CHAPTER 8

Hyperthermia Applications, Conclusions and Future Scope

8.1 Introduction

The integration of silver metal with magnetite nanoparticles is employed to impart multimodality. This attachment can also lead to formation of a Janus shaped structure other than core-shell morphology. Till now, there is limited study on the synthesis methods and physical properties of silver-magnetite Janus structured systems. In this chapter, we have investigated the different physical parameters such as zeta potential, and hyperthermic response of the magnetite and its based nanoparticles that also play a crucial role in implementation of these particles for various applications. The synthesized nanoparticles are found to be highly stable and display good hyperthermic response.

8.2 Fe_3O_4 and Ag-Fe_3O_4 as Hyperthermic Agents

The magnetite and silver- iron oxide nanoparticles have been investigated for their application as hyperthermic agents. The hyperthermic response for Fe_3O_4 has been recorded for alternating magnetic field (AMF) of strength 17 mT and 25 mT with frequency 737.9 kHz and 110 kHz, respectively. For Janus shaped silver-Fe_3O_4

nanoparticles, the data have been recorded at a magnetic field of 25 mT and nominal frequency of 110±1.0 kHz. With a concentration of 0.03 mg/μL and magnetic field amplitude 17 mT, the magnetite nanoparticles can reach temperature from 29 °C to 43 °C in merely 12 minutes (see Figure 8.1). For alternating magnetic field amplitude 25 mT, for Fe_3O_4 nanoparticles, with concentration 0.01mg/μL, the temperature elevates from 31^0 C to 46^0 C in a span of merely 400 seconds (less than 10 minutes). For same magnetic field strength and frequency, in case of silver-magnetite Janus nanoparticles, the temperature reaches 42^0 C from 31^0 C in similar time span for a concentration of

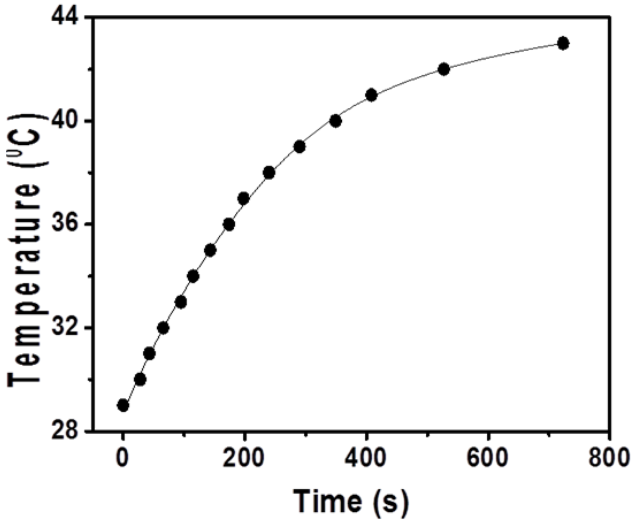

Figure 8.1 Variation of temperature with time on application of 17 mT magnetic field for uncoated magnetite nanoparticles.

0.02 mg/μL dispersed in oleic acid.

Figure 8.2 shows response of magnetite and silver-magnetite nanoparticles in presence of alternating magnetic field. The hyperthermic response of materials is quantified by specific absorption rate (SAR), given by the equation, $SAR = \frac{C}{m}\left(\frac{dT}{dt}\right)\Big|_{t=0}$ that measures the efficiency of conversion from electromagnetic energy into heat. Here, C and m represents the heat capacity of dispersion medium and mass of suspended magnetic

particles, respectively [208]. The value $\left(\frac{dT}{dt}\right)\Big|_{t=0}$ denotes the initial rate of change in temperature with respect to time. The value of SAR is found to be equal to 4.91 W/g and 7.58 W/g for bare magnetite in AMF amplitude 17 mT and 25 mT, respectively. In presence of AMF 25 mT, this value of SAR is obtained to be 1.28 W/g for silver-magnetite nanoparticles, when samples in all three cases are placed in vial of diameter 10 mm.

