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A Novel Poly (Taurine)/Nano Gold Modified Electrode for the Determination of Arsenic in Various Water Samples

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Poly taurine nano gold film has been fabricated on glassy carbon electrode (GCE) and ITO using cyclic voltammetry. Fabricated poly taurine nano gold film modified GCE has been successfully employed for the detection of arsenic in lab analysis and real drinking water sources like mineral water, spring water and tap water samples etc. The poly taurine nano gold film modified GCE successfully detects the arsenic in the linear range of 6 to 28 µM with the detection limit of 0.46 µM in lab samples. Also, the proposed film successfully detects the arsenic in drinking water sources like spring water samples (1 and 2) in the linear range of 10 to 34 µM with a detection limit of 0.91 µM, 5to 28 µM with a detection limit of 0.58 µM, respectively.

Keywords: Taurine, gold nanoparticles, arsenic, cyclic voltammetry, differential pulse voltammetry

1. INTRODUCTION

Arsenic is a poisonous substance and widely distributed in the earth crust. In the ground water arsenic exists in many chemical forms such as arsenite and arsenate. In general, arsenic is toxic and direct exposure to humans, animals and ecosystem [1, 2]. It is also associated with cancer in lungs, skin, and bladder and kidney diseases. India, China, Bangladesh, Mexico, Argentina and the USA and many other countries in the world reported the arsenic contamination in the ground water [3]. According to the world health organizations (WHO) report [4], the maximum permissible contamination of arsenic in the drinking water level is 10 ppb.

So, we need a sensitive and reliable method for detection of arsenic**.** Analytical methods, such as atomic absorption spectrometry, atomic fluorescence spectrometry and inductively coupled plasma with mass spectrometry have been used for the accurate detection of arsenic at the laboratory levels [5-

8]. However, these methods are expensive and need to be done in a large scale experiments and the well trained technicians are needed to handle these instruments. Comparing with above methods, we need a simple, highly sensitive and low cost instrument for the detection of arsenic. Electrochemical methods are found to be convenient, reliable, cheapest and important one for the arsenic detection [9-12]. For example, inorganic arsenic species have been detected in the sea water using a stripping chronopotentiometric (SCP) method [13]. In virtue of the electrochemical deposition, we can realize the successful determination of arsenic with a low detection limit, but it suffers from the interference by various metals like Cu, especially when it presents in a large amount in water systems. Copper can be easily co-deposited with the arsenic at the certain potential. Presence of copper can easily reduce the signal of the arsenic [14-16].

Taurine is a well-known dissociated amino acid, which exhibits important physiological functions and pharmacological characteristics. It has widely been used as food nutrition enhancer and common drug [17]. Various types of electrochemical analysis have been reported for the detection and determination of arsenic [18]. Compare with various analytical techniques, modified electrodes shows a keen special attention for the detection and determination of important chemical compounds due its easy preparation method, compatibility, reliability and wide electro analytical applications [19-30]. For example, arsenic oxidation at platinum electrode [31], detection and determination of copper and arsenic by stripping voltammetry [32] and poly (3, 4-ethylenedioxythiophene) (PEDOT) film modified electrode to monitor iodide and arsenic sensing were reported [33]. These reports clearly show the importance and the pathway for the arsenic detection using electrochemical methods. Therefore, in this report, we have attempted to fabricate a simple, rapid and reliable film for the sensitive detection and determination of arsenic at the micro levels in both the lab and real samples. Novel Poly (Taurine)/Nano Au film has been fabricated on GCE and ITO by using cyclic voltammetry (CV). Surface morphological study has been analyzed using field emission scanning electron microscopy (FE-SEM). Fabricated poly taurine/Nano gold film modified GCE showed significant response for the detection of arsenic in lab and real samples using differential pulse voltammetry and impedimetric analysis.

2. MATERIALS AND METHODS

2.1 Apparatus

Electrochemical measurements like cyclic voltammetry (CV) was performed by a CHI 1205A electrochemical analyzer and differential pulse voltammetry (DPV) was performed by CHI 750A analyzer. A conventional three-electrode cell were used at room temperature with glassy carbon electrode (GCE) (Surface area =0.07cm^2) as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphological of the film was studied by SEM (Hitachi S-3000H, Japan) and AFM (Being Nano-Instruments, CSPM- 4000, and China). Indium tin oxide (ITO) thin film coated glass electrodes have been used for SEM and AFM analysis. Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co KG, Germany).

