

Full Paper

Voltammetric Response of Furazolidone on Multi-walled Nanotube Film Coated Carbon Paste Electrode Using Ionic Liquid

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Abstract- A film of multiwalled carbon nanotubes (MWCNT) was casted on the surface of an ionic liquid (IL) modified carbon paste electrode (CPE) to established a modified electrode denoted as MWCNT/IL/CPE. The electrochemical reduction of furazolidone (Fu) was investigated with cyclic voltammetry. The constructed electrode (MWCNT/IL/CPE) exhibited excellent electrocatalytic behavior toward the reduction of Fu as evidenced by the enhancement of the reduction peak current and the shift in the cathodic potential to less negative values (by 20 mV) in comparison with the bare CPE. The formal potential, E^0 , of Fu is pH dependent with a slope of -53.1 mV per unit of pH, close to the anticipated Nernstian value of -59 mV for a 4-electron and 4-proton process. A detailed analysis of cyclic voltammograms gave fundamental electrochemical parameters including the electroactive surface coverage (Γ), the transfer coefficient (α) and the standard rate constant (k_s). A linear calibration curve was obtained for Fu detection in the concentration range of 50-800 $\mu\text{mol L}^{-1}$ of detection limit 33 $\mu\text{mol L}^{-1}$.

Keywords- Ionic Liquid, Cyclic Voltammetry, Multiwalled Carbon Nanotubes, Furazolidone, Modified Electrode

1. INTRODUCTION

Furazolidone is a synthetic nitrofuran which widely used in human and veterinary medicine, food additives and preservatives [1]. The main pharmaceutical uses of nitroaromatic compounds (RNO_2) are as antibacterial and anticancer agents [2]. Reduction of these compounds is believed to be due to flavoproteins known as "nitroreductases" which have the ability to use nitro compounds as acceptors of one or two electrons [3].

Carbon nanotubes are an interesting class of nonmaterial offering high electrical conductivity, high surface area, significant mechanical strength and good chemical stability. They have been known to promote electron transfer reactions when used as electrode modifying material. On the other hand, some temperature ionic liquids are liquid electrolytes composed entirely ions have valuable properties such as high ionic conductivity, electrical and thermal stability and catalytic activity. Recently, Safavi and coworkers [4-6] reported the application of ILs in electrochemical analysis. They reported the direct electrochemistry of hemoglobin based on its direct immobilization on carbon ionic liquid electrode and its electrocatalytic behaviors [7].

In recent years, modified electrodes are increasingly used in biological chemistry [8-10]. The combination of CNTs and ionic liquids as modifying reagents is interesting because of their unique properties [11]. To our knowledge, reduction of Fu using both MWCNT and IL has not been reported yet. In previous works, we reported on the stabilization of RNO_2^- at a glassy carbon electrode and obtained some of its kinetic parameters [12-14]. In continuation of our study [15-16], we have investigated the electroreduction of Fu at the MWCNT/IL/CPE based on the unusual properties of both MWCNT and IL as modifying reagents.

2. EXPERIMENTAL

2.1. Apparatus

Electrochemical measurements were carried out with a Metrohm model 746VA trace analyzer connected to a 747 VA stand. The working electrode was a composed of a MWCNT film-modified IL/CPE. A platinum wire and a commercial Ag/AgCl saturated KCl electrode from Metrohm were used as auxiliary and reference electrodes, respectively.

2.2. Reagent

Furazolidone was obtained from Sigma. All other reagents used were of analytical grade without further purification. A Fu solution (1 mM) was used in a Britton-Robinson (B-R) buffer (pH 7.0)-10% DMF solution. Multi-walled carbon nanotubes with purity 95% (10-30 nm diameters and 5 μm length) were obtained from io-li-tec, Ionic Liquid Technologies. DNA solution (4.0 mg L^{-1}) were prepared with B-R buffer (0.04 M, pH 7.0), and stored at

4 °C. The ionic liquid, 1-butyl-3-methyl imidazolium hexafluoro phosphate (BMIMPF₆), was purchased from io-li-tec and used as received. Solutions were deaerated by bubbling high purity argon gas for 10 min through them prior to the experiments.

