CHAPTER 7

Synthesis and study of fluorescence properties of Cu nanoparticles

In this chapter, we describe synthesis of Cu nanoparticles by employing an electro-explooding wire technique. The synthesized Cu nanoparticles have been characterized by X-ray diffraction, TEM, AFM, UV-visible spectroscopy and their results discussed. Surface charge of the Cu nanoparticles has been studied using Zeta potential measurements. Fluorescence peaks at ~296 nm have been observed at excitation wavelength in the ranges 200-240 nm and 250-280 nm. Position of the fluorescence peaks remain fixed irrespective of the excitation wavelength used. Associated with these, two resonant absorptions are observed at ~213 nm and ~269 nm, evident from fluorescence excitation spectrum, which allow us to give a description of the electronic levels operating in this system. Hence, fluorescence emission is attributed to the electronic transitions from the excited states to the 3d levels of the Cu nanoparticles. Also, with increase in the concentration of Cu nanoparticles in the range $0.5 \times 10^{17}$ - $6.45 \times 10^{18}$ atoms/cc, intensity of the fluorescence peak at ~296 nm increases. Further, we have studied effect of temperature and solvent on the fluorescence emanating from the Cu nanoparticles. We have also established effect of the temperature and emission wavelength on the probability of resonant absorptions. We have also established fluorescence emission from trap states of the Cu nanoparticles.
7.1 Introduction

In recent years, much attention has been given to metal nanoparticles [1-3] due to remarkable physical and chemical properties exhibited by them, owing to their high aspect ratio and quantum size effect [4]. Besides their usefulness in various fields and their ability to promote surface enhanced optical phenomenon [5, 6], it is discovered that noble metals clusters display intense visible fluorescence. The study of their fluorescence properties yields new insight into the energy band structure of the nanoparticles and also it is prerequisite for their practical applications in integrated optical devices [1, 7], in bio-labeling and as a sensor [8, 9]. Fluorescence spectroscopy has proved as a very reliable and sensitive technique to study the fluorescence properties of nanoparticles dispersed in a solvent.

Recently fluorescence from noble metal nanoparticles of Ag and Au has been reported [3, 10-12]. While, there is no literature report to the best of our knowledge on study of the fluorescence properties of the Cu nanoparticles alone. However, Cu nanoparticles influence on the fluorescence properties of silica and alumina has been studied [13]. For both samples, shift in the peak wavelength towards longer wavelengths and strong long wavelength emission bands have been observed. Also, Manikandan et al. [14] reported a fluorescence peak at 500 nm of embedded Cu nanoclusters in soda-lime glass at an excitation wavelength ($\lambda_{ex}$) of 270 nm. While, Annapurna et al. [15] have reported the fluorescence peak at 500 nm of Cu$^+$ embedded in zinc borosilicate glass at $\lambda_{ex}$ = 296 nm, 310 nm and 360 nm. Fluorescence has been attributed to transitions between the Cu$^+$ 3d$^9$4s$^1$ and 3d$^{10}$ electronic configurations [14, 15].

In this chapter, our objective is to report synthesis of the Cu nanoparticles by employing a novel, physical and top-down technique of electro-exploding wire (EEW). Further, our objective is to characterize the synthesized Cu nanoparticles employing various characterization techniques. To study the phase and crystallinity of Cu nanoparticles, XRD has been used. To analyse the size and shape of Cu nanoparticles, we have used TEM, AFM, and to measure the surface charge on the Cu nanoparticles, Zeta potential measurements have been carried out. To study the absorption properties of Cu nanoparticles, UV-visible spectroscopy has been employed. Our primary objective,
however, is to study in detail fluorescence properties of the Cu nanoparticles at $\lambda_{ex}$ in the ranges 200-240 nm and 250-280 nm. In addition, we have studied in details effect of Cu nanoparticles concentration, surrounding medium and temperature on the fluorescence of the Cu nanoparticles. Also, in conformity with these, we have studied the effect of emission wavelength and temperature on the excitation spectrum. Furthermore, we have studied fluorescence from trap states of the Cu nanoparticles.

### 7.2 Synthesis of Cu nanoparticles

Various techniques have been employed for synthesis of Cu nanoparticles, such as, chemical reduction [16], radiolytic reduction [17], laser ablation [18], flow levitation [19], reverse micelles [20], hydrothermal method [21] and sputtering [22]. Cu nanoparticles, reported here, have been synthesized by employing a novel, physical, top-down process of EEW.

