

## 1.1 Brief historical background on nanoscience and nanomaterials:

Nanoscience is the branch of science which deals with study of phenomenon and manipulation of materials at atomic/molecular scales, where properties fluctuate significantly from those at a larger scale. In the International System of Units, the prefix "*nano*" means one-billionth of a meter or  $10^{-9}$ , therefore one can practically visualize that a human hair is approximately 80,000–100,000 nanometers wide or a strand of human DNA is 2.5 nanometers in diameter [El-Sayed, 2004, Daniel *et al.*, 2004]. Studies on atoms and molecules are the conventional field of chemistry and physics from very of the beginnings. Scientific community generally attributes the first acknowledgement to brilliant Nobel Laureate physicist Richard Feynman for the importance of nanoscience. At the annual meeting of the American Physical Society on 29 December 1959 lecture, Richard Feynman addressed the audience with his historical and legendary lecture under the title “There's Plenty of Room at the Bottom” in which he first proposed that, properties of materials and devices at the nanometer range would be future opportunities. The term reached greater public awareness in 1986 with the publication of “Engines of Creation: The Coming Era of Nanotechnology” by Eric Drexler. Invitation to enter a new field of science which is so called nanoscience/nanotechnology [Feynman, 1960].

The classical example for this nano-effect could be best illustrated by observing the change in the color of gold. In its bulk structure gold exhibits a bright yellow color, but it appears pink-red in color when colloidal nanosized particles are prepared in aqueous solution. Similarly silver in bulk form looks whitish grey but when it is synthesized in colloidal nanosized form, exhibits yellowish grey [Link *et al.*, 1999]. A well-known example is the Lycurgus Cup that was fabricated in 4<sup>th</sup> century A.D. It displays red in transmitted light and greyish green in reflected light as shown in figure 1.1. The detailed study of the glass's composition was carried out in the late 20<sup>th</sup> century, revealed that remarkable color is due to the

presence of colloidal gold (Au) and silver (Ag) (with the average diameter of 40 nm) in the glass consisted of a gold (30%) and silver (70%) spherical particles [Faraday, 1857].

Noble metal nanomaterials are referred to as the materials produced from metallic ions precursor which have at least one dimensional and in range of nanometer scale (1–100 nm) [Burda, *et al.*, 2005]. Noble metal nanoparticles, especially gold and silver nanoparticles, exhibit intense scattering and absorption of light in the visible spectrum which is the source of the attractive colors in stained glass (Lycurgus Cup) kept in British Museum as shown in figure 1.1.



**Figure 1.1:** The Lycurgus Cup, appearing green in (A) reflected light and red in (B) transmitted light, – [El-Sayed, 2004].

### **1.2 Quantum confinement, size factor and origin of intense color of noble metallic nanomaterials:**

In this section, some basic fundamental concepts of nanomaterials science including basic of quantum mechanical aspects, unique features of nanomaterials, generalized mechanism of formation of metallic nanomaterials and its widespread applications are described. We have focused closely on the implications of those concepts to nanomaterials science for applications purposes which are frontier of nanoscience and technology. It is fundamentally important to revisit these topics

which help to understand the depth of subject. To understand why materials in nano size would be interesting from a quantum mechanical point of view, considering that if a electron is excited from the valence band to the conduction band in a materials then vacancy created in the valence band is a “hole”, which can be thought of as a particle with its own charge and effective mass. The electron and hole are considered “bound” to each other via columbic attraction and this quasi particle is then known as an “exciton”. The electronic excitation consists of loosely bounded electron hole pair and usually delocalized over a length much larger than the lattice constant. Such a distance is called as Bohr radius which is in the order of few nanometers [El-Sayed, 2004]. Exciton can be considered hydrogen like system and Bohr approximation of an atom can be used to calculate the spatial separation of the electron–hole pair of the exciton by following equation:

$$r = \epsilon h^2 / \pi m_r e^2$$

where  $r$  is the radius of the sphere (defined by the 3-D separation of the electron–hole pair),  $\epsilon$  is the dielectric constant of the semiconductor,  $m_r$  is the reduced mass of the electron–hole pair,  $h$  is Planck’s constant, and  $e$  is the charge on the electron. Physical dimensions of a these nanomaterials can be smaller than the exciton diameter, so that semiconductors is a good example of the “particle-in-a-box” calculations of undergraduate physical chemistry which is mathematically represented as the following given equation.

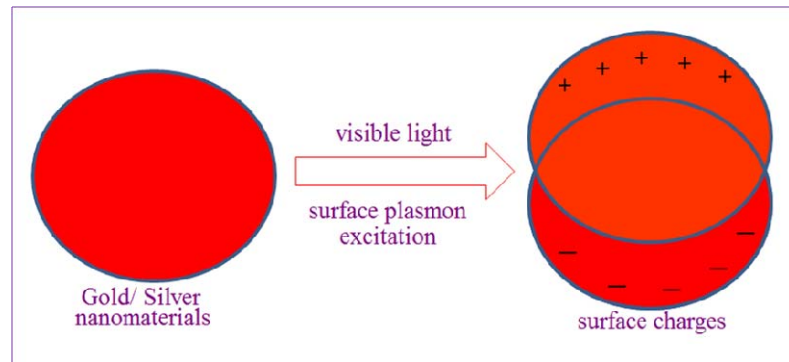
$$E = n^2 h^2 / 8mL^2$$

Where  $E$  is the energies of the particle in the box,  $n$  is particular quantum number,  $h$  is the plank constant,  $m$  is the mass of the particle and  $L$  is the length of the box. In those calculations, the energies of the particle in the box depend on the size of the box. This is how, energy band gap becomes *size-dependent*. As the particle size decreases below the Bohr radius of the semiconductor material, the electron becomes more confined in the particle and it leads to an increase in the band gap

energy. Furthermore the valence and conduction bands break into *quantized energy* levels. When the size of the semiconductor material becomes comparable or smaller than Bohr radius so the space decreases in which the charge carriers move and this is called *quantum confinement* in semiconductor nanomaterials [Link *et al.*, 2000; Horvath, 2009].

Gustav Mie was first to explain the observed intense color of dispersed colloidal gold particles in 1908. A mathematically rigorous description of the color of gold particles was demonstrated in terms of classical electromagnetic theory. James Maxwell Garnett and Gustav Mie independently described the interaction of metallic nanoparticles with light and rationalized the observed colors of the nanomaterials using classical electromagnetism hypothesis. This purely classical description of light absorption and scattering by metal nanoparticles still dominates today and is a source of advancement in scientific findings in current times. Gustav Mie calculated the absorbance of colloidal gold particles as a function of the particle size using classical electromagnetic theory with the bulk optical properties of metallic gold. The main assumption of Mie's theory of the optical absorption by small particles is that, particle and its surrounding medium are each homogeneous and describable by their bulk optical dielectric functions. Since nanoparticles have a high surface area to volume ratio so resonance frequency is highly sensitive to the shape/size of nanoparticles and dielectric nature of local environments [Mie, 1908].

In semiconductor nanomaterials, mechanism of optical absorption is different as compared to bulk scale. Nanostructured noble metals such as gold and silver nanoparticles exhibit distinct optical properties from the bulk metals, typically exhibiting strong absorption bands in the visible region [Eustis *et al.*, 2006]. When the nanoparticles interact with visible light, electron clouds of the nanoparticles interact with it and hence the *new electronic state* is generated, thus electron distribution is *perturbed* [Link *et al.*, 1999]. This electron oscillation creates *surface polarization* and causes the formation of a dipole as shown in figure 1.2.



**Figure 1.2:** Schematic illustration of surface plasmon resonance (SPR) by interaction of light with surface dipole of nanomaterials [El-Sayed, 2004].

