Chapter 4

Synthesis of carbon nanonoions by a novel and cost effective method and evaluation of its structural, magnetic, microwave absorbing and optical limiting properties

Multifunctional properties can be imparted to magnetic metal nanoparticles by forming hybrid nanostructures. This chapter discusses the major findings on the studies carried out on passivated cobalt nanostructures synthesized by a modified chemical processes. The properties of cobalt can be enhanced by embedding them within graphitic layers. This provides passivation as well as possibilities for applications. Unlike available literature reports, cobalt nanoparticles within graphitic layers were prepared by a simple scalable two step process. Graphitic layers were found to evolve over the surface of cobalt nanoparticles during thermal treatment by the decomposition of organic molecules surrounding the metal nanoparticles which serve as a catalyst. These were analyzed employing techniques like powder X-ray diffraction, transmission electron microscopy, micro-Raman spectroscopy and vibrating sample magnetometry. The microwave absorbing properties as well
as the nonlinear optical limiting properties of cobalt carbon nanostructures were also investigated.

4.1 Introduction

Though carbon nanostructures existed earlier, research in carbon nanomaterials received a fillip immediately after the discovery of fullerene (C\textsubscript{60}) molecule [23, 36]. In the early 1990s research on fullerenes (C\textsubscript{60}) were accelerated by the production of adequate amount of material using high pressure arc discharge method, first demonstrated by Krastchmer et al [24]. Filling the cavities of carbon nanostructures like carbon nanotubes (CNTs), carbon nano fibres, carbon nano onions (CNOs) with magnetic nano particles is exciting and expected to give rise to interesting materials with immense scope for applications [59]. They display interesting and unique properties for applications in optical limiting, catalysis, gas storage, additives for aerospace applications, magnetic metal based composite coatings, solar cells, light-emitting devices, fuel-cell electrodes etc [60, 184, 185].

With nanometer-scale quasi-spherical shape, perfectly arranged outer shell and stability, CNOs are attractive materials for studies for tribological applications [37]. Their advantage over graphite is that they have no edges where chemical attack can occur while maintaining the thermal stability of graphite. If magnetic properties can be incorporated to these structures, their applications are immense. The encapsulated magnetic nanomaterials can find applications in magnetic inks, magnetic recording media, toner for xerography and ferrofluids for biomedical applications [59, 60]. The carbon coating protects the magnetic nanoparticles against environmental degradation [186]. Moreover, carbon coatings can impart biocompatibility and stability in many organic and inorganic media. Therefore, carbon-coated magnetic nanoparticles have been recognized as interesting candidates for many bio-engineering applications including biosensors, drug delivery and magnetic contrast agents for magnetic resonance imaging [152, 153, 187].

Ultrafine elemental cobalt, which is ferromagnetic, readily oxidizes upon exposure to air, resulting in the formation of antiferromagnetic cobalt oxide layer [188]. Bulk cobalt possess a large room temperature saturation magnetization
of 162 emu/g. Major efforts are on in encasing these magnetic metal nanoparticles in a chemically inert oxygen-impermeable layer/matrix like gold, silica or carbon [49-54]. In some cases organic compounds, surfactant and polymers are also being tried. This approach also prevents unavoidable agglomeration which reduces their surface energy. Besides being a protective coating, they act as a means for attaching complex structures to biological systems like DNA, antibodies, proteins and cells in order to target them to specific sites. Cobalt carbon nanoparticles are reported as materials of great potential for in vivo tumor thermal ablation, bacteria killing, and various other biomedical applications [187]. Thus the other aspect of this method is that it will facilitate the passivation of otherwise highly reactive cobalt nanoparticles tuning the physical, mechanical and optical properties. Controlling the size of the magnetic nanoparticles and the thickness of the encapsulating graphitic layer is crucial for the design of devices. A survey of literature points towards the fact that the organic capping material and metal precursor governs the temperature of graphitization as well as size of nanostructures.

