

Photoluminescence from Gold and Silver Nanoparticles

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Abstract. This review is an attempt to highlight some of the significant results of the work carried out on the photoluminescence from nanoparticles of the noble metals, particularly gold and silver, over the past two decades. Although quite an immense amount of reports can be found, those that have contributed in throwing some light on the underlying mechanism behind photoluminescence have been considered here. Interband radiative recombination of electrons in metals or photoluminescence (PL), though very weak, was first reported in Au, Cu and Au-Cu alloys. A simple model attributes the PL to the radiative recombination of conduction band electrons below the Fermi energy with d-band holes. Most of the mechanisms are based on this concept. Only small sized clusters are known to exhibit luminescence, with the appearance of additional features which changed with the surfactants suggesting ligand to metal charge transfer. Further, the observation that more polar ligands do indeed enhance the luminescence intensity supports ligand to metal charge transfer. A non-radiative decay of excited electrons from 6sp-band to interface electron energy levels or bands (IEEB), that could be created due to charge transfer from the ligand to the metal core, followed by radiative recombination of electrons from these levels with the hole in the d-band could be another possible mechanism, which is supported by the size independence of the PL emission peak position. However, it is possible that these mechanisms operate independently or even simultaneously depending on various factors like size, ligands, dispersion medium, particle surface topography and so on.

Introduction

The unique optical and electronic properties of metal nanoparticles have opened a range of applications, these include SERS based biosensing [1], cancer diagnostics and therapy [2], vapor sensing [3], catalysis [4] to cite a few. The quantum size effect, observed when the particle size approaches the electron Fermi wavelength, is predicted to cause a discretization of the energy levels of the conduction electron [5]. The appearance of the discrete energy levels can also be expected to give rise to other optical effects, not seen in the bulk. Relatively intense, and to a certain extent size dependent photoluminescence from metal nanoparticles, first reported by Wilcoxon et al. [6], is an example of a property exhibited by a metal only in nano size regime but not expected in bulk.

An examination of the basic requirements for observing this phenomenon would help in understanding why a bulk metal is not expected to show photoluminescence. Photoluminescence is a consequence of the interaction of light with matter. When electromagnetic radiation is incident on a material, it absorbs the energy and a fraction of the absorbed energy may be re-emitted in the form of electromagnetic radiation in the visible or near visible region. This is referred to as photoluminescence. Luminescence is a process which involves at least two steps: the excitation of the electronic system of the solid and the subsequent emission of photons. These steps may or may not be separated by intermediate processes. An intermediate process is implied if the emitted radiation is of a lower energy, which is usually the case. Therefore, only a part of the absorbed energy is transformed into luminescent light. The rest of the energy is lost by non-radiative means, such as the excitation of phonons in a solid, or molecular vibrations, or heat. Photoluminescence can be classified into fluorescence and phosphorescence. In fluorescence the time delay between the absorption and emission of energy is short, whereas in phosphorescence this delay can be relatively long. A decay time of $\sim 10^{-8}$ second can be taken as a demarcation line between fluorescence and phosphorescence.

In a simple model of a semiconductor, photoluminescence results due to the relaxation of an electron excited from the valence to the conduction band. This relaxation would be radiative in nature, resulting in the emission of photons of energy at least equal to the band gap of the material. Non-radiative decay, in this case, is less probable as the energy is too high to be dissipated via a phonon. However, the absence of a finite band gap between occupied and unoccupied electronic states in a metal makes photoluminescence exceedingly improbable. This is so because a photoexcited electron can relax non-radiatively back to the ground state by energy transfer through the closely spaced energy levels. The discretization of the energy levels in metal nanoparticles, arising from the quantum confinement effects, can lead to changes in the optical properties. The fluorescence reported from metal nanoparticles in the last two decades is associated with the changes in the fundamental properties of the electronic energy levels in metals. Therefore, an in-depth study of photoluminescence/fluorescence from metal nanoparticles would provide means for understanding the properties of matter in the nanoscale.

This article is an attempt to highlight some of the significant results of the work carried out in this field over the past two decades. Although quite an immense amount of reports on the photoluminescence from nanoparticles of the noble metals have been reported, those that have contributed in throwing some light on the underlying mechanism behind this phenomena have been considered here. Luminescence spectroscopy is among the simplest and versatile technique for many applications, such as molecular recognition and labeling, for medical, biological and general analytical purposes [7]. Research on fluorescent nanoparticles has mainly been concentrated on semiconductor nanoparticles such as CdSe, in which the fluorescence can easily be tuned to span over the visible region of the electromagnetic spectrum. But the possibility of use of these nanoparticles *in-vivo* appears very limited due to their toxicity [8]. Nanoparticles of noble metals are better suited for biological applications because of their reduced toxicity and the innumerable easy synthetic methods available yielding highly stable colloids. Among the noble metals, gold (AuNP)

and silver nanoparticles (AgNP) are the ones that have been investigated the most. Hence, we first look into the results of luminescence from AuNP followed by AgNPs.

Photoluminescence

From Au Nanoparticles. Interband radiative recombination of electrons in metals or photoluminescence (PL), though very weak, was first reported by Mooradian [9] in Au, Cu and Au-Cu alloys when excited by an argon-ion laser emitting in the range 457.9 nm to 514.5 nm or from Hg arc lamp emitting in the 300-400 nm range. Irrespective of the excitation wavelength the Au emission was found to be at a higher energy of 2.2 eV (~ 564 nm) compared to the Cu emission at 2.0 eV (~ 620 nm) and the emission peaks of the alloys were found to lie in between these two. The emission energies are close to the energy gap between the upper d-band and the Fermi energy and appeared as a broad peak centered near their respective interband absorption edge.

Mooradian [9] proposed a simple model to explain the PL from noble metals and it is noteworthy that many of the mechanisms proposed for PL from noble metal nanoparticles are to a large extent, based on this model. A few aspects of the band structure of noble metals, such as the interaction between the conduction band and the d-band at the region of crossover and the band being made up of a number of closely spaced bands in k space, are not explicitly detailed in the representation. However, the simple model suffices to understand the underlying mechanism for the PL emission. A photoexcited electron from upper states in the d-band makes a transition to levels at and above the Fermi energy, without any change in momentum. PL can be expected when the conduction band electrons below the Fermi energy recombines radiatively with d-band holes with $k < k_F$. Quite early, in 1986, Boyd et al. [10] undertook a comprehensive study, both experimental as well as theoretical, to understand the mechanism of single and multiphonon induced luminescence from smooth and rough surfaces of Au, Ag and Cu films. Based on calculations and experimental observations of single photon induced emissions from these films, it was shown that the features in the emission spectra depended on both the roughness as well as the metal studied. Whereas the emission from

smooth films of Au and Cu could be attributed to direct radiative recombination of electrons below the Fermi level with holes in the d- bands around the X and L symmetry points, those from Ag appeared to be predominantly due to radiative emission from the surface and volume plasmons.

The work by Boyd was further investigated in more detail by Apell et al. [11] for bulk noble metals. Who developed a theory based on the optical constants and density of states of the metal being probed. According to this theory, the process of luminescence emission proceeds with the initial excitation of an electron in the d-band to states above the Fermi level. The hole left behind is scattered to a different state in the d-band by a phonon. Another electron from the filled sp- band, with energy less than the Fermi energy, transits directly into this hole emitting a photon of lower energy in the process.