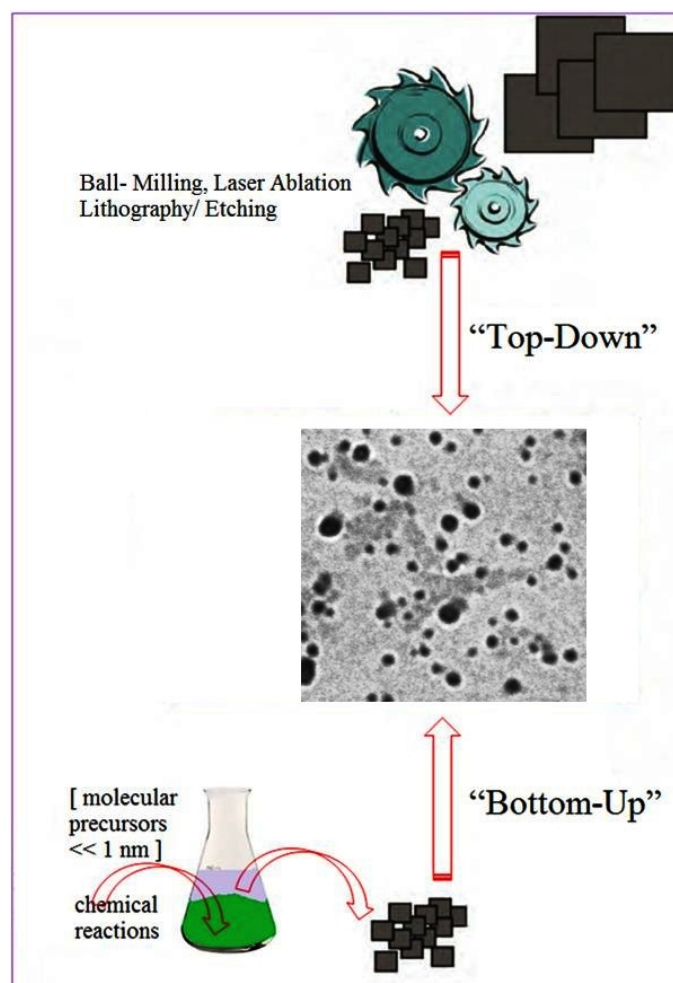
The dipole of the particle is what ultimately causes, appearance of a resonance at a definite wavelength. When light interact with nanomaterials that are much smaller than the incident wavelength, free electrons in the metal move to the surface and oscillate in resonance with photon's frequency. Hence, light scattering due to collective oscillation of the conduction electrons induced by the incident radiation in colloidal metal nanomaterials is known as *surface plasmon resonance* (SPR) [Mie, 1908; El-Sayed, 2004]. When the particles are not spherical but elongated, two dipole oscillation modes are possible: first one is along the transverse and another one is along the longitudinal axis. Therefore, when two different dipoles are formed, two plasmon bands are expected in the absorption spectrum. Metal nanoparticles of gold, silver and copper are well known to possess such plasmon resonances in the visible region, but for nanoparticles of most other metals, plasmon bands occur in the UV region and hence cannot be easily figure out. Without going into the lengthy mathematical details, Mie equation as given below explain the strong absorption of gold and silver nanomaterials in visible region of electromagnetic spectrum [Mie, 1908; Mulvaney, 1996].

$$E(\lambda) = \frac{[\epsilon_i] \quad 24 \pi N_A a^3 \epsilon_m^{3/2}}{[(\epsilon_r + \chi \epsilon_m) + \epsilon_i^2] \quad \lambda \ln 10}$$

Where  $E(\lambda)$  is the extinction (extinction = scattering + absorption),  $N_A$  is the number of nanoparticles,  $a$  is the radius of the nanosphere,  $\epsilon_m$  is the dielectric constant of the medium surrounding the nanosphere,  $\lambda$  is the wavelength of the absorbing radiation,  $\epsilon_i$  and  $\epsilon_r$  correspond to the imaginary and real portions of the spherical metal's dielectric function and  $\chi$  is a shape factor dependent upon the aspect ratio of the nanoparticles (equal to 2 for a sphere). It is evident that SPR spectrum of a single metallic nanosphere suspended in a dielectric medium relies on the nanoparticle size and the dielectric constant of the surrounding environment. Moreover, the extinction spectrum also depends upon the shape  $\chi$  factor which becomes an important parameter in the case of non-spherical nanoparticles.

### 1.3 Synthetic methodology for nanostructure generation:

There are two major schematic approaches for synthesis of nanomaterials i.e. top-down and bottom-up as illustrated in figure 1.3. In its earlier days, majority of nanodevices utilized a top-down approach as their primary method of fabrication. One of the best known types for the top-down approach is a lithographic etching of the silicon semiconductor. Richard Feynman suggested the bottom up approach of manipulating things at the atomic level will be the major interest of the future in the advancement of nanoscience/technology [Feynman, 1960]. The first one is the breakdown (top-down) method by which an external force is applied to a matter that leads to its break-up into smaller particles. The second is the building-up (bottom-up) method that produces nanostructures starting from atoms of gas or liquid phases based on atomic transformations or molecular scale synthesis. Bottom-up approaches is a versatile method to make nanomaterials and interconnects from scientific advancements to the technological applications.



**Figure 1.3:** Top-down Vs Bottom-up approach.

#### **1.4 Glimpse over the vital synthesis on gold and silver nanomaterials (Important literatures review):**

In this section, we have discussed a glimpse over the important breakthrough (conventional and unconventional methods) in synthesis of gold (Au) silver (Ag) nanomaterials and their advantages/drawbacks. There are thousands of review literatures, featured articles and books published on nanoscience and nanotechnology exclusively on noble metallic nanomaterials synthesis and their probable practical applications during last three decades. It is very difficult to cover entire spectrum of nanomaterials synthesis however, unique as well as

improved methods are continuously being studied and developed which has been discussed in proceeding section.

### 1.4.1 Faraday methods:

The very first scientific report on gold was recognized in research community by Michael Faraday named “The Bakerian Lecture: Experimental relations of Gold (and other metals) to Light”. In 1857, Michael Faraday prepared deep red colloidal gold by reducing aqueous solution of  $\text{AuCl}_4^-$  with phosphorus in  $\text{CS}_2$  as shown in figure 1.4. He called the gold nanoparticles as “divided state of gold” [Faraday, 1857].



**Figure 1.4:** Faraday is credited as the discoverer of metallic colloid, he prepared gold colloids that were purple red in color by the reduction of gold salts with phosphorous, courtesy– Royal Institution of Great Britain available from: <http://www.rigb.org/rimain/heritage/faradaypage.jsp>.

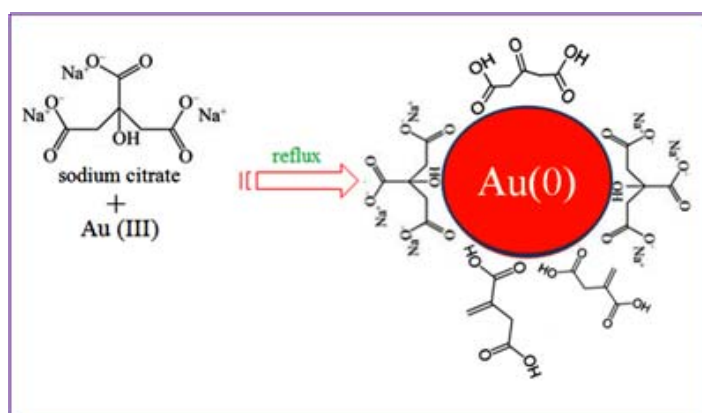
He was the first to attribute the red color to finely divided gold particles. He investigated the optical properties of thin films prepared from dried colloidal solutions and observed reversible color changes of the films upon mechanical compression (blue–purple→green). Faraday found that colloids did not settle readily over time, unfortunately, the microscopic tools available to Faraday did not allow him to see the gold particles and consequently he could not answer the



questions about their behavior. In 1908, Mie developed a solution to Maxwell's equations that describes the scattering and absorption spectra of spherical particles of arbitrary size. That Historical background can now be seen as the foundation of development in modern colloid/nanoscience and opened up a new avenue from both point of views, fundamental academic interest as well as technological applications in a wide range of fields.

## 1.4.2 Turkevich method:

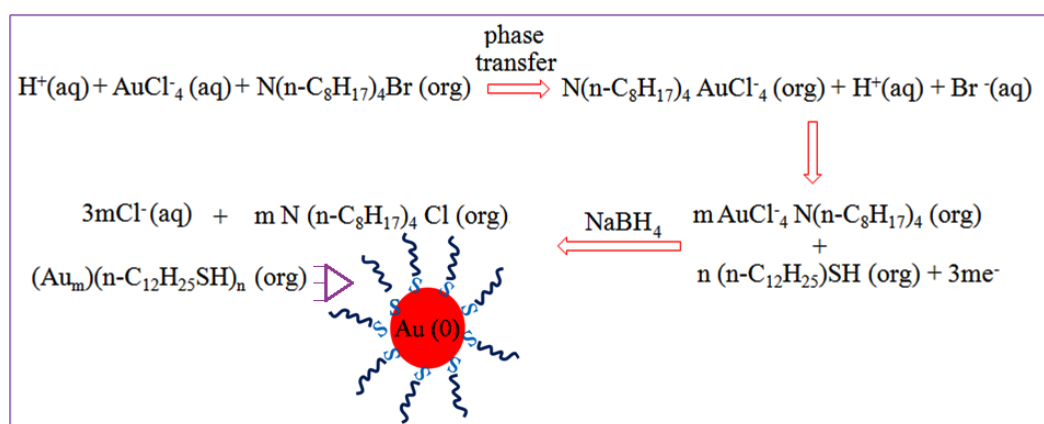
In 1951, Turkevich described a synthesis of hydrophilic gold nanoparticles by the reduction of chloroauric acid with sodium citrate in an aqueous solution on refluxing, as schematics shown in figure 1.5. Moreover, the oxidation products of citrate anions (acetonedicarboxylic and itaconic acids) can adsorb on the nanoparticles surface provide the stabilization [Turkevich *et al.*, 1951]. Despite its considerable drawbacks, citrate method was widely used for the synthesis of silver/gold nanoparticles. A distinguishing feature of the Turkevich method is that citrate ions simultaneously act as a reducing agent and stabilizer. This complicates the selection of their optimal concentration because its variations simultaneously affect the reduction rate, nucleation and growth of nanoparticles. Similar procedure is also applicable to produce other noble metallic (e.g. Ag) nanomaterials as well.



