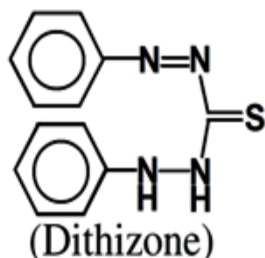


### 3.1. Introduction:

The last three decades have witnessed the successful synthesis of metal nanocrystals because of their attractive chemical, optical and electronic properties as well as biocompatibility which make it suitable and promising material for photoelectric devices, health & nutrition sciences, catalysis, bio-imaging and sensing [Murphy *et al.*, 2006; Das *et al.*, 2012; Pina *et al.*, 2008]. The very first literature on gold colloid was documented in scientific community by Michael Faraday, who prepared deep red colloidal gold by reducing aqueous solution of  $\text{AuCl}_4^-$  with phosphorus in  $\text{CS}_2$  [Faraday *et al.*, 1857]. In this approach, metal salt is reduced by a strong reducing agent to produce dispersed gold nanoparticles. Thereafter In 1951, subsequent advancements were done by Turkevich who synthesized hydrophilic gold nanoparticles by the reduction of chloroauric acid with refluxing in an aqueous solution of sodium citrate [Turkevich *et al.*, 1951]. A distinguishing feature of the Turkevich method was that citrate ions simultaneously act as a reducing agent as well as stabilizer. In 1994 Brust and Schiffrin method of nanomaterials synthesis is one of the most remarkable milestones in the development of two-phase water/ organic synthesis of metallic nanomaterials. In this two-phase method,  $\text{AuCl}_4^-$  in the aqueous phase is transferred to an organic phase of toluene using tetraoctylammonium bromide as the phase transfer catalyst, followed by the addition of a thiol and subsequent reduction using an aqueous solution of sodium borohydride produces metal colloids [Brust *et al.*, 1994]. Organic thiol molecules present in solution adsorb onto the surface of the newly formed nanoparticles, providing colloidal stability and thus preventing sedimentation.

Still it is the popular method of choice because of its simplicity and rapid preparation but substantial 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 nanocrystals, thus preventing their further use in the application purposes [Chaudhuri *et al.*, 2012]. The reducing agent in metal nanoparticle synthesis can be any molecule that can reduce the metal

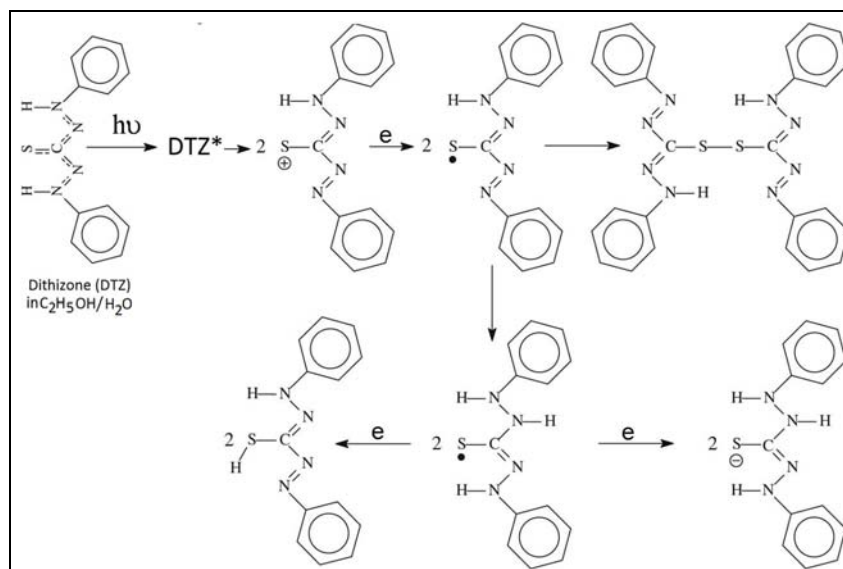
precursor into the zerovalent state. The standard reducing agents are: aminoboranes, borohydrides, ascorbic acid, hydrazine, hydroxylamine, formaldehyde, citric acid, alcohols, polyols, sugars and carbon monoxide etc [Clary *et al.*, 2012; Mandal *et al.*, 2002; Korchev *et al.*, 2004; Weaver *et al.* 1996]. Photochemical assisted synthesis of noble metallic nanoparticles is versatile method for generating metal nanostructures which includes both scientific as well as technological interests in recent time. The use of light as a driving force in noble metal salt reduction provides an interesting tool for the generation of colloidal particles [Sun *et al.*, 2004; Kim *et al.*, 2002; Gobbo *et al.*, 2012; Clary *et al.*, 2012; Pienpinijtham *et al.*, 2012].



Dithizone molecule consists of phenyl ring which is highly aromatic resonance stabilized system. Dithizone can serve a dual purpose: 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 hetero atom present in its molecular structure [Meriwether *et al.*, 1965; Sertova *et al.*, 2000].

In the present work we adopted relatively green route of synthesis of gold nanoparticles using dithizone, which have well established complexation and photochromic properties with metal ions as reported in the available literature [Eschwege *et al.*, 2011]. It is how, we employ that analytical reaction in a different approach and revisited the chemistry of dithizone in the regards of its complexation & redox properties, oxidation product, stability, etc. Although dithizone (DTZ) 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 using dithizone (DTZ) as a reductant as well as stabilizer.



**Figure 3.1:** Photochemically generated electron utilizing the reduction of noble metal ions and possible oxidation product of dithizone.

