

Novel approach to design magnetic-plasmonic nanohybrids



Thesis Submitted towards the Partial fulfilment of

BS-MS dual degree programme

By

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DEDICATED TO

**ALL THE PEOPLE WHO HAVE BEEN A PART OF
THIS WONDERFUL JOURNEY AT IISER**

CERTIFICATE

This is to certify that this dissertation entitled “**Novel approach to design magnetic-plasmonic nanohybrids**” towards the partial fulfilment of BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Akula Venumadhav**, IISER Pune under the supervision of **Dr. Seema verma**, IISER Pune during the academic year 2013-2014.

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Place:

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Head (Chemical Sciences)

Date:

Date:

Place:

Place:

Declaration

I hereby declare that the matter embodied in the report entitled “**Novel approach to design magnetic-plasmonic nanohybrids**” are the results of the investigations carried out by me at the Department of Chemistry, IISER Pune, under the supervision of **Dr. Seema Verma** and the same has not been submitted elsewhere for any other degree.

AKULA VENUMADHAV

Date:

Place:

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ABSTRACT

Multifunctional magnetic-plasmonic nanohybrid architecture has attracted much interest in the recent years due to its unique magnetic and optical properties. Coupling of these two kind of unique materials is a challenge, which is expected to broaden and open the door for many new exciting applications. With this motivation in mind, the present investigation is planned and demonstrated in different chapters of the thesis. First chapter gives the short introduction to the field of magnetic nanoparticles and their enhanced applications upon integrating with the plasmonic nanoparticles. Though brief but a critical review of literature on the motivation behind the work is presented mainly to answer the following questions: (i) how the combination of unique plasmonic characteristics and integrated functions of multi-component magnetic nanoparticles will find modern applications, especially in the area of biomedicine and electronics. (ii) how the magnetic functionality permits the control of the plasmonic properties by an external magnetic field, which allows the development of active plasmonic devices. (iii) what should be the strategy to obtain stable magnetic-plasmonic nanohybrids since silver is prone to get oxidized. The second chapter presents the brief description of the novel low temperature synthetic routes which allows obtaining multifunctional magnetic - plasmonic nanohybrids. Novel approach to further design the nanohybrid structures by appropriate surface functionality is briefly discussed in the second chapter. A brief discussion on different experimental tools employed to characterize the nanohybrids for structural, magnetic, optical behaviour. Results and discussion chapters are planned according to the systematic progress in the synthetic routes and the challenges faced to obtain the stable silver nanoparticles while integrating that to the magnetic nanocrystals. We have put an attempt to introduce a new synthetic route and demonstrate a generic approach to form stable dispersion of magnetic-plasmonic nanohybrids in hydrophobic media by using appropriate surface functionalities.

CHAPTER I

INTRODUCTION

This chapter demonstrates a brief introduction to the field of magnetic nanoparticles and their enhanced applications upon integrating with the plasmonic nanoparticles. A brief but a critical review of literature on the motivation behind the work is presented mainly to address how the combination of unique plasmonic characteristics and integrated functions of multi-component magnetic nanoparticles will find applications, especially in the area of biomedicine and electronics.

1. Introduction

Nanoscience is the study of structures and materials on the scale of nanometers. It has gained a lot of prominence because of the properties exhibited by nano-size particles in the size range of 1-100 nm which differ greatly from the bulk materials.¹ The properties exhibited by nanomaterials are due to the high surface to volume ratio and the quantum effects. Nano materials are pursued not only because of the novel properties that are shown at the nano level but also because of the wide range of technological applications like high performance materials, energy production and storage information processing.² Combination of the properties of various nano-scale components to make hybrid nanomaterials has been the aim in the recent years. Such approaches give enhancement in chemical reactivity, optical, electronic, thermal properties. In this present investigation, we present novel synthetic routes to obtain multifunctional magnetic - plasmonic nanohybrids. An effort is made to further coat the nanohybrids with a shell layer of silica and then with silver nanoparticles which improves stability of the nanohybrids and facilitates the easy labelling of the silica surface with small biological molecules suitable for biomedical applications.

1.1 Magnetic Nanoparticles

Magnetic nanoparticles have been of great interest for a very long time because of the diverse physical phenomena it exhibits. The numerous applications of magnetic materials, ranging from compass to spintronics make them one of the most important and extremely interesting areas of modern materials research. The main emphasis, at present, is on the synthesis and multi-functionalization of the nanoparticles in order to explore variety of modern technological and biomedical applications for the benefit of human kind. Magnetic nanoparticles have been extensively studied for their application in various disciplines like magnetic fluids,³ catalysis,^{4,5} biotechnology, biomedicine,⁶ magnetic resonance imaging,^{7,8} data storage,⁹ and environmental remediation.^{10,11}

Magnetism in a solids is an intrinsic property that is exhibited by different magnetic ions or atoms distributed throughout a regular crystalline lattice or equivalent sites.

Nanosized magnetic materials are of special interest because the magnetic properties change drastically when the size of a magnetic particle is reduced below 100 nm and the modified properties are useful in many applications and devices. When bulk magnetic materials are reduced to nanometer size range, changes in several magnetic properties take place. The interesting and sometimes unexpected properties of the magnetic nanoparticles are partly due to the aspects of the surface of the materials dominating the properties in lieu of the bulk properties. The percentage of atoms at the surface of a particle becomes significant as the size of the material approaches the nanoscale. Depending upon the magnitude and the interactions between different magnetic ions, there exist different types of magnetization behaviour which are paramagnetism, ferromagnetism, ferrimagnetism and antiferromagnetism. The essence of paramagnetism lies in the criterion that there is hardly any interaction between the individual magnetic moments in a long range ordered crystalline lattice. In order to achieve the saturation magnetization of a paramagnet, where all the moments align parallel to the direction of the applied field, very high magnetic fields are required, simultaneously with very low temperatures. Ferromagnetic, ferrimagnetic and antiferromagnetic materials exhibit long-range cooperative ordering of the moments in the lattice. For ferro- and ferrimagnetic substances, the field dependence of magnetization is nonlinear and at large values of H , the magnetization M becomes constant at its saturation value M_s , as shown in Figure 1.1. But once saturated, a decrease in H to zero does not reduce M to zero. Hence it possesses some magnetization called remnant magnetization (M_R). In order to demagnetize the substance after saturation, a reverse field is required. The magnitude of this field is called coercivity (H_c). The M - H curve in the case of ferro- and ferrimagnets is called the magnetic hysteresis loop. Depending upon the value of magnetocrystalline anisotropy energy values which is responsible for holding the magnetic moment vectors along a particular preferred crystallographic axis, the hysteresis loop can be fat (for hard magnetic materials) or thin (for the soft magnetic materials)¹². The mechanism of magnetization is a result of conversion of multidomain structure to the single domain structure owing to the domain wall motion and domain rotation as represented in the Figure 1.2.

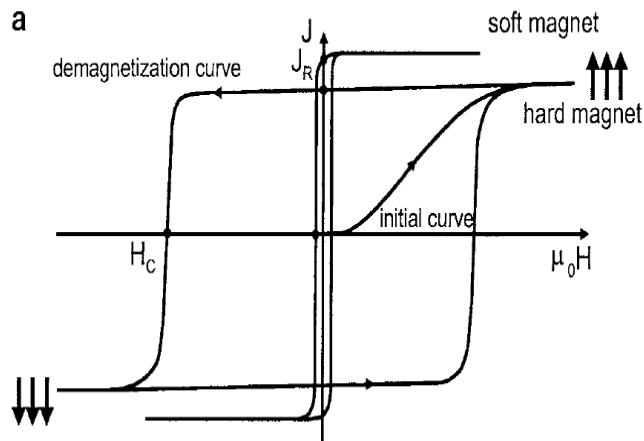


Figure 1.1: Field dependent magnetization in the hard and the soft magnetic materials.

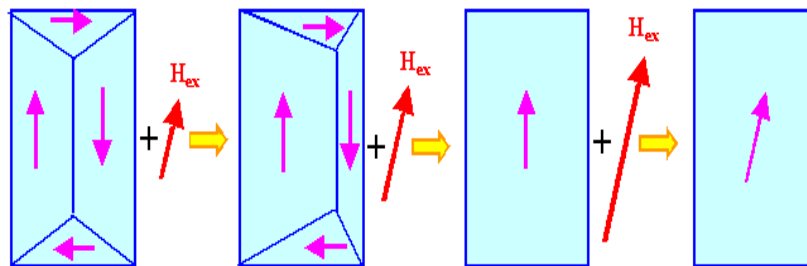


Figure 1.2: Growth of the favorably oriented domain towards the direction of field.

Fine particle magnetism has been traditionally dealt with the size effect, which is based on the magnetic domain structure of the magnetic materials. It assumes that the state of lowest free energy of ferromagnetic particles has uniform magnetization for the particles less than a certain critical size (single domain particles) and non uniform magnetization for the particles larger than the critical size (multi domain particles). As the particle size decreases toward some critical particle diameter, the formation of domain walls becomes energetically unfavorable and the particles are called single domain. Changes in the magnetization can no longer occur through domain wall motion and instead require the coherent rotation of spins, resulting in large coercivities. Nanosized magnetic materials exhibit behavior similar to paramagnetism at temperatures below the Curie or the Neel temperature. Consider an assembly of uniaxial, single-domain particles, each with an anisotropy energy density $E = K \sin^2\theta$, where K is the anisotropy constant and θ the angle between M_s

and the easy axis. If the volume of each particle is V , then the energy barrier ΔE that must be overcome before a particle can reverse its magnetization is KV . Now in any material, fluctuations of thermal energy are continually occurring on a microscopic scale. In 1949 Néel pointed out that if single-domain particles became small enough, KV would become so small that energy fluctuations could overcome the anisotropy forces and spontaneously reverse the magnetization of a particle from one easy direction to the other, even in the absence of an applied field. This is just like the behavior of a normal paramagnetic, with one notable exception. The magnetic moment per atom or ion in a normal paramagnetic is only a few Bohr magnetons. But a spherical particle of iron 50\AA in diameter contains 5560 atoms and has the relatively enormous moment of $(5560)(2.2) = 12,000 \mu_B$. As a result, Bean coined the very apt term superparamagnetism to describe the magnetic behaviour of such particles¹³. Superparamagnetism is a unique and important feature of magnetism in the nanosized particles. When E_A becomes comparable to thermal activation energy $k_B T$ where k_B is the Boltzmann constant, the magnetization direction starts flipping randomly and goes through rapid superparamagnetic relaxation. The temperature above which the thermal activation energy overcomes the magnetic anisotropy energy barrier and the nanoparticles become superparamagnetically relaxed is known as the superparamagnetic blocking temperature, T_B . Saturation magnetization of nanoparticle is also strongly dependent on their size. Intrinsically, magnetic materials possess magnetically disordered spin glass like layers near the surface due to the reduced coordination and broken exchange interactions at the surface.¹⁴ In bulk cases, since the disordered surface layer is minimal compared with the total volume of the magnet, such surface spin canting effects are negligible.¹⁵ Usually, superparamagnetic particles are characterized by a maximum in the temperature variation of ac susceptibility and zero-field-cooled (ZFC) susceptibility measured in a small dc magnetic field. The temperature at which a maximum is observed is the superparamagnetic blocking temperature T_B . When the same sample is cooled under a magnetic field (FC), the magnetization remains almost constant or deviates below the blocking temperature and overlaps with the ZFC magnetization when the temperature rises above T_B . Such temperature dependence of the ZFC magnetization and the divergence of ZFC and FC magnetization below T_B are the characteristic features of superparamagnetism. Typical low temperature

magnetization behaviour and the expected opening of the hysteresis loop are shown in the Figure 1.3.

