Chapter 4

Halide ion effect on shape of Au nanoparticles: Fluorescence and white light emission

This chapter discusses the effect of anions on the shape of Au nanoparticles synthesized in presence of cetyltrimethylammonium salts. Reduction of Au$^{3+}$ ions is carried out using tryptophan. Spherical nanoparticles formed in case of cetyltrimethylammonium chloride (CTAC) while triangular shaped particles are formed when cetyltrimethylammonium bromide (CTAB) is used. The possible reasons for such a difference have been presented and are the focal point of this chapter. Interestingly emission of white light is observed from the triangular nanoparticle solution when exposed to UV-light. The possible cause for such emission characteristics has also been delineated.

Part of the work described in this chapter has been published in:

4.1 Introduction:

Usage of stained glasses to decorate windows has been practice a wide spread from ancient times. Recently it has been realized that the beautiful colours that these glasses display are due to the noble metal nanoparticles like silver, gold, copper and their alloys that get incorporated in them during their prepartation. It has been realized that the color (optical absorbance) of the nanoparticle varies more dramatically with shape than size. With advancement of synthetic methods, recent focus has been shifted to the controlled synthesis of anisotropic noble metal nanoparticles like nanotrianlges/prism or nanorods as these evince properties such as NIR absorption, anisotropic electrical conductivity and strong enhancement of electric fields at the vertices. Shape dependent properties of these nanomaterials enable their application in fields like cancer hyperthermia, electromagnetic waveguides, SERS and infrared radiation absorbing optical coatings, imaging, enhanced fluorescence. These exciting properties and various applications have encouraged researchers to take up the challenge to synthesize anisotropic nanoparticles more vigorously.

Synthetic methods used for making of anisotropic materials include photochemical transformation of spherical particles, wet chemical synthesis with, or without template etc. Methods that utilize liquid crystals and polymer templates have also been found to be effective to control the shape of nanoparticles. A recent trend that has emerged in the syntheses of anisotropic nanoparticles is use of biological routes using plant extract, bacteria etc. Synthesis of nanoparticles of various morphologies using droplet based microfluidic techniques are also gaining lot of interest these days.

Inorganic fluorescent materials are of great interest and are considered as replacement for dyes in biolabeling and as solid state emitters. Amongst all the nanoparticles, semiconductor nanoparticles are well known for their unique size dependent emission characteristics. A clever combination of different sized semiconductor nanoparticles could lead to white light emission. So lots of investigations are on to develop semiconducting nanoparticle mixtures that may emit white light. However, considering the toxicity of the Cd$^{2+}$metal ions that
constitute many of these semi-conducting nanoparticles, greater attention is being paid to the search for the substitutes of such systems. One of the features noble metal nanotriangles/prism display is enhancement of fluorescence of fluorophores attached to them. Aslan et al. have shown fluorescence enhancement of Indocyaninegreen (ICG) in presence of silver nanoprisms. It is reported that presence of metal in the proximity of fluorophores also decreases the life time thus increasing the photo stability due to less excited state time for photochemical process to occur. Thus it is observed that presence of metal in the vicinity of fluorophore leads to increased intensity and a reduction in fluorophore lifetime.

Work presented in this chapter deals with formation of different shapes of Au nanoparticles in presence of different surfactants. We have used two surfactants, namely cetyltrimethyl ammonium chloride (CTAC) and cetyltrimethyl ammonium chloride (CTAB) for synthesis of gold nanoparticles. Tryptophan which is an amino acid was used as reducing agent in these experiments. Particles with different morphologies are observed for CTAC (monodispersed spherical particle) and CTAB (triangular particles). The difference in the type of halide ion present with these surfactants is probably one of the main factors for the formation of different shapes. The most exciting observation is white light emission from the oxidized tryptophan–gold nanotriangular combination when exposed to UV light of 365 nm.
**Part A**

### 4.2 Synthesis of Au nanoparticles:

**Figure 4.1:** Method for synthesis of Au nanoparticles using CTAB and CTAC as surfactants and tryptophan as reducing agent.

