

CHAPTER 5

Study of Optical Characteristics of Ag@Fe₃O₄ Core-Shell Nanoparticles

5.1 Introduction

In chapter 3, a theoretical investigation for the silver coated magnetite nanoparticles with distinct core sizes and shell thickness have been discussed to obtain the appropriate size range for desired applications. It was found that the plasmon resonance of noble metal nanoparticles is highly susceptible to their shape and size. The strong local electric field, also referred as “hotspots”, in the vicinity of the noble metal nanostructures can be used to enhance the luminescence properties of magnetic/ rare-earth materials on condition of overlapping SPR absorption spectra corresponding to noble metal with luminescence peak or absorption wavelength of the other material [72].

Correspondingly magnetite nanoparticles coated with silver shells have been synthesized in the size range of 6-24 nm (including the silver shell). The modification in energy level of magnetite nanoparticles upon silver coating is shown by considering the diagram proposed by Sadat et al which suggests the appearance of a charge transfer

band corresponding to silver metals between the conduction and valence band corresponding to magnetite nanoparticles [76]. In this chapter, we have studied the effect of silver shell coating and increasing shell thickness on the absorption and luminescence properties of these magnetite nanoparticles.

5.2 SPR Properties of the Fe₃O₄ and Ag@Fe₃O₄ Nanoparticles

The localized SPR absorption of noble metal nanoparticles can be considered as a promising approach for enhancement of photoluminescence of magnetic nanoparticles. A noble metal such as silver or gold can increase the luminescence of a weakly luminescent material manifold if there is an overlap of SPR absorption peak of the noble metal with luminescence or absorption wavelength of the other material. The overlapping between the SPR absorption peak of silver and luminescence or absorption wavelength of Fe₃O₄ makes it suitable for enhancement of luminescence properties [47]. The SPR absorption peak of silver nanoparticle is located in the blue region of spectrum which lies in similar wavelength region of luminescence peak measured for magnetite nanoparticles. This combination makes the Ag@Fe₃O₄ the most suitable candidate to be used as a multimodal imaging agent.

To check the suitability of the synthesized nanostructures as visible range SPR absorbance material, the absorption spectra of ~4 nm thick silver shell coated magnetite nanoparticles was recorded, as shown in Figure 5.1, and compared with experimental and theoretical data reported for silver nanoparticles of same size range [67,71]. The theoretical investigations have been already carried out in order to show the tunability of absorbance across visible region of electromagnetic spectrum by variation of core-shell ratio. The result for resonance peak obtained for ~4 nm silver shell and ~6 nm magnetite core nanostructures is in agreement with the theoretical investigation, the

small difference in maxima position and shape occur due to certain limitations such as size distribution and refractive index of surrounding media in case of real systems [69].

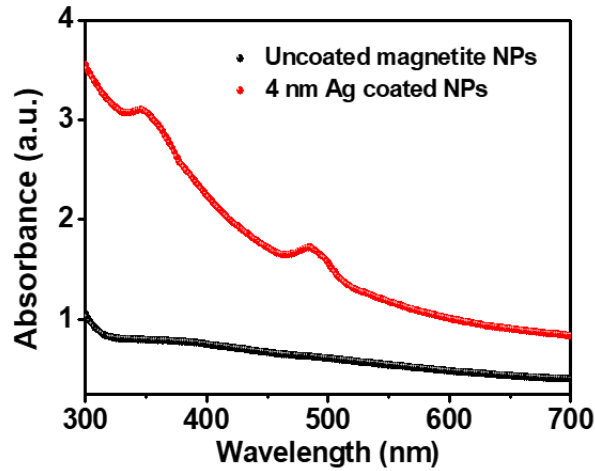


Figure 5.1 UV-Vis absorbance spectra of uncoated and silver coated magnetite nanoparticles.

As it has been explained that, the atomic structure of magnetite is inverse spinel, comprising O^{2-} ions in face-centered cubic lattice i.e. half of the trivalent Fe ions occupy tetrahedral voids while other half along with equal number of divalent Fe cation occupies octahedral voids [125]. The separation between valence band of 2p orbital in oxygen and empty 4s orbital of iron is found to be 4-6 eV in Fe_3O_4 as reported by Zaanen et al [182].

