

Full Paper

Preparation, Characterization and Electrochemical Application of ZnO Nanorods for Voltammetric Determination of Hypericin using Modified Carbon Paste Electrode

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Abstract- The direct electrochemistry of hypericin on a modified carbon paste electrode (CPE) was described. The electrode was modified with zinc oxide (ZnO) nanorods and n-hexyl-3-methylimidazolium hexafluoro phosphate as a binder. The oxidation peak potential of hypericin at the surface of the ionic liquid / ZnO nanorods / CPE (ILZNCNPE) appeared at 320 mV, which was about 100 mV lower than the oxidation peak potential at the surface of the traditional carbon CPE under a similar condition. The linear response range and detection limit were found to be 2.5×10^{-6} - 2.0×10^{-4} M and 9.1×10^{-7} M, respectively.

Keywords- Hypericin, ZnO nanorods, Drug analysis, Ionic liquids, Carbon paste electrode

1. INTRODUCTION

Hypericin, a naphthodianthrone, is one of the major active components of St John's Wort. It is available as an "over-the-counter" drug. Patients with malignant diseases undergoing radiation therapy often use it for self-medication [1]. It is also shown to be clinically effective in treating mild to moderate forms of depression [1] and HIV infection [1]. In particular, several phosphorylation of signaling pathways, such as extracellular signal-regulated kinases (ERK) could be suppressed by hypericin in cultured cells.[1]. Therefore, determination of this compound is very important. Various methods including chromatography [2], chemiluminescence [3], capillary electrophoresis [4] and electrochemical methods [5,6] have been used for the detection of hypericin.

Since the discovery of the carbon paste electrode (CPE) by Ralph N. Adams in 1958 and its introduction as an alternative to the dropping mercury electrode, particularly in anodic polarography [7]. Type of electrode (and sensors based on it) has undergone considerable development. The scope for the development is due to several advantages, such as low cost, low background current, wide potential window, high sensitivity, and renewable surface. However, because the fabrication process involves simply mixing graphite with suitable binders to form a paste, modification of this material has branched out across several lines of innovation. Between the more relevant ones are: research into alternative binding components such as Teflon, sol-gel, and ionic liquid, modification of the paste with polymers, redox mediators and recognition elements to construct electrochemical sensors and biosensors, and the doping of the electrode with different materials such as clay, carbon nanotubes and metal nanoparticles to enhance the analytical performance of the associated electrochemical devices [9-17].

Room temperature ionic liquids (RTILs) are beginning to be used as a new kind of binder to make an ionic liquid modified electrode [18]. Because RTILs have many specific electrochemical properties such as wide electrochemical window, high ionic conductivity and good solubility, they have been recognized as a useful non-aqueous media for various electrochemical processes [19-28].

Nanostructured materials particularly carbon nanomaterials including nanoparticles, nanowires and nanotubes 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 [29-35] . Among them, zinc oxide (ZnO), an environment-friendly semiconductor (band gap of 3.37 eV) is an interesting metal oxide with several scientific and engineering based applications [36-46].

In the present work, we describe the preparation of a new carbon paste electrode modified with an ionic liquid and ZnO nanorods (ILZNCPE) and investigate its performance for the determination of hypericin in aqueous solutions.

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 ILZNCPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

Hypercin 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. ZnO nanorods were synthesized in our laboratory according to the method described in literatures [37]. A typical SEM image of the synthesized ZnO nanorods is shown in Fig. 1.

