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$ZnIn_2S_4$ Nanoparticles Modified Carbon Paste Electrode for Voltammetric Determination of Penicillamine

Ehsan Pourtaheri,[1,2,*] Mohammad Ali Taher,[1] Hadi Beitollahi[3] and Mehdi Ranjbar[1,2]

[1]*Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran*

[2]*Young Researchers Society, Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran*

[3]*Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran*

*Corresponding Author, Tel.: +98 341 3220041; Fax: +98 341 3643853

E-Mail: e.pourtaheri94@gmail.com

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Abstract- An ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate)– $ZnIn_2S_4$ nanoparticles modified carbon paste electrode (ZISILCPE) was used as a fast and sensitive tool for the investigation of the electrochemical oxidation of penicillamine using voltammetry. The modified electrode offers a considerable improvement in voltammetric sensitivity toward penicillamine, compared to the bare electrode. Using differential pulse voltammetry (DPV), the electrocatalytic oxidation peak current of penicillamine shows a linear calibration curve in the range of 5.0×10^{-7} to 8.0×10^{-5} M penicillamine. The limit of detection was equal to 3.0×10^{-7} M. The electrode was also employed to determination of penicillamine in real samples.

Keywords - Penicillamine, $ZnIn_2S_4$ nanoparticles, Ionic liquids, Carbon paste electrode

1. INTRODUCTION

Electrochemical techniques have become of growing importance in industrial process control, environmental monitoring and different applications in medicine and biotechnology, due to their simplicity, reasonable accuracy and precision, low cost, and rapidity [1-12].

There is no need for derivatization or time-consuming extraction steps in comparison with other techniques because of less sensitivity of electroanalytical methods to the matrix effects [13-18]. Carbon paste electrodes (CPEs) are widely utilized to perform the electrochemical determinations of a variety of biological and pharmaceutical species owing to their low residual current and noise, ease of fabrication, wide anodic and cathodic potential ranges, rapid surface renewal, and low cost [19-24]. Moreover, chemically modified electrodes (CMEs) can be easily prepared by adding different substances to the bulk of CPEs in order to increase sensitivity, selectivity, and rapidity of determinations [25-30].

Determination of amino acids has been attracting increasing attention because they are the basic units of enzymes and proteins. Many research papers related to the electroanalytical determination of amino acids by chemically modified electrodes have been published in the last few decades [31-33].

Penicillamine (PA) is a sulfur-containing amino acid which is generally considered to be in a family of aminothiols [34]. It is a pharmaceutically essential chiral compound which is a degradation product of penicillin [35]. It can typically be classified into two forms including D-penicillamine (DPA) and L-penicillamine (LPA). The pharmaceutical form is DPA whereas LPA is clinically toxic since it inhibits the action of pyridoxine [36]. DPA is therefore favorable in the treatment of clinical pathology [37]. Various analytical techniques, including high performance liquid chromatography [38], chemiluminescence, flow injection analysis [39, 40], capillary electrophoresis [41], electrochemistry [42-45], spectrophotometry [46], and fluorometry [47] have been reported for identification of DPA in both pharmaceutical preparations and biological samples.

Nanostructured materials have attracted considerable interests and have become a vast area of research owing to their unique physical and chemical properties which can provide an important and feasible platform for electroanalysis particularly in the design of modified electrodes for electrochemical sensing [48-53]. Applications of nanocomposites in electroanalytical studies display extraordinary advantages over conventional electrodes including enhanced mass transport and catalysis, highly effective surface areas, high porosity, more absorption and reactive sites and control over the electrode macro-environment [54-56]. Ionic liquids (ILs) have been generating increasing interest over the last decade [57,58]. Ionic liquids have a great potential for possible electrochemical applications because these compounds possess high thermal stability, no volatility, high polarity, large viscosity, high intrinsic conductivity, and wide electrochemical window [59,60].

In the present work, we describe the preparation of a new carbon paste electrode modified with an ionic liquid and $ZnIn_2S_4$ nanoparticles (ZISILCPE) and investigate its performance for the determination of penicillamine.

2. EXPERIMENTAL

2.1. Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25±1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and ZISILCPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

Penicillamine and all of the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0. Ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) was purchased from Sigma Aldrich Co. $ZnIn_2S_4$ nanoparticles were synthesized in our laboratory as reported previously [61]. A typical SEM of the $ZnIn_2S_4$ nanoparticles are shown in Fig. 1.