**Figure 4.2:** Structure of cetyltrimethyl ammonium chloride (CTAC), cetyltrimethyl ammonium bromide (CTAB) and tryptophan.
Schematic of the Au nanoparticle preparation as used for the work described in this chapter is shown in Figure 4.1. As seen from the scheme we have used CTAC and CTAB as surfactants and tryptophan as reducing agent. Structures for CTAC, CTAB and tryptophan are shown in Figure 4.2. It is well known that the critical micelle concentration (CMC) for CTAC is $16 \times 10^{-3} \text{ M}$ while that of CTAB is $1 \times 10^{-3} \text{ M}$. In our study we considered three different concentrations of CTAC and CTAB (at CMC, above CMC $10^{-2} \text{ M}$ and below CMC $10^{-4} \text{ M}$). In a typical experiment, to 100 mL solution of CTAC/CTAB, tetrachloroauric acid ($\text{HAuCl}_4$) was added so that it yields a final concentration of $10^{-3} \text{ M}$. $\text{HAuCl}_4$ which is now present with CTAB or CTAC is reduced by adding $10^{-3} \text{ M}$ tryptophan. Immediate colour change from orange yellow to wine red was observed for solution where the surfactant concentration is at CMC or below CMC, while in case of solution above CMC, no immediate change was observed. These solutions were kept in static condition. For CTAC slight colour change was observed after 5 min and with increase in time the colour changed from faint red to deep wine red. After about 45 min, colour change is complete. In case of CTAB colour change was observed only after 2.5 hrs and gradually as time increases the colour developed to reddish brown. Complete colour change was observed after 6 hrs. Samples were purified by centrifuging them at 8000 rpm for 15 min. Pellet obtained were re-dispersed in de-ionized water. Centrifugation was carried out twice to ensure complete removal of excess surfactant and tryptophan.
4.3 Results:

4.3.1: UV-visible

**Figure 4.3:** UV-Visible spectra recorded for Au nanoparticles synthesized using tryptophan as reducing agent in presence of CTAC (A) and CTAB (B). Curve 1-3 corresponds to CTAC/CTAB concentration below CMC, at CMC and above CMC respectively.

Figure 4.3 shows the UV-spectra for Au nanoparticles synthesized in presence of CTAC (A) and CTAB (B) at different concentrations as illustrated. It is seen that for CTAC at all concentrations only one peak centered around 520 nm is present. This peak is the feature of UV-visible spectra for Au nanoparticles which occurs due to surface plasmon resonance. In case of CTAB for concentration at CMC and below CMC are similar to the case of CTAC. But at a concentration above CMC, we observe two peaks one centered around 520 nm and other appearing at 710 nm. This indicates the formation of anisotropic nanoparticles or aggregated spherical structure. However transmission electron microscopy images (vide infra) conclude that the absorbance features are due to the formation of anisotropic triangular particles. Time dependent UV-visible spectra were recorded for this sample in order to see the development of the peak.
Chapter IV

Figure 4.4: Time dependent UV-visible spectrum for Au nanoparticles synthesized in presence of CTAB with concentration above CMC. Curves 1-5 correspond to time interval of 2, 5, 8, 24 and 70 h respectively.

Figure 4.4 shows the time dependent UV-visible spectra, which shows that at about 2 h only peak at 520 nm is dominant (curve1). As time increases absorbance at around 700 nm starts increasing. In the anisotropic particles the absorbance at 520 nm is attributed to the dipolar plasmonic vibrations perpendicular to the plane of the particle called the transverse peak while that at 700 nm is attributed to the longitudinal vibrations. In the present case as time increases the longitudinal peak starts developing and becomes stronger with time and dominates the transverse peak. Finally after 5 h the longitudinal peak is observed at 620 nm which gradually shifts to 780 nm with advancement of time (by 70 h).