2.2. Reagents

Potassium tetra chloro Aurate (III) was purchased from Stem chemicals (USA) and Taurine and Sodium meta arsenite were purchased from Sigma – Aldrich (USA). The other chemicals (Merck) that are used in this investigation were of analytical grade (99%). All the solutions are prepared using double distilled water. Electro catalytic studies were carried out in phosphate buffer solution (PBS) of pH 7.0 was prepared from Na_2HPO_4 (0.05 M) and NaH_2PO_4 (0.05 M). While performing experiments pure nitrogen gas was passed through all solutions. Danshui river water (Taiwan (R.O.C)) obtained for the river water analysis. This water has been filtered several times before the analysis. Tap water was obtained from Taipei Water Department (www.twd.gov.tw). Tap water has been filtered several before the analysis. Two types of natural drinking spring water bottles obtained from local convenient store. Drinking spring waters directly employed without any further pretreatment process. Drinking spring water sample (1) contains, ((Ca^+) 8–20, (Mg^+) 2–6, (Na^+) 6–15, (K^+) 0.3–2 and (SiO_2) 23–35 ppm; pH: 6.5–8.5). Drinking spring water type (2) contains Ca = 14.8 – 27.6, Mg = 8.8 – 16.4, Fe < 0.018, F < 0.1, and Na = 2.7–11.3 mg/L; pH 6.0–8.0). As (III) was dissolved in this samples and the stock solution have been prepared and these solutions directly injected in the pH 7.0 PBS for the analysis.

2.3. Modification of the electrodes

Prior to the electrodeposition process, the bare glassy carbon electrode was initially polished with 0.05µm alumina powder on BAS polishing pad and ultrasonically cleaned in water for a minute. The electrode was then successfully washed with double distilled water and used. The glassy carbon electrode was modified by electrochemical deposition of gold nanoparticles (10^{-3} M) and Taurine (2mM) in PH 7 solution, with a potential scan between -0.5 and 1.2 V, at the scan rate of 0.1 V s^{-1} for ten cycles. The modified electrode was then rinsed with double distilled water and used for further electrochemical studies.

3. RESULTS AND DISCUSSION

3.1 Characterization of poly taurine nano gold film

Figure 1(A) displays the electrochemical deposition process of poly taurine nano gold film which begins at the negative potential of -0.5V and ends in the positive potential 1.2 V at the scan rate of 0.1 V/s for ten cycles. Here the reduction of Au takes place at the potential of 0.51 V and continues up to 1 V and at the higher reduction peak current occurred at the 0.5 V in the first scan process. This shows the initial nucleation of Au at the electrochemical deposition process, respectively. For the continuous cycles, this peak current decreases with the potential shift and initiates at 0.48 V. During the electrochemical deposition process, the continuous growth of the reduction and oxidation peak currents of Au validates the electrochemical deposition process of poly taurine film on the GCE surface. One obvious anodic wave at 0.96 V and two cathodic waves at 0.16 and -0.26 V are seen for the deposition of poly taurine. An increase in cycle number results in the enhancement of the peak currents and a slight shift of the peak potentials. The shift of peak potential is possibly related to the change in resistance of the electrode during polymerization. Based on this result we conclude that the electrochemical deposition of poly taurine occurs with the nano Au deposition process and it exhibits as a thin layer on the electrode surface, respectively.