It is interesting to note that a detailed study of luminescence from Au nanoparticles was carried out and the anticipated mechanism proposed for this phenomenon in one of the first known reports of photoluminescence from metal nanoparticles by Wilcoxon et al. [6]. Their work encompasses studies on the PL from Au nanoparticles synthesized by different methods, its behavior with change of particle size, the effect of different ligands and solvents. They have resorted to a rather different technique to purify and identify the size of Au clusters formed in water by the citrate method. Size exclusion liquid chromatography, used for determining the size distribution of water soluble organic polymers, was used to separate and purify the clusters. Clusters of different sizes eluted from the column at different times (larger clusters eluted at shorter times) and their absorption and PL spectra were recorded. Since this study was the first report on PL from metal nanoparticles, precautions were taken by the authors to confirm that the observed emission is indeed PL from Au clusters. It was concluded that the peak in the PL spectra obtained at ~ 440 nm is indeed that due to small Au clusters because (i) clusters of different sizes showed different PL intensities although the concentration of the reagents was the same and therefore, that of the by-products are the same, (ii) water containing the precursor ionic chemicals did not exhibit any photoluminescence and (iii) small Au clusters synthesized by the inverse micellar method in organic solvents too exhibited PL.

Wilcoxon et al. [6] observed that the 15 nm clusters elute from the column after time $t = 8.9$ min, whereas clusters of 5 nm dimension elute at $t = 13.2$ min. A highly intense PL signal at 440 nm (excitation wavelength 230 nm) is obtained during the passage of the 5 nm fraction through the column whereas no PL is observed from the fraction eluting at 8.9 min. ie. the 15 nm clusters. But this fraction exhibited an absorption peak at 520 nm. The quantum yield from the 5 nm clusters had a very modest value of $\sim 10^{-4} - 10^{-5}$, yet 10^5 more than that reported from bulk surfaces. Further, the 15 nm Au clusters were etched using KCN. After etching for ~ 30 min, the PL spectra and absorption spectra of the fractions eluting at different periods of time were studied. It was observed that there was no absorption peak of the 15 nm clusters. At the same time PL peaks at 440 nm were observed from fractions eluting at $t = 12.5$ and 13.8 min. This suggests that only clusters of certain specific size among the etched clusters exhibit photoluminescence. Because the PL peaks are shown only from clusters eluting at $t \sim 13$ min., the corresponding size of 5 nm seems to be favorable for PL emission. Interestingly, the absorption spectra of these small luminescent clusters obtained by etching the 15 nm clusters invariably showed additional features in the UV region, not seen for the larger clusters. It was therefore concluded that the smaller clusters have surface characteristics which makes them conducive for emitting PL. That only small sized clusters would luminesce was further confirmed from PL spectra of samples prepared in inverse micelles. However, the PL spectra of small clusters synthesized in tetrahydrofuran (THF) exhibited additional features in the range ~ 600 nm to ~ 750 nm not observed for clusters synthesized in water. The ionic nature of the citrate groups protecting the clusters in water and the non-ionic polyether surfactant attached to the clusters in THF is thought to account for the additional features. This was further confirmed by attaching several other surfactants on to the Au core and observing that the PL features changed with the type of surfactant used.

Based on these observations it was concluded that (i) The emission occurring near 440 nm is due to the radiative recombination of Fermi level electrons with sp- or d- band holes (ii) the surface ligands attached to the Au core play a role in determining the non-radiative energy loss paths and therefore the shape and position of the final emitted signal and (iii) an efficient coupling between the incident radiation and the surface plasmon enhances the strength of the emitted radiation.

Varnavski and co-workers [12] reported ultrafast time resolved PL from Au and Ag nanoparticles- polyaminoamine (PAMAM) nanocomposites. The fluorescence efficiency was estimated to be three orders higher than that from bulk metals. The emission maximum was found to be close to the absorption peak at around 550 nm. The formation of elongated non-spherical clusters is reported to be the cause for the high enhancement in efficiency.

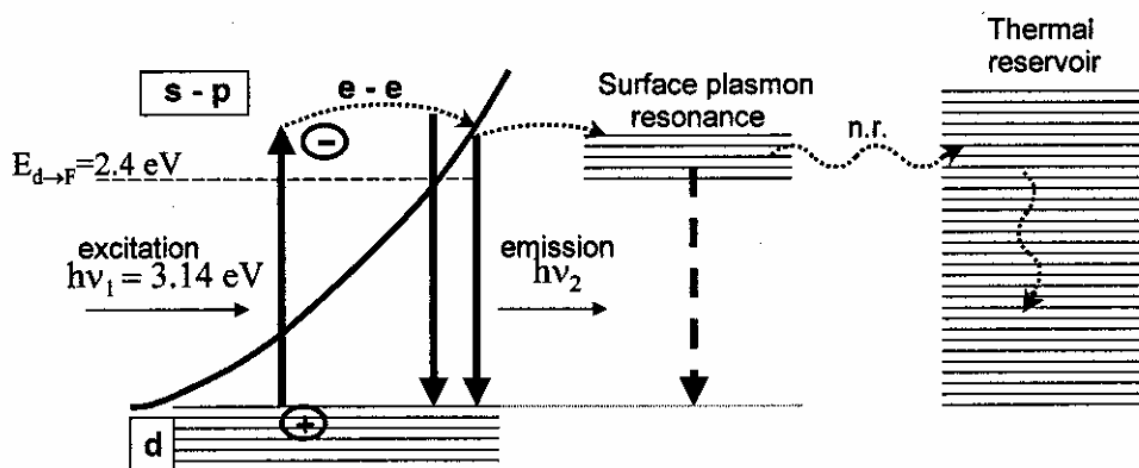


Fig.1. Schematic illustration of the dynamics of PL from Au-dendrimer nanocomposites.

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Fig. 1 is the proposed model for the PL from Au–dendrimer nanocomposites. The authors suggest the electron-phonon coupling and the energy loss by an excited electron via the thermal reservoir of the dendrimer PAMAM attached to the Au surface to be responsible for the non-radiative energy loss. The possibility of the coupling between the emission dipole moment of the surface plasmon

with that of the dendrimer to be one more possible mechanism for the ultrafast luminescence emission observed in dendrimer encapsulated non-spherical Au particles is also suggested.

Zheng and co-workers [13] synthesized poly(amidoamine) dendrimer (PAMAM) encapsulated Au nanodots having high quantum yield and whose absorption and fluorescence could be tuned from the UV to the NIR region by controlling their size, achieved by varying the relative Au:PAMAM concentration. These nanodots are anticipated to have good potential for application in biolabelling as their synthesis requires neither complicated high temperature procedures with toxic precursors nor difficult overcoating with surface passivation. The photophysical properties such as the excitation and emission wavelengths and the quantum yields varied with size of the clusters. Emission wavelengths varied from 385 nm to 879 nm, with the varying excitation wavelengths from 330 nm to 765 nm for the cluster size variation from Au₅ to Au₃₁. The quantum yield decreased from 70% to 10% for the corresponding variation in cluster size [13].

The quantum yields of these clusters, especially the smaller ones, are claimed to be comparable to the best water soluble emitters available. The observed decrease in the quantum yield with increase in cluster size has been attributed to the increased radiation pathways at lower energies. The authors observed that the emission energy scaled inversely with the cluster radius as $N^{-1/3}$, as per the jellium model, which indicates that not only are the electronic structure of these clusters determined by the metal cores but also that they are approximately spherical. Hence, these clusters have been called “multielectron artificial atoms” with the difference that in a true atom the electron density changes with atomic number whereas it does not in these clusters. The discrete excitation and emission spectra exhibited by these artificial atoms is therefore argued to be due to the conduction electrons making intraband transitions between nanocluster electronic states of well defined angular momenta.