2.3. Fabrication of MWCNT/IL/CPE

The IL/CPE was fabricated with the following procedure: 0.093 g of graphite powder, 0.024 g paraffin oil and 0.016 g of IL were mixed thoroughly in an agate mortar to form a uniform paste. A portion of the resulted carbon paste was filled into one end of a teflon tube (diameter 1.8 mm) and a copper wire was inserted through the opposite end to established an electrical contact. The traditional carbon paste electrode (CPE) was prepared according to the reference [4] by hand mixing of graphite powder with paraffin oil at a ratio of 70/30 (w/w).

MWCNT (4 mg) was added to 1 mL DMF. A homogeneous and stable suspension of 4 mg mL⁻¹ MWCNT was achieved with the aid of ultrasonic agitation for about 30 min.

The MWCNT/IL/CPE was prepared by casting 4.0 μL of the suspension of MWCNT on the surface of an IL/CPE, which was dried in air for 30 min at room temperature.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of Fu at the MWCNT/IL/CPE

Fig. 1 compares the cyclic voltammogram responses at unmodified and modified CPEs in the presence and absence of Fu in B-R buffer (0.04 M, pH 7.0)-10% DMF solution. In the absence of Fu, no redox peaks were observed at the bare CPE during the cyclic voltammetry measurements within the potential window of -0.20 to -0.55 V (Fig. 1, curves a). Compared with the bare CPE a large background current was observed at the modified CPEs during the cyclic voltammetric scan, indicating that the use of both modifying reagents MWCNT and IL significantly enhanced the electrical double layer of the electrode. Cyclic voltammogram of Fu at the unmodified CPE (Fig. 1A, curve b) showed only a small and broad cathodic peak occurs at about -0.476 V and no corresponding oxidation peak was observed in the reverse scan, which indicates that the electrochemical behavior of Fu at unmodified CPE is an irreversible and sluggish electron transfer process due to the 4electron- reduction of the nitro group to hydroxylamine [17]. While at a MWCNT/CPE (Fig. 1A, curve c) the cathodic peak was observed at less negative potential, -0.466 V with increasing peak current about two orders of magnitude compared with bare CPE. The increased current as well as the positive shift of the cathodic peak demonstrated an efficient electrocatalytic reduction of Fu on the MWCNT/CPE. In order to test the electrocatalytic activity of the IL, the cyclic voltammograms at both IL/CPE and MWCNT/IL/CPE were recorded in the presence of Fu (Fig. 1B). As shown in Fig. 1B (curve c) the cathodic peak current at MWCNT/IL/CPE was obviously increased about two times (with a 20 mV positive potential shift) compared with

both MWCNT/CPE (Fig. 1A, curve c) and IL/CPE (Fig. 1B, curve b) which is due to the electrical conductivity of the electrode in the presence of IL as well as MWCNT.

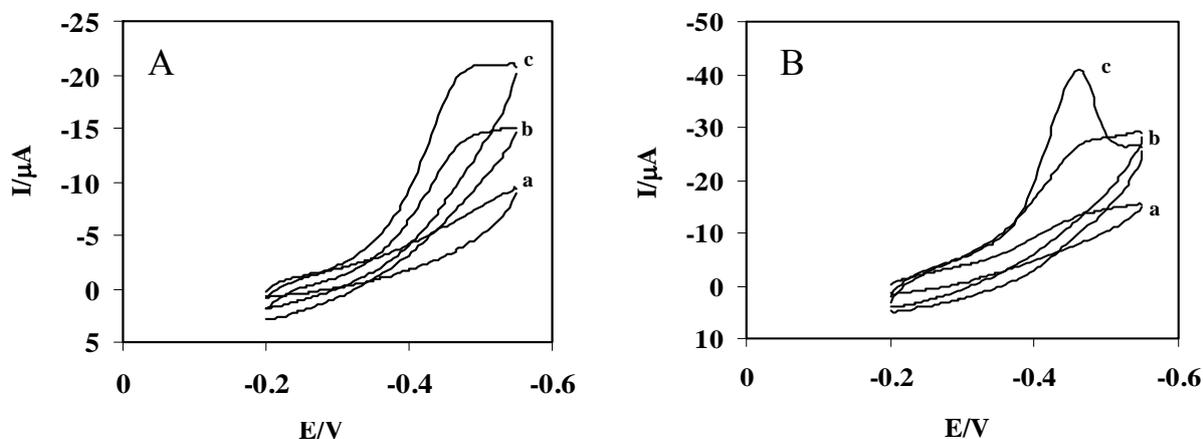
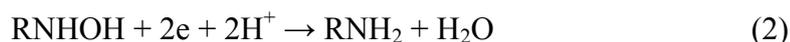
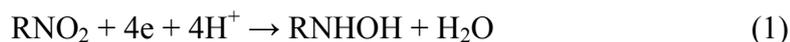


