Preface

Amidst all types of available nanoscale materials, superparamagnetic iron oxide nanoparticles (SPIONs) of different nanostructures are the most widened studied types of nanoparticles for successful use in biomedicine. The utmost interest for their use in diagnostics and therapeutics is attributed to its room temperature superparamagnetic properties, intoxicity and low-cost easy synthesis. SPIONs have already been approved by Food and Drug Administration (FDA), USA to be implemented in clinical use for human patients to enhance MRI signals, hyperthermic and targeted drug delivery agents. To impart multifunctionality to the synthesized SPIONs, they are coated with optically active metals which are very effective contrast enhancement agent.

The iron oxide nanoparticles are functionalized or coated with several dyes, surfactants, polymers, silica, decorated with carbon dots or sometimes dispersed in a matrix in order to prevent them from oxidation as well as to make them optically active. These functionalized nanomaterials exhibit superior optical as well as magnetic properties but also have some serious disadvantages such as toxicity, photobleaching, non-biodegradability, low blood circulation time, complex synthetic procedures and not so cost effective.

The superparamagnetic iron oxide nanoparticles possess combination of most of the desirable properties such as superparamagnetism, high saturation magnetization values, stability, biocompatibility, imaging capabilities and flexible surface modification/conjugation which make them very efficient to be used in various biological applications. The integration of these SPIONs with electron rich metal i.e.

silver makes them optically active and acts as luminescence enhancer for magnetite nanomaterials.

The overall aim of the work was to synthesize monodispersed bare magnetite and silver coated magnetite nanoparticles of different shell thickness and study their structural, optical and magnetic properties which could be employed as multifunctional materials in biological imaging, drug delivery and hyperthermic treatment of cancerous tissues or tumors. The silver coated iron oxide nanoparticles are the most appropriate choice with all of the desirable and essential qualities for a contrast agent. It can be suitably used both in optical imaging as well as MR imaging modalities with excellent colloidal stability and biocompatibility. They show efficient luminescence response in blue-emission range as well as higher values of magnetic moments and saturation time which directly affects the longitudinal and transverse relaxation time for the nanoparticles.

The specific objectives of the PhD thesis are as follows:

1. Theoretical investigation of the critical size range/ core-shell ratio of magnetite-silver nanoparticles as well as tuning of synthesis parameters to obtain uncoated and silver coated magnetite nanoparticles in the desirable size range (<40 nm) and their effect on particle morphology and size.

2. Effect of silver coating on different optical characteristics such as luminescence and absorption spectra of uncoated magnetite nanoparticles.

3. Structural and magnetic investigation of the synthesized magnetite and silver coated magnetite nanoparticles using different characterization tools.

Important findings of the present thesis are as follows: -

1. Effect of silver coating on the luminescence properties of magnetite core-shell nanoparticles having a core size of 6 nm and shell thickness of 1-9 nm shows effectiveness of silver as luminescence enhancer for these magnetite

nanoparticles. A blue photoluminescence (PL) peak observed in the visible region of spectrum, brighten further with the increase in the thickness of silver shell. The energy band diagram indicates towards the presence of a charge transfer band corresponding to silver near electron trap level present at octahedral site of Fe_3O_4.

2. The structural and magnetic analysis of uncoated and silver coated magnetite nanoparticles shows a trilayer structure. The occurrence of an intermediate layer with magnetically disordered spins is identified in between the innermost magnetically ordered magnetite core and outermost non-magnetic silver shell. The thickness of this magnetically disordered layer increases with the shell thickness showing a saturating trend.
3. The dynamical magnetic response of magnetite nanoparticles of diameter ~6 nm coated with ~2 nm and ~4 nm thick silver shell under the influence of external magnetic field is heavily affected by the intermediate magnetically disordered spin layer. The Néel Arrhenius formalism, Vogel-Fulcher and Power law model shows the presence of superparamagnetic and spin-glass behavior for bare Fe_3O_4 and $Ag@Fe_3O_4$ core-shell nanoparticles, respectively. The time decay of magnetization relaxation suggests consolidated presence of two characteristic relaxation times corresponding to superparamagnetic and spin-glass behavior for both uncoated and silver coated magnetite nanoparticles.
4. The possibility of the synthesized magnetite and silver coated magnetite nanoparticles to be used in magnetic hyperthermia has been explored. The absolute increase in temperature and specific absorption rate were measured for bare magnetite and silver-magnetite nanoparticle. The value of SAR is obtained to be 7.58 and 1.28 W/g for magnetite and silver-magnetite Janus nanoparticles,

respectively, thus making these systems to be used for both therapeutics and diagnostics applications.

