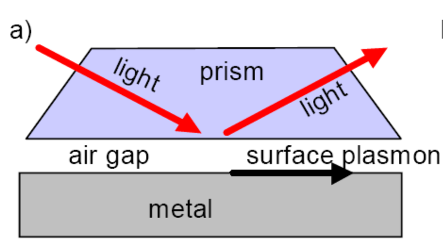
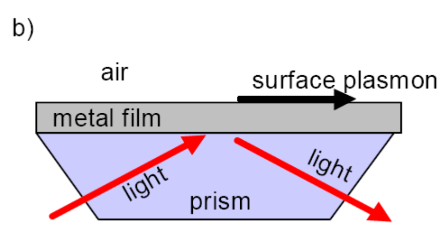
Studies on Surface Plasmons of Metal Nanoparticles

Plasmons are produced by the quantization of plasma oscillation. Plasmons are quasi particles formed by the oscillation of electrons present on the metals. When the surface of the metal is illuminated by light at right angle to the metal , the energy required for electron oscillation is used[1]. This phenomenon evolves the quasi particles known as plasmons. The plasmonic property can be analyzed using UV-spectroscopy. UV absorption frequency differs from metal to metal. It also depends upon refractive index, metal composition and surrounding of the metal. Since electrons carry charge the electrical field is associated around the electrons. It shows interplay between charges and field[1]. The field varies among the bulk, surface and particle. Surface plasmons can not be excited by plane waves as the Plasmon modes have larger momentum regardless of the angle of incidence. Thus additional momentum has to be provided to excite the plasmons. This is usually done by placing grating structure between metal and light source such as prism[1]. where gap is formed between metal and prism . The light passes through prism used and falls on the metal producing dispersion of plasmons. This is known as Otto-configuration. In the Kretschmann configuration thin film of the metal is used and light passes through prism where no gap is provided.

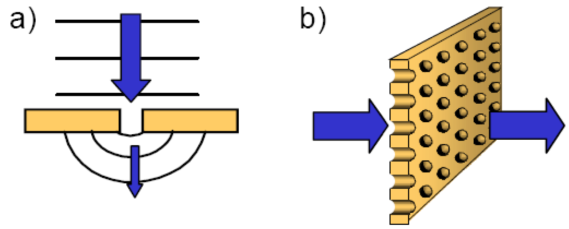




a) Otto configuration

b) Kretschamnn configuration

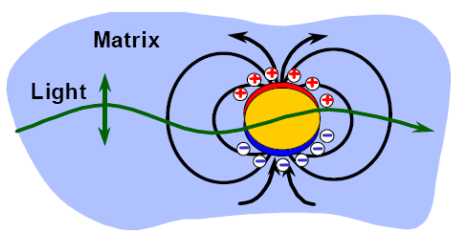
The surface plasmons produced at the interface of dielectric medium and metal surface can be affected by dimples, holes and rims present on surface of the metal. Surface plasmons can be coupled when light passes through holes in the metal. Optical property of the metal is studied from its opaque surface[2]. The light is passed through sub-wavelength sized nanohole . The metal film is larger than expected from diffraction theory. This fascinating effect has been used in optical properties of metals such as filters or displays. The Plasmons formed in the holes are believed to couple and intensity of the Plasmons produced is larger than the light source used. If it is passed through a single hole the intensity of excited Plasmon is less as the coupling of plasmons is less[1].



a) Single hole transmission is very small b) Transmission through a number of holes and intensity is higher when normalized to total area

