CHAPTER 4

Synthesis and study of fluorescence properties of Ag nanoparticles

In this chapter, we start with a brief introduction to Ag nanoparticles. Synthesis of the Ag nanoparticles employing the electro-explooding wire technique is presented next. Synthesized Ag nanoparticles are characterized by using X-ray diffraction, transmission electron microscopy, atomic force microscopy, Zeta potential, UV-visible spectroscopy and their results discussed. Fluorescence properties of the Ag nanoparticles dispersed in water have been studied in details at different excitation wavelengths. Associated with the fluorescence emission, resonant absorptions are observed in the fluorescence excitation spectra. This allows us to establish the electronic levels operating in the Ag nanoparticles. Hence, fluorescence has been assigned to electronic transitions from different higher excited states to d levels. Also, the effect of solvent on the fluorescence of Ag nanoparticles is established by studying the fluorescence of the Ag nanoparticles dispersed in methanol and hexane. In addition, effect of concentration and temperature on the fluorescence of the Ag nanoparticles dispersed in water has been studied. In conformity with these, effect of the temperature and the emission wavelength has been studied on the excitation spectra. In the last section of the chapter, we discuss the fluorescence from trap states of the Ag nanoparticles.
4.1 Introduction

Noble metal nanoparticles [1-3] have been a source of immense interest due to their novel properties, different from those of the metal atoms and the bulk metal as well. Uniqueness in properties of the metal nanoparticles arise due to their high aspect ratio and quantum size effect [4], resulting from their reduced size. Metal nanoparticles have remarkable electrical, optical, electronic, physical, chemical and magnetic properties. Besides their usefulness in various fields and their ability to promote surface enhanced optical phenomenon [5, 6], it has been discovered that noble metal clusters display intense visible fluorescence. The study of their fluorescence properties yields new insight into the energy band structure of the nanoparticles and it is prerequisite for their possible practical applications in integrated optical devices [1, 7], in bio-labeling [8, 9], and as a sensor.

There are two types of interaction [10] of incident radiation with the metal clusters. In one type, interaction between the valence electrons is more significant than their interaction with atomic cores and results in the surface plasmon oscillations. In the second type, primary interaction takes place between the valence electrons and their atomic cores, yielding transitions similar to those occurring in solitary atoms. Fluorescence from the noble metal nanoparticles are presaged by the work of A. Mooradian [11], who observed broad fluorescence peaks centred near the interband absorption edge (2.0 eV, 2.2 eV), from Cu and Au metals for excitation at 488 nm. Further, it was observed that at different excitation wavelengths, (457.9 nm to 514.5 nm and 300 nm to 400 nm) the fluorescence peaked at the same energy, while, the high energy tail increases slightly with higher photon energy pumping. After a span of around two decades, a detailed experimental study of this phenomenon was undertaken by Boyd et al. [12], who elucidated the effect of excitation energy and surface roughness on the fluorescence of the Cu, Ag, and Au films. At higher excitation energy, additional peaks in the fluorescence spectrum are observed. Fluorescence from the noble metals has been attributed to transitions between electrons in the conduction band below the Fermi level and holes in the d bands. Recently, there are reports of fluorescence from Ag nanoparticles, whereby various explanations are given for the observed fluorescence. Jiang et al. [3] have reported fluorescence peak for the Ag nanoparticles dispersed in
water at 465 nm for excitation wavelength ($\lambda_{ex}$) = 290 nm, which has been assigned to transition of electrons involving the interface electron energy bands of fluorescence. Basak et al. [13] have shown shift in the fluorescence peak position towards longer wavelengths for Ag nanoparticles dispersed in PMMA matrix with increasing $\lambda_{ex}$ in the range \~370-550 nm and speculated fluorescence due to resonance between the luminescence transition and silver plasmons. Also, Treguer et al. [14] assigned the fluorescence peaks at 550, 700 nm for $\lambda_{ex}$ at 300, 350 nm, respectively, for Ag nanoparticles in aqueous medium to the presence of oligomeric clusters of Ag$_{4x}^{x+}$ and Ag$_{7}^{3+}$. While, Jian et al. [14] reported two fluorescence peaks for the Ag nanoparticles. A peak fixed at 315 nm, irrespective of the $\lambda_{ex}$ ($\lambda_{ex} < 280$ nm), has been assigned to the local field enhancement, while the second peak red shifts from 540 nm to 595 nm with change in $\lambda_{ex}$ from 380 to 440 nm and its origin has been speculated to the electron interband transitions. However, Xu et al. [15] reported a fluorescence peak at 448 nm for $\lambda_{ex}$ at 309 nm for Ag nanoparticles and attributed the fluorescence to metal to ligand charge transfer absorption. From the above review of the literature on the fluorescence studies of the Ag nanoparticles, it is clear that detailed analysis is required for the fluorescence properties of the Ag nanoparticles. In this chapter we present such a study of the fluorescence properties of the Ag nanoparticles along with their synthesis using electro-exploding wire technique (EEW) and characterization using various techniques.

4.2 Synthesis of Ag nanoparticles

Various techniques have been employed for synthesis of Ag nanoparticles such as gas evaporation [16], arc plasma [17], sputtering [18], chemical reaction [19], electrochemical method [20] and laser ablation [21]. EEW technique has been employed by us [22-25] for preparation of Ag nanoparticles, a process in which high current density is passed through a metal in wire-plate geometry. EEW is a novel, physical, top-down, semi-continuous approach to synthesize the Ag nanoparticles, where a thin Ag wire is exploded on a plate of Ag metal by passing a current density \~10^{10} A/m$^2$, in a time \~10^{-6} sec. Flow of current through the Ag wire-plate leads to heating of wire-plate at the point of contact, followed by melting. The melted Ag metal at the point of contact is further
heated by the ever increasing current density due to increase in the resistance. This leads to evaporation of the material (Ag metal), followed by plasma formation. This plasma is contained by the self induced magnetic field. When the vapour pressure of the plasma overwhelms the self induced magnetic field, explosion occurs and plasma products are dispersed in the medium, leading to formation of the Ag nanoparticles. Ag nanoparticles are thus synthesized by fragmentation of the parent Ag metal in water medium, which simultaneously caps and collects the particles. The synthesized Ag nanoparticles are free from extraneous impurities as no chemicals have been used in the nanoparticles synthesis. Parameters, like, current density, material type, wire-plate dimension and the medium in which explosion is carried out, are monitored to have control over the entire process of exploding the wire [16-19]. A schematic diagram of the apparatus and process details has already been presented in chapter 2.