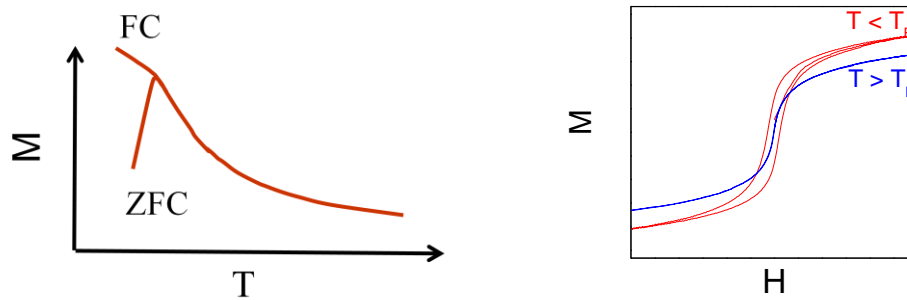


Figure 1.3: Typical FC and ZFC magnetization curves and field dependent magnetization behaviour below and above the blocking temperature of superparamagnetic nanoparticles

Cobalt ferrite is a hard magnetic material (hard to magnetize and demagnetize) which has the spinel structure and they exhibit high coercivity values. It is known for the high electromagnetic performance and photomagnetism. It has high wear resistance, chemical stability and high Curie temperature value. This makes cobalt ferrite one of the most promising and most effective materials to be used for applications like MRI, data storage, magneto-optic devices, and high performance catalysts. The properties of the magnetic field depend mostly on the morphology of the nanoparticles which in turn depends on the method of preparation of the compound. The other magnetic material mostly studied for its biomedical applications is iron oxide. Though, like cobalt ferrite nanoparticles iron oxide also possesses spinel structure, due to its small anisotropy energy value it is considered to be a soft magnetic material (easy to magnetize and demagnetize) is suitable for microwave applications. The distinguishing characteristic of these materials is high permeability, and it is chiefly this flux-multiplying power of the magnetically soft materials that fits them for their job in machines and devices.

1.2 Metal Nanoparticles:

Metal nanoparticles have fascinated scientist for more than a century due to its huge potential applications in the area of biomedicine and engineering. Metal nanoparticles like gold and silver have achieved great prominence in recent times because of their unique electronic, optical and catalytic properties different from the corresponding bulk materials. These properties depend mainly upon the size, shape and composition of nanoparticles.¹⁶ As the size and shape of the noble metal nanoparticles changes, the observed colour also changes. The change in colour is due to the collective oscillation of the electrons in the conduction band, also known as surface plasmon oscillation. The surface plasmons are the waves that propagate along the surface of the metal. These waves are essentially the light waves trapped on the metallic surface due to their interaction with the free electrons. The interaction of the light with the metal nanoparticles results in the collective oscillation in the free electrons in resonance with the light wave. This resonant interaction between the surface charge oscillations and the electromagnetic field of light constitutes unique phenomena called surface plasmon resonance (SPR). SPR is related to the localization, guiding and manipulating the electromagnetic waves down to the nanometer-length scale. Also, by altering the structure of the metal surface, the properties of the surface plasmons especially their interaction with light can be tailored which can be explored further for their potential applications in optics, magneto-optic data storage, light propagation and bio-photonics etc.¹⁷ The noble metals exhibit a strong surface plasmon resonance in the range of visible light which can be further explored in the development of biosensors for detecting biologically interesting molecules.¹⁸ The SPR can be utilized for electric field enhancements that can be used to manipulate light – matter interactions. For example, metallic structure much smaller than that of the wavelength of light is vital for the signal enhancement important for the many fold enhancement concentrate light In terms of plasmonics. It is important to choose a metal that can support a strong SP at the desired resonance wavelength. Among all the metals, Ag has played the most important role in the development of plasmonics, and its unique strong SPR properties make it well-suited for most of the next generation plasmonic technologies. However, poor chemical and structural stability of Ag nanoparticles prevents the broad applications of Ag in place of Au nanoparticles in the SPR sensing. It has been observed that the plasmonic

behavior of Ag is almost destroyed when it is exposed to air, oxidative agents etc making it unsuitable for SPR sensing. Therefore, it is essential to develop the strategies to stabilize the silver nanoparticles while retaining their excellent plasmonic behaviour for effective use in SPR sensing. There are many strategies which can be utilized to stabilize the silver nanoparticles. The surface of the silver nanoparticles can be protected by modifying the surface of the particles either by organic or inorganic materials. In this respect, mesoporous silica coating is the most important step which not only enhances the stability of the silver nanoparticles but also allows further loading of the silica shell with various functional groups for biomedical applications. One of the most important biomedical applications of silver nanoparticles is that they act as effective antimicrobial agents.¹⁹ Recent studies indicate that gold and silver have ability to inactivate protein expression and weaken DNA replication. Bacteria develop resistance to all the antibiotic drugs whereas they cannot easily develop any resistance to noble metals because of the multiple target sites. Antimicrobial properties of these metals are due to their affinity to sulphur and oxygen. The cells are affected by the interaction of noble metals with thiol-containing proteins and DNA. Noble metals are also used for photo thermal applications. Due to the absorption of radiation by different materials they release thermal energy which is effectively and specifically kill cancer cells only.

1.3 Multifunctional magnetic-silver nanohybrids

Multifunctional magnetic-plasmonic nanohybrid architecture has attracted much interest in the recent years due to its unique multimodal magnetic and optical properties. Magnetic nanoparticles have been utilized for its technological and biomedical application such as in high density magnetic recording media, magnetic field driven drug delivery, separation, and hyperthermia and MRI contrast agent. Metallic nanoparticles on the other hand, possess exciting surface Plasmon behaviour to offer capabilities to detect single molecule via surface-enhanced Raman Scattering (SERS), optical imaging via wavelength-tuneable elastic light scattering, photo thermal therapy etc. Indeed, coupling of these two kind of unique materials is a challenge which is expected to broaden and open the door for many new exciting applications. In the present investigation we propose to integrate

magnetic and plasmonic nanoparticles to have multifunctional nanohybrids. It is known that the SERS enhancement of Ag nanoparticles is greater than Au, there has been some concern regarding the biocompatibility, physical and chemical stability of Ag²⁰. Use of transparent mesoporous silica coating on the surface of as-prepared magnetic-Ag nanohybrids will not only increase the biocompatibility of Ag for any biomedical applications on one hand, it would also allow further surface functionalities by embedding silica sphere with Ag nano particles which may act as SERS-dots.

1.4 References:

- (1)Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M *Science* **2001**, 293, 1289–1292
- (2)Wiley, B.; Sun, Y. G.; Xia, Y. *Acc. Chem. Res.* **2007**, 40, 1067–1076.
- (3)S. Chikazumi, S. Taketomi, M. Ukita, M. Mizukami, H. Miyajima, M. Setogawa, Y.Kurihara, *J. Magn. Magn. Mater* **1987**, 65, 245
- (4)A.-H. Lu, W. Schmidt, N. Matoussevitch, H. Bonnermann, B. Spliethoff, Tesche, E.Bill, W. Kiefer, F. Schuth, *Angew. Chem.* **2004**, 116,4403;
- (5)S. C. Tsang, V. Caps, I. Paraskevas, D. Chadwick, D. Thompsett, *Angew.Chem.***2004**,116,5763;
- (6)A. K. Gupta, M. Gupta, *Biomaterials* **2005**,26,3995.
- (7)S. Mornet, S. Vasseur, F. Grasset, P. Verveka, G. Goglio, A. Demourgues, J. Portier,E Pollert, E. Duguet, *Prog. Solid State Chem.* **2006**, 34, 237.
- (8)Z. Li, L. Wei, M. Y. Gao, H. Lei, *Adv. Mater.* **2005**, 17, 1001.
- (9)T. Hyeon, *Chem Commun.* **2003**, 927.
- (10)D. W. Elliott, W.-X. Zhang, *Environ. Sci Technol.* **2001**, 35, 4922.

- (11)I. S. Jacobs, C. P. Bean, Magnetism, Ed. by G. T. Rado and H. Suhl, Academic Press, New York, **1963**, vol. III
- (12)Pastoriza-Santos, Liz-Marzán, L. M. *Adv. Funct. Mater.* **2009**, *19*, 679.
- (13)Bao, J.; Chen, We.; Liu, T. T.; Zhu, Y. L.; Jin, P. Y.; Wang, L. Y.; Liu, J. F.; Wei, Y. G.; Li, Y. D. *ACS Nano* **2007**, *1*, 293–298
- (14)Wang, D.; Li, Y. *Inorg. Chem.* **2011**, *50*, 5196
- (15)Wiley, B.; Sun, Y. G.; Xia, Y. N. *Langmuir* **2005**, *21*, 8077–8080.
- (16)McFarland, A. D.; Van Duyne, R. P. *Nano Lett.* **2003**, *3*, 1057.
- (17)Li, Y. N.; Wu, Y. L.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 3266.
- (18)Wang, W.; Asher, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 12528.
- (19)Henglein, A.; Giersig, M. *J. Phys. Chem. B* **1999**, *103*, 9533.
- (20)Yang, Q.; Wang, F.; Tang, K. B.; Wang, C. R.; Chen, Z. W.; Qian, Y. T. *Mater. Chem. Phys.* **2002**, *78*, 495.

CHAPTER II

Synthesis and Characterization Techniques

This chapter presents a brief description of one-pot wet chemical synthetic routes used for obtaining magnetic-plasmonic nanohybrids. Various relevant synthetic protocols employed to stabilize the silver nanoparticles especially by coating the magnetic-plasmonic nanohybrids by a shell of silica layer are discussed in this chapter. The characterization tools required to characterize structural, magnetic, optical etc. properties of the multifunctional nanohybrids are discussed in detail in this chapter.

2.1 MATERIAL CHARACTERISATION TECHNIQUES

2.1.1 X-RAY DIFFRACTION

X-rays are electromagnetic waves with the wavelength same as the size of the spaces between atoms, so the rays get diffracted. If the atoms of a compound are arranged in a periodic pattern the X-rays get diffracted giving a characteristic Diffraction pattern. Each material has its own diffraction pattern and can be easily identified based on the diffraction pattern. The purity of the sample can be found from the diffraction pattern. It can also be used to find the crystallite size, lattice parameter, and orientation of single crystals, preferred orientation of polycrystals, defects, and strains. The technique can be used to characterize the bulk materials as well as nanomaterials.¹

A powder X-ray diffractometer consists of an X-ray source, a sample stage, a detector and the angle is varied to measure the diffraction pattern. The X-Ray is incident on the sample at an angle of θ and the diffracted ray is measured at angle of 2θ . The incident angle changes with time and the diffracted ray is always at an angle twice of the incident ray. Constructive interference occurs only for a certain angle diffracted where the path difference between them is an integral multiple of the wavelength of light. The equation for constructive interference is given by Braggs Law

$$2d\sin\theta = n\lambda$$

Where, λ is wavelength of the incident X-ray,

d is the interplanar distance,

' θ ' is the scattering angle and

n is an integer-called order of diffraction.

