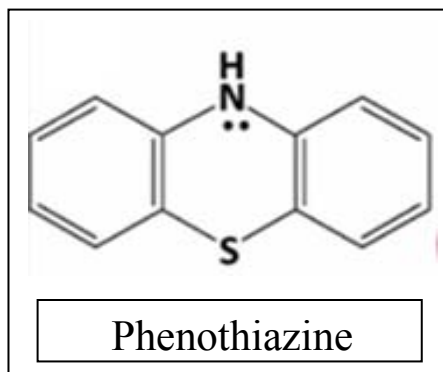


### 5.1. Introduction:

Enjoying the history dating back to the days of Faraday's pioneer efforts, a lot of research activity on gold nanoparticles have been seen during the last two to three decades because of their attractive chemical, electronic and optical properties as well as biocompatibility which make it suitable and promising material for photoelectric devices, catalysis, electrochemical sensing and bio-imaging applications [Chen *et al.*, 2002; Sato *et al.*, 1994; Mallon *et al.*, 2010; Sun *et al.*, 2004; Sanchez *et al.*, 2011]. Increasing awareness toward utilization of light in the green route synthesis of noble metallic nanomaterials which have scientific as well as technological interest. Photochemical assisted synthesis of noble metallic nanomaterials is versatile method to generate metal nanostructures for advancement in nanomaterials synthetic procedure [Mallik *et al.*, 2001; Mandal *et al.*, 2002]. In the field of colloid chemistry, light remains an interesting tool that might be used to control particle shape, size and composition. Photochemical approach however remains one of the less 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 [Sinha *et al.*, 2013; Ghosh *et al.*, 2007]. Photochemical assisted synthesis, as compared to standard chemical approaches, provides the benefits of a homogeneous distribution of the reducing process in the entire solution content. However, photochemical method also do not utilise any external reducing agent, it has an advantage over common existing methods in which excess of reducing agent (e.g. hydrazine, sodium borohydride) 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 nano particle surface which contaminates the nanomaterials resulting into the poor sensitivity in electroensing of analytes or improper electrode modification/applications purposes [Aslam *et al.*, 2004; Sharma *et al.*, 2004].

We limit our beginning mostly in frontier of generation of photoelectron by photoactive organic molecule i.e. phenothiazine and proposal of synthetic approach in synthesis of gold nanoparticles using light as an energy input. The reaction of Au (III) with phenothiazine (PTZ) is an analytical reaction, generally utilized for quantitative and qualitative determination of phenothiazine in clinical samples [Nemcova *et al.*, 1990]. Analytical spectrophotometric determination of gold with Phenothiazine was reported by Nemcova and their research group. They have shown the reaction of Au (III) with phenothiazine which produces green colored solution but they did not report the formation of Au nanostructures and also did not go for microscopy i.e. SEM, TEM etc. This is how, we employ that frame as an analytical reaction to synthesize the metallic nanomaterials in a different approach and revisited the chemistry of phenothiazine in the light of its photooxidation/ photoelectron generation, stability, redox properties, etc.

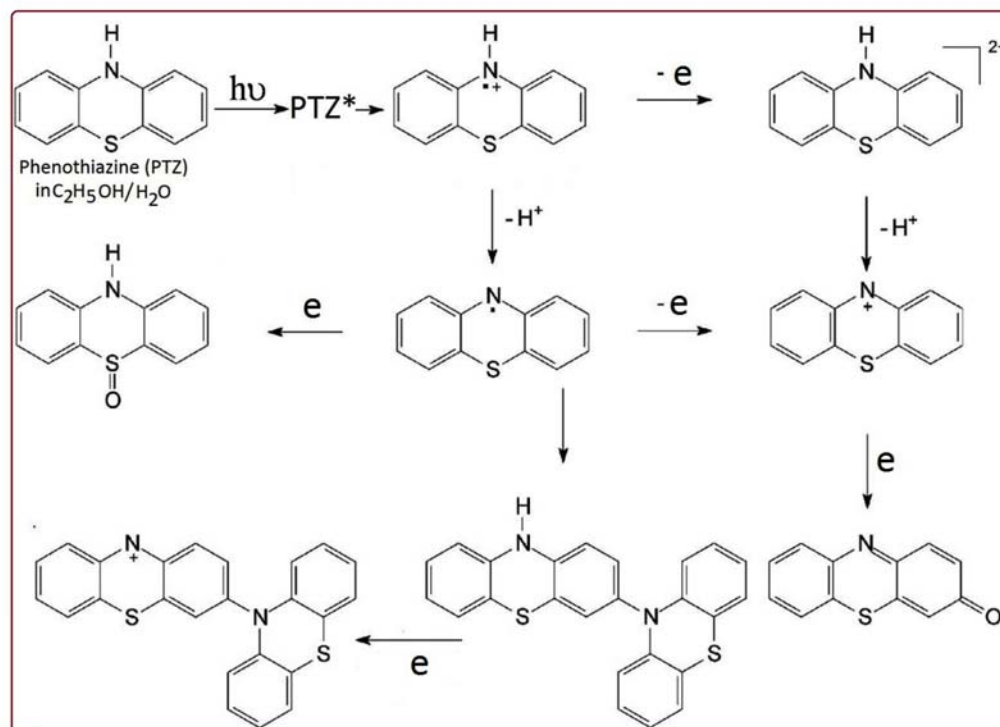
Phenothiazine molecule consists of two phenyl ring and bridged by sulphur and



nitrogen atom respectively. This molecule is highly aromatic resonance stabilized system. Phenothiazine (PTZ) plays as a dual task in nanomaterials synthesis: It can initiate the reduction of Au (III) in the presence of light and at the same time it interacts with the nanomaterials surface to protect nanomaterials via interaction with sulphur and nitrogen hetro

atoms present in its molecular structure [Kumar *et al.*, 2003; Turro *et al.*, 1995]. In the other words, oxidized phenothiazine molecules present in solution adsorb onto the surface of the newly formed nanoparticles, providing colloidal stability and thus preventing agglomeration. Phenothiazine (PTZ) is an electron donor compound having low ionization potential, so readily get photo-oxidized and also easily form radical-cations. Photo-oxidation of phenothiazine yielding the stable radical cation that has been well studied by several research groups [Xiang *et al.*,

1994; Beckett *et al.*, 1978]. Rodrigues and their research group have also studied photochemically generated stable radical cation of phenothiazine by using electron spin resonance spectroscopy as well as flash photolysis studies [Kadirov *et al.*, 2003; Rodrigues *et al.*, 2006].



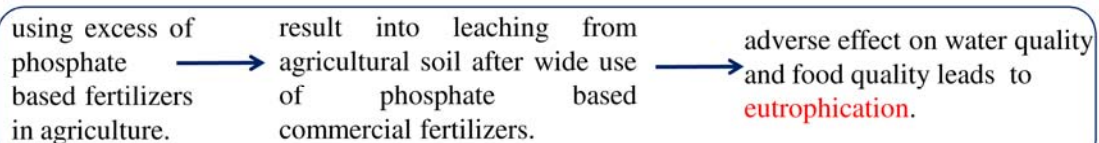
**Figure 5.1:** Photochemically generated electron utilizing the reduction of noble metal ions and possible oxidation product of phenothiazine.