4.3.2: TEM Measurements

TEM measurements were carried out for Au nanoparticles synthesized in presence of CTAC (Au_CTAC) and CTAB (Au_CTAB) with their concentration
above CMC. Figure 4.5 demonstrates the TEM images of Au_CTAC along with particle size distribution.

**Figure 4.5**: TEM micrograph image for Au_CTAC at different magnifications (A-C). Particle size distribution is shown in figure D indicating average particle size to be 13 nm. Inset in B shows the electron diffraction which is indexed as shown.

TEM analysis shows that the particles obtained in this case are spherical and mono-dispersed in nature. The average particle size obtained is 13 nm as can be observed from the histogram plotted. TEM measurements were also carried out for Au_CTAB.
Figure 4.6: (A-C) TEM micrographs of Au_CTAB recorded at different magnifications. (D) Shows the edge length measurement for the triangular nanoparticles. Inset in B shows the electron diffraction which clearly shows the hexagonal arrangement.

Figure 4.6 (A-C) shows the representative transmission electron microscopy (TEM) images of Au nanotriangles synthesized using CTAB as surfactant when its concentration is above CMC (10^{-2} M). Selected area electron diffraction (SAED) was also recorded for Au_CTAC (Figure 4.6B, inset) and Au_CTAB (Figure 4.6B, inset). For Au_CTAC the particles are clearly polycrystalline and the rings could be indexed based on the fcc structure of Au. While SAED pattern for Au_CTAB shows a hexagonal arrangement again corresponding the fcc phase of Au nanoparticles. TEM images are recorded at different magnifications as can be seen form the scale bars. It can also be concluded that nanotriangles have varied edge length from 40 nm to 105 nm. The sizes of the nanotriangles were also verified with
atomic force microscopy measurements that are presented in Figure 4.7. The thickness obtained from AFM measurement is 27 nm.

![Atomic Force microscopy image of nanotriangle in contact mode](image1.png)

**Figure 4.7:** Atomic Force microscopy image of nanotriangle in contact mode (A). Height and length profile is shown in figure B.

4.3.3: X-ray Diffraction Measurements (XRD)

![XRD measurements for Au_CTA (A) and Au_CTAB (B)](image2.png)

**Figure 4.8:** XRD measurements for Au_CTA (A) and Au_CTAB (B). Au_CTA can be indexed to fcc gold while we see that Au_CTAB is single crystalline in nature.

Powder diffraction pattern was recorded for Au_CTA and Au_CTAB nanoparticles. Figure 4.8A corresponds to Au_CTA while Figure 4.8B corresponds to Au_CTAB. The XRD pattern in case of Au_CTA corresponds well to the fcc crystalline phase of Au. In case of Au_CTAB we observe a single peak.
corresponding to (111) Bragg reflection of fcc gold. Magnified pattern (inset 4.8 B) of Au_CTAB indicates absence of peaks other than those form (111) planes from other Bragg plane of fcc gold.

4.3.4: Fourier Transform Infrared Spectroscopy (FTIR)

Interaction of tryptophan with surface of Au nanotriangles was studied by FTIR analysis that is shown in Figure 4.9. Curve 1 corresponds to pure tryptophan while curve 2 represents tryptophan reduced Au nanotriangles. An FTIR spectrum of pure tryptophan shows a peak at 2073 cm$^{-1}$ (marked by circle) due to the combination of the asymmetrical NH$_3^+$ bending vibration and the torsional oscillation of the NH$_3^+$ group. This peak is absent after reduction of chloroaurate ions with tryptophan. This is the main difference between the two spectra.