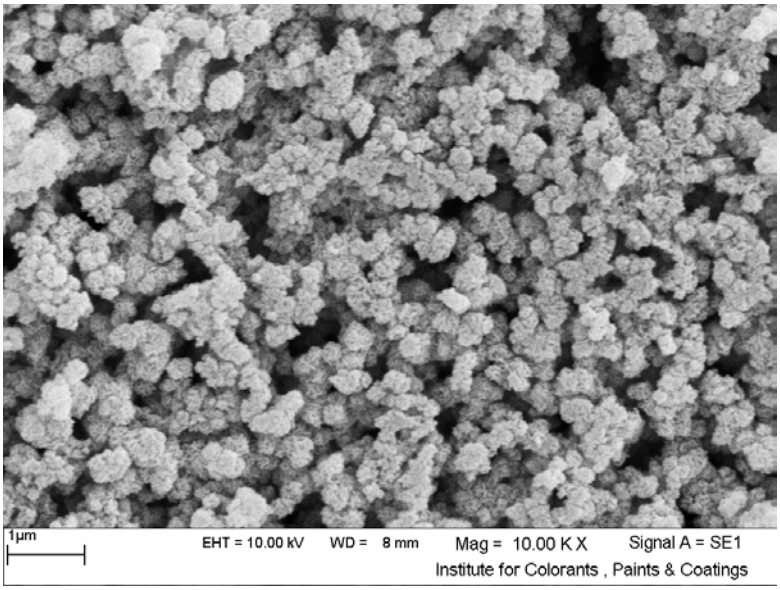

Fig. 1. SEM image of synthesized $ZnIn_2S_4$ nanoparticles

2.3. Preparation of the electrode

ZISILCPEs were prepared by mixing 0.04 g of $ZnIn_2S_4$ nanoparticles with 0.96 g graphite powder and approximately, ~ 0.8 mL of ionic liquids with a mortar and pestle. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact.

For comparison, ionic liquid/carbon paste electrode in the absence of $ZnIn_2S_4$ nanoparticles (ILCPE), $ZnIn_2S_4$ nanoparticles carbon paste electrode (ZISCPE) consistent of

$ZnIn_2S_4$ nanoparticles**,** graphite powder and paraffin oil, and bare carbon paste electrode (CPE) consisiting of graphite powder and paraffin oil were also prepared in the same way.

3. RESULT AND DISCUSSION

3.1. Electrochemical behavior of penicillamine at the surface of various electrodes

Fig. 2 displays cyclic voltammetric responses from the electrochemical oxidation of 80.0 µM penicillamine at the surface of ZISILCPE (curve d), ILCPE (curve c), ZISCPE (curve b) and bare CPE (curve a). The results showed that the oxidation of penicillamine is very weak at the surface of the bare CPE, but the presence of ILs in CPE could enhance the peak current and decrease the oxidation potential (decreasing the overpotential). A substantial negative shift of the potential starting from oxidation potential for penicillamine and dramatic increase of the current indicates the catalytic ability of ZISILCPE (curve d) and ILCPE (curve c) to penicillamine oxidation. The results showed that the combination of $ZnIn_2S_4$ nanoparticles and the ionic liquid (curve d) definitely improved the characteristics of penicillamine oxidation. However, ZISILCPE shows much higher anodic peak current for the oxidation of penicillamine compared to ILCPE, indicating that the combination of $ZnIn_2S_4$ nanoparticles and IL has significantly improved the performance of the electrode toward penicillamine oxidation.