Since the discovery of carbon nano structures, lot of efforts has gone into in reducing the synthesis temperature of ordered carbon nano structures. Typical temperatures for graphitic carbon production by direct current arc discharge method are >1200 K. To date, various techniques are in vogue for synthesizing carbon-coated magnetic nanoparticles, such as conventional arc-discharge, modified arc-discharge and ion-beam sputtering methods [24-31]. Thermal transformation of carbonaceous compounds under pressure leading to structural reorganization of carbon residues formed is also reported [32, 33]. Pressure, temperature or the duration of heat treatment are also significant parameters which modifies the properties. Cobalt filled carbon nanoparticles or nanotubes are being studied by several groups [189-191]. However, all the above studies were based on the materials prepared by the conventional arc or modified arc method. In this work we have tried to develop a modified approach for obtaining cobalt embedded in CNOs employing simple and inexpensive techniques.

Metal carbon nanostructures are ideal optical limiting (OL) materials too. Carbon black, fullerene , or CNT suspensions have been extensively investigated in this regard and are considered as benchmark OL materials [77 84]. Metal
nanowires (Co, Cu, Ni, Pd, Pt or Ag) have shown broadband optical limiting properties comparable to materials like CNT which are dominated by nonlinear scattering [34]. However, not much literature exists on the nonlinear optical properties of magnetic metal nanoparticles probably because of their reactive nature and high work functions. Passivation of metal nanoparticles with an inert material like carbon can enhance their thermal stability and offers resistance to laser damages. These nanostructures have an added advantage of being a potential optical limiting candidate thereby enhancing the nonlinear optical properties. These materials should possess sensitive broadband response to long and short pulses, high linear transmission throughout the sensor bandwidth, resistance to laser-induced damages and invariably have high stability. Moreover, these cobalt-carbon nanostructures can be candidates as microwave absorbers once the metal core size is well below their skin depth [192]. Layered graphitic shells can tune the dielectric properties thereby improving the impedance matching criteria [181].

4.2 Experimental

4.2.1 Synthesis

Cobalt nanoparticles were prepared by the borohydride reduction of cobalt salts in the presence of stabilizing surfactant, which is a modified procedure of previously reported method [6]. 0.2 M sodium borohydride (NaBH₄, AR grade, purity >95%, Merck Ltd, Mumbai) was added dropwise to a solution of 0.1 M cobaltous sulphate (CoSO₄·6H₂O, AR grade, purity >98%, CDH (P) Ltd, New Delhi) containing 5 ml of oleic acid (C₁₈H₃₄O₂, Merck Ltd, Mumbai) at 353 K. The mixture was thoroughly stirred keeping the reaction temperature at 353 K for 1 h. A black precipitate was obtained which was magnetically separated, washed with acetone and dried in a hot air oven at 373 K for 3 h to obtain oleic acid coated cobalt nanoparticles. The sample was labelled as Co-S. The same reaction procedure was adopted with cobalt chloride as metal precursor. The resulting product was labelled as Co-Cl. These samples were thoroughly characterized. Co-S was heat treated in air for 12 h at 573 K (Co300), 873 K (Co600) and 1073 K (Co800) and were further investigated using various analytical tools.
4.2.2 Characterization

Transmission electron microscope (TEM) with an accelerating voltage of 200 kV (JEOL JEM 2200 FS) was used to characterize the morphology and particle size of the synthesized nanostructures. Micro-Raman spectroscopy, which is widely used to probe the quality of carbon structures, was carried out using S2000 Raman spectroscopy equipped with an argon laser ($\lambda_{ex} = 514.5$ nm). The structural analysis was carried out in a powder X-ray diffractometer (Rigaku Dmax-C) using CuKα radiation ($\lambda = 1.5406$ Å) [118] with a scanning rate of 5°/min in the 2θ range 20-80°. Room temperature magnetic measurements were carried out using a vibrating sample magnetometer (EG&G PAR 4500). Complex dielectric permittivity and magnetic permeability were determined with the help of a vector network analyzer in the S (2-4 GHz, Rohde & Schwarz-ZVB4) and X-band (8-12 GHz, Agilent-8510C) by employing the cavity perturbation technique. The nonlinear optical applications were probed via an open aperture z-scan measurement technique.