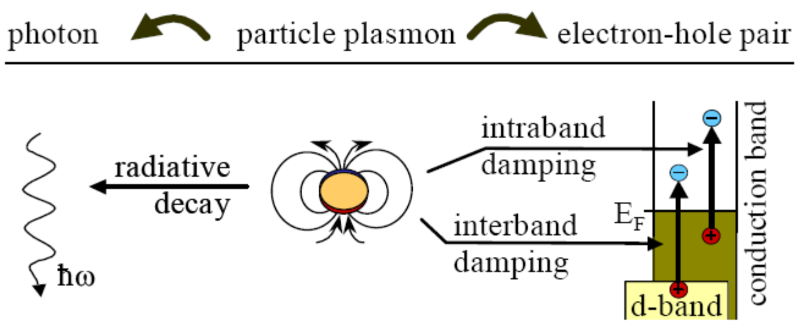
Simple semi-classical model

The particle to be used can be qualitatively considered that the wavelength of light used is on the order of particle size. When light passes through the particle negative and positive charges are separated. The frequency of light used depends on the restoring force of negative and positive charges[1]. That is, the magnitude of separation depends upon the excitation light field which is required to separate the opposite charges present in the local field of particle.



Damping mechanism

The collective oscillation of electrons is produced when light falls on a metal and the electrons undergo resistance due to radiative and nonradiotive process[1]. In the radiative process the energy is consumed by photons. In the nonradiative decay electrons are transferred from one band to another known as interband transition. The electrons also move in a same band known as intraband transition. In order to understand non radiative decay the electrons are considered as independent. Thus superposition of these independent electrons form plasmons , collective oscillation of electrons, neglecting the many body effects such as collective scattering with phonons[2,3]. Damping is due to resistance experienced by electrons when electrons are excited to higher energy states as per Pauli-exclusion principle electrons move to empty states.



Where the moment of electrons form conductivity(σ) and it is derived from the imaginary part of the dielectric function (ε) = $\sigma/\varepsilon_0\omega$. The energy dissipated in the nonradiative process is transferred into heat.

Quasi-Static approximation

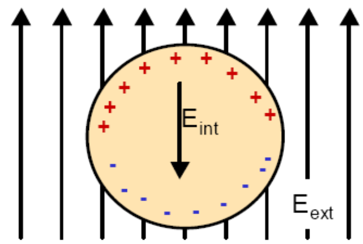
A simple metal particle is considered to study about particle Plasmon neglecting the effects due to self-induction of electromagnetic field. Where a region of space is considered and it is smaller than the wavelength of light. Electromagnetic phase is constant throughout the region of interest. The particle smaller than 40nm proves the quasi-static approximation and it has the advantage of simple electro-statics to calculate the response of particle to electromagnetic field(1).

Conductivity of the metal is related to dielectric constant of metal and medium as follows

$$\varepsilon_r = \varepsilon_r' + i\varepsilon_r'' = \varepsilon_{\text{metal}}/\varepsilon_{\text{medium}}$$

or

$$\alpha = \varepsilon_0 3V \frac{\varepsilon_r - 1}{\varepsilon_r + 2}$$



The plasmon absorption can be observed from UV-spectroscopy and it depends on shape, size, composition of metal nanoparticle and refractive index of surrounding medium(2). The shift in UV spectrum has been observed because of change in the structure of liquid crystals deposited on a metal when light falls on it.(2) As the Plasmon absorption depends on shape of nanoparticle Ag-nanodisks are prepared by sol-gel reverse micelle method method using AOT(4,5). We also prepared silica nanodisks spotted with Ag by Tollens reagent method to study plasmonic properties with other external compounds(6). These nanodisks are trapped using thiol funtionalised compound which also has nitrogroup responsible for H-bonding. This property is used for aminesensing(7). Primary amines having two hydrogen atom makes H-bonding with nitro group and this interaction provides the change in absorption spectrum of nanodics-amine system from that of nanodisk alone. This property has been studied with aromatic amines and aminoacids.The effect of absorption spectrum of aminoacids with buffer solution has been studied(8). Absorption enhancement and Fluorescence decay has been observed when we study this interaction between amine and nanodisk system especially 3-AQ (3-aminoquinoline)(9). Life time studies of nanoparticle and amine interaction has also been done to study dynamics of species involved in the excited state.