In the EEW technique, a thin Cu metal wire is exploded on a thin Cu metal plate by passing current density $\sim 10^{10}$ A/m$^2$; in a time $\sim 10^{-6}$ sec. A schematic diagram and details of the EEW technique have already been described in chapter 2. To describe it in brief, heating of Cu wire-plate at the point of contact takes place due to the flow of high density current, which is followed by melting. The melted Cu wire-plate is further heated by the ever increasing current density due to increase in resistance, which leads to evaporation of the material and subsequent plasma formation. This plasma is contained by the self induced magnetic field. When vapour pressure of the plasma overwhelms the self induced magnetic field, explosion occurs and plasma products are dispersed in the medium with high speed, which leads to formation of the Cu nanoparticles. Hence, following the above mechanism Cu nanoparticles have been synthesized. Synthesized Cu nanoparticles are free from any extraneous impurities as no chemicals have been used during/ after synthesis of the Cu nanoparticles. Parameters like current density, wire-plate dimension and medium in which explosion is carried out are monitored to have control over the entire process of exploding the wires [23-26] to synthesize the Cu nanoparticles.
7.3 X-ray diffraction analysis of Cu nanoparticles

From XRD analysis, we can find out the amorphous or crystalline nature of the material. If the synthesized material is crystalline, we can determine its basic lattice structure (e.g. cubic or face centred cubic etc.) by indexing its lattice planes. Details of the sample preparation and instrumentation have already been given in previous chapters. In Figure 7.1, we show XRD patterns of the Cu nanoparticles, synthesized using the EEW technique. There are peaks at 2θ (degree) = 43.50, 50.51, 74.25 and 90.05. The XRD peaks position for the Cu nanoparticles matches with those from the bulk Cu in face centred cubic (fcc) phase and correspond to the (hkl) planes (111), (200), (311) and (220), respectively.

![XRD pattern of Cu nanoparticles](image)

Figure 7.1. Powder X-ray diffraction patterns of the Cu nanoparticles.

**Preferential orientation:** By preferential orientation we mean that atoms may get preferentially oriented along specific planes. Preferential orientation [27] of atomic planes make a material further tuned to specific properties. As nanomaterials are, altogether, a different class of materials having different properties from atoms and bulk, their specific orientation is of special interest. The preferential orientation of the synthesized nanoparticles is extracted through an evaluation of the orientation index (M).
Details about how to calculate $M$ are given in chapter 3. $M$ is more than 1 for (111) plane ($M_{111} = 1.41$), indicating preferential orientation of nanoparticles along this plane. $M$ is less than 1 for (200), (220) and (311) planes ($M_{200} = 0.95$, $M_{220} = 0.85$ and $M_{311} = 0.71$), indicating that orientation has been suppressed for these planes. From this analysis of orientation index, we can say that Cu nanoparticles synthesized by employing the EEW technique are specifically oriented along the (111) plane. In the process of electro-explosion of wires, high density current is passed, which leads to plasma formation and subsequent explosion at tip-plate interface. This is followed by ejection of nanoparticles from the tip-plate interface at high speed. This EEW is a non equilibrium process, responsible for the reorientation of atoms along specific planes.

**Crystallite size:** Here, crystallite size $(d)$ has been calculated using the ‘Debye-Scherrer’ Formula [28].

$$d = \frac{k\lambda}{\beta \cos \theta} \quad 7.1$$

where symbols have their usual meaning, details of which are given in chapter 3. Crystallite size is calculated by taking the XRD peak corresponding to the (111) plane. The crystallite size calculated using Debye-Scherrer formula comes out to be 12.4 nm.

### 7.4 Transmission electron microscopy of Cu nanoparticles

For TEM investigations, a small drop of the Cu nanoparticles dispersed in water is put on a carbon coated copper grid. After drying the grid, TEM characterization is carried out employing a JEOL JEM-2000EX transmission electron microscope. Figure 7.2 shows, the TEM image and selected area electron diffraction pattern (SAD) of the Cu nanoparticles. Average size of the Cu nanoparticles is ~10 nm (Figure 7.2 a). Further, any particle chosen randomly exhibits SAD patterns (Figure 7.2 b), clearly demonstrating that the synthesized nanoparticles are crystalline, also confirmed by the XRD analysis. We believe that particle size is much smaller than what has been observed. For that, we have recorded high resolution TEM images of the Cu nanoparticles. Figure 7.3a shows, TEM image of the Cu nanoparticles at high resolution. Particles of size 2-5 nm are observed. There are few particles whose size $> 5$ nm but mostly there are particles, whose size is $\leq$
5 nm. Further, Figure 7.3b shows, high resolution TEM image of a representative Cu nanoparticle, showing particle size ~5 nm.

Figure 7.2. (a) TEM image of the Cu nanoparticles (b) SAD of a Cu nanoparticle.