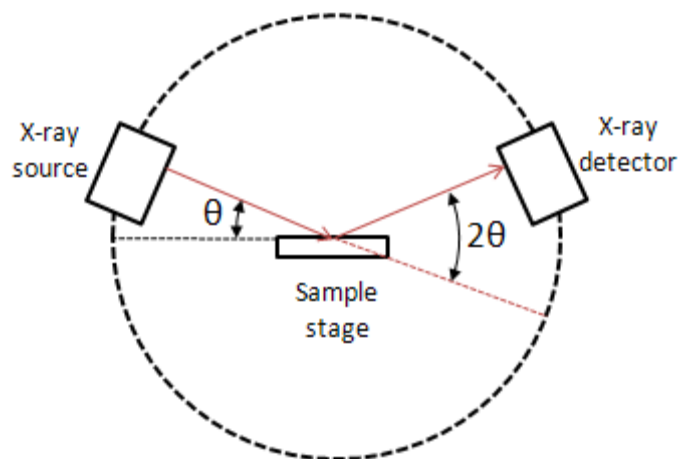


Figure 2.1: Representation of X-ray Diffraction

Characterization and phase purity of the samples were done at room temperature using a model D8 ADVANCE BRUKER diffractometer at IISER Pune equipped with Ni-filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 30 mA). The diffraction patterns obtained (I/I_0 vs. d-spacing) were matched with JCPDS standards. Crystallite size was calculated using Scherrer formula in the framework of the X-ray line broadening technique.²

2.1.2 Microscopy Tools

For the Determination of size and morphology of the nanohybrids Transmission electron microscopy (TEM) & Field Emission Scanning Electron Microscopy (FESEM) were used.

2.1.2a Transmission electron microscopy (TEM)

The working principle of transmission electron microscope is the same as that of a conventional light microscope. The difference between two microscopic techniques is that in the conventional light microscope we use light whereas in transmission electron microscope we use electrons. TEM gives us much better resolutions (thousand folds) because of the smaller wavelengths of the electrons compared to that of the light. So the resolution limit is dependent on the wavelength used. An object of few nanometres can also be seen and studied. Electron beam travels through the sample and depending on the density, the electrons get scattered and some of them pass through the sample giving rise to a shadow image of the sample displaying the densities of the material under study on a fluorescent screen. The

possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research.

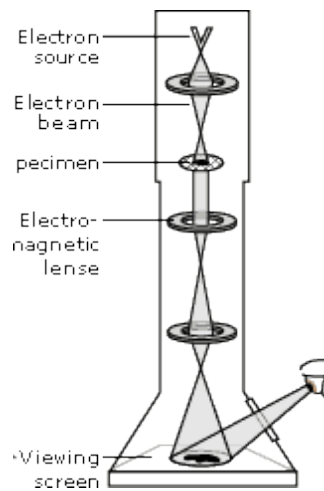


Figure 2.2: Schematic of Transmission electron microscope³

2.1.2b Field Emission Scanning Electron Microscopy (FESEM)

The SEM is a technique that gives detailed information about the morphology of the material. In Field emission microscopy the electrons are ejected from the surface of a conductor caused by electric field. An extremely thin and sharp tungsten needle (tip diameter 10–100 nm) works as a cathode. The Field Emission source reasonably combines with scanning electron microscopes (SEMs). The acceleration voltage between cathode and anode is commonly in the order of magnitude of 0.5 to 30 kV, and the apparatus requires an extreme vacuum ($\sim 10^{-6}$ Pa) in the column of the microscope. Because the electron beam produced by the FE source is about 1000 times smaller than that in a standard microscope with a thermal electron gun, the image quality will be markedly improved; for example, resolution is on the order of ~ 2 nm at 1 keV and ~ 1 nm at 15 keV. Therefore, the FE scanning electron microscope (FE-SEM) is a very useful tool for high resolution surface imaging in the fields of nanomaterials science.

2.1.3 Spectroscopy Tools

With the help of spectroscopic tools extremely sensitive aspects of the electronic structure of multifunctional nanohybrids were studied.

2.1.3a UV-VIS Spectroscopy

It is a technique which deals with the absorption spectrum because of the electronic transitions that occur in compounds. In metals, the free electrons on the surface vibrate with a given absorption frequency and the absorption spectrum is recorded. Absorbance is directly proportional to the path length, l , and the concentration, c , of the absorbing species.

Beer's Law states that,

$$A = \epsilon lc,$$

where ϵ is a constant of proportionality, called the molar absorptivity.

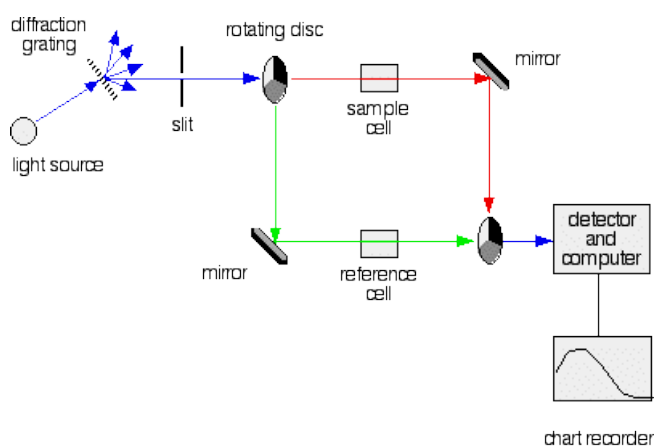


Figure 2.3: Schematic representation of UV –Visible spectrophotometer⁴

All the measurements were conducted in the PERKIN ELMER UV- VIS absorption spectrophotometer at IISER PUNE

2.1.3b Fourier Transform IR Spectroscopy

IR spectrum is a characterization tool to identify the particular bond vibration which has a permanent dipole moment change.⁵ Usually the vibrational features of the bonds are studied in the mid Infrared region from $4000 - 400 \text{ cm}^{-1}$. The energies of the bond vibrations depend on the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling. It helps us to characterize the bonding of the surfactants on the surface of nanoparticles. Mostly covalent compounds can be characterized by this technique.⁶ A compound with few bonds gives simple and highly pure spectrum whereas the compounds with more bonds give complex structures. The detection limit for IR measurements is very low.

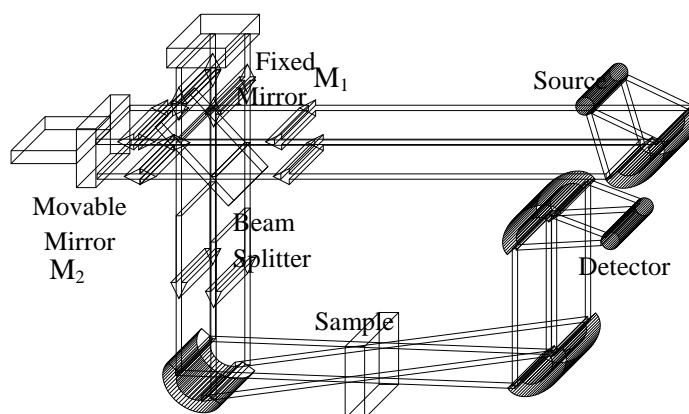


Figure 2.4: Schematic diagram of the IR spectrometer⁷

The final data obtained is fourier transformed. The final signals give transmission of light and wavelength on Y& X-Axis respectively. All the measurements were taken by preparing pellets of IR transparent KBr(Sigma Aldrich, spectroscopy grade) & respective samples in the $400-4000 \text{ cm}^{-1}$ range (Nicolet 6700).The FTIR measurements of these samples were carried out on a Nicolet 6700 FTIR spectrometer at IISER, Pune, INDIA.

2.1.4 Magnetic Property Measurement System (MPMS)

The MPMS SQUID uses a Superconducting Quantum Interference Device (SQUID) Magnetometer to measure very small changes in magnetic flux and so discover the magnetic properties of samples. It is extremely sensitive for all kinds of AC and DC magnetic measurements. Magnetic Moment of the sample can be measured by SQUID. Magnetization and magnetic susceptibility of the samples can be calculated. Measurements of small quantities of paramagnetic ions, characterization of magnetic materials, and determination of the number of unpaired electrons in samples include the applications of MPMS. The MPMS helps to determine sensitive magnetic measurements in key areas such as high-temperature superconductivity, biochemistry, and magnetic recording media.⁸Data can be collected between $H = 0$ to ± 50 kOe and $T = 1.7$ K to 400 K. The sensitivity of this instrument is 10^{-9} emu.

20 to 40 mg is usually required for the measurements but strongly magnetic materials can be taken in lesser quantities. All the magnetic measurements were done in Quantum design MPMS XL instrument at IISER PUNE

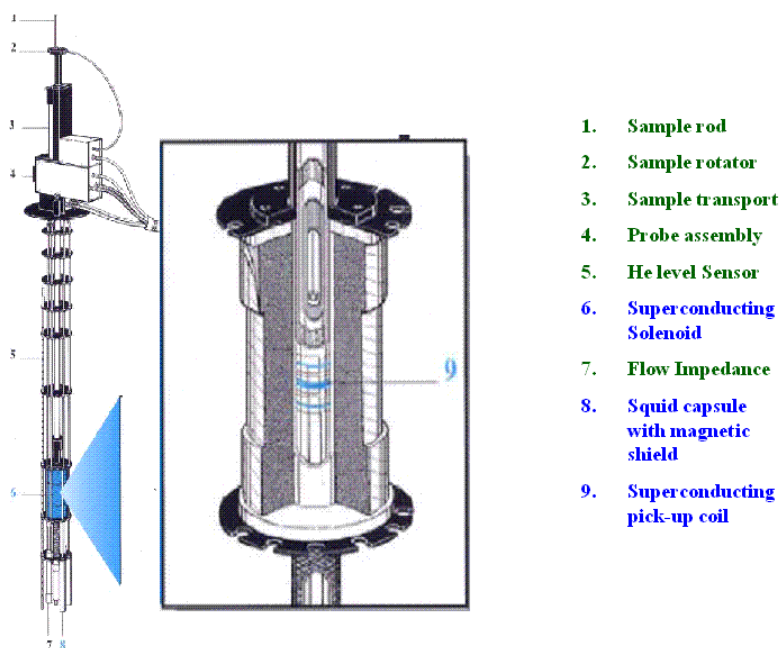


Figure 2.5: Schematic diagram of Magnetic Property Measurement System.⁸

2.2 EXPERIMENTAL

2.2.1 Chemicals

Iron acetylacetonate, Cobalt acetyl acetonate, Cetyl trimethylammonium bromide (CTAB), 1,2 dodecane thiol, 3-Amino propyl Triethyl silicate (APTES), oleic acid (Oa), and oleylamine (Oam), Silver nitrate, Ammonia, TEOS, MUA, MSA, Igepal were purchased from Aldrich Chemicals. N-methyl 2-pyrrolidone (NMP) was purchased from RANKEM Chemicals. All the Chemicals were of analytical grade or better.

2.2.2 One - pot synthesis of CoFe_2O_4 -Ag nanohybrids

Iron acetyl acetonate (0.1M) and cobalt (0.05M) acetyl acetonate were dissolved in 15 ml of NMP. In an RB flask NMP, Oleic acid, oleylamine, 1, 2 dodecanethiol were taken and magnetically stirred in air. The mixture was heated and refluxed at 200 °C. To this solution the magnetic salt solution was injected instantaneously and was further refluxed for 2 hrs. This was followed by a slow addition of 0.15 M silver nitrate solution. The solution was further stirred for another 1 hr under reflux condition. Extraction and magnetic separation was done and the product was collected and dried in vacuum oven.