Experimental

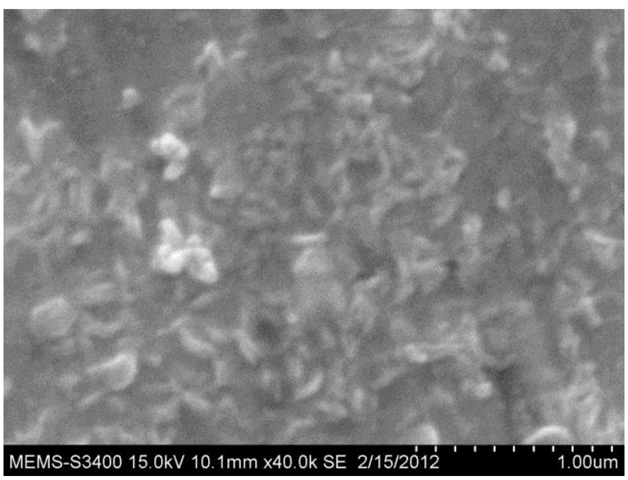
AOT and $AgNO_3$ purchased from Sigma-Aldrich are used to prepare nanodisk by sol-gel reverse micelle method. All amine and amino acids have been purchased from sigma-alrich.

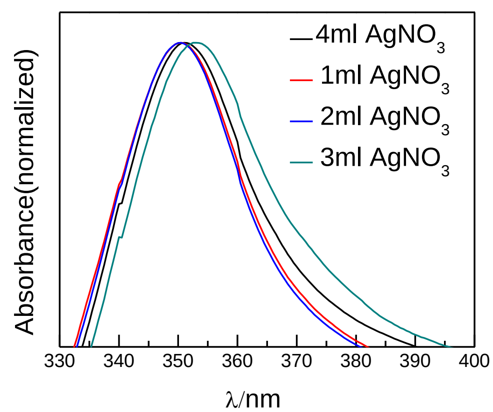
Instruments

Uv-spectroscopy, Fluorescence spectroscopy, TCSPC, SEM and TEM.

Synthesis

Since AOT contains water molecules, it must be removed to calculate *w*=[H2O] / [AOT] value(4,5). To dry AOT, We prepared saturated solution of AOT in HPLC methanol in a 100ml Rb. We dried 1gm of charcoal to absorb moisture from the AOT used. We have increased surface area of the charcoal by drying it for 3 hours. Then 10gm AOT was saturated with HPLC methanol. The whole mixture was refluxed for 24 hours using water condenser and guard tube which is used to absorb moisture from outside. Thus it protects entering of moisture. After 24 hours, the mixture is filtered using celite and sintered crucible to remove charcoal. The filtrate is dried to remove methanol by using rotavapour for two hours. Then the dried AOT is used to prepre lamellar micelles. Lamellar micelles are disc-like micelles which act as templates to prepare silver nanodisks. Lamellar micelles were prepared at different conditions. 4ml of 0.1M $AgNO_3$ solution was added to 2gm of AOT and allowed to stirring for 8 hours to form lamellas micelles and 1ml of 0.1M $NaBH_4$ were added to reduce the $AgNO_3$ added. The whole mixture was mixed by manual for 30 minutes. This mixture was allowed to stand for 7 hours to form Ag-nanodisks. Then 20ml of 1-dodecanethiol was used to extract Ag-nanodisks. The mixture with 1-dodecanethiol was centrifuged for 20 minutes[(5)]. It was done for 10 times to extract Ag-nanodisks completely .Then the mixture was washed with ethanol to remove excess 1-dodecanethiol and then the Ag-nanodisks prepared was dispersed in n-hexane to take SEM image of the sample. Lamellar micelle was also prepared by adding 4ml of 0.1M $NaBH_4$ solution first and then 1ml of 0.1M $AgNO_3$ solution. Nanodisks are also trapped by 4-nitrothiophenol and used for amine sensing. This system has been studied with amino acids and aromatic amines.