**Figure 1.5:** Formation of gold nanoparticles coated with citrate and its oxidation product by reaction of sodium citrate with chloro auric acid.

### 1.4.3 Brust-Schiffrin method:

The Brust-Schiffrin method for gold nanoparticles synthesis was reported in 1994. This method has a substantial impact because it allowed the facile synthesis of thermally and air-stable gold nanoparticles and controlled size for the first time. It is one of the most remarkable milestones in the development of two-phase water organic synthesis of metallic nanoparticles was achieved by the Brust research group [Brust *et al.*, 1994; Brust *et al.*, 1995]. Still it is the popular method of choice because of its simplicity and rapid preparation but considerable drawback of the Brust and Schiffrin method is the use of a large number of chemicals, particularly the phase transfer agent that contaminates the surface of formed nanocrystal thus preventing their further use in the application purposes. This method was developed based on earlier works: e.g. Faraday's approach of two phase synthesis of gold nanoparticles using an aqueous solution of chloroauric acid and phosphorus dispersed in carbon disulfide and role of long chain thiols in protecting the gold surface through monolayer coverage. The important steps in the reaction are as follows and schematics shown in figure 1.6.



**Figure 1.6:** General scheme for borohydride Brust-Schiffrin method for gold nanomaterials functionalized with thiols. In figure, where  $m$  and  $n$  represent the stoichiometric ratio.

- Transfer of  $\text{AuCl}_4^-$  from aqueous to the organic medium (e.g. toluene) using a phase-transfer reagent (e.g., tetra octyl ammonium bromide).
- Reduction of metal cations to zerovalent form through a reducing agent in aqueous phase (e.g., sodium borohydride).
- Stabilization of growing metal nuclei by the use of a long-chain thiol (e.g., dodecane thiol).

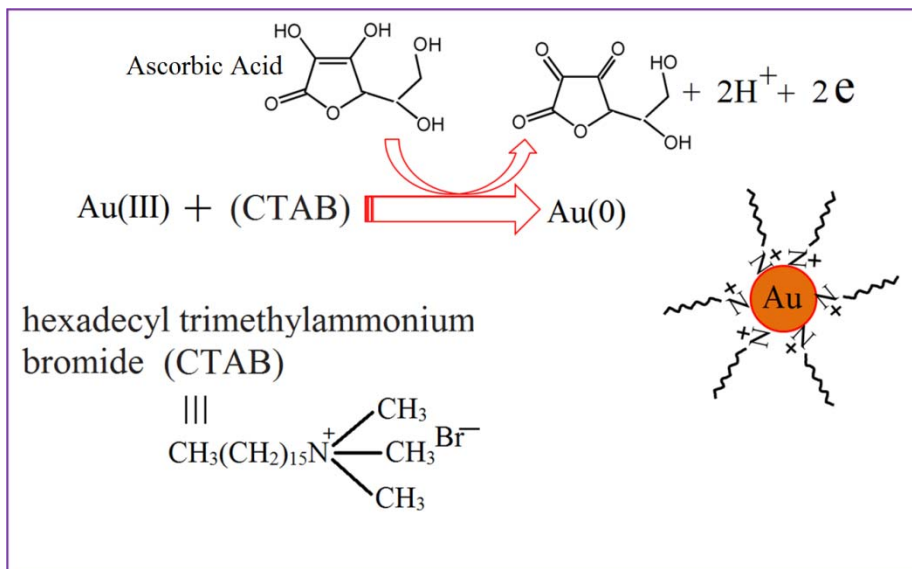
The characterization of gold nanoparticles prepared by Brust- Schiffrin method leads to a few remarkable points as follows:

- ✓ The size of the particle was in the range of 1–3 nm.
- ✓ Gold was present in the zero valent state and thus the gold–thiol bond did not have the characteristics of gold sulfide (no chemical bonding Au–S) which means there was a particular type of interaction had taken place between sulphur and gold surfaces which may be Van der Waals/electrostatic interaction depending upon the implemented procedure.
- ✓ Elemental analysis along with IR confirmed the presence of thiol on the nanomaterials surface.

### 1.4.4 CTAB and ascorbic acid method:

Synthesis of gold nanocrystals can be achieved by using ascorbic acid, hexadecyltrimethylammonium bromide (CTAB) and  $\text{HAuCl}_4$ . Ascorbic acid rapidly reduces the gold salt from its Au (III) to Au (I) state, leading to meta-stable solution at room temperature [Busbee *et al.*, 2003]. CTAB was used as a structural stabilization of surface and the diameters of such made gold were typically less than 10 nm. The stability of the nanoparticles produced in CTAB can be explained as follows: CTAB has a positively charged trimethyl ammonium group ( $-\text{N}^+(\text{CH}_3)_3$ ) and a long carbon chain ( $\text{C}_{16}\text{H}_{33}^-$ ) [Kimling *et al.*, 2006]. Generalized reaction scheme as shown in figure 1.7 and this approach of aqueous phase reduction of metal ion salts have been widely adopted for the synthesis of other noble metal nanoparticles as well. This method is also one of most pragmatic and

preferred protocol and key features of this method are mono-dispersity, short-time preparation and high yield, nanocrystal with size and shape tunability.

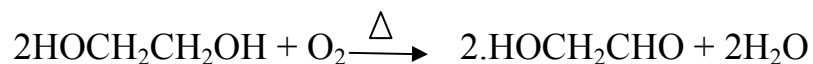


**Figure 1.7:** Ascorbic acid mediated synthesis of gold nanoparticles.

#### 1.4.5 Polyol method of noble metallic nanomaterials:

Polyol synthesis is a popular method of preparing metal nanostructures, but still the mechanism by which metal ions are reduced is poorly understood. Heating ethylene glycol (EG) in air results in the oxidation to glycolaldehyde (GA), a reductant, which is capable of reducing noble metal ions. The dependence of reducing power on temperature for ethylene glycol can be explained by this temperature-dependent oxidation and the factors influencing glycolaldehyde production can have a profound impact on the nucleation and growth kinetics. Metal colloids such as Au, Ag, and Pd could be formed in air-saturated aqueous solutions of poly (ethylene glycol) (PEG). The polyol synthesis provides a simple and versatile approach to metal nanostructures generation [Longenberger *et al.*, 1995; Skrabalak *et al.*, 2008]. These new results provide critical insight into why the polyol synthesis has been so successful in generating metal nanostructures with well defined and controllable shapes. Yet the best possible mechanism was fairly satisfactory to explain the chemistry of reaction. Since heating EG in air may

generate glycolaldehyde, a reductant for many metal ions. NMR, gas chromatography and mass spectrometry spectrophotometric method proved for confirming glycolaldehyde production as intermediate reductant in the reaction and quantified its concentration.