4.3 X-ray diffraction analysis of Ag nanoparticles

![X-ray diffraction patterns of the Ag nanoparticles synthesized by EEW.](image)

Figure 4.1. X-ray diffraction patterns of the Ag nanoparticles synthesized by EEW.
With the help of the XRD analysis, we can find out the crystal phase and amorphous or crystalline nature of the new material. If the prepared material is crystalline, we can determine its basic lattice structure (e.g. cubic or hexagonal etc.) by indexing its lattice planes. Details of the sample preparation and instrumentation have already been presented in chapter 3. In Figure 4.1, we show the XRD patterns of the Ag nanoparticles. There are peaks at $\theta = 38.14^\circ$, $44.34^\circ$, $64.54^\circ$ and $77.47^\circ$ in the XRD spectra of the Ag nanoparticles. The XRD peaks position matches with that of the metallic Ag in face centred cubic (fcc) phase (at $\theta = 38.11$, $44.27$, $64.42$, $77.47$) and corresponds to the reflections from the (111), (200), (220) and (311) planes, respectively. Further, the XRD pattern shows that the synthesized Ag nanoparticles are crystalline.

**Crystallite size:** Scherrer observed that small crystallite size could give rise to line broadening of the XRD peaks [26]. Here, crystallite size ($d$) has been calculated using the ‘Debye-Scherrer’ formula.

$$d = \frac{k\lambda}{\beta \cos \theta}$$

where the symbols have their usual meanings, details of which are given in chapter 3. The crystallite size, as calculated by taking the XRD peak corresponding to (111) plane, comes out to be $\sim 35$ nm.

### 4.4 Transmission electron microscopy of Ag nanoparticles

For TEM investigations a small drop of the Ag nanoparticles dispersed in water is put on a carbon coated copper grid. TEM characterization is carried out employing a JEOL-2010F, UHR electron microscope, operating at 200KV. Figure 4.2 shows, TEM images of a large number of Ag nanoparticles at a magnification of 30,000. Though, it appears that the size of such particles is in the range of $\sim 15$ nm or larger, we believe that these large sized particles are composed of van der Waals clusters of smaller entities [24]. To demonstrate this, we show, a TEM image at high resolution (Figure 4.3a) and a high resolution TEM image (magnification = 800,000) of two almost spherical particles joined in the middle (Figure 4.3b). From the information present in the high resolution TEM...
image, shown in Figure 4.3b, it is clear that these individual particles are 6-7 nm in diameter, while the composite particle in lower resolution would appear to be in the range of ~15 nm. Further, in the high resolution TEM image, we can see the crystal planes and this support the XRD analysis, demonstrating crystalline nature of the Ag nanoparticles.

Figure 4.2. TEM images of the Ag nanoparticles (a) and (b).

Figure 4.3. (a) TEM image of a large collection of nanoparticles, (b) High resolution TEM image showing van der Waals cluster of two particles.
4.5 Atomic force microscopy of Ag nanoparticles

We have spin coated the Ag nanoparticles dispersed in water on optically flat glass substrates and after drying the sample, AFM images are recorded (details of sample preparation and instrumentation have already been given in chapter 3). Figure 4.4 shows, the AFM images of the Ag nanoparticles at various scan sizes: (a) 2×2 μm (b) 2×2 μm (c) 1×1 μm (d) 644.5×644.5 nm, images taken from various samples.

Figure 4.4. AFM images of the Ag nanoparticles at scan sizes: (a) 2×2 μm (b) 2×2 μm (c) 1×1 μm (d) 644.5×644.5 nm.

Average particle size, from the AFM data analysis, comes out to be ~50 nm. The average size observed in the AFM analysis is much larger than observed in TEM analysis or XRD analysis. We believe this can be because of the coalescence of the Ag nanoparticles on the glass substrate due to van der Waals forces of interaction. Coalescence of the Ag
nanoparticles has also been seen in the TEM data. This will be clear in the later part of the discussion in this chapter, where we have observed fluorescence emission of the Ag nanoparticles, possible only from atom-like states.

4.6 Zeta potential measurements of Ag nanoparticles

Zeta potential is a physical property, which is a measure of the effective charge on the particles dispersed in a liquid/solvent and therefore related to the electrostatic repulsion between them. Zeta potential measurement is done by employing computer operated ZEECOM-2000 from Microtec, Japan (other details about instrumentation are given in chapter 3). Diluted samples of the Ag nanoparticles dispersed in water are used for Zeta potential measurement. Figure 4.5 shows, the frequency plot of the Zeta potential of the Ag nanoparticles. Average value of the Zeta potential of the Ag nanoparticles is -17.14 mV.

![Figure 4.5. Zeta potential measurement of the Ag nanoparticles dispersed in water.](image)

The DLVO (Derjaguin, Landau, Verwey and Overbeek) theory for colloidal interactions dictates that a colloidal system will remain stable if and only if the Coulombic repulsion, arising from the net charge on the surface of the particles is greater than the van der Waals forces of attraction between the particles. Here, negative value of the Zeta
potential for the Ag nanoparticles dispersed in water indicates that there is negative surface charge on the Ag nanoparticles dispersed in water. But, the Coulombic repulsion between the Ag nanoparticles due to negative surface charge, providing a Zeta potential of ~ 17 mV, is not enough to stop aggregation of the Ag nanoparticles, as have been seen in AFM and TEM analysis.

4.7 UV-visible spectroscopy of Ag nanoparticles

Absorption of UV-visible light by metal nanoparticles can be either due to the surface plasmon oscillation or due to the electronic transitions, depending on the energy of the incident radiation, as discussed in details in chapter 1 and 3. After ultrasonication for 10 min, Ag nanoparticles dispersed in water are employed to record the absorption spectrum, employing a Hitachi 3300 UV-visible double beam spectrophotometer. Figure 4.6 shows, the UV-visible absorption spectrum of the Ag nanoparticles dispersed in water. There are peaks at ~ 400 nm, ~270 nm and ~215 nm in the absorption spectrum of the Ag nanoparticles dispersed in water.

![Absorption Spectrum](image)

Figure 4.6. UV-visible absorption spectrum of Ag nanoparticles dispersed in water.
The peak at 400 nm is assigned to surface plasmons [13], which arise due to collective oscillations of the valence electrons in the electromagnetic field of the light radiation and is characteristic of the Ag nanoparticles. The peaks at 270 nm and 215 nm are similar to those reported by others [23, 27] and are due to transition of the valence electrons to higher energy states. We will discuss these electronic transitions in detail in the next section on the fluorescence properties of the Ag nanoparticles.

4.8 Fluorescence properties of Ag nanoparticles

After ultrasonication for 10 min of Ag nanoparticles dispersed in water, fluorescence measurements are done by using a Carey Eclipse fluorescence spectrophotometer from Varian, equipped with a Xenon light source, two Czerny-Turner monochromators for excitation and emission, and accessories to monitor and control the sample temperature. It is well established that fluorescence is a three step process involving excitation (by high energy radiations) of an electron from ground state to higher energy states, relaxation of the excited electron, followed by fluorescence emission [28, 29].