Blue emission from second and fourth generation OH terminated PAMAM stabilized Au₈ nanodot had earlier been reported by Zheng and co-workers[14], but no emission was observed from the clusters stabilized with zeroeth generation dendrimer. An increase in the quantum yield in methanol had also been reported. Fluorescence lifetime measurements showed the presence of a

short lifetime (7.5 ns) component, thought to arise from electronic transitions between the d and sp-band and a long lifetime (2.8 μ s) component argued to be a result of triplet-singlet intraband transition. While most researchers have studied the effect of particle size on the optical properties of metal nanoparticles, Longo et al. [15] have studied the effect of alloying on the PL emission from Au-Ag nanoparticles of different compositions, but all with size around 1.5 nm. The nanoparticles were generated by simultaneous thermal decomposition of Au and Ag mercaptides and films of polystyrene-mercaptide blends were obtained by solution casting. Different composition of Au-Ag nanoparticles were obtained by varying the concentration of both Au and Ag mercaptides. The PL emission peak for the maximum excitation wavelength of 280 nm was observed at 633 nm and this was found to red shift linearly as a function of Ag mercaptide concentration. A reduction in the PL emission intensity with increasing Ag mercaptide concentration was also observed. The red shift has been explained using a simple jellium model but assuming that the total number N of atoms inside the basic Au structure is increased due to the inclusion of Ag atoms (δN_{Ag}). Replacing N with $(N_{Au} + \delta N_{Ag})$ to determine the emission energy E_0 in the jellium model $E_0 = E_F + N^{1/3}$ and by considering a first order expansion of the jellium law as a function of a small parameter $\delta N_{Ag}/N_{Au}$ it can be found that the normalized PL energy would decrease by an amount $\delta N_{Ag}/3N_{Au}$ which very well explained the red shift that was observed. The authors caution that the red shift could also be the result of an Au core with Ag atoms at the surface. The reduction in PL intensity has been attributed to either a change in the number of Au clusters in unit volume or the Ag atoms incorporated into the Au structure producing larger electron diffusion lengths across the sample, thereby reducing the possibility for recombination processes.

Farrer et. al. [16] have reported multiphoton -absorption -induced luminescence (MAIL) from Au nanoparticles. In this technique the sample is illuminated with multiphotons from a near IR ultrafast laser that produces sub 100-fs pulses at a repetition rate of 76 MHz centered at 790 nm. The emitted photons are collected by single-photon-counting avalanche photodiodes. The emission from irregular shaped AuNPs of sizes ranging from 125 nm to 2.5 nm exhibits more efficient MAIL compared to

symmetrical smaller NPs. The asymmetries present in the irregularly shaped particles are said to cause large electric field enhancements which results in an increased multiphoton absorption cross section. The observation that the spectrum and emission efficiency is similar in different environments of the AuNPs, have led the authors to suggest that the electronic density of states of the particles have an important role in the emission from these nanostructures.

Huang and Murray [17] reported PL from four water-soluble, monolayer protected clusters (MPC) of Au in which the protecting ligands were the thiolates of tiopronin, 3-mercapto-1-propanesulfonic acid (MPSA), mercaptosuccinic acid (MSA) and glutathione. The attached ligand was found to significantly affect the PL emission peak, as evidenced from table 1 below, which lists the PL profile of a 1 μ M solution of the MPCs excited at 451 nm, in order of decreasing emission intensity.

Table 1. Photoluminescence emission profiles for Au clusters protected with monolayers of different ligands [17].

Ligand	PL profile
Tiopronin	Broad band with maxima at ~ 770 nm
MSA	Broad band peaking at ~ 787 nm
MPSA	Broad band with peak at ~ 802 nm* and a shoulder at ~ 700 nm
Glutathione	*Peak position uncertain due to the limitation of spectrometer at lower energies.

The excitation wavelength was chosen as 451 nm so as to compare the quantum yield with respect to $[\text{Ru}(\text{bpy})_3]_{2+}$ and a 0.03% yield was determined for 1.8 nm core size tiopronin protected clusters. The authors have also observed a linear increase in the fluorescence intensity with concentration for the tiopronin MPC at low concentrations, whereas at a concentration of 1mM there was no fluorescence. The latter effect could be either due to absorption of the exciting beam by the dark MPC solution or

due to self quenching by the tiopronin MPC. The authors propose one of the first, and what they believe to be an over simplified, model for the emission process from Au nanoparticles wherein excitations may probably be from a broad band of $5d^{10}$ states to unoccupied $6sp$ states above the Fermi level as shown in Fig. 2.

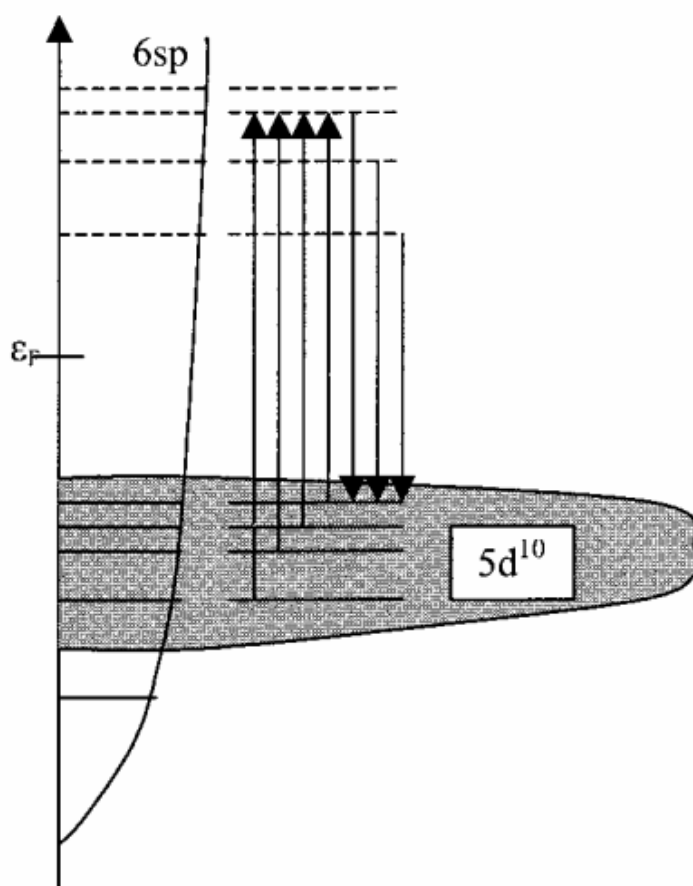


Fig. 2. Schematic model of interband excitation and emission. Reprinted with permission from Ref.17. Copyright ©2001, American Chemical Society.

The ensuing emission is thought most likely to occur from the lower edge of the sp band to the holes below the Fermi level. The observed differences in the position and intensity of the emission peak indicate that the $6sp$ emitter states can be regarded as a kind of surface electronic state of the MPC molecule, which is influenced by the attached thiolate ligand. Their results also suggest a shift in the PL emission to longer wavelengths with increasing core size. Lee and coworkers [18] have synthesized 1.1 nm phenylethylthiolate $Au_{38}(PhC_2S)_{24}$ nanoparticles exhibiting highest occupied

molecular orbital (HOMO)-lowest unoccupied molecular orbitals (LUMO) gap energy~ 1.33 eV as measured by voltammetry and absorbance spectra. When these particles were ligand exchanged to give $\text{Au}_{38}(\text{PEG}_{135}\text{S})_{13}(\text{PhC}_2\text{S})_{11}$, where PEG_{135}S is $-\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, it exhibited a broad photoluminescence emission band. The intensity of the emission spectra varied considerably with excitation wavelength, with indications that the short wavelength emissions were more favoured with higher energy excitations. While the 1.38 eV emission favours the argument that it could arise due to HOMO-LUMO transitions of electrons, the 1.2 eV emission is thought to arise due to sub-bandgap transitions.

A similar result has also been observed by Link et al. [19] in a Au_{28} gold core protected by a monolayer of 16 tripeptide glutathione units. Absorbance studies indicated a HOMO-LUMO gap at 1.3 eV and PL emission spectra was obtained as a broad band with clear indications of the presence of two spectrally overlapping emission bands with maxima at ~ 1.5 eV and ~ 1.15 eV, implying radiative transitions from two different electronic states. Since no dependence of the luminescence intensities on the excitation power is observed, it could be concluded that the excitations involve one photon processes. Additionally, since neither emission occurred at 1.3 eV it was surmised that the emissions do not originate from radiative transitions across the HOMO-LUMO gap. Several possible mechanisms have been suggested for these observations. Firstly, if the Au_{28} compound is considered a cluster, then the visible luminescence could arise due to the radiative recombination of electrons excited to sp- band with a hole in the d-band in addition to an initial relaxation of the electron. The IR emission could be the relaxed radiative recombination of an excited electron between the HOMO-LUMO gap (Fig. 3a).