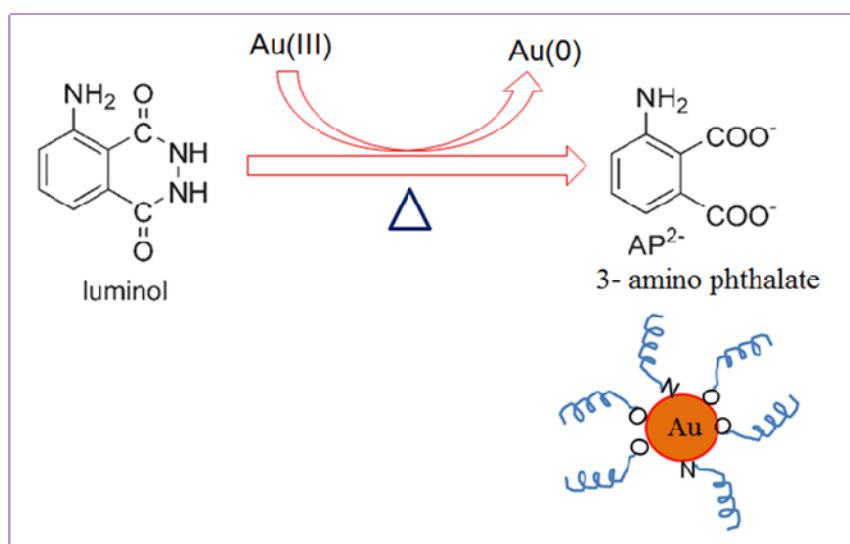


It was suggested that PEG molecules might be coiled to form pseudo-crown ether cavities for the binding and reduction of metal complexes on the oxy-ethylene groups. This provided a simple method for the synthesis of metal nanoparticles [Chen *et al.*, 2002; Sato *et al.*, 1994; Liu *et al.*, 2009; Sun *et al.*, 2002]. PEG simultaneously plays the roles of protective agent and reducing agent. Gold nanocrystals were produced by a modified Polyol process with the presence of surface regulating polymer [Poly (vinyl-pyrrolidone) (PVP)]. Briefly, ethylene glycol solutions of hydrogen tetrachloroaurate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and PVP were injected simultaneously into boiling ethylene glycol. Ethylene glycol served as both solvent as well as reducing agent for the reaction. PVP not only stabilized the particles but also controlled the shape of the particles. The optimum ratio between the PVP and gold precursor is enough to form the gold nanoparticles within few minutes. On the other hand, the disadvantage of this polyol method is the high boiling point which makes the removal of the solvent difficult.

### 1.4.6 Luminol catalyzed reduction method:

Many of nitrogen containing organic molecules like amine compounds, including aliphatic amines, aromatic amines and several amino acids having ability to reduce noble metal precursors to metallic colloids and get stabilized by its oxidation products in both aqueous and organic solutions [Pethkar *et al.*, 2001; Chaki *et al.*, 2002; Kumar *et al.*, 2003; Aslam *et al.*, 2004]. The interaction linking of gold/silver nanomaterials and amine molecules was attributed to the weak covalent interaction between noble metals and nitrogen atoms. Electrostatic interactions also take place between negatively charged metal nanoparticles and positively charged

amines. Luminol is a type of reductive compound with an aromatic amine functional group. It was found by Cui and their group that chloroauric acid ( $\text{HAuCl}_4$ ) can be directly reduced by the luminol in aqueous solution to form gold nanoparticles (AuNPs), at the same time get stabilized by its oxidation product [Cui *et al.*, 2007]. The morphology and surface state of the resulting gold nanoparticles were confirmed by transmission electron microscopy (TEM), UV/visible spectroscopy, X-ray photoelectron spectroscopy (XPS), FTIR spectroscopy.

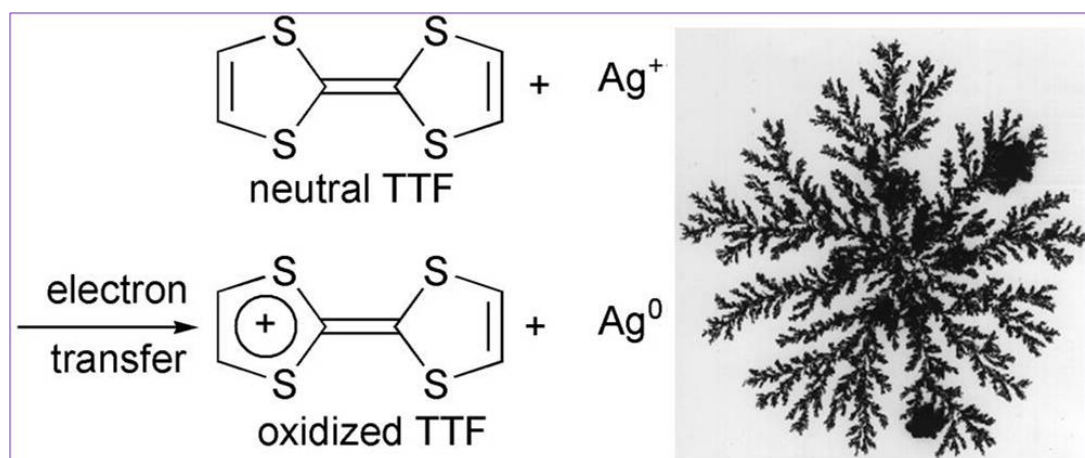


**Figure 1.8:** Proposed reaction scheme illustrating luminol- reduced gold nanoparticles

Luminol and its oxidation product 3- aminophthalate ( $\text{AP}^{2-}$ ) were capped on the surface of gold nanoparticles as stabilizers and coexisted on the surface of gold nanoparticles through the weak covalent interaction between gold and nitrogen atoms in their functional amino groups as shown in figure 1.8. Luminol-reduced gold nanoparticles might be further linked to the electrode by virtue of bridging which have affinity to adhere on electrode surface by linking through nitrogen atom for applications in electrocatalysis/electron transfer studies.

### 1.4.7 Tetrathiafulvalene catalyzed reduction method:

Silver dendritic nanostructures protected by tetrathiafulvalene (TTF) were synthesized via redox electron transfer from tetrathiafulvalene to silver ions in acetonitrile [Wang *et al.*, 2003; Wang *et al.*, 2002]. The metallic silver was stabilized by the resulting oxidized TTF and its radical cations, which had dual purpose as a reducing agent and stabilizer. The reduction of silver ions by electron-rich TTF is schematically illustrated in figure 1.9.



**Figure 1.9:** Reaction scheme for tetrathiafulvalene (TTF) catalyzed formation of silver dendritic nanostructures [Wang *et al.*, 2002].

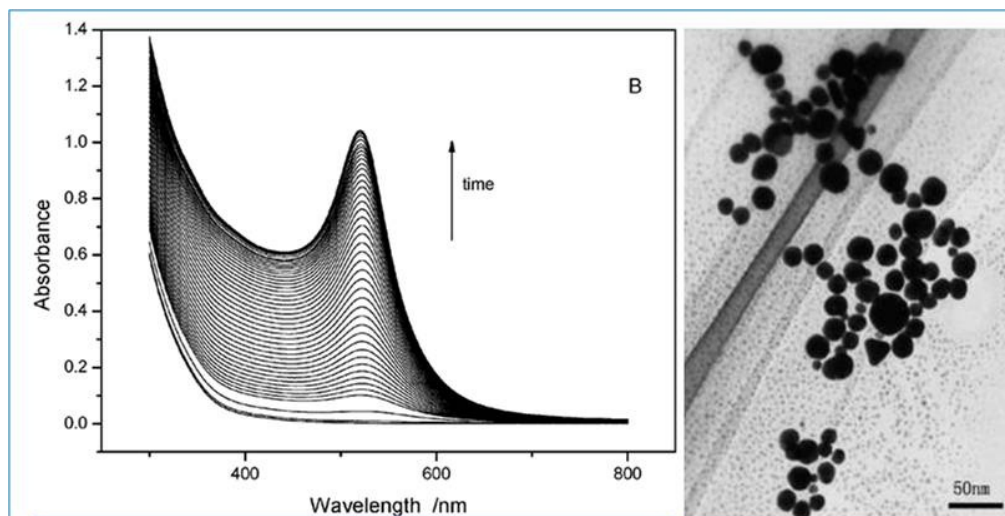
Positively charged TTF radical cations form network with the surface of the silver dendrites and get adsorb via interaction with sulphur atom present in its structure [Mallik *et al.*, 2001]. This research work proposed a new mechanism for dendrite formation & suggested a new perception for preparing a nanosized composite of metal nanostructures and  $\pi$ -electron rich organic molecules.

### 1.4.8 Chitosan reduction method:

HAuCl<sub>4</sub> can be reduced into zerovalent gold nanoparticles by chitosan [Huang *et al.*, 2004]. It was found that, chitosan plays a role as a reducing agent, but the exact mechanism of the reduction is not clear. Glucose is a well known reducing sugar and also in chitosan's chemical structure, it is a polysaccharide, which can hydrolyze in an aqueous acid to give D-glucosamine, a derivative of



glucose. So it was suggested the same mechanism of reduction of metal salts as for glucose. On the other hand,  $-OH$  (hydroxyl) group in molecular chitosan may also act as a reducing functionality in the formation of gold nanoparticles.