![Figure 4.7. Optical micrographs of Ag nanoparticles dispersed in water and kept in (a) daylight, (b) UV-light.](image)

We show in Figure 4.7, the optical micrographs of the Ag nanoparticles (concentration of the Ag nanoparticles is \( \sim 10^{19} \) atoms/cc) dispersed in water and kept in (a) daylight, (b)
UV-light. The Ag nanoparticles dispersed in water are black in colour under daylight but when kept under UV light, they appear deep-blue. Colour of the nanoparticles dispersed in a solvent depends upon many factors like light scattering, absorption and emission; size and shape of the nanoparticles; dielectric constant of the solvent and the nanoparticles. We are not going into address some of these details.

To study in detail, the fluorescence properties of the Ag nanoparticles dispersed in water, fluorescence measurements at various $\lambda_{ex}$ has been carried out. We show in Figure 4.8, the fluorescence emission spectra of the Ag nanoparticles dispersed in water at $\lambda_{ex} = 215$ nm (squares), 225 nm (spheres), 230 nm (triangles) and 235 nm (stars).

![Figure 4.8](image.png)

**Figure 4.8.** Fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex} = 215$ nm (squares), 225 nm (spheres), 230 nm (triangles) and 235 nm (stars).

There are strong emission peaks at $\sim 300$ nm (the exact positions of the 3 emission peaks are 299 nm). The position of the emission peaks remain approximately same with change in $\lambda_{ex}$ and hence, are assigned to fluorescence emission from the Ag nanoparticles. The maximum fluorescence (as estimated from intensity of fluorescence peaks) is observed for $\lambda_{ex} = 215$ nm, decreasing thereafter, which indicates maximum transition probability/
resonant absorption at 5.76 eV (corresponds to $\lambda_{ex} = 215$ nm). In addition, the same fluorescence emission peaks at $\sim 300$ nm are also seen at $\lambda_{ex} \sim 270$ nm. In order to demonstrate this, we show in Figure 4.9a, fluorescence emission spectra of the Ag nanoparticles dispersed in water at $\lambda_{ex} = 255$ nm (squares; red), 260 nm (spheres; blue), 265 nm (triangles; olive), 270 nm (circles; orange), 275 nm (pentagons; magenta) and 280 nm (stars; black).

![Figure 4.9a](image)

**Figure 4.9.** (a) Fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex} = 255$ nm (squares; red), 260 nm (spheres; blue), 265 nm (triangles; olive), 270 nm (circles; orange), 275 nm (pentagons; magenta) and 280 nm (stars; black), (b) Plot of the fluorescence peak intensity at 300 nm with $\lambda_{ex}$.

The high intensity peaks at $\lambda_{ex} = 255, 260, 265, 270, 275$ and 280 nm are Rayleigh scattering peaks, whose position changes with change of $\lambda_{ex}$. Rayleigh scattering lines have indeed been reported in conjunction with the fluorescence emission from the metal nanoparticles in H$_2$O [3]. The peaks at $\sim 300$ nm are fluorescence emission peaks of the Ag nanoparticles, because their position remains fixed with change in $\lambda_{ex}$. In Figure 4.9b, we plot the intensity of the fluorescence peak at 300 nm for excitations in the range 255-280 nm. The peak intensity goes through a maxima at $\lambda_{ex} = 270$ nm, indicating thereby resonant absorption by a level at $E = 4.59$eV from the ground state, corresponding to $\lambda_{ex} = 270$ nm.
Further, to look into details of electronic levels operating in the fluorescence of the Ag nanoparticles, we recorded the fluorescence excitation spectra. The transitions between two states can be detected in the absorption spectrum as long as the transitions are not forbidden, no matter, whether the transitions are radiative or not. However, in fluorescence excitation spectrum only the radiative transitions can be observed. This is the basic difference between the UV-visible absorption and fluorescence excitation spectrum. Due to this difference between absorption and excitation spectra, the inhomogeneous broadening of the absorption bands can be resolved in the fluorescence excitation spectrum. Because, in a fluorescence excitation spectrum, by monitoring a specific spectral band of the full fluorescence range and then scanning the excitation energy, transitions that overlapped in direct absorption spectrum (UV-visible absorption) are resolved in the excitation spectrum [28, 29]. Further, intensity of a peak excitation/emission depends upon the transition probability between two states \( s \) and \( n \) which is given by the formula [30]:

\[
p_{sn} = q \int \psi_s^*(r) \psi_n(r) dr = q \langle s | r \rangle | n \rangle \tag{4.2}
\]

Solving the time dependent Schrödinger equation by using the wavefunction \( \psi(r, t) = \sum_n C_n(t)e^{-i\omega_{n}}\psi_n(r) \), it can be easily demonstrated that the coefficient \( C \) is given by

\[
C_s(t) = A \left[ \frac{e^{i\omega_{sk}t/2} \sin(\omega_{sk} + \omega)t/2}{(\omega_{sk} + \omega)/2} + \frac{e^{i(\omega_{sk} - \omega)t/2} \sin(\omega_{sk} - \omega)t/2}{(\omega_{sk} - \omega)/2} \right] \tag{4.3}
\]

where \( A \) is a constant. For large value of \( t \), the function \( \frac{\sin(\omega_{sk} - \omega)t/2}{(\omega_{sk} - \omega)t/2} \) peaks around \( \omega = \omega_{sk} \) and is negligible elsewhere. Thus, transition probability between states for which \( \omega_{sk} \) is significantly different from \( \omega \) will be negligible. In an emission spectrum \( E_k > E_s \) and hence \( \omega_{sk} = (E_k - E_s)/\hbar \) is negative, then it is the first term which contributes. While, in an absorption process \( E_k < E_s \) and hence \( \omega_{sk} \) is positive and consequently, it is the second term which contributes. In conformity with this, we show in Figure 4.10a, the fluorescence excitation spectra of the Ag nanoparticles dispersed in water, when emission wavelength (\( \lambda_{em} \)) is fixed at 300 nm, i.e., at the highest intensity of
the fluorescence peak. The spectrum is marked by two broad peaks centred at \(\sim 215\) nm and \(\sim 270\) nm. This demonstrates transitions in the Ag nanoparticles to higher energy levels, corresponding to transitions between pairs of levels \(s\) and \(k\) in the formula above. Intensity of these peaks are maximum at 215 nm and 270 nm, indicating maximum transition probability and hence resonant absorption at 5.76 eV (corresponds to \(\lambda_{ex} = 215\) nm) and 4.59 eV (corresponds to \(\lambda_{ex} = 270\) nm).

![Fluorescence excitation spectrum of Ag nanoparticles dispersed in water](image)

Figure 4.10. Fluorescence excitation spectrum of Ag nanoparticles dispersed in water (a) at \(\lambda_{em} = 300\) nm, (b) at \(\lambda_{em} = 290\) nm (squares; orange), 300 nm (triangles; blue), 310 nm (circles; olive), 320 nm (stars; magenta).