2.2.3 Mesoporous silica coating on the CoFe_2O_4 -Ag nanohybrids

A micro-emulsion of magnetic particles and CTAB was prepared. Then the emulsion was heated at 60°C for 20 min. This results in water dispersible particles. EtOAc, NH_4OH and TEOS were further added to the water solution. The resulting mixture was stirred for 30 sec, and then aged for 3 h. This resulted in silica coated particles

2.2.4 Water dispersible silver nanoparticles:

AgNO_3 & trisodium citrate solution was prepared in water. A solution of sodium borohydride was prepared. Both the solutions were cooled in an ice bath for 15 min. Then the Sodium borohydride solution was added all at once to the water solution of silver nitrate. The solution was stirred for 30 sec to get nanoparticles. The obtained solution was centrifuged at 5000rpm to collect the silver nanoparticles

2.3 References:

(1) *Elements of X-ray Diffraction*, ed. by B. D. Cullity (Addison Wesley Publishing **1978**).

(2) H.P. Klug, L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd edn., *J. Wiley & Sons, New York, 1974*, 618.

(3) The Transmission Electron Microscope, <http://www.nobelprize.org/tem>

(4) A Double beam UV Visible spectrophotometer

<http://www.chemguide.co.uk/analysis/uvvisible/spectrometer.html>

(5) C. N. Banwell, E. M. McCash, *A Book: Fundamentals of Molecular Spectroscopy*, 4th Ed., Tata McGraw Hill Publishing Co. Ltd., **2002**

(6) J. Coates, *Interpretation of Infrared Spectra: A Practical Approach, Encyclopedia of Analytical Chemistry*, R.A. Meyers (Ed.), 10815, *John Wiley & Sons Ltd, 2000*

(7) Dhanapal Pravarthana, *Multifunctional Magnetic Nanoparticles for Biomedical Applications*, BS-MS Dissertation, **2011**, IISER PUNE.

(8) Materials Research Laboratory at UCSB:

<http://www.mrl.ucsb.edu/tempo-facility/instruments/quantum-design-mpms-5xl-squid-magnetometer>

CHAPTER III

Section I: Results and Discussion

In the present study we provide a simple method to obtain nearly mono-dispersed magnetic - plasmonic CoFe_2O_4 -Ag nanohybrids. We demonstrate a one-pot synthetic route utilizing a high boiling strong polar solvent and oleylamine which acts both as a surfactant and reducing agent. The silver nanoparticles attached to the tiny magnetic nanoparticles are stabilized by silica shell. We discuss the importance, drawbacks and the challenges involved in the present synthetic route adopted for obtaining stable silver nanoparticles. The nanohybrids obtained are characterized by XRD, UV-VIS, FT-IR, FESEM, TEM and MPMS magnetometer.

3.1 INTRODUCTION

In recent times lot of effort is put towards developing a new simple synthetic route to obtain mono-dispersed, uniform nanoparticles.¹ Earlier, we introduced N-methyl 2-pyrrolidone (NMP) as a strong polar solvent for the synthesis of highly mono-dispersed magnetic nanocrystals following thermal decomposition route.^{2,3} In the present investigation we put an attempt to obtain magnetic-plasmonic nanohybrids by a simple one-pot synthetic route utilizing NMP as a high boiling solvent and oleylamine as a surfactant and a good reducing agent. The high boiling point of oleylamine enables it to employ high reaction temperatures which are necessary for the thermal decomposition methods. Earlier, oleylamine is shown to act as a surfactant, solvent, and reducing agent, as a function of other synthesis parameters. Though there are few reports on the synthesis of magnetic oxides, Ag and Ag-Au nanoparticles utilizing oleylamine,⁴ there is no report on integrating the two systems at low temperature utilizing oleylamine and NMP. Therefore, in the present investigation we put an effort to integrate both magnetic oxide and silver nanoparticles in a simple one-pot reaction utilizing NMP as a solvent and oleylamine as a surfactant and reducing agent to convert Ag ion to Ag nanoparticles.

Figure 3.1 shows the representative TEM and FESEM images of CoFe_2O_4 -Ag nanohybrids synthesized utilizing oleylamine. An analysis of TEM micrographs clearly indicated the formation of composite materials with nearly monodispersed silver nanoparticles of average particle sizes of 22 (± 2 nm) and tiny CoFe_2O_4 nanocrystals of an average particle sizes of 4 (± 1 nm). It is important to note that the present results, with the reaction protocol as mentioned in the experimental section of chapter II is not giving the core-shell structure and this is likely to be related to the higher concentration used for obtaining large scale CoFe_2O_4 -Ag nanohybrids. Indeed, further work is needed to obtain core-shell structure in a simple one-pot reaction. The work in this direction by varying the reaction conditions like concentration, injection rate etc is in progress.

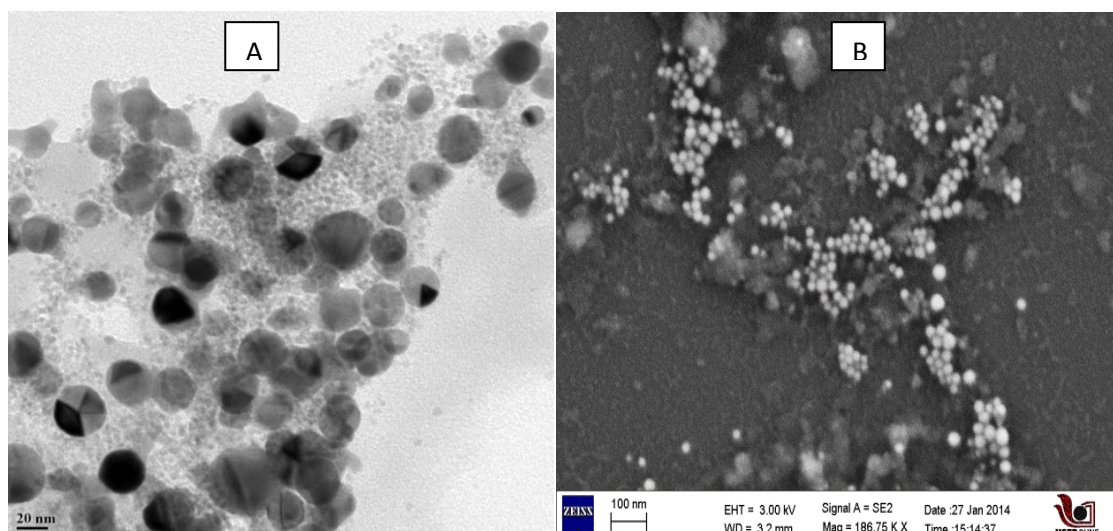


Figure 3.1: (A) TEM and (B) FESEM images of CoFe_2O_4 -Ag nanohybrids

Figure 3.2 shows the XRD spectrum of the CoFe_2O_4 - Ag nanohybrids and is compared to the simulated patterns of bulk Ag and CoFe_2O_4 particles. The XRD peak positions and the relative intensity of all diffraction peaks matches well with the simulated standard patterns of Ag single crystal ($a = 4.086 \text{ \AA}$, JCPDS no.652871). The presence of characteristic peaks of face-centered-cubic (FCC) metallic silver (37.7° , 43.82° and 63.71°) is clearly observed, which confirms the reduction of Ag^+ to Ag.

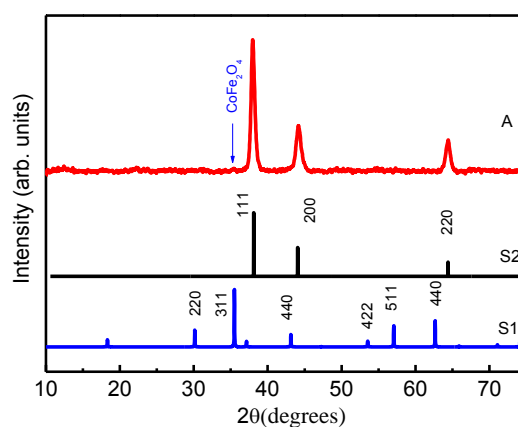


Figure 3.2: (A) XRD pattern of CoFe_2O_4 - Ag nanohybrids. S1 and S2 are the simulated patterns with $a = 4.086 \text{ \AA}$ and $a = 8.3919 \text{ \AA}$, respectively for Ag single crystals and bulk CoFe_2O_4 particles

It is interesting to see that the reflection only due to Ag phase is dominating and the diffraction from the magnetic CoFe_2O_4 phase (see S1 simulated with $a = 8.39 \text{ \AA}$, JCPDS no. 22-1086) is too weak to be observed due to the heavy atom effect of Ag on the surface of the magnetic particles. Moreover the crystallite size calculated from the Debye Scherrer formula indicates the average crystallite sizes of the particles is $24 (\pm 1 \text{ nm})$ which is in clear agreement with that of the TEM particle size.

Figure 3.3 illustrates the characteristic UV - Vis spectra of the $\text{CoFe}_2\text{O}_4\text{-Ag}$ nanohybrids. It clearly shows the red shift and broadening of the characteristic plasmon resonance of oleylamine coated particles. This significant broadening and red shift may be attributed to the presence of larger fraction of aggregates formed with time (see Fig. 3.3 B). It is possible that with the present synthetic protocol having oleylamine acting both as reducing agent and a surfactants for integrating magnetic oxide and silver nanoparticles, results arrangement of closely spaced silver nanoparticles leading to their aggregation with time which can be seen in the figure3.3B

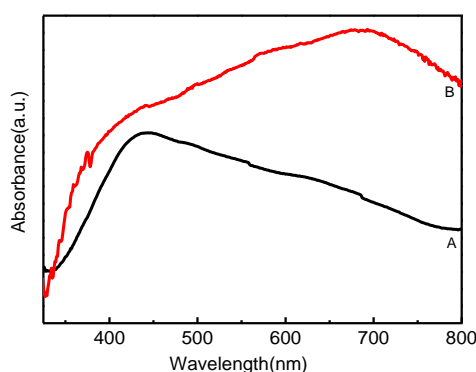


Figure 3.3 :UV - visible spectra of $\text{CoFe}_2\text{O}_4\text{-Ag}$ nanohybrids (A) measured after 24hr of synthesis (B) measured after 3 months of synthesis

In order to understand the adsorption mechanism of the surfactants on the surface of the $\text{CoFe}_2\text{O}_4\text{-Ag}$ nanohybrids, FTIR analysis were performed. Figure 3.4 represents the FTIR spectrum of the nanohybrids obtained with oleylamine as a surfactant. A broad absorption peak corresponding to the antisymmetric deformation of the NH^{3+} group at around 1610 cm^{-1} which is superimposed with that of C=C stretching mode at 1638 cm^{-1} . This clearly reveals the presence of the protonated amines. The characteristic spinel absorption bands at 603 cm^{-1} confirm the formation of

CoFe₂O₄ ferrite phases.^{3a} A strong peak at 3430 cm⁻¹ represents the NH stretching mode clearly indicate the presence of amine group.