The band gap (E_g) of materials is determined effectively by employing the use of UV-visible absorption spectroscopy. For an allowed indirect transition, the band gap can be calculated using tauc equation [183]: $(\alpha h\nu)^2 = h\nu - E_g$, where α is the absorption coefficient of materials and $h\nu$ is the photon energy. The extrapolation of $(\alpha h\nu)^2$ to photon energy axis determines the band gap energy of material. The band gap of the ~9 nm silver coated magnetite is estimated to be 5.12 eV. The silver coated magnetite nanoparticles with varying thickness were subjected to different emission wavelengths

in order to find the appropriate excitation wavelength. The excitation spectra for light of wavelength 463 nm gave a maximum intensity band at 306 nm revealing the value of excitation wavelength. As seen from figure 5.2 (a), the excitation wavelength for all sets of Ag@Fe₃O₄ core-shell nanoparticles was found to be same irrespective of their shell thickness. Further, the emission spectra was recorded for the uncoated and silver coated magnetite nanoparticles with shell thickness ~1, ~2, ~3, ~4 and ~9 nm for an excitation wavelength 306 nm. The emission spectra show nearly same trend for all the samples under consideration (figure 5.2 (b)). Thus, the details analysis of principle behind these transitions has been performed for selected samples i.e. Ag@Fe₃O₄ core-shell nanoparticles with shell thickness ~3, ~4 and ~9 nm.

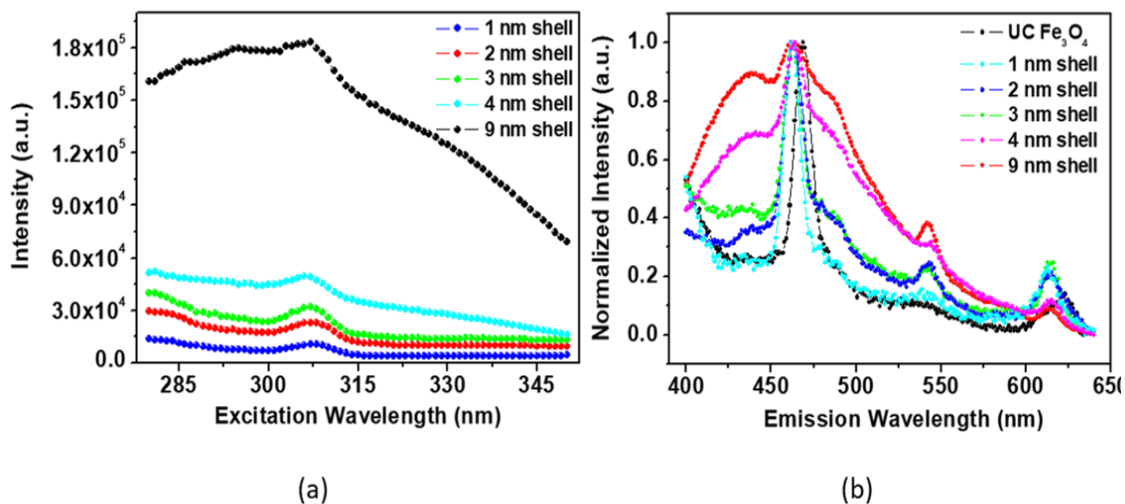


Figure 5.2 Photoluminescence (a) excitation spectra (b) emission spectra for uncoated (UC) Fe₃O₄ and silver coated Fe₃O₄ nanoparticles with different shell thickness.

5.3 Photoluminescence Properties and Energy Level Diagram of Fe₃O₄ and Ag@Fe₃O₄ Nanoparticles

On illumination with an excitation wavelength of 306 nm, in case of uncoated and silver coated nanoparticles, the spectra reveal three main emission bands in wavelength range

of 400-700 nm. The three peaks corresponding to wavelength 469 nm, 538 nm and 622 nm are clearly visible in the PL spectra (Figures 5.3(a) and (b)). The crystal field bands of tetrahedral and octahedral sites, composed of 3d transition metal atomic orbitals are present in between O (2p) and Fe (4s) states, have been taken into account. Based on the earlier measurements and calculations reported in literature [184], the crystal field splitting on the octahedral and tetrahedral site shows an energy gap of $\Delta_{cf,o} \sim 2.2\text{eV}$ and