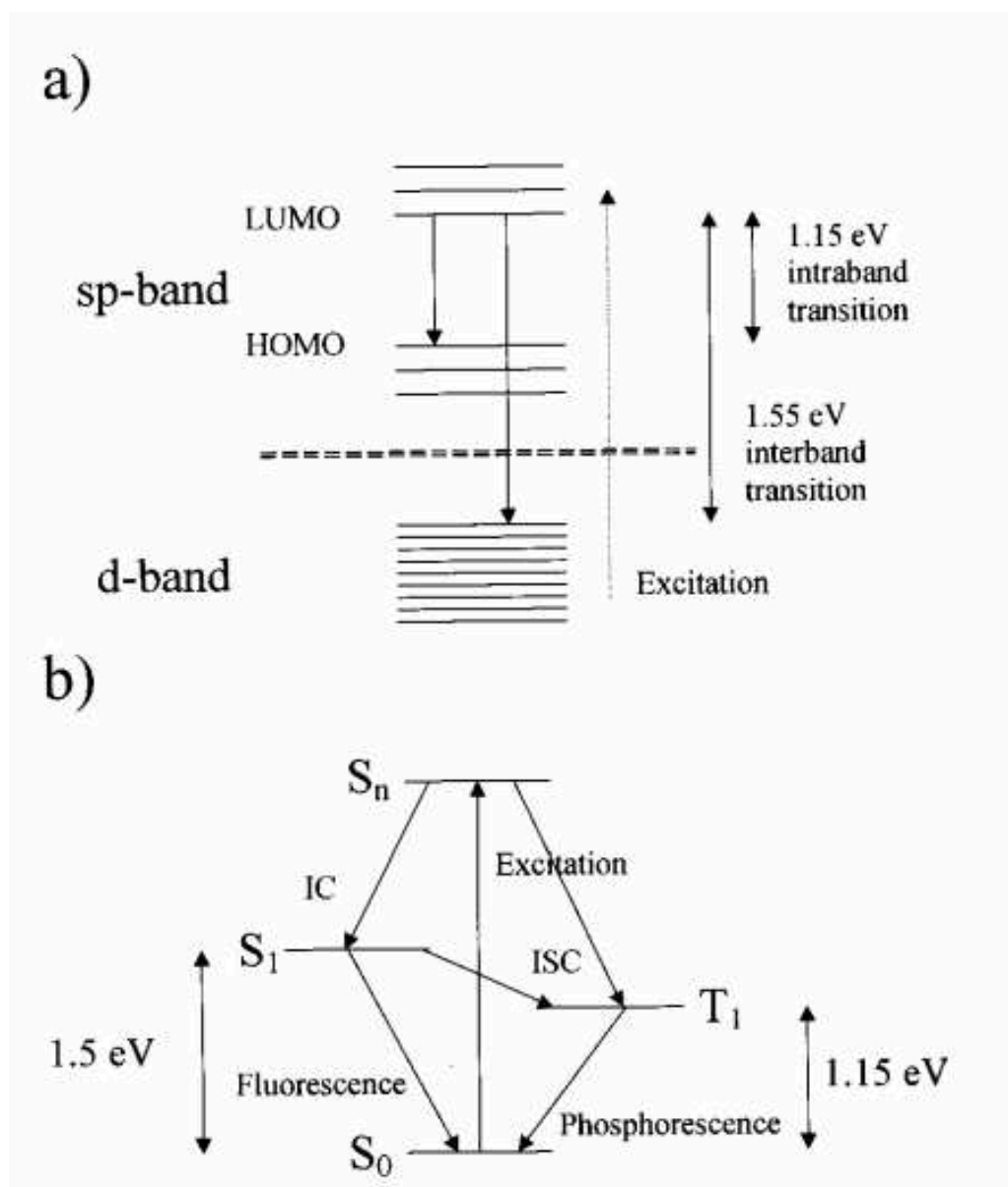


Fig. 3. Schematic (a) Solid state model and (b) Molecular model for the origin of the two luminescence band. Reprinted with permission from Ref.19. Copyright © 2002, American Chemical Society.

From a different point of view, the two luminescence band has been explained based on a molecular model wherein the Au_{28} is considered to be a large molecule. Accordingly, photoexcitation would excite electrons to higher excited states. De-excitation from the higher excited electronic state to a lower energy state in the molecule can take place by two non-radiative processes- internal conversion (IC) and intersystem crossing (ISC), the difference being that in IC the molecular spin state remains the same whereas it changes in ISC. Accordingly, following internal conversion or

intersystem crossing relaxation, they relax to the lowest excited singlet state or triplet state respectively. A singlet state is one in which all of the electrons in the molecule have their spins paired. Triplet states are those in which one set of electron spin have become unpaired. Triplet states and singlet states differ significantly in their properties due to inherent energy differences. A molecule may be considered to undergo internal conversion to the lowest vibrational level of its lowest excited singlet state in a time that is short, relative to photon emission, regardless of the singlet state to which it was excited initially. If a molecule is placed in a rigid medium where collisional processes are minimized, a radiative transition between the lowest triplet state and the ground state is observed. This emission is called phosphorescence. The singlet state being at a comparatively higher energy than the triplet state, radiative relaxation from the singlet state to the ground state can account for the high energy emission and that from the triplet state to the ground state would result in the low energy emission (Fig. 3b). The possibility that the low energy emission could also originate as a result of ligand to metal charge transfer is also briefly discussed.

Wang et al. [20] have shown that MPCs with different core sizes and attached with different ligands all emit over a broad range of energies extending from ~ 700 nm to ~ 1.3 μ m depending on the ligand attached. The emission intensities depend on the core metal as well as the polar nature of the attached ligands with more polar ligands emitting with higher intensity. Absorption studies gave values of optical “band gap” that increased with decreasing size of the Au clusters but no such size dependence was observed for the luminescence emission energy. These make the authors propose that localized core surface states may probably play a role in the emission from the Au nanoparticles. The surmise that the ligands attached to the Au core affects the luminescence from these particles was studied in more detail by Wang et al. [21]. In this, luminescence from clusters of Au with 38 and 140 atoms were recorded with a wide range of ligands with the specific aim to elucidate the effect of the polar nature of the ligand. The experiments were carried out with ligand place exchange reactions which were tracked with ^1H NMR. Ligand exchange was carried out on phenylethanethiolate stabilized Au_{38} clusters and alkanethiolate stabilized Au_{140} clusters. Many important observations

could be made and conclusions arrived at from the detailed studies. It was shown clearly that irrespective of the number of atoms in the cluster, the intensity of luminescence emission increased linearly with the number of exchanged ligands when more polar ligands than the original were incorporated on to the cluster surface. Fig. 4 shows unambiguously this result for the Au_{38} cluster and confirms the initial findings that more polar ligands do indeed enhance the luminescence intensity.