**Figure 1.10:** Time-dependent UV-vis absorption spectra of solutions containing  $HAuCl_4$  and medium molecular weight chitosan and corresponding TEM image of the gold nanoparticles [Huang *et al.*, 2004].

TEM images and SAED proved that these particles cannot be the aggregates of small gold particles also it was not observed the formation of chitosan nanoparticles in that synthetic procedure (figure 1.10). Proposed method for the preparation of gold nanoparticles is considered to be a green approach because of the use of naturally occurring polysaccharide chitosan, as both reducing as well as stabilizing agent. Similar method is also widely applicable to the silver nanoparticles synthesis as well.

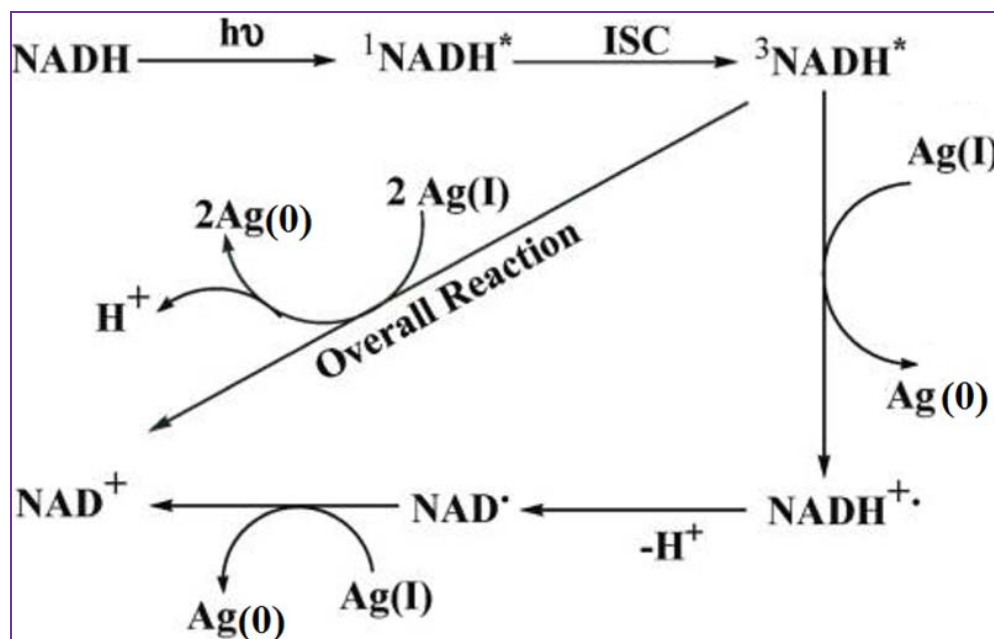


### **1.5 Photochemical mediated synthesis of noble metallic nanomaterials:**

We have come across the conventional synthesis of metallic nanomaterials so far, hereafter we have taken glimpse on some recent literatures in the area of photochemical synthesis of nanomaterials where no external reducing agents & not any additional protecting functionality has been used. Thousand of the improved synthetic method of metallic nanomaterials synthesis is being developed day by day as the research cultivates. However, photochemical approach remains one of the less explored protocols as compared to other “bottom up chemical synthesis” of nanomaterials by using photochemically active molecules and its practical applications. Photochemical assisted synthesis of noble metallic nanostructures is versatile method for generating metal nanostructures which includes both academic as well as technological awareness in recent time.

#### **1.5.1 Photochemical synthesis of silver nanoparticles using enzyme cofactor reduced nicotinamide adenine dinucleotide (NADH):**

Bera and their group described a rapid green photochemical route for the synthesis of polyhedral Ag nanostructures, using the enzyme cofactor reduced nicotinamide adenine dinucleotide (NADH) [Bera *et al.*, 2010]. The synthesis of anisotropic silver nanostructures involves the reduction of  $\text{Ag}^+$  by photo-excited NADH in its triplet state as shown in figure 1.11. The photoexcited enzyme cofactor nicotinamide adenine dinucleotide (NADH) act as an effective reducing agent in its triplet excited state assist in the reduction of Ag (I) ions. The progress of the reaction was monitored by spectral and electron microscopic measurements. Reduction of Ag (I) by NADH does not proceed in darkness and the reaction was very slow in room light indicated that light controls the reduction of Ag (I) and the growth of nanoparticles.



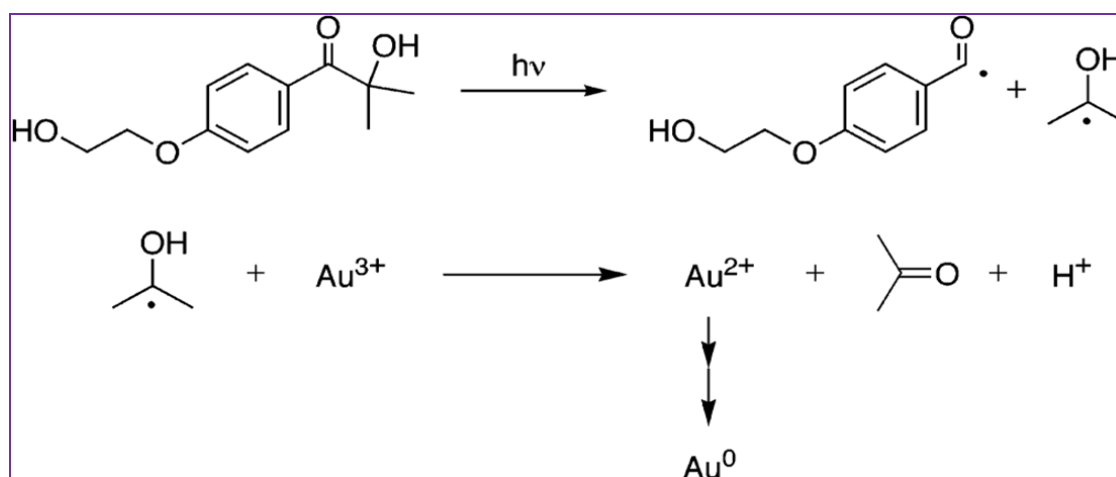
**Figure 1.11:** Proposed scheme illustrating the photochemical reduction of Ag (I) and the growth of polyhedral silver nanostructures [Bera *et al.*, 2010].

The Synthetic methodology does not require any additional seeds, surfactant, or stabilizer/external reducing agent. Even though this synthetic procedure may require few optimizations to produce slightly smaller nanoparticles for applications purpose.

### 1.5.2 Photochemical synthesis of gold nanoparticles by Irgacure-2959:

McGilvray and their group presented a reaction scheme in which gold nanoparticles can be prepared in a few minutes by reduction of  $\text{HAuCl}_4$  by photochemical decomposition of I-2959 (1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-1-propane-1-one), a water-soluble benzoin [McGilvray *et al.*, 2006]. A wide range of particle sizes can be prepared by controlling the intensity of light used. One-pot synthesis can be performed in seconds to minutes, rather than hours under mild conditions using readily available precursors. Synthesis of

aqueous gold nanoparticles was performed using Irgacure-2959. Upon 350 nm excitation, I-2959 yields ketyl radicals via Norrish type-I cleavage these ketyl radicals function as reducing agents that are capable of reducing  $\text{Au}^{3+}$  to  $\text{Au}^0$  and form gold nanoparticles as illustrated in figure 1.12.



**Figure 1.12:** Photochemical scheme illustrating the step wise reduction of Au (III) [McGilvray *et al.*, 2006].

A small excess of I-2959 is required to generate sufficient acetone ketyl radicals, which reduce tetrachloroaurate to form  $\text{Au}^{2+}$  it further disproportionate to  $\text{Au}^{3+}$  and  $\text{Au}^+$ , whereby  $\text{Au}^+$  is then reduced to  $\text{Au}^0$ , leading to nanoparticle formation [Kim *et al.*, 2002; Monti *et al.*, 2004]. Gold nanoparticles have previously been synthesized photochemically using other ketyl radicals as reducing agents, such as benzophenone-15 or benzoin-16 but these have been carried out in polymers, dendrimers or micelles and frequently required working under an inert conditions. This method is based upon simple aqueous photochemistry which is very rapid, requires no protective groups/ stabilizer/ additional reducing agent and is performed under mild conditions.

## 1.6 Diversified applications of noble metallic (gold and silver) nanomaterials:

The development of nanoscience and nanotechnology has inspired the researcher to continuously explore the nanomaterials for constructing an enhanced and cost effective quality product for consumer applications [Maillard *et al.*, 2003; Kapoor *et al.*, 1998]. Here we have taken a sight on such nanomaterials utilized commercial product which achieved trade success, as shown in figure 1.13.



