

*Full Paper*

## **Preparation, Characterization and Electrochemical Application of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> Nanocomposite for Voltammetric Determination of D-Penicillamine**

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**Abstract-** A novel carbon paste electrode modified with ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite and an ionic liquid (ZZ/IL/CPE) was fabricated and used for the electrochemical study of D-penicillamine (D-PA). This modified electrode offers a considerable improvement in voltammetric sensitivity toward D-PA, compared to the bare electrode. Square wave voltammetry (SWV) exhibits a linear dynamic range from  $5.0 \times 10^{-7}$  to  $3.0 \times 10^{-4}$  M and a detection limit of  $1.0 \times 10^{-7}$  M for D-PA. Finally, the proposed method was successfully applied to the determination of D-PA in real samples.

**Keywords-** D-Penicillamine, Carbon paste electrode, ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite, Chemically modified electrodes

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### **1. INTRODUCTION**

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 (CMEs) have been published in the last few decades [1–3]. D-Penicillamine (D-PA) is an aminothiols and a potent copper chelating agent [4]. D-PA is currently approved for the treatment of Wilson's

disease and rheumatoid arthritis. Based on its ability to effectively chelate and remove copper, it has also been investigated as an antiangiogenic agent [5]. Several different methods have been proposed for the determination of D-PA in biological specimens and pharmaceutical formulations, such as chromatography [6], chemiluminescence [7], spectrophotometric [8] and electrochemical methods [9–14]. Although these methods have been successfully employed, some of them suffer from interference from the pharmaceutical or biological matrix, and others are time consuming or require expensive equipment and consequently are not suitable for routine analysis in common laboratories. Therefore, a simple, rapid and sensitive determination of D-PA is of great importance. One of these methods is electrochemical method. The poor selectivity, slow kinetics of electro-oxidation and very weak voltammetric responses of D-PA at bare (unmodified) electrodes are often serious problems in detection with these electrodes. The chemical modification of electrodes using modifier is an interesting field in this area. Some chemically modified electrodes with various modifier [15–18] are used as modified electrodes.

Electrochemical methods for the detection of inorganic and organic compounds are selective and sensitive [19–25]. Chemically modified electrodes (CMEs) are extensively researched for applications in medical diagnostics, food analysis, and environmental monitoring [26–32]. An important property of CMEs is their ability to catalyze the electrode process to significantly decrease the overpotential and give more selective interaction of the electron mediator with the target analyte. These electrodes can enhance the selectivity in the electroanalytical methods.

Carbon paste electrodes (CPEs) represent one of the most convenient materials for the preparation of modified electrodes. CPEs are widely applied in both electrochemical studies and electroanalysis for their advantages such as very low background current (compared to solid graphite or noble metal electrodes), easy to prepare, low cost, large potential window, simple surface renewal process, and ease of miniaturization [33–51].

Nanostructured materials have attracted considerable interests and have become a vast area of research owing to their unique physical and chemical properties such as large ratio of surface area to volume and high activity, which can provide an important and feasible platform for electroanalysis particularly in the design of modified electrodes for electrochemical sensing [52–57]. Core-shell nanocomposites are of special interest due to the combination of several very different properties. The growth of shell on a core material to form a heterostructure has been a successful route in the surface modification of nanostructured materials.

Ionic liquids (ILs) have been generating increasing interest over the last decade [58–60]. ILs 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 windows [61–63].

To the best of our knowledge, no study has been reported so far on the determination of D-PA by using ZZ/IL/CPE. Although, there are many reports about the determination of D-PA using electron transfer mediator, but in this study, we report the preparation and application of a ZZ/IL/CPE for the determination of D-PA without any additional modification such as addition of electron transfer mediator or specific reagents for the first time. The main objectives of this ZZ/IL/CPE for determination of D-PA are: wide linear dynamic range, short time of the procedure and no use of electron transfer mediator.

## 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  $25 \pm 1$  °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and ZZ/IL/CPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. D-PA 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 (Darmstadt, Germany).