Figure 4.9: FTIR analysis for pure tryptophan (curve 1) and tryptophan reduced Au nanotriangles (curve 2).
4.4 Discussion:

In this section, detail discussion on formation of anisotropic nanoparticles will be stressed upon. Various factors that could be infusing the formation of anisotropic nanoparticles are delineated. The synthesis was carried out in the presence of two surfactants namely cetyltrimethyammonium chloride (CTAC) having CMC as $16 \times 10^{-3}$ M and cetyltrimethyammonium bromide (CTAB) with CMC as $1 \times 10^{-3}$ M. Tryptophan was used as reducing agent. Three different concentrations of both the surfactant as mentioned in section 4.2 were considered for the synthesis purpose. From the UV visible results obtained for Au nanoparticles for CTAC and CTAB at all the three different concentrations the following observations have been made.

a. For CTAC the surface plasmon resonance (SPR) peak corresponding to Au nanoparticles is centered at 520 nm which is the characteristic for spherical Au nanoparticles. For all the three concentrations (above, at and below CMC) SPR peak is centered at 520 nm.

b. In case of CTAB for concentration above CMC ($10^{-2}$ M) we observe two SPR peaks positioned at 520 nm (transverse) and 700 nm (longitudinal).

c. Time dependent UV-visible for CTAB above CMC concentration shows that at start, the transverse peak is more prominent than the longitudinal peak. But with progress in time, the longitudinal peak becomes more sharp and strong.

TEM images recorded (Figure 4.5 and 4.6) for the samples above CMC for both the surfactants show that spherical nanoparticles are obtained in case of CTAC while for CTAB formation of triangular nanoparticles resulted. These nanoparticles are also observed to be arranged edge to edge. Selected area diffraction pattern clearly shows that the Au_CTAC nanoparticles are polycrystalline in nature and the rings can be indexed to face centered structure of gold. While the SAED pattern for Au_CTAB reveals that it is single crystalline. The hexagonal nature of the diffraction spots is a clear indication that the triangular gold nanoprisms are highly [111] oriented with the top normal to the electron beam. The spots could be indexed based on the face centered cubic (fcc) structure of gold. The circled spots, boxed
spots and spots circumscribed by triangles correspond to the forbidden $1/3\{422\}$, allowed $\{220\}$ and $\{311\}$ Bragg reflections with lattice spacing of 2.5, 1.44 and 1.23 Å respectively. The presence of the $1/3\{422\}$ reflections indicates that the gold triangles could have stacking faults along the $<111>$ direction.\textsuperscript{42,43}

X-ray diffraction studies carried out for CTAC and CTAB also reveals preferential orientation in $<111>$ directions for nanotriangles while the XRD data obtained for Au\_CTAC can be indexed to fcc phase of gold particles. Thus XRD results also support the TEM measurements.

The mechanism of formation of anisotropic nanoparticles like nanosheets, nanotriangles, rods etc has been very intriguing. Reasons cited for formation of anisotropic particle formation include preferential binding of surfactant,\textsuperscript{44,45} oriented attachment,\textsuperscript{45} soft templates,\textsuperscript{3,46} aggregation of spherical particles\textsuperscript{8} and kinetic control.\textsuperscript{5,44,46-48}

Studies carried out by Xia and co-workers clearly illustrated the role of reaction rates on the morphology of Pd nanoparticles.\textsuperscript{48} The thermodynamically favorable shapes of Pd nanocrystals are cubooctahedral and multiple twinned particles (MTT). It was observed that when PdCl$_4^{2-}$ is reduced by ethylene glycol to generate Pd(0), atoms formed at relatively higher rates will mould into the thermodynamically stable forms of cubooctahedral and multiple twinned particles. Slowing down the reduction rates resulted in reduction of nucleation and growth and deviation in shape from its thermodynamic state. Thus transformation from cubooctahedral and MTT to triangular nanoplates or hexagonal shape is observed on reduction of reaction rate.