Photochemically generated electron can be used for the reduction of noble metal ions and oxidized fragments of the phenothiazine provides the stability to the nanostructures via interaction with sulphur and nitrogen hetero atom present in its molecular structure as shown in figure 5.1. Zhu and their research group have well studied the chemistry of phenothiazine and provided the experimental evidence of electron transfer ability of phenothiazine, formation of stable radical cations of phenothiazine and also radical cations of phenothiazine exist stably quite enough to be detected at room temperature by using EPR [Ghosh *et al.*, 1997; Kadirov *et al.*, 2003; Rodrigues *et al.*, 2006; Zhu *et al.*, 2008]. Phenothiazine and its oxidation fragments have been well studied by liquid chromatography and mass

spectrometry techniques [Hayen *et al.*, 2003]. Although phenothiazine chemistry has been documented extensively in the scientific report, but it is amazing to note that there is scarcely any report published so far on photochemically mediated formation of gold nanostructures by using phenothiazine as a reductant as well as stabilizer.

One of the objectives of present finding is to utilize the nanomaterials based platform for the amperometric sensing of phosphate. The concept of chemically modified electrode is one of the exciting developments in the field of electroanalytical chemistry. Thin film (nm/ $\mu\text{m}$ ) of the desired material on the bare electrode surface through the method of self-assembly is called modified electrodes and have a potential application in electro analytical techniques as electrosensing of environmentally & biologically hazardous analytes. They show several advantages over conventional macro electrodes viz. increased mass transport, decreased influence of solution resistance, less electrode fouling problem and better detection limits [Kumar *et al.*, 2011]. As such synthesized hybrid nanomaterials were used for the modification of the electrodes and efforts have been made to develop a sensitive platform for the amperometric detection of phosphate.

Dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ) plays key role in biological, environmental and many industrial processes.



In recent years phosphate levels of water have significantly increased because of leaching from agricultural soil after wide use of phosphate based commercial fertilizers, which may have an adverse effect on water quality and food quality [Moss *et al.*, 2011; Norouzi *et al.*, 2012; Berchmans *et al.*, 2011].

Therefore, detection of phosphate ions, both inorganic and organic, is important in biological, environmental and biomedical samples. On the basis of previous literature reports several colorimetric probes, so-called “naked eye chemosensors” have been developed for the detection of phosphate anion based upon the selective recognition unit, hydrogen-bonding receptors etc [Cao *et al.*, 2011; Liao *et al.*, 2011; Tobey *et al.*, 2003]. Also great efforts have been devoted to design advanced hybrid electrode materials for the detection of phosphate based on chemical modification of electrode using electrochemical technique [Lu *et al.*, 2005; Berchmans *et al.*, 2012]. However we have developed the amperometric technique which is sensitive towards phosphate addition with nanomaterials modified electrode which is simplest, pragmatic and without any pre sample treatment.

### **5.2. Experimental Section**

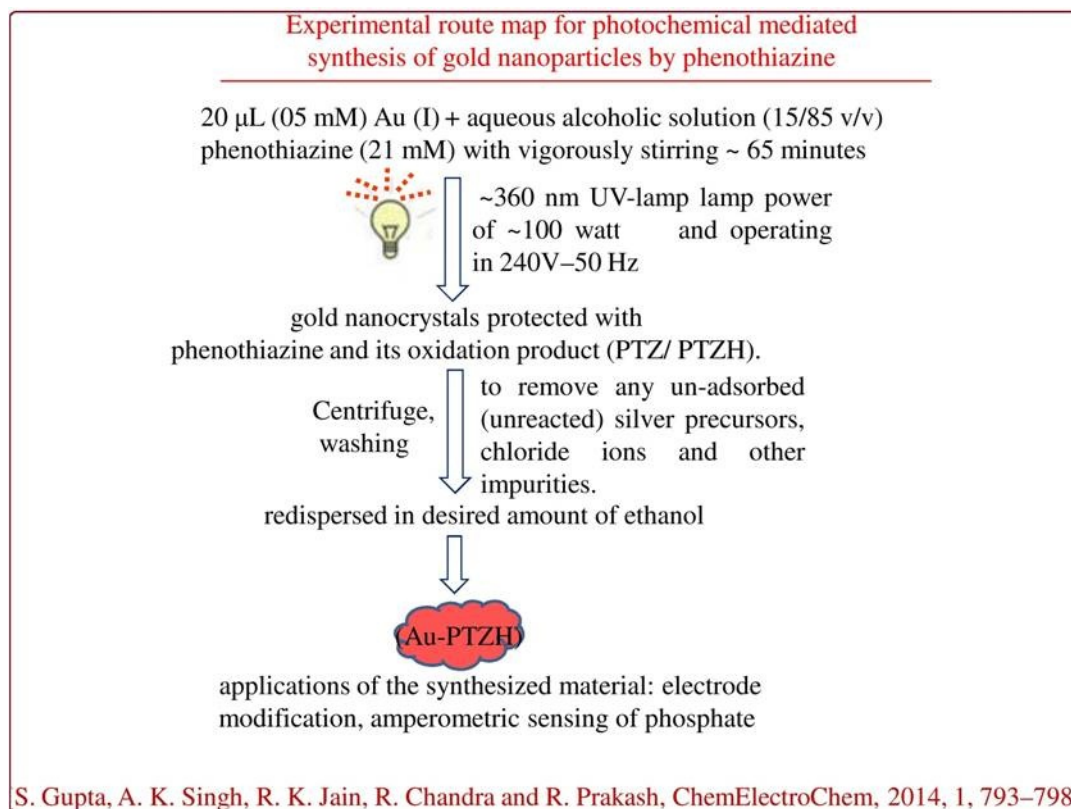
#### **5.2.1 Materials:**

HAuCl<sub>4</sub>.3H<sub>2</sub>O (Sigma-Aldrich), Phenothiazine (Sigma-Aldrich), Indium tin oxide (ITO) plates (Asahi Beer Optical Ltd, Japan), Ethanol (99.5%) and Sodium dihydrogen phosphate (Merck Germany), were used. All the chemicals were used as received, unless otherwise mentioned. The glassware used in the preparation of gold nanocrystals was cleaned with freshly prepared aqua regia (3:1, HCl/HNO<sub>3</sub>) and rinsed comprehensively with ultrapure millipore water (18.2 MΩ cm) before use (Caution! Aqua regia is a powerful oxidizing agent, and it should be handled with extreme care). Tris buffer (pH 7.2) was prepared from 0.1 M Tris (hydroxymethyl) – amino methane. The pH was adjusted with 0.1M HCl. Deaerated Tris buffer (pH 7.2) was used as a supporting electrolyte in electroanalytical detection of phosphate.