**Figure1.13:** Diversified applications of nanomaterials ranging from consumer applications → healthcare → electronics → commercial power devices products [Sanchez *et al.*, 2011].

Gold/silver nanomaterials are very much attractive noble metallic materials because of their attractive chemical, optical, electronic and biocompatibility properties which make it suitable and promising material for photoelectric devices, health & nutrition sciences, catalysis, bio-imaging, screen printing electronic

sensor and power storage devices [Sanchez *et al.*, 2011; Ghosh *et al.*, 2007; Wang *et al.*, 2013].

### **1.7 Room for research in the area of photochemical synthesis of noble metallic nanomaterials and its practical applications:**

Vital synthetic methodology of noble metallic nanomaterials have been discussed in last section so far, however *photochemical approach* remains one of the fewer explored protocols as compared to other “bottom up chemical synthesis” of nanomaterials where, harsh conventional reducing agent/phase transfer agent/external seeds etc. are used. Utilizing harsh chemical reducing agent ( $\text{NH}_2\text{-NH}_2$ ,  $\text{NaBH}_4$ ), nanomaterials get contaminated with their counter ions e.g.  $\text{BH}_4^-$ , which make difficult to use these nanomaterials as an electrode modifier for electroensing applications. Another problem with these conventional reducing agent is that during the course of reaction,  $\text{P}^{\text{H}}$  of the reaction content changes abruptly, this is also one of the drawbacks of conventional methods.

Photochemical assisted synthesis of noble metallic nanoparticles is versatile method for generating metal nanostructures which includes both scientific as well as technological interests [Mandal *et al.*, 2002; Sun *et al.*, 2004]. Still, there is a scope for the photochemical assisted synthesis of nanomaterials by using photochemical active organic molecules [Clary *et al.*, 2012; McGilvray *et al.*, 2006; Mandal *et al.*, 2002; Korchev *et al.*, 2004; Weaver *et al.* 1996]. Undoubtedly the fundamental science i.e. chemistry, physics, life science etc. collaborate with nanoscience and nanotechnology, serves as a multidisciplinary interface. The development of nanoscience and nanotechnology has inspired the researcher to continuously explore new electro active materials for constructing an enhanced electrochemical platform for sensing & brought the great momentum to applied electrochemical fields [Mallon *et al.*, 2010; Freund *et al.*, 2014]. Present thesis fills this gap in the area of photochemical synthesis of noble metallic nanostructures and its application in electroensing of hazardous analytes. Considerable attention has been drawn during the last two decades to functionalize

the hybrid nanomaterials on electrode surfaces by forming films of few nm to several  $\mu\text{m}$  thicknesses on the polycrystalline electrode surface for electroensing devices applications. Modification of an electrode surface can be achieved by different methods such as chemisorption, covalent binding, electro polymerization, etc. Molecular level modification on electrode surfaces through a self-assembly approach is gaining importance in view of its many functional applications in areas such as molecular electronics, molecular recognition, electron transfer studies and electroanalysis. Thin film (nm/ $\mu\text{m}$ ) of the desired material on the bare electrode surface through the method of self-assembly is called chemically modified electrodes and have a potential application in electroanalytical techniques/electrosensing device [Zhang *et al.*, 2006; Tang *et al.*, 2013; Sagara *et al.*, 1996].

### **1.7.1 Generalized overview of photochemical mediated synthesis of metallic nanomaterials:**

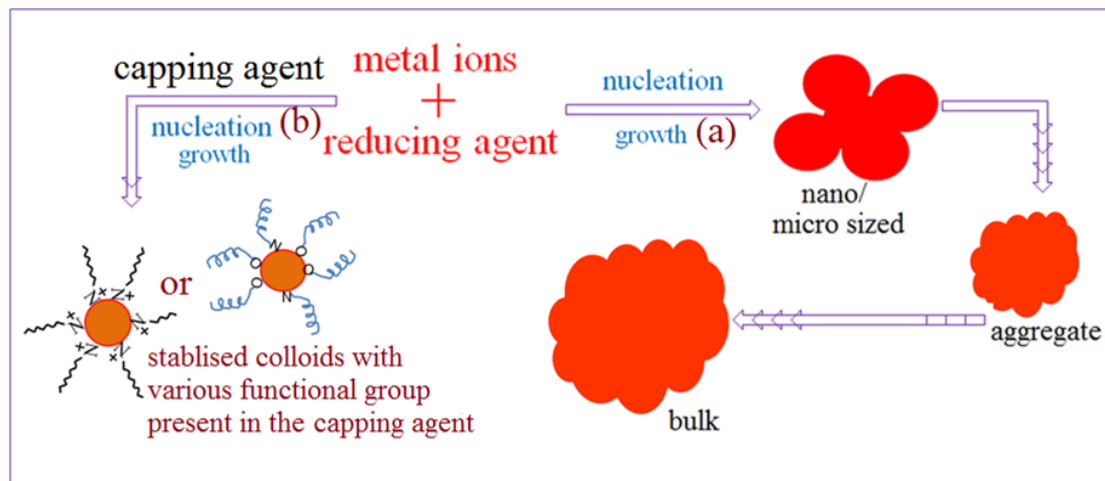
Reduction of  $\text{M}^{\text{n}+}$  (noble metal salt) ions is initiated by the excitation of the photoactive organic molecule with light. It is a particular kind of chemical redox reaction, where oxidation of the photoactive organic molecule produces the photo electron for the reduction of metal ions precursors. In recent years, numerous interesting efforts have been anticipated to generate metal nanostructures by using photoactive molecules organic molecule [Sato *et al.*, 1994; Sato *et al.*, 1999]. The use of thiol/ amine containing organic molecule as a photosensitizer may serve as dual purpose e.g. it can initiate the reduction of metal ions and at the same time it can bind with the metal surface to protect nanomaterials. Specific organic molecule containing functional groups, like  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{NH}_2$ ,  $-\text{COOH}$  etc., can stabilize metal nanoparticles on their surfaces through electrostatic/ covalent/ Van der Waals interaction [Chien *et al.*, 2011; Gachard *et al.*, 1998]. The proposed mechanism suggests a two-step process, first one is nucleation and second one is consecutive growth of the particles. In the first step, metal ions in solution are reduced. The atoms thus formed, agglomerate to form small clusters. Nanoclusters

thus formed act as nucleation centers and catalyze the whole reduction process of the remaining metal ions present in the bulk. Thereby, result is the autocatalytic growth of the nucleating particles [Sun *et al.*, 2002; Sharma *et al.*, 2004; Zhou *et al.*, 1999].

### **1.7.2 Stepwise formation of metallic nanomaterials, generalized mechanism and role of capping agent:**

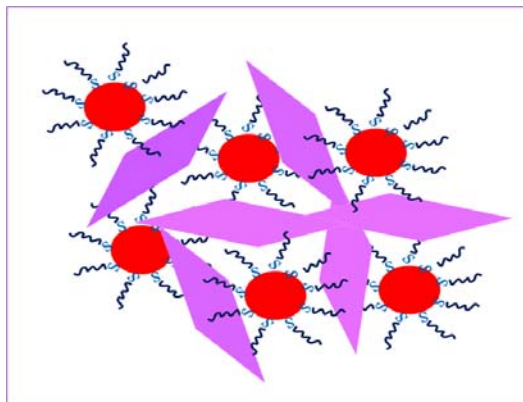
When a solid is suspended in a liquid solvent without causing its precipitation, we refer to such two phase mixture as colloids. Indeed, nanoparticles are true colloids if they remain in the solution and do not precipitate w.r.t. time. This is because nanoparticles are not just very small in size, but they are also highly stabilized by the organic functional molecule on their surfaces. Colloid is a heterogeneous system in which one substance is dispersed (*dispersed phase*) as very fine particles in another substance called *dispersion medium*. Colloidal particles are larger than simple molecules but small enough to remain suspended in *dispersion medium*. They have a range of diameters lies in between 1 and 1000 nm. Organic functional molecule acts as protecting groups that protect particles by sterically hindering their surfaces from each other, thus preventing agglomeration and enhancing their solubility. When the metallic nanoparticles are formed, external stabilizer molecules adsorbed on the nanoparticles surface and stabilize them in nanosized and keep them from further aggregating by reducing their surface energy [Sharma *et al.*, 2004; Kamat *et al.*, 2002; Sun *et al.*, 2004]. Furthermore, surfactants guide the particles growth and used as method of control over particular size and their monodispersity. In fact, if the stabilizer is already present in solution when the reduction is initiated, it prevents the growth of large particles. Initially formed clusters are very small in size and have extremely high surface energy, which drives them to aggregate into larger particles [Xia *et al.*, 2009; Sardar *et al.*, 2009; Eustis *et al.*, 2005]. In many cases, external stabilizer (long chain thiol, amine, charged species) is added into the synthesis system to stabilize metallic nanoparticles and prevent them from further aggregating as shown in figure 1.14.