Pileni et al have demonstrated that the particle shape can be controlled by using different anions.\textsuperscript{49,50} They have studied the effect of different anions on shape of nanoparticles keeping all the other preparation conditions same. In absence of any external anions, added spherical particles were obtained. Presence of ions like Cl$^-$ during the synthesis resulted in rod formation. In case of Br$^-$ ions, formation of rod with higher aspect ratio is observed. Addition of NO$_3^-$ ions addition resulted in formation of aggregates. In case of SO$_4^{2-}$, slight elongation was observed. To explain the change in shape of nanoparticles on addition of these ions, Pileni and co-
workers have considered the Hofmeister series. The Hofmeister series for anions is given as follows

$$SO_4^{2-} > CO_3^{2-} > HPO_4^{2-} > F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > SCN^-$$

When these above mentioned anions are added to an organic solvent/water-surfactant mixture, solubility of surfactant in the aqueous phase increases from left to right. The anions desorb at the water-oil interface and then decrease the solubility between water and surfactant. Water molecules are highly bound to surfactant and induce high rigidity of the water-surfactant interface. They hypothesized that such changes result in decreasing the desorption of metal ions to the water phase and thus resulting in more spherical particles than cylindrical without perturbing the template.

Ravishankar and co-workers have based their argument related to formation of anisotropic nanoparticles on a morphology diagram formulated by them. As a representative the morphology diagram for Au is shown in Figure 4.10. Here their argument is based on the fact that crystal growth occurs through nucleation and growth where the driving force is the volume free energy change. They have observed that depending on the nature of the driving force, the nucleation and growth pattern takes different routes as shown in Figure 4.10 A & B. Large driving force leads to continuous growth while at low driving force, growth resulted in formation of steps and a lateral motion of steps on the surface. In the morphology diagram for Au the region represented by grey colour represents the condition of $\Delta G > 0$ thus no reduction occurs in this region. As the reactant conditions are changed the free energy reverses its sign from positive to negative. In the region represented by yellow the condition is -$\Delta G<\Delta G_{2D}^{crit}$ and favors 2D structure formation. 3D structures are obtained when the free energy condition is -$\Delta G>\Delta G_{3D}^{crit}$ which is represented by the red portion. Transition from 2D to 3D is represented by the green portion. Thus, from the morphology diagram it is found that at lower temperature and low pH anisotropic nanoparticles can be obtained.
Another reason cited for formation of anisotropic nanoparticles is the differential stress caused by the adsorption effect of halide ions. Br$^-$ and Cl$^-$ are known to form a hexagonal close packed adlayer on gold nanosurface. Slight mismatch between the halide adlayers and the atomic Au (111) lattice planes might cause some residual strain at the surface and lead to the development of the defects like twin planes. This may be one of the factors that influence the formation of triangular nanoparticles as reported by Lofton and Sigmund.\textsuperscript{43} This has been postulated as the reason for the observation that anisotropic particles are preferentially formed in presence of the Br$^-$ ions and not in presence of Cl$^-$. Murphy and co-workers also have employed CTAB for formation of nanorods. They postulated that CTA$^+$ head group binds to the side surface with some preference. The preferential binding is based on steric - the Au atom spacing on the side faces is more comparable to the size of the CTA$^+$ head group than the close-packed \{111\} face of gold, which is at the ends of the nanorods. Such binding stabilizes the side faces, which have relatively large surface energy and stress (tension) compared to
other faces. This allows material addition along the [110] common axis on \{111\} faces, which do not contain the CTA\(^+\) headgroups.\(^{57}\)

In the present case, formation of triangular nanoparticles in presence of CTAB can be attributed to preferential binding of bromide ions to the specific planes. There have been many reports where in presence of CTAB as surfactant leads to formation of anisotropic nanoparticles. Various reports suggest that Br\(^-\) ions chemisorbs onto the surface of Au more strongly and form hexagonal packed adlayer on the Au (111) surface.\(^{58-62}\) Earlier report suggest that the edges of triangle are bound by the (110) and (111) faces\(^{42}\) but it appears that Br\(^-\) ions are strongly adsorbed on to (110) thus enhancing growth of nanotriangles in <111> direction. It is also known that there is a mismatch between the Br\(^-\) ion adlayer and gold lattice plane which results in strain on the small particles synthesized at initial stages. This strain leads to defect formation like twin boundary resulting in orientational growth of small nanoparticles to form nanotriangles.\(^{43}\)

We also noticed that the reaction rates with CTAB are lower than those with CTAC. Therefore this also could have had an effect on the formation of triangular particles. Apart from the above reasons, role of tryptophan and the oxidized products of tryptophan influences the shape of resulting nanoparticles cannot be ruled out.