The possible oxidation product of dithizone (figure 3.1) serve as protecting agent for metallic nanomaterials through interaction with nitrogen and sulphur hetro atom present in its molecular structure and this photochemically generated electron can be used for the reduction of noble metal ions [Grzelczak *et al.*, 2014]. We revisited the redox chemistry of dithizone (DTZ) and made a remarkable conclusion that Au (III) ions may get reduced by exposing the photo-light by using dithizone [Gupta *et al.*, 2015]. An outline of reaction between Au (III) and dithizone has been presented and further this synthesized hybrid nanomaterials used as modification of electrode and electro-sensing of thiocyanate [Gupta *et al.*, 2015]. We found hardly any evidence/ discussions of such photochemical synthesis scheme for preparation of gold nanomaterials by using dithizone and utilization as a modification of electrode for electro-sensing purposes.

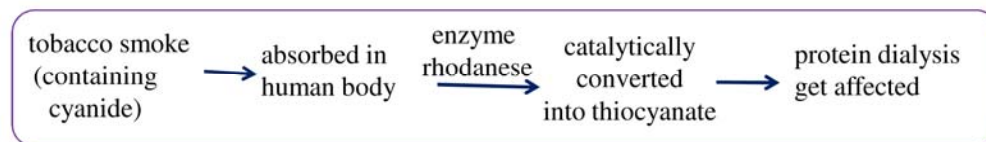
Considerable awareness has been drawn during the last two decades to functionalize the hybrid nanomaterials on electrode surfaces by forming films of few nm to several  $\mu m$  thicknesses for electrosensing devices applications. Modification of an electrode surface can be achieved by different methods 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 [Walcarius *et al.*, 2013; Mallon *et al.*, 2010]. 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 electrode and have a potential application in electro analytical techniques as screen printed modified electrode chips. The focus of this study was to synthesize hybrid nanomaterials Au-DTZH with a different route and connect this nanomaterials to nano electroanalytical chemistry which is a growing interdisciplinary field, combines characteristics of electrochemistry (e.g., high sensitivity, tiny electrode dimension, rapid detection, cost effective and compatibility by means of micro fabrication technology) with unique properties of nanomaterials (e.g., electronic, optical, catalytic) in the electro sensing application. 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 [Hutchings *et al.*, 2008; Freund *et al.*, 2014].

We have utilized this prepared electroactive hybrid nanomaterials for amperometric sensing of thiocyanate. Our group is interested in the development of advanced electroactive materials for electrochemical sensors devices. One of the objectives of the present finding was to utilize the nanoparticles based platform for the electrocatalytic sensing of hazardous thiocyanate. Nanomaterials modified electrode do not undergo fouling at problems, decrease the overpotential, also facilitated electron transfer can help in better sensitivity for detection of thiocyanate as compared to existing instrumental technique [Gupta *et al.*, 2015].

Thiocyanate present in humans as a result of the digestion of some vegetables and as a metabolic product of compounds in tobacco smoke, containing cyanide, once absorbed, is going to catalytically converted into thiocyanate by

the enzyme rhodanese, which is found in the human mitochondria of liver and kidney cells [Bristow *et al.*, 2010; Casella *et al.*, 1998].



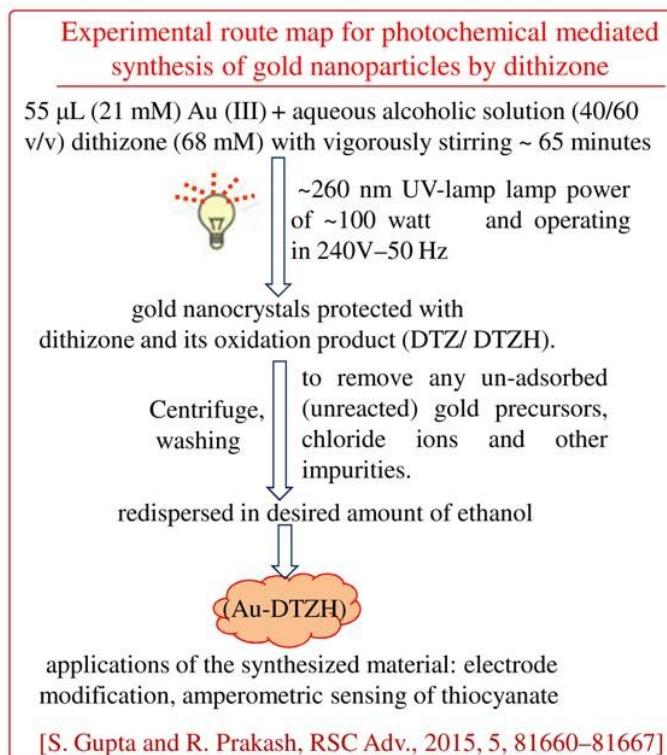
Therefore, the concentration of thiocyanate has long been considered an important biomarker for distinguishing among non-smokers from smokers. Thiocyanate is also known to block iodine uptake by the thyroid gland. It is also found in certain individuals because it is prescribed as a drug in the treatment of thyroid conditions and arterial hypertension. If the content of thiocyanate ion is a little higher in the body than normal, the protein dialysis will be affected and it may even result in coma. The classical spectrophotometric method makes use of a chemical reaction between acidified  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  in the presence of some suitable indicator, to form an intense red colored complex and the produced intensity of red colored complex is directly proportional to the thiocyanate concentration. Many instrumental techniques are available e.g. chromatography, potentiometry and fluorometry etc for the determination of environmentally hazardous thiocyanate [Zhang *et al.*, 2012]. However, most of them require colorimetric probe, redox dye indicator etc. and also they are time consuming, costly or require sophisticated instrumentation work up, high detection limit which prevent them from being used for on-site measurement and field tests [Casella *et al.*, 2002]. Thiocyanate is harmful to aquatic life. Hence determination of thiocyanate in water and industrial effluents is therefore important. Trace detection of thiocyanate is required not only in the field of human health but also quality control for food and eatable items, to make sure its optimum quality parameter in industrial manufacturing processing. So it is essential to develop a simple, rapid, cheap and sensitive electrochemical amperometric technique for the determination of thiocyanate.

