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## Photochemical Assisted Formation of Silver Nanoparticles by Dithizone and its Application in Amperometric Sensing of Cefotaxime

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### Abstract:

This paper reports a convenient approach for one pot facile photochemical assisted synthesis of stable silver colloids (Ag) by using dithizone (DTZ)/its oxidation products (DTZH) as a reductant/particle stabilizer without any extra control viz. surfactant, pH etc. Although dithizone chemistry has been studied extensively, but it is surprising to note that there is hardly any report published so far on photochemical assisted formation of metallic nanomaterials using dithizone. We revisit the chemistry of dithizone based upon the previous reports and synthesize silver nanoparticles (Ag-DTZH) photochemically using dithizone. It is characterized by UV-visible spectroscopy, infrared spectroscopy, cyclic voltammetry, transmission electron microscopy, field emission scanning electron microscopy and X-ray photoelectron spectroscopy techniques. Nano silver formation by exposure of light is studied for various time intervals using UV-visible spectroscopy as well as TEM. This hybrid material derived from nanoscale silver protected with dithizone and its oxidation product has been further utilized for electro-sensing of Cefotaxime (CFX) a third-generation cephalosporin antibiotic drug. Also, a possible reaction mechanism for the formation of silver nanostructure has been proposed. Modified electrode with hybrid nanomaterial (Ag-DTZH) efficiently electro-catalyzes the oxidation of cefotaxime at the potential of 0.789 V vs.

AgCl/Ag and shows linear response toward cefotaxime sensing with  $0.244 \mu\text{A}/\mu\text{M}$  sensitivity and  $15.32 \text{ nM}$  limit of detection at S/N (signal-to-noise ratio): 3. Electrochemistry behind this sensing of cefotaxime is probably due to high connectivity throughout silver nanostructure (Ag-DTZH) capped with dithizone and its oxidation product over the modified electrode. It exhibits high electron transfer kinetics via interaction of Ag-DTZH with  $-\text{NH}_2$  and  $-\text{COOH}$  groups present in CFX. The present finding will open new avenues in the field of electro-sensing of analyte with this hybrid material modified electrode.

**Keywords:** Photochemical synthesis, Dithizone, Silver nanoparticles, Hybrid electrode materials, Modified electrode, Electro-sensing, Amperometric sensing of cefotaxime.

## 1. Introduction:

Photochemical assisted formation of metallic nanoparticles is versatile method for generating metal nanostructures which includes both academic as well as industrial interests [1-4]. Reducing the bulk size of metals to nanoparticles and further to few-atom nanoclusters, new properties appear which are different from bulk and allow fascinating applications in various areas. In past few decades, noble metal particles have been widely studied for their excellent properties (which are different from bulk) and their potential applications in catalysis, biological labeling, surface enhanced Raman scattering, microelectronics, optical, biological and magnetic devices etc. [5-8]. A lot of effort has been devoted to the synthesis and characterization of stable dispersions of nanoparticles made of silver, gold and other noble metals. Silver nanoparticles with different morphology and size have attracted a lot of interest because silver exhibits the highest electrical and thermal conductivities among all metals [8]. It is well known that preparation of silver nanoparticles with well-defined shape and well-controlled dimensions was more difficult than that of other nanoparticles due to the higher reactivity of silver compounds [9]. Rich varieties of recipes are now available in the literature for the synthesis of Ag nanoparticles. Several routes for chemical reduction of noble metal ions for preparing metallic colloids have been studied in the past few decades. A number of reports are available in the literature to synthesize nano silver by reducing silver salts as precursors by several methods [10-12]. Reduction routes involved in these studies may be classified in three broadly defined categories as (i) use of relatively strong reducing agents, such as sodium borohydride, hydrazine and tetrabutylammonium borohydride to prepare metallic nanomaterials, (ii) heating of solution of metallic salt with commonly used reductants such as glucose, sodium citrate, dimethylformamide, ascorbic acid, alcohols or polyols and its oxidation products may serve as a particle stabiliser and (iii) irradiation of the

solution containing noble metal ions with ultraviolet or visible light, microwave and ultrasound irradiation without using external reducing agent [13-17, 2].

