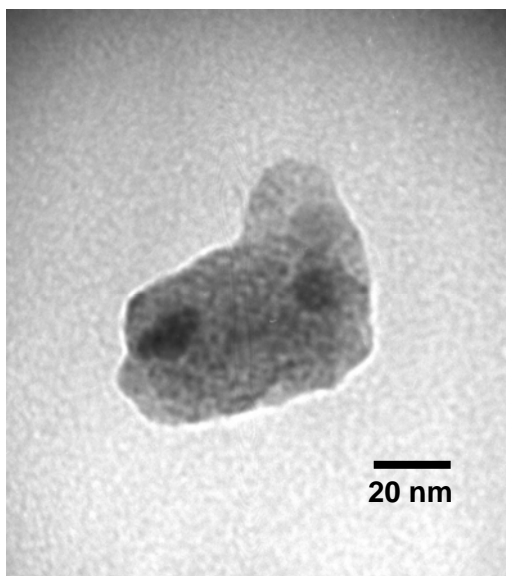
**Figure 18.** The smaller white particles are Au and the large gray particles are TiO<sub>2</sub>.



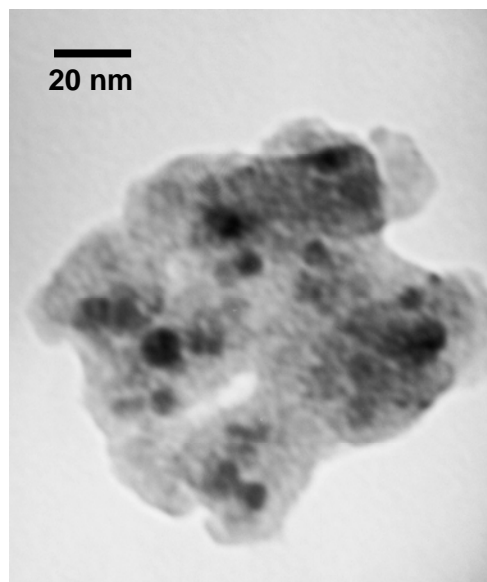
**Figure 19.** TEM image of Au nano particles adhered to the larger TiO<sub>2</sub> particles

Since this was successful we now tried to make these particles magnetic in nature. This would give the particles more useful properties. Firstly they will be magnetic in nature, secondly they will have a photocatalytic surface and moreover it will have a functionizable surface of gold. For this purpose we followed the procedure by R. Amal *et al*<sup>31,32</sup>. They have shown that they were able to coat magnetite with titanium. A sol-gel technique was used during the coating process. This involved the hydrolysis of titanium butoxide in the presence

of magnetite seed particles, and resulted in the deposition of titanium dioxide layer onto the surface of the magnetite particles. The magnetite particles were dispersed in ethanol in an ultrasonic bath. Water was added followed by the rapid addition of titanium butoxide which has been dissolved in a separate volume of ethanol. The final reaction mixture was aged in an ultrasonic bath at a temperature of 20 °C. The reaction was stopped by immersion in an ice-water bath and dilution with ethanol. The grayish black particles that were formed were magnetically separated and washed three times with ethanol followed by two rinses with water. These particles were then dissolved in ethanol and the resulting solution was used for TEM measurements. Several sets of experiments were performed to figure out the appropriate amount of titanium butoxide that needs to be dissolved in ethanol. The Figures 20 and 21 show the TiO<sub>2</sub>-magnetite nanocomposites that were formed when a higher concentration of