Figure 7.3. High resolution TEM images of (a) the large number of Cu nanoparticles, (b) a representative Cu nanoparticle.
7.5 Atomic force microscopic analysis of Cu nanoparticles

Samples of Cu nanoparticles for AFM analysis are prepared by spin coating of the Cu nanoparticles dispersed in water on a clean and optically flat glass substrate. Figure 7.4 shows, the AFM images of the Cu nanoparticles at scan sizes: (a) 1×1 μm (b) 1×1 μm (c) 968.7×968.7 nm (d) 1.02×1.02 μm. Average size of the Cu nanoparticles in AFM analysis is ~30 nm. Size of the Cu nanoparticles observed in AFM analysis is bigger than what has been observed in TEM and XRD analysis. This can be due to van der Waals interaction between the Cu nanoparticles that the small size Cu nanoparticles coalesce to form bigger particles on a surface.
7.6 Zeta potential measurements of Cu nanoparticles

Zeta potential is a physical property, which is a measure of the effective charge on the particles dispersed in a solvent and therefore related to the electrostatic repulsion between them. Details of the sample preparation and instrumentation are given in chapter 3.

![Graph showing Zeta potential measurements](image)

**Figure 7.5. Zeta potential measurement of Cu nanoparticles dispersed in water.**

Figure 7.5 shows, the Zeta potential measurement for Cu nanoparticles dispersed in water. Average value of the Zeta potential for Cu nanoparticles dispersed in water is −23.12 mV. Here, negative value of the Zeta potential for Cu nanoparticles dispersed in water indicates that there is negative surface charge on the Cu nanoparticles dispersed in water. But, negative surface charge on the Cu nanoparticles dispersed in water is not strong enough to stop their aggregation due to van der Waals forces, which has been observed in AFM and TEM analysis.

7.7 UV-visible spectroscopy

Absorption of UV-visible light by metal nanoparticles can be either due to surface plasmon oscilllation or due to electronic transitions. An absorption spectrum is a plot of
the changes in absorption intensity versus wavelength. Details about the sample preparation and instrumentation used have already been given in chapter 3. In Figure 7.6, we show UV-visible absorption spectrum of the Cu nanoparticles dispersed in water. Although, a surface plasmon peak is expected at ~580 nm for the Cu nanoparticles [29], we observe no surface plasmon peak in the absorption spectrum of the Cu nanoparticles. We, further, observe sharp intensity maxima in the absorption spectrum in the range 200-350 nm (at λ (nm) = 222, 244, 280, 336). To the best of our knowledge, no one has reported such atom like electronic transition in the absorption spectrum (below 350 nm) for Cu nanoparticles. Absorption in this range is also reported by others [30, 31] and attributed to oligomeric clusters of the Cu.

![Figure 7.6. UV-visible absorption spectrum of Cu nanoparticles dispersed in water. Inset shows first-order differential of the absorption spectrum.](image)

These sharp transitions observed in the UV region can be correlated with electronic transitions arising from occupied valence band density of states in the Cu clusters of size < 30 atoms. In the inset to Figure 7.6, we have shown plot of the first-order differential of the absorption spectrum, which shows a peak at 586 nm (2.11 eV). This peak indicates the absorption edge, where absorption starts. This absorption edge coincides with the
position of the surface plasmon peak, which has been totally suppressed due to quantum confinement effect in our case due to small size of the Cu nanoparticles. Pileni and Lisiecki [20] have demonstrated the broadening of the surface plasmon peak on decrease in particle size in case of Cu nanoparticles. Further, they have shown total disappearance of surface plasmons for particles having size below 3 nm. We observe total suppression of the plasmon resonance for the Cu nanoparticles (data presented in Figure 7.6), and hence, particle size of our nanoparticles should be less than 3 nm. For such small particles collective oscillation of electrons are no longer available due to quantum confinement effect and for dissipating the incident energy, other routes open up in the ultraviolet region and correspond to transitions from discrete states in the Cu nanoparticle atoms. By comparing with data available in the literature for the absence of surface plasmon in nanoparticles and occupied valence band density of states, we project the size of our nanoparticles less than 3 nm. Also, distinct peaks in the absorption spectrum can be seen as electronic transitions in the Cu nanoparticles.