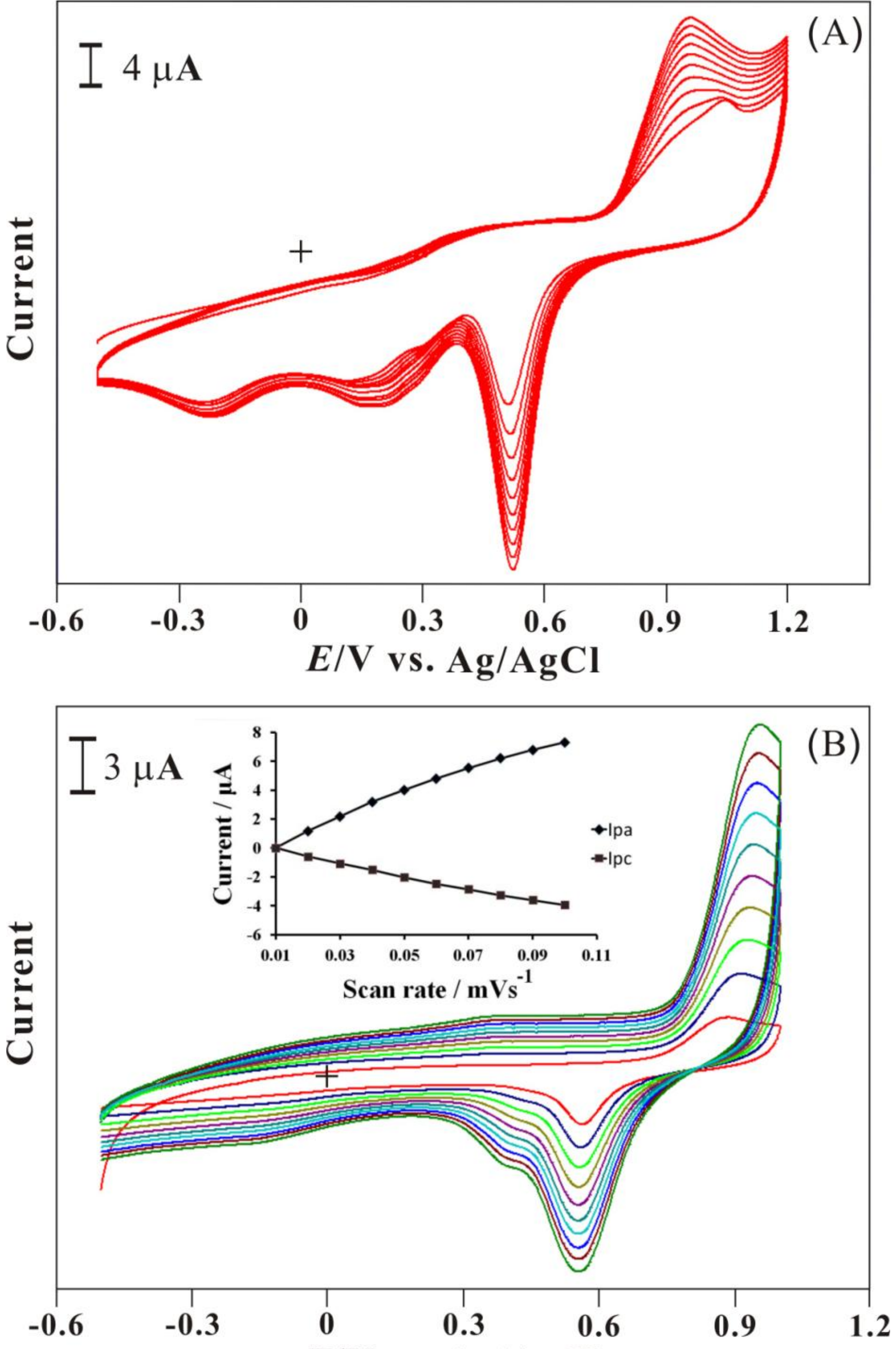

Figure 1.(A) Cyclic voltammogram of poly Taurine nano gold film electrodeposited on the GCE from pH7 containing Taurine (2mM) and $KAuCl_4.3H_2O$ (1x 10^{-3} M) and potential scan between -0.5 to 1.2 V for 10 cycles at the scan rate of 0.1 V/ S.(B) Different scan of the poly Taurine nano gold modified electrode in pH 7 at scan rate varies from 0.01, 0.02, 0.03, 0.04 , 0.05, 0.06, 0.07, 0.08, 0.09, 0.1V/S. Inset shows a current vs. scan rate plot at pH7.

Next the poly taurine nano gold film modified GCE was employed for the different scan rate studies in pH 7.0 PBS. Figure 1(B) displays the different scan rate studies of the poly taurine nano gold film at the scan rate of 0.01-0.1 V/s. For the increasing scan rates, the reduction peak current of Au increases and shifts to positive potentials. Peak currents were linearly dependent on the scan rate illustrates that the poly taurine nano gold film possesses the surface controlled electrochemical activity, respectively.

3.2 SEM analysis

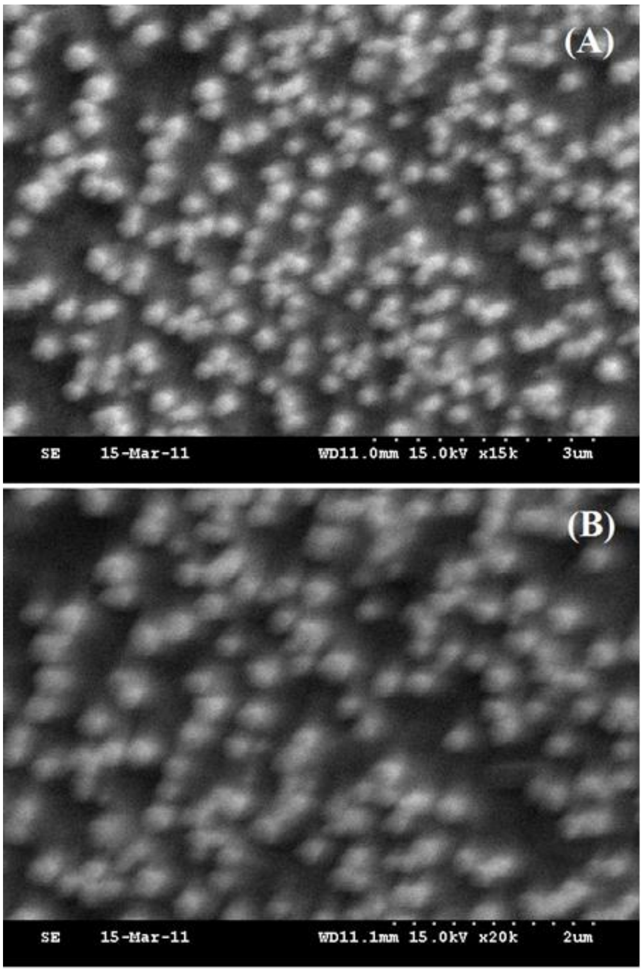

Figure 2. SEM images of Poly taurine nano gold film modified ITO (magnifications x20,000 (2µm) and x30,000 (3µm)).