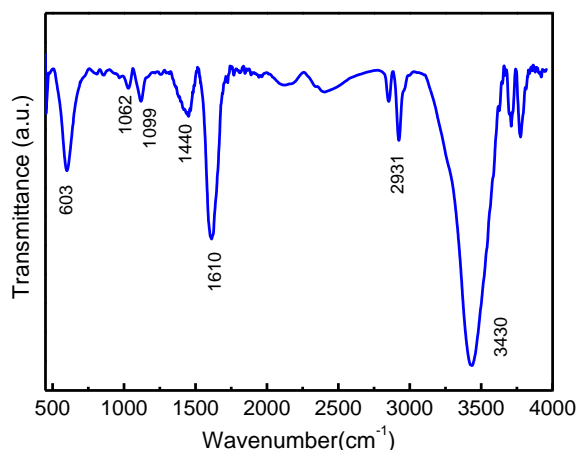


Figure 3.4: FT-IR spectrum of CoFe₂O₄-Ag nanohybrids

Figure 3.5 illustrates the magnetic behaviour of the multifunctional CoFe₂O₄-Ag nanohybrids, investigated with a quantum design MPMS system. Field dependent magnetization behaviour measured at 300 K and 5K is represented in Fig. 3.5A. At room temperature, it is clear that the magnetization does not saturate, even for a strong applied field of 60 kOe and also no hysteresis is observed. This type of MH characteristic is typical of superparamagnetic behaviour.

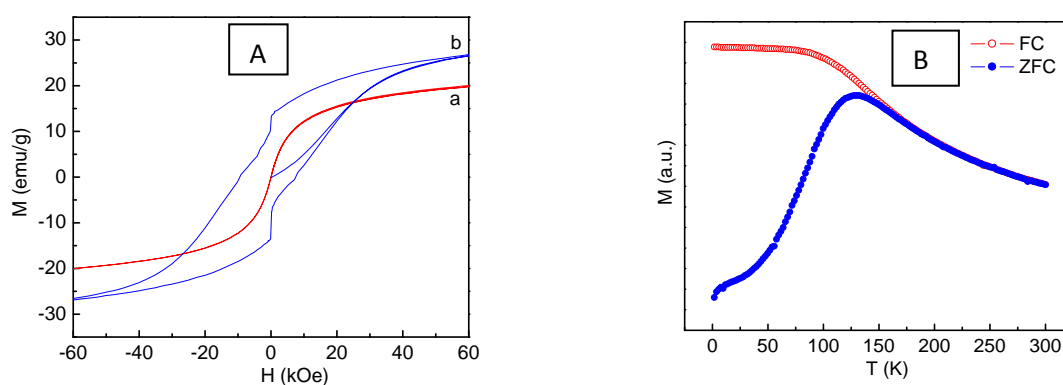


Figure 3.5. Magnetic behaviour of the CoFe₂O₄- Ag nanohybrids. (A) Field dependent magnetization behaviour measured at (a) 300 K and (b) 5K. (B) ZFC and FC magnetization measured at 50 Oe.

The room temperature saturation magnetization value obtained after extrapolating the M vs. $1/H$ curve to the limit of $1/H \rightarrow 0$ is ~ 35 emu/g, which is much less than that of the bulk value of 80 emu/g. The substantial loss in the saturation magnetization value is attributed to the presence of spin canting predominantly on the surface of the nanoparticles. The non-collinear spin structure originates mainly from the reduced coordination and broken exchange interactions on the surface of each particle.

Figure 3.5 B represents the characteristic zero field cooled (ZFC) and field cooled (FC) magnetization measured at a magnetic field of 50 Oe. In ZFC magnetization the sample is cooled from room temperature down to 5 K in the absence of any external applied field and the magnetization is measured while warming the sample in the presence of small magnetic field of 50 Oe. In the field cooled magnetization, the sample is cooled from room temperature down to 5K under the magnetic field of 50 Oe and after reaching the temperature of 5K, the magnetization is measured while warming the sample, in the presence of same magnetic field. In the ZFC magnetization curve, presence of a maximum (T_{max}) is a characteristic feature of superparamagnetism which is observed at ~ 125 K. The bifurcation between ZFC and FC magnetization starts just above the T_{max} . This temperature at which the bifurcation starts is called the irreversibility temperature (T_{irr}). The value of T_{irr} is ~ 142 K which is only ~ 17 K higher than that of T_{max} . T_{max} represents the blocking of particles with mean particle sizes which is also referred as blocking temperature (T_B) whereas the T_{irr} is related to the blocking of largest particles. A smaller difference between the T_{irr} and T_{max} is due to the narrow distribution of anisotropy energy barrier which clearly indicate that the magnetic nanocrystals obtained are highly mono-dispersed. Interestingly, nature of FC plot (a constant magnetization value below T_{max}) indicates the presence of strong inter particle interactions.

Opening of the hysteresis measured below its blocking temperature is expected (see Figure 3.5A). The coercivity calculated is as high as 8585 Oe for this particle and the larger value is due to higher anisotropy energy value associated with CoFe_2O_4 nanoparticles.

3.2 Silica coating on CoFe₂O₄-Ag nanohybrids

The reverse micro emulsion technique has been used to generate hydrophilic particles. The hydrophilic particles are then used for silica coating using modified stober method. The growth of silica particle takes place via Lamer model in which nucleation occurs very fast followed by growth of silica without further nucleation.^{3b}

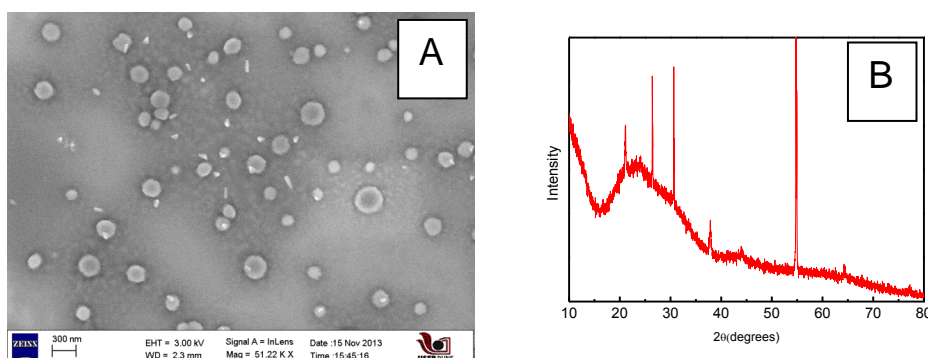


Figure 3.6 : (A) FESEM Image (B) XRD spectrum of silica coated CoFe₂O₄-Ag nanohybrids

Figure 3.6(A) shows the silica coated nanohybrids. The image clearly shows the nanohybrids coated by silica. The particles are spherical and the size of the particles is around 80-100 nm. In the process of silica coating on the nanohybrids the particles were oxidized. The phase transfer of the nanohybrids resulted in the oxidation of CoFe₂O₄-Ag nanohybrids. Figure 3.6(B) shows the XRD spectrum of the oxidized silica coated nanohybrids. This image clearly shows the peaks of both silica and oxidized silver.

3.3 Challenges:

Silver is prone to oxidation even under ambient conditions, and this results in significant changes in the chemical and plasmonic properties of Ag nanoparticles (Ag NPs).⁵ For example, exposure to air or oxygen has been reported to cause a red shift of Ag NP plasmonic bands.⁶ Another example is an interesting observation of the dependence of oxidation of AgNPs on the NP size.⁷ The conversion of particulate Ag⁰ to aqueous Ag⁺ requires an oxidation reaction. It has been observed numerous times that AgNPs are highly sensitive to air and apparently form a surface silver oxide or silver carbonate layer when exposed to air or aerated water, acids,

bases which may make dissolved oxygen the most relevant oxidant for AgNPs in the environment.⁸ The excess electron density is accepted by the particle interior and imparts a more negative redox potential to the AgNP, and thus lowers the free energy barrier to oxidation of nanoparticles.⁹ So this makes silver a very difficult substrate to be used for various SERS applications although it has much better optical properties than gold.¹⁰

3.4 References:

- (1) Yanglong Hou ,Hongjun Gao , and Shouheng Sun *Chem. Mater.* **2009**, 21, 1778–1780
- (2) Liz-Marzan et al *Chem. Mater.* **2013**, 25, 1465–1476
- (3)(a) Seema Verma and D. Pravarthana *Langmuir* **2011**, 27, 13189–13197;
(b) Stober, Fink *Journal of colloid and Interface science* Volume 26, January **1968**, 62-69.
- (4) Hiroki Hiramatsu and Frank E. Osterloh *Chem. Mater.*, **2004**, 16 (13), pp 2509–2511
- (5) Lok, C. N.; Ho, C. M.; Chen, R.; He, Q. Y.; Yu, W. Y.; Sun, H.; Tam, P. K. H.; Chiu, J. F.; Che, C. M. *J. Biol. Inorg. Chem* **2007**, 12, 527–534.
- (6) Ivanova, O. S.; Zamborini, F. P. *J. Am. Chem. Soc.* **2009**, 132, 70–72.
- (7) Yin, Y.; Li, Z. Y.; Zhong, Z.; Gates, B.; Xia, Y.; Venkateswaran, *J. Mater. Chem.* **2002**, 12, 522–527.
- (8) Henglein, A. *Chem. Mater.* **1998**, 10, 444–450.
- (9) Henglein, A. *J. Phys. Chem.* **1993**, 97, 5457–5471.
- (10) Qi, H.; Alexson, D.; Glembocki, O.; Prokes, S. M. *Nanotechnology* **2010**, 21, 215

CHAPTER IV

Section II: Results and Discussion

The present study shows the synthesis of magnetic plasmonic $\text{CoFe}_2\text{O}_4\text{-Ag}$ nanohybrids using both oleylamine and oleic acid as a capping reagents. In order to see whether there is any change on the optical and magnetic properties of the nanohybrids with the change in the molar ratio of silver ions for a fixed amount of magnetic ions, a systematic increase in the amount of silver ions were made. Temperature control experiments were also conducted to see the effect of size, shape & morphology of the nanohybrids. The nanohybrids were coated with silica surface and the details of the synthetic routes, difficulties involved in getting the stable pure phase of silver nanoparticles are discussed in detail. An effort to further decorate the silica nanosphere with that of silver nanoparticles as SERS dots is discussed in this chapter. The nanohybrids were characterized by XRD, UV-Vis spectroscopy, FTIR, FESEM, TEM and MPMS magnetometer.

4.1 CoFe₂O₄-Ag Nanohybrids using both oleic acid & oleylamine

The stability and the assembly of the nanoparticles are largely governed by the properties of their surface. Fatty acid, especially oleic acid, C₁₇H₃₃COOH, is a successfully used surfactant to stabilize the magnetic oxide. Also, oleylamine is well known reducing and stabilizing reagent for metal nanoparticles. Therefore, an appropriate amount of both the surfactants will incorporate the goodness of both the surfactants while coating the magnetic and silver nanoparticles. Introduction of oleic acid may help to prevent the tendency of silver nanoparticles aggregation, its oxidation and further degradation with time. Oleylamine helps the deprotonation of oleic acid and itself gets protonated, thereby forming an acid-base complex.¹ The resulting acid-base complex now acts as a binary capping agent and prevents further oxidation of the nanohybrids.² The binary surfactants will allow COO⁻ to bind to the oxide surface, leaving NH³⁺ to bind to the metal nanoparticles, thereby rendering particle surface hydrophobic which are stable for longer time and are well dispersed in different organic solvents.

In order to grow the silver nanoparticle sizes, we adopted a simple strategy of varying the concentration of silver ions systematically for a fixed amount of the magnetic ions. Change in concentration affects the growth of the particles and is likely to change the diffusion mechanism of silver ions. The variation of the metal ions concentration and the corresponding sample codes with their XRD crystallite sizes are mentioned in the Table 4.1. In order to see the effect of reaction temperature on size, we have adopted another strategy of first synthesizing the magnetic nanoparticles at 200°C and further the silver ions were injected to the magnetic seeds at much lower temperature of 150°C and 80°C. The sample codes and corresponding XRD crystallite sizes are mentioned in the Table 4.2.