Fig. 1. Cyclic voltammograms in the absence of IL (A) and presence of IL (B) at (a) CPE in blank, (b) CPE in 0.5 mM Fu, (c) MWCNT/CPE in 0.5 mM Fu; B-R buffer (0.04 M, pH 7.0)-10% DMF solution, scan rate 50 mV s^{-1}

3.2. The effect of pH

In our previous reports [12-14], we showed that voltammetric reduction of nitro group depends significantly on the solvent system and pH of medium. In protic media (low percent of DMF and acidic pH media) Fu is reduced at two reductive potentials due to the following well known mechanism for aromatic nitro compounds.



Cyclic voltammograms of Fu at various pH-values at MWCNT/IL/CPE are shown in Fig. 2A. By increasing the pH from 3.0 to 7.0, the cathodic peak potential of Fu shifts to more negative potentials up to pH 7.0 (Fig. 2B). The formal value of E^0 is linear with pH in the range 3.0-7.0, with a slope 53.1 mV/pH (Fig. 2C). This value is close to the theoretical value of 59 mV/pH [18] indicating the participation of the same proton and electron numbers in the electrochemical process.

The position of the break in the E^0/pH plot implies that the protonation site is associated with the electrode reaction, which has an apparent pK_a value of about 7.0.

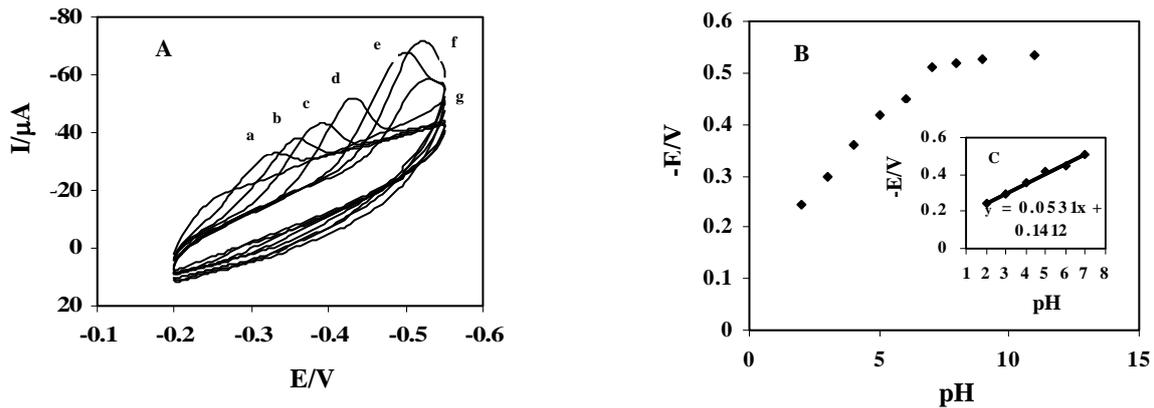


Fig. 2. (A) Cyclic voltammograms of 2 mM Fu at MWCNT/IL/CPE for pH values of a) 3.0, b) 4.0, c) 5.0, d) 6.0, e) 7.0, f) 8.0 and g) 9.0 in B-R buffer (0.04 M)-10% DMF solutions, scan rate 50 mV s^{-1} . (B) Plot of $E^{0'}$ vs. pH (C) Linear plot $E^{0'}$ vs. pH