![Structure of kynurenine](image)

Figure 4.11: Structure of kynurenine, the products obtained when tryptophan is oxidized.

It is well known that tryptophan in process of reducing Au\(^{3+}\) ions gets oxidized and leads to formation of kynurenine.\(^{63}\) In our FTIR studies we noticed that absence of peaks corresponding to pure tryptophan but could not detect any
specific peaks that confirm the formation and adsorption of kynurenine on the gold surface. But the fluorescence studies indicate the tryptophan is getting oxidized.

**Part B**

### 4.5 White light emission:

This section of the chapter deals with emission of white light observed from Au_CTAB when exposed to UV light of 365 nm. This phenomenon was not observed for Au_CTAC (spherical nanoparticles). Experimental observations are shown in Figure 4.12 with UV light **ON** and UV light **OFF**.

**Figure 4.12:** Photographs of Au_CTAB solution when UV-light is **OFF** (A) Au_CTAB solution exposed to UV-light of wavelength 365 nm (B). Au_CTAC solution when UV-light is **OFF** (C) and when exposed to UV-light of wavelength 365 nm (D).
The Au-CTAB solution is reddish brown in colour. Interestingly, when unexposed to UV-light (Figure 4.12A) of wavelength 365 nm we observe an intense white light (Figure 4.12B) from the same sample. In case of Au_CTAC no such emission is observed when the solution is exposed to same UV-light (Figure 4.12C and D). In order to confirm the white light which was emitted is not due to scattering it was passed through the prism. Similar experiment was carried out with just tryptophan. The observed results are shown in Figure 4.13.

**Figure 4.13:** (A) Light spectrum obtained when white light emitted from Au_CTAB nanotriangles is passed through prism. (B) Spectrum obtained when light emitted from tryptophan is passed through prism.

In the case of white light emitted from Au_CTAB the splitting into various components (red, green, cyan and blue) is clearly observed (Figure 4.13 A). When same experiment was carried out by illuminating pure tryptophan only blue light was observed. To entice more information about this phenomenon detailed fluorescence and life-time measurements were carried out.
4.6: Fluorescence measurements

Figure 4.14: Fluorescence measurements carried for pure tryptophan (A). Excitation wavelength was 280 nm. Fluorescence spectrum for oxidized tryptophan is shown in figure B, curve 1 while fluorescence for Au_CTAB nano-triangles is represented by curve 2. For both the samples excitation was 365 nm.

Fluorescence for pure tryptophan is shown in Figure 4.14 A. The excitation for this was 280 nm. We observe that the emission for pure tryptophan is centered around 350 nm. It is known that during the reduction of Au$^{3+}$, the tryptophan will be oxidized. Mandal et al.$^{63}$ have confirmed that the oxidized product of tryptophan in this reaction would be kynurenine. But in our studies we could not confirm the formation of kynurenine and hence we would restrict calling the formed product as oxidized tryptophan. To see what emission characteristic this oxidized product will have, we prepared oxidized tryptophan with H$_2$O$_2$. Spectrum for oxidized tryptophan excited at 365 nm is shown in Figure 4.14 B. A clear peak with a weak intensity is observed at 460 nm (curve 1). In the emission spectra for Au_CTAB nanotriangles again a peak centered at 460 nm could be seen. The total initial concentration of tryptophan used to obtain the spectrum 1 and 2 is the same. From the spectra we can see that the intensities of the emission peak in case of Au_CTAB sample is much higher than that observed with H$_2$O$_2$ oxidized tryptophan. This suggests that in presence of Au_CTAB the emission intensity of oxidized tryptophan is getting enhanced.
The results obtained from the fluorescence were supported by life time measurements. Measurements were recorded for excitation of 365 nm and collected at 460 nm with accordance with fluorescence measurements. Milk was used as the reference to eliminate scattering effects. Life time measurements recorded for milk as background and oxidized tryptophan are shown in Figure 4.15.