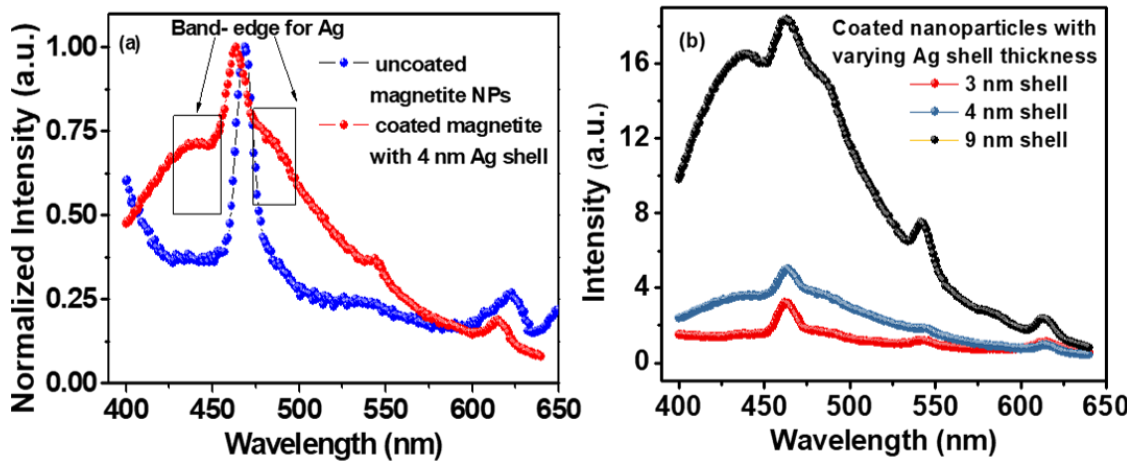


Figure 5.3 Photoluminescence emission spectrum for (a) uncoated and 4 nm Ag coated magnetite nanoparticles, (b) coated nanoparticles with varying shell thickness.

$\Delta_{cf,t} \sim 0.9\text{ eV}$, respectively. The crystal field e_g , t_{2g} of tetrahedral and octahedral site, respectively, is further separated by energy of 0.9 eV from valence band of O (2p). It can be stated that an electron requires a minimum energy of 3.1 eV to make transition from valence O (2p) to the crystal field site (e_g) for the octahedral site.

Considering the energy band gap model proposed by Sadat et al. [76], the peaks at 469 nm (2.64 eV) corresponds to transfer of trapped electrons at octahedral site to valence band of O (2p). The electrons in the octahedral levels relax from Fe-O charge transfer band (CTB) to electron trap level via non-radiative loss which is immeasurable with the PL detector being used. The luminescence peak at 538 nm is obtained due to radiative

recombination of electrons from $e_g \rightarrow t_{2g}$ crystal field on octahedral site. The peak at 622 nm (1.99 eV) can be related to transfer of electrons taking place from t_2 crystal field to O (2p) at tetrahedral site. The transition scheme for uncoated and silver coated magnetite nanoparticles is schematically shown in the Figure 5.4 (a) & (b), respectively. The PL spectra for ~4 nm thick silver shell coated magnetite in Figure 5.3(a) shows the emission peaks corresponding to silver and magnetite with a slight observable shift to higher energies in Fe₃O₄ characteristic peaks after coating. The visible peaks for silver can be attributed to the radiative recombination of electrons at or above Fermi energy level with the holes present in upper level of sp- or d-bands [185]. The electron, upon excitation by incident light of suitable wavelength, reaches to the highest vibrational level of excited state. The electron then reaches the lowest level of excited state via non-radiative relaxation by dissipating extra energy to the local environment.