The major aim of the work was to develop silver coated magnetite nanoparticles as potential candidate for multimodal imaging and applications. This thesis includes in **Chapter 1**, a basic introduction to the various essential properties and choice of materials suitable as multimodal agents. The desired structural, optical properties and magnetic spin dynamics of the materials has been focused. This chapter also reviews the possibility of these materials to be used in multiple biological applications.

The optimization of various synthesis parameters in order to obtain the uncoated and silver coated magnetite nanoparticles is described in **Chapter 2**. The effect of various synthesis parameters on nanoparticle phase, morphology and size is also presented in this chapter. The experiments find that the critical concentration of ferrous- ferric solution to obtain particles in single phase is ≤ 0.09 M and ≤ 0.184 M, respectively. The variation of molar concentration ($0.01\ M \leq x \leq 0.1\ M$) of CTAB leads to formation of Fe_3O_4 nano-scale particles of distinct morphologies e.g. nano-cubes, pentagons and spheres. The number of ferrous and ferric ions involved in the formation decides the size of the nanoparticles. The single crystallographic phase is obtained in reaction temperature range of $65\ ^0C < T < 72\ ^0C$. The method facilitates to produce nanostructures having narrower size distribution along with good reproducibility.

Chapter 3 aims towards the theoretical investigation of the critical size range and core-shell ratio for gold and silver coated magnetite nanoparticles using MATLAB programs. This chapter emphasizes on the excellent tunability of SPR maxima of core-shell nanostructures over single metal nanostructures. The critical diameter of magnetite core with 1 and 2 nm gold nanoshells for SPR peak to lie in the visible region of electromagnetic spectrum has been found to be 12 and 24 nm, respectively. This critical

diameter value for silver coated magnetite nanoparticles is 16 and 32 nm for 1 and 2 nm thick nanoshells, respectively.

The effect of silver coating on the luminescence properties of magnetite nanoparticles has been studied extensively in **Chapter 4**. The effectiveness of silver as luminescence enhancer for magnetite nanoparticles is evident from the studies presented in the chapter. A blue photoluminescence (PL) peak observed in the visible region of spectrum, brighten further with the increase in the thickness of silver shell.

In **Chapter 5**, the structural investigation of the synthesized silver coated magnetite nanoparticles has been carried out using various characterization techniques. The analysis presents an interesting trilayer structure in a single nanoparticle system which has a significant impact on the properties of nanoparticles. It also focuses on the impact of non-magnetic shell on the magnetic properties of magnetic shell. From structural and magnetic analysis, we report that the structure is not exactly bilayer core shell but a trilayer structure with disordered magnetic shell in between magnetic core and outermost silver layer. The structural and magnetic sensitivity of these coated nanoparticles are found to be altered up to a considerable extent when compared to the uncoated ones of same magnetic core size.

Chapter 6 describes the magnetic spin relaxation behavior of uncoated magnetite and silver coated magnetite nanoparticles using magnetic ac susceptibility measurements and remanent magnetization curves. From analysis of ac susceptibility measurements, a hint of superparamagnetic and spin-glass behavior has been found for uncoated and 1 nm thick silver shell coated magnetite nanoparticle, respectively. The time-decay measurement of magnetization data for both uncoated and silver coated magnetite nanoparticles, however, suggests presence of two different characteristic relaxation times. On further comparison of experimental data with combination of magnetic

relaxation functional forms, the uncoated and coated nanoparticles were observed to have integrated magnetic behavior of superparamagnetic as well as spin glass systems.

Chapter 7 focuses on the possibility of the synthesized magnetite and silver coated magnetite nanoparticles to be used in therapeutic applications such as magnetic hyperthermia. The value of SAR is obtained to be 7.58 and 1.28 W/g for magnetite and silver-magnetite Janus nanoparticles, respectively. The experimental analyses of silver-magnetite nanoparticles suggest the feasibility of these nanoparticles as multimodal agents.

The final conclusions and outcomes drawn from this work have been summarized in **Chapter 8**.