7.8 Fluorescence properties of Cu nanoparticles

It is well established that fluorescence is a three step process involving excitation of an electron from the ground state to the high energy states, then relaxation of the excited electron followed by fluorescence emission [32]. The details of the sample preparation and instrumentation have been already given in previous chapters. In Figure 7.7, we show optical micrographs of the Cu nanoparticles dispersed in water and kept in (a) day light, (b) UV-light. Under daylight Cu nanoparticles dispersion in water are rust brown in colour and while, under UV-light, they are green. Further, we have studied in detail fluorescence properties of the Cu nanoparticles dispersed in water. Figure 7.8a shows, the fluorescence emission spectra of the Cu nanoparticles dispersed in water (concentration of Cu nanoparticles is \(\sim 6.0 \times 10^{18}\) atoms/cc) at \(\lambda_{ex} = 205\) nm (squares; red), 210 nm (spheres; blue), 213 nm (triangles; olive), 220 nm (stars; royal), 225 nm (hexagons; magenta), 230 nm (circles; green) and 240 nm (pentagons; orange). There are peaks at \(\sim 296\) nm, the position of which remains fixed irrespective of the \(\lambda_{ex}\) employed and hence, are assigned to fluorescence emission from the Cu nanoparticles.
Figure 7.7. Optical micrographs of Cu nanoparticles dispersed in water and kept in (a) day light, (b) UV-light.

Figure 7.8. (a) Fluorescence emission spectra of Cu nanoparticles dispersed in water at $\lambda_{ex}=205$ nm (squares; red), 210 nm (spheres; blue), 213 nm (triangles; olive), 220 nm (stars; royal), 225 nm (hexagons; magenta), 230 nm (circles; green) and 240 nm (pentagons; orange), (b) shows variation of maximum intensity of the fluorescence peak at 296 nm with $\lambda_{ex}$.

Also, in Figure 7.8b, we show the variation of maximum intensity of the fluorescence peak at $\sim296$ nm with $\lambda_{ex}$ in the range 200-240 nm. The intensity of the fluorescence peak at $\sim296$ nm increases as $\lambda_{ex}$ increases from 200 nm, is highest at $\lambda_{ex}=213$ nm and
decreases thereafter as $\lambda_{\text{ex}}$ increases to 240 nm. Further, same fluorescence peak is also observed at $\lambda_{\text{ex}} \sim 269$ nm. For this, we show in Figure 7.9a, fluorescence emission spectra of the Cu nanoparticles (concentration of Cu nanoparticles is $\sim 6.0 \times 10^{18}$ atoms/cc) dispersed in water at $\lambda_{\text{ex}} = 250$ nm (cyan), 255 nm (green), 260 nm (magenta), 265 nm (olive), 269 nm (red), 275 nm (blue), 280 nm (purple). The high intensity peaks at 250, 255, 260, 265, 269, 275, 280 nm are Rayleigh scattering peaks, position of which shift with change in $\lambda_{\text{ex}}$. Rayleigh scattering lines have indeed been reported in conjunction with fluorescence emission spectra of the noble metal nanoparticles in H$_2$O [3].

Also, there are peaks at $\sim 296$ nm, which we assign to fluorescence emission from the Cu nanoparticles, because their position remains fixed with change of $\lambda_{\text{ex}}$ in the range 250-280 nm. Further, in Figure 7.9b, we show variation of the maximum intensity of the fluorescence peak at 296 nm with $\lambda_{\text{ex}}$ in the range 250-280 nm. Intensity of the fluorescence peak increases as $\lambda_{\text{ex}}$ increases from 250 nm, is highest at $\lambda_{\text{ex}} = 269$ nm and decreases thereafter as $\lambda_{\text{ex}}$ increases from 269 nm to 280 nm. Hence, transitions at $\lambda_{\text{ex}} = 213$ nm and 269 nm corresponds to the maximum transition probability/ resonant absorption.
We now proceed to measure the exact position of the transitions, which are accountable for fluorescence emission by recording excitation spectrum of the Cu nanoparticles dispersed in water with fluorescence emission wavelength ($\lambda_{em}$) fixed at the highest intensity of the fluorescence peak. The inhomogeneous broadening of the absorption bands can be resolved in the fluorescence excitation spectrum. Because, in the fluorescence excitation spectrum by monitoring a specific spectral band of the full fluorescence range and scanning the excitation energy, absorption features that overlapped/ weakly resolved in the direct absorption spectrum (UV-visible absorption) get resolved [32]. In conformity with this, we show in Figure 7.10a, fluorescence excitation spectrum of the Cu nanoparticles dispersed in water for $\lambda_{em}$ fixed at 296 nm, i.e., at maximum intensity of the fluorescence emission peak. There are peaks at $\sim$213 nm and $\sim$269 nm in the fluorescence excitation spectrum of the Cu nanoparticles dispersed in water. The highest intensity of these peaks (observed in the excitation spectrum) is at 213 nm and 269 nm, which corresponds to maximum transition probability/ resonant absorption. This allows us to establish the electronic levels operating in the Cu nanoparticles. There are two excited states corresponding to $\lambda_{ex}$ = 213 nm and 269 nm, evident from the excitation spectrum. The excitation peak with maximum intensity at $\sim$269 nm is for the transitions between the ground state ($E_0$) and the first excited state ($E_1$), and the excitation peak with maximum intensity at $\sim$213 nm, corresponds to the transitions between the ground state and the second excited state ($E_2$). The transitions are then $E_0 \rightarrow E_1$, at $\lambda_{ex}$ = 269 nm (from the ground state to the first excited state) and $E_0 \rightarrow E_2$, at $\lambda_{ex}$ = 213 nm (from the ground state to the second excited state), respectively. However, both these absorption pathways yield fluorescence at 296 nm (Figure 7.8 and 7.9) which we will discuss in detail in the latter part of this section. Further, fluorescence excitation spectrum is also in conformity with the fluorescence emission spectra presented in Figure 7.8 and 7.9, where variation in the fluorescence peak intensity has been observed with change in $\lambda_{ex}$ and highest fluorescence emission intensity is observed at $\lambda_{ex}$ = 213 nm and 269 nm. Also, we have studied effect of change in $\lambda_{em}$ on the excitation spectrum. In Figure 7.10b, we show excitation spectra of the Cu
nanoparticles dispersed in water at $\lambda_{em} = 290$ nm (squares; red), 296 nm (triangles; blue), 305 nm (circles; olive) and 310 nm (stars; magenta).