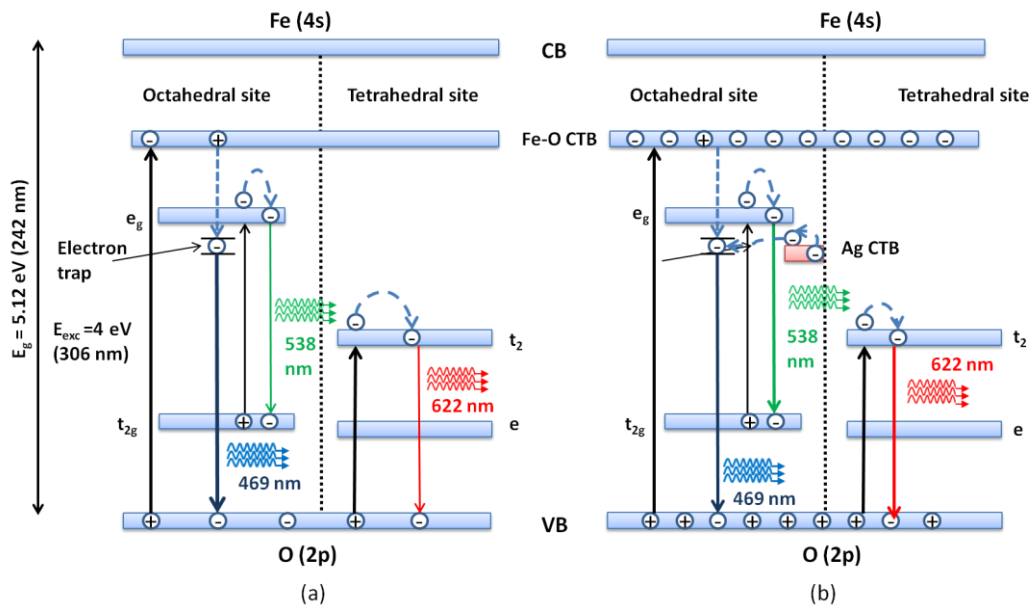


Figure 5.4 Proposed Energy Level diagram for (a) magnetite, and (b) silver coated magnetite nanoparticles. The dashed lines (--->) represent non-radiative recombination of electrons. [CB- conduction band, VB- valence band, E_g - band gap, E_{exc} - excitation energy, CTB-Charge Transfer Band].

On incorporation of silver shell onto the magnetite core, an additional charge transfer state related to d- band of silver appears at 2.61 eV and 2.82 eV (figure 5.4 (b)). Since this level is very near to the energy levels of trapped electrons at octahedral site of Fe-O, the transfer of few electrons may take place from d-level of Ag along with emission that appears as hump in the curve range 470- 500 nm. As the population of trapped electrons increases, number of electrons that participate in the transition corresponding to peak 469 nm becomes larger. This is well exhibited by increase in the intensity of the peak, as intensity being a direct measure of number of photons being emitted. This supports the enhancement of luminescence in the blue region. The effect of increase in silver shell thickness on PL spectra has also been studied.

Figure 5.3(d) shows the spectrum of silver coated magnetite nanoparticles with shell thickness ~9 nm, ~4 nm and ~3 nm. The peak positions and their shape are almost independent of the shell thickness. However, the intensity of the peak increases with the thickness of silver shell coating. Nanoparticles offer larger surface to volume fraction, therefore, also resulting in higher defect densities at surfaces. These defects result in broadening of emission peaks, thus lowering the PL intensity [186]. The surface defects can lead to reduction in band gap. In uncoated magnetite nanoparticle system, electrons can move between various defects through non-radiative recombination by dissipating energy thermally. Tongay et al reported increasing PL intensities for higher defect densities in case of monolayer transition metal dichalcogenides [187]. Arras et al showed the modification of electronic states caused due to formation of oxygen vacancies in Fe₃O₄ defects [188]. Taking the integrated area under the curve ratio of transitions corresponding to trapped electrons and crystal field levels (e_g and t_{2g}) of octahedral site as $\frac{A_{green}}{A_{blue}} \left(\frac{G}{B}\right)$ gives an indication of number of conduction electrons participating in electron transition from associated levels. The calculated integrated area