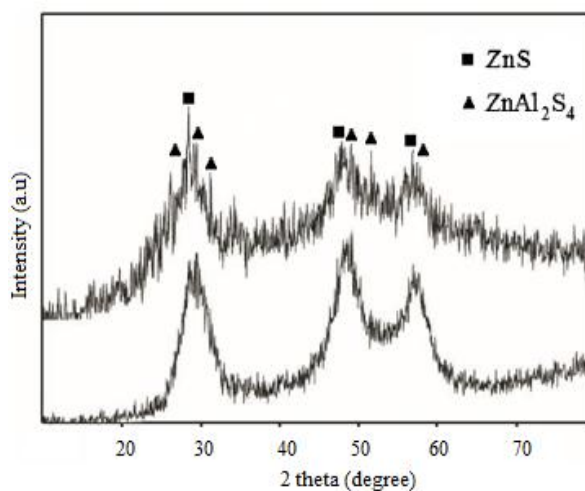
**Table 1.** Reaction conditions for ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposites

Sulfide Source	Temperature(°C)	Time (min)
Thioacetoamid	200	6

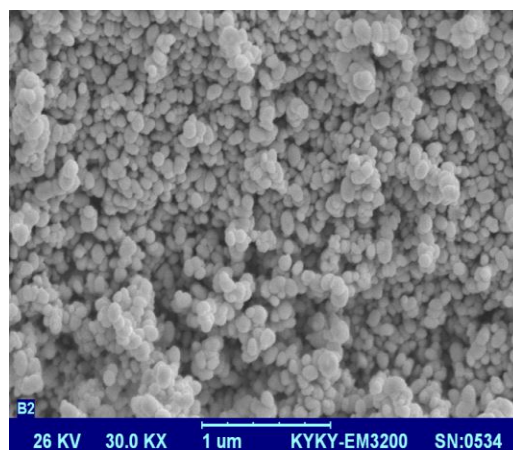
### 2.2. Synthesis of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> Core-shell nanocomposites

In a typical experimental procedure, ZnAl<sub>2</sub>S<sub>4</sub> was prepared from a mixture of Zn(OAc)<sub>2</sub> (1 mmol), Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (2 mmol), and sulfide source (4 mmol) with the molar ratio of 1:1:2 in the 30 ml propylene glycol. The earlier mentioned mixture was continuously stirred for 2 h and then was placed in a Teflon-lined stainless steel autoclave of 55 mL capacity. The autoclave was sealed and maintained at 200 °C for 4 h in an electric oven and reaction was performed in the various conditions (Table 1). After the reaction, the autoclave was allowed to cool naturally to room temperature. The yellow precipitate was centrifuged, washed out with alcohol and distilled water for three times and dried under vacuum at 75 °C for 4 h. The

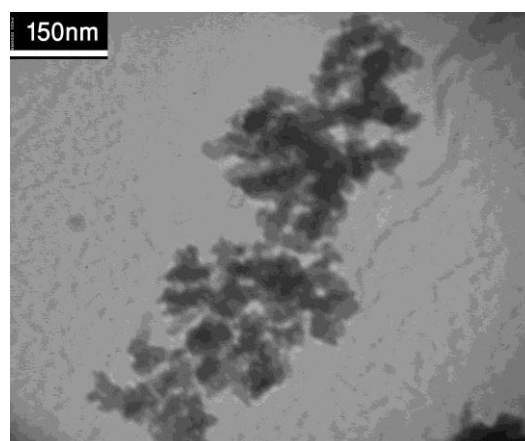
purity and morphology of the as-prepared product was characterized by XRD (Fig. 1), SEM (Fig. 2) and TEM (Fig. 3).



**Fig. 1.** XRD patterns of (a) ZnS/ZnAl<sub>2</sub>S<sub>4</sub> hollow/ micro sphere nanocomposites and (b) ZnS nanoparticle