The Poly taurine nano gold film modified ITO has been employed for the SEM analysis. Figure (A) and (B) shows the large scale view [x20,000 (2µm)]] and magnified views [(x30, 000 (3µm)] of electrodeposited poly taurine nano gold film modified ITO. Based on Fig. (A) and (B) we can clearly see the existence of electrodeposited nano Au particles on the ITO surface. Here the poly taurine has been co-deposited as thin film on the ITO surface. Therefore, visibility of the poly taurine as a thin layer is not distinguishable in the SEM analysis. Further the electrodeposited nano Au particles sizes were found in the range of 20-80 nm. During the electrodeposition process, few nano Au particles coagulated together and deposited as group of nanoparticles. These nanoparticles size falls in the range of 100-150 nm, respectively. Finally, SEM results clearly explicate the surface morphological nature of the poly taurine nano gold film.

3.3 Electrochemical detection of arsenic

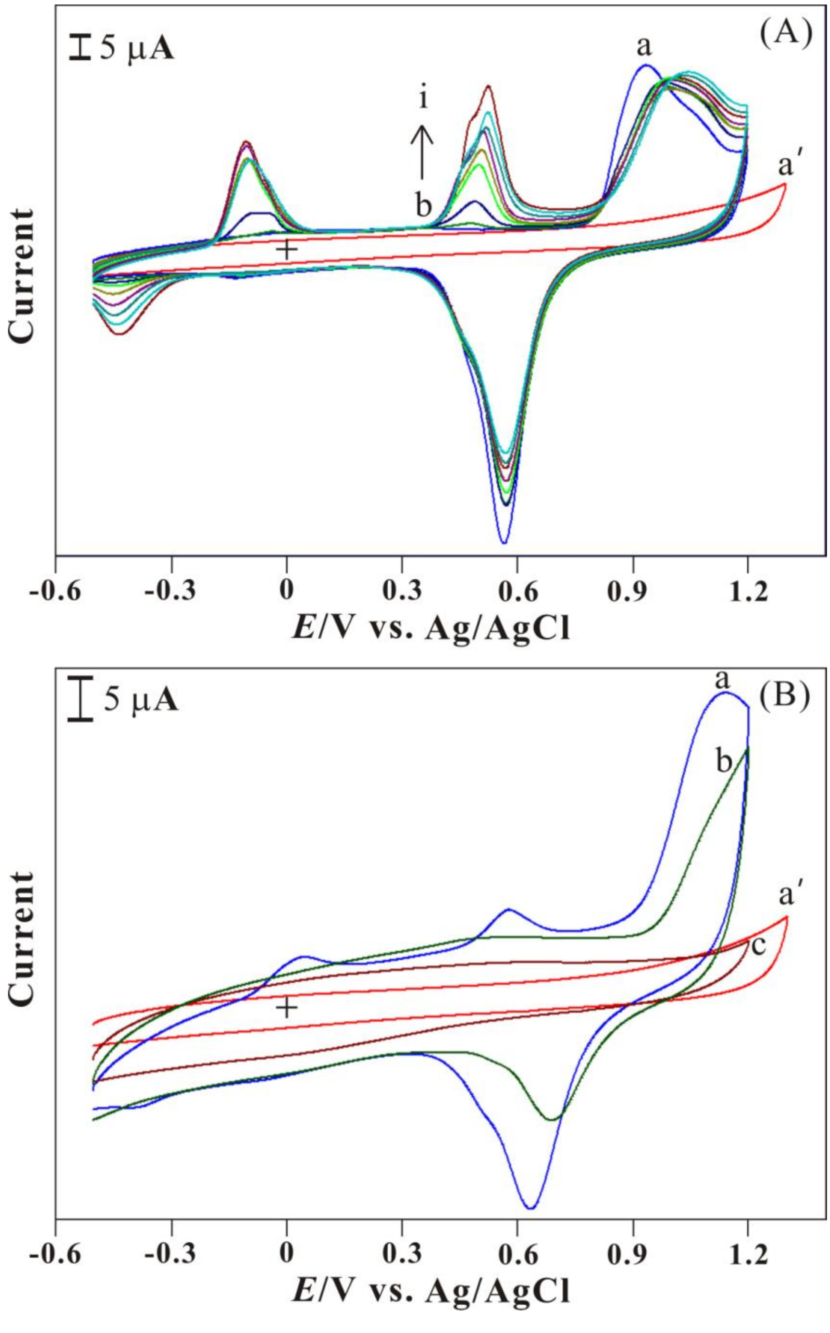

Figure 3. (A) Electro catalytic response of (a) modified electrode at Blank pH 7 (b-i) Poly Taurine nano gold modified electrode at addition of arsenic concentration and (a') Bare GCE, Arsenic Concentration: 6* 10^{-6}M to $2.8*10^{-5}$M. (**B**) Electrocatalytic response of (a) Poly Taurine nano gold modified electrode at arsenic (b) only nano gold (c) only poly Taurine and (d) Bare GCE, arsenic concentration: $2.8*10^{-5}$M.