#### **5.2.2 Photochemical synthesis of gold nanoparticles by phenothiazine:**

In a typical synthesis, 20 μL of HAuCl<sub>4</sub> (5 mM) was mixed with continuously stirred phenothiazine (21mM) solution (Since phenothiazine is insoluble in water and is soluble in ethanol, aqueous ethanolic (15: 85 v/v) solution was made to

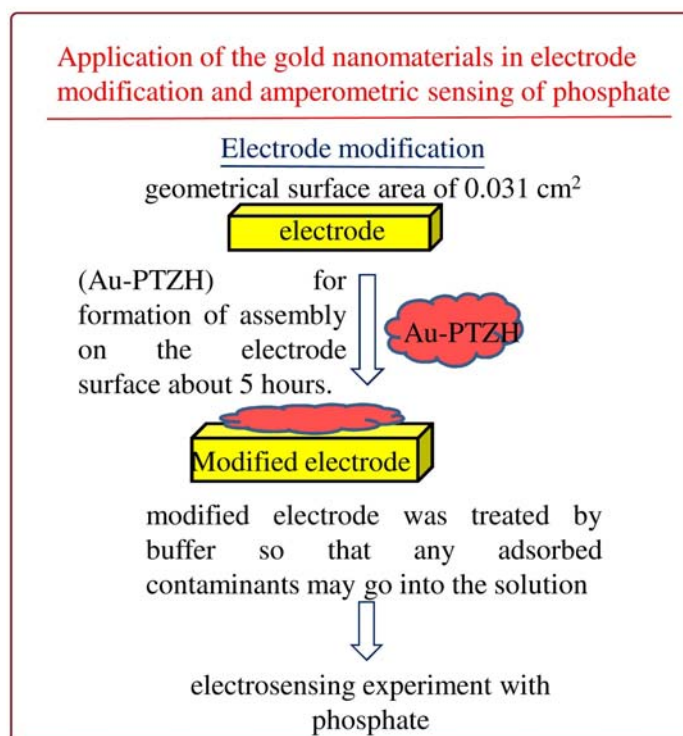
dissolve the phenothiazine) and the whole reaction content was irradiated using a 100W sun lamp having spectral output of  $\sim 360$  nm.



The glass vial was kept at a distance of 12 cm from the light source to avoid heating of the solution. After completion of reaction, resulting solution was centrifuged at 12000 rpm for 4 min, to obtain the content of gold nanocrystals protected with phenothiazine and its oxidation product (PTZ/ PTZH) [Gupta *et al.*, 2014]. This process is repeated for twice. The obtained content was washed several times with mixture of isopropyl alcohol and milli-Q-water (v/v: 40/60) to remove any un-adsorbed (unreacted) gold precursors, chloride ions and other impurities. Thus, the obtained content is redispersed in desired amount of ethanol so that it can be used for further applications/experiments purposes.

### 5.2.3 Preparation of gold nanoparticles modified electrode for amperometric sensing of phosphate:

Prior to the surface modification of polycrystalline gold electrode (geometrical surface area of electrode  $0.031 \text{ cm}^2$ ) was kept in piranha solution (v/v 3:1  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) for 10 min. Thereafter electrodes were cleaned by sequential 15 min sonications in acetone, ethanol and water, respectively followed by rinsed thoroughly in milli-Q-water and dried under flowing nitrogen gas for further surface modification.



The thoroughly cleaned polycrystalline Au electrode was soaked in ethanolic solution of gold nanomaterials (Au–PTZH) for the formation of assembly on the electrode surface for 6 hours. Finally modified electrode was treated by buffer so that any adsorbed contaminants may go into the solution and this modified electrode is ready for electrochemical experiments. Reduction potential, i.e.  $-0.336$  volts Vs Ag/AgCl was chosen for amperometric analysis of phosphate ions under optimized conditions and aliquots of phosphate were injected into a stirred



supporting electrolyte (Tris Buffer Buffer-pH 7.2) solution. A systematic change in the current was noticed after each addition of phosphate into the supporting electrolyte solution.

### **5.2.4 Instrumentation:**

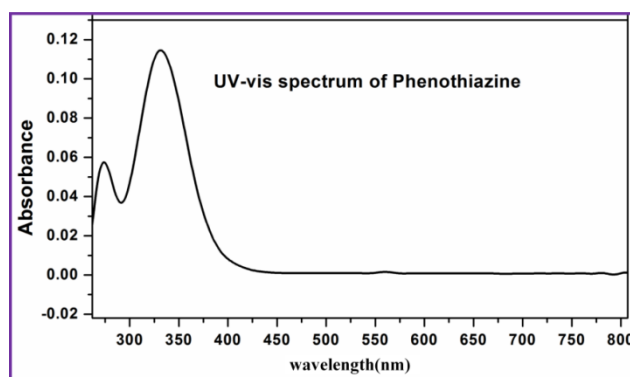
UV-visible absorption spectra were recorded using Lambda-25 Perkin Elmer (Germany) spectrophotometer by using a quartz cuvette having optical path length of 10 mm. The microscopic views of samples were examined using transmission electron microscope (TEM Tecnai G2, 20 FEI Corporation Netherlands) operating at 200 kV. Few  $\mu\text{L}$  of the colloidal gold nanoparticles was dropped on the carbon-coated copper grids (obtained from Pelco International, USA) and allowed to dry and fabricated electrode with gold nanoparticles was examined by SEM images, recorded with a JEOL JEM 6700F field emission scanning electron microscope (FESEM). FT-IR studies of PTZ and PTZH-AuNPs were carried out using Nicolet Thermo Scientific 6700 Germany. Cyclic voltammogram and amperometric analysis for modified electrode with Au-PTZH was performed using Autolab potentiostat-galvanostat (PG-STAT, 302, Netherlands) using computer controlled GPES software. A conventional three-electrode system consisting modified electrode with Au-PTZH served as the working electrode, Pt foil as the counter electrode, and Ag/AgCl as the reference electrode, were used for all the electrochemical measurements. Tris buffer (pH 7.2) was used as a supporting electrolyte and the scan rate was kept 50mV/sec for each measurement. Elemental analysis/ oxidation studies on gold nanocrystals was confirmed by X-ray photoelectron, kratos analytical instrument, Shimadzu group company Amicus XPS (UK).