4.3 Morphology

The TEM images and histogram showing the size distribution of oleic acid coated cobalt nanoparticles prepared from sulphate and chloride precursors are depicted in Figure 4.1 and 4.2 respectively. The dark regions indicate the formation of cobalt nanoparticles with spherical morphology. The average grain size of Co in Co-Cl is found to be $\sim 26$ nm, which is higher than the average grain size of Co-S (12 nm). Oleic acid coating of $\sim 2$ nm thickness was found for Co-S. The length of an oleic acid molecule is 2 nm and hence the observed thickness for oleic acid in Co-S suggests that a monolayer of oleic acid is being coated over the metal surface. However, this is not the case with Co-Cl samples. Here the particles are nonuniformly coated with the surfactant. This result indicates that the size of cobalt nanoparticle as well as the surfactant thickness varies significantly with the type of metal precursor used, which is directly related to the rate of reaction [193].
Figure 4.1: (a-c) Transmission electron microscope image of Co-S. (d) Histogram showing the particle size distribution of Co-S

Figure 4.2: (a-c) Transmission electron microscope image of Co-Cl. (d) Histogram showing the grain size distribution of Co-Cl
The energy dispersive spectra of Co-S and Co-Cl (Figure 4.3) indicate the formation of elemental cobalt. It is to be noted that there are traces of chlorine contamination in Co-Cl emanating from the trapped NaCl, a byproduct formed during the precipitation of cobalt nanoparticles, from the cobaltous chloride precursors. These could not be washed off thoroughly since this lead to the removal of oleic acid coating. Such impurities were absent in the EDS spectrum of Co-S establishing the effectiveness of the sulphate precursor route.

![Energy dispersive spectra of (a) Co-S and (b) Co-Cl](image)

Figure 4.3: Energy dispersive spectra of (a) Co-S and (b) Co-Cl

Further, investigations were carried out on Co-S by heat treating at different temperatures (573, 873 and 1073 K). They were extensively analysed using transmission electron microscopy, selected images of which are depicted in Figure 4.4. The cobalt particles of average grain size of 13 nm, are found to be uniformly coated with an organic layer leaving behind no bare metal nanoparticles preventing oxidation by exposure to environmental oxygen. Moreover, it can also be seen that there is no noticeable grain growth taking place by heating at 573 K. The thickness of the coating was found to be $\sim 2.2-3.8$ nm, which prevents agglomeration or coalescence of cobalt nanoparticles.
Figure 4.4: TEM of (a-c) Co300, and (d) histogram showing the grain size distribution of Co300

Figure 4.5: (a,b) TEM and (c, d) HRTEM of Co600
TEM and HRTEM images of Co600 are depicted in Figure 4.5. Annealing at a temperature of 873 K caused the neighbouring cobalt grains to coalesce forming larger grains. TEM image clearly showed lattice fringes of Co core corresponding to the (111) plane of fcc cobalt (marked in Figure 4.5b). The average grain size is found to increase to \( \sim 19 \) nm (Figure 4.5d). Thus, annealing enhanced the crystallinity of cobalt nanoparticles along with an increase in their grain size. High resolution TEM image focused on the outer surface of the particles (Figure 4.5c,d) establishes the formation of graphite layers (with interlayer spacing of \( \sim 0.34 \) nm) surrounding the cobalt grain. Atleast \( \sim 43 \) atomic layers are visible over cobalt nanoparticles.

**Figure 4.6:** (a) Bright field image, (b) carbon mapping, (c) cobalt mapping, and (d) histogram showing the particle size distribution of cobalt in Co600

It may be noted here that the formation of concentric graphitic layers of carbon or CNOs at relatively low temperatures by employing cost effective and scalable experimental techniques is reported for the first time [194]. It was found that the coating thickness as well as the number of graphitic layer over cobalt particles, all depends not only on the initial thickness of organic layer coating but also on the geometry of the particles [195]. Since the initial cobalt core
possesses spherical morphology, concentric graphitic shells are formed. Formation of graphitic shells instead of carbon nanotubes are observed earlier during carbon deficient conditions in CVD [43, 44].

The sample was further subjected to elemental mapping. The bright field image and elemental mapping corresponding to carbon and cobalt further confirms the formation of carbon coated cobalt nanostructures and are shown in Figure 4.6a-c.