The peaks at 215 nm and 270 nm, in the excitation spectra of the Ag nanoparticles dispersed in water, allow us to establish the electronic levels operating in the Ag nanoparticles. The peak at \(\sim 270\) nm, corresponds to the transitions from the ground state to the first excited state and the excitation peak at \(\sim 215\) nm, corresponds to the transition from the ground state to the second excited state. However, both these absorption pathways yield fluorescence at 300 nm.

We have also studied the effect of change in \(\lambda_{em}\) on the excitation spectra of the Ag nanoparticles dispersed in water. In Figure 4.10b, we show the excitation spectra of the Ag nanoparticles dispersed in water at \(\lambda_{em} = 290\) nm (squares; orange), 300 nm (triangles; blue), 310 nm (circles; olive) and 320 nm (stars; magenta). Intensity of the absorption...
peaks at ~215 nm and ~270 nm decreases as the $\lambda_{em}$ changes from 300 nm (maximum fluorescence emission intensity). This allows us to establish that the transition probability decrease as the $\lambda_{em}$ changes from the position of maximum intensity. However, no observable change in the position of the absorption peaks at ~215 and ~270 nm has been observed with change in $\lambda_{em}$ from the position of maximum intensity. These are also in conformity with the fluorescence emission spectra, where the maximum intensity of the fluorescence peak at 300 nm is observed at $\lambda_{ex} = 215, 270$ nm.

For metal nanoparticles, it is well known that energy bands split into a series of energy levels as a result of the quantum size effect. Further, splitting of the energy levels will be more distinct as the size of the nanoparticles becomes smaller. The relationship between level spacing ($\delta$) and particle size is given by $\delta = \frac{4E_F}{3N}$, where $E_F$ denotes Fermi energy, $N$ denotes number of conduction electrons or $\delta \propto \frac{1}{d^3}$, where $d$ is particle size (for a spherical particle) [4, 31]. Hence, the energy level splitting makes the electronic transition abundant. With increasing excitation energy electrons will be excited into higher energy levels, which are discrete too, as in solitary atoms.

In the region of fluorescence emission observed by us (i.e., at 300 nm), a peak at 315 nm has been reported only by Jian et al. [14], who assigned its origin to local field enhancement, while, an early investigation by Boyd et al. [12] for Ag thin films has assigned this to volume and surface plasmons. Our careful $\lambda_{ex}$ and $\lambda_{em}$ dependence study of the fluorescence properties of the Ag nanoparticles allow us, however, to assign these to pure fluorescence involving more than one excited state. In conformity with the results discussed so far, we construct an energy level diagram, which is shown in Figure 4.11. The upward transitions from the d level of Ag nanoparticles to the excited states are marked by thick arrows in the upward direction and their labels, namely, UP2 ($5.76\, eV$), which results in the excitation from the ground state to the second excited state and UP1 ($4.59\, eV$), which results in the excitation from the ground state to the first excited state, are marked next to these arrows. Also marked are the downward transitions taking place from the bottom of the first excited state, which gives rise to the fluorescence emission,
At \( \lambda_{em} = 300 \text{ nm} \) (DN1, DN2= 4.1 eV). The difference between UP1 and the fluorescence emission energy, i.e., \( \sim 0.5 \text{ eV} \), is probably a measure of the width of the first excited state, as the emission takes place from the bottom of the first excited state.

\[ \lambda_{em} = 300 \text{ nm} \] (DN1, DN2= 4.1 eV). The difference between UP1 and the fluorescence emission energy, i.e., \( \sim 0.5 \text{ eV} \), is probably a measure of the width of the first excited state, as the emission takes place from the bottom of the first excited state.

At \( \lambda_{ex} = 270 \text{ nm} \), transition of electrons take place from the ground state to the first excited state and at \( \lambda_{ex} = 215 \text{ nm} \), transition take place from the ground state to the second excited state, as established by us. However, both these absorption pathways yield fluorescence at 300 nm. The second excited state (UP2) deexcites via DN2, also shown in the Figure 4.11, that is possible only through a transition or a major reorganization DN*. A measure of the width of the second excited state, as well as, the presence or absence of DN* can not be verified, as we have no possibility of detection of the radiation emanating with an energy of 1.2 eV. It is known as a general rule in the fluorescence that a molecule deexcites to the lowest vibrational level of its lowest excited state prior to photon emission in a time short enough as compared to the photon emission times [29]. The only way photon emission at 300 nm from both these excited states can be achieved, though
these are separated by 1.2 \textit{eV}, is through an internal conversion involving these excited states.

Our observation of a unique fluorescence at 300 nm from different excited states allows us to establish a combination of pathways, not possible in ordinary molecules. To the best of our knowledge, this special feature has not been reported earlier for metal nanoparticles. This is in conformity with the fluorescence excitation spectra, where two peaks have been observed at ~270 nm and ~215 nm. These resonant levels are also corroborated by UV-visible absorbance spectra, where weakly resolved absorption peaks are observed at 215 nm, 270 nm. In this scenario, the excited states should be sensitive to the surrounding medium, which is exactly what we find, when the Ag nanoparticles are dispersed in other solvents such as methanol or hexane.

4.8.1 Solvent effect on the fluorescence of Ag nanoparticles

Although, the simple picture of photon absorption by the nanoparticles and subsequent reemission of photons to give fluorescence seems to be quite straightforward, this is not entirely so. There are various factors/ nonradiative processes, which precede/ compete with the photon emission. When measuring the fluorescence of the Ag nanoparticles dispersed in a solvent, the most common state for the fluorescence measurements, it is important to note that the effect caused by the solvent are quite varied and complex [28, 29]. Typically, the fluorophore has a larger dipole moment in the excited state than in the ground state. Also, following excitation, solvent dipoles reorient or relax around the excited state of the fluorophore, which lowers the energy of the excited state. As the solvent polarity is increased, this effect becomes larger, resulting in emission at longer wavelengths (Red Stokes shifts or polarisation shift). In addition to specific solvent-fluorophore interactions, many fluorophores can form an internal charge transfer state. For instance, after excitation there can be increase in charge separation within the fluorophore. In case of a polar solvent, a fluorophore with charge separation may become the lowest energy state. However, in a nonpolar solvent the fluorophore without charge separation may have the lowest energy.