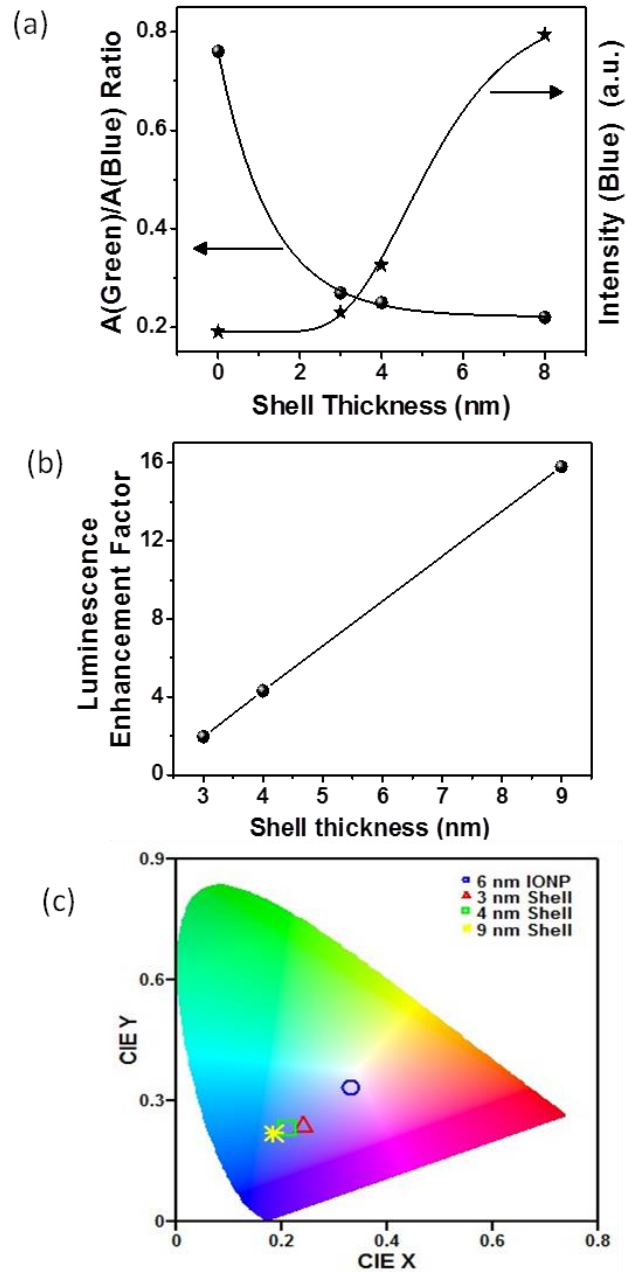


Figure 5.5 Different properties studied using PL spectrum for uncoated and silver coated iron oxide nanoparticles (a) Integrated area ratio curve and highest intensity variation with silver shell thickness; (b) Linear dependence of Luminescence Enhancement Factor on shell thickness; (c) Chromaticity diagram for uncoated and silver coated nanoparticles.

ratios are indicated in Figure 5.5(a). It can be noticed that G-B ratio decreases for

thicker silver shells. This indicates the decrease in electron transitions from e_g to t_{2g} level of octahedral sites, which corresponds to green emission line.

It seems that, on increasing the shell thickness, there is an increase in population of conduction electrons in trap level of octahedral site. An enhancement in the intensity of blue-emission peak with increasing silver shell thickness is also worth noticing. Consequently, the band-edge in the wavelength range 430-450 nm and 470-500 nm corresponding to silver appears increasing with thicker shells as shown in Figures 5.3(a) and (b) indicating the rise in number of electrons participating in due to transfer of electrons to electron trap levels from d-bands of Ag which accounts for high intense peaks at 469 nm. Such observations suggest enhancement and occurrence of excellent photoluminescence properties can be achieved by silver coating onto the magnetite core. The maximum luminescence intensity was obtained for thickest silver shell of ~9 nm that can be measured as Luminescence Enhancement Factor (LEF). It is defined as the ratio of maximum luminescence peak for coated nanoparticles to that of uncoated ones [189]. The maximum LEF is 1.97, 4.32 and 15.85 factors with calculated quantum yield ~4%, ~7% and ~22% for ~3 nm, ~4 nm and ~9 nm shell thickness, respectively. The LEF shows a linear variation with shell thickness as represented by Figure 5.5(b).

The two-dimensional (x, y) CIE color space chromaticity diagram of uncoated and silver coated magnetite nanoparticles is shown in Figure 5.5(c). The CIE coordinates are found to be (0.33, 0.33), (0.24, 0.24), (0.21, 0.23) and (0.19, 0.22) for bare magnetite and ~3 nm, ~4 nm, ~9 nm silver coated magnetite, respectively. The color co-ordinates of bare magnetite nanoparticles lie in the cool white emission region. The CIE co-ordinates observe a blue shift on silver coating making them very efficient for imaging applications.