## 3.2. Experimental Section

### 3.2.1. Materials:

HAuCl<sub>4</sub>, Ammonium thiocyanate and Dithizone (Sigma-Aldrich, USA), Ethanol (99.5%), potassium chloride and HCl (SRL, India), Tris Buffer (Merck India) were used as received, unless otherwise mentioned. The glassware used in the preparation of gold nanostructures were cleaned with freshly prepared aqua regia (3:1, HCl/HNO<sub>3</sub>) and rinsed comprehensively with ultrapure millipore water. Solutions used for electrochemical measurements were made with ultrapure millipore water (18.3 MΩ cm) and extensively purged with nitrogen gas before use.

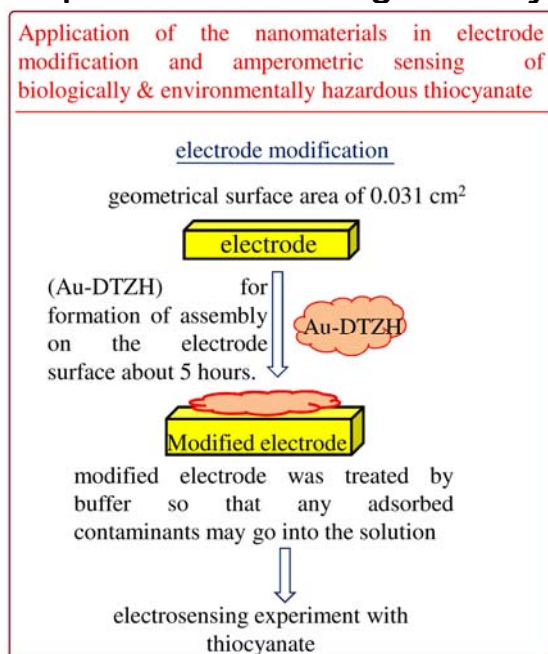
### 3.2.2. Photochemical Synthesis protocol of gold nanoparticles:



In a typical synthesis, 55 μL of HAuCl<sub>4</sub> (21 mM) was added drop wise in water alcoholic (40/60 v/v) solution of dithizone (68 mM) with vigorously stirring and at the same time, whole reaction content was irradiated with an ~ 260 nm UV-lamp (Black Ray, UVP, B-100) having a lamp power of ~100 watt/cm<sup>2</sup> and

operating in 240 V–50 Hz to undergo photochemical reduction of Au (III) about ~ 65 minutes [Gupta *et al.*, 2015]. The glass vial was kept at a distance of 16 cm from the light source to avoid unwanted heating of the solution. After completion of reaction, resulting solution was centrifuged at 12000 rpm for 6 min, to obtain the content of gold nanocrystals protected with dithizone and its oxidation product (DTZH). This process is repeated for twice. The obtained content was washed thrice 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 application/ experiments.

### 3.2.3. Fabrication of gold nanomaterials modified electrode for amperometric sensing of thiocyanate:



Prior to the surface modification of polycrystalline gold electrode (geometrical surface area of electrode 0.031 cm<sup>2</sup>) was kept in piranha solution (v/v 3:1 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) 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. Thoroughly cleaned polycrystalline gold electrode was soaked in ethanolic solution of hybrid nanomaterials (Au-DTZH) for formation



of assembly on the electrode surface about 5 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.

### **3.2.4. Instrumentation:**

Spectral changes were recorded using UV-visible spectrophotometer (Perkin Elmer Lambda-25 Germany) by using a quartz cell (10 mm path length), where the spectral background was subtracted using the same solvent. The microscopic morphological properties of samples were examined using transmission electron microscope (HRTEM Tecnai G2, 20 FEI Corporation Netherlands) operating at 200 kV by taking a few  $\mu\text{L}$  of the ultrasonicated test solution on the carbon-coated copper grids (obtained from Pelco International, USA). Hybrid nanomaterials material Au-DTZH adhere on electrode surface was examined by FESEM, JEOL JEM 6700F for surface morphology of electrode and energy dispersive X-ray spectroscopy (EDS) analysis was done with the same TEM instrument as a separate EDS detector was connected with that instrument. Cyclic voltammogram and amperometric analysis of modified electrodes were performed using computer controlled (GPES software) Autolab Potentiostat-Galvanostat (PG-STAT, 302, Netherlands).

A conventional three-electrode system consisting modified electrode 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 at room temperature  $27^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . 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).

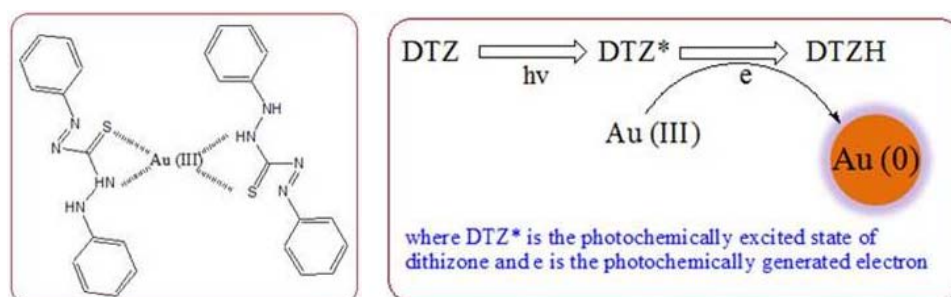
## **3.3. Results and Discussion**

### **3.3.1 Characterizations of photochemically synthesized gold nanoparticles by dithizone:**

The photoinduced reduction of Au (III) ions is accelerated by excitation of dithizone molecule with light. Here, the use of dithizone as a photo active can