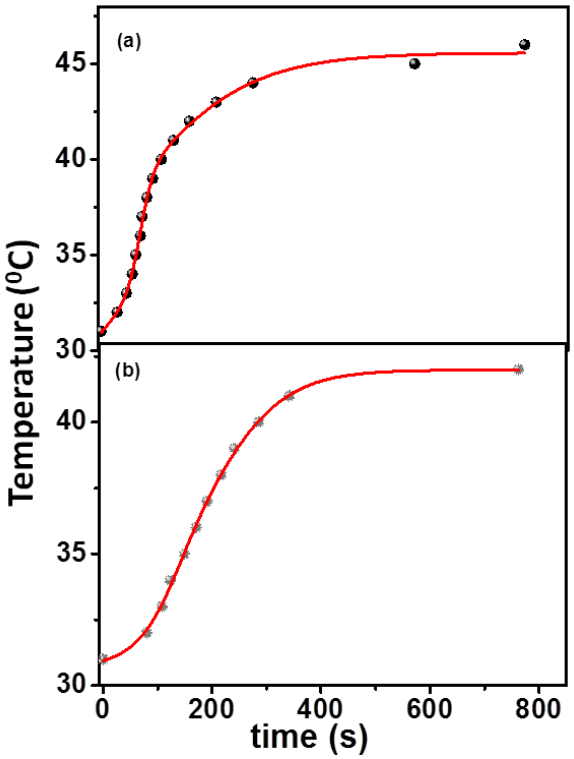

Figure 8.2 Temperature raise with elapsed time on application of alternating magnetic field 25 mT with frequency 110 kHz for (a) bare magnetite nanoparticles; (b) silver coated magnetite nanoparticles.

Based on the measurements and analysis carried out in the chapter, it is evident that the magnetite and Janus shaped silver-magnetite nanoparticles have quicker and higher response rate of the nanoparticles to alternating magnetic field. This opens up the possibility of these materials to be used for hyperthermia treatments.

8.3 Conclusions and Future Scope

On the basis of work carried out, result obtained and the discussion presented in the preceding chapters, the following conclusions can be drawn:

The optimization of various synthesis parameters in order to obtain the uncoated and silver coated magnetite nanoparticles is presented. 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 ≤x≤ 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 ^{0}C<T< 72 ^{0}C. The method facilitates to produce nanostructures having narrower size distribution along with good reproducibility.

The theoretical investigation shows the excellent tunability of SPR maxima of core-shell nanostructures over single metal nanostructures. The critical maximum 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. A linear relationship of SPR wavelength is observed with core-shell ratio as well as core size with fixed shell thickness 1 and 2 nm. The SPR peak wavelength belonging to blue-green region lies between 450-560 nm for which the corresponding particle size for Ag@Fe_3O_4 nanoparticle having shells of thickness 1-2 nm turns out to be around 6 nm.

The study on effect of silver coating on the luminescence properties of magnetite nanoparticles shows effectiveness of silver as luminescence enhancer for 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.

The structural and magnetic analysis of uncoated and silver coated magnetite nanoparticles indicates formation of a trilayer structure in case of core-shell nanoparticles. 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 value of saturation magnetization are smaller than those obtained for bulk magnetite emphasizing the presence of a disordered spin layer due to unsaturated iron ions at the surface in case of uncoated magnetite nanoparticles and at the interface for coated ones.

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. The characteristic relaxation time corresponding to superparamagnetic contribution decreases for silver coated magnetite nanoparticles.

The possibility of the synthesized magnetite and silver coated magnetite nanoparticles to be used in magnetic hyperthermia is 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.

8.4 Suggestions for Further Study

- The longitudinal and transverse relaxivity values of silver coated magnetite nanoparticles can be measured. These relaxivities can further be increased or decreased by changing the shape and size of the nanoparticles. The core size and shell thickness is one of the best controlling parameters in case of core-shell nanoparticles. This will further help in exploring the suitability of these silver coated magnetite nanoparticles as MRI contrast enhancement agents.
- The *in vitro* fluorescence imaging of silver coated nanoparticles can be done to check their potential as optical imaging agent. The colour of light emission can be tuned across entire visible region of optical spectra by changing core to shell ratio. The coating of combination of different noble metals can be tried to improve the sharpness or proper lineation of the specimen after under investigation.
- The functionalized silver coated nanoparticles with appropriate proteins can be tested in laboratory for *in vivo* biological imaging. These magneto-plasmonic nanostructures can be studied as an efficient targeted drug delivery agent which can be efficiently detected for their appropriate delivery location.