**Fig. 2.** SEM images of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposites



**Fig. 3.** TEM image of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite

### 2.3. Preparation of the electrode

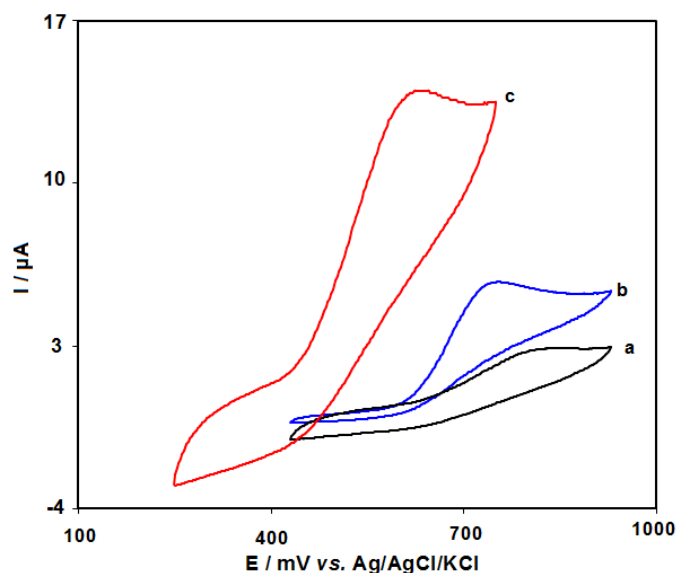
The ZZ/IL/CPEs were prepared by hand mixing 0.04 g of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite with 0.96 g graphite powder and approximately, ~0.8 mL of ionic liquids with a mortar and pestle. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite carbon paste electrode (ZZ/CPE) consistent of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite, graphite powder and paraffin oil, and bare carbon paste electrode (CPE) consistent of graphite powder and paraffin oil were also prepared in the same way.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Cyclic voltammetric study of D-PA oxidation

Fig. 4 displays cyclic voltammetric responses from the electrochemical oxidation of 150.0  $\mu$ M D-PA at the surface of bare CPE (curve a), ZZ/CPE (curve b) and ZZ/IL/CPE (curve c). The results showed that the oxidation of D-PA is very weak at the surface of the bare CPE, but the presence of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite in CPE could enhance the peak current and decrease the oxidation potential (decreasing the overpotential).

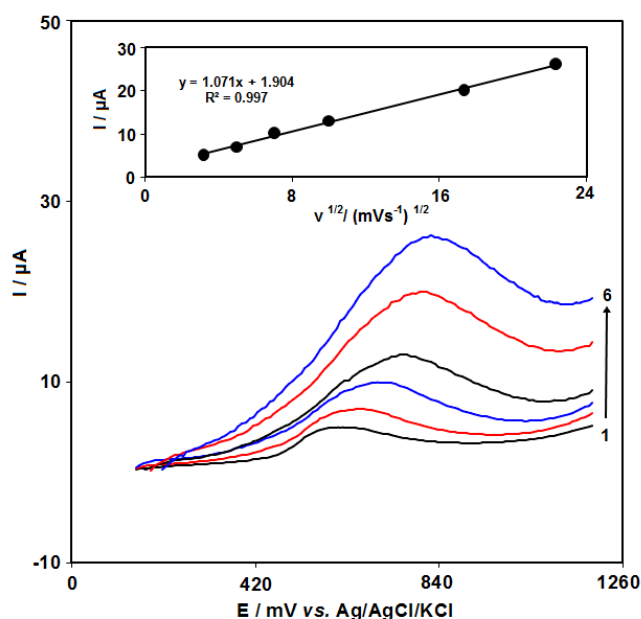


**Fig. 4.** CVs of 150.0  $\mu$ M D-PA in 0.1 M PBS at the surface of CPE (a), ZZ/CPE (b) and ZZ/IL/CPE (c) in scan rate of 50  $\text{mVs}^{-1}$

A substantial negative shift of the potential starting from oxidation potential for D-PA and dramatic increase of the current indicates the catalytic ability of ZZ/IL/CPE (curve c) to D-PA oxidation.

The results showed that the combination of ZnS/ZnAl<sub>2</sub>S<sub>4</sub> nanocomposite and the ionic liquid (curve c) definitely improved the characteristics of D-PA oxidation.

The effect of potential scan rate on the electrocatalytic oxidation of D-PA at the ZZ/IL/CPE was investigated by LSV (Fig. 5). A plot of peak height ( $I_p$ ) vs. the square root of scan rate ( $v^{1/2}$ ) was found to be linear in the range of 10-500 mVs<sup>-1</sup>, suggesting that, at sufficient over potential, the process is diffusion rather than surface controlled (Fig. 5 inset).