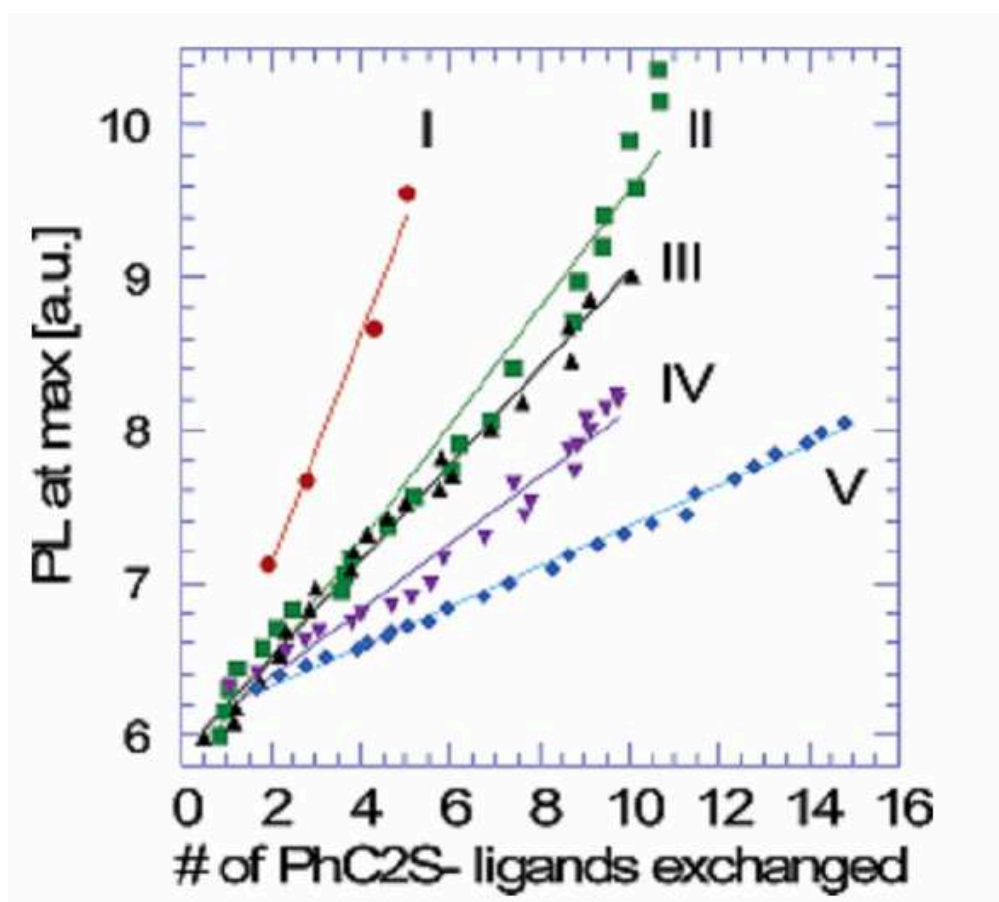


Fig.4: Plot of luminescence intensities versus number of exchanged ligands for (I) 4-nitrothiophenol (95%) (II) 4-chlorothiophenol (98%) (III) 4-bromothiophenol (95%) (IV) *p*-toluenethiol (98%) and (V) 4-methoxybenzenethiol (98%). Reprinted with permission from Ref.21. Copyright © 2006,

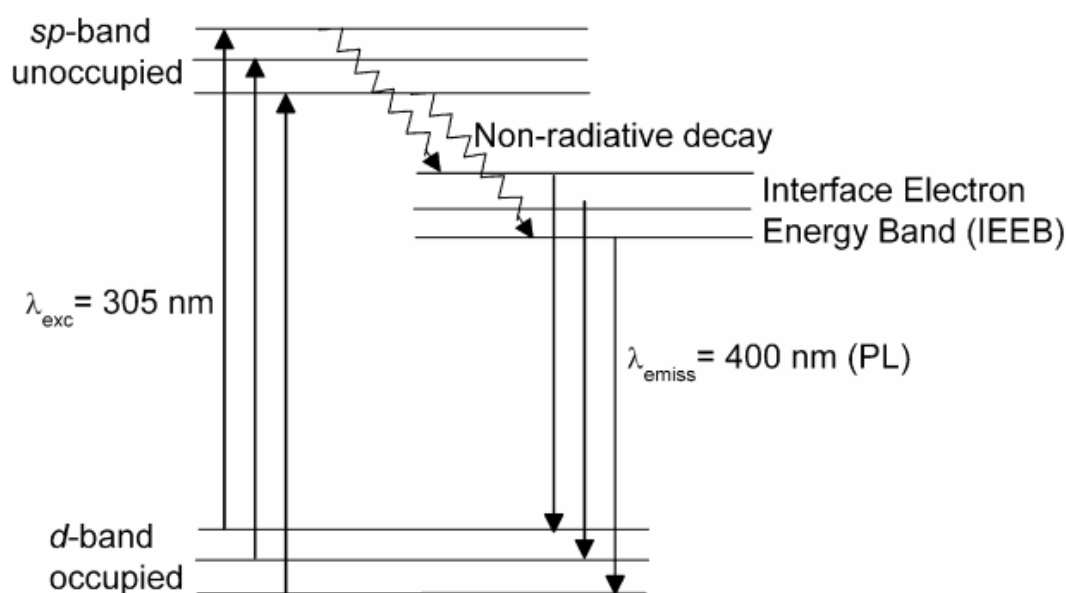
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Fig. 4 also illustrates that as the electron withdrawing capacity increases from thiol V to I so does the emission intensity per exchanged ligand. Increased luminescence was also observed when polar functionalities were placed nearer to the Au-S interface and also by directly removing the electrons from the Au surface by electrolysis. All these results strongly points to a close link between the Au-S bond polarization and the luminescence intensity. Au nanoparticles of size ~ 2.5 nm luminescing at about 810 nm was synthesized [22] by reducing HAuCl_4 in the presence of glutathione (GSH) at 90°C . The simple synthesis method with the natural peptide GSH used as both reductant and stabilizer, together with the strong emission, long PL lifetime, large Stoke's shift, stability towards chemical oxidation and photobleaching makes these nanoparticles to be well suited for *in vitro and in vivo* NIR imaging.

Lin and Chen [23] assign a different reason for the UV emission they observed from Au nanoparticles of size 18 nm and 13 nm. Their observation that the PL excitation (PLE) maximum occurs at approximately 255 nm which is about half the SPR peak position of ~ 526 nm make them conclude that intense PL emission occurring at an excitation wavelength of ~ 250 nm should be due to second harmonic surface plasmon resonance. The observed blue shift in the PLE for smaller Au NPs are said to provide confirmatory evidence for their argument. NIR luminescence from small dodecanethiolate stabilized AuNPs of size 1.1 nm and 1.7 nm was reported by Bigioni et al. [24]. Since an electronic energy gap of 0.9 eV and 0.5 eV respectively was observed in the absorption spectra of these particles the authors expected and did find a broad luminescence emission in the NIR region of the electromagnetic spectrum. Since the excitation wavelength used was 1064 nm the authors conclude that the luminescence emission is not associated with the ligand shell since the electronic transition in alkanethiols is in the deep ultraviolet region. Metal-ligand charge transfer or vice-versa is also ruled out due to the inaccessibility of the states in the ligand molecule. Since the emission range is of low energy, 6sp-5d transition is also ruled out. Similarly a radiative transition across the HOMO-LUMO gap again cannot explain the broad emission observed. It is therefore

concluded by the authors that the photoluminescence could be due to intraband gold sp to sp-like transition.

PL from thiosalicylic acid stabilized AuNPs of average size 5, 8 and 11 nm were studied by Pattabi and Pattabi [25]. When colloidal solutions of the samples in water were excited at 300 nm, emission maximum was observed at ~ 400 nm, irrespective of sample size. The size independence of the PL emission peak is propounded to arise due to non-radiative decay of excited electrons from 6sp-band to interface electron energy levels or bands (IEEB) that could be created due to charge transfer from the ligand to the metal core followed by radiative recombination of electrons from these levels with the hole in the d- band. The position of the interface electron energy levels depend only on the ligand and the metal and therefore, can be expected to be unaffected by the particle size. The above argument can explain the independence of the PL emission peak position with size of the particle. The schematic diagram of the proposed mechanism for the observed photoluminescence is shown in Fig. 5. The role of IEEB in the PL emission is further strengthened by the observations that AuNPs stabilized with three aromatic thiols having the general formula $\text{HS-C}_6\text{H}_4\text{-X}$, where (i) X=OH is 4-hydroxythiophenol (4-HTP), (ii) X= NH_2 is 4- aminothiophenol (4-ATP) and (iii) X=COOH , viz. 2- carboxythiophenol (2-CTP), showed different emission characteristics [26].



d-electrons excited to unoccupied states in *sp*- band by 305 nm excitation. Non-radiative exchange of energy with states in IEEB and subsequent recombination with holes in *d*- band with emission at ~400 nm.