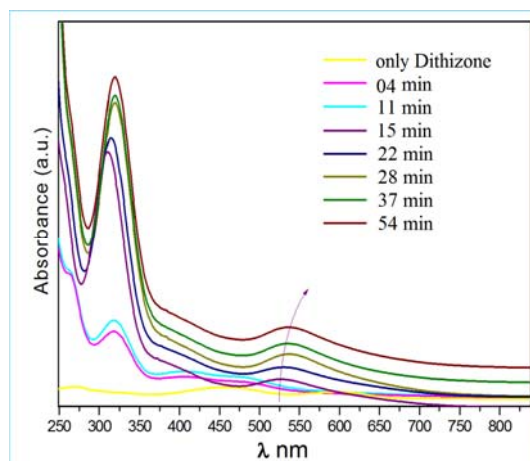


serve a dual purpose: It can initiate the reduction of Au (III) and simultaneously, it interacts with the nanomaterials surface to protect gold nanoparticles via interaction with sulphur and nitrogen hetero atom present in its molecular structure as shown in figure 3.2. Dithiozone molecule which is known for its strong complexation tendency with metal ions depending upon their charge/size ratio, which influence rate of nucleation of the metal nanoparticles formation [Eschwege *et al.*, 2011].



**Figure 3.2:** Reaction of Au (III) with dithiozone.

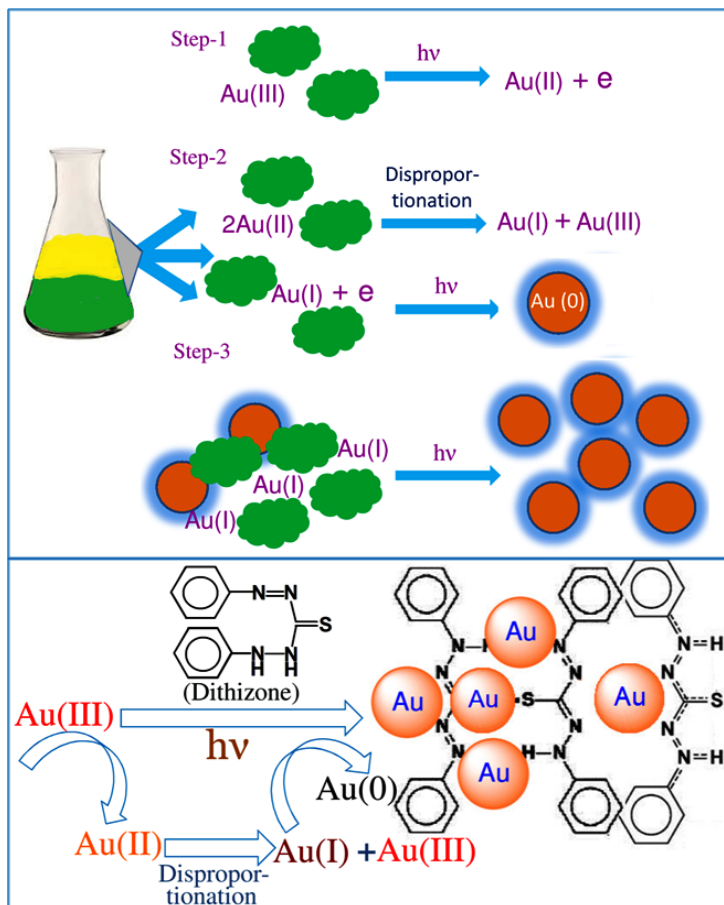
Progress of spectral changes was monitored by UV-visible spectrum as shown in figure 3.3 and feature gradually grows as a clear peak at ~528 nm corresponds to characteristic SPR band nano gold [Cui *et al.*, 2007].



**Figure 3.3:** Time dependent UV-visible spectrum of the photochemical assisted formation of gold nanoparticles.

Purposely, dithiozone (DTZ) and its oxidation product (DTZH) not only serves as a capping agent to selectively gold facets, but also coordinates/chelates with gold ions to form a complexes which further start reducing in presence of

photon/light. The recommended mechanism suggests 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 consequence in the autocatalytic growth [Gupta *et al.*, 2015].

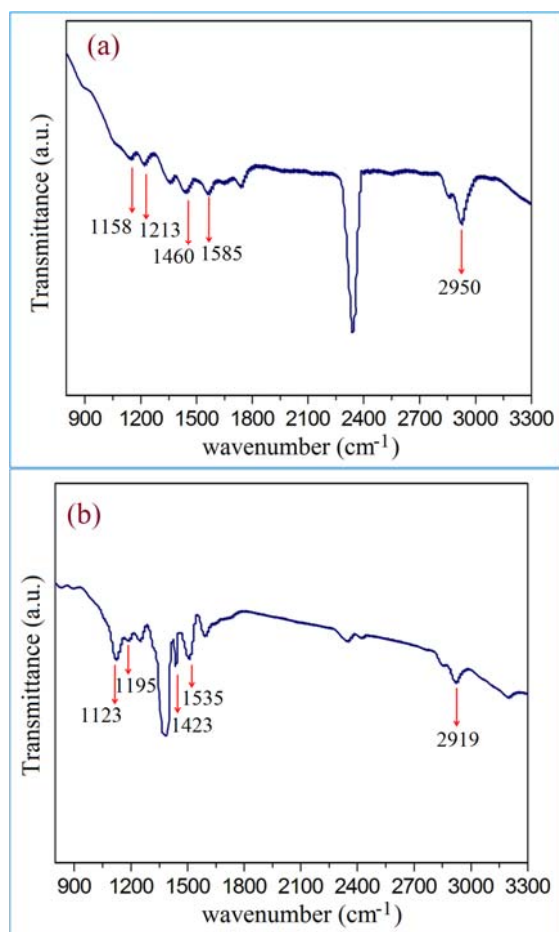


**Figure 3.4:** Reaction scheme for the photochemical step wise reduction of Au (III) to Au (0).

The photo chemical reduction of Au(III) to Au(0) is not a single step process, firstly Au (III) ions form complexes with the dithizone 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 reaction scheme

(figure 3.4) of formation of gold nanoparticles. Eschwege and their research group have studied extensively on oxidation product of dithizone. They have elucidated the several possible structures of oxidation products on the basis of X-ray crystallographic and DFT quantum computational techniques [Eschwege *et al.*, 2008; Meriwether *et al.*, 1965]. On the basis of previous documented result in literature related to oxidation product on dithizone we conclude that metal nanoclusters is stabilized/protected by that oxidized product via interaction with nitrogen and sulphur coordinating sites present in its structure [Eschwege *et al.*, 2011].