Table 4.1: Sample codes, molar ratio of magnetic and silver ions, XRD crystallite sizes for the nanoparticles synthesized at 200°C

Sample Codes	Molar ratio of magnetic : silver ion	XRD crystallite size (± 2 nm)
COFAG-1-1	0.15: 0.15	12
COFAG-1-2	0.15: 0.30	22
COFAG-1-3	0.15: 0.45	23
COF	0.15: 00	5

Table 4.2: The sample codes, reaction temperature of silver nanoparticles and XRD crystallite sizes of the nanoparticles

Sample Codes	Reaction temperature	XRD crystallite size (± 2 nm)
COFAG 150C	150°C	9
COFAG 80C	80°C	6

Figure 4.1- S1 illustrates the UV-Vis spectra of the samples obtained at 200°C. The UV-Vis spectrum of the COFAG-1-1 exhibits a narrow plasmonic distribution around 410 - 415 nm which is a characteristic plasmonic behaviour of small silver nanoparticles. The narrow distribution concludes that the particles produced are highly mono-dispersed.³ For the COFAG-1-2 and COFAG-1-3 nanohybrids a broad distribution and a red shift of absorption spectrum is observed which may be due to the growth and aggregation of the silver nanoparticles. Figure 4.1-S2 shows the UV-Vis spectra of the silver nanoparticles obtained at lower temperature. The nature of the UV-Vis spectra clearly indicates that at lower temperature much smaller particles are obtained and is also evident from the XRD crystallite sizes (see Table 4.2).

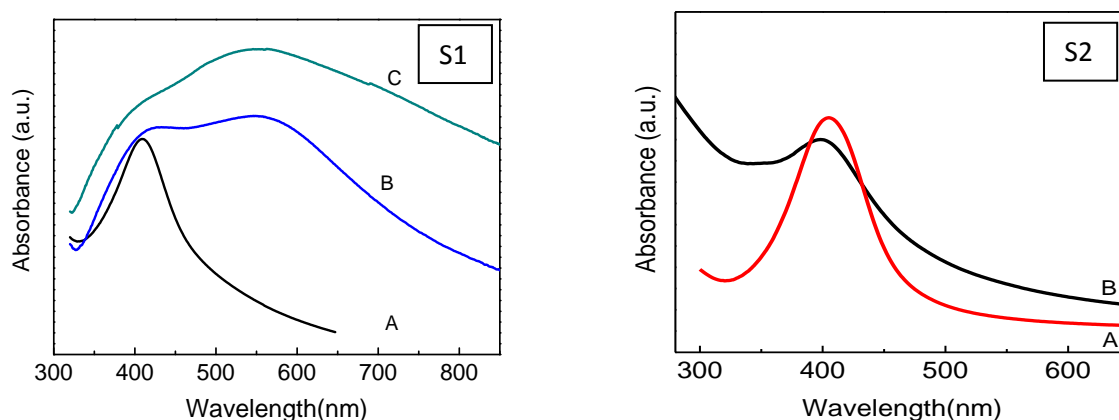


Figure 4.1: (S1): The UV-Vis spectra CoFe₂O₄ Ag nanohybrids synthesized at 200°C for (A) COFAG-1-1 (B) COFAG-1-2 and (C) COFAG-1-3. (S2): Corresponding UV-Vis spectra for (A) COFAG 150C and (B) COFAG 80C

Figure 4.2 A shows the XRD spectrum of the CoFe₂O₄ - Ag nanohybrids and is compared to the simulated patterns of bulk Ag and CoFe₂O₄ particles. The XRD peak positions and the relative intensity of all diffraction peaks matches well with the simulated standard patterns of Ag single crystal ($a = 4.086 \text{ \AA}$, JCPDS no.652871). The presence of characteristic peaks of face-centered-cubic (FCC) metallic silver (37.7° , 43.82° and 63.71°) is clearly observed, which confirms the reduction of Ag⁺ to Ag. It is interesting to see that the reflection only due to Ag phase is dominating and the diffraction from the magnetic CoFe₂O₄ phase (see S1 simulated with $a = 8.39 \text{ \AA}$, JCPDS no. 22-1086) is too weak to be observed due to the heavy atom effect of Ag on the surface of the magnetic particles.

Figure 4.2 B illustrates the XRD diffraction patterns of nanohybrids prepared at different temperatures. Ag nanoparticles prepared at 80°C show the presence of reflections corresponding to both CoFe₂O₄ and Ag particles indicating presence of very small silver nanocrystals with very weak heavy atom effect. However, it is interesting to see that with the increase in the reaction temperature, the XRD reflections corresponding to CoFe₂O₄ disappears on one hand & the broadening of the XRD peak decreases on the other. The XRD crystallite sizes calculated from the XRD line broadening utilizing Scherrer formula is mentioned in the Tables 4.2 and

4.3. It is clear that the heavy atom effect is much prominent for the bigger particles of Ag nanoparticles formed.

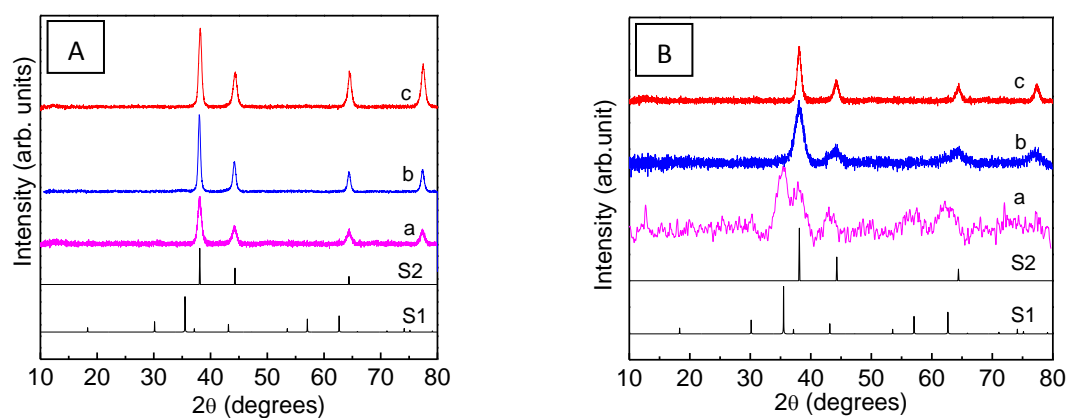


Figure 4.2: (A): X-Ray diffraction patterns of a) COFAG-1-1 (b) COFAG-1-2 (c) COFAG-1-3. S1 and S2 are the simulated patterns with $a = 4.086 \text{ \AA}$ and $a = 8.3919 \text{ \AA}$, respectively for Ag single crystals and bulk CoFe_2O_4 particles. (B): X-Ray diffraction patterns of (a) COFAG-80C (b) COFAG-150C (e) COFAG-1-1

Figure 4.3 shows the FTIR spectra of $\text{CoFe}_2\text{O}_4 - \text{Ag}$ nanohybrids synthesized at conditions. Appearance of symmetric (vs (COO^-)) stretch at ~ 1570 and 1440 cm^{-1} confirm the formation of deprotonated carboxylate.⁵ Moreover, strong bands at 1099 , 1062 cm^{-1} arising from the C-O stretching reveal that two oxygen atoms in the carboxylate are coordinated onto the surface of the nanocrystals. Absence of any 1700 cm^{-1} clearly indicate the absence of any free carboxylic acid due to the presence of unprotonated oleic acid. Presence of peaks around 3430 may be due to the stretching mode of NH bond. However, the broad peak at ~ 3430 may also be due to the presence of OH stretching mode. The characteristic spinel absorption bands at 603 cm^{-1} confirm the formation of CoFe_2O_4 ferrite phases.

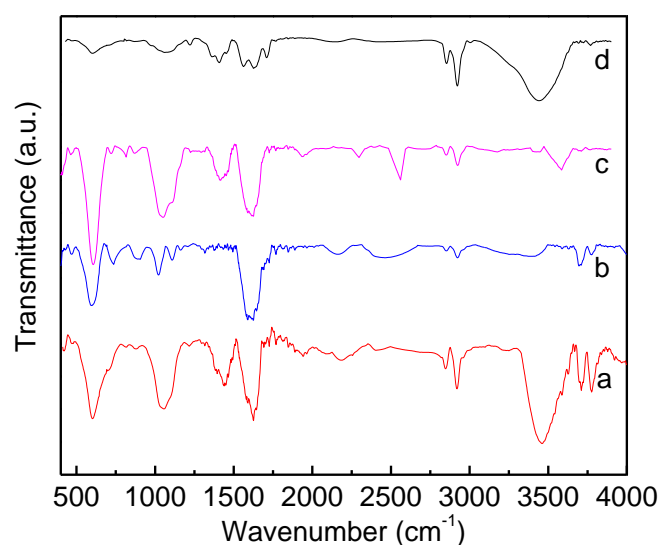


Figure 4.3: IR vibrational frequencies of the $\text{CoFe}_2\text{O}_4\text{-Ag}$ nanohybrids a) COFAG-1-1 (b) COFAG-1-2, (c) COFAG 80Cand (d) COFAG 150C

The morphology and the particle sizes were studied by FESEM and TEM analysis. Figure 4.4 illustrates the FESEM and TEM images of COFAG-1-2. An analysis of TEM micrographs clearly indicated the formation of much denser hybrid materials with nearly monodispersed silver nanoparticles of average particle sizes of $22 (\pm 2 \text{ nm})$ and tiny CoFe_2O_4 nanocrystals of an average particle sizes of $4 (\pm 1 \text{ nm})$. The particle size obtained from the TEM micrograph is in good agreement with that calculated from XRD line broadening using Scherrer formula (see Table 4.1).