![TEM images with elemental mapping](image)

**Figure 4.7:** a) Low resolution TEM image, (b, c) HRTEM, and (d) EDS pattern of Co800

Further, these hybrid nanostructures were heated to 1073 K and characterized using TEM (Figure 4.7). It was interesting to note the dominance of the evolved graphitic structures over cobalt particles. The presence of cobalt was further verified from the energy dispersive spectra of Co800 (Figure 4.7d).

### 4.4 Micro-Raman spectroscopy analysis

Micro-Raman spectra of Co-S, Co300, Co600 and Co800 are depicted in Figure 4.8a. It clearly indicates the evolution of carbonaceous structure formed upon
heat treatment. The peak near 1600 cm\(^{-1}\) known as the graphitic or G-band, the characteristic \(E_{2g}\) mode, is related to the stretching vibration of sp\(^2\) carbon-carbon bond within the ordered graphitic layers of CNO. The disorder induced Raman breathing mode, D-band at \(\sim 1300\) cm\(^{-1}\), assigned to disordered carbon species, are associated with the vibrations of carbon atoms with dangling bonds at the curvatures or defects. Thus, the D-band is also used as a proof of disruption of the aromatic system of \(\pi\)-electrons in the nano-onions framework due to the sp\(^3\) states of carbon. One can observe the signatures of multilayer structure of graphitic carbon with fingerprint peaks at \(\sim 1290\) and \(1595\) cm\(^{-1}\) in Co300, Co600 and Co800, while they are absent in Co-S as expected. This observation has additional support from TEM results. It is clear that the carbon layers are being evolved over cobalt particles by the pyrolysis of carbon rich oleic acid coating. The metal particles act as catalyst for the precipitation of carbon layers [162, 166, 196].

**Figure 4.8:** (a) Micro-Raman spectrum Cobalt carbon nanostructures (b) Variation of \(I_D/I_G\) with temperature treatment.

The ratio of the intensity of the D-band (\(I_D\)) to that of the G-band (\(I_G\)) for the samples annealed at different temperatures are shown in Figure 4.8b. \(I_D/I_G\) decreased from 1.01 to 0.91 suggesting an increase in the graphitization of carbon layers formed in the composite. That is, the Raman intensity of the sp\(^2\) carbon related mode has surpassed the sp\(^3\) mode. This point towards the rise in the abundance of graphitic carbon with increase in annealing temperatures. The absence of any shoulder peak for the G-band confirms no lattice distortion in the
carbon layers formed [197].

**Mechanism of growth:** The mechanism leading to the growth of carbon nano onions assume importance because of their multifaceted properties and evolution of various carbon nano structures during the process. The mechanism can be properly elucidated by carefully analyzing the structure of cobalt-carbon nanostructures. It is well known that the explosion of carbon rich materials leads to carbon nanostructures [21, 22, 172, 191, 198-200]. Usually this process occurs at high temperature and under adequate pressure. Various transition metals accelerate graphitization of carbon by the solution precipitation mechanism [200, 201]. This results in the rupture of C-C bond by the catalytic transition metal particles. The carbon atom dissolves in the metal particle, diffuse and precipitates as graphite at the particle surface [202].

Formation of onion like structure requires a high degree of graphite like order. In the present system carbon rich organic surfactant (oleic acid) undergoes pyrolysis. They decompose precipitating carbon nanostructures. At high temperatures, thermal energy is absorbed leading to the breakage of some of the C-C bonds with high defect density and high energy and eventually the structure collapses. To reduce the surface energy, the broken domains tends to close from inside to outside resulting in the formation of carbon nano onions. Due to the lower radius and lower energy level contained at the outer layers, these broken C domains cannot be converted into an associated crystal form leaving a carbon nano sheath by amorphous carbon. Addition of layers results from a precipitation of C previously dissolved by the metal. If the solubility of C is low, it prevents this possibility. Annealing provides additional thermal energy that makes the structural rearrangement possible long after the initial deposition process. There are reports of energy transfer from the electron beam and catalytic effects from metal in the carbon onion formation around Pd clusters [55]. The driving force for graphitization would be the free energy difference between the initial and final form of carbon.