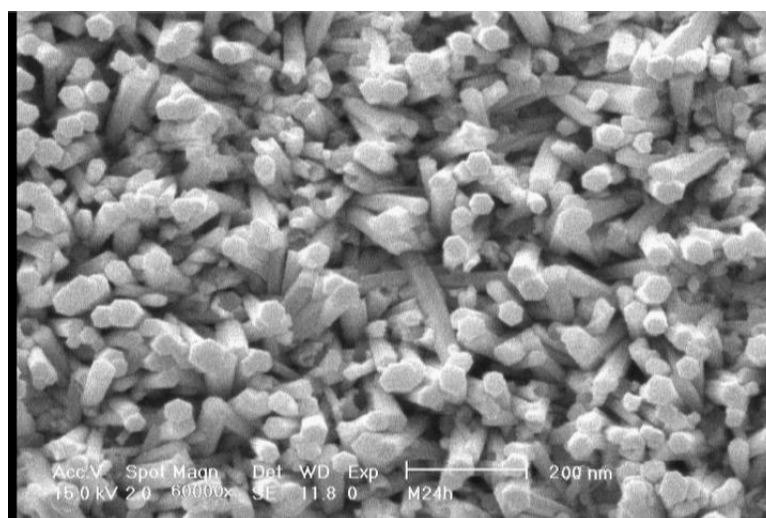


Fig. 1. SEM image of synthesized ZnO nanorods

2.2. Preparation of the electrode

ILZNCPEs were prepared by mixing 0.04 g of ZnO nanorods 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 ZnO nanorods (ILCPE), ZnO nanorods carbon paste electrode (ZNCPE) consistent of ZnO nanorods

graphite powder and paraffin oil, and bare carbon paste electrode (CPE) consisting of graphite powder and paraffin oil were also prepared in the same way.

3. RESULT AND DISCUSSION

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

Fig. 2 displays cyclic voltammetric responses from the electrochemical oxidation of 40.0 μM hypericin at the surface of ILZNCPE (curve d), ILCPE (curve c), ZNCPE (curve b) and bare CPE (curve a). The results showed that the oxidation of hypericin 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 hypericin and dramatic increase of the current indicates the catalytic ability of ILZNCPE (curve d), ILCPE (curve c) to hypericin oxidation. The results showed that the combination of ZnO nanorods and the ionic liquid (curve d) definitely improved the characteristics of hypericin oxidation. However, ILZNCPE shows much higher anodic peak current for the oxidation of hypericin compared to ILCPE, indicating that the combination of ZnO nanorods and IL has significantly improved the performance of the electrode toward hypericin oxidation.

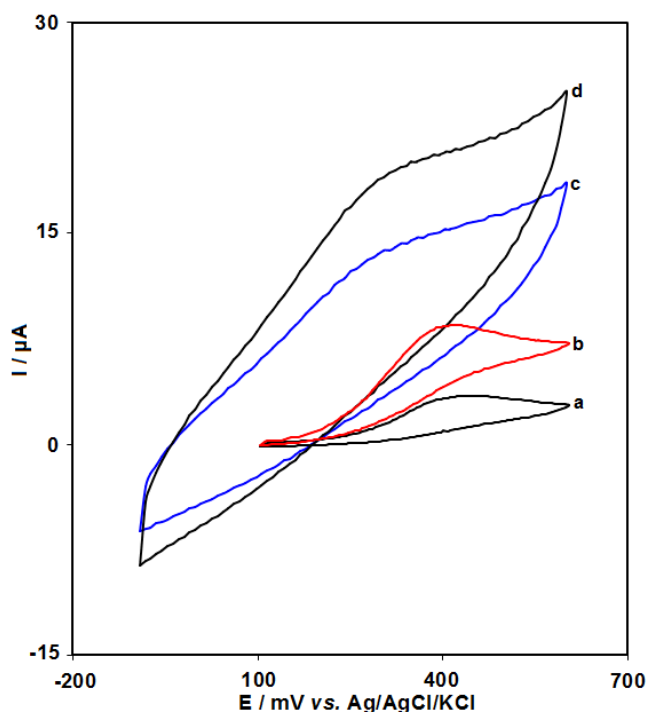


Fig. 2. CVs of a) CPE, b) ZNCPE, c) ILCPE and d) ILZNCPE in the presence of 40.0 μM hypericin in 0.1 M PBS (pH 7.0), respectively. In all cases the scan rate was 50 mV s^{-1}

3.2. Effect of scan rate

The effect of potential scan rates on the oxidation current of hypercin 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 [47] 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 10 to 400 mV s^{-1} .