An important observation is the intensity of the excitation peaks at ~213 nm and ~269 nm, which decreases as $\lambda_{em}$ changes from 296 nm (maximum intensity of fluorescence peak) to 310 nm or 290 nm. This allows us to establish that the transition probability decrease as the $\lambda_{em}$ changes from the position of maximum intensity of the fluorescence peak and maximum intensity of the fluorescence peak at ~296 nm corresponds to maximum transition probability.

It is well established that fluorescence from the noble metals take place due to the transitions of electrons in the conduction band below the Fermi level to the holes in the d bands [33]. Also, fluorescence from Au nanoparticles has been attributed to interband electronic transitions between the 6sp$^1$ conduction band and the 5d$^{10}$ valence levels [12]. However, our careful $\lambda_{ex}$ and $\lambda_{em}$ dependence study of the fluorescence of Cu nanoparticles allows us to assign this to electronic transitions from the excited states to the d levels of the Cu nanoparticles. In conformity with the experimental results observed by us, we construct an energy level diagram, shown in Figure 7.11, where $E_0$ represents the ground state and $E_1, E_2, \ldots$ etc. represent the excited states. Transitions in the Cu
nanoparticles take place from the ground state ($E_0$, i.e., 3d levels) to the excited states ($E_1, E_2, ...$), depending upon the excitation energy, and shown by arrows in the upward direction. When excited electrons, after relaxation, deexcites to the 3d levels, fluorescence emission takes place as explained in Figure 7.11 and shown by arrows in downward direction.

![Figure 7.11. Schematic of the energy levels for fluorescence mechanism of Cu nanoparticles.](image)

Although, at $\lambda_{ex} \sim 213$ nm and $\sim 269$ nm, electrons are excited from the ground state to the different excited states, i.e., $E_0 + \frac{hc}{\lambda_{270nm}} = E_1$ (from the ground to the first excited state) and $E_0 + \frac{hc}{\lambda_{213nm}} = E_2$ (from the ground to the second excited state), also evident from the excitation spectrum, Figure 7.10, they yield the same fluorescence at $\sim 296$ nm. As a general rule in fluorescence, an excited electron deexcites nonradiatively to the lowest excited state prior to photon emission in a time short enough compared to the photon emission times. The only way fluorescence emission at 296 nm from these excited states can be achieved is through an internal conversion involving these excited states as shown in Figure 7.11. In this respect, fluorescence behaviour of the Cu nanoparticles is similar to those from solitary atoms or molecules.
So far, we have established that intensity of a fluorescence emission/excitation peak depends upon the transition probability between the two levels involved, in accordance with Fermi Golden Rule [34]. When $\lambda_{ex}$ changes, transition probability between levels changes and hence, intensity of the fluorescence peak changes. Consequently, at $\lambda_{ex}$ in the range 200-240 nm, intensity of the fluorescence peak at $\sim$296 nm increases as $\lambda_{ex}$ increase from 200 nm and is maximum at $\lambda_{ex} = 213$ nm, corresponding to resonant absorption/maximum radiative transition probability and then decreases as $\lambda_{ex}$ increases to 240 nm. Further, for $\lambda_{ex}$ in the range 250-280 nm, intensity of the fluorescence peak increases as $\lambda_{ex}$ increase from 250 nm, is highest at $\lambda_{ex} = 269$ nm, corresponding to maximum radiative transition probability and thereafter intensity of the fluorescence peak decreases as $\lambda_{ex}$ increase to 280 nm. So, there are most probable excitation wavelengths $(\lambda_{M1}, \lambda_{M2})$, i.e., 213 nm for $\lambda_{ex}$ in the range 200-240 nm and 269 nm for $\lambda_{ex}$ in the range 250-280 nm, at which intensity of the fluorescence peak is highest and intensity of fluorescence peak decreases for excitation at $\lambda_{ex} \neq \lambda_{M1}, \lambda_{M2}$. This is corroborated by the fluorescence excitation spectrum, where we observe two peaks centred at $\sim$213 nm and $\sim$269 nm, corresponding to resonant absorption. This is also corroborated by the UV-visible absorption spectrum as well, where sharp peaks have been observed in this range. We observe the same fluorescence emission peak at $\sim$296 nm for $\lambda_{ex}$ at $\sim$213 nm and $\sim$269 nm, although, electrons are excited to different excited states, clear from the excitation spectrum. This is due to the fact that the electrons excited to second excited state at $\lambda_{ex} \sim 213$ nm, nonradiatively relaxes to the first excited state due to internal conversion, following which fluorescence emission takes place. Experimental analysis shows that the fluorescence behaviour of the Cu nanoparticles is similar to that of the solitary atoms/molecules. In this scenario the excited states of the Cu nanoparticles should be influenced by the surrounding medium too and hence the position of the fluorescence peak will depend on the medium surrounding the nanoparticles. In this respect the nanoparticles can act as a sensor for the surrounding medium.
7.8.1 Solvent effect on the fluorescence of Cu nanoparticles