Here, cobalt particles act as a nucleation center for the growth of carbon nanostructures. The decomposition of organic compound into molecular fragments and their transformation or precipitation forming carbon nanomaterial is promoted by the transition metal catalysts, cobalt. Hence a metal mediated
graphitization occurs. It is observed that the amorphous carbon in contact with Co fully crystallize between 773-873 K [21, 22]. Carbon atoms dissolve onto the metal and upon supersaturation, graphite precipitates outwardly at the interfaces. Metallic cobalt simply acts as a template for carbon nano onion formation.

4.5 Structural analysis using X-ray diffraction

The structure of cobalt nanoparticles thus formed is further investigated by analyzing the XRD pattern of Co-S, Co300, Co600 and Co800 and are depicted Figure 4.9.

![Figure 4.9: XRD patterns of Co-S at different annealing (in air) temperatures (a) Co-S, (b) Co300, (c) Co600, and (d) Co800](image)

Co-S show an amorphous nature, but when heat treated at 573, 873 and 1073 K broad peaks at $2\theta = 44.2^\circ$ corresponding to (111) plane of fcc cobalt emerges (ICDD file no. 15-0806). It is to be noted that other planes of Co are not prominent in the XRD pattern, and the elemental cobalt is confirmed from EDS analysis. Signatures of cobalt oxide (CoO or Co$_3$O$_4$) are absent in the XRD pattern which confirms the effectiveness of the passivation of cobalt core within the graphitic carbon shells or CNOs. The lattice constant is found to be 3.57 Å which is in line with the ICDD values.
4.6 Magnetic properties

The determination of the saturation magnetization ($M_s$) of the fine particles is one way of securing information about their magnetic characteristics. The room temperature hysteresis loops of amorphous cobalt (Co-S and Co-Cl) are depicted in Figure 4.10a. A saturation magnetization of 5.4 emu/g and 4.4 emu/g with a remanence of 0.94 emu/g and 0.64 emu/g are obtained for Co-Cl and Co-S respectively. Slightly higher $M_s$ for Co-Cl when compared to that of Co-S may be due to the larger grain size of Co-Cl (25 nm) when compared to Co-S(12 nm), as observed from the TEM images.

![Figure 4.10: (a) M-H curves of Co-Cl and Co-S (b) M-H curves of Co300, Co600, Co800 (Inset: enlarged view showing coercivity)](image)

The saturation magnetization for bulk cobalt is $\sim$162 emu/g [2, 4]. Although oleic acid coating protects the core, it affects the magnetic properties of the nanocrystalline cobalt through the contribution of surface anisotropy and interparticle interaction. In the nanoregime, as the surface to volume ratio increases, the saturation magnetization is found to decrease. Several factors determine the magnetic properties of nanocomposite. Disordered surface spins, non-magnetic surface coating and amorphous nature of cobalt particles in the system are the main factors for reduced magnetization.

Cobalt has an inherently high magnetocrystalline anisotropy resulting in high coercivity [2]. This also leads to a lower value of superparamagnetic size limits. The magnetization saturates at 15 kOe for both the samples. Upon heat
treatment, cobalt particles undergo crystallization and the magnetic properties undergo drastic changes [203]. When Co-S is heated at 573 K (Co300), the coercivity is found to increase from 43 Oe to 717 Oe whereas there is only a marginal increase in $M_s$. For Co600, $M_s$ drastically increases to 78 emu/g from $\sim$5 emu/g with a coercivity of 62 Oe. These observations show that there is a strong relation between the magnetic properties and heat treatment on the nanomaterials. Generally, it is known that the coercivity increases as the single domain grain size increases. When the size of the grain attains a value at which it becomes multidomain, the coercivity starts decreasing [2]. Moreover the enhancement of coercivity may be attributed to the variation of both particle size and ordering of the particles with annealing [31]. On heat treatment, the crystallinity increases as evident from XRD and HRTEM. The particle size also increases which accounts for the decrease of $H_c$.