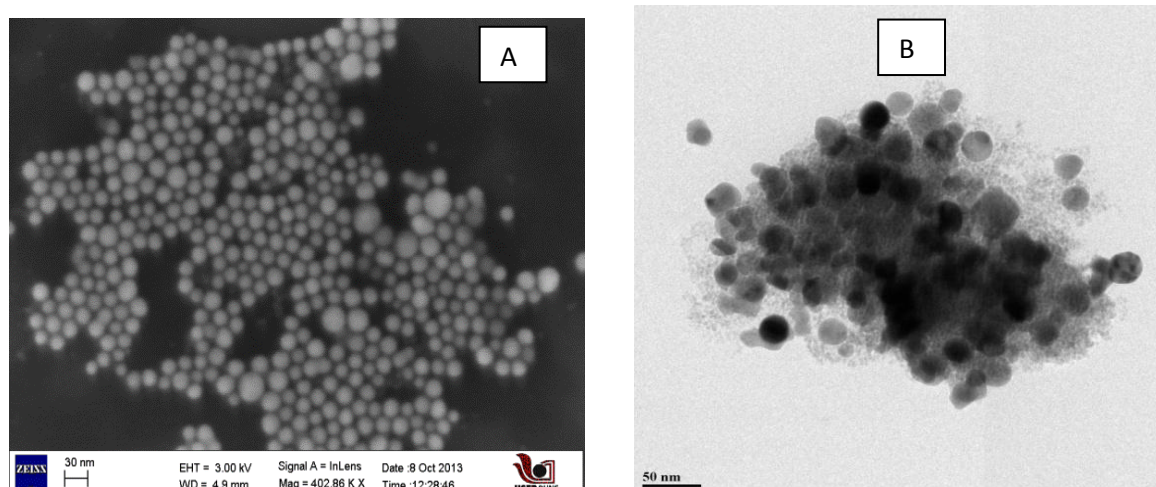


Figure 4.4 (A): The FESEM images and (B) TEM images of COFAG-1-2

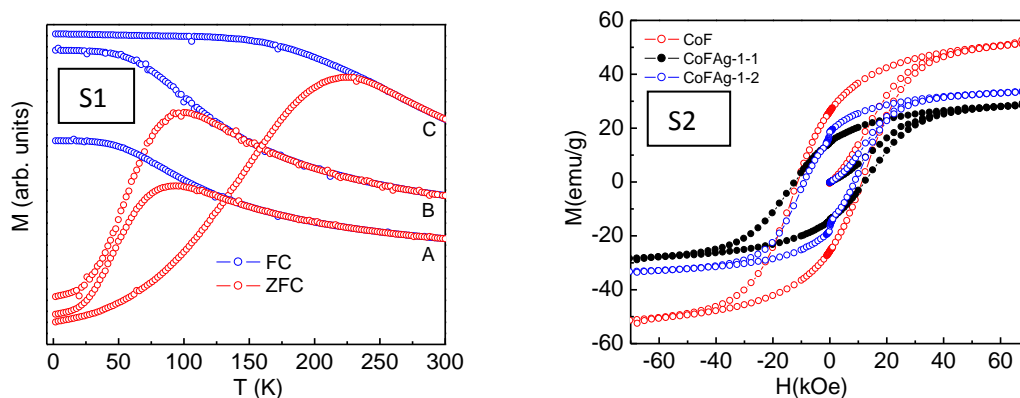


Figure 4.5: (S1): ZFC and FC magnetization curves for (A) CoFe_2O_4 nanoparticles, (B) CoFag1-1 and (C) CoFag-1-2 nano hybrids measured at 50 Oe. (S2): Corresponding field dependent magnetization curves measured at 5 K.

A comparative magnetic behaviour study of the magnetic – plasmonic nano hybrids with that of CoFe_2O_4 nanoparticles is shown in the Figure 4.5. Presence of maxima in ZFC magnetization is a characteristic of the superparamagnetic particles. It is indeed interesting to see that in spite of obtaining the CoFe_2O_4 and magnetic – plasmonic nano hybrids with the fixed initial amount of magnetic ions (see Table 4.1) and having similar sizes of magnetic nanoparticles (see TEM images); the nature of ZFC and FC magnetization curves are significantly different for the COFAG-1-2 nano hybrids as compared to that of CoFe_2O_4 nanoparticles. The blocking temperatures (T_B) are found to increase with the increase in Ag fraction. The blocking temperature values of CoFe_2O_4 nanoparticles and COFAG-1-1 nano hybrids are 89 K and 97 K respectively. Interestingly, for COFAG-1-2 nano hybrids, a large increase in the T_B value to 221 K is observed. Almost constant value of FC magnetization value below T_B clearly indicates that there is a strong interparticle interaction. Therefore, an increase in the anisotropy energy barrier is expected for COFAG-1-2. Figure 4.5S2 represents the field dependent magnetization behaviour of the corresponding samples. It is expected to observe the opening of the hysteresis loop below the T_B values for these superparamagnetic particles.

Phase transfer of these hydrophobic particles has been done using various reagents like Igepal, mercapto undecanoic acid, mercapto succinic acid, CTAB.⁶ In order to counter the oxidization of silver, we tried phase transfer in the presence of strong

reducing agents such as hexadecanediol, sodium borohydride.⁷ In the present investigation we adopted modified Stober method by using combinations of amino acids and reducing agents instead of ammonia. The modified Stober method using acetic acid and citric acid was found to be the better method for obtaining a pure phase of silica coated core-shell structures of nanohybrids. Various concentrations of TEOS have been adjusted to modify the size and thickness of the silica coated particles. In order to confirm the phase purity we performed XRD and UV-Vis spectra of silica coated samples after magnetic separation. To confirm that the silica is coating the magnetic-plasmonic nanohybrids, we have done magnetic separation till the supernatant doesn't give any characteristic UV-Vis absorption. Figure 4.6 represents the FESEM images and corresponding UV-VIS spectra after coating with silica. Presence of plasmonic behaviour even after silica coating confirms that the Ag nanoparticles are stable.

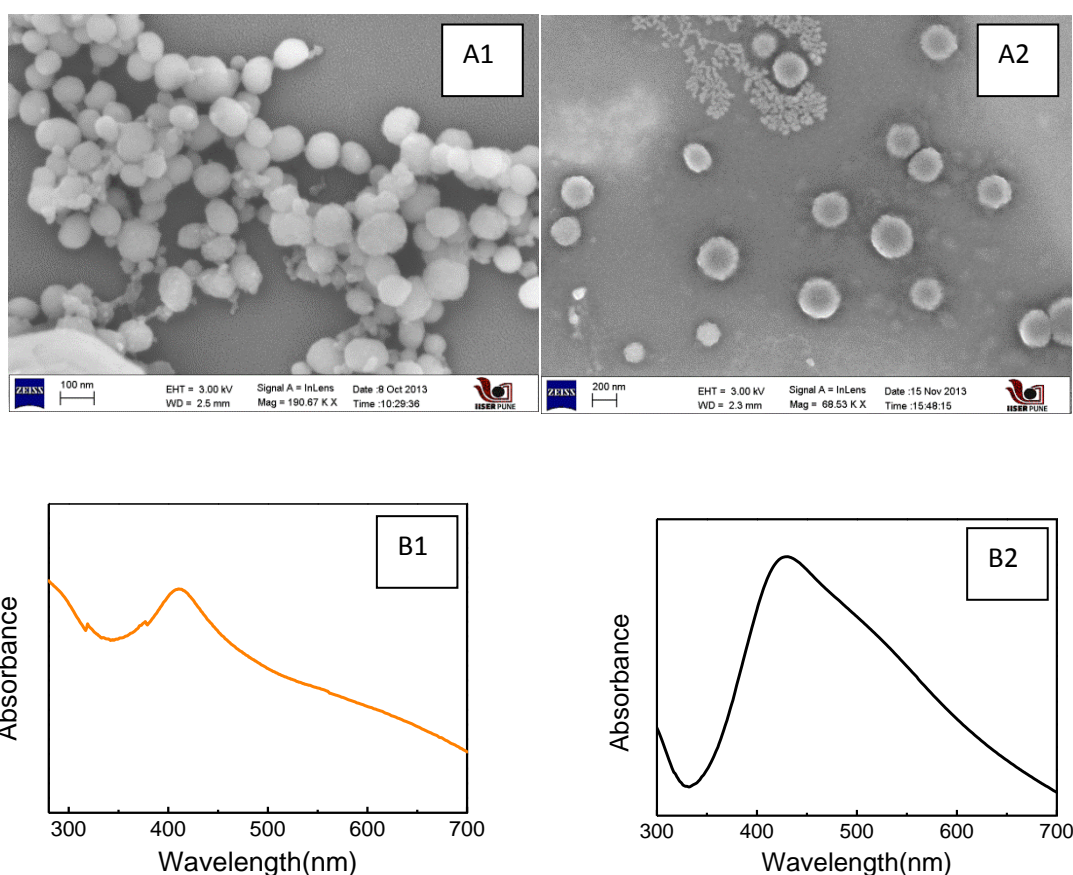


Figure 4.6: (A1 and A2) FESEM images of COFAG-1-1 and COFAG-1-2. (B1 and B2) Corresponding UV-Vis spectrum using Tyrosine, hexadecane diol and CTAB

Figure 4.7 represents the FESEM and TEM images of the silica coated COFAG-1-1 using acetic acid as a stabilizer. Corresponding XRD and UV-Vis spectra of the samples after magnetic separation is shown in the figure 4.7 C and D respectively. The silica coated particles have a spherical morphology and they have retained the plasmonic behaviour of the silver nanoparticles. The size of the silica coated particles obtained was around 60 – 80 nm. More work is indeed needed to vary the thickness of the silica shell in order to have SERS studies.

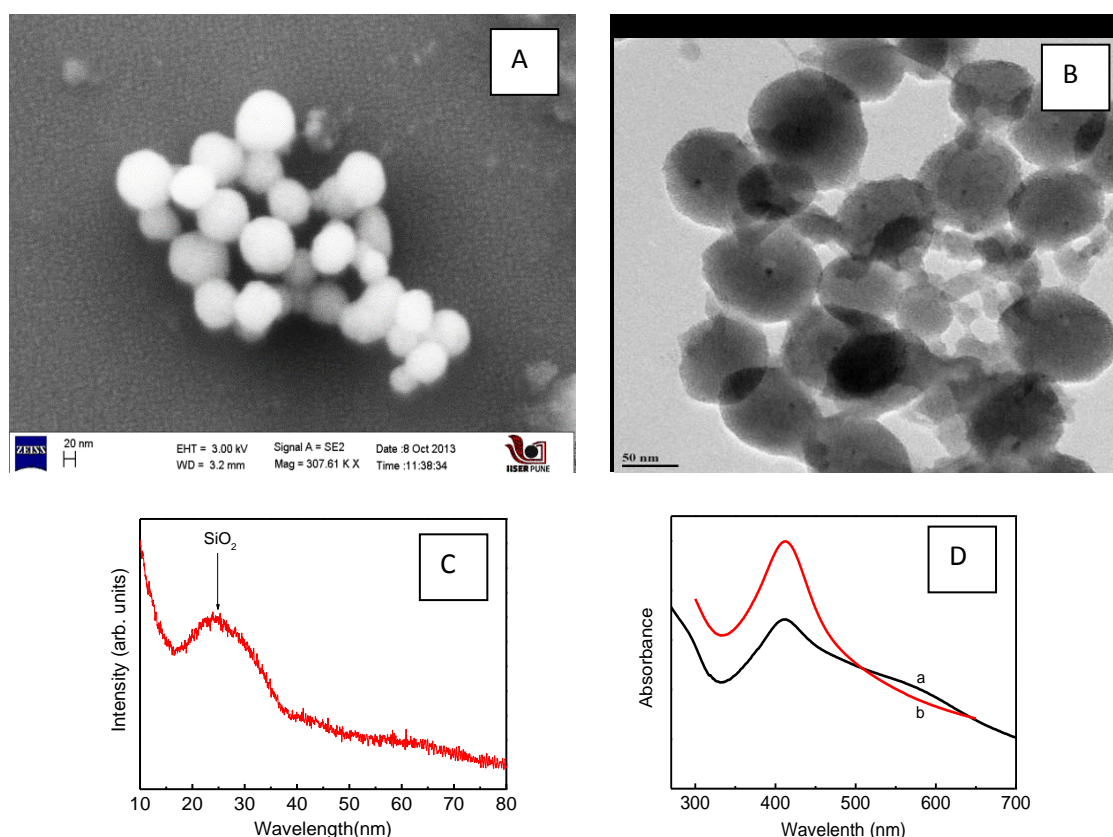


Figure 4.7: (A) FESEM image, (B) TEM images of silica coated COFAG-1-1 using acetic acid. Corresponding (C) XRD pattern and (D) UV-Vis spectra spectra (a) silica coated COFAG1-1 (b) COFAG-1-1

The silica coated nanohybrids were further treated with APTES in order to functionalize the silica shell with the amine group.⁹ The presence of amine group on the surface were confirmed by the high positive zeta potential value as seen from the zeta potential plot in the Figure 4.8. Silica coated nanohybrids had a – ve zeta potential value of -10.4 mV before the APTES treatment. A high + ve zeta potential

value of + 27.0 mV after the APTES treatment confirms the formation of a stable amine functionalized silica coated nanohybrids.