When measuring the fluorescence of Cu nanoparticles dispersed in a solvent, most common state for the fluorescence measurements, it is important to note that effect caused by the solvent are quite varied and complex. Typically, a fluorophore has a larger dipole moment in the excited state than in the ground state. Following excitation the 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 Polarization 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. Hence, the role of solvent polarity is not only to lower the energy of the excited state due to general solvent effects, but also to govern which state has the lowest energy [32].

In order to study the effect of the surrounding medium on fluorescence emission from the Cu nanoparticles, we recorded fluorescence emission of the Cu nanoparticles dispersed in methanol, at similar excitation wavelengths as has been used for Cu nanoparticles dispersed in water. Figure 7.12a shows, fluorescence emission spectra of the Cu nanoparticles dispersed in methanol at $\lambda_{ex} = 225$ nm (stars; olive), 230 nm (spheres; blue) and 239 nm (triangles; orange). The maximum intensity of the fluorescence peaks are at 356 nm for excitation at 225 nm, 230 nm and at 368 nm for excitation at 239 nm. Further, Figure 7.13b shows the fluorescence emission spectra of the Cu nanoparticles dispersed in methanol at $\lambda_{ex} = 265$ nm (stars; blue), 280 nm (spheres; red), 290 nm (triangles; olive). There are fluorescence peaks at 376 nm. Now, we compare the fluorescence of the Cu nanoparticles dispersed in water and methanol. The primary difference in fluorescence emission spectra of the Cu nanoparticles dispersed in water and methanol is in the position of the fluorescence emission peak, which has red-shifted in case of methanol. Shift in the emission peak position due to a solvent's dielectric constant have been well researched in the literature [32] and is known to provide a polarization shift. 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, methanol is 33.6).
A possible reason for the shift in the fluorescence peak position observed for solvents of different polarity is the formation of an internal charge transfer states [32], discussed in details in chapter 4. After excitation, there can be increase in charge separation within the fluorophore. In case of a polar solvent (water), a fluorophore with charge separation becomes the lowest energy state, while, in a relatively nonpolar solvent like hexane or methanol the fluorophme without charge separation has the lowest energy. So, this red shift in the fluorescence peak position in case of the eu nanoparticles dispersed in methanol than water is due the formation of the internal charge transfer state, whereas, in solvents of different polarity one state of the fluorophore has the lowest energy than the other.

7.8.2 Effect of Cu nanoparticles concentration on their fluorescence

To look into how concentration will effect the fluorescence emission of the Cu nanoparticles, we performed fluorescence measurements at various concentrations (in the range $0.5 \times 10^{17}$ atoms/cc - $6.45 \times 10^{18}$ atoms/cc) of the Cu nanoparticles dispersed in water. Figure 7.13a shows, the fluorescence emission spectra of the Cu nanoparticles dispersed in water at $\lambda_{ex} = 215$ nm and at concentration $= 0.5 \times 10^{17}$ atoms/cc (squares), $1.0 \times 10^{17}$ atoms/cc (stars), $4.0 \times 10^{17}$ atoms/cc (spheres), $0.8 \times 10^{18}$ atoms/cc.
(pentagons), $3.22 \times 10^{18}$ atoms/cc (circles) and $6.45 \times 10^{18}$ atoms/cc (triangles). The peaks at $\sim 296$ nm are fluorescence emission peaks of the Cu nanoparticles as established already. An important observation, here, is scaling of the fluorescence intensity with the Cu nanoparticles concentration, which increases as the concentration of Cu nanoparticles increases from $0.5 \times 10^{17}$ atoms/cc to $6.45 \times 10^{18}$ atoms/cc. As concentration of the Cu nanoparticles increases, number of fluorescence centres increases, which contribute to the increased fluorescence peak intensity.