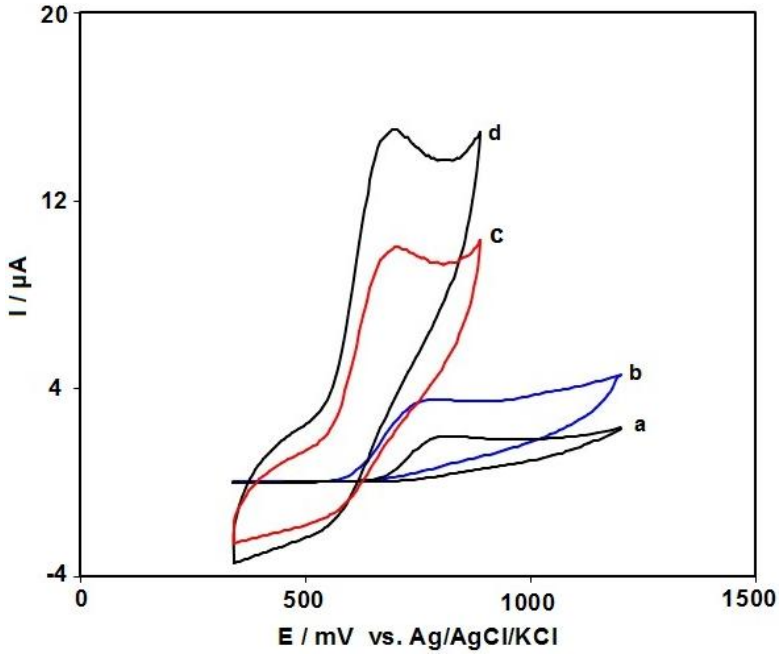

Fig. 2. CVs of a) CPE, b) ZISCPE, c) ILCPE and d) ZISILCPE in the presence of 80.0 µM penicillamine at a pH 7.0, respectively. In all cases the scan rate was 50 mV s^{-1}

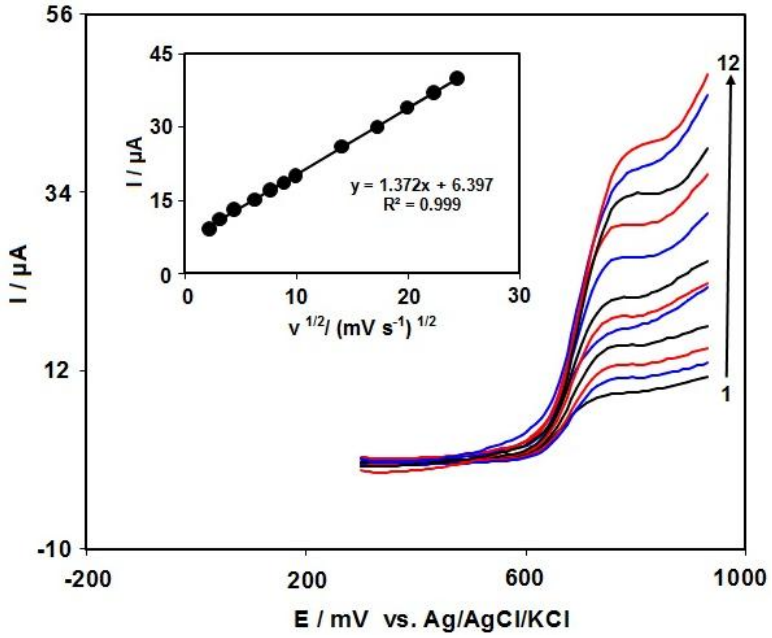

Fig. 3. LSVs of ZISILCPE in 0.1 M PBS (pH 7.0) containing 80.0 µM penicillamine at various scan rates; numbers 1-12 correspond to 5, 10, 20, 40, 60, 80, 100, 200, 300, 400, 500 and 600 mV s^{-1}, respectively. Inset: Variation of anodic peak current *vs*. square root of scan rate

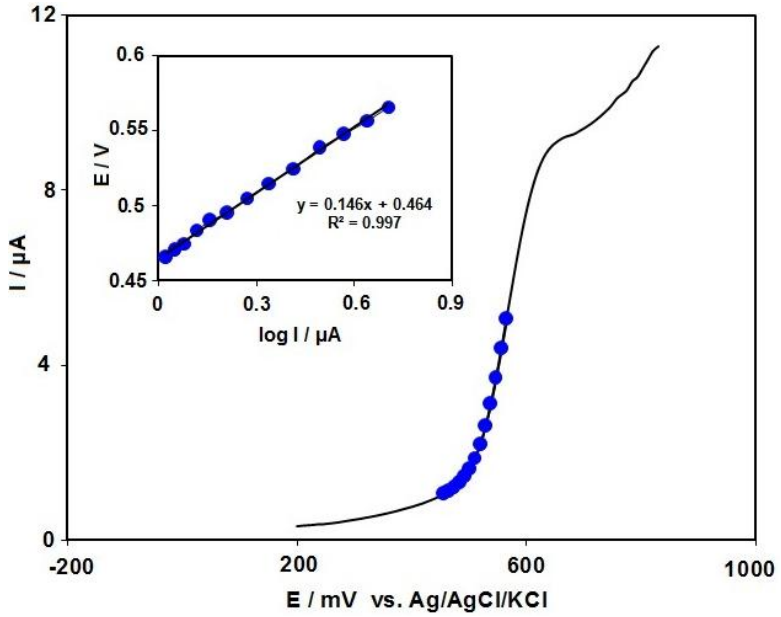

Fig. 4. LSV (at 5 mV s^{-1}) of a ZISILCPE in 0.1 M PBS (pH 7.0) containing 80.0 µM penicillamin; the points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