The PL spectra for magnetite nanoparticles of average size ~8 nm coated with ~1, ~2 and ~3 nm were also recorded in order to check the effect of increase in core size as shown in Figure 5.6. The spectral properties were found to remain almost similar to the one with average size ~6 nm magnetite core.

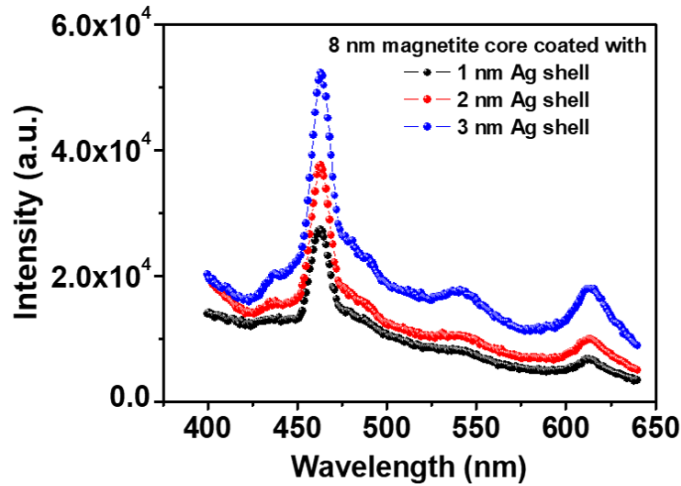


Figure 5.6 PL emission spectrum for ~1, ~2 and ~3 nm Ag coated ~8 nm magnetite core nanoparticles for $\lambda_{\text{ex}}=306$ nm.

Apart from core-shell nanoparticles, in order to study the effect of integration of silver magnetite nanoparticles, the SPR and PL response of Janus shaped silver-magnetite nanoparticles were also studied, which has been discussed in the following section.

5.4 SPR and PL Response of the Janus Shaped Silver-Magnetite Nanoparticles

The optical characteristics of the magnetite and silver-magnetite Janus structured samples have been studied in order to analyze their absorption wavelength and band gap. Figure 5.7 shows the measured UV-Vis spectra for silver-magnetite nanoparticles. A SPR band at 372 nm and 474 nm corresponding to the silver-magnetite Janus nanoparticle appears in the spectrum. There is a noticeable shift and change in the

nature of curve for the resonance peak position as compared to those for individual silver nanoparticles due to difference in morphology and local environment.

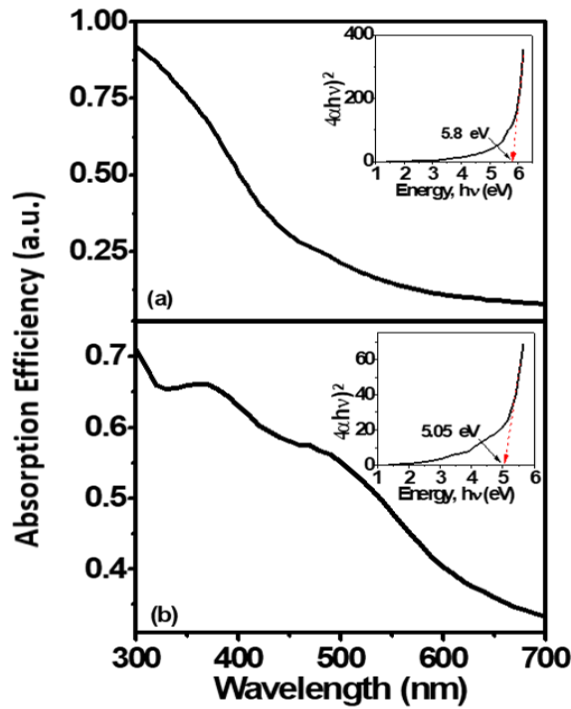


Figure 5.7 UV-Vis spectra for synthesized nanoparticles (a) pure phase Fe₃O₄ nanoparticles; (b) Janus shaped Ag-Fe₃O₄ nanoparticles. The inset in figure show Tauc plots for the system to obtain their energy band gap.