The FT-IR spectrum of DTZ was assigned from the literature for various functional groups present in its structure [Salih *et al.*, 1998].

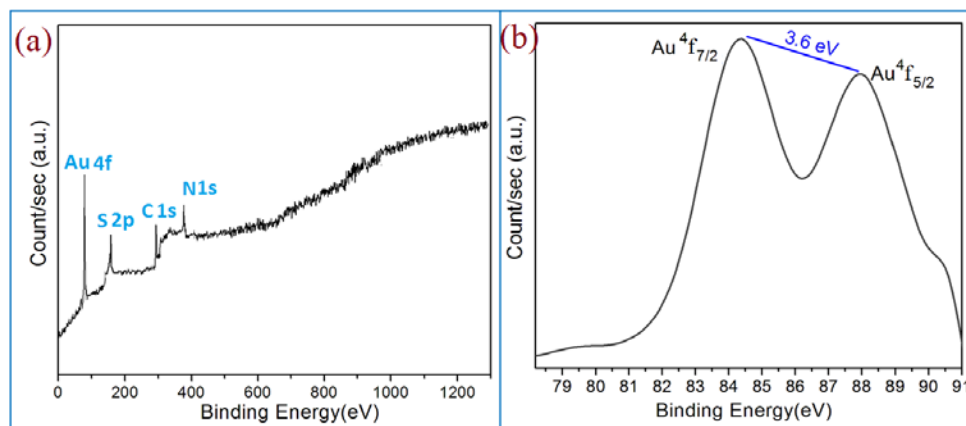


**Figure 3.5:** (a) FT-IR of DTZ (b) FT-IR of Au-DTZH

In FT-IR spectrum we focus on the regions where we can see some major changes of assign band of DTZ and Au-DTZH and thus highlighted the

spectrum in the region  $\sim 800\text{--}3300\text{ cm}^{-1}$  as shown in figure 3.5. Assignment of DTZ band indicates that N-C-S stretching at  $1158\text{ cm}^{-1}$ , C=S stretching vibration at  $1213\text{ cm}^{-1}$ , N-H bending at  $1460\text{ cm}^{-1}$ , N=N stretching at  $1585$ , N-H adjacent to C=S at  $2950\text{ cm}^{-1}$ . Interpretation of Au-DTZH spectrum reveals that peaks were observed at slightly lower frequency e.g.  $1123$ ,  $1195$ ,  $1423$ ,  $1535$  and  $2919\text{ cm}^{-1}$  respectively. Since gold having affinity towards nitrogen and sulphur hence if interaction takes place in C-N-Au, C-S-Au, then there might be shift in IR stretching frequencies. The decrease in assigned stretching frequency is due to the transfer of electron density from the sulphur and nitrogen atoms to gold, resulting in the electrostatic interaction with sulphur and nitrogen atom with gold which provides stability to gold nanostructures [Sharma *et al.*, 2004; Cui *et al.*, 2007].

The XP spectrum in figure 3.6 indicates  $4f_{7/2}$  peak at  $84.2\text{ eV}$  and a  $4f_{5/2}$  peak at  $87.9\text{ eV}$ , respectively confirms that Au is in zero oxidation state [Cui *et al.*, 2007]. 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).

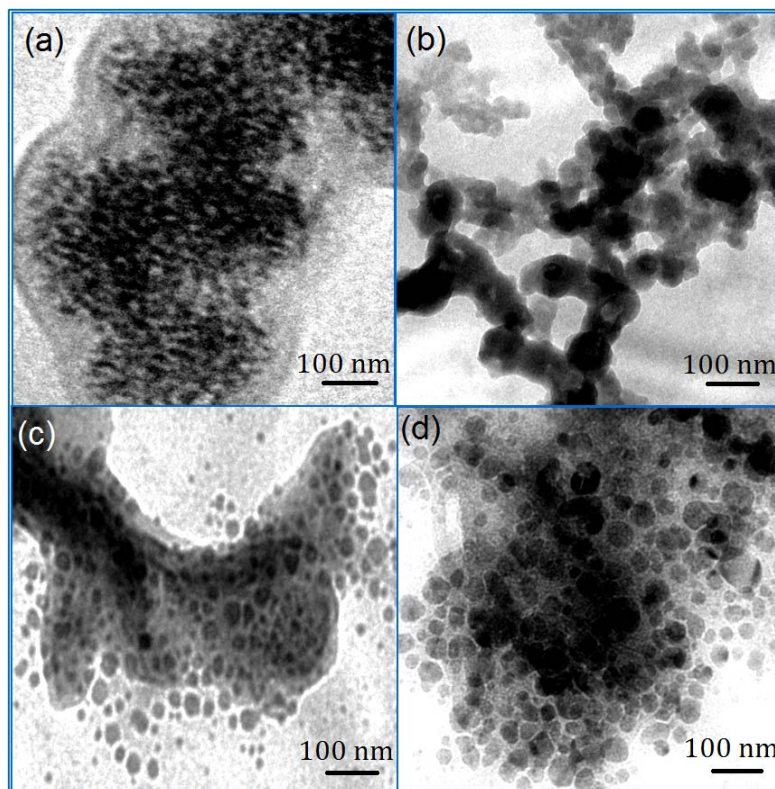


**Figure 3.6:** (a) XPS survey spectrum of Au-DTZH in full range (b) X-ray photoelectron spectra of Au (4f).

Binding energy observation, described here justify that dithizone molecule reacts with gold ions in a redox photochemical reaction yielding a gold colloid and oxidation product which are essentially dithizone and its fragments as revealed by infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS)