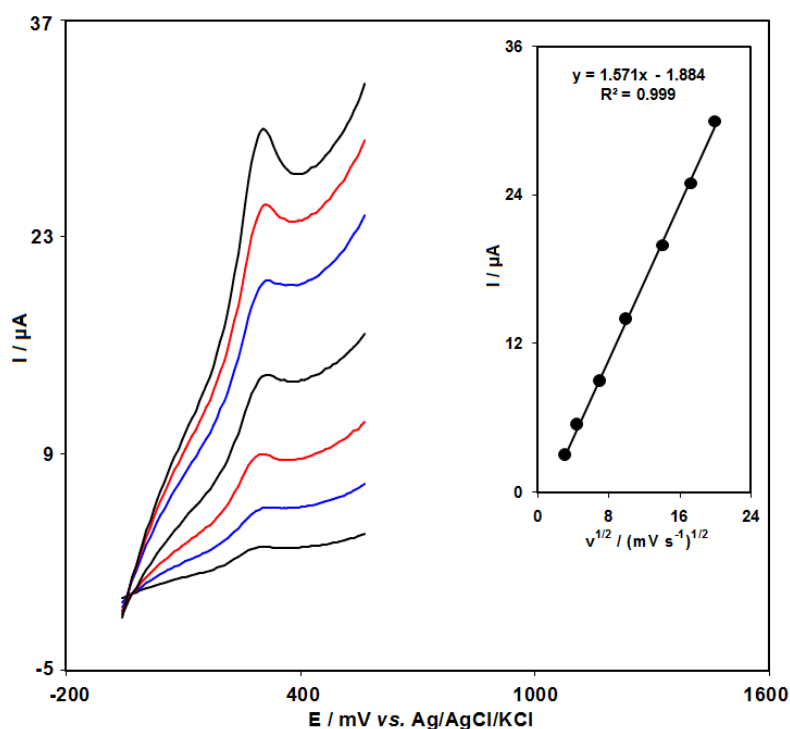


Fig. 3. CVs of ILZNCPE in 0.1 M PBS (pH 7.0) containing 15.0 μM hypercin at various scan rates; (10, 20, 50, 100, 200, 300 and 400 mV s^{-1}) Inset: Variation of anodic peak current vs. square root of scan rate

3.3. Chronoamperometric measurements

Chronoamperometric measurements of hypercin at ILZNCPE were carried out by setting the working electrode potential at 0.4 V vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of hypercin in PBS (pH 7.0) (Fig. 4). For an electroactive material (hypercin 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 [47].

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

Where D and C_b are the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) 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 hypercin (Fig. 4A). The slopes of the resulting straight lines were then plotted vs. hypercin concentration (Fig. 4B). From the resulting slope and Cottrell equation the mean value of the D was found to be $1.3 \times 10^{-5} \text{ cm}^2/\text{s}$.