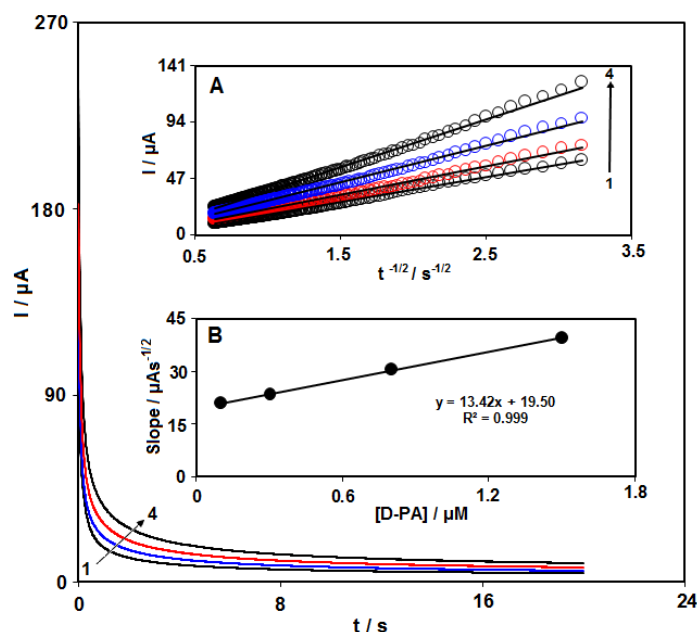
**Fig. 5.** LSVs of ZZ/IL/CPE in 0.1 M PBS (pH 7.0) containing 75.0 μM D-PA at various scan rates; numbers 1-6 correspond to 10, 25, 50, 100, 300 and 500 mV s<sup>-1</sup>, respectively. Inset: Variation of anodic peak current vs.  $v^{1/2}$

### 3.2. Chronoamperometric measurements

Chronoamperometric measurements of D-PA at ZZ/IL/CPE were carried out by setting the working electrode potential at 0.7 V versus Ag/AgCl/KCl (3.0 M) for the various concentrations of D-PA in buffered aqueous solutions (pH 7.0) (Fig. 6). For an electroactive material (D-PA 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 [64]:

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

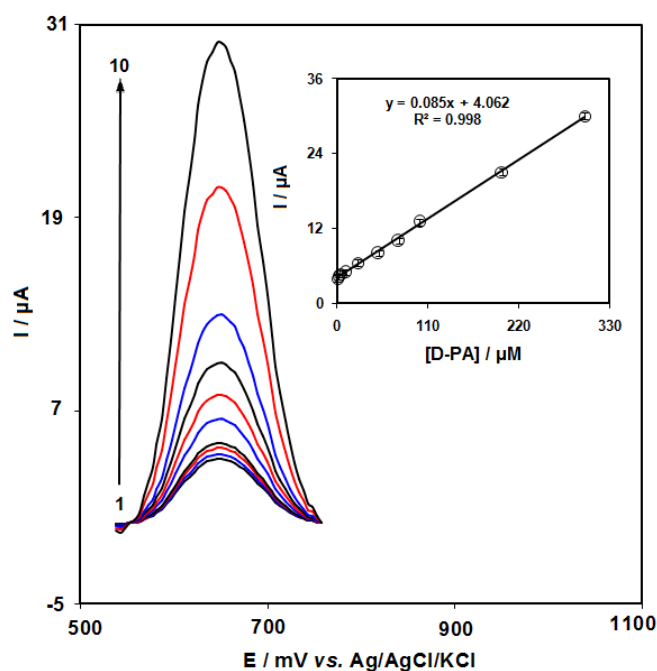
Where  $D$  and  $C_b$  are the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) and the bulk concentration ( $\text{mol cm}^{-3}$ ), respectively. Experimental plots of  $I$  vs.  $t^{-1/2}$  were employed, with the best fits for different concentrations of D-PA (Fig. 6A). The slopes of the resulting straight lines were then plotted vs. D-PA concentration (Fig. 6B). From the resulting slope and Cottrell equation the mean value of the  $D$  was found to be  $7.5 \times 10^{-6} \text{ cm}^2/\text{s}$ .