## 5.3 Results and Discussion

### 5.3.1 Characterizations of the photochemical mediated synthesis of gold nanoparticles by phenothiazine:

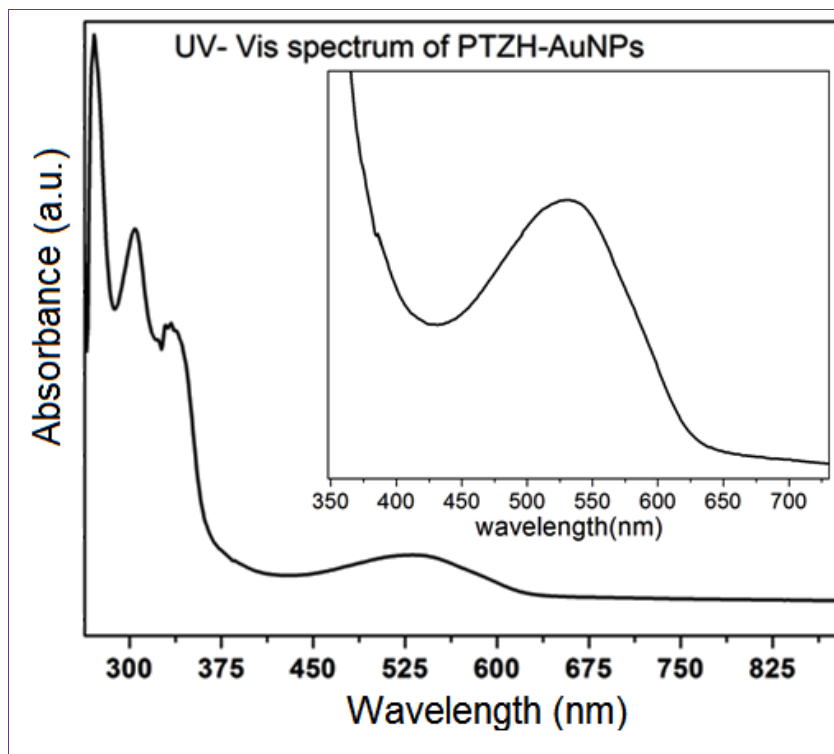
To the best of our knowledge, the reducing/stabilizing capability of phenothiazine has not been applied to preparing metal nanostructures so far. Phenothiazine was selected on the basis of its unique property, as a reducing capability under UV-visible light as well as capability to stabilize the gold nanoparticles through the interaction with sulphur and nitrogen coordinating sites present in phenothiazine. Few amines and amino acids have capability to reduce Au (III) as well as stabilize the nanoparticles through weak covalent as well as weak electrostatic interaction between gold and nitrogen atoms as discussed in introductory chapter. Also it is well known that thiols based ligands stabilize gold nanoparticles through Au-S interaction. Although phenothiazine and its product do not have long chain structure, yet it stabilizes Au nanoparticles through coordination with nitrogen and sulphur site present in its structure. This is because of its planer radical cation structure formation after oxidation, which is highly aromatic resonance stabilized system [Rawashdeh *et al.*, 2005].



**Figure 5.2:** UV-visible spectrum of phenothiazine.

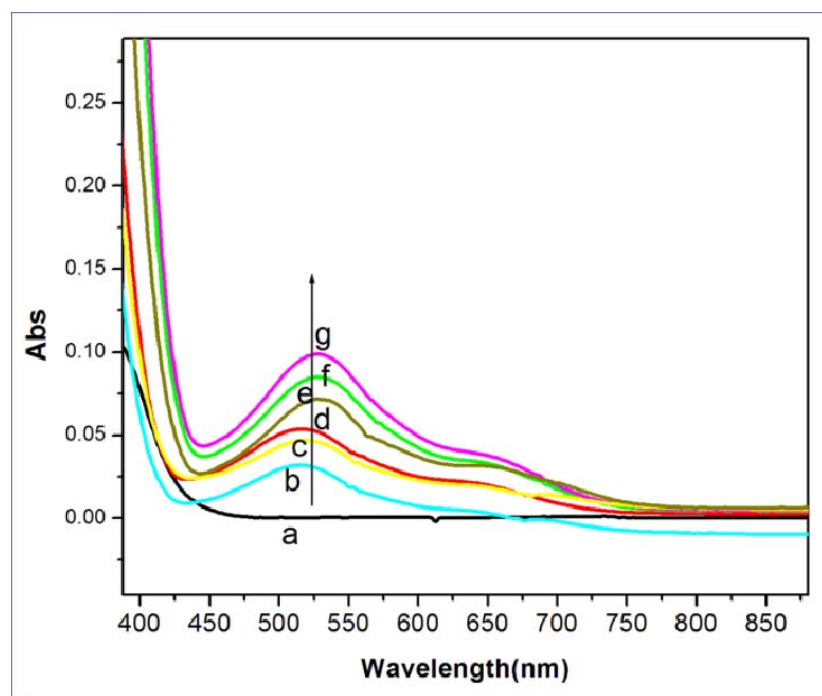
The UV-vis spectrum of phenothiazine shows two absorption bands at 273 nm and 332 nm as shown in figure 5.2. It did not show any absorption in the range 400-750

nm, whereas the gold nanoparticles exhibits a distinct absorption band  $\sim 526$  nm corresponding to Surface Plasmon Resonance (SPR) band of gold nanoparticles as shown in figure 5.3.



**Figure 5.3:** UV-Vis spectrum of gold nanoparticles, *Inset:* zoom view of SPR band of gold nanoparticles.

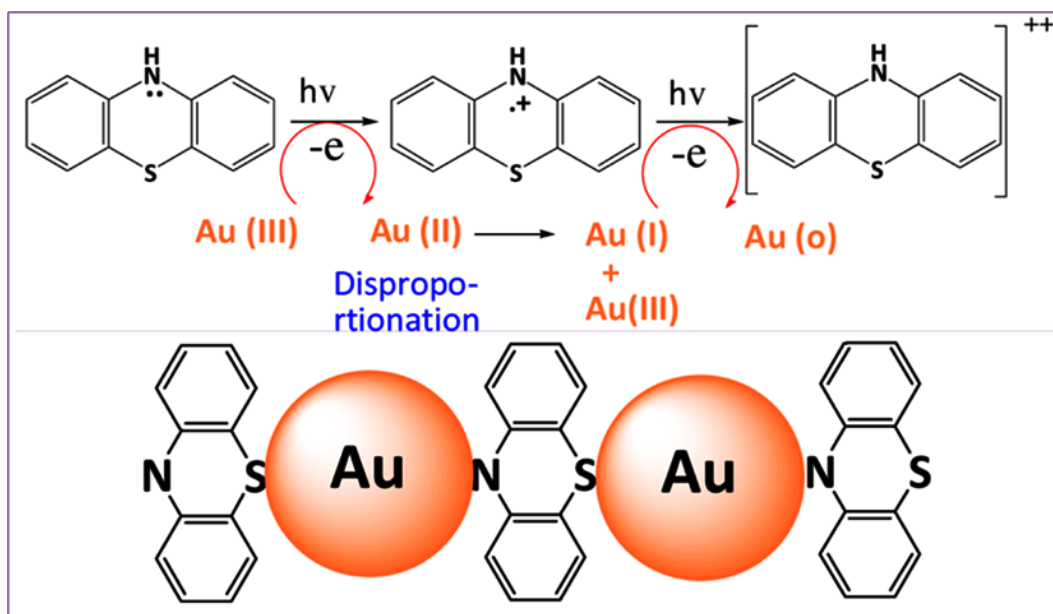
Progress of spectral changes was monitored by UV-visible spectrum as shown in figure 5.4 and feature gradually grows as a clear peak at  $\sim 526$  nm corresponds to characteristic SPR band nano gold [Thomas *et al.*, 2002]. The photoinduced reduction of Au (III) ions is accelerated by excitation of phenothiazine with light. Here, the use of phenothiazine as a photo active can serve a dual purpose: It can initiate the reduction of Au (III) and simultaneously, it interacts with the nanomaterials surface to protect gold nanoparticles via interaction with sulphur and nitrogen hetro atom present in its molecular structure.



**Figure 5.4:** Time dependent UV-visible spectrum of gold nanoparticles formation, a: 0 min, b: 2 min, c: 5 min, d: 12 min, e: 22, min, f: 32 min, g: 50 min.