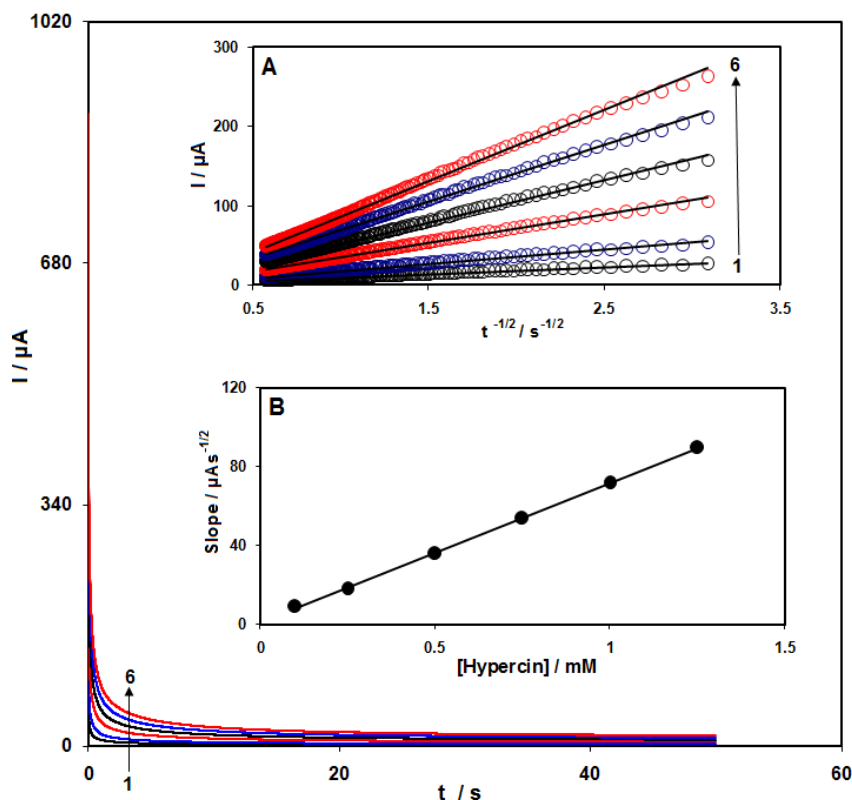


Fig. 4. Chronoamperograms obtained at ILZNCPE in 0.1 M PBS (pH 7.0) for different concentrations of hypercin. The numbers 1–6 correspond to 0.1, 0.25, 0.5, 0.75, 1.0 and 1.25 mM of hypercin. Insets: (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–6; (B) Plot of the slope of the straight lines against hypercin concentration

3.4. Calibration plot and limit of detection

The peak current of hypercin oxidation at the surface of the modified electrode can be used for determination of hypercin in solution. Therefore, square wave voltammetry (SWV) experiments were done for different concentrations of hypercin (Fig. 5). The oxidation peak currents of hypercin at the surface of a modified electrode were proportional to the concentration of the hypercin within the ranges 2.5×10^{-6} to 2.0×10^{-4} M with detection limit (3σ) of 9.1×10^{-7} M.

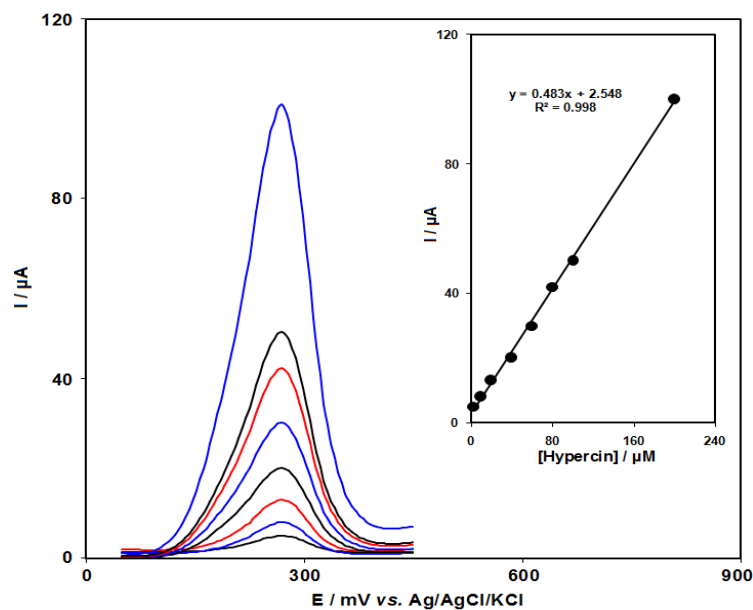


Fig. 5. SWVs of ILZNCNPE in 0.1 M PBS (pH 7.0) containing different concentrations of hypercin (2.5, 10.0, 20.0, 40.0, 60.0, 80.0, 100.0 and 200.0 μM). Inset shows the plots of the peak current as a function of hypercin concentration in the range of 2.5-200.0 μM

4. CONCLUSION

Zinc oxide nanorods were incorporated onto the surface of a carbon paste electrode in the presence of ionic liquid as a binder. The direct electrochemistry of hypercin at the surface of ILZNCNPE was assessed by cyclic voltammetry, chronoamperometry and SWV methods. The presence ionic liquid and zinc oxide nanorods helped hypercin have a favoured orientation and reduce the effective electron transfer distance.

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