In order to study effect of the solvent on the fluorescence emission of Ag nanoparticles, we record the fluorescence emission of Ag nanoparticles dispersed in methanol and
hexane, at similar excitation wavelengths as has been used for Ag nanoparticles dispersed in water. In Figure 4.12a, we show the fluorescence emission spectra of Ag nanoparticles dispersed in methanol at $\lambda_{ex} = 210$ nm (squares; black), 220 nm (spheres; red), 225 nm (triangles; blue), 230 nm (rectangles; olive), 235 nm (stars; magenta), 240 nm (circles; purple), 250 nm (pentagons; royal). There are peaks at ~310 nm, for Ag nanoparticles dispersed in methanol, position of which remains fixed with change in $\lambda_{ex}$ and hence, are attributed to fluorescence emission of the Ag nanoparticles dispersed in methanol. Further, intensity of the fluorescence emission peak increases as the $\lambda_{ex}$ increase, is maximum at $\lambda_{ex} = 225$ nm and decreases thereafter as the $\lambda_{ex}$ increase. Maximum fluorescence emission intensity at $\lambda_{ex} = 225$ nm, indicates that $\lambda_{ex} = 225$ nm, corresponds to maximum transition probability/ resonant absorption for Ag nanoparticles dispersed in methanol. Also, Figure 4.12b shows, the fluorescence emission spectra of Ag nanoparticles dispersed in methanol at $\lambda_{ex} = 255$ nm (squares; orange), 260 nm (pentagons; royal), 265 nm (rectangles; olive), 270 nm (spheres; red), 275 nm (triangles; black), 285 nm (circles; blue), and 290 nm (stars; magenta). Here too, fluorescence peaks are observed at ~310 nm, irrespective of $\lambda_{ex}$ employed. The intensity of the fluorescence emission peak again goes through a maximum at $\lambda_{ex} = 275$ nm, corresponding to maximum transition probability for Ag nanoparticles dispersed in methanol. There are also high intensity peaks at 255, 260, 265, 270, 275, 285 and 290 nm, which are Rayleigh scattering peaks, as discussed previously in this chapter. To summarize, as for water discussed earlier, similar fluorescence emission is observed at ~310 nm, for the Ag nanoparticles dispersed in methanol at $\lambda_{ex}$ in the ranges (a) 210-250 nm and (b) 255-290 nm. However, the primary difference in fluorescence emission of the Ag nanoparticles dispersed in water and methanol is in the position of the fluorescence emission peak, which has red-shifted in the later. Shift in the emission peak position due to a solvent’s dielectric constant have been well researched in the literature [29] and is known to provide polarization shifts. Thus, the red-shift in methanol is unexpected, as methanol is a relatively non-polar solvent compared to water (dielectric constant of water is 80.3 and of methanol is 33.6). Also, a shift per se may not mean much if this is not compared with
the excitation peak position. Polarization shifts take place when energy absorbed during excitation is lost from the fluorophore due to availability of other channels in its immediate surrounding, namely, the solvent molecules.

![Fluorescence emission spectra of Ag nanoparticles dispersed in methanol](image)

Figure 4.12. Fluorescence emission spectra of Ag nanoparticles dispersed in methanol (a) at $\lambda_{ex} = 210$ nm (squares; black), 220 nm (spheres; red), 225 nm (triangles; blue), 230 nm (rectangles; olive), 235 nm (stars; magenta), 240 nm (circles; purple), 250 nm (pentagons; royal), (b) at $\lambda_{ex} = 255$ nm (squares; orange), 260 nm (pentagons; royal), 265 nm (rectangles; olive), 270 nm (spheres; red), 275 nm (triangles; black), 285 nm (circles; blue), and 290 nm (stars; magenta).

We now proceed to measure the exact location of the absorption maxima by recording the excitation spectrum of the Ag nanoparticles dispersed in methanol with $\lambda_{em}$ fixed at the location where highest intensity of the fluorescence peak is observed. Figure 4.13 shows, the fluorescence excitation spectrum of the Ag nanoparticles dispersed in methanol for $\lambda_{em}$ fixed at 310 nm. In the excitation spectrum of the Ag nanoparticles dispersed in methanol, there are peaks at ~225 nm and ~275 nm, corresponding to maximum transition probabilities. This is in conformity with the fluorescence emission data, where intensity of the fluorescence peak of the Ag nanoparticles dispersed in methanol is maximum at $\lambda_{ex} = 225$ nm and 275 nm.

A red shift of 10 nm in the fluorescence emission from the Ag nanoparticles dispersed in methanol, a less polar solvent compared to water, can now be commented upon. In a polarization shift scenario, the excitation peak holds its position, while the emission peak
shifts. This is in accordance with the access to other energy loss pathways, namely, the reorientation of solvent molecules by the fluorophore through dipolar interactions. However, evidence of such energy loss is absent here as the separation between emission and excitation remains constant. Thus, the observed shift has its origin somewhere else.

Figure 4.13. Fluorescence excitation spectrum of Ag nanoparticles dispersed in methanol for $\lambda_{em}$ fixed at 310 nm.

It is known as a general rule in fluorescence that a molecule deexcites to the lowest vibrational level of its lowest excited state prior to photon emission, in a time short enough compared to photon emission times [29]. We have already established the fluorescence of the Ag nanoparticles due to transitions of electrons from the excited states to the d levels. In conformity with the fluorescence emission observed from the Ag nanoparticles dispersed in water or methanol, we show in Figure 4.14, a schematic diagram showing energy levels in order to describe the solvent effect on the fluorescence of the Ag nanoparticles. Electron excitation takes place from 4d levels to various excited states, depending upon the excitation energy. Fluorescence emission takes place, when excited electrons, after relaxation, are deexcited back to the 4d levels. A level scheme (solid lines) describes the absorption in and emission from the Ag nanoparticles dispersed.
in water. And level scheme (dotted lines) describes the absorption in and emission from the Ag nanoparticles dispersed in methanol.

![Energy Level Diagram](image)

**Figure 4.14.** Schematic energy level diagram for fluorescence mechanism of the Ag nanoparticles in different solvents.

The other details, in the Figure 4.14, have already been discussed. Metal to ligand charge transfer and electron interband transitions have been put forth in the literature [14, 24] to explain the fluorescence of the Ag nanoparticles. These reports, however, lacked the possibility of observing fluorescence from pure nanoparticles, substantially smaller, as reported here. This has allowed us identification of fluorescence peaks, which are considerably narrow and hence allow tracking minor shifts. The proposal for fluorescence emission put forth in Figure 4.14 is a result of such a capability. Together with monitoring fluorescence shifts, there is a lack of correlation with polarization shifts in presence of solvents. Thus, the shifts observed need to be based on an independent origin. If the nanoparticles atoms are considered as having an effective central potential with an effective positive charge $Z_{\text{eff}}$, any charge transfer from the metal to ligand will stabilize the electronic levels (due to an increase in $Z_{\text{eff}}$), this will include the excited states. From photoemission studies [32] involving water and methanol adsorption on metallic surfaces, a larger charge transfer from the metal is observed in the case of water as compared to
methanol. Thus, if the excited states depicted in Figure 4.14 were to be on the metal site, a greater stabilization of these levels would ensue in the case of water. We, however, find just the opposite.