**Figure 1.14:** Thermodynamically favored bulk agglomerated particle in the absence of any stabilizer (route a). stepwise formation of metallic nanomaterials and at the same time Electrostatic/Van der Waals interaction of metal nano particles with capping agent provide the stabilization of metal nanostructures (route b).

The nanoparticles having large surface energy coalesce to give thermodynamically favored bulk particle. In the absence of any counteractive repulsive forces, the Van der Waals forces between two metal nanoparticles would lead towards agglomeration [Kamat, 2000].



**Figure 1.15:** Steric stabilization of nanostructured metal colloids capped with protecting agent.



Hence for spatial confinement of the particles in nano range it is essential to stabilize the particles. This can be achieved by either electrostatic or steric stabilization by using a capping agent such as polymer, surfactant, solid support or some selective organic molecule having suitable functional groups as shown in figure 1.15.

### **1.8 Chemically modified electrode for electroensing applications:**

Electron transfer between the solid (electrode) and liquid phases (electrolyte) is the fundamental aspect of electrochemistry and is affected directly by substrate adhere on it & its interfacial properties such as conductivity, roughness, cleanliness etc. Therefore, construction of well-defined and highly controllable electrochemical interfaces is significant for both fundamental as well as applied studies in electrochemistry. Polycrystalline bare electrode is coated with particular hybrid electroactive nanomaterials/electrodeposited thin film of nanomaterials/conducting polymer film etc. which exhibits chemical, electrochemical, optical features of the film and these properties may be utilized in application proposes [Chaki *et al.*, 2002]. Chemically modified electrode comprise a relatively recent approach to electrode systems in a wide spectrum of basic electrochemical investigations and the design of electrochemical devices in the applications of chemical sensing, energy conversion, storage, molecular electronics, electrochromic displays, corrosion protection and electro-organic syntheses [Murray *et al.*, 1980; Pumera *et al.*, 2007 ]. Chemically modified electrode has ability to enhance the sensitivity and selectivity of electroanalytical techniques. Monomolecular level modification of electrode surfaces through a self-assembly approach is also gaining importance in view of its many functional applications in area of molecular electronics, molecular recognition, electron transfer studies and electroanalysis etc [Cheng *et al.*, 2002; Tang *et al.*, 2013]. The term ‘Self-assembly’ involves the arrangement of atoms and molecules into an ordered or even aggregate of functional entities towards an energetically stable form. Formation of SAM is essentially an

organization of molecules at the solid (electrode)–liquid (electrolytes) interfaces induced by strong chemisorption between the substrate and the modifier [Ganesh *et al.*, 2006; Ganesh *et al.*, 2008; Raj *et al.*, 2007; Guoa *et al.*, 2007]. One of the important advantages of SAM is that it can be prepared in laboratory using a very simple method. SAMs exhibit a high degree of organization and are spontaneously formed as a consequence of immersing a solid surface into a solution consisting of desired materials. Thiols/amines capped nanomaterials are generally used to modify the electrode surface via attachment or bridging through sulphur/nitrogen atoms [Thomas *et al.*, 2003; Xia *et al.*, 1999].

### **1.8.1 Convenient methods for the chemical modification of electrode and its surface investigation at a glance:**

The chemical film is strongly and ideally, irreversibly adsorbed (chemisorbed) onto the electrode surface and some of the practical and handy methods of electrode modification are discussed below:

#### **Dip-coating-**

- This procedure consists of immersing the thoroughly cleaned bare electrode in a solution of the electro active nanomaterials for a period sufficient for spontaneous film formation to occur by chemical adsorption followed by washing the chemically modified electrode with desired buffer solution.

#### **Solvent evaporation-**

- Fine droplet of a solution of the hybrid electro active nanomaterials is applied to the electrode surface and the solvent is allowed to evaporate slowly. Drop casting is the handy way to fabricate the desired film thickness of nanomaterials on the bare electrode surface.

#### **Spin coating-**

- It is also called spin casting, a droplet of a dilute solution of the desired materials is applied to the surface of a rotating electrode and excess solution is spun off the surface and the remaining nanomaterials film is allowed to

dry. Multiple layers are applied in the same way until the desired thickness is obtained. This procedure typically produces pinhole-free thin films which is long-lasting film.

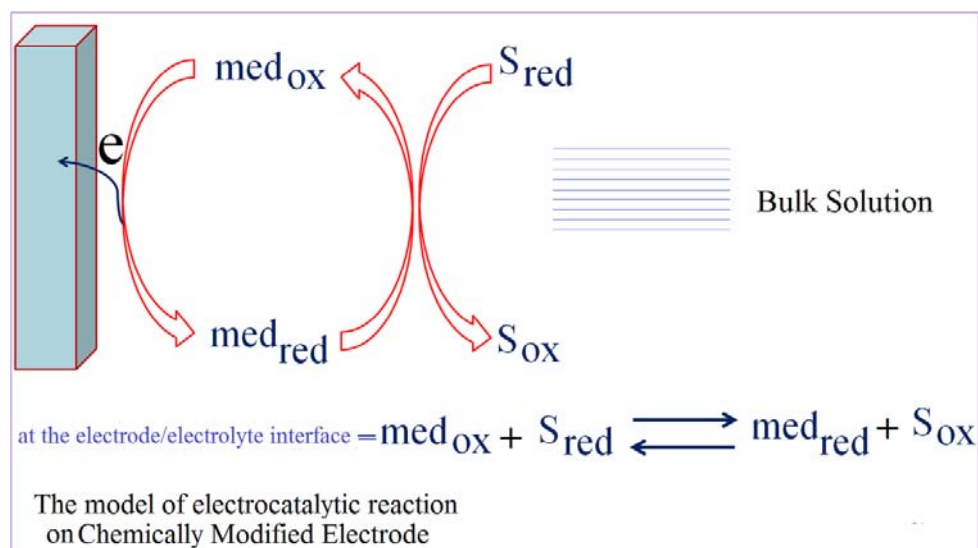
The chemically modified electrode can be characterized by a variety of methods including physical measurements like different voltammetric & impedance measurement, infrared, X-ray photoelectron spectroscopy, field emission scanning electron microscopy etc. and more specifically electrochemical techniques like cyclic voltammetry (CV), impedance spectroscopy are especially useful for checking their surface modification/ electron transfer process [Chaki *et al.*, 2002; Raj *et al.*, 2007].

### **1.8.2 Need of chemical modification of electrode:**

Many analytes which are biologically and environmentally hazardous show no response within a potential window at bare electrodes or direct electrochemical detection usually requires high potential for such compounds. This can produce large background current, resulting in inferior detection limits/sensitivity. Bare electrode suffers electrode fouling problem. It is also of the main disadvantages of using bare electrode in electrosensing purposes, due to the unwanted adsorption of heavy molecular masses species/reaction products during the course of electrochemical reaction. Moreover, coexisting foreign components, which may be present in concentrations much larger than the analytes, may interfere with the determination of trace analytes. Hence complicated sample pre-treatment work up is often employed to eliminate/separate the interfering components.

### **1.8.3 Mechanism of electrocatalysis on chemically modified of electrode:**

An important motivation for modifying the electrode surface is, *electrocatalysis* on the electrode of an analytically desired analyte, being one of the most fascinating areas of research on chemically modified electrodes [Liu *et al.*, 2011; Jena *et al.*, 2006].



**Figure 1.16:** Mechanism of electrocatalysis on chemically modified electrode.

This type of mediated electrocatalysis process with the chemically modified electrode can be represented by the scheme as shown in figure 1.16. The explanations of the receiving electrochemical signal of the analytes with nanomaterials modified electrode are as follows:

- ❖ Nanomaterials consist of thousands of atoms, in principle which can be oxidized/ reduced/ interacts with analytes through various type of interaction like van der waals/electrostatic/hydrogen bonding/difference in the electronegativity etc.
- ❖ Nanomaterials which have large surface to volume ratio which increase the loading of electrochemically detectable species, since every nanomaterials contains thousands of atoms thus are the driving force in nanomaterials-assisted electrocatalysis.
- ❖ Since efficient electron transfer take place when,  
 Potentiostats/ Galvanostat  $\xleftarrow{e^-}$  electrode || nanomaterials || analytes are in electronic communication/ interaction with the electrode surface. Under these conditions, the electrochemical sensor behaves like an ultra microelectrode array thus, quantity of nanomaterials labeled on the electrode surface, which

is again a function of the analytes concentration, can be determined indirectly by monitoring much amplified current produced by the electrochemical faradic reaction process.