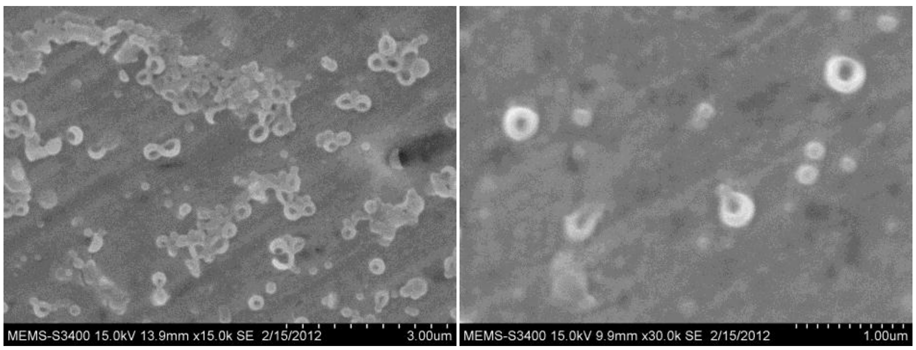




SEM image of Ag-nanodisk trapped with 1-dodecanethiol

Synthsis of silica nanodisk results the Si-nanodisk having hole at the centre. This was prepared by phase separation method when we tried preparing Si-nanodisk[(10)]. It was prepared when we maintained the value $w_0 = 6$. For this 2.88gm AOT, 23.4ml water and 160ml of n-heptane are taken in a separating funnel. They are mixed and left undisturbed for 24 hours (remove the pressure from time to time). The lower layer was removed using syringe with disturbing the upper layer slightly and transferred into a beaker. If we don't disturb the upper layer silica nanodicks are formed. Where upper layer is disturbed to form ring like lamellar micelles in which the hydrophobic part is present inside the hydrophilic part. 1ml of TEOS (Tetraethylorthosilicate) was added to this lamellar micelles after 3 hours.To this, 0.7ml of 4N NaOH was added after 10 hours and left undisturbed for 24 hours. Ethanol has been used to remove AOT completely from this mixture by washing the hole mixture 8 or 10 times. Then the silica nanoring is formed by drying the residue in oven. The silica nanoring is Useful to study the effect of the hole to plasmonic property of nanoring and could be compared with spectral studies of silicananodisk.

Ag spotted silica wafers were prepared using silica nanodisks by Tollens reagent method. Silver mirror preparation was done in presence of silica nanodisks to provide Ag spotted silica wafers.



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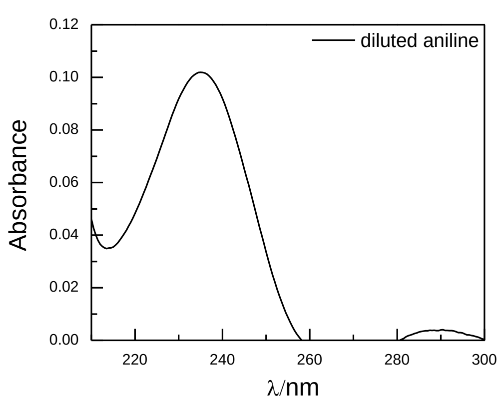
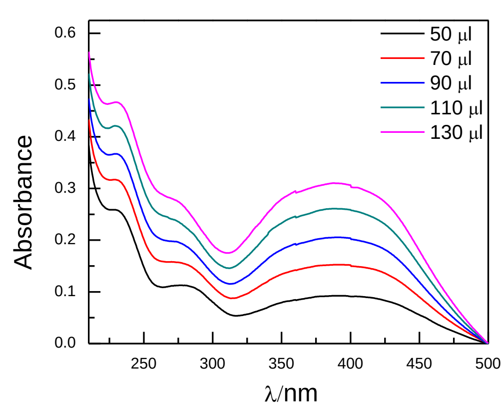
Results and discussion