Electrochemical detection of As (III) has been examined by CV (Figure 2(A)). Figure 2(A) curve (b) shows the detection of As (III) (2.8× 10^{-5} M) at poly Taurine nano gold film modified GCE. Here the As (III) electrochemical detection signal appears at 0.5 V at poly taurine nano gold film modified GCE in pH 7.0 PBS. Bare GCE (curve a') also showed the null response for the detection of As (III) detection. We have also employed the detailed detection of As (III) with individual films. Figure 2(B) shows the electrochemical detection of As (III) by CV curve (a) shows the detection of As(III) (2.8× 10^{-5} M) at poly taurine nano gold film at the same time only gold and poly taruine film modified GCE (Curve b and c) not showed any obvious response for the detection of As(III). Bare GCE (curve a') also showed the null response for the detection of As (III) detection. This result clearly shows that the poly Taurine nano gold film modified GCE shows excellent response for the detection of As (III) in pH 7.0 PBS. Based on this examination further we have employed the poly taruine nano gold film modified GCE for the detailed detection of As (III) using DPV.

3.4 Detection of arsenic in various water samples

The DPVs of poly taurine nano gold film modified GCE in pH 7.0 PBS for the various concentrations of As (III) in figure.3. (A). Here the electrochemical detection signal of As (III) appears at the 0.40 V. Poly taurine nano film modified GCE also exhibits a small oxidation peak current for As (III) detection at around 0.067 V. For the continuous additions of As (III), the modified film shows well distinguished anodic oxidation peaks which linearly dependent on the increasing concentrations of As (III), respectively. This result validates the capability of the proposed film will be suitable for the detection of As (III) in the certain linear ranges (6-28 μM) in pH 7.0 PBS. The inset of Figure 3(A) shows the current versus calibration plot for the As (III) detection. The sensitivity and the detection limit of the As (III) detection at the poly taurine nano gold film modified GCE was found as 1.365μA $\mu M^{-1} cm^2$ and 0.46 μM, respectively.

The real sample analysis has been carried out using real world drinking water sources like river water (Danshui River, Taipei, Taiwan (ROC), spring waters (sample 1 and sample 2) and tap water (Taipei water department, Taiwan (ROC)). As (III) dissolved in the tap water has been spiked in pH 7.0 PBS (Figure 3(B)). Here the poly taurine nano gold film modified GCE clearly exhibits the As (III) detection signals (at 0.40 V) in the linear range of 6-24 μM. The sensitivity and detection limit of the poly taurine nano gold film for the As (III) detection was found as 1.0151μA $\mu M^{-1} cm^2$ and 0.45 μM. This shows that the proposed film holds the capability to detect the As (III) in tap water.

Next the drinking spring water samples (sample-1(Figure-4 (A)) and sample-2 (Figure-4 (B)) (mineral content details has been included in the experimental section)) have been employed for the detection of As (III). Here in the spring water sample-1 the linear range of detection of As (III) was found as 6-28 μM. Further the sensitivity and the detection limit of the poly taurine nano gold film for As (III) detection in the sample-1 was found as 1.00μA $\mu M^{-1} cm^2$ and 0.58 μM. Next, in the sample-2 poly taurine nano gold film modified GCE detects the As (III) in the linear range of 10-34 μM with the sensitivity and detection limit of 0.968μA $\mu M^{-1} cm^{2-}$ and 0.91 μM. These two results clearly explicates that the proposed film successfully detects the As (III) in the drinking spring water samples, respectively.