We, thus, propose the origin of the excited states to electronic states at the surface of the nanoparticle in the central potential $Z_{\text{eff}}/R$ of the nanoparticle atom, where $R$ is the radius of the nanoparticle. In the presence of molecules such as water, with which hybridization of such electronic states are possible, these are destabilized due to involvement of the ligand states through the exchange term. Under this description, a ligand which is expected to be least hybridized to the nanoparticle would produce the most stable excited state. We indeed find such a situation, when fluorescence of the Ag nanoparticles dispersed in hexane (a nonpolar solvent) is measured, where the fluorescence emission is further red-shifted to 330 nm, as compared to methanol (at 310 nm). In conformity with this, Figure 4.15a shows, the fluorescence emission spectra of the Ag nanoparticles dispersed in hexane at $\lambda_{\text{ex}} = 215$ nm (squares; red), 225 nm (triangles; blue) and 230 nm (spheres; olive). There are several fluorescence emissions, however, the primary fluorescence emission is at ~330 nm.

![Fluorescence emission spectra of Ag nanoparticles dispersed in hexane](image)

Figure 4.15. Shows the fluorescence emission spectra of Ag nanoparticles dispersed in hexane (a) at $\lambda_{\text{ex}} = 215$ nm (squares; red), 225 nm (triangles; blue) and 230 nm (spheres; olive), (b) at $\lambda_{\text{ex}} = 265$ nm (squares; red), 280 nm (triangles; violet) and 295 nm (spheres; olive).
Also, Figure 4.15b shows, the fluorescence emission spectra of the Ag nanoparticles dispersed in hexane at $\lambda_{ex} = 265$ nm (squares; orange), 280 nm (triangles; violet) and 295 nm (spheres; olive). High intensity peaks at 265, 280, 295 nm are Rayleigh scattering peaks and the peaks at $\sim 330$ nm are fluorescence emission peaks of the Ag nanoparticles dispersed in hexane, as already established. Fluorescence emission peak has further red shifted for Ag nanoparticles dispersed in hexane as compared to Ag nanoparticles dispersed in methanol (fluorescence peak is at $\sim 310$ nm) or for Ag nanoparticles dispersed in water (fluorescence peak is at $\sim 300$ nm).

### 4.8.2 Ag nanoparticles concentration effect on their fluorescence

Another important factor, which can affect the fluorescence emission of the Ag nanoparticles, is the concentration of nanoparticles. In order to establish this, concentration of the Ag nanoparticles has been varied in the range $0.15 \times 10^{17} - 2.0 \times 10^{18}$ atoms/cc and fluorescence studied.

![Figure 4.16](image_url)

**Figure 4.16.** Fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex} = 225$ nm and at concentration $= 0.15 \times 10^{17}$ atoms/cc (circles), $0.3 \times 10^{17}$ atoms/cc (stars), $0.6 \times 10^{17}$ atoms/cc (squares), $0.5 \times 10^{18}$ atoms/cc (spheres), and $2.0 \times 10^{18}$ atoms/cc (triangles).
Figure 4.16 shows, the fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex} = 225$ nm and at concentration $= 0.15 \times 10^{17}$ atoms/cc (circles), $0.3 \times 10^{17}$ atoms/cc (stars), $0.6 \times 10^{17}$ atoms/cc (squares), $0.5 \times 10^{18}$ atoms/cc (spheres) $2.0 \times 10^{18}$ atoms/cc (triangles). There are peaks at ~300 nm, which are fluorescence peaks of the Ag nanoparticles, as established in the previous section. The important observation, here, is that intensity of the fluorescence peaks at ~300 nm increases as concentration of Ag nanoparticles increases in the range $0.15 \times 10^{17}$ - $2.0 \times 10^{18}$ atoms/cc. As the concentration of Ag nanoparticles increases, the number of fluorescence centres increases, which contributes to the increased intensity observed by us.

4.8.3 Temperature effect on the fluorescence of Ag nanoparticles

Another important factor is temperature, which is known to affect fluorescence properties of the fluorophores. Nanoparticles in size range 1-100 nm, dispersed in a solvent, are colloidal dispersion, which are larger than most ordinary molecules, but still fairly small. In accordance with the kinetic theory of liquids, nanoparticles dispersed in a solvent are in a state of constant random motion called Brownian motion arising from collisions with solvent molecules, which themselves are in motion [33]. So, it is quite interesting to study the effect of temperature on the fluorescence of Ag nanoparticles dispersed in water, when Ag nanoparticles are in a state of random motion. To study this in detail, we performed experiments, to see variation in the fluorescence spectra of Ag nanoparticles dispersed in water, with varying temperature.

Figure 4.17a shows, the fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex} = 215$ nm and in temperature range 20-90 °C. There are peaks at ~300 nm, which are fluorescence peaks of the Ag nanoparticles dispersed in water as already established. Also, Figure 4.17b shows, the fluorescence emission spectra of the Ag nanoparticles dispersed in water at $\lambda_{ex} = 270$ nm, recorded also in temperature range 20-90 °C. Here, the high intensity peaks at ~270 nm are Rayleigh scattering peaks and peaks at ~300 nm are fluorescence peaks of the Ag nanoparticles dispersed in water. The important observation, here, is that intensity of the fluorescence peak at ~300 nm decreases as the temperature increases in the range 20-90 °C and vice-versa. So, at a
particular temperature, the fluorescence intensity is fixed and this is repeatable, which is quite interesting.

![Figure 4.17. Fluorescence emission spectra of Ag nanoparticles dispersed in water at temperature in the range 20-90 °C (a) at $\lambda_{ex}=215$ nm (b) at $\lambda_{ex}=270$ nm.](image)

According to the Stokes-Einstein equation [34] of Brownian motion of a spherical particle of radius $R$, suspended in a liquid of viscosity $\eta$, rotational and translational diffusion coefficient, $D_{rot}$ and $D_{trans}$, of the particle are given by

$$D_{rot} = \frac{kT}{6\pi\eta R}, D_{trans} = \frac{kT}{6\pi\eta R},$$

where $K$ is Boltzmann’s constant and $T$ is temperature.

During the lifetime of an excited state, a particle will undergo many collisions with other particles in solution and with the molecules of solvent. Some of these collisions will be such that the excitation energy can be transferred to other particles in the ground state or perhaps to the solvent molecules and completely lost nonradiatively. Hence, some fluorescence intensity is always lost in this process. Also, the viscosity of water is primarily a decreasing function of temperature in the range 20-90 °C and is inversely proportional to the diffusion coefficient. So, as the temperature increases, diffusivity of the nanoparticles will increase. As diffusivity increases, number of collisions of a nanoparticle with other nanoparticles in the medium and as well with the molecules of solvent increases. This increases the probability of radiationless loss of excitation energy by collisional transfer and results in the diminishing fluorescence intensity with increasing temperature.
In line with the temperature dependence of the fluorescence emission spectra, we also performed the temperature dependence of the excitation spectrum. Figure 4.18 shows, the temperature dependence of the excitation spectrum at $\lambda_{em} = 300$ nm and in the temperature range 20-90 °C.