In the present work we adopted relatively green route of synthesis of silver nanoparticles using dithizone, which have well established complexation and photochromic properties with silver as reported in the available literature [18-20]. It triggered us that silver ions may get reduced by exposing the photo-light by using dithizone [21-23]. An outline of reaction between silver ions and dithizone has been presented and further this synthesized hybrid material used as modification of electrode and electro-sensing of cefotaxime. We found hardly any evidence/ discussions of such photochemical synthesis scheme for preparation of silver nanomaterials by using dithizone and utilization as a modification of electrode for electro-sensing purposes. Design of analytical hybrid electrode material containing functionalized nanomaterials for electro-sensing of biological and chemical species has attracted increasing attention. Since hybrid nanomaterials modified electrode show excellent response towards electro-sensing of analyte. Chemically hybrid nanomaterials functionalized electrodes that lead to improve electrocatalytic properties have been actively studied, especially toward the development of matrixes for catalysis, sensing, and other electrochemical applications. Traditional approach for electro-sensing of toxicants involves the use of redox mediators/enzyme that can mediate the analyte to take part in electrochemical electron transfer reaction at electrode surface. However, the utility of an enzyme-based electrode may be limited by the gradual fouling of its surface/loss of enzyme activity and also not reusable. Such problems may be minimized with the use of hybrid nano materials modified electrodes to decrease the overpotential and electrode fouling problem. In the present study hybrid nano silver modified electrode is explored for the trace sensing of cefotaxime (CFX) a third-generation cephalosporin antibiotic drug. This drug is commonly used to treat infections caused by bacteria, mostly respiratory and urinary infections in

addition to protection of infections in the infected part of human body during surgery [24-25]. Because of its important role in numerous pathological processes, detection and quantification of CFX is an essential task in pharmaceutical and clinical procedures. Numerous methods have been reported for the quantification of CFX, including spectrophotometry and chromatographic techniques [26-27]. Although these methods give good sensitivity and selectivity but they have disadvantages including high costs, long analysis time, requirement of complex and tedious sample pre-treatment etc. On the other hand, electrochemical methods have attracted great interest because of their simplicity, rapidness and high sensitivity in the detection of analyte [28-33]. We demonstrated the electroensing of cefotaxime by nanomaterials modified electrode which showed upto nanomolar detection limit which is better than other polymer modified electrodes or spectrophotometric determination of CFX (generally reported in the range of  $\mu\text{M}$  viz.  $0.085 \mu\text{M} - 88 \mu\text{M}$  etc.). Such lower detection by using electrochemical technique is attributed to catalytic efficiency of nanosized materials which mainly depends on (i) the surface-to-volume ratio of the material and (ii) the electronic interactions between the material and the analyte, which results in the lower detection limit. Also facilitated electron transfer can help in better sensitivity for detection of CFX. However, our reported technique is sensitive, ease to handle and cheap for detection of analytes Hence Quantification of CFX drug is required not only in the field of human health but also for quality control in food and fermentation packaging industry to make sure their misuse in food preservation and processing.

## **2. Experimental Section:**

### **2.1 Materials:**

Silver Nitrate and Dithizone (Sigma-Aldrich, USA), Ethanol (99.5%), cefotaxime, potassium chloride and HCl (SRL, India), Tris Buffer (Merck India) were used in the present work. All the chemicals were used as received, unless otherwise mentioned. The glassware used in the

preparation of silver nanostructures were cleaned with freshly prepared aqua regia (3:1, HCl/HNO<sub>3</sub>) and rinsed comprehensively with ultrapure millipore water.

## 2.2 Instrumentation:

UV-vis absorption spectrum was recorded using Lambda-25 Perkin Elmer (Germany) spectrophotometer by using a quartz cuvette having optical path length of 1 cm. The microscopic 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 test solution on the carbon-coated copper grids (obtained from Pelco International, USA). Modified electrode with hybrid material Ag-DTZH was examined by FESEM, JEOL JEM 6700F. 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  $25^\circ\text{C} \pm 2^\circ\text{C}$ . Tris buffer (pH 7.2) was used as a supporting electrolyte and the scan rate was kept 50mV/sec for each measurement. Elemental analysis was recorded with X-ray photoelectron, kratos analytical instrument, Shimadzu group company Amicus XPS (UK).

## 2.3 Synthesis of silver nanoparticles:

In a typical synthesis of the silver nanoparticles 40  $\mu\text{L}$  of AgNO<sub>3</sub> (17 mM) was added drop wise in water alcoholic (40/60 v/v) solution of dithizone (52 mM) with vigorously stirring condition and at the same time, whole reaction content was irradiated using a 100W sun lamp having spectral output of  $>360\text{ nm}$  to undergo photochemical reduction of Ag (I) for  $\sim 2$  hrs. The glass vial was kept at a distance of 10 cm from the light source to avoid heating of the solution. After completion of reaction, resulting solution was centrifuged at 12000 rpm for 6

min, to obtain the content of nanosilver protected with 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) silver, nitrate ions etc and other impurities. Then, the obtained content is redispersed in desired amount of ethanol so that can be used for further application/ experiments.