![Figure 4.11: ZFC-FC curve for Co600](image)

Further, vibrating sample magnetometer was employed to study the variation of magnetization with temperature in Co600. The ZFC-FC curves depicted in Figure 4.11 shows the absence of any superparamagnetic blocking in the temperature range measured (4-340 K).
4.7 Optical limiting property using z-scan technique

The optical limiting properties of cobalt-carbon nanostructures were evaluated using the traditional open aperture z-scan measurements. A frequency doubled Q-switched Nd:YAG laser (Minilite, Continuum) having a nominal pulse width of 5 ns at 532 nm wavelength was used for the measurements. The sample was dispersed in ethanol by sonicating for 10 min and was taken in a 1 mm glass cuvette mounted on a stepper motor controlled linear translation stage. The laser beam was focused using a plano-convex lens and the focal spot radius \( \sigma_o \) was around 17 \( \mu \text{m} \). The laser propagation direction was taken as the z-axis. The sample was translated in the z-direction in small steps, and the transmitted energy was measured at each z position, using a pyroelectric laser energy detector (Laser Probe Inc.). The experiment was completely automated in a linux platform.

The Co300 and Co600 samples were dispersed in ethanol with concentrations such that their linear transmission was 50% at the laser wavelength, when taken in the 1 mm glass cuvette. The samples show a decrease in the transmittance at higher input intensities. The obtained z-scan curves fit well to a two-photon process, in which the net transmission 'T', of the sample is given by

\[
T = \left( \frac{\left(1 - R\right)^2 \exp(-\alpha_0 L)}{\sqrt{\pi q_0}} \right) \int_{-\infty}^{+\infty} \ln\left[ \sqrt{1 + q_0 \exp(-t^2)} \right] dt \tag{4.1}
\]

where 'L' and 'R' are the sample length and surface reflectivity respectively, and \( \alpha_0 \) is the linear absorption coefficient. Here \( q_0 \) is given by \( \beta(1 - R)I_z L_{eff} \), where \( \beta \) is the two-photon absorption coefficient, and \( I_z \) is the intensity of the laser beam at position z. \( L_{eff} \) is the effective sample thickness given by \( [1 - \exp(-\alpha_0 L)]/\alpha_0 \). The obtained z-scan curves alongwith the theoretical fit to the experimental data are presented in Figure 4.12.

Both samples exhibit good optical limiting properties. The two photon absorption coefficients \( (\beta_1) \) were evaluated to be \( 1.8 \times 10^{-10} \text{ m/W} \) and \( 1.2 \times 10^{-10} \text{ m/W} \) for Co300 and Co600 samples respectively.
Figure 4.12: Optical limiting property of (a) Co300 and (b) Co600

The origin of this nonlinearity can be explained from the absorption spectra of the samples. The optical absorption spectrum of cobalt-carbon nanostructures (Co300 and Co600) dispersed in ethanol recorded in the range 200-1000 nm is depicted in Figure 4.13. The spectrum shows broad absorption peak at around 300 nm and is characteristic of $\pi - \pi^*$ electron transition in the polyaromatic system of curved graphitic layers [39]. Weak optical absorption of these nanostructures is due to the higher value of work function and first ionization potential of cobalt. The broad absorption band in the range 240-330 nm (band gap $\sim$4eV) is emanating from the carbonaceous structures formed around the cobalt nanoparticles. Reports reveal the variation of band gap of carbon nanostructures is in the range of 0.25 eV to 5.5 eV [21, 22, 40].

From the optical absorption spectrum, it can be seen that the samples have a strong absorption at 266 nm, which is the two-photon absorption level corresponding to the excitation wavelength of 532 nm. Considering the fact that there is a small residual absorption at 532 nm and that the samples are prepared in a concentration such that 50% of the incident photons are absorbed, the optical nonlinearity could be predominantly from a two-step excited state absorption rather than a pure two-photon absorption. The two-photon absorption coefficient evaluated thus can be termed as an effective two photon absorption coefficient.
Figure 4.13: UV-vis NIR spectrum of (a) Co300 and (b) Co600

Nonlinear scattering, free carrier absorption, two/multi-photon absorption and reverse saturable absorption are the main mechanisms attributed to the optical limiting effects in nanomaterials [79–84]. It is a cumulative effect, rather than a contribution from one mechanism alone. The particle size, morphology, aggregation state, the local environment or the host matrix, all contribute to the limiting phenomenon. Pan et al. [34] has studied the optical limiting properties of nickel and cobalt [204] and found that nonlinear scattering, resulting from a photoionisation of metal atoms and subsequent expansion of the microplasmas in the suspension produces the optical limiting effects. Moreover, the laser parameters like wavelength, pulse duration or repetition rate of the laser source, plays a crucial role in the process.