![Image](https://via.placeholder.com/150)

Figure 7.13. Fluorescence emission spectra of Cu nanoparticles dispersed in water (a) at $\lambda_{ex} = 215$ nm and at concentration = $0.5 \times 10^{17}$ atoms/cc (squares), $1.0 \times 10^{17}$ atoms/cc (stars), $4.0 \times 10^{17}$ atoms/cc (spheres), $0.8 \times 10^{18}$ atoms/cc (pentagons), $3.22 \times 10^{18}$ atoms/cc (circles) and $6.45 \times 10^{18}$ atoms/cc (triangles), (b) at $\lambda_{ex} = 265$ nm and at concentration = $2.5 \times 10^{16}$ atoms/cc (spheres), $2.0 \times 10^{17}$ atoms/cc (squares), $4.0 \times 10^{17}$ atoms/cc (circles), $0.8 \times 10^{18}$ atoms/cc (stars), $3.2 \times 10^{18}$ atoms/cc (pentagons), and $6.45 \times 10^{18}$ atoms/cc (triangles).

In addition, similar dependence is observed for fluorescence emission at a different $\lambda_{ex}$.

For that, we show in Figure 7.13b, fluorescence emission spectra of the Cu nanoparticles dispersed in water at $\lambda_{ex} = 265$ nm and at concentration = $2.5 \times 10^{16}$ atoms/cc (spheres), $2.0 \times 10^{17}$ atoms/cc (squares), $4.0 \times 10^{17}$ atoms/cc (circles), $0.8 \times 10^{18}$ atoms/cc (stars), $3.2 \times 10^{18}$ atoms/cc (pentagons), and $6.45 \times 10^{18}$ atoms/cc (triangles). The high intensity peaks at $\sim 265$ nm are Rayleigh scattering peaks and peaks at $\sim 296$ nm are fluorescence emission peaks of the Cu nanoparticles dispersed in water, as established previously. Here, also, intensity of the fluorescence peak at $\sim 296$ nm increases with increase in
concentration of the Cu nanoparticles due to increase in the number of fluorescence centres.

7.8.3 Effect of temperature on fluorescence of Cu nanoparticles

Nanoparticles dispersed in a solvent are in a state of constant random motion called Brownian motion, arising due to the collisions with solvent molecules, which themselves are in motion, as discussed in details in chapter 4.

So, it is quite interesting and important to study the effect of temperature on the fluorescence of the nanoparticles, when the nanoparticles themselves are in Brownian motion. To study this in detail, we performed experiments to see variation in the fluorescence spectra of the Cu nanoparticles dispersed in water with varying temperature. Figure 7.14a shows, fluorescence emission spectra of the Cu nanoparticles dispersed in water at $\lambda_{ex} = 213$ nm and in temperature range 20-90 °C. The peaks at $\sim 296$ nm are due to fluorescence emission from the Cu nanoparticles, as established by us previously. Important observation to be mentioned is the intensity of the fluorescence peak at $\sim 296$ nm, which decreases as the temperature increases in the range 20-90 °C and vice-versa. So, the intensity of the fluorescence peak has a fixed value at a particular temperature.
This is in conformity with the results of temperature dependence observed for the Ag nanoparticles, discussed in chapter 4.

As the temperature of the sample (Cu nanoparticles dispersed in water) increases, diffusivity of the nanoparticles increases, according to Stokes-Einstein equation (discussed in detail in chapter 4). As diffusivity increases, the number of collisions of the nanoparticles with other nanoparticles in water and as well with molecules of the water 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 addition, same fluorescence behaviour of the Cu nanoparticles with temperature is also observed with changes in $\lambda_{ex}$. For that, we show in Figure 7.14b, the fluorescence emission spectra of the Cu nanoparticles dispersed in water at $\lambda_{ex} = 265$ nm and also in the temperature range 20-90 °C. Here also, decrease in intensity of the fluorescence peak at ~296 nm has been observed with increase in temperature.

![Fluorescence excitation spectra of Cu nanoparticles dispersed in water](image)

**Figure 7.15.** Fluorescence excitation spectra of Cu nanoparticles dispersed in water at $\lambda_{em} = 296$ nm and in temperature range 30-90 °C.