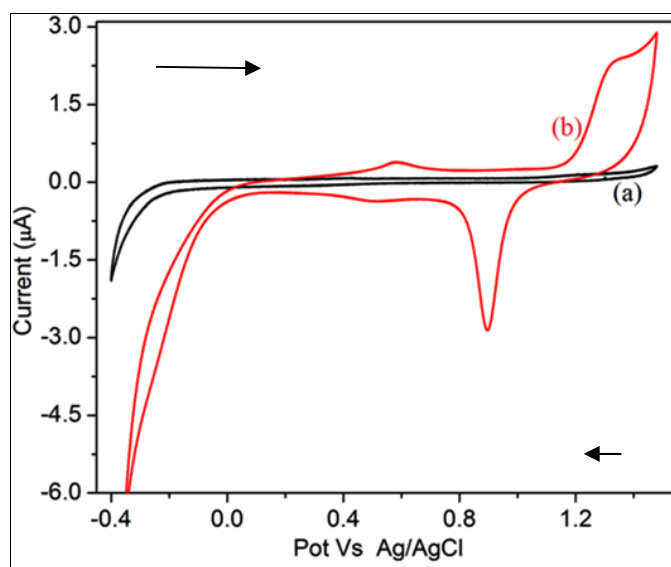
Purposely, phenothiazine and its oxidation product (PTZH) not only serves as a capping agent to selectively gold facets, but also coordinates with gold ions to form a complexes which further start reducing in presence of photolight [Gupta *et al.*, 2014]. The recommended mechanism put forward a two-step process, i.e., nucleation and the successive growth of the particles. In the first step, metal ions in solution are reduced and atoms thus produced agglomerate to form small clusters. Nanoclusters thus formed act as nucleation centers and catalyze the reduction process of the remaining metal ions present in the bulk thus result in the autocatalytic growth [Gupta *et al.*, 2014]. The photo chemical reduction of Au(III) to Au(0) is not a single step process, firstly Au (III) ions form complexes with the phenothiazine molecule and this coordination significantly reduces the concentration of free Au (III) ions, thus photochemically reduced to form Au (II) which further disproportionate to Au (III) and Au (I). Consequently unstable photo

generated Au (I), get reduced to metallic Au (0) leading to formation of nano gold as shown in figure 5.5 of reaction scheme of formation of gold nanoparticles.

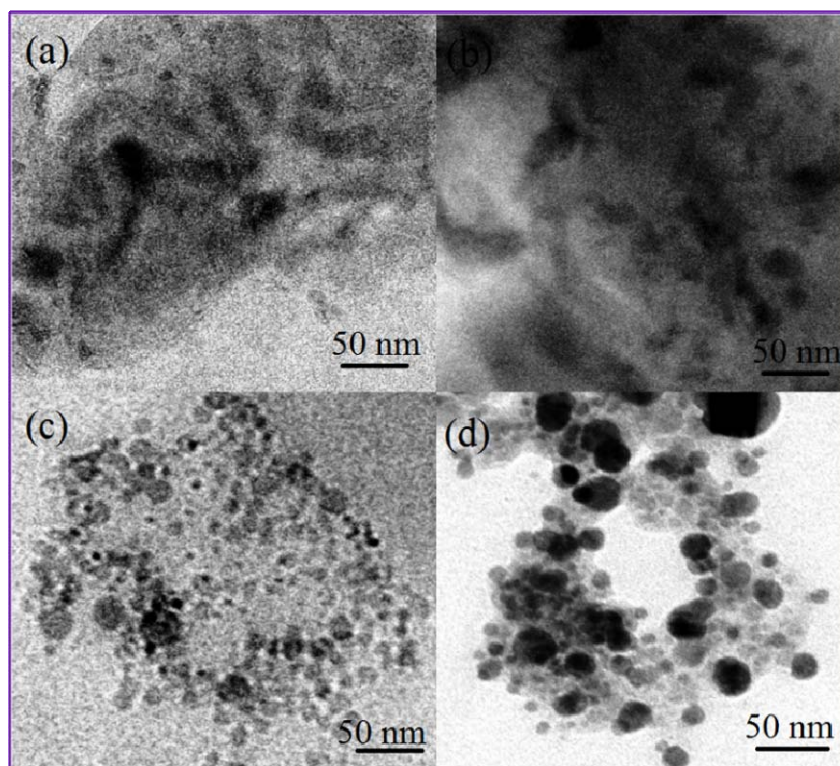


**Figure 5.5:** Plausible reaction scheme for the photochemical formation of gold nanoparticles and their stabilization by phenothiazine and its oxidation product.

On the basis of previous documented result in literature related to oxidation product on phenothiazine, we conclude that metal nanoclusters are stabilised/protected by that oxidized product via interaction with nitrogen and sulphur coordinating sites present in its structure. Gold nanocrystals can also be characterized by electrochemical cyclic voltammogram [Yancey *et al.*, 2010]. The cyclic voltammogram of Au nanoparticles on ITO electrode surface is similar to the gold electrode in 0.5 M  $H_2SO_4$  as shown in figure 5.6. The characteristic gold surface oxidation and the corresponding oxide reduction confirmed that the ITO surfaces were modified with gold nanoparticles.