Fig. 5. Schematic diagram of the mechanism of photoluminescence involving interface electron energy bands (IEEB). Reprinted with permission from Ref.25. Copyright © 2009, Elsevier B.V.

Fluorescent Au and Ag nanoclusters in bovine serum albumin (BSA) was demonstrated by Guével et al. [27]. The smaller Au₈-BSA clusters prepared at pH 8 exhibited a maximum emission at 450 nm whereas the Au₂₅-BSA prepared at pH 11 was red emitting. Their studies highlighted the nature of the reducing agent and pH on the oxidation state and therefore the stability of the clusters in the protein. Liu et al. [28] also found a correlation between the solution pH and fluorescence emission from DNA template Au nanoparticles with weakly acidic conditions favouring the formation of small fluorescent Au particles. Because these nanoclusters are stable in biological conditions, it is anticipated that they would prove useful for biological applications in the future.

Recently, from time resolved-PL measurements, Shu et al. [29] demonstrated that the capping molecule plays a vital role in determining the optical behavior of nanocrystals. Their study, on dodecanethiol (DDT) and dihydrolipoic acid (DHLLA) stabilized Au nanocrystals of size ~ 1.9 nm, showed that the PL profile for the both the systems exhibited a peak at ~ 1.95 eV but that for the latter, it appeared as a broad band centered at ~ 1.95 eV. The PL decay profile of both the compounds was recorded and it was revealed that the profile from DDT Au nanocrystals involve only a fast decay component whereas that from DHLLA Au nanocrystals involve both a fast and a slow component. The presence of the slow component suggests carrier localization. The presence of localized carriers implies lesser mobility and therefore, a prolonged decay time. This result, though not directly related to PL emission does support the various observations that metal-ligand bonding does depend on the ligand involved.

Lin et al. [30] further investigated Au nanoclusters (AuNCs) stabilized with DDT and DHLLA. They performed experiments determining the change in the PL emission spectra at different excitation energy E_{ex} and observed that the emission spectra exhibited different characteristics at different energy ranges of the excitation which is termed as “site selective excitation”. In the emission energy range of 1.55 eV to 1.6 eV, the PL emission spectra remains the same, exhibiting a peak at ~ 1.35 eV. The emission peak blue shifted from ~ 1.35 eV to ~ 1.4 eV when the excitation energy is scanned from 1.7 eV to 2.1 eV. This was also accompanied by a broadening of the PL spectra. No change in the emission was observed when the excitation was again scanned from 2.1 eV to 3.1 eV. From time resolved PL measurements it was concluded that the PL lifetime decreases with increasing emission energy, which again signifies carrier localization in this energy range.

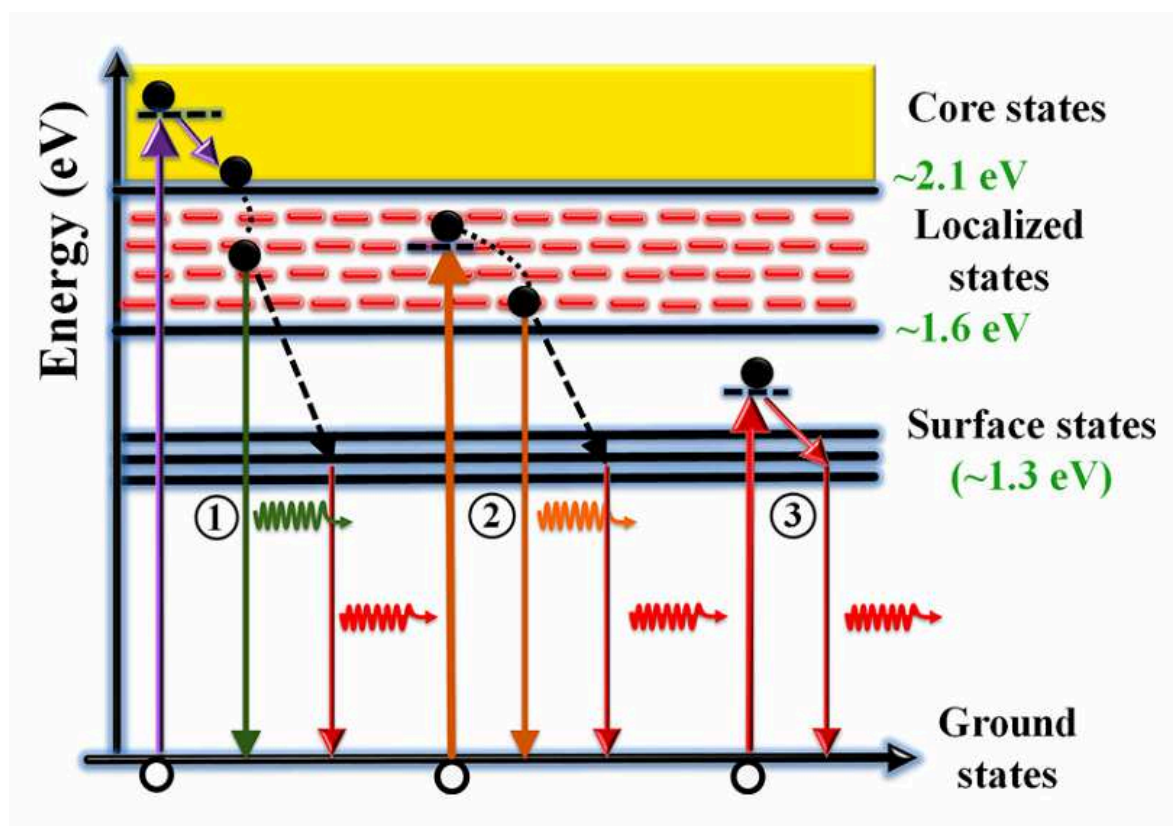


Fig. 6. A schematic description of the excitation, relaxation, and luminescence processes in AuNCs under different excitation energy. Reprinted with permission from Ref. 30. Copyright 2012, AIP Publishing LLC.

The schematic shown in Fig. 6 has been proposed by Lin et al. [30] to explain the PL behavior at different excitation energies. When excited at energies in the range 1.7 to 2.1 eV, the electrons transit to the localized states. The lesser mobility of these electrons results in a slow relaxation and therefore shifts in the PL emission energy. Dissociation of glutathione-gold (I) polymers in water yielded small luminescent AuNPs and XPS studies on them indicate that the Au(I) oxidation state in the AuNPs is responsible for the observed emission [31]. Emission from Au colloids with diameter 50 nm, spin coated on to glass substrates was reported by Geddes et al. [32]. When excited at 532 nm, the emission intensity gradually increased up to 5 minutes after which it remained a constant. But no change in the PL line shape was observed with constant illumination. BSA coated monodispersed Au nanoparticles, 5.1 nm in diameter, was reported to fluoresce at 404 nm when excited at 320 nm [33].