3.2. Effect of scan rate

The effect of potential scan rates on the oxidation current of penicillamine has been studied (Fig. 3). The results showed that increasing in the potential scan rate induced an increase in the peak current. In addition, the oxidation process is diffusion controlled as deduced from the linear dependence of the anodic peak current (I_p) on the square root of the potential scan rate ($v^{1/2}$) over a wide range from 5 to 600 mV s^{-1}.

Fig. 4 shows the Tafel plot for the sharp rising part of the voltammogram at the scan rate of 5 mV s^{-1}. If deprotonation of penicillamine is a sufficiently fast step, the Tafel plot can be used to estimate the number of electrons involved in the rate determining step. A Tafel slope of 0.146 V was obtained which agrees well with the involvement of one electron in the rate determining step of the electrode process [62], assuming a charge transfer coefficient, α of 0.6.

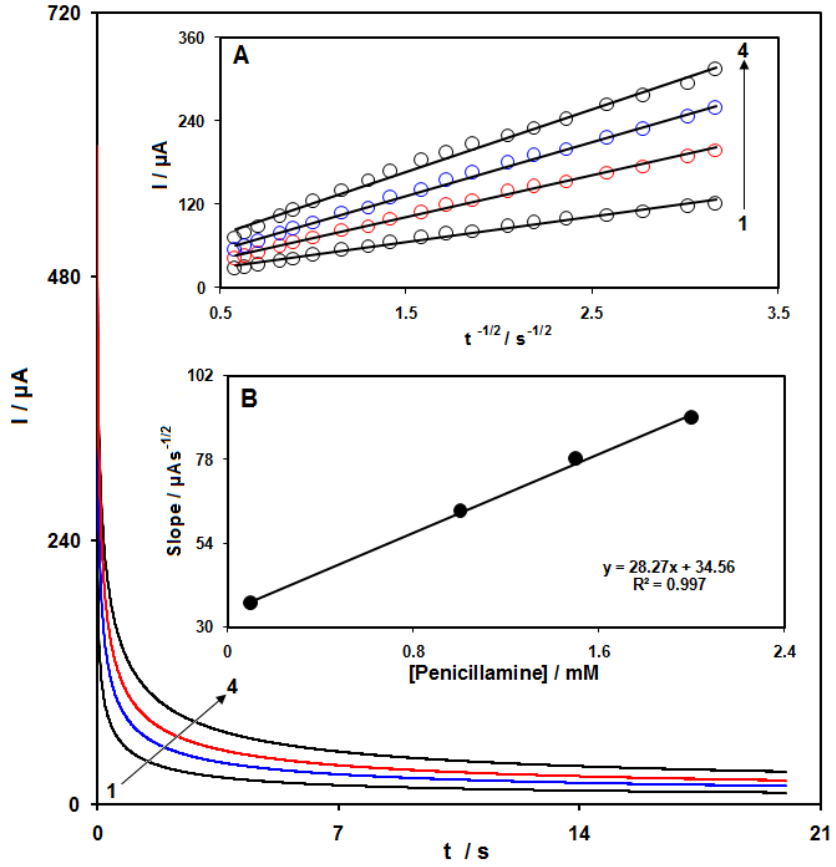

Fig. 5. Chronoamperograms obtained at ZISILCPE in 0.1 M PBS (pH 7.0) for different concentration of penicillamine. The numbers 1–4 correspond to 0.1, 1.0, 1.5 and 2.0 mM of penicillamine; insets: (A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against penicillamine concentration

3.3. Chronoamperometric measurements

Chronoamperometric measurements of penicillamine at ZISILCPE were carried out by setting the working electrode potential at 0.8 V *vs*. Ag/AgCl/KCl (3.0 M) for the various concentrations of penicillamine in PBS (pH 7.0) (Fig. 5). For an electroactive material (penicillamine in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [62].

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D and C_b are the diffusion coefficient ($cm^2\ s^{-1}$) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I *vs*. $t^{-1/2}$ were employed, with the best fits for different concentrations of penicillamine (Fig. 5A). The slopes of the resulting straight lines were then plotted *vs*. penicillamine concentration (Fig. 5B). From the resulting slope and Cottrell equation the mean value of the D was found to be 3.3×10^{-5} cm^2/s.