In corroboration with temperature dependence of the fluorescence emission spectra, we also performed temperature dependence of the excitation spectra of the Cu nanoparticles...
dispersed in water. Figure 7.15 shows, the temperature dependence of the excitation spectra of the Cu nanoparticles dispersed in water, in the temperature range 30-90 °C and at $\lambda_{em} = 296$ nm. Intensity of the excitation peaks at ~213 nm and ~269 nm decreases as the temperature increases from 30 to 90 °C, indicating maximum transition probability and hence resonant absorption at ~213 nm and ~269 nm decreases as the temperature increase. This is in conformity with the fluorescence emission spectra (Figure 7.14), where intensity of the fluorescence emission peak decreases with increase of the temperature.

7.8.4 Fluorescence from trap states of the Cu nanoparticles

So far, we have discussed fluorescence of the Cu nanoparticles, where energy of the excitation photon is more than the energy required for the fluorescent transitions. What will happen, when the energy of the pumping source is lower than the energy required for the fluorescent electronic transition? To study this, we show in Figure 7.16a, the fluorescence spectra of the Cu nanoparticles dispersed in water at $\lambda_{ex} = 510$ nm (red), 520 nm (blue), and 530 nm (olive).

Figure 7.16. Fluorescence emission spectra of Cu nanoparticles dispersed in water (a) at $\lambda_{ex} = 510$ nm (red), 520 nm (blue) and 530 nm (olive), (b) at $\lambda_{ex} = 370$ nm (red), 380 nm (blue), and 390 nm (olive).
High intensity peaks at 510 nm, 520 nm and at 530 nm are Rayleigh scattering peaks, as established in previous sections. There are peaks at ~418 nm, 450 nm, and 488 nm, position of which is fixed with change in $\lambda_{ex}$. Due to their location with respect to the Rayleigh peak, these peaks can be assigned to anti-Stokes fluorescence emission from the Cu nanoparticles dispersed in water, as these peaks are on the high energy side of the $\lambda_{ex}$. This can be quite an interesting observation of the upconversion of energy observed in Cu nanoparticles. So, how this will behave at higher energy excitation but lower than the fluorescent electronic transition? For that, Figure 7.16b shows, the fluorescence spectra of the Cu nanoparticles dispersed in water at $\lambda_{ex} = 370$ nm (red), 380 nm (blue), and 390 nm (olive). The high intensity peaks at 370 nm, 380 nm and at 390 nm are Rayleigh scattering peaks. No peaks at energy higher than $\lambda_{ex}$ are observed, instead, there are peaks at 422 nm, 450 nm, 488 nm, whose position is fixed irrespective of excitation wavelength. These peaks can be assigned to the Stokes fluorescence emission from the Cu nanoparticles as there energy is lower than the $\lambda_{ex}$. Further, there are peaks at 510 nm (for $\lambda_{ex} = 370$ nm), at 524 nm (for $\lambda_{ex} = 380$ nm) and at 534 nm (for $\lambda_{ex} = 390$ nm), position of these peaks changes with change in $\lambda_{ex}$ but remains fixed with respect to the Rayleigh scattering peak. These are Raman peaks of the Cu nanoparticles. Interesting point to mention is the position of these fluorescence peaks, which is same for $\lambda_{ex} \sim$380 nm and ~520 nm. So, these fluorescence peaks do originate from the same energy levels and may not have any relation to Stokes/anti-Stokes emission. These energy levels are nothing but the trap or surface states of the Cu nanoparticles. Effects of the temperature, solvent and UV-exposure on the fluorescence from the trap states of the metal nanoparticles has already been discussed in detail in chapter 4. Similar dependences are seen here as well.

7.9 Conclusions

In conclusion, we have been able to demonstrate synthesis of extremely small Cu nanoparticles by EEW technique. Novelty in these Cu nanoparticles is their small size and preferred orientation along specific planes. The preferred orientation is induced by
the noneqilibrium process of EEW. These small particles (size ~5 nm) show no surface plasmon and are crystalline having bulk-like lattice periodicities. The bare Cu nanoparticles, obtained with no extraneous capping agents, allow us to demonstrate in detail fluorescence never reported earlier for Cu nanoparticles at various $\lambda_{ex}$ in the ranges 200-240 nm and 250-280 nm. A fluorescence peak ~296 nm has been observed at different $\lambda_{ex}$, also corroborated by the excitation spectrum. This allows us, for the first time, to establish existence of the different excited states in the Cu nanoparticles, which always decay through the lowest excited state to give fluorescence emission form the Cu nanoparticles, similar to that observed from the solitary atoms/molecules. Further, we have been able to establish effect of Cu nanoparticles concentration, solvent and temperature on their fluorescence properties. In corroboration with this, we have also established effect of the temperature and emission wavelength on the probability of resonant absorptions. Also, we have studied fluorescence from the trap states of the Cu nanoparticles

**References**