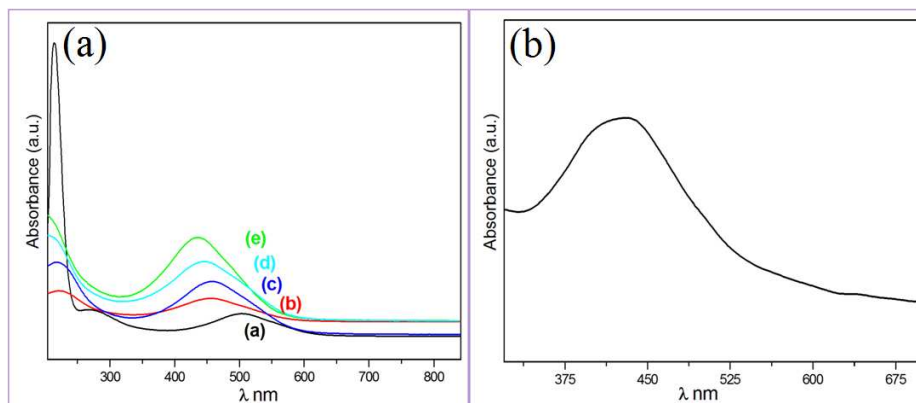
#### **2.4 Electro-sensing of cefotaxime with Ag-DTZH modified electrode:**

A polycrystalline gold electrode with a geometrical surface area of  $0.031 \text{ cm}^2$  was used as a substrate for fabrication of nanostructured platform with prepared hybrid nanomaterial. Thoroughly cleaned polycrystalline gold electrode was soaked in ethanolic solution of hybrid nanomaterial (Ag-DTZH) for formation of assembly on the electrode surface for 5 hours. Solutions used for electrochemical measurements were made with ultrapure millipore water ( $18.3 \text{ M}\Omega \text{ cm}$ ) and extensively purged with nitrogen gas before use.

### **3. Results and Discussion:**

Although dithizone chemistry has been studied so extensively, but it is surprising to note that there is hardly any report has been published so far on photochemical assisted formation of metallic nanomaterials by using dithizone [34-36]. The key point here is that dithizone itself, an efficient reductant of silver in the presence of photo light and no additional reductant/stabilizer is required for such typical synthesis indicated by our experimental observations. Facile photochemical method of preparing highly dispersed silver nanocrystals by reducing silver ions with dithizone silver nanoparticles having spherical morphology were formed in a few hours.



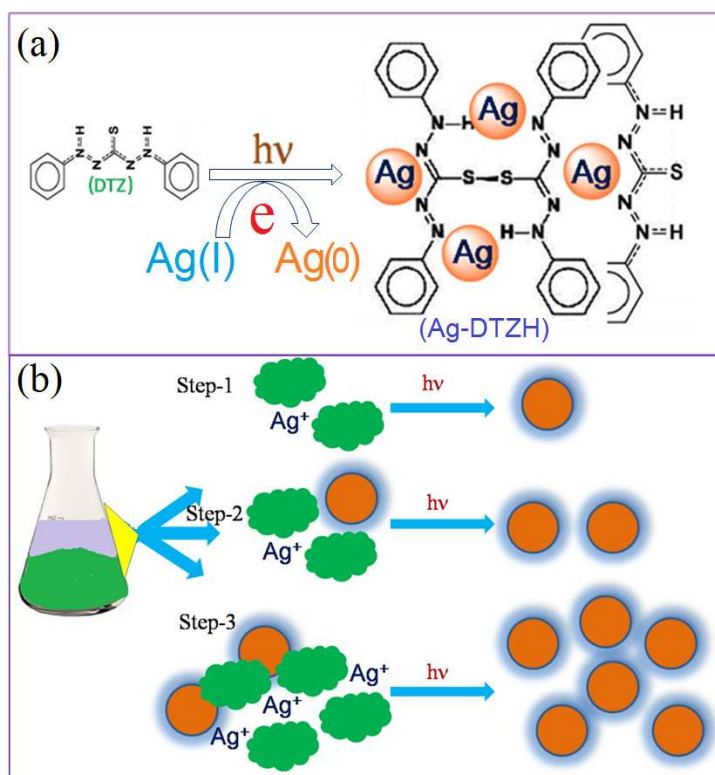


**Figure 1.** (a) Time dependent UV-vis spectrum of the formation of nanosilver, a-only dithizone, b-at 6 min, c-at 16min, d-30 min, e-55min, (b) UV-vis spectrum of the nanosilver at the completion of reaction (after 2 hrs).