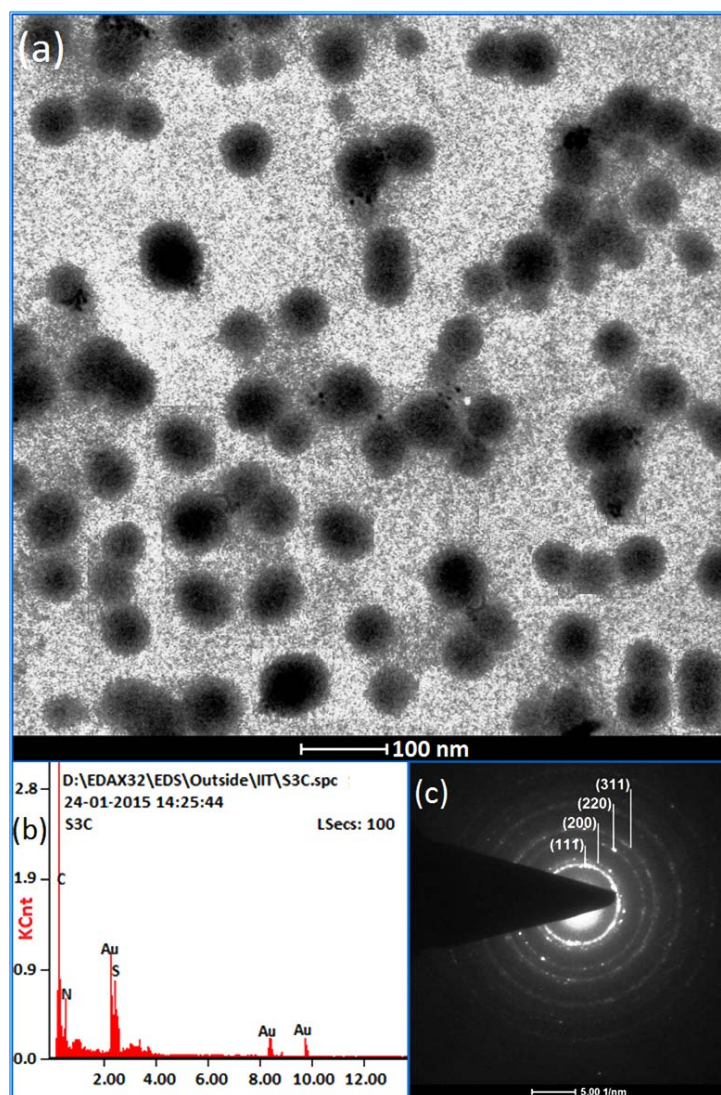
studies, that both the sulphur and nitrogen atoms get adsorb on surface of photo-reduced gold [Thomas *et al.*, 2000].

Photochemical formation of gold nano crystals w.r.t. time is pictorially micrographed in different time interval shown in figure 3.7. It is very interesting to note from TEM images that, w.r.t. time gold nano crystals are growing and after ~65 minutes we get a 40 nm average spherical sized gold nanoparticles as shown in figure 3.8 (a) and the corresponding EDX spectrum is shown as figure 3.8 (b). The selected-area electron diffraction (SAED) pattern confirms that the nanoparticles formed in this stage are not a single crystal. Scherrer ring of the (SAED) pattern obtained for the gold nano crystal, as shown in figures 3.8 (c) can be indexed as the (111), (200), (220), and (311) planes of a face-centered cubic (FCC) lattice of Au atom [Sharma *et al.*, 2004].



**Figure 3.7:** (a) TEM studies for the formation of nano gold w.r.t. time of light exposure a=09 min, b=17 min, c=28 min, d=54 min.



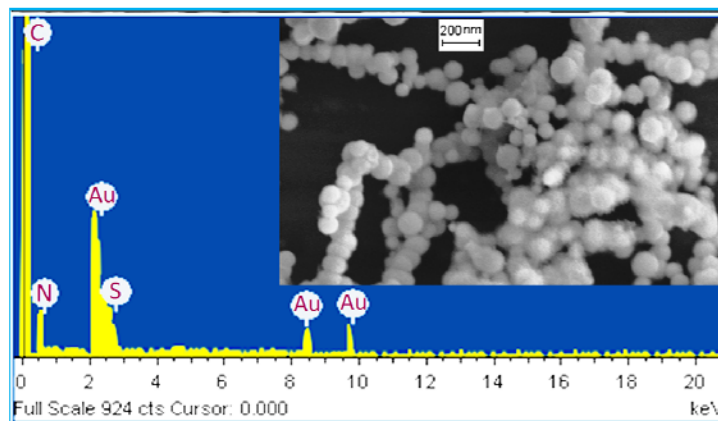


**Figure 3.8:** (a) TEM image of gold nanoparticles at the completion of reaction and the respective (b) EDX and (c) SAED pattern.

### 3.3.2 Amperometric sensing of thiocyanate by gold nanoparticles modified electrode:

To the best of our knowledge, no attempts have been made previously to synthesise such hybrid electroactive nanomaterials by photochemical method and its utilisation in electrode modification for amperometric sensing of thiocyanate, however dithizone modified nanomaterials have been used for optical and heavy metal ions electrochemical sensing applications [Zhai *et al.*, 1996; Pemberton *et al.*, 1981; Eschwege *et al.*, 2008]. Nanomaterials modified

electrode configuration developed can be used for environmental cleanup by converting hazardous unstable thiocyanate into non-hazardous compound.