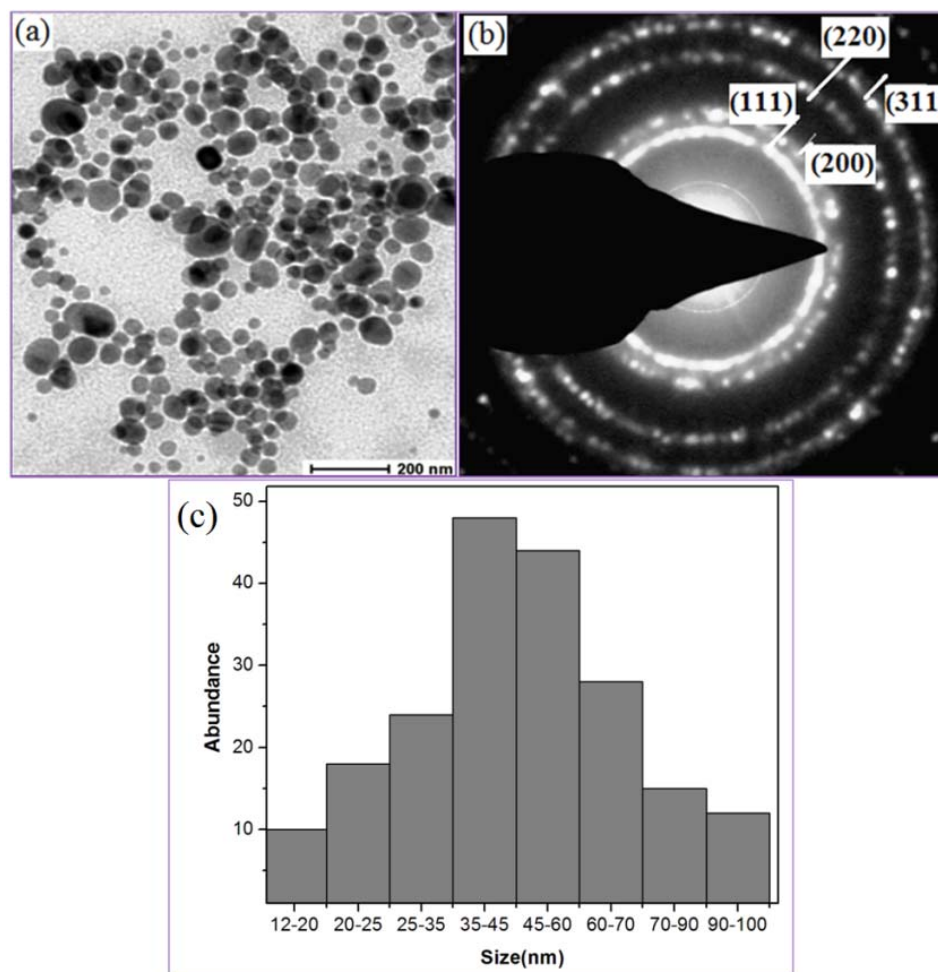


**Figure 5.6:** (a) Cyclic voltammogram of unmodified ITO electrode (b) CV of gold nanomaterials on ITO electrode surface in 0.5 M  $\text{H}_2\text{SO}_4$ .



**Figure 5.7:** (a) TEM studies for the formation of nano gold w.r.t. photo-light exposure, recorded at different time interval a: 0 min, b: 5 min, c: 22 min, d: 32 min.

The photochemical formation of gold nano crystals w.r.t. time is pictorially micrographed in different time interval shown in figure 5.7. It is very interesting to note from TEM images that, w.r.t. time gold nano crystals are growing and after ~32 minutes we get a 40-45 nm average spherical sized gold nanoparticles as shown in figure 5.8.

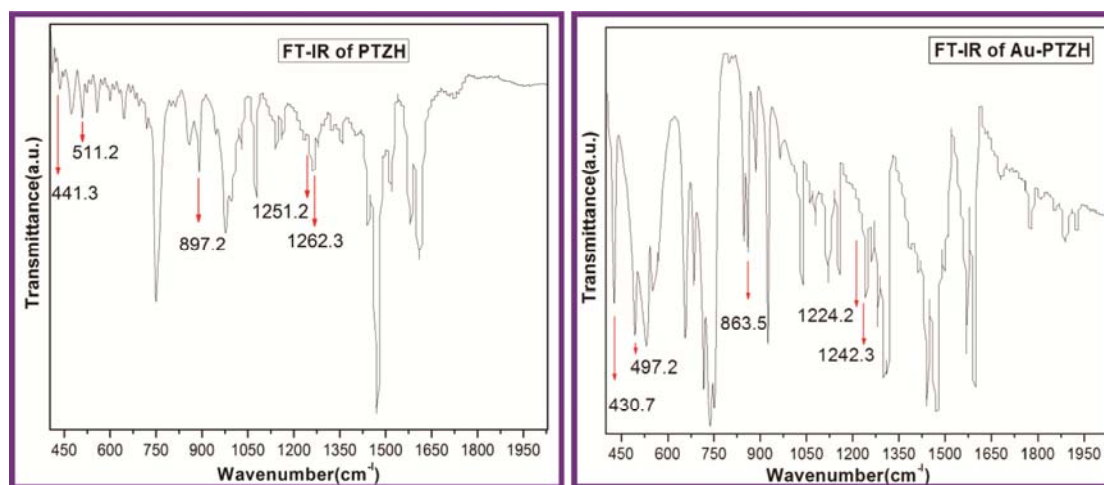


**Figure 5.8:** (a) TEM image (b) SAED pattern of gold nanoparticles. (c) size distribution of prepared nanomaterials.

The TEM image shown in figure 5.8 (a) reveals that the average particle size of Au nanoparticles is ~45 nm and corresponding size distribution of gold nanoparticles has been shown in figure 5.8(c). The Scherrer ring of the selected area electron

diffraction (SAED) pattern obtained from the gold nanoparticles as shown in figure 5.8(b) were indexed as the (111), (200), (220), and (311) planes of a face-centered cubic (FCC) lattice of gold atom [Lee *et al.*, 2011].

In FT-IR spectrum (figure 5.9), we focus on the regions where we can see some major changes of assign band of PTZ and Au-PTZH and thus highlighted the spectra in the region  $\sim 400\text{--}2000\text{cm}^{-1}$ . The FT-IR spectrum of phenothiazine was assigned from the literature [Palafox *et al.*, 2002]. It shows that angle bending of  $\delta$  (C-S), asymmetric angle bending of  $\delta$  (C-S-C), angle bending of  $\delta$  (C-N), symmetric  $\nu_s$  (C-N-C) and asymmetric stretching of  $\nu_{as}$  (C-N-C) is appeared at 441.3, 511.2, 897.2, 1251.2 and 1262.3  $\text{cm}^{-1}$ , respectively. In the FT-IR spectrum of AuNPs-PTZH these peaks are observed at 430.7, 497.2, 863.5, 1224.2 and 1242.3  $\text{cm}^{-1}$ , respectively.

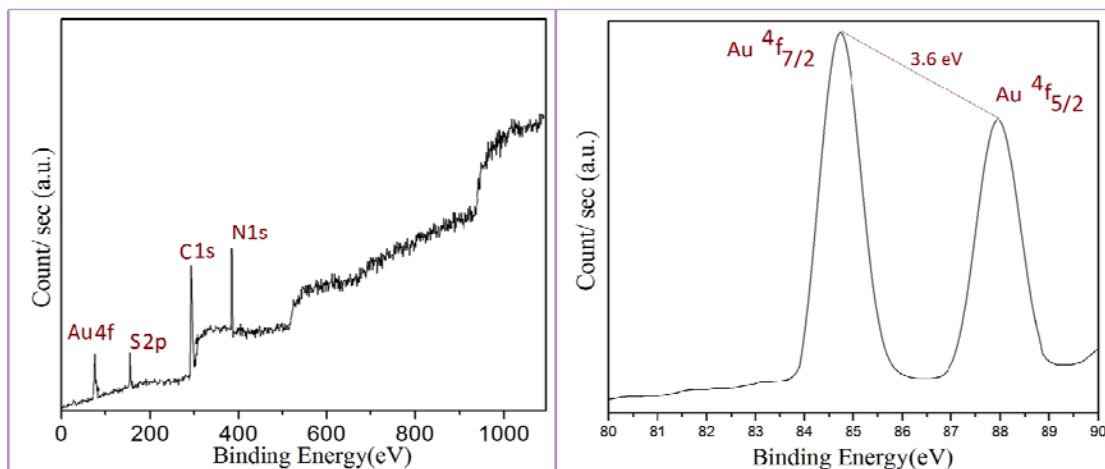


**Figure 5.9:** FT-IR Spectrum of PTZ and Au-PTZH.

The lowering in these peaks indicated the decrease in the bond strength of C-S as well as C-N in the AuNPs-PTZH. The decrease in assigned stretching frequency is due to the transfer of electron density from the S and N atoms to gold atom, resulting in the electrostatic interaction with sulphur and nitrogen atom with gold nanocrystals [Cheng *et al.*, 2004]. With this experimental FT-IR result it is reasonable to say that gold nanoparticles are co-adsorbed on the PTZH surface



through electrostatic interaction with Sulphur and Nitrogen atom [Gupta *et al.*, 2014].