The kinetics of the initial stage of formation of silver nanoparticle has been monitored by UV-visible absorbance spectroscopy. We focused on the initial stages of the reaction, when nucleation is the dominating process. Progress of reaction was monitored by UV-visible spectra as shown in figure 1(a) and feature gradually grows as a clear peak at  $\sim 430$  nm corresponds to characteristic SPR band nano silver [6]. Dithiozone molecule which is known for its strong complexation tendency with silver, which affects the rate of nucleation of formation of the silver nanostructures [35]. Specifically, dithiozone and its oxidation product not only serves as a capping agent to selectively bind nano silver facets, but also coordinates with  $\text{Ag}^+$  ions to form a variety of complexes which further reduces silver ions in presence of photo-light. Plausible mechanism of the formation of the nanoparticle has been suggested with chemical reactions as shown in figure 2 (a).

Von Eschwege et. al. [20] has studied extensive study on oxidation product of dithiozone. They have elucidated the several possible structures of oxidation products on the basis of X-ray crystallographic and DFT quantum computational techniques. Dithiozone-disulfide, dehydro-dithiozone, etc. oxidation product may adsorb on the surface of nano silver via

attachment with nitrogen, sulphur atom present in its structure and protect silver nanoparticles for agglomeration.

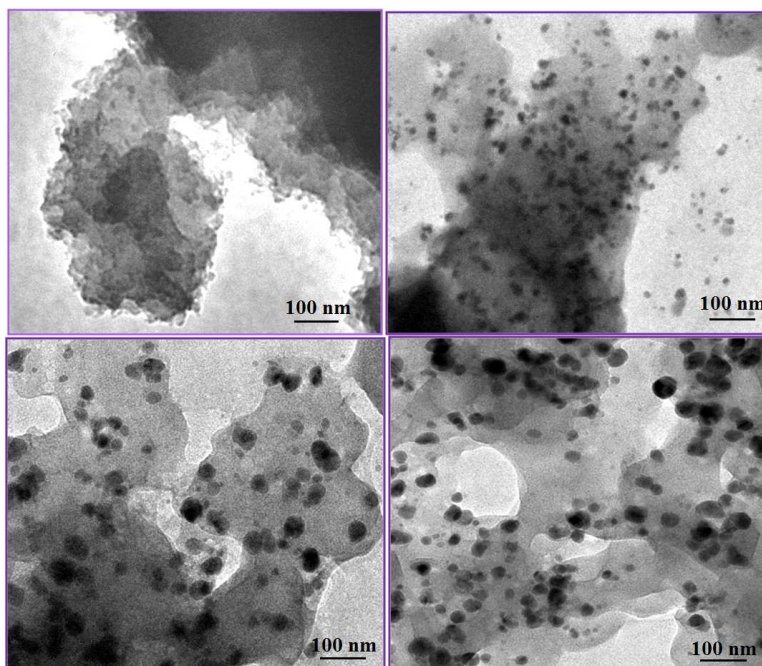


**Figure 2. (a)** Reaction scheme for the photochemical assisted formation of nano silver by dithizone where photochemically generated electrons can easily captured by  $Ag^+$  ions to generate silver nanostructures via photo-reduction. **(b)** This figure schematically illustrates that how silver nanoparticles is protected by DTZH matrix and how nucleation and growth phenomenon promotes the silver nanoparticles formation within DTZH matrix.

Firstly silver ions form complexes with the dithiozone molecule and this coordination significantly reduces the concentration of free  $Ag^+$  ions, thus slowing down the reduction step and enabling a kinetic control which favours nanoparticles formation [37-38]. With the irradiation of photo light, dithiozone molecules form its oxidation product, thereby silver ions get reduced and co-adsorbed onto the surface of silver nanoparticles. The production of metal colloids by the reduction of their ions in solution involves two distinct stages nucleation and growth respectively. The relative rates of these two processes determine the final size