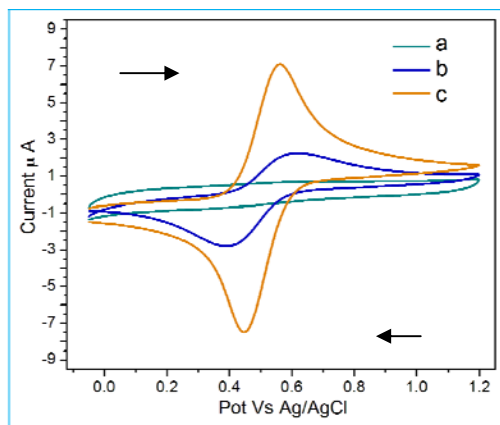
**Figure 3.9:** FESEM and EDAX image of chemically modified electrode Au-DTZH platform.

The assembled Au-DTZH on the gold electrode surface was examined by taking FESEM images as shown in figure 3.9. SEM image is showing uniform distribution of the Au-DTZH over the electrode surface.

Chemically modified electrode generally suffer leaching problem in the supporting electrolyte solution but remarkable properties of Au-DTZH is that it completely adheres on the electrode surface [Wang *et al.*, 2004; Gupta *et al.*, 2014]. Traditional approach for electroensing of analytes involves the use of redox mediators or enzyme to facilitate electrochemical electron transfer reactions. However, the utility of an enzyme-based modified electrode may be limited by the gradual fouling and loss of enzyme activity, also not reusable. Such problems may be minimised with the use of hybrid nanomaterials modified electrodes to decrease the overpotential and electrode fouling problem [Cheng *et al.*, 2002]. Fe (II)/ Fe (III) redox system shown in figure 3.10, reveals that modified electrode with Au-DTZH, efficiently facilitates the electron transfer as compared to bare electrode because it significantly enhances the current (3.10c vs. 3.10b). Au-DTZH modified electrode not only maximizes the availability of nanosized surface area for electron transfer but also provides better mass transport to the analyte [Wang *et al.*, 2013; Wittstock *et al.*, 2010]. Gold nanocrystal can also be characterized by its characteristics cyclic

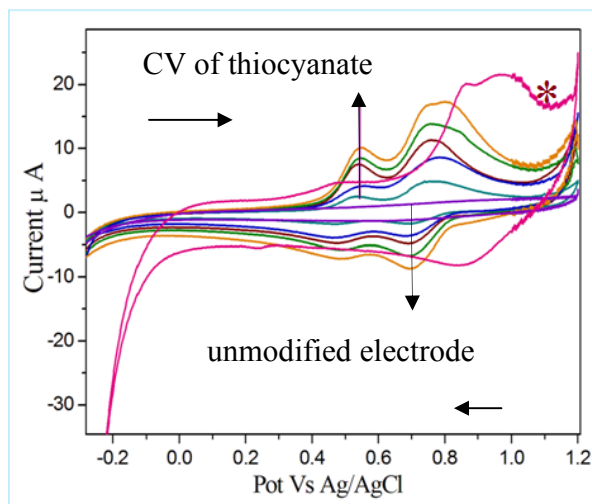


voltammogram. The modified electrode shows the gold oxidation peak at 0.947 V and corresponding gold oxide reduction peak at 0.82 which is attributed to the characteristics peak for nano gold as shown in figure 3.11 as asterisk marked curve [Yancey *et al.*, 2010].



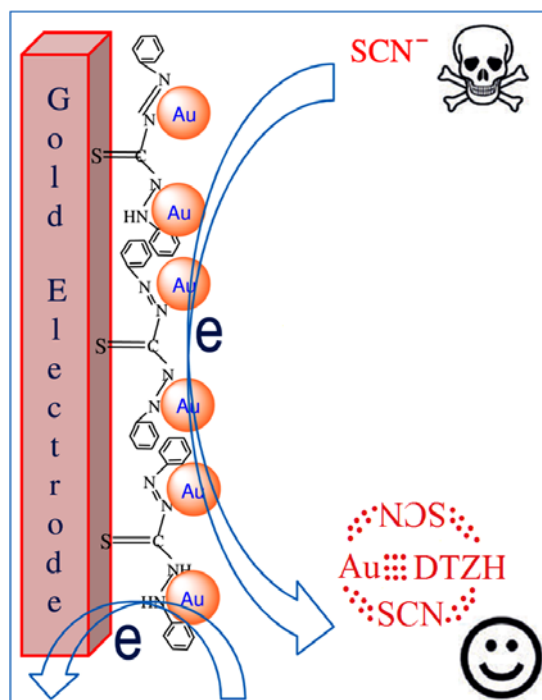
**Figure 3.10:** CV Response for (a) Bare electrode (b) CV of  $\text{Fe}(\text{CN})_6^{4-/3-}$  redox couple on without modified electrode (c) CV of  $\text{Fe}(\text{CN})_6^{4-/3-}$  redox couple on Au-DTZH modified electrode.

The direct oxidation of thiocyanate is difficult and it requires very high overpotential on unmodified electrodes and the electrodes often undergo fouling problem [Cheng *et al.*, 2003]. However, well-defined voltammetric responses are obtained for the successive thiocyanate addition suggests the Au-DTZH efficiently catalyze the oxidation process at modified electrode as shown in figure 3.11.



**Figure 3.11:** Cyclic voltammogram response of successive addition of thiocyanate in 0.1 M tris buffer at pH 7.2. Asterisk marked curve: characteristics CV of gold nano crystals.