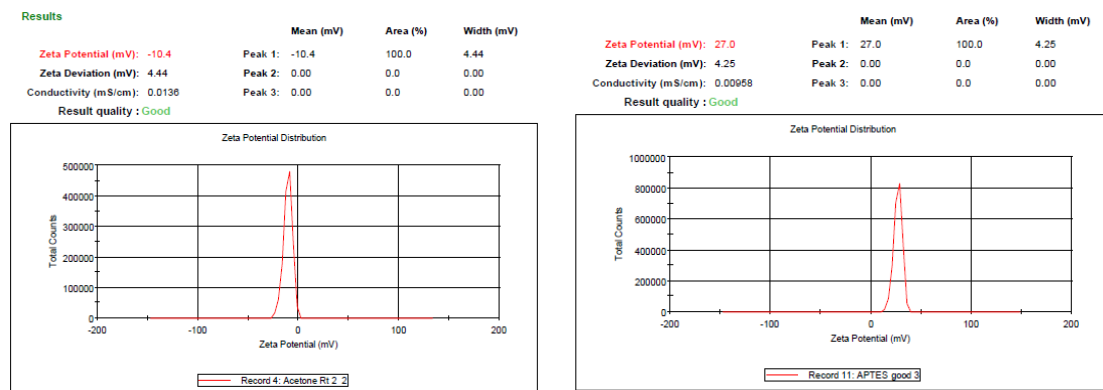


Figure 4.8: Image on the left & right shows corresponding –ve and +ve zeta potential of the silica coated nanohybrids and APTES coated silica particles respectively

The zeta potential was measured after washing the sample with water and further doing magnetic separation. As the amine group has affinity to the silver, this could prove to be an excellent surfactant for the further attachment of silver nanoparticles.¹⁰ This amine functionalized silica coated particles are further treated with silver nanoparticles to embed the surface of the mesoporous silica, which may possess exciting surface plasmon behavior to offer capabilities to detect single molecule via surface-enhanced Raman Scattering (SERS).

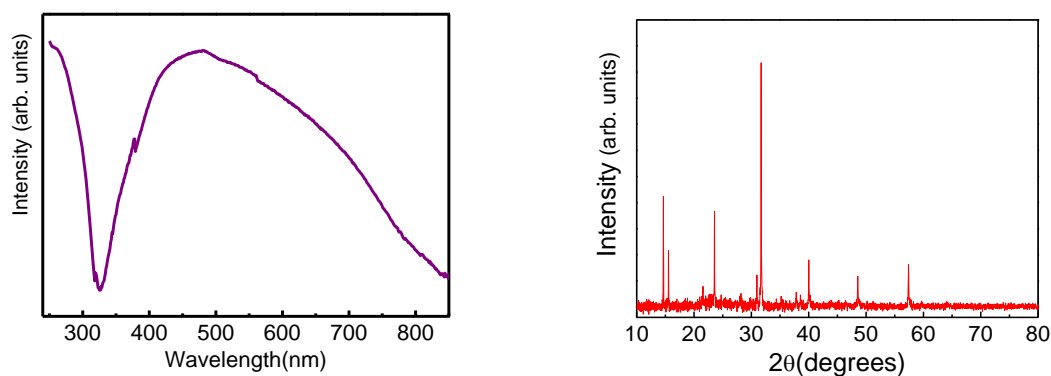


Figure 4.9: UV-Vis spectra and corresponding XRD after treating amine functionalized silica with of silver nanoparticles

Figure 4.9 clearly show the presence of plasmonic behaviour indicating the attachment of Ag nanoparticles on the surface of mesoporous silica. However, XRD analysis done on the same sample after a few weeks indicated the oxidation of the

silver nanodots adsorbed on the surface of the silica. Indeed, more work is needed with the aim of getting stable silver nanoparticles. In this direction, other functionalization reagents such as MPTMS has also been used to give the surface sulphur functionalized silica coated particles, which has better affinity for Ag nanoparticles.¹¹

In order to see whether the present synthetic route can be generally adopted for other magnetic oxide also, we made an attempt to obtain the iron oxide-silver nano hybrid. Figure 4.10 represents corresponding XRD diffraction pattern and the UV-Vis spectra of the nano hybrids obtained at 200°C. Homogeneous phase formation and a narrow distributed absorption spectrum clearly demonstrate that the present synthetic route can be utilized for integrating any spinel oxides with that of the silver nanoparticles.

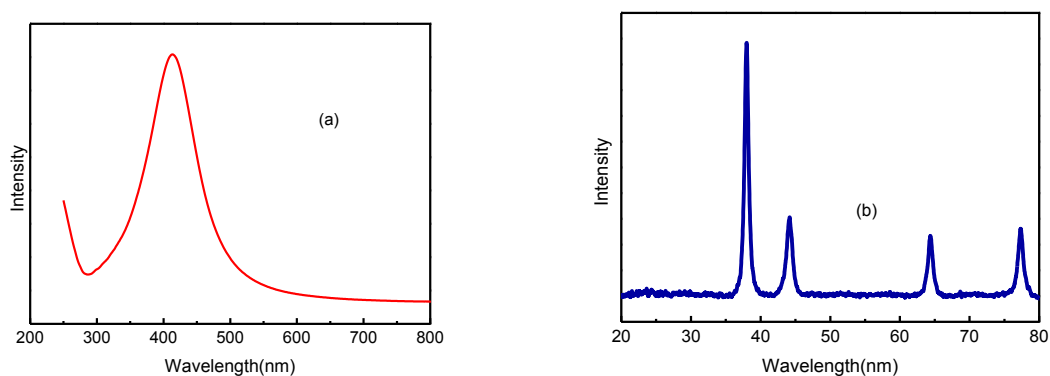


Figure 4.10: (a) UV visible spectrum and (b) X-ray diffraction pattern of $\gamma\text{-Fe}_2\text{O}_3\text{-Ag}$ nano hybrids

4.2 Challenges

Silver has very efficient optical, thermal and physical properties which makes it a very interesting prospect for SERS studies, biomedical applications etc. But the easy oxidation of silver and its strong affinity to various groups such as amines, sulphides makes it vulnerable for oxidation. The pH conditions also affect the silver oxidation. Silver nanoparticles are extremely sensitive to oxygen.¹³ $\text{CoFe}_2\text{O}_4\text{-Ag}$ nano hybrids on the exposure to basic conditions like ammonia gets oxidised thereby destroying the plasmonic behaviour of silver nanoparticles. Indeed, it is a highly

challenged task to develop the hybrid structures which are stable and can retain the plasmonic properties and much work in this direction is in progress.

4.3 Conclusions

In the present work we have tried to develop magnetic - plasmonic nanohybrids composed of a magnetic component (CoFe_2O_4) and plasmonic component (Ag). The effects of surfactant, temperature and concentration of silver on the diffraction patterns, magnetic and the plasmonic properties have been explored. The nanohybrids synthesized were coated with silica to give rise to plasmonic core-shell silica coated nanohybrids. We have tried to coat the silica coated nanohybrids with silver nanoparticles which enables it to form an excellent substrate for SERS and therapeutic applications. Studies have shown that the size, morphology, stability and properties (chemical and physical) of the metal nanoparticles are strongly influenced by the experimental conditions, the kinetics of interaction of metal ions with reducing agents, and adsorption processes of stabilizing agent with metal nanoparticles.¹⁴ Hence, the design of a synthesis method in which the size, morphology, stability and properties are controlled has become a major field of interest.¹⁵

4.4 Future prospects

We are in the process of establishing a strategy for the formation of silver shell on the silica coated nanohybrids. SERS studies of the CoFe_2O_4 - Ag nanohybrids, silica coated nanohybrids, and the Ag nanoparticles treated silica coated particles are yet to be studied. These materials can also be further explored for biomedical applications and photothermal applications. More recent studies have shown that integrating single molecule SERS with optically tweezing methods such as holographic optical trap (HOT) lead to a local field enhancement capability at nano scale. To the best of our knowledge there is no report on the effect of a magnetic field on SERS properties. Therefore, it would be interesting to see the effect of magnetic field produced by the multifunctional magnetic – plasmonic nanohybrids on SERS properties.

4.5 References

- (1) Cornell, R. M.; Schwertmann, U.; VCH: *Weinheim*, **1996**.
- (2) N. Insin J. B Tracy, H. Lee, J. P. Zimmer, R.M. Weservelt, M.G Bawendi, *ACS Nano* **2008**, 2, 197-202.
- (3) Urban, J. J.; Talapin, D. V.; Shevchenko, E. V.; Murray, C. B. *J. Am. Chem. Soc.* **2006**, 128, 3248.
- (4) Batlle. X; Labarta. A *J. Phys. D: Appl. Phys.* **2002**, 35(6), R5-R42.
- (5) Murray, C. B.; Norris, D.j; Baendi. M; g. *J. Am. Chem. Soc* **1993**, 115(19), 8706-8715.
- (6) Roduner, E. *Chem. Soc. Rev.* **2006**, 35(7), 583-592.
- (7) Alivisatos, P. *Nat. Biotechnol.* **2004**, 22(1), 47-52.
- (8) Tartaj. P.: Morales, M. P; Veintemillas-Verdaguer, S.; Gonzalez-Carreño. T.; Serna.C.J. *J. Phys. D: Appl. Phys.* **2003**, 36(13), 15.
- (9) Liu, M. Z.; Guyot-Sionnest, P. *J. Phys. Chem. B* **2004**, 108, 5882.
- (10) Kreibitz, U.; Frauth, K.; Granqvist, C. G.; Schmid, G. Z. *Phys. Chem.* **1990**, 169,
- (11) Lee, J. H.; Huh, Y. M.; Jun, Y. W.; Seo, J. W.; Jang, J. T.; Song, H. T.; Kim, S. G.; Suh, J. S.; Cheon, J. W. *Nat. Med.* **2007**, 13, 95.
- (12) Zhao, W.; Gu, J.; Zhang, L.; Chen, H.; Shi, J. *J. Am. Chem. Soc.* **2005**, 127 8916
- (13) Zhichuan Xu, Yanglong Hou, and Shouheng Sun *J. Am. Chem. Soc.* 9 VOL. 129, NO. 28, **2007**.
- (14) Knoll B, Keilmann F. *Nature* **1999**, 399, 134.
- (15) Wiley B, Sun Y, Xia Y. *Acc Chem Res* **2007**, 40, 1067.

Conferences:

- (1) Akula Venumadhav and Seema Verma, multifunctional silver nanowires coated with magnetic nanoparticles as SERS nanoprobe, Poster Presentation in 3rd International Conference on Advanced Nanomaterials and Nanotechnology (ICANN), Dec 1-3, 2013, IIT Guwahati.
- (2) Akula Venumadhav and Seema Verma, one-pot synthesis of monodispersed multifunctional magnetic-plasmonic nanohybrids, Poster presentation in 6th International Conference on Nanoscience and Technology (ICONSAT), March 3-5, 2014, INST Chandigarh, Punjab.