3.3. Determination of electrochemical active surface area

Electrode reaction rates and most double layer parameters are extensive quantities and have to be referred to the unit area of the interface. Knowledge of the real surface area of electrodes is therefore needed. In order to measure the electrochemically active surface areas of the modified electrode, the chronoamperogram of 0.1 mM potassium ferrocyanide as the redox probe was recorded. In chronoamperometric studies, the current for the electrochemical reaction of ferrocyanide (at a mass-transfer-limited rate) that diffuse to a electrode surface is described by the Cottrell equation [18]:

$$i = nFAD^{1/2}C^* / \pi^{1/2}t^{1/2} \quad (3)$$

Where A is the electrochemical active area, D is the diffusion coefficient, C^* is the bulk concentration of ferrocyanide and the other parameters having their usual meanings. Under diffusion control, a plot of i vs. $t^{-1/2}$ will be linear and from the slope, the value of A can be obtained, since the precise value of the diffusion coefficient of ferrocyanide is well known ($6.20 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The electrochemically active area of the MWCNT/IL/CPE was 0.50 cm^2 .

3.4. The effect of the scan rate

Useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. Fig. 3A shows the cyclic voltammograms of Fu at the MWCNT/IL/CPE when the scan rate (ν) varies from 10 to 120 mV s^{-1} . A linear relationship ($y = -474.73x - 25.07$) with a correlation coefficient of $R = 0.977$ was observed between the peak current and the scan rate (Fig. 3B), which indicates that the electrode process is surface-controlled. From the slope of the linear plot of I vs. ν the surface

concentration of the electroactive species (Γ) can be estimated to be about 6.3×10^{-11} mol cm^{-2} according to the following equation [18]:

$$i_p = n^2 F^2 A \Gamma \nu / 4RT \quad (4)$$

As shown by increasing the scan rate, the peak potential is shifted to a more negative potential. Because of the irreversible electrode process of the reduction reaction of Fu, the Laviron's equation [19] was used to estimate αn and k_s values as follows:

$$E_p = E^0 + (RT/\alpha nF) [\ln(RT k_s / \alpha nF) - \ln \nu] \quad (5)$$

Where α is the electron transfer coefficient, k_s is the standard rate constant of the surface reaction, ν is the scan rate, n is the electron transfer numbers and E^0 is the formal potential. k_s and αn values can be concluded from the intercept and slope of the linear plot of E_p with respect to $\ln \nu$, if the value of E^0 is known.

The E^0 value at MWCNT/IL/CPE can be deduced from the intercept of E_p vs. ν plot on the ordinate by extrapolating the line to $\nu=0$ (Fig. 3C). Knowing E^0 , and from the graphical representations of E_p vs. $\ln \nu$ for Fu (Fig. 3D), the values of $\alpha n=2.04$ and $k_s=1.0 \text{ s}^{-1}$ were obtained from the slope and intercept, respectively. Since for a totally irreversible electron transfer, α was assumed as 0.5, the n was calculated to be 4 which indicated that four electrons were involved in the reduction of Fu on the MWCNT/IL/CPE.