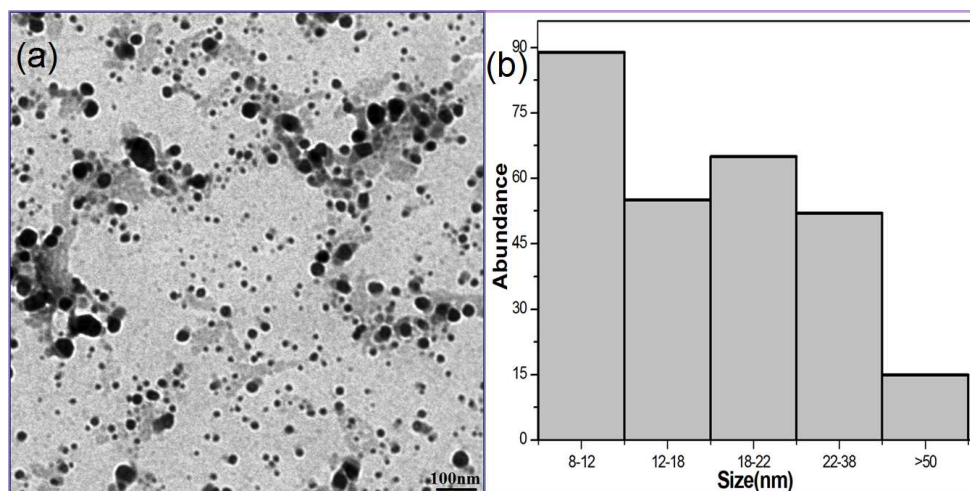
distribution of the nanoparticles. Oxidizing dithizone acts as nucleation centers for silver nanoparticles growth (Step-1), photochemically assisted formed silver nanoparticles by dithizone acts as a seed for further growth of silver nanoparticles (Step-2) and by repeating steps 1 and 2, several silver nanoparticles starts forming within DTZH matrix (Step-3) as shown in figure 2b. where, green cartoon stands for dithizone, orange for nanosilver and light blue for capped product to protect nanosilver respectively. The most notable feature of this approach is the in-situ stabilization of silver nanoparticles with dithizone and its oxidation products. When the silver ions are reduced into metallic silver, the silver atoms first aggregate into clusters. The clusters are very small in size and have extremely high surface energy, which drives them to aggregate into larger particles. In many cases, a surfactant is added into the synthesis system to stabilize silver nanoparticles and prevent them from further aggregating. In this case when the silver nanoparticles are formed, dithizone and its oxidation products molecules adsorbed on the nanoparticle particle surface and stabilize them in nanosize and keep them from further aggregating by reducing their surface energy.

We studied the TEM images for the nano silver formed by exposure of light for various time intervals as shown in figure 3 to show the nano silver formation and effect of exposure of photo-light.



**Figure 3.** (a) TEM studies for the formation of nano silver with respect to time of light exposure a=6 min, b=16 min, c=30 min, d=60 min.

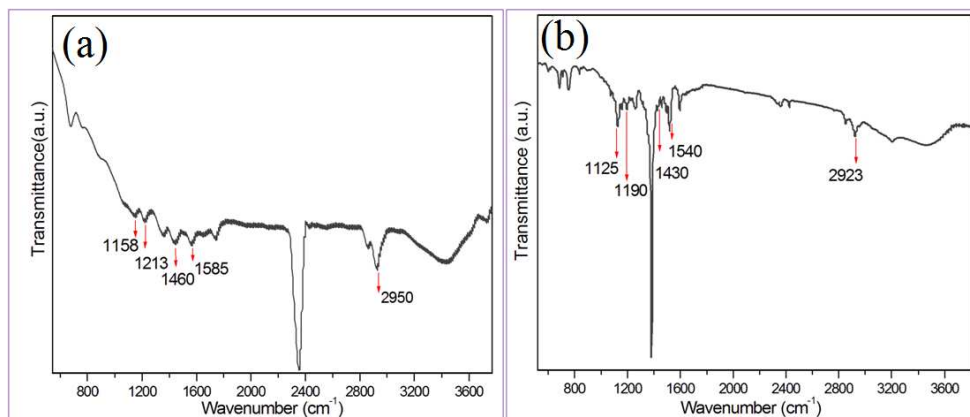
It is very interesting to note from TEM images that, w.r.t. time nanosilver are growing and after some time remains constant (>1 h). We also performed the chemical test, whether all  $\text{Ag}^+$  ion reduce into  $\text{Ag}(0)$  or not after 2 h of reaction time. For this we took the test colloidal solution of prepared silver nanomaterial and introduced chloride ions solution externally. We did not observe any white/cloudy precipitate of  $\text{AgCl}$ , which suggested that all  $\text{Ag}^+$  ions have been reduced into  $\text{Ag}(0)$ . It is also observed that the 2 h exposure of light for the given concentration is sufficient for the nano silver formation.



**Figure 4.** (a) TEM image of nanosilver at the completion (after 2 hrs.) of reaction (b) corresponding size distribution of nanoparticles.

One can get silver nanoparticles protected with dithizone and its oxidation product with this presented reaction scheme. At the completion of the reaction we have taken TEM images as shown in figure 4 (a). Most of the nanoparticles size lies in the 8-12 nm and 18-22 nm as shown in size distribution figure 4(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 silver nano crystal as shown in associated content of SI-1, can be indexed as the (111), (200), (220), and (311) planes of a face-centered cubic lattice of Ag atoms.