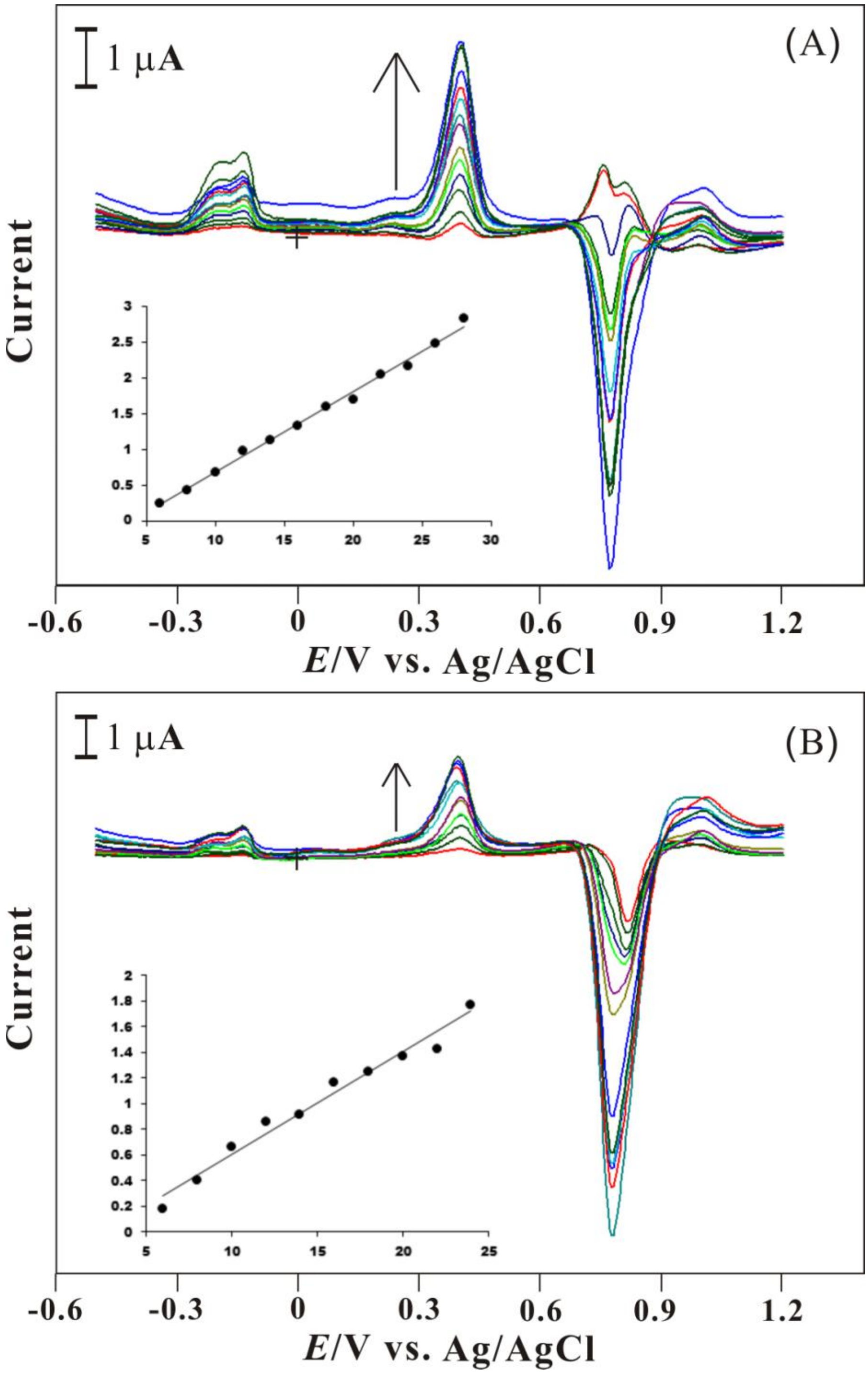

Figure 4. (A) DPV of poly Taurine nano gold film modified electrode for the different concentrations of Arsenic (Lab Sample) in pH 7 (a-t; 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40μM) Inset shows a current vs. Concentration plot of arsenic. **(B)** DPVs of poly Taurine nano gold film modified GCE for As (III) detection (dissolved in tap water) in pH 7 PBS (As (III) concentration (a-v): 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24μM). Inset shows calibration plot of As (III) in tap water.