The band gap of materials can also be evaluated using UV-Vis absorption spectroscopy by employing the use of Tauc equation [183]: $(\alpha hv)^2 = hv - E_g$, where α and hv represents the absorption co-efficient of nanoparticles and incident photon energy, respectively. The band gap of material is determined by extrapolating $(\alpha hv)^2$ to the incident photon energy axis which is found to be 5.7 eV and 4.9 eV for magnetite and silver- magnetite nanoparticles, respectively. The values of energy gap for magnetite nanomaterials have been reported to lie in the range 4-6 eV [182]. The luminescence emission spectrum has also been recorded in a wavelength range of 420 nm to 700 nm upon illumination by an excitation wavelength of 390 nm as shown in Figure 5.8. Two

major emission peaks at 440 nm and 574 nm are observed for bare magnetite nanoparticles along with some less significant peaks. The silver integration with magnetite nanoparticle makes the two peaks more prominent and shift towards lower energy. The two maxima for silver-magnetite nanostructure appear at 450 nm and 587 nm with relatively larger intensities indicating an increase in the number of electrons participating in electron transfer from various energy levels due to match in energies between charge transfer band (CTB) of silver and Fe-O states.

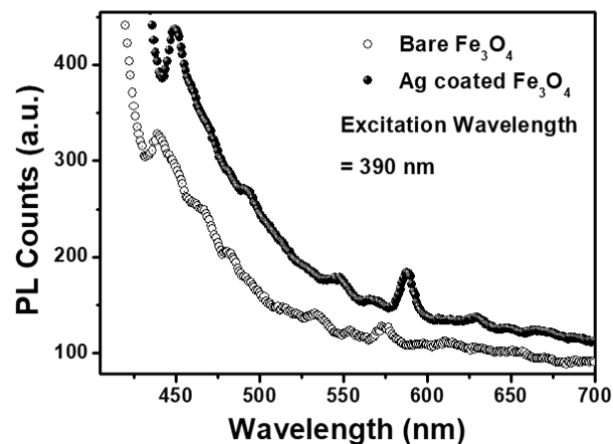


Figure 5.8 Photoluminescence spectra for uncoated and Janus shaped silver-magnetite nanoparticles.

The silver-magnetite nanoparticles have blue-emission in visible region of electromagnetic spectrum. The significance of blue emission nanomaterials in bioimaging applications has been studied by several researchers who have performed the imaging on human brain tumor cells using carbon dots and fluorescent carbon nanoparticles [190-191]. The particles exhibiting emission in blue region provides a better contrast in the images which helps in easy identification of abnormal cells.

5.5 Conclusions

In the present chapter, the influence of Ag coating on photoluminescence of Fe₃O₄ was investigated. The luminescence of Fe₃O₄ was effectively enhanced by surface plasmon

absorption of silver present in the shell. The peak intensity of green emission decreases for thicker silver shells indicating lowering of energy gaps between crystal fields of octahedral levels leading to increase in transitions corresponding to octahedra levels. The luminescence enhancement factors are 1.97, 4.32 and 15.85 factors for ~3, ~4 and ~9 nm thick silver shell coated magnetite nanoparticles, respectively. The estimated quantum yield was found to be ~4% for ~3 nm thick silver shell, ~7% for 4 nm thick silver shell and ~22% for ~9 nm thick silver shells. The Ag coating enhanced luminescence is due to the transfer of electrons from d-band of silver to electron trap level of Fe-O at octahedral sites increasing the population of electrons and thus intensifying the emission peak corresponding to blue emission. The influence of thickening of shell on the magnetic core was investigated. The CIE coordinates of bare magnetite in two-dimensional chromaticity diagram are found to lie in cool white emission range which makes a more blue-shift on increasing shell thickness.

After an investigation of the absorption and luminescence properties of Ag@Fe₃O₄ nanoparticles, which confirm the optical activity in the entire visible region, the next part of our study is directed towards the detailed analysis of the magnetic behavior of the synthesized uncoated and silver coated magnetite nanoparticles. The upcoming chapter discusses the details of the magnetic behavior of these uncoated and core-shell Ag@magnetite nanoparticles.