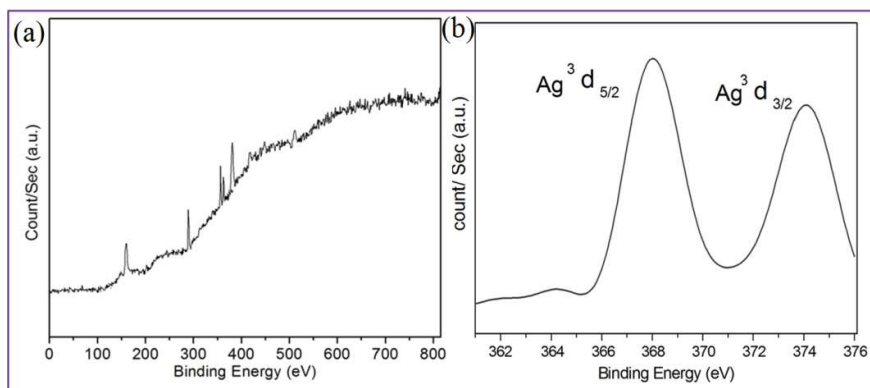
The FT-IR spectrum (figure 5) of dithizone was assigned from the literature for various functional groups present in its structure [39]. This shows N-C-S stretching at  $1144\text{ cm}^{-1}$ , C=S stretching vib at  $1213\text{ cm}^{-1}$ , N-H bending at  $1497\text{ cm}^{-1}$ , N=N stretching at  $1590$ , N-H adjacent to C=S at  $2961$  was appeared respectively. In the FT-IR spectrum of Ag-DTZH, these peaks were observed at slightly lower frequency e.g.  $1125$ ,  $1190$ ,  $1430$  and  $2923\text{ cm}^{-1}$ , respectively. Silver having affinity towards nitrogen and sulphur hence if interaction takes place in C-N-Ag, C-S-Ag, then there might be shift in IR stretching frequencies.



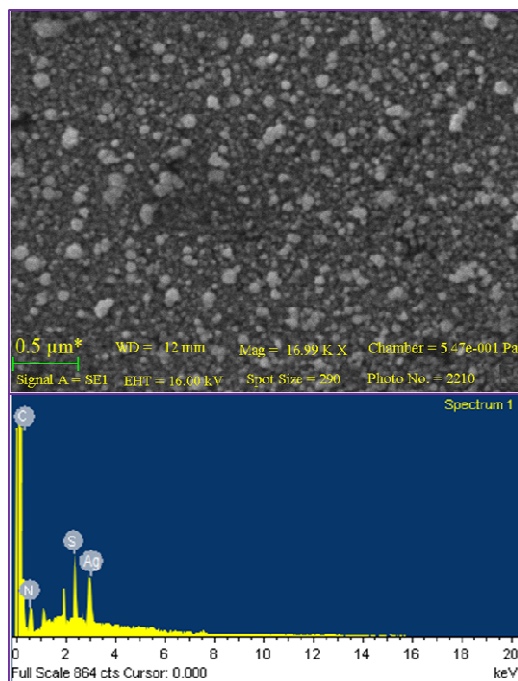
**Figure 5.** (a) FT-IR of DTZ (b) FT-IR of Ag-DTZH

The decrease in assigned stretching frequency is due to the transfer of electron density from the S and N atoms to silver atom, resulting in the electrostatic interaction with sulphur and nitrogen atom with silver which provides stability to silver nanostructures.

Photo-reduced silver show peaks in XPS spectrum as shown in figure 6 at 374.1 and 368.1 eV which can be assigned to  $\text{Ag}^3 d_{3/2}$  and  $\text{Ag}^3 d_{5/2}$ , respectively, this confirms that silver is in zero oxidation state (reduced silver). From the experimental result described here in this paper we see that dithizone molecule reacts with silver ions in a redox reaction yielding a silver colloid and products which are essentially dithiozone and its fragments, as revealed by infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) studies, both the sulphur and nitrogen atoms get adsorb on surface of Ag (0) [40].



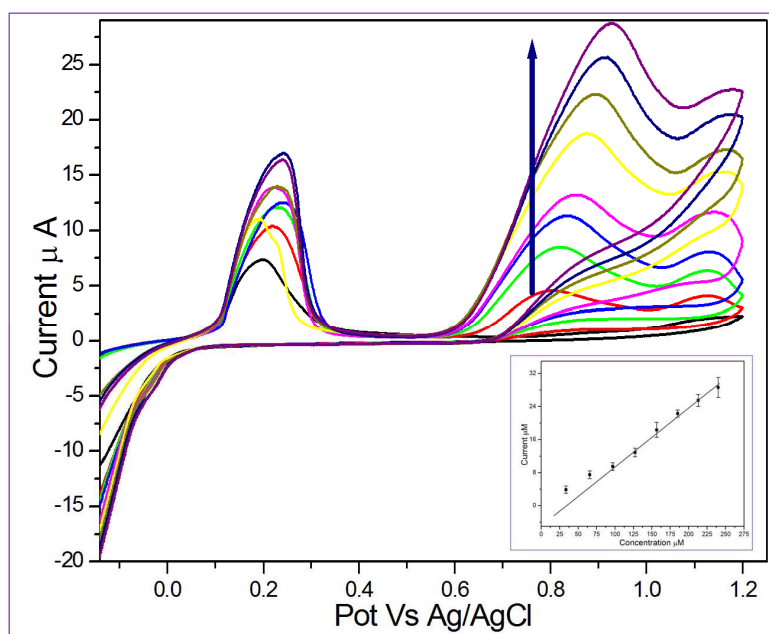
**Figure 6.** (a) XPS survey spectrum of Ag-DTZH in full range (b) X-ray photoelectron spectra of Ag (3d).