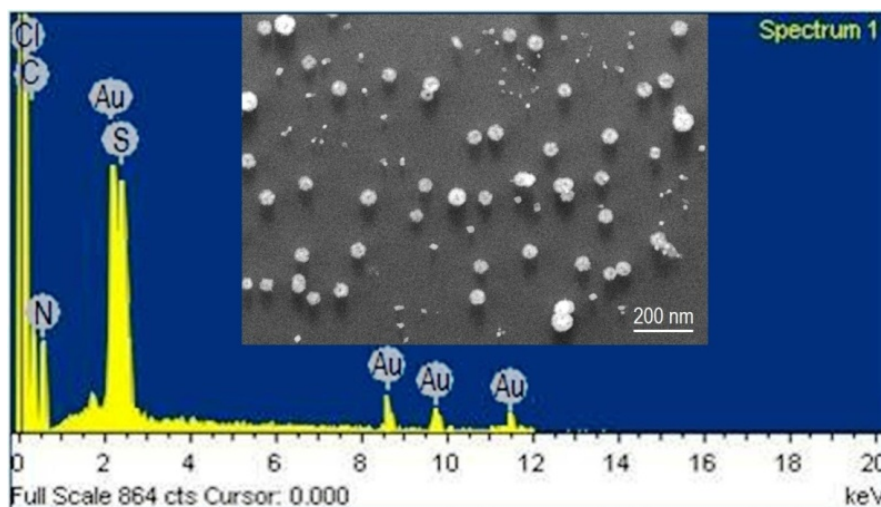
**Figure 5.10:** (a) XPS survey spectrum of Au-PTZH in full range (b) X-ray photoelectron spectra of Au (4f).

The XP spectrum in figure 5.10 indicates  $4f_{7/2}$  peak at 84.2 eV and a  $4f_{5/2}$  peak at 87.9 eV, respectively confirms that Au is in zero oxidation state. XPS analysis also reveals that -N as well as -S elements are attached on the nanoparticles surface and Au (III) is photoreduced to Au (0) [Kumar *et al.*, 2003]. Binding energy observation, described here justify that phenothiazine molecule reacts with gold ions in a redox photochemical reaction yielding a gold nanoparticles and oxidation products which are essentially phenothiazine and its fragments as revealed by infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) studies, that both the sulphur and nitrogen atoms get adsorb on surface of photoreduced gold [Gupta *et al.*, 2014].

### 5.3.2 Application of the gold nanoparticles in Amperometric sensing of phosphate

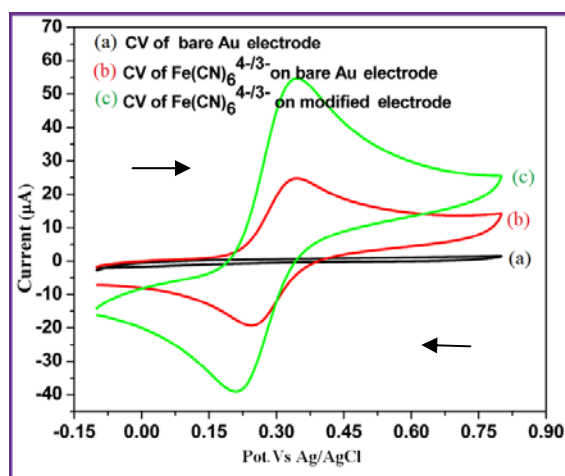
Gold nanoparticles capped with phenothiazine and its oxidation product can be used as modifiers of electrode surfaces due to some of the special characteristics: it is fairly soluble in water so that leaching of material from the electrode surface can

be avoided and can be easily adsorbed on gold surface through interaction with sulphur and nitrogen. The assembled Au–PTZH on the gold surface was examined by taking FESEM image as shown in Figure 5.11. The majority of gold nanoparticles modified interfaces are based on the affinity between thiols and gold (S–Au) interaction or the affinity between amines and gold (N–Au) interaction.



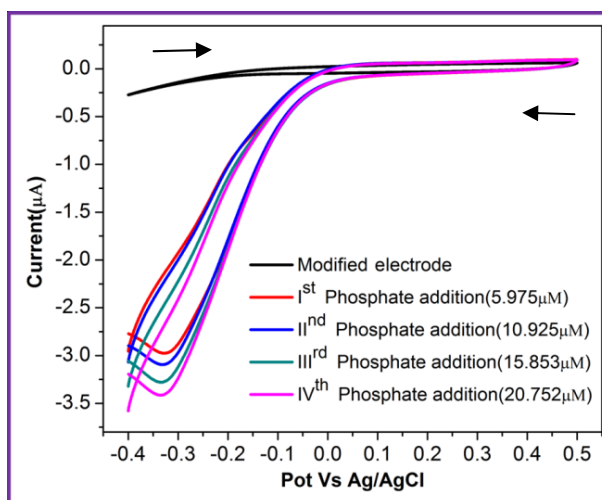
**Figure 5.11:** FESEM and EDAX image of the Au–PTZH nanostructured platform (gold nanomaterials modified electrode).

Cyclic voltammetric responses of the polycrystalline gold electrode, and modified electrode with Au–PTZH were examined by taking the 0.1mM  $\text{Fe}(\text{CN})_6^{4-/3-}$  in tris buffer solution. Significant increase in the peak current was observed for the same amount of  $\text{Fe}(\text{CN})_6^{4-/3-}$  for modified electrode as compared to unmodified polycrystalline gold electrode as shown in a figure 5.12, indicating that the modified electrode with Au–PTZH favors the enhanced electron-transfer reaction. Catalytic efficiency of nanosized materials mainly depends on (i) the surface-to-volume ratio of the material and (ii) the electronic interactions between the material and the analyte. The nanoparticles are very different from their bulk counterparts, since the catalytic activity originates from their quantum-scale dimensions [Kumar *et al.*, 2011].



**Figure 5.12:** Cyclic voltammograms response for  $\text{Fe}(\text{CN})_6^{4-/3-}$  redox couple.

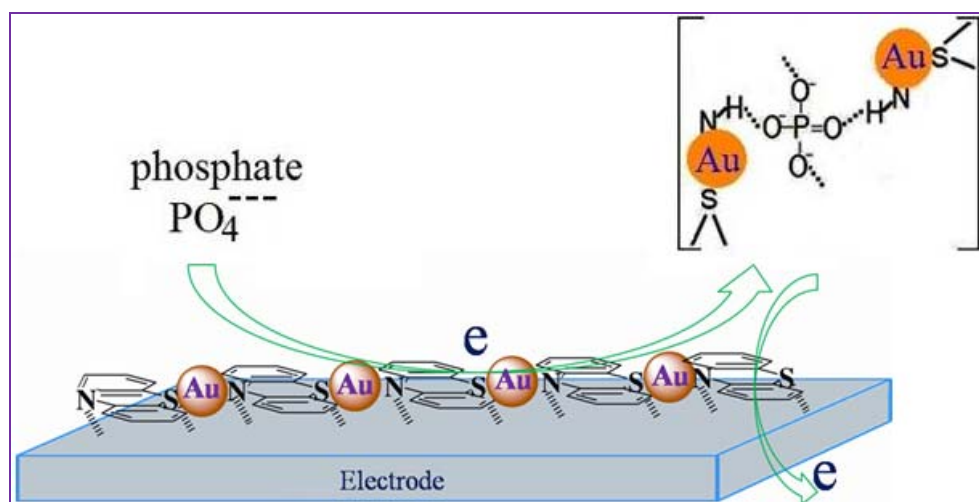
The gold nanoparticles modified electrode did not show any redox peak in the potential window  $-0.4 \text{ V}$  to  $0.5 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  in blank. We selected particular potential window regions where there is no another redox peak of the material appears/ interferes. However, it can be seen well-defined voltammetric responses were obtained for successive additions of phosphate as shown in figure 5.13.