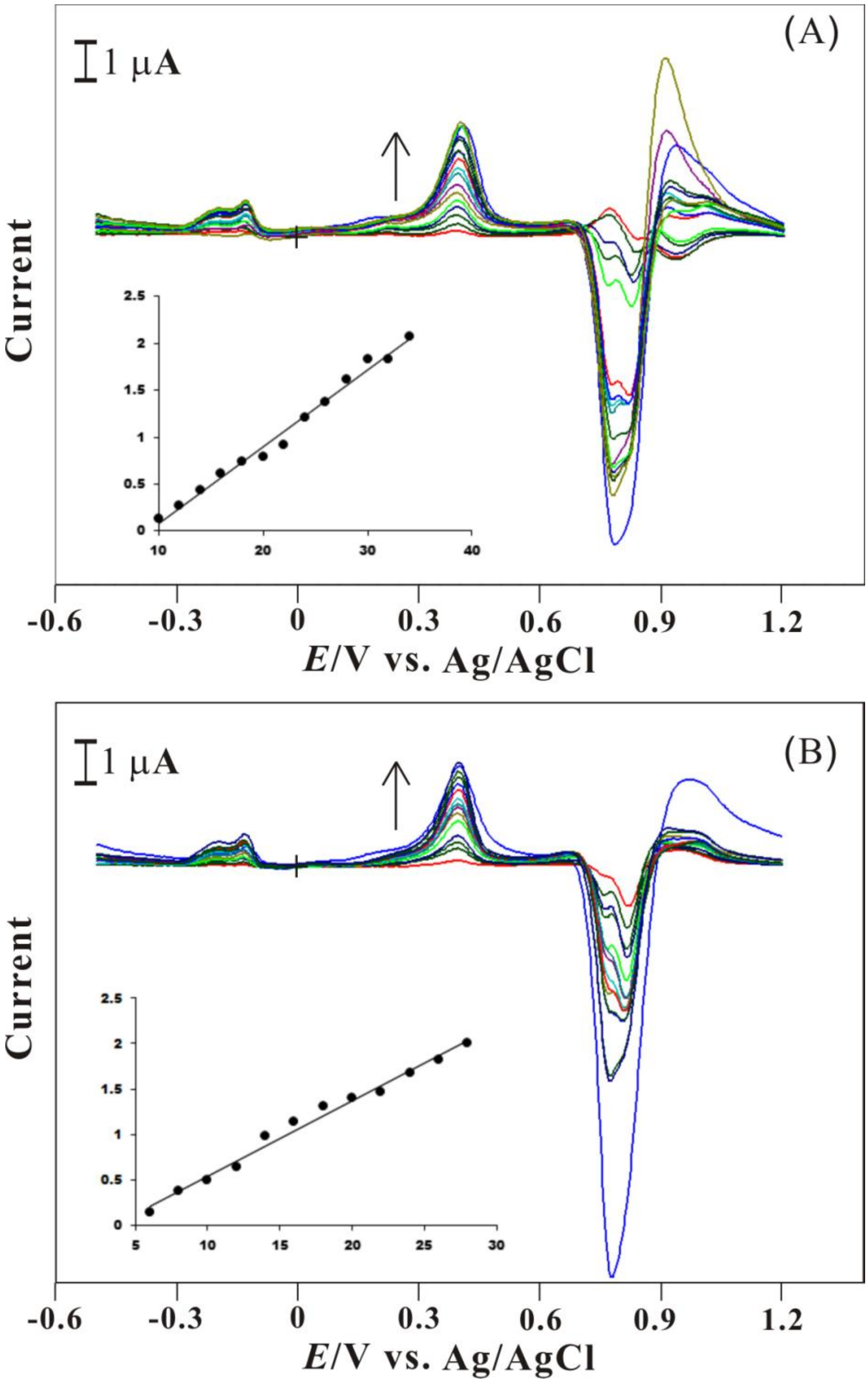

Figure 5. (A) DPVs of poly Taurine nano gold film modified GCE for As (III) (dissolved in spring water-1) in pH 7 PBS (As (III) concentration: 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28μM). Inset shows calibration plot of As (III) in drinking mineral water. (B) DPVs of Poly Taurine nano gold film modified GCE for As (III) detection (dissolved in spring water-2) in pH 7 PBS (As (III) concentration (a-y): 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34 μM). Inset shows calibration plot of As (III) in drinking mineral water.

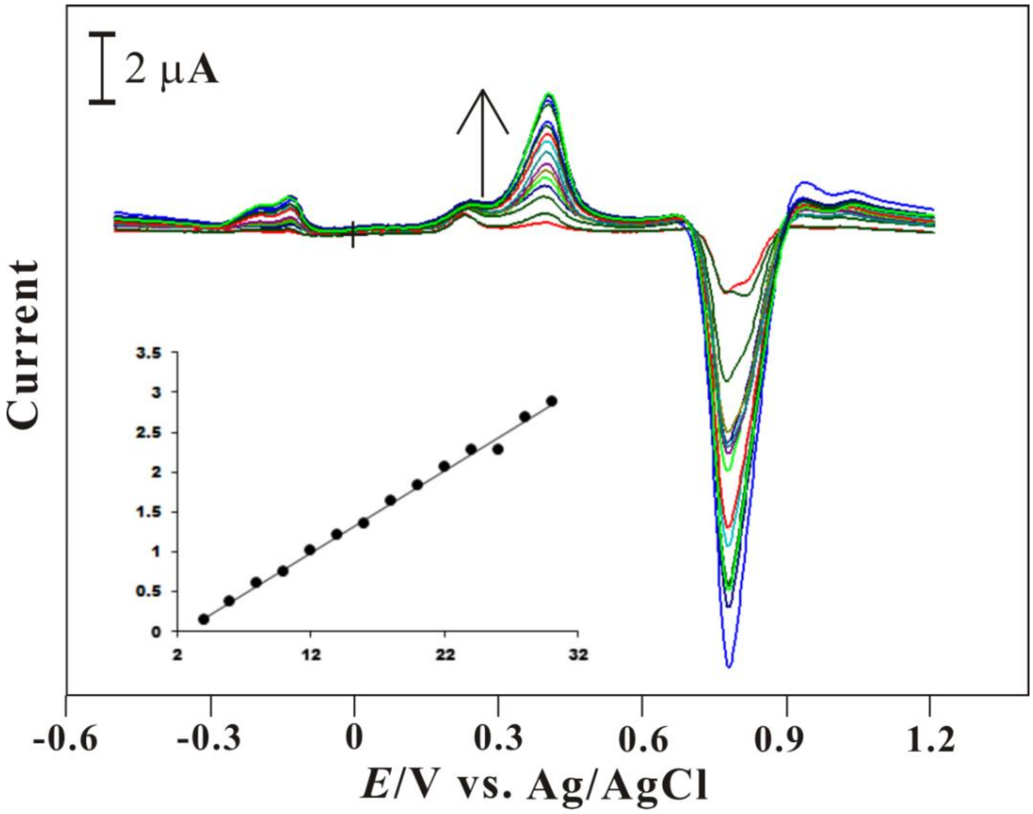

Figure 6. DPVs of poly Taurine nano gold film modified GCE for As (III) detection (dissolved in river water) in pH 7 PBS (As (III) concentration: 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30μM). Inset shows calibration plot of As (III) detection in river water.