**Figure 7.** FESEM and EDAX image of modified electrode Ag-DTZH platform.

The modified electrode with hybrid silver nanomaterial is represented as Ag-DTZH. This assembled on the polycrystalline gold electrode surface very easily via interaction with nitrogen and sulphur [41]. The assembled Ag-DTZH on the gold electrode surface was examined by taking FESEM images as shown in figure 7. SEM image is showing uniform distribution of the hybrid nano silver over the gold electrode surface, however, some agglomeration of the nanoparticles occurred while modification of electrode (increase in particle size observed). The modified electrode shows peak at 0.188 V, it is attributed to the Ag-DTZH characteristics peak as shown in SI-2 for silver oxidation [42]. The modified electrode does not show any characteristic signature in the potential window 0.6 V to 1.2 V. However, well-defined voltammetric responses are obtained for the oxidation of CFX peak at  $\sim 0.789$  (figure 8) suggest the Ag-DTZH efficiently catalyze the oxidation process at modified electrode.

DTZH-Ag based modified electrodes show excellent response on successive addition of cefotaxime in the range of  $\sim 30 \mu\text{M}$  to  $\sim 240 \mu\text{M}$  as shown in figure 8 (inset). The direct oxidation of such bigger molecule like cefotaxime on unmodified electrode requires large overpotential and the electrodes often undergo fouling by the oxidation/bi products. In our adopted method, we did not use any external reducing agents like  $\text{NaBH}_4$ ,  $\text{NH}_2\text{NH}_2$  etc. for reduction of silver ions which is advantage of this synthesis. Generally such reducing agent is required to prepare such metallic nanomaterials but excess or unreacted  $\text{NaBH}_4$ ,  $\text{NH}_2\text{NH}_2$  may cause the change in pH of the resultant colloidal solution and also the counter ions e.g. unused  $\text{BH}_4^-$  may get adsorb and contaminate on the nanomaterials surface. If nanomaterials surface is contaminated with some counter ions then it also interferes in the electro-analysis of analytes which is immobilized on electrode surfaces for the use of electro-sensing devices.

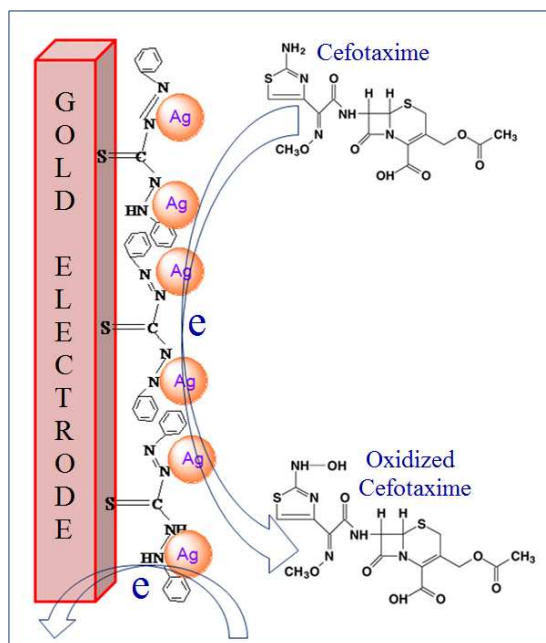


**Figure 8.** Cyclic voltammogram response of successive addition of cefotaxime in 0.1 M tris buffer at pH 7.2.

The electro-sensing behind CFX molecule is that having  $-\text{COOH}$  and  $-\text{NH}_2$  functional group, which probably get electro-oxidised by using hybrid nanomaterials Ag-DTZH on modified electrode. Silver nanoparticles enhance the electrode conductivity and facilitate the electron