![Figure 4.18](image)

Intensity of the absorption peaks at ~215 nm and ~270 nm decreases as the temperature increases from 20 to 90 °C, indicating maximum transition probability and hence resonant absorption at ~215 nm and ~270 nm decreases. This is in conformity with the temperature dependence of the fluorescence emission spectra, where intensity of the fluorescence emission peak decreases with increase in temperature.

### 4.9 Fluorescence from trap states of the Ag nanoparticles

It is well known that fluorescence is usually initiated using the energy of the pumping source above the energy of the fluorescent electronic transition and energy of the fluorescence photons is lower than the excitation photons. The positive difference
between the energy of the exciting photon and the energy of the electronic levels is expended on the creation of phonons or other relaxation processes. Till now, we have discussed fluorescence of Ag nanoparticles, where the energy of excitation is greater than the energy of the fluorescent electronic transition. In keeping with observations reported in literature for semiconducting quantum dots [35, 36], we query if it is possible to achieve fluorescence emission, where the energy of excitation is lower? To present such a possibility, we show in Figure 4.19a, the fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex} = 500$ nm (red), 520 nm (blue) and at 530 nm (green). The high intensity peaks at $\lambda_{ex} = 500, 520, 530$ nm are Rayleigh scattering peaks, as discussed in previous sections. There are peaks at $\sim 418, \sim 450, \sim 488$ nm, which are at higher energy side of the excitation peaks and their position remains fixed irrespective of the $\lambda_{ex}$. These peaks can be interpreted as anti-Stokes fluorescence peaks of the Ag nanoparticles dispersed in water, as their energy is higher than the excitation energy. In addition, as $\lambda_{ex}$ increases, the intensity of these fluorescence peaks decreases.

Figure 4.19. Fluorescence emission spectra of Ag nanoparticles dispersed in water (a) at $\lambda_{ex} = 500$ nm (red), 520 nm (blue), 530 nm (olive), (b) at $\lambda_{ex} = 370$ nm (red), 380 nm (blue), 390 nm (green).

Further, at high energy excitation but still lower than the energy of the fluorescent electronic transition, it is of interest to see if any fluorescence peaks of the Ag nanoparticles exist. To see this, we show in Figure 4.19b, the fluorescence emission
spectra of the Ag nanoparticles dispersed in water at $\lambda_{ex} = 370$ nm (red), 380 nm (blue) and 390 nm (green). The high intensity peaks at $\lambda_{ex} = 370, 380, 390$ nm are Rayleigh scattering. In addition, there are peaks at $\sim 420$ nm, $\sim 450$ nm and $\sim 488$ nm, whose position remains fixed irrespective of the $\lambda_{ex}$ employed. From the position of these peaks with reference to the excitation energy, they can be interpreted as Stokes fluorescence peaks of the Ag nanoparticles, as their energy is lower than the excitation energy. There are also peaks at 510 nm (at $\lambda_{ex} = 370$), 524 nm (at $\lambda_{ex} = 380$), 535 nm (at $\lambda_{ex} = 390$), whose position changes with $\lambda_{ex}$ but remains fixed with respect to the Rayleigh scattering peaks. These are Raman peaks of the Ag nanoparticles. To confirm presence of Raman peaks, we show in Figure 4.20, the fluorescence emission spectra of pure water at $\lambda_{ex} = 370$ nm (red), 380 nm (blue) and 390 (olive). The high intensity peaks at 370, 380, 390 nm are Rayleigh scattering peaks, as explained previously. There are peaks at $\sim 427$ nm ($\lambda_{ex} = 370$ nm), $\sim 439$ nm ($\lambda_{ex} = 380$ nm), $\sim 454$ nm ($\lambda_{ex} = 390$ nm), whose position shifts with the change in $\lambda_{ex}$ but remains fixed with respect to the Rayleigh scattering peak. These are Raman peaks of water.

![Fluorescence emission spectra](image)

Figure 4.20. Fluorescence emission spectra of water only at $\lambda_{ex} = 370$ nm (red), 380 nm (blue), 390 nm (olive).
When Ag nanoparticles are dispersed in water, these Raman peaks are observed at 510, 524, 535 nm for $\lambda_{ex} = 370, 380, 390$ nm, respectively but there character remains same. The usefulness of the metal nanoparticles for surface enhanced optical phenomenon is well known. Till now, the interesting point to note has been the position of the fluorescence peaks, which remains same for $\lambda_{ex} \sim 380$ nm and $\sim 520$ nm. Hence, these fluorescence peaks originate from the same energy levels. Further to look into some more details, we show in Figure 4.21, the fluorescence emission spectra of the Ag nanoparticles dispersed in water for excitation at $\lambda_{ex} = (a) 420$ nm, (b) 450 nm. The high intensity peaks at 420 nm in Figure 4.21a and 450 nm in Figure 4.21b are Rayleigh scattering peaks. At $\lambda_{ex} = 420$ nm, there are fluorescence peaks at $\sim 488$ nm and 532 nm, i.e., at lower energy than the excitation energy. At $\lambda_{ex} = 450$ nm, there are fluorescence peaks at 358 nm, 424 nm, i.e., at higher energy than the excitation energy and at $\sim 488$ nm, 532 nm, i.e., at lower energy than the excitation energy. Further, peaks at 575 nm for $\lambda_{ex} = 420$ nm and at 617 nm for $\lambda_{ex} = 450$ nm are Raman peaks of the Ag nanoparticles dispersed in water.

![Figure 4.21. Fluorescence emission spectra of Ag nanoparticles dispersed in water at $\lambda_{ex}$ (a) 420 nm, (b) 450 nm.](image-url)
At $\lambda_{ex} = 450$ nm, fluorescence peaks both at high and lower energy than the excitation energy are observed and more interesting to see that at excitation $= \lambda_1$ (380 nm) some particular peak (~424 nm) is at lower energy and at $\lambda_2$ (450 nm) excitation, the same peak appears at higher energy than the excitation energy. This is also evident from fluorescence analysis in Figure 4.19, where the fluorescence peaks at $\lambda_{ex} \sim 380$ nm and at $\lambda_{ex} \sim 520$ nm are at the same position. This indicates, again, that these fluorescence peaks are originating from the same energy levels. Hence, we infer that these peaks are neither Stokes nor anti-Stokes fluorescence, are just fluorescence peaks, originating from states within the ground and first excited states of the Ag nanoparticles.