Finally river water has been examined for the As (III) detection process (Figure5). As (III) dissolved river water was spiked in pH 7.0 PBS and the poly taurine nano gold film modified GCE clearly shows the electrochemical detection signals of As (III) (at 0.40 V) in the linear range of 4-30 μM. Here the sensitivity and the detection limit of the proposed film for the As (III) detection was 1.310μA $\mu M^{-1} cm^{2-}$ and 0.20 μM. Here the sensitivity and the detection limit of the poly taurine nano gold film for As (III) detection in this analysis may vary due to the different types of the real samples. Finally, all these water sample analysis results clearly show that the proposed film possesses the capability to detect the As (III) successfully in the real samples, respectively.

3.5 *Stability Studies*

Stability of the poly taurine nano gold film modified GCE was investigated by storing it in air at 4 ºC and further checking the back-ground current response in pH 7.0 PBS. It was stable for 2 days and few gradual decreases occurred in the reduction and oxidation peak potentials (Fig.5). Further by increasing the number of cycles and other factors, we can improve the stability of this type of modified electrodes.

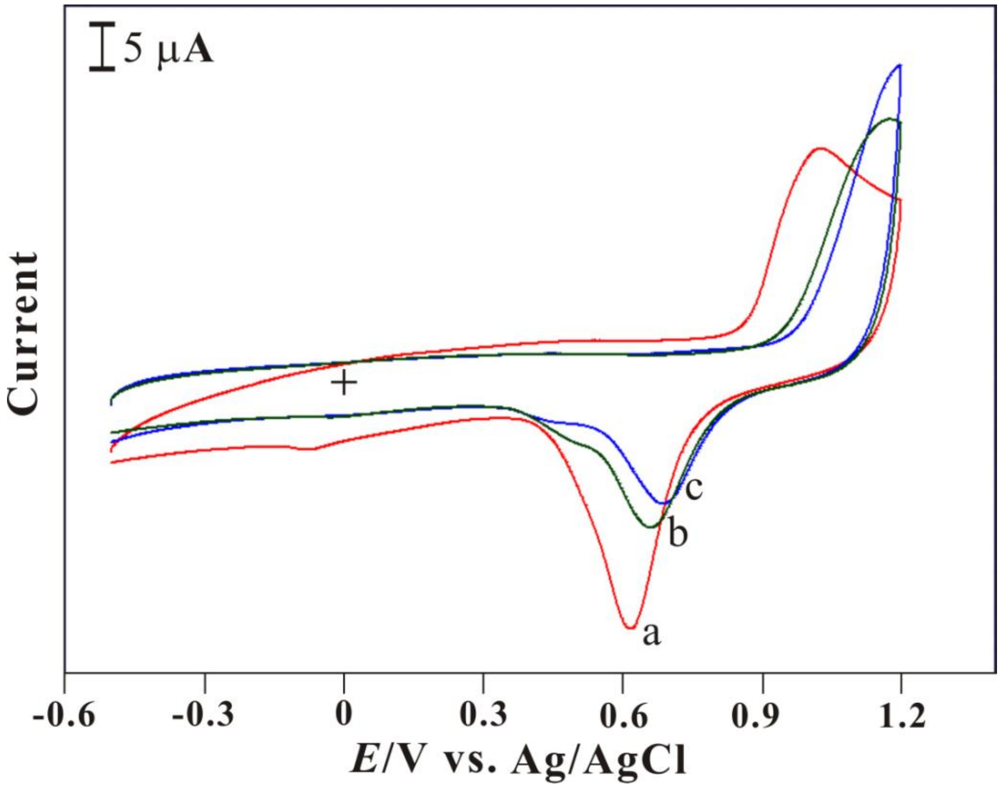

Figure 7. CV response of Poly Taurine nano gold film modified GCE in the pH 7.0 PBS: a first day, b after 4 hrs, and c second day.

4. CONCLUSIONS

Electrochemically fabricated poly taurine nano gold film modified GCE successfully employed for the detection of As (III) using CV and DPV. The proposed film shows the As (III) detection signals at the stipulated conditions. Also, the poly taurine nano gold film successfully employed for the detection of As (III) in the micro molar concentration ranges in the real drinking water samples such like, river water, spring water and tap water samples. The proposed film will be a promising method for the detection of As (III) in electroanalysis and this method could be utilized for the detection of As (III) in the lab and real samples along with verification of other analytical techniques, respectively.

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