The quantum yield was observed to be around eight orders of magnitude higher than that from Au films. The PL intensity was found to be pH and solvent dependent. PL intensity was maximum for pH of 11 and 12, decreased sharply below this value and showed an increase again at 8. The intensity decreased again for lower values of pH. The PL intensity was almost the same when the nanoparticles were dispersed in water, methanol and ethanol but there was a sharp increase in the emission intensity in acetonitrile. It was also observed that in acetonitrile, there was a shift in the maximum excitation wavelength from 320 to 308 nm and emission maximum from 404 to 413 nm, compared to the other dispersing media studied. Philip reported PL from Au nanoparticles of different sizes prepared by different methods [34]. While the 3 and 4 nm sized particles obtained by borohydride reduction in the presence of polyethylene glycol (PEG) and the 9 nm particles synthesized by citrate reduction exhibited PL emission maxima at 408 nm, the 6 nm tannic acid/citrate reduced particles luminesced at 456 nm. The emission intensity was observed to increase upon addition of KCl upto an optimum value after which it decreased. The initial increase has been attributed to the electrostatic stabilization of the Au nanoparticles by Cl^- and the decrease to the aggregation of the particles. Although a size dependent shift in the PL is observed it could also be attributed to the different synthesis method / stabilizers used.

Luminescence from nanorods of Au has been reported [35-38]. Highly enhanced two photon luminescence with a broad emission in the 400-650 nm region was observed from Au nanorods excited at 830 nm [35]. From the overlap of the PL excitation spectrum and the longitudinal plasmon band in the 700-900 nm region it has been concluded that the local field enhancement from the plasmon resonance has a role in dictating the intensity of the emission. Very large enhancement in fluorescence quantum yield from Au nanorods, compared to that from Au metal, was reported by Mohammed et al. [36]. The emission maximum was found to red shift from 548 nm to 588 nm as the aspect ratio of the rods change from 2 to 5.4 for rods having more or less the same width of ~ 20 nm. Although the longitudinal plasmon resonance peak also red shifts with increasing aspect ratio, the fact that the resonance peak occur at much higher wavelengths (~ 630 nm for rods with aspect ratio

2) suggests that the emission is not associated with surface plasmon radiative relaxation. The local field theory developed by Boyd et. al. [10] was applied to explain the data. Using this it was shown that the excitation at 480 nm caused both the excitation of surface plasmon oscillation and the d-electrons. The emission is a result of slow relaxation of the plasmon oscillation followed by radiative recombination of the electrons in the sp band with holes in the d- band. The same theory also supported the argument that the high intensity was due to large enhancement of the exciting field and the emitted field through the excitation of the surface plasmon resonance which is made possible by the rod shape.

From the applications point of view, nanoparticles embedded in solid matrices have the advantage that they are mechanically stable. In addition, such matrices allow for flexible control of the optical properties of the particles by proper choice of the embedding material. Photoluminescence have been reported from Au nanoparticles embedded in several solid matrices [39-42]. PL spectra of AuNPs sandwiched between oxide layers of SiO₂, ZnO and TiO₂ were studied by Liao et. al. [39]. It was observed that the PL emission intensity is appreciable only in the composite multilayers in which the Au particles have sizes greater than 20 nm. The PL peak position was always found to be red shifted with respect to the SPR peaks for all samples except the Au:TiO₂ composite. The PL and SPR from the Au:ZnO multilayers were studied for different thickness of the Au layer. The AuNPs formed after thermal annealing were of different sizes. The PL peak position was always found to lie on the longer wavelength side with respect to the SPR peak for the Au:ZnO films with different Au particle sizes. However, the separation between the SPR and PL peak positions was found to increase for larger values of SPR peak position. The PL emission energy from the composite multilayers seem to be influenced by the surface plasmons, but a definite correlation between the SPR and PL emission peak energies, among the different composites studied, is lacking.

PL from AuNPs embedded in germane-silicate glass matrix [40] was observed to exhibit a broadband visible emission at ~ 833 nm as well as a narrowband emission at 1536 nm when excited at 488 nm from an Argon-ion laser. The broadband emission in the visible region has been attributed to interband transitions and the emission centered at 1536 nm to a relaxed radiative recombination across the HOMO-LUMO gap. Eichelbaum et al. [41] observed multiphoton induced white luminescence from Au nanoparticles generated inside thin glassy silicate-titanate films. From the slope of the logarithmic plot of the integrated emission intensity versus the integrated laser intensity it was deduced that at high gold concentration the excitation is a three photon process. The observed PL is again attributed to a radiative recombination of electrons excited to the 6 sp band of Au with the hole in the d band.

Silica beads labeled with luminescent tiopronin protected Au nanoparticles (stabilized with succinimidyl ester terminated ligands) and with size 1.6 nm were shown to have potential to be developed into molecule imaging agents because of their good photostability and bright signals [42]. The fluorescence images were obtained with scanning confocal microscopes. The labeling of the silica beads with the Au nanoparticles was achieved by covalent bond formed between the 3-aminopropyltrimethoxysilane on the silica bead surface and the succinimidylated Au. The emission images of the AuNPs were enhanced upon conjugation with silica beads and more bright images were obtained when the AuNP/silica bead ratio increased. The better photostability of the AuNP labeled beads (compared to quantum dots) together with their enhanced emission suggest a possibility of them being used as fluorescent probes in molecular imaging.

From Ag Nanoparticles. Zheng and Dickson [43] reported one of the first observation of fluorescence from Ag nanoclusters created inside poly(amidoamine) fourth and second generation-OH dendrimer “cages”. The fluorescence from these dendrimer encapsulated, water soluble Ag nanoclusters was observed by irradiating it with blue light from a band-pass filtered mercury lamp through standard epifluorescence microscope. The photoactivation resulted in the formation of Ag_2 - Ag_8 nanodots which displayed multicoloured fluorescence throughout the visible region. The size as

well as the emission intensity remained stable after photoactivation, thus the “cage effect” of the dendrimers also protects the nanodots from quenchers in solution. Ag_n clusters with $n < 8$ only exhibited emission thereby proving the necessity of the dendrimer to produce fluorescent clusters. The work thus demonstrated the feasibility of synthesizing stable, highly fluorescent clusters by simple methods without resorting to expensive laser sources.

Huang and Murray [17] had observed emission appearing as a broad band centered at ~ 770 nm from tiopronin coated Au nanoparticles. The same researchers observed size independent luminescence emission at 500 nm from tiopronin coated Ag nanoparticles [44]. Their work was also an elegant demonstration of the PL emission from tiopronin coated Ag shifting gradually to that of Au when Ag was replaced with Au by reacting the Ag monolayer protected cluster with a thiolate complex of Au. When Ag was thus exchanged with Au, the surface plasmon resonance peak of Ag at 380 nm diminished in intensity. As expected, no Au peak was observed due to their size being less than 2 nm. As for the PL spectra, the emission peak of Ag at 500 nm diminished with increasing Au atoms, accompanied by the growth of an emission peak at 700 nm corresponding to that of Au. A conclusion drawn from their study is that the emission is controlled by surface atoms rather than the core atoms. The Ag NP emission has been attributed to interband recombination of d band holes with sp band electrons, further intensified due to a strong coupling with SPR excitation. Gao et al. [45] studied the optical properties of Ag nanoparticles stabilized with [poly(styrene)]-dibenzo-18-crown-6-[poly(styrene)] and observed a blue shift in the PL emission from 486 nm to 442 nm with increase in the photoexcitation energy. Since, the excitation wavelength producing the emission at 442 nm was 343 nm, they have associated this to a metal-ligand charge transfer.

Jiang et al. [46] observed fluorescence at 465 nm for excitation at 290 nm from Ag nanoparticles synthesized by microwave irradiation. The intensity of the emission depends on the concentration of the surfactant used, the fluorescence being quenched for higher concentrations. Alqudami and Annapurni [47] synthesized Ag nanoparticles dispersed in water by bringing a 0.2 mm thick Ag wire into contact with a silver plate while a potential difference of 30 V was maintained between the wire

and the plate. When these nanoparticles were excited at 390 nm, two fluorescence emission peaks were obtained, one at 450 nm and another at 490 nm. The intensity as well as the peak position was found to depend on the medium in which the nanoparticles were dispersed and the stabilizer used. When bovine serum albumin was attached to the particle surface only the 490 nm peak blue shifted by about 20 nm, but in cyclohexane both the peaks were observed to blue shift by ~ 30 nm. The appearance of two emission signals is accounted for by the argument that the large interface area presented by small metal particles in solution causes chemical modification of the surface due to the decreased density of states and increased concentration of electrons. This leads to the formation of interface electron energy bands (IEEB) characteristic of the core material. Electrons photoexcited into the lowest unoccupied energy levels of the IEEB may undergo non-radiative decay into two different lower energy levels. A radiative transition from these two levels is proposed to be the reason for the two emission peaks observed. In an earlier work, fluorescence occurring as a broad peak extending from 500 to 600 nm was observed for excitation at 390 nm from Ag nanoparticles synthesized by the same electro-exploding wire technique [48] which has been assigned to emission from various small sized clusters in the solution. The gemini surfactant 2-hydroxy-1, 3-bis(octadecyldimethylammonium) propane dibromide stabilized Ag nanoparticles [49] exhibited luminescence at 448 nm when excited at 309 nm. This has been attributed to metal- ligand charge transfer absorption.