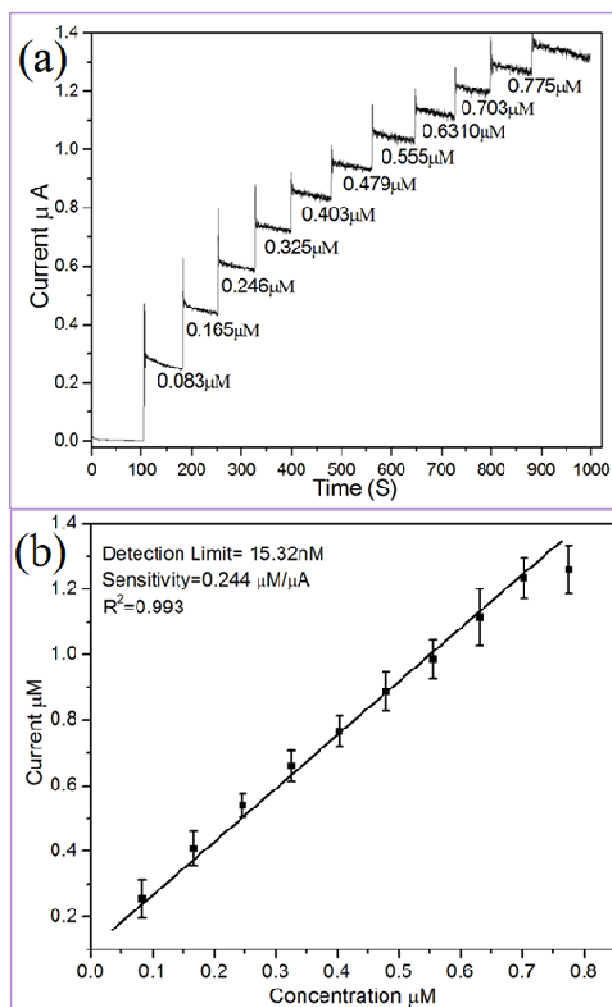
transfer thus improving the analytical selectivity and sensitivity towards the detection of analyte [43]. It seems from the molecular structure of dithizone that sulphur and nitrogen hetro atom served as a bridging to electrode surface as shown figure 9 of schematic representation of modified electrode with Ag-DTZH [42, 44].



**Figure 9.** Schematic representation of the nano integrated platform of the Ag-DTZH as a modified electrode for electro-sensing of cefotaxime.

One of the aim of the present finding was to utilize the nanoparticles based platform for the amperometric sensing of trace levels of CFX under optimized conditions at fixed potential. Oxidation potential, i.e. 0.789 V vs. AgCl/Ag was selected for amperometric analysis of cefotaxime from CV studies under optimized conditions. A systematic change in the chronoamperometric current was noticed after each addition of cefotaxime into the supporting electrolyte solution as shown in figure 10(a). Amperometric experiments were repeated four times with (Ag-DTZH) modified electrode and experiments were highly reproducible. We believe that the analytical approach presented in this paper can be extended to other toxicants analytes and this amperometric technique becomes a very effective route

for quantification of the sample. Efforts in this direction are currently being done in our laboratory. The mean deviation of the current values was within  $\sim 6\%$  for repeated chronoamperometric experiment and detailed investigation of mechanism of electrocatalysis of modified electrode with Ag-DTZH, achieving to low detection limit and electroanalytical determination of cefotaxime in real systems is likely to be addressed in our future studies.



**Figure 10.** (a) Amperometric response at an applied potential of 0.789 V vs. Ag/ AgCl for successive addition of cefotaxime in 0.1 M tris buffer at pH 7.2 under stirred condition. (b) Corresponding standard addition calibration plot of chronoamperometric current vs. cefotaxime concentration.

Analytical performance of the developed amperometric sensor shows excellent chronoamperometric response towards cefotaxime additions with a sensitivity and limit of detection  $0.244 \mu\text{A}/\mu\text{M}$  and  $15.32 \text{ nM}$  respectively, as shown in figure 10 (b). The presented strategy could afford a simple and applicable way for CFX quantification with appropriate sensitivity and good reproducibility.

#### 4. Conclusions:

This article reports a systematic study of the time dependent growth of silver nanocrystals. The key to the success of this synthesis is to photo-irradiation of the silver ions using dithizone without introducing additional stabilizers. We limit ourselves to general suggestions, that silver nanoparticles has been synthesized photochemically by using dithizone, that seems to be consistent with the results of the present studies presented in this article. The prepared hybrid nanomaterials Ag-DTZH having potentially high surface areas, high electroactivity and connected structures could find use as a new class of hybrid nanomaterials for electro-sensing applications and fabrication of sensing devices. The sensing platform is highly sensitive and showed linear response toward cefotaxime additions with a sensitivity and limit of detection  $0.244 \mu\text{A}/\mu\text{M}$  and  $15.32 \text{ nM}$  respectively at S/N(signal-to-noise ratio): 3. The method described in this work offers a selective, sensitive, enzyme and mediator less electroanalytical determination of cefotaxime. It is believed that the publication of present finding will strongly promote the fast development of the photochemical driven synthesis of other noble metallic nanomaterial by dithizone and its application in modified electrode chemistry.

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