### **1.8.4 Benefits of utilizing the nanomaterials modified electrode in electroensing:**

Several instrumental techniques are available ICP-OES or spectrometers e.g. chromatography, potentiometry and fluorometry etc. for the determination of environmentally such hazardous species. However, most of them require colorimetric probe, redox dye indicator etc. and also they are time consuming, costly or require sophisticated instrumentation work up, which prevent them from being used for on-site measurement/ field tests [Cheng *et al.*, 2003; Cheng *et al.*, 2002; Nagaraju *et al.*, 2008]. In earlier time, electrode modified with enzymes and heavy molecular masses conductive polymers are utilized for electroensing of the analytes but the major drawbacks of using such modified electrode suffer several problems as follows:

- Very careful pre-treatment of enzyme, since it very much sensitive to pH, temperature and local environment etc.
- Enzymes having high molecular masses which cause electrode fouling problem/ increase the solution resistance thereby decreasing sensitivity.

Enzyme-based modified electrode is fragile in nature so storage and stability of the electrode is the practical concern but with latest advancement in the hybrid nanomaterials modified electrode, such problems have been minimized upto better extent. Specially, electrochemical methods have attracted great interest because of their simplicity, affordable price, rapidness and high sensitivity in the detection of analytes. Benefits of utilizing the nanomaterials for electrochemical detection of analytes are as follows:

- ❖ Nanoparticles are very different from their bulk counterparts since the catalytic activity originates from their quantum-scale dimensions.

Micro/nano electrode ensembles show several advantages over conventional polycrystalline electrodes viz. increased mass transport, decreased influence of solution resistance, less electrode fouling problem and better detection limits due to high ratio between faradic and non faradic current.

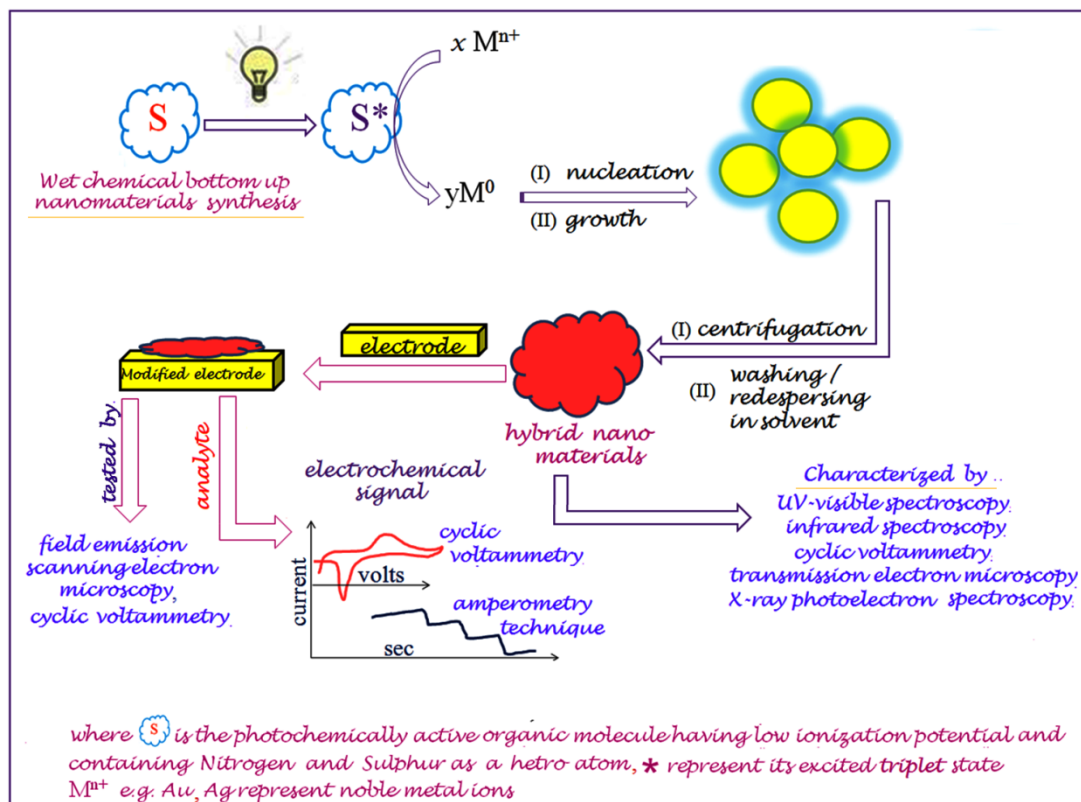
- ❖ Gold/silver noble nanomaterials are most widely used to functionalize the polycrystalline electrode for electroensing purposes. Electrochemical sensing is generally monitored in aqueous electrolyte media, so interfacial electrochemical reaction that occurs in the potential region, which must be safe within the potential limit in aqueous electrolyte media if otherwise solvent itself may decompose and hydrogen or oxygen gas evolution take place along with some electrochemical side reaction.

### **1.9 Motivation & objective of the thesis:**

We have exclusively revisited the concept of nanoscience & nanotechnology, fundamentally important terminology, versatile synthetic scheme of nanomaterials and its mechanism of formation in introductory section so far. Bottom-up synthetic approach using colloidal nanomaterials ensembles, is extremely controllable strategy for chemical modification of electrode. Recent development in wet chemical bottom-up synthesis offers an exciting opportunity for tailoring the bare electrode with nanomaterials for the advancement in chemically modified electrode for electroensing applications. Use of light as a driving force in the reduction of noble metal ions provides an attractive tool for generation of metallic nanomaterials which is relatively green route as it uses photolight and utilize less number of chemicals.

The focus of present thesis is to synthesize noble metallic nanomaterials with a different route (i.e. photochemical route) and connect these nanomaterials to nano electroanalytical chemistry which is a growing interdisciplinary field, combines characteristics of electrochemistry with unique properties of nanomaterials for

electrosensing applications. It is area of interest in the “*room at the bottom*” research on “*Small particles for solving Big Problem*”. In view of preceding context discussed in the chapter, we made the Point wise strategy for the thesis which is as follows and shown in Schematic 1.17:



**Figure 1.17:** Schematic outline illustrating the objectives of thesis.

1. Choosing some photoactive molecule (should have low ionization potential, some hetro atom present in its structure) which can be photochemically oxidized and reduce precursor noble metal ion leading to formation of metallic nanostructures without use of any external conventional reducing agent (i.e. green route).
2. Extensively investigation of as such prepared electro active noble metallic nanomaterials by various characterization methods including UV-visible spectroscopy, infrared spectroscopy, cyclic voltammetry, amperometry, field

emission scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy.

3. Modification of polycrystalline electrodes surface with electro active hybrid nanomaterials by the virtue of attachment to the electrode surface via sulphur, nitrogen hetro atoms present in its structure for electrosensing of biologically and environmentally hazardous analytes.

### **1.10 Benefits of the proposed scheme in perspective of synthetic procedure and practical applications**

Rationalized scheme of this thesis may have advantages over conventional existing method which is structured below:

- 1) Why Gold & Silver ?



- ✓ Easily reducible.
  - ✓ Excellent electro-catalytic properties.
  - ✓ Affinity towards sulphur & nitrogen.
  - ✓ Characteristics signature (peak) in the electrochemical (safe) window (i.e.  $-0.4 \text{ V}$  to  $+1.3 \text{ V}$ ).
- 2) Photochemical assisted synthesis of noble metallic nanoparticles do not require any external stabiliser/conventional harsh reducing agent/phase transfer agent/seeds which is the simplest, most straight forward, limited post synthesis work up and pragmatic.
  - 3) The prepared hybrid nanomaterials may have potentially high surface areas, high electroactivity and connected structures could find use as a new class of advanced electrode hybrid nanomaterials for promising applications in electrosensing of biologically & environmentally hazardous analytes and fabrication of nano-devices in electron transfer studies.
  - 4) Photochemical scheme do not utilise any external reducing agent, it has an advantage over common existing methods in which excess of reducing agent (e.g. hydrazine  $\text{NH}_2\text{-NH}_2$ , sodium borohydride  $\text{NaBH}_4$ ) may cause in



the sudden  $P^H$  change in the colloidal solution, at the same time their counter ions like  $NH_2^-$ ,  $BH_4^-$  may get adhere on the nanoparticles surface which contaminates the nanomaterials surfaces resulting into poor sensitivity in electrosensing of analytes or improper electrode modification.

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