**Figure 5.13:** Cyclic voltammogram response of successive addition of phosphate in  $0.1 \text{ M}$  tris buffer at  $\text{pH } 7.2$ .

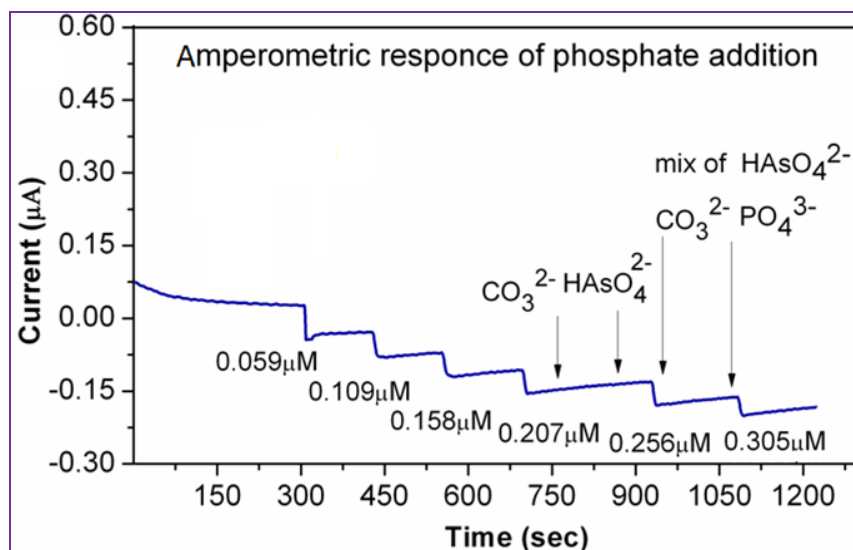
On successive addition of phosphate substantial increase in the peak current reflects fast electron-transfer reaction on the  $\text{Au-PTZH}$  modified electrode owing

to the high electrocatalytic effect of the nanostructured platform. Electrochemistry behind the electrocatalytic sensing of phosphate is possibly due to electrostatic interactions attributed as (PTZH $\cdots$ PO $_4^{3-}$  $\cdots$ Au $^{m+}$  $\cdots$  PO $_4^{3-}$  $\cdots$ DTZH complexation) and conducting gold nanoparticles facilitates the efficient collection and transfer of electrons to the collecting electrode surface schematically shown in figure 5.14 [Gupta *et al.*, 2014].



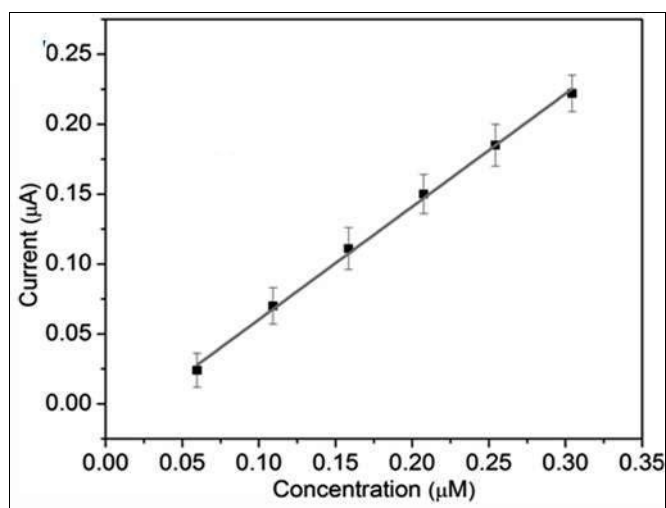
**Figure 5.14:** Schematic representation of the nano integrated platform of the Au–PTZH as a modified electrode.

For amperometric study a fixed reduction potential  $-0.336$  volts Vs AgCl/Ag was chosen from cyclic voltammetry studies and aliquots of phosphate were injected into a stirred supporting electrolyte solution. A systematic change in the current was noticed after each addition of phosphate into the supporting electrolyte solution, and a steady state response was attained within 2-3 sec. After the fourth standard addition of phosphate, equal quantities of  $0.03 \mu\text{M}$  of carbonate and arsenate were added in sequence, and their influence on the current response was noted.



**Figure 5.15:** Amperometric response at an applied potential of -0.336 volts Vs Ag/AgCl for successive addition of phosphate in 0.1 M tris buffer at pH 7.2 under stirred condition.

However, it can be seen from the figure 5.15, added possible interfering anions (carbonate and arsenate) had no effect on the chronoamperometric current.



**Figure 5.16:** Corresponding standard addition calibration plot of chronoamperometric current vs phosphate concentration.

The sensing platform is highly sensitive and showed linear response toward phosphate additions with a sensitivity and limit of detection  $0.794\mu\text{A}/\mu\text{M}$  and  $(0.022\pm 0.0016)\mu\text{M}$  respectively at S/N (signal-to-noise ratio): 3 as shown in chronoamperometric calibration plot figure 5.16.

The amperometric experiments were repeated four times with modified electrode and experiments were highly reproducible. The mean deviation of the current values was within  $\sim 8\%$  and detailed investigation of mechanism of electrocatalysis of the modified electrode with Au-PTZH, achieving to low detection limit and electroanalytical determination of phosphate in biological systems is likely to be addressed in our future prospects.

### **5.4 Concluding Remarks of the chapter:**

We have successfully presented the outline on a photochemical assisted synthesis of gold nanoparticles by photoactive phenothiazine molecule, without the aid of any external stabiliser/reducing agent/seeds which is the simplest, most straight forward, limited post synthesis work up and pragmatic. This study not only provides a simple photochemical synthetic route but also opens a new room for developing amperometric sensing techniques with hybrid nano materials modified electrode. The prepared hybrid nanomaterials Au-PTZH having 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 electro-sensing and fabrication of nano-devices in electron transfer studies. Method described in this work offers a selective, sensitive, enzyme less electroanalytical determination of phosphate and field deployable onsite measurements where one cannot afford to carry costly equipments like ICP-OES or spectrometers. Sensing platform is highly sensitive and showed linear response toward standard phosphate additions with a sensitivity and limit of detection  $0.794\mu\text{A}/\mu\text{M}$  and  $(0.022\pm 0.0016)\mu\text{M}$  respectively.