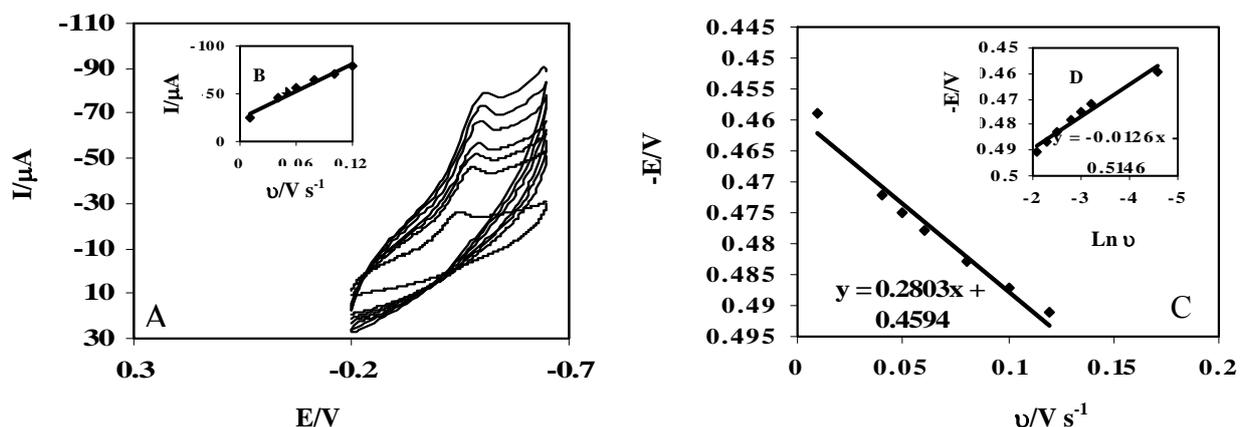


Fig. 3. (A) Cyclic voltammograms of 2.0 mM Fu at MWCNT/IL/CPE in B-R buffer (0.04 M, pH 7.0)-10% DMF solution at scan rates (inner to outer) 10, 40, 50, 60, 80, 100, 120 mV s^{-1} . (B) The plot of peak current vs. scan rate. (C and D) The variations of peak potential vs. ν and $\ln \nu$ at MWCNT/IL/CPE, respectively

3.5. The effect of the amount and injected volume of MWCNT composite

The effect of the amount of MWCNT on the anodic peak was examined by varying the amount of 1.0 to 5.0 mg in 1.0 mL of DMF. The results showed that peak current reached a maximum at 4.0 mg value and decreased after that. The effect of the injected volume of MWCNT composite film was also investigated and maximum current is obtained at 4.0 μL .

3.6. Analytical application, analytical figures of merit

Under the optimum conditions there was a linear relationship between peak current and Fu concentration in the range 50 to 800 $\mu\text{mol L}^{-1}$ ($R=0.962$) (Fig 4). The limit of detection (LOD), was obtained as $Y_{\text{LOD}}=X_{\text{B}}+3S_{\text{B}}$, where Y_{LOD} is the signal for limit of detection, X_{B} and S_{B} are the mean and the standard deviation of the blank signal, respectively. Under optimum experimental conditions the limit of detection (LOD) was obtained as 33 $\mu\text{mol L}^{-1}$.

The reproducibility of the method was checked by successive determinations ($n=8$) of Fu. The relative standard deviations (RSD) were lower than 0.69%.

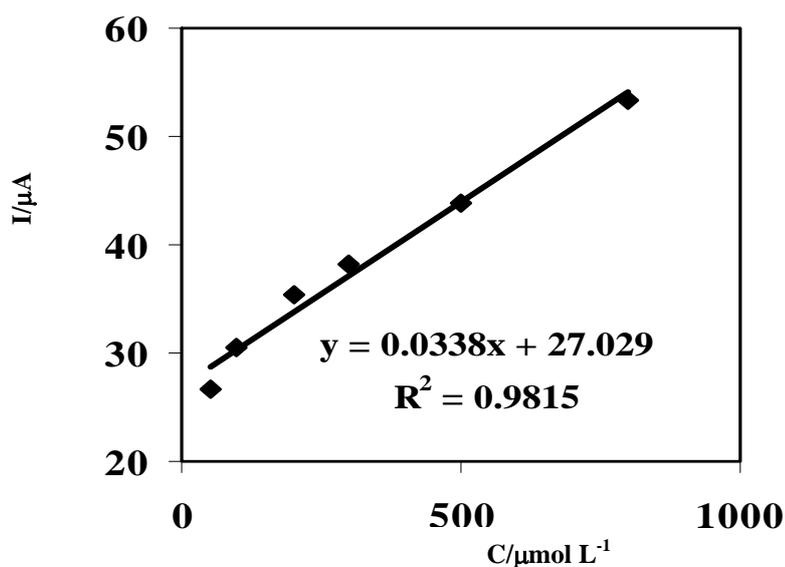


Fig. 4. The plot of the current vs. Fu concentration; scan rate 50 mV s^{-1}

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