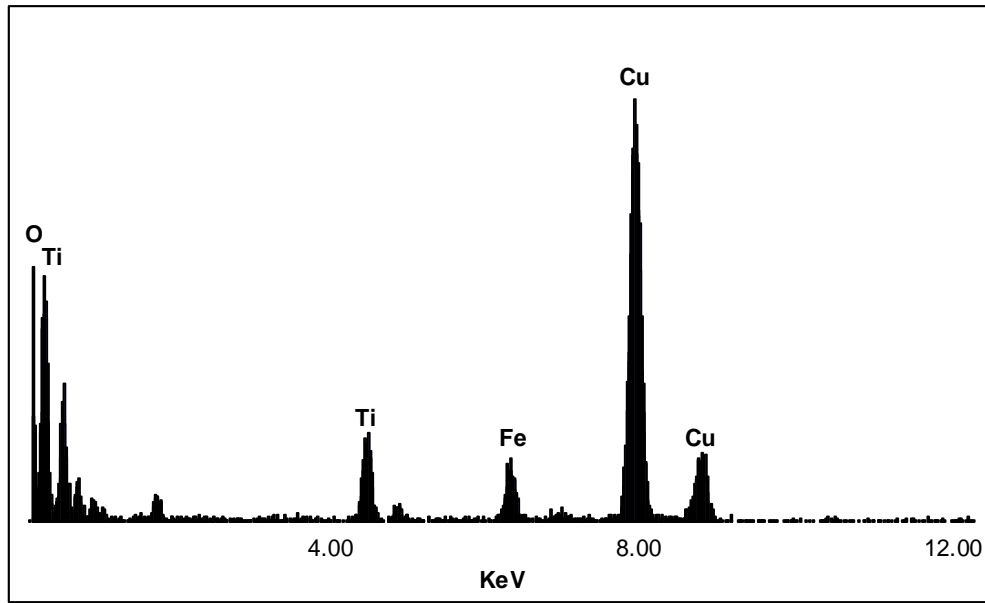


**Figure 20.** TEM image of Titaniumdioxide magnetite



**Figure 21.** TEM image of another Titanium dioxide magnetite nanoparticles

titanium butoxide was added. From the figures it is evident that the darker magnetite particles are covered with the titanium dioxide layer. EDS spectra were taken which show the presence of both Ti and Fe. (Figure 22)



**Figure 22.** EDS spectrum of titanium dioxide – magnetite nanocomposite corresponding to Figure 20



## **Conclusion**

The experiments conducted to date have resulted in a novel method for preparation of gold-magnetite nanocomposite materials. These materials substantially maintain the optical properties of gold. At the same time, the gold can be separated or otherwise manipulated with a magnetic field. The new methodology also includes parameters that can be adjusted to vary the Au/Fe ratio and particle sizes of the gold structures within the nanocomposites. These new particles have potential use in biomedical applications, in sensor applications, and in electronic, optoelectronic, and magneto-optic devices. Furthermore, the fundamental interactions occurring at the gold-magnetite interface are poorly understood. These new nanocomposite materials provide an opportunity to study these interfaces and gain knowledge about interparticle interactions within nanoscale materials.

## Future Research

The future research plan can be broadly divided into three parts:

### a) **Gold magnetite research:**

Further research work will include

- Measuring the magnetic properties as well as the magneto-optical properties of the nanoparticles. But for these experiments we will need large amounts of Au-magnetite nanocomposites.
- Change the concentration of the gold and see the shape and morphology of the particles. All the experiments need to be verified by TEM, EDS, SQUID and ICP.
- Synthesis of gold nanoparticles as well as the synthesis of magnetite particles.
- Further modify the shape and size of the nanocomposites by reacting the preformed gold and preformed magnetite nanoparticles.

### b) **Biomagnetic research**

Nanomaterials are at the leading edge of the rapidly developing field of nanotechnology. Their unique size-dependent properties make these materials superior and indispensable in many areas of human activity. A list of some of the applications of nanomaterials to biology or medicine is given below:

- Probing of DNA structure

- Fluorescent biological labels
- Detection of proteins

The fact that nanoparticles exist in the same size domain as proteins makes nanomaterials suitable for bio tagging or labelling. It can be used as a convenient surface for molecular assembly, and may be composed of inorganic or polymeric materials. There are some developments in directing and remotely controlling the functions of nano-probes, for example driving magnetic nanoparticles to the tumour and then making them either to release the drug load or just heating them in order to destroy the surrounding tissue. The major trend in further development of nanomaterials is to make them multifunctional and controllable by external signals or by local environment thus essentially turning them into nano-devices.

### c) **Titanium-gold-magnetite nanocomposite**

In this part the main focus would be

- Synthesizing smaller Ti nanoparticles
- Varying the irradiation time of the UV light to cover surface of TiO<sub>2</sub> with gold nanoparticles
- Synthesis of Gold coated Magnetite-TiO<sub>2</sub> core shell particles

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## VITA

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