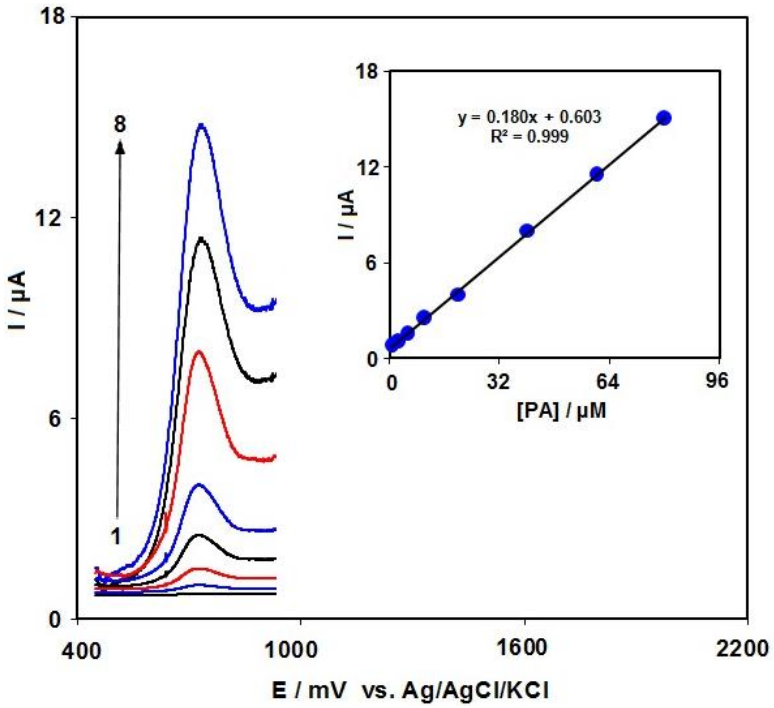

Fig. 6. SWVs of ZISILCPE in 0.1 M PBS (pH 7.0) containing different concentrations of penicillamine (0.5, 2.5, 5.0, 10.0, 20.0, 40.0, 60.0 and 80.0 µM). Inset shows the plot of the peak current as a function of penicillamine concentration in the range of 0.5-80.0 µM

3.4. Calibration plot and limit of detection

The peak current of penicillamine oxidation at the surface of the modified electrode can be used for determination of penicillamine in solution. Therefore, DPV experiments were

done for different concentrations of penicillamine (Fig. 6). The oxidation peak currents of penicillamineat the surface of a modified electrode were proportional to the concentration of the penicillamine within the ranges 5.0×10^{-7} to 8.0×10^{-5} M with detection limit (3σ) of 3.0×10^{-7} M.

3.5. Drug Analysis of penicillamine Capsules

In order to demonstrate the electro-oxidation of penicillamine in pharmaceutical preparations, we examined this ability in the voltammetric determination of penicillamine in penicillamine capsules (containing 250 mg penicillamine) purchased from Laboratories Rubio, SA, Spain. The penicillamine content in penicillamine capsules was determined by the standard addition method in order to prevent any matrix effects. The results for the analysis of penicillamine capsules using the voltammetric method are summarized in Table 1. The results in Table 1 show that the relative standard derivations (RSD%) and recovery rates of the spiked samples are acceptable. Thus the modified electrode can be efficiently used for determination of penicillamine in pharmaceutical preparations.

Table 1 The application of ZISILCPE for determination of penicillamine in penicillamine capsule. (n=5)

Spiked (µM)	Found (µM)	Recovery (%)	R.S.D. (%)
0	11.0	-	3.4
7.5	18.9	102.1	2.7
17.5	28.2	98.9	2.1
27.5	38.3	99.5	1.9
37.5	50.0	103.1	2.9

4. CONCLUSION

In this work a carbon paste electrode was modified with $ZnIn_2S_4$ nanoparticles and an ionc liquid and used for determination of penicillamine. The voltammetric investigation demonstrates that electrooxidation of penicillamine at the surface of modified electrode showed very distinct characteristics due to the presence of $ZnIn_2S_4$ nanoparticles and ionic liquid layer on the surface of electrode. In addition, a selective voltammetric sensor for the determination of penicillamine with simple, sensitive, and rapid characteristics was developed. The proposed modified electrode presented a low detection limit and good linear range and reproducibility which make it a suitable penicillamine sensor for practical applications.

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