**Fig. 6.** Chronoamperograms obtained at ZZ/IL/CPE in 0.1 M PBS (pH 7.0) for different concentration of D-PA. The numbers 1–4 correspond to 0.1, 0.3, 0.8 and 1.5 mM of D-PA. Insets: (A) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against D-PA concentration

### 3.3. Calibration plot and limit of detection

The electrocatalytic peak current of D-PA oxidation at the surface of the ZZ/IL/CPE can be used for determination of D-PA in solution. Therefore, square wave voltammetry (SWV) experiments were performed using modified electrode in 0.1 M PBS (pH 7.0) containing various concentrations of D-PA (Fig. 7). The plot of peak current vs. D-PA concentration consisted of a linear segment with a slope of  $0.085 \mu\text{A} / \mu\text{M}$  in the concentration range of  $5.0 \times 10^{-7}$ – $3.0 \times 10^{-4}$  M and the detection limit ( $3\sigma$ ) was obtained  $1.0 \times 10^{-7}$  M. These values are comparable with values reported by other research groups for electro-oxidation of D-PA (Table 2).



**Fig. 7.** SWVs of ZZ/IL/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of D-PA. Numbers 1-10 correspond to 0.5, 2.0, 5.0, 10.0, 25.0, 50.0, 75.0, 100.0, 200.0 and 300.0  $\mu\text{M}$  of D-PA. Inset: The plot of the electrocatalytic peak current as a function of D-PA concentration in the range of 0.5-300.0  $\mu\text{M}$

**Table 2.** Comparison of the efficiency of some modified electrodes used in the electro-oxidation of D-PA

Electrode	Method	LOD (M)	LDR (M)	Ref.
Carbon paste	Voltammetry	$1.0 \times 10^{-7}$	$1.0 \times 10^{-7} - 1.0 \times 10^{-4}$	[10]
Carbon paste	Voltammetry	$1.0 \times 10^{-7}$	$1.0 \times 10^{-6} - 1.0 \times 10^{-4}$	[12]
Glassy carbon	Voltammetry	$3.5 \times 10^{-6}$	$1.0 \times 10^{-5} - 4.8 \times 10^{-4}$	[13]
Carbon paste	Voltammetry	$7.6 \times 10^{-7}$	$8.0 \times 10^{-7} - 1.4 \times 10^{-4}$	[18]
Carbon paste	Voltammetry	$1.0 \times 10^{-7}$	$5.0 \times 10^{-7} - 3.0 \times 10^{-4}$	This Work

### 3.4. Determination of D-PA in D-PA capsule and urine samples

In order to evaluate the analytical applicability of the proposed method, also it was applied to the determination of D-PA in D-PA capsule and urine samples. The results for



determination of the D-PA in real samples are given in table 3. Satisfactory recovery of the experimental results was found for D-PA. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.).

**Table 3.** The application of QDMCPE for determination of D-PA in some real samples (n=5). All concentrations are in  $\mu\text{M}$ .

Sample	Spiked	Found	Recovery	R.S.D.
D-PA capsule	-	8.0	-	3.2
	2.5	10.8	102.8	1.7
	5.0	12.8	98.5	2.9
	7.5	15.6	100.6	2.4
	10.0	17.6	97.8	2.7
Urine	-	-	-	-
	5.0	4.9	98.0	1.9
	10.0	10.1	101.0	2.8
	15.0	15.5	103.3	3.4
	20.0	19.8	99.0	2.2

#### 4. CONCLUSION

This work demonstrates the construction of a chemically modified carbon paste electrode by the incorporation of  $\text{ZnS}/\text{ZnAl}_2\text{S}_4$  nanocomposite and ionic liquid as modifying species. The results show that the oxidation of D-PA is accelerated at pH 7.0, with the peak potential of D-PA shifted by 200 mV to a less positive potential at the surface of the ZZ/IL/CPE. SWV exhibits a linear dynamic range from  $5.0 \times 10^{-7}$  to  $3.0 \times 10^{-4}$  M and a detection limit of  $1.0 \times 10^{-7}$  M for D-PA. Finally, the proposed method was successfully applied to the determination of D-PA in real samples.

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