![Figure 4.22. Schematic of the energy levels for fluorescence from trap states of the Ag nanoparticles.](image)

A schematic of the energy levels is shown in Figure 4.22, to explain the fluorescence from such states, which we now call trap states of the Ag nanoparticles. Where, $E_0$ & $E_1$ represents the ground state and excited state in the Ag nanoparticles. There are trap states near the ground state (ground trap states) and excited state (excited trap states) of the Ag nanoparticles, shown by dotted lines in Figure 4.22. Excitations take place from the ground state to the excited trap state or via ground trap states to the excited state and excited trap states. There is no possibility of direct excitation from the ground state to the
excited state, as the energy of the excitation (~380 nm, ~520 nm) is lower than the energy of the fluorescent electronic transition (~300 nm). Also, no fluorescence is observed for transitions from the excited states to the ground state, which confirm the no direct involvement of the excited state. So, whatever excitations are taking place to the excited states, they nonradiatively relax to the excited trap states as shown in Figure 4.22. Fluorescence peaks are observed, when the electrons from the excited trap states deexcites to the ground states. At $\lambda_{ex}=380$ nm or ~520 nm fluorescence emission occurs, when the deexcitation take place from the excited trap states to the ground states. So, fluorescence emission occurs between the same energy levels for excitation at ~380 nm or ~520 nm. And we observe the same fluorescence peaks involving transitions from the same trap states, creating a false impression of Stokes and anti-Stokes lines. In subsequent discussions, we will establish the effect of various factors on the fluorescence from the trap states of the Ag nanoparticles.

To study the solvent effect on the fluorescence from the trap states of the Ag nanoparticles, we dispersed the Ag nanoparticles in methanol and studied the fluorescence properties at similar excitation energies. Figure 4.23a shows, the fluorescence emission spectra of the Ag nanoparticles dispersed in methanol at $\lambda_{ex}=370$ nm (red), 380 nm (blue) and 390 nm (olive). The high intensity peaks at $\lambda_{ex}=370, 380, 390$ nm are Rayleigh scattering peaks. There are peaks at ~423 nm, ~488 nm, whose position is almost fixed irrespective of $\lambda_{ex}$ and are attributed to fluorescence from the trap states of the Ag nanoparticles. There are also peaks at 510 nm (at $\lambda_{ex}=370$), 522 nm (at $\lambda_{ex}=380$), 535 nm (at $\lambda_{ex}=390$), position of which changes with change in $\lambda_{ex}$ but remains fixed with respect to Rayleigh peak, are Raman peaks. Also, Figure 4.23b shows, the fluorescence emission spectra of the Ag nanoparticles dispersed in methanol for excitation at $\lambda_{ex}=510$ nm (squares), 520 nm (circles) and at 530 nm (triangles). The high intensity peaks at $\lambda_{ex}=500, 520, 530$ nm are Rayleigh scattering peaks. There are peaks at 412, 450, 488 nm, whose position remains fixed with change in $\lambda_{ex}$ and hence, are assigned to fluorescence from the trap states of the Ag nanoparticles. Fluorescence from
the trap states has been observed for Ag nanoparticles dispersed in water and methanol at the same position. So, from the above analysis, it is clear that the solvent has no significant effect on the fluorescence from the trap states of the Ag nanoparticles, as the transitions are internal to the nanoparticles, bearing no effect from its surroundings.

Further, to confirm absence of the surrounding effect on the fluorescence from the trap states, we have studied the temperature dependence of the fluorescence emitted from the trap states of the Ag nanoparticles dispersed in water. Figure 4.24a shows, the temperature dependence of the fluorescence emission spectra of the Ag nanoparticles dispersed in water at $\lambda_{ex} = 380$ nm and at temperature 20°C (red), 50°C (blue), 90°C (olive). With increase in temperature, intensity of the fluorescence from trap states of the Ag nanoparticles decreases marginally with no dramatic intensity change as observed earlier (see Figure 4.17). Further, this temperature dependence of the fluorescence from trap states of the Ag nanoparticles is non-reversible, as shown in Figure 4.24b. After increasing the temperature to 90°C, when temperature is decreased to 20°C, no increase in intensity of fluorescence peaks has been observed. This behaviour is quite different, when transitions involved the first excited state of the nanoparticles (Figures 4.17 and 4.18).
Similarly, intensity of the fluorescence peaks from the trap states of the Ag nanoparticles at $\lambda_{ex} = 520$ nm, decreases marginally with increase of temperature in the range 20-90°C, shown in the Figure 4.25a and this is also not reversible (Figure 4.25b). This non-reversibility allows us to infer annealing of trap states with temperature rise. As such trap
states are no longer available, no increase in intensity of fluorescence emission is observed with decrease in temperature. The underlying physics is thus entirely different from the temperature cycling effects observed earlier, resulting from nonradiative decay due to collisional scattering (Figure 4.17).

An idea, which further confirms this point is an enhancement of trap states using an external influence. In this regard, we have studied the effect of UV-light (\( \lambda \sim 254 \) nm) exposure before measuring the fluorescence from the trap states of the Ag nanoparticles dispersed in water. Figure 4.26 shows, the fluorescence emission spectra of the Ag nanoparticles dispersed in water at \( \lambda_{ex} = 520 \) nm and for UV-light exposure time = 0 minute (red), 3 minute (blue), 7 min (olive) and 11 min (magenta). As time of UV-light exposure to the sample increases, the intensity of the fluorescence peaks from trap states increases. This is due to the fact that as the UV-light exposure increases, more trap states are created, which give rise to the increased intensity observed by us. Unlike, increase in temperature, which helps annealing the trap states, increase in UV-light exposure helps creating more trap states.
4.10 Conclusions

We have successfully synthesized the Ag nanoparticles employing a physical, top-down approach of electro-explosion of wires. The synthesized nanoparticles are characterized by XRD, TEM and AFM for size, shape and crystallinity. Further, UV-visible absorption spectrum shows a surface plasmon peak at 400 nm, characteristic of the Ag nanoparticles. The bare particles, obtained with no extraneous capping agents, allow us to demonstrate fluorescence pathways never reported earlier for excitation wavelengths $\lambda_{\text{ex}} < 290$ nm. Thus, we identify here, discrete higher excited electronic states in the Ag nanoparticles (dispersed in water) system, whose relaxation takes place always through the lowest excited state. In addition, we have established effect of the concentration of the Ag nanoparticles, and solvent on the fluorescence of the Ag nanoparticles. Further, we have established the effect of the temperature on the fluorescence of the Ag nanoparticles in the temperature range 20-90 °C, which allows us to establish that Ag nanoparticles dispersed in water are in a state of constant random motion. Also, we have established the effect of temperature and emission wavelength on the excitation spectra. Finally, we have identified and studied in details the fluorescence from trap states of the Ag nanoparticles.

References