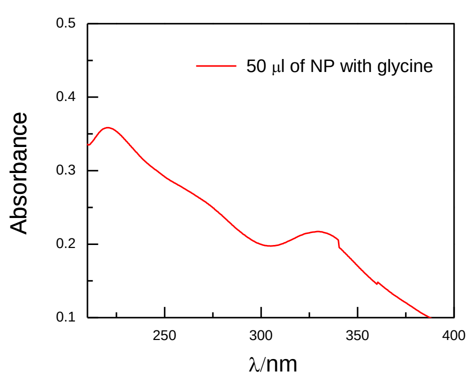
4-nitrothiophenol trapped nanodisks have been used to sense amines such as aniline, benzyl amine and cyclohexyl amine. When the nanodisk system interacts with amine the change in absorption maximum has been observed indicating the presence of amines. This is because of the formation of H-bonding between nitrogroup and H-atom attached to nitrogen atom of amine. The less amount of amine has been used to study its presence. The shift in absorption maximum and enhancement in absorption spectrum of amines with nanodisks have been observed.

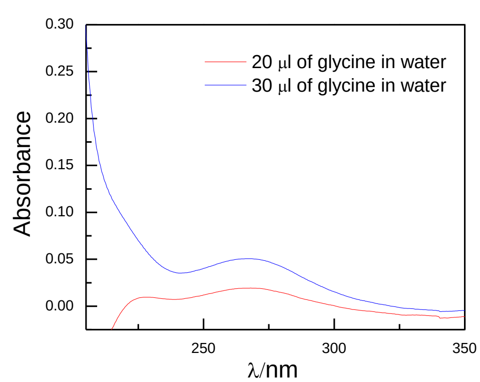




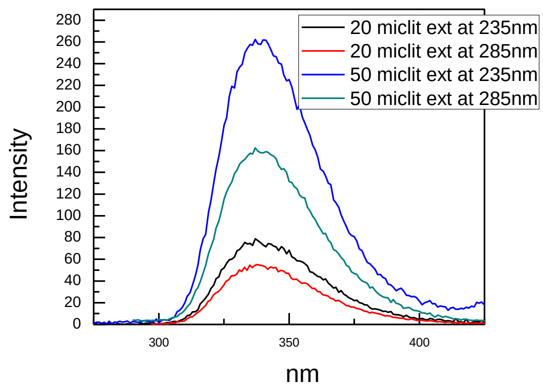
The same phenomenon has been observed with benzyl amine. Even tertiary amines show absorption enhancement with our nanoparticle system. Though it has no N-H bond nanoparticle system enhances the absorption spectrum of TEA (Tertiary ethyl amine). This interaction between amine and nanoparticle favors the enhancement studies of nanoparticle system with different compounds to analyse weather the system enhances the absorption spectrum of amine compounds only or other compounds also. Like this, amino acids have been studied to sense the presence of them in different environment. But water is the best solvent to study the spectroscopic properties of amino acids. Sensing of amino acids has been done in both hydrophilic and hydrophobic environment. Spectral studies of amino acids in hydrophilic environment are useful and helpful to study their property in vivo. Both aromatic and aliphatic amino acids have been studied to analyze the solvent in which it gives good interaction with nanoparticle system. But spectral studies of them in hydrophilic environment are favorable.

Water soluble amino acids such as glycine, proline, serine and threonine were taken to analyze their spectral properties as in vivo. The actual properties in vivo can be studied by using different pH solution which is to be used as a solvent. The change in absorption maximum and absorption enhancement has been observed with NP-system and glycine and absorption enhancement has been observed with increase in concentration of NP system. Thus the presence of amino acid can be studied in water environment and different pH solutions. Its UV absorption of glycine confirms this. That is, glycine absorbs at 267nm in water but it absorbs at 220nm in presence of NP system. To study the fluorescence properties of amino acids those which give fluorescence spectrum has been taken. Glycine, proline are not fluorescence molecules and not taken for their fluorescence property with NP system.