4.7: Life time measurements:

![Figure 4.15](image)

**Figure 4.15**: Life-time measurements recorded for milk as reference (A) and life time data for tryptophan collected at 350 nm.

The lifetime data for milk does not show any decay as can be seen form Figure 4.15 A. Lifetime measurement for tryptophan (Figure 1.15 B) was carried out by exciting the sample at 280 nm and collecting the data at 350 nm which is the wavelength of emission of pure tryptophan. The experimental data could be fitted to decay with two different life time values of 2.7 ns (90.7%) and 5.9 ns (9.3%). Our experimental life time values are in good agreement with reported values ($\tau_1=2.1 \pm 0.2$ and $\tau_2=5.4 \pm 1.1$ ns).\textsuperscript{64}

The lifetime measurements carried out for oxidized tryptophan and the Au_CTAB nanotriangles are shown in Figure 4.16. Excitation of the sample was carried out at 365 nm and the data was collected at 450 nm. The obtained lifetime values are $\tau_1=0.23$ ns (2%), $\tau_2=2.32$ ns (10%), $\tau_3=13.9$ ns (88%) for H$_2$O$_2$ oxidized
tryptophan and $\tau_1=1.99$ ns (9 %), $\tau_2=3.71$ ns (16 %), $\tau_3=18.2$ ns (75 %) for Au_CTAB.

Figure 4.16: (A) Lifetime measurement for oxidized tryptophan. (B) Lifetime measurement for Au_CTAB nano-triangular solution. Both the samples were excited at 365 nm while the emission was recorded at 450 nm.

4.8 Discussion

Observance of white light from Au nanotriangles (Figure 4.12 A and B) is well studied by fluorescence and life time measurements (Figure 13-16). Tryptophan has earlier been used as reducing agent for gold nanoparticles. Fluorescence of pure tryptophan occurs at 345 nm when excited at 280 nm, which is also observed by us for pure tryptophan (Figure 4.14 A). The most striking result in the emission experiments, is the observation of a broad peak from Au_CTAB where emission maximum is centered at 450 nm (Figure 4.14 B, curve 2). From our control experiments we could surmise that the origin of the emission could be from the oxidized tryptophan. Accordingly fluorescence was recorded for oxidized tryptophan prepared using H$_2$O$_2$ as oxidizing agent. As expected a clear peak with emission maximum again centered at 450 nm could be clearly seen (Figure 4.14 B, curve1). However the intensity of peak for Au_CTAB is much higher than the oxidized tryptophan. This enhancement is attributed to binding of oxidized tryptophan molecule to the tips of nanotriangles. Aslan et al. have shown enhancement in fluorescence spectra by ten orders of magnitude in presence of
anisotropic metal nanoparticles.\textsuperscript{16,17} This enhancement is attributed to increased local excitation fields around the edges of the triangles and interaction of excited state fluorophores with free electrons in the metal (surface plasmon electron).\textsuperscript{40,68,69} El-Sayed and co-workers have demonstrated the lightning gold nanorod effect, which is explained based on electron hole recombination and the increase in the emission yield results from the enhancement effect of the incoming and outgoing electric fields via coupling to the surface plasmon resonance in the rods.\textsuperscript{70}

Thus, our fluorescence data clearly point out the possibility of attachment of oxidized tryptophan molecules to the sharp edges of nanotriangles. The enhanced intensity of this emission which is very broad with these different life times could be the cause for white light emission observed.

\textbf{4.9 Conclusion:}

Au nanoparticles were prepared with two different surfactants (CTAB and CTAC) with tryptophan as reducing agent. Spherical particles are obtained in case of CTAC while use of CTAB resulted in formation of Au nanotriangles. White light emission was observed from nanotriangles when illuminated with UV-light of 365 nm. Occurrence of white light is attributed to the enhancement of fluorescence of oxidized tryptophan attached to sharp tips of nanotriangles.
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