From initial studies, it can be inferred that cobalt carbon nanostructures are good optical limiters. Further studies on their nonlinear refractive index and fabrication of devices based on these nanostructures can be carried out.

4.8 Microwave absorbing property

Extensive use of electronic gadgets in communication devices for domestic, military as well as industrial purposes using microwave frequencies has caused environmental pollution that causes health hazards and interference problems. One
way of sorting out this issue is to develop a microwave absorbing material in a scalable and cost effective manner. The cobalt carbon nanostructures are one such candidate that would tune the dielectric and magnetic properties thereby manipulate the microwave absorbing properties.

Cobalt nanoparticles embedded within carbon nano onions (Co600) were investigated for their microwave absorbing properties in the S and X-bands by measuring their complex dielectric permittivity and complex magnetic permeability using cavity perturbation technique. The details of measurements are explained in Chapter 2. Cobalt carbon nanostructures (Co600) was pressed into rectangular rod like pellets of dimension 1 mm x 2 mm x 4 cm with 1% poly vinyl alcohol added as binder. This was dried and subjected to microwave measurements.

Figure 4.14 and 4.15 depicts the variation of complex dielectric permittivity and magnetic permeability of Co600 in the S and X-band respectively. $\epsilon'$ is found to be more or less $\sim 20$ while $\epsilon''$ is found to increase from 0.25 to 1.15 in the S-band with frequency, whereas these parameters are almost constant in the X-band ($\epsilon' \sim 18, \epsilon'' \sim 1.5$).

![Graphs](image)
Figure 4.15: Variation of (a) complex dielectric permittivity and (b) complex magnetic permeability for Co600 in the X-band

The layered carbon structures formed over the cobalt particles causes a capacitive effect that increases the dielectric permittivity of the composite. With increase in frequency, the capacitive effect gradually vanishes. The nanocrystalline cobalt particles on the other hand improve the permeability values of Co600. Permeability values are found to reduce with increase in frequency. It is found that $\mu'$ is $\sim 1.5$ while $\mu''$ is $\sim 0.3$ in the S-band whereas in the X-band $\mu' \sim 1.25$ and $\mu'' \sim 0.25$. Thus from the measured values of permittivity and permeability, the reflection loss of Co600 was simulated using the single layer absorber model [181] using Equation 3.3.

Figure 4.16: Reflection loss simulated for different absorber layer thickness of Co600 in the (a) S-band and (b) X-band

From these studies it can be seen that the reflection loss decreases with in-
creasing frequency (Figure 4.16) in accordance with the conventional theories [75, 181]. Also for increased thicknesses, the reflection loss minimum shifted to lower frequencies. A minimum reflection loss over -10 dB was obtained for a thickness of 4.2-4.6 mm in the S-band while this thickness is lowered to 1.5-2.25 mm in the X-band. This suggests the effectiveness of the cobalt-carbon nanostructures for the development of microwave absorbing materials.

4.9 Conclusion

Production of metal nanoparticles by bottom-up solution phase approach offers several advantages including easiness of surface modification, control of size, functionalization, prevention from agglomeration and oxidation. Stable cobalt nanostructures passivated by oleic acid was initially prepared by a controlled borohydride reduction technique. Effect of particle size and surfactant thickness with change in cobalt metal precursor were also looked into. Cobalt particles were formed in metallic form with no traces of cobalt compounds. Oxygen impermeable stealth, which is a prerequisite for use of these metal nanoparticles for several applications, was fabricated successfully. This was done by the heat treatment of oleic acid coated cobalt particles which lead to the evolution of carbon nano onions. The structure and morphology of the composites were extensively investigated using TEM, Raman spectroscopy and XRD studies. Room temperature magnetic properties of these nanoparticles determined using vibrating sample magnetometry revealed the effectiveness of the method developed for obtaining stable magnetic cobalt carbon nanostructures. These cobalt-carbon nanostructures were oxidatively stable and chemically resistant having desirable optical limiting and microwave absorbing properties.