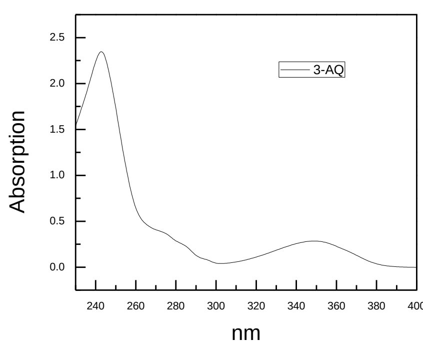


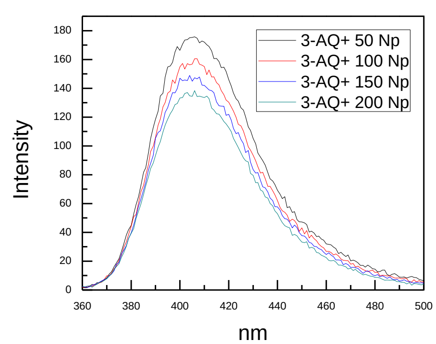


Aromatic amines like aniline, benzyl amine are fluorescent molecules and they give both absorption and fluorescence studies. Since aniline is a good fluorescent molecule it has been taken to observe its fluorescence properties with NP system. It shows fluorescent enhancement with increase in concentration of nanoparticle. It is due to H-bond between N-H-atoms of aniline and nitro group when it was excited at 235nm and 285nm. This fluorescence enhancement studies of nanoparticle with fluorescent amines help in finding the molecule which shows less fluorescence. Thus these less fluorescent molecules can be found out with high concentration of nanoparticle. These studies are helpful in detecting amino acids which are less fluorescent.

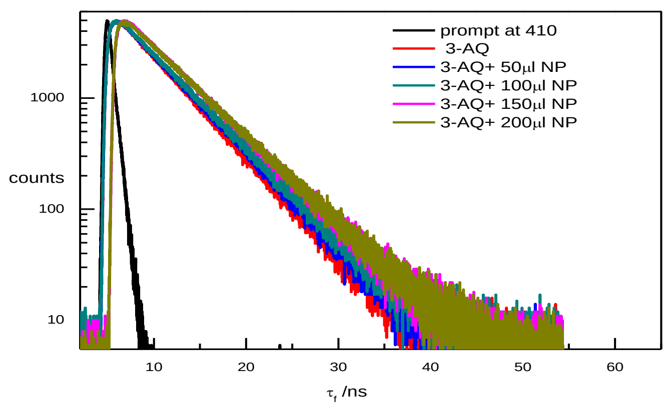


This NP system also shows fluorescent decay with aromatic amine 3-aminoquinoline (3-AQ). 3-AQ is a heterocyclic aromatic organic compound. The absorption spectrum of 3-AQ shows band at 245nm, 272nm and 350nm. The maximum absorption is observed at 245nm.





Fluorescent decay was observed with increase in concentration of NP. Emission spectrum of 3-AQ shows peak at 410nm in ethanol. The H-atoms attached to nitrogen interacts with nitro group of nanoparticle forming H-bond and positive charge is created in the aromatic ring of 3-AQ. This charge is stable in the excited state of the molecule and high concentration of NP system. This fluorescent quantum yield is very small and confirmed from fluorescence decay spectrum. The increase in polarity of the solution by increasing the concentration of NP system stabilizes the excited state and this stabilization is very low. It is observed from the lifetime measurement. Life time of 3-AQ with NP system in the excited state is 7ps. When the polarity is very low the tetrahedral amino group undergoes flip-flop motion and destabilizes the excited state. The stability of excited state is increased by increasing the NP concentration and ICT (Intramolecular charge transference) process is also enhanced. Where the flip-flop motion of amino group is restricted due to the formation of planar amino group and ICT is enhanced. When the polarity is very low the tetrahedral amino group undergoes flip-flop motion and destabilizes the excited state. The



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Conclusion

The plasmonic property of metals could be studied using Ag nanoparticles trapped using 4-nitrothiophenol. Amines can be sensed using NP synthesized and it could be observed from fluorescence enhancement for some amines and fluorescent decay for others.

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