PL emission wavelength shifting linearly to higher wavelengths with increase in the excitation wavelength was observed by Basak and co-workers [50]. This shift in the emission peak was observed only when the excitation wavelength was above 370 nm and when the excitation wavelength was increased from 380 nm to 500 nm, the emission peak red shifted from ~ 590 nm to ~ 750 nm. Since the size of the particles was ~ 8 nm, it is argued that the observed PL is not due to quantum confinement effects. At the same time, an enhancement in the peak intensity up to an excitation wavelength of 410 nm which lies in the region of the SPR peak of Ag is also observed.

Based on these two observations, a significant role of the surface plasmon resonance on PL emission is inferred.

Solid phase synthesis of Ag nanoparticles by thermal reduction of silver ions in glycine matrix yielded nanoparticles of different sizes ranging from 2 to 30 nm which could be separated by centrifugation [51]. Luminescence could be observed at the single particle level. The absorption spectra of red emitting 18 nm Ag particles were broader than those from similar sized non-luminescent particles synthesized by solution phase method, indicating the presence of additional optical transitions other than plasmons. TEM and XPS studies showed that whereas the non-luminescent particles had a single crystalline or twined structure made up of ~ 8 nm sized domains, the luminescent particles were polycrystalline with domains sized about 1- 2 nm. It is suggested that the scaling down of the domains towards the electron Fermi wavelength is responsible for the appearance of discrete energy states that give rise to optical transitions. This would also lead to the appearance of emission at different wavelengths depending on the domain size.

Luminescence at 380 and 510 nm was observed from PVA stabilized Ag nanoparticles when excited at 325 nm [52]. The peak intensity was enhanced with increase in the particle size. While the peak in the UV range is thought to be due to radiative recombination of Fermi level electrons and sp- or d- band holes, the probable origin of the 510 nm peak has been reasoned either be due to the formation of irregular shaped and sized clusters during their deposition on glass slides or due to coupling of the surface plasmon with the Fermi level electrons. The luminescence at two wavelengths, 330 nm and 520 nm, from Ag sol, observed by Zhang et al. [53] and its shift with changes in the particle size has been interpreted as arising due to the formation of hybrid surface energy states due to the mixing, splitting and shifting of the primary plasmon energies.

Maretti et al. [8] synthesized Ag nanoparticles having size ~ 3.4 nm by reducing silver trifluoroacetate in cyclohexylamine with ketyl radicals. The ketyl radicals were photogenerated by irradiating I-2959 with UV light from four lamps. Luminescence was observed at ~ 530 nm when the particles were dispersed in toluene which red shifted to 580 nm in tetrahydrofuron (THF).

Absorbance peak from the fluorescent Ag nanoparticles was close to 450 nm which is close to that reported for Ag dimers. The fluorescence decay could be fitted to a monoexponential function with a lifetime of 2.6 ± 0.1 ns. The emission from Ag₂, Ag₃ and Ag₄ clusters have relatively long lifetimes and the emission and absorption are found to have a mirror-image relationship. The reported lifetime of Ag₂ clusters in Ar matrices is 4.6 ns [54]. These factors support the claim that the emission observed is likely to be from the Ag₂ clusters supported on the nanoparticle surface. The Ag nanoparticles generated by the electro-exploding wire technique resulted in the formation of Ag nanoparticles in the size range 8-20 nm [55]. In water as the dispersing medium, fluorescence emission was observed at 300 nm for excitation wavelengths ranging from 215-235 nm. A decrease in the fluorescence intensity with increasing excitation wavelengths was also observed.

Application

Several researchers have succeeded in synthesizing luminescent particles and demonstrated their applications in various fields. The GSH stabilized nanoparticle's capacity to sense Cu²⁺ ions was demonstrated [22] by observing the PL quenching in the presence of these ions and has been attributed to the formation GSH-Cu²⁺ complex which induces aggregation of the particles making them less luminescent. The applicability of the Au nanorods synthesized by Wang et al. [35] as two photon luminescence imaging agents was demonstrated *in vivo* by imaging the flow of single gold nanorods through the blood vessels in mouse ear. Au₁₅ clusters protected with glutathione and further stabilized in cyclodextrin cavities were incorporated into chitosan films to obtain free standing films of Au₁₅ clusters [56]. The luminescence from these films were quenched on exposure to Cu²⁺ ions thus making them useful as a metal ion sensor. Liu et. al. have synthesized NIR emitting Au nanoclusters capable of detecting Cu²⁺ ions at concentrations as low 0.3 nM [57]. The emission at ~ 657 nm from very small lysozyme stabilized Au nanoclusters of diameter ~ 1 nm, was shown to be effectively quenched by Hg²⁺, demonstrating their applicability for the detection of Hg²⁺

ions with a detection limit of 10 nM [58]. Comparatively large sized, fluorescent (>16 nm) AuNPs, synthesized by citrate reduction technique were investigated for their viability for the imaging of cervical cancer HeLa cells [59]. The particles all fluoresced at 610 nm when excited at 514.5 nm and the emission peak was invariant with size. AuNPs of size 38 nm were bio-conjugated and were then targeted to the cancer cells. The cancer cells could be imaged by recording the fluorescence from the AuNPs. Au₈ clusters encapsulated with fourth generation polyamidoamine dendrimers with amine terminated groups was also found suitable for intra-cellular imaging of cancer cells by monitoring their fluorescence emission [60]. Glutathione stabilized Au nanoparticles, 2 nm in size, showed extremely high renal clearance while at the same time exhibiting good stability in the blood stream. They appear to be promising candidates for biological imaging [61]. The feasibility of detecting calf thymus-DNA (*ct*-DNA) by spectrofluorometric method was demonstrated by Liu et al. [62] using AgNPs synthesized by an aqueous gas phased reaction of AgNO₃ and ammonia gas. The fluorescence from these particles quenched upon addition of calf thymus-DNA. Since the fluorescence intensity depended on the *ct*-DNA concentration, these particles are suggested to be useful in their detection.

Conclusion

Numerous studies have been carried out over the past two decades with an aim to elucidate the mechanism for photoluminescence from metal nanoparticles, especially those of the noble metals. The results have been at variance, in terms of the size effect on the luminescence, the ligand effect on this phenomena and the effect of the core metal as well as the luminescence efficiency. A few theories have been proposed to explain PL based on either an interband sp to d transitions of the photoexcited electrons or on the formation of an interface electron energy band and the transitions through these IEEB. The concept of metal-ligand charge transfer and the formation of IEEB is contained in many of the results including the first report of Wilcoxon et al.[6], much earlier to the explicit mention of that. It is possible that these mechanisms operate independently or even

simultaneously depending on various factors like size, ligands, dispersion medium, particle surface topography and so on. A consensus has still not been arrived at as to the mechanisms involved in PL from metal nanoparticles. Therefore, still more concerted effort, with good control over the growth process, is required to achieve a fundamental understanding of photoluminescence from metal nanoparticles. Only then, can it be hoped that PL from metal particles can find *in vivo* applications.

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