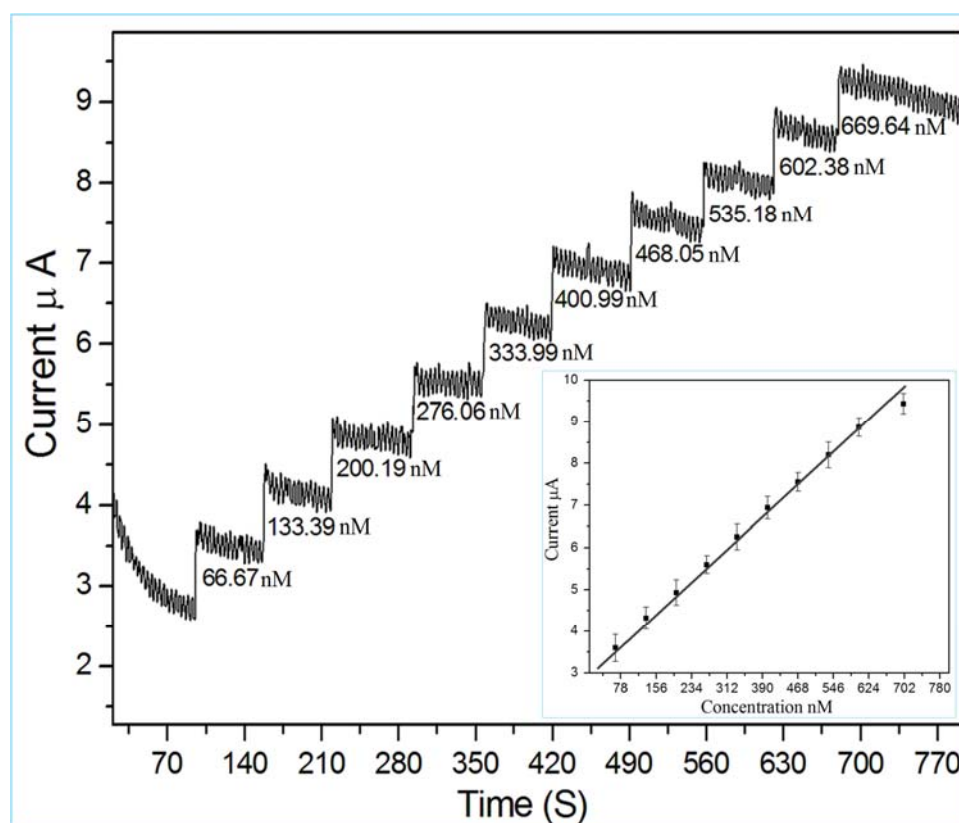
During the course of electrochemical reaction occurring at the electrode surface, thiocyanate may interact with electrochemically oxidize  $\text{Au}^+$  or  $\text{Au}^{+++}$  giving rise to two peaks at 0.547 V and 0.753 vs. Ag /AgCl. Thiocyanate ( $\text{SCN}^-$ ) which is similar to  $-\text{SH}$ , can interact strongly onto the of nano gold surface [Dawson *et al.*, 2000; Gupta *et al.*, 2015]. Electrochemistry behind the sensing of thiocyanate is possibly due to electrostatic interactions attributed as ( $\text{DTZH} \cdots \text{SCN}^{n-} \cdots \text{Au}^{m+} \cdots \text{SCN}^{n-} \cdots \text{DTZH}$  complexation) and conducting gold nanoparticles facilitates the efficient collection and transfer of electrons to the collecting electrode surface schematically shown in figure 3.12.



**Figure 3.12:** Schematic representation of the nano integrated platform of the Au-DTZH as a modified electrode for electro-sensing of thiocyanate.

One of the aims of the present finding is to utilize the hybrid nanomaterials modified platform for the amperometric sensing of trace levels of thiocyanate under optimized conditions at fixed potential. Since energetically favorable

peak at 0.547 V (less potential is required *c.f.* 0.753 volts), this is why we chose the oxidation potential i.e. 0.547 V vs. Ag /AgCl optimized for amperometric analysis of thiocyanate from CV studies. A systematic change in the chronoamperometric current was noticed after each addition of thiocyanate into the supporting electrolyte solution as shown in figure 3.13. Amperometric experiments were repeated four times with (Au-DTZH) modified electrode and experiments were highly reproducible. The mean deviation of the current values was within ~5 % for repeated chronoamperometric experiment. Analytical performance of the developed amperometric sensor shows excellent chronoamperometric response towards thiocyanate additions with sensitivity and limit of detection 0.016  $\mu\text{A}/\text{nM}$  and  $(23.348 \pm 0.506) \text{ nM}$  respectively.



**Figure 3.13:** Amperometric response at an applied potential of 0.547 V vs. Ag /AgCl for successive addition of thiocyanate in 0.1 M tris buffer at pH 7.2 under stirred condition. *Inset:* corresponding standard

addition calibration plot of chronoamperometric current vs. thiocyanate concentration.

We believe that the analytical approach presented with this hybrid nanomaterials can be extended as well, to other electrochemical application/ electron transfer studies. This presented method may offer a new cost-effective, rapid and simple solution to the inspection of  $\text{SCN}^-$  ion in saliva and environmental aqueous samples. The method is simple, sensitive, requires no labelling of the analyte with enzyme/biomolecule. Under optimized conditions, this method yields excellent response toward  $\text{SCN}^-$  since our presented approach is simple and of low cost, it can be extendable to prepare a thiocyanate amperometric sensor on disposable screen-printed electrode.

### **3.4. Concluding remarks of the chapter:**

We have successfully presented a outline on a photochemical assisted synthesis of gold nanoparticles 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-DTZH 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. To achieve commercial success, it is important to further research on modified screen printed electrode for electro-sensing of hazardous thiocyanate in real sample, which will be anticipated in future scheme. The sensing platform is highly sensitive and showed linear response toward thiocyanate additions with a sensitivity and limit of detection  $0.016 \mu\text{A/nM}$  and  $(23.348 \pm 0.506) \text{ nM}$  respectively at S/N (signal-to-noise ratio): 3.