Full Paper

Zinc Oxide Modified Carbon Paste Electrode Sensor for Uric Acid: A Cyclic Voltammetric Study

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Abstract- Zinc oxide (ZnO) modified carbon paste electrode (MCPE) was used for the electrochemical studies of potassium ferrocyanide (K₄[Fe(CN)₆]) and uric acid (UA). The effect of amount of ZnO in carbon paste electrode (CPE), scan rate and concentration studies of K₄[Fe(CN)₆] and UA were carried out. The electrochemical sensitivity of CPE/Triton X-100(TX-100), CPE/ZnO/TX-100, CPE/cetyltrimethyl ammonium bromide (CTAB), CPE/ZnO/CTAB, CPE/Polyglycine (PG) and CPE/ZnO/PG were studied towards uric acid.

Keywords- Zinc oxide, Polyglycine, Uric acid, Modified Carbon paste electrode, Cyclic voltammogram

1. INTRODUCTION

The semiconductor ZnO has gained substantial interest to researchers because it is a unique material with a direct band gap (3.37 eV) and large exciton binding energy of 60 meV. It has been widely used in near uv-emission, gas and chemical sensors, transparent electrodes, photo catalysts, solar cells and piezoelectric applications [1-10]. ZnO can be
prepared by several methods such as chemical precipitation [11], sol-gel synthesis [12] and solvothermal/hydrothermal reaction [13-15].

The prepared ZnO as in the literature [16], along with surfactants (TX-100 and CTAB) and polyglycine (PG) was used as a modifier in carbon paste electrode (CPE) for the detection of uric acid (UA). The electrochemical response of bare carbon paste electrode (BCPE), ZnO and surfactants modified carbon paste electrode (MCPE) in the presence of potassium ferrocyanide in 1M KCl solution was studied.

Potassium ferrocyanide is the chemical compound with the formula K₄[Fe(CN)₆]. This lemon yellow salt consists of the co-ordination compound [Fe(CN)₆]⁴⁻, it is soluble in water. Potassium ferrocyanide is used in the separation of copper from molybdenum ores and the purification of tin. Potassium ferrocyanide is also used in the production of wine and citric acid [17]. Swamy et al. studied potassium ferrocyanide as a standard for Poly (Aniline Blue) Modified Carbon Paste Electrode [18].

UA is a primary product of purine metabolism in the human body [19]. In human the UA concentration in urine and serum are certain ranges (0.21 to 0.42 mmol/L in men and 0.16 to 0.36 mmol/L in women [20]), because of its abnormal concentration level causes many disease such as gout, hyperuricaemia and Lesch-Nyan disease [21]. There are many methods for the detection of UA including spectrophotometry [22], chromatography [23] and electroanalytical methods [24]. Among these methods electroanalytical detection is an important technique because it is a simple, sensitive, reliable, repeatable, low costs and more convenient. The chemically modified electrode was used for the electrochemical detection of UA [25-27].

In this work, synthesized ZnO was used as modifier for studying electrochemical response towards K₄[Fe(CN)₆] and for detection of UA. The modified ZnO/TX-100, ZnO/CTAB and ZnO/PG carbon paste electrode was studied for electrochemical investigation of UA in 0.2 M phosphate buffer at pH 7.4 at the scan rate of 0.1 Vs⁻¹. Thus the present study shows CPE/ZnO/PG is an excellent modifier electrode for the selective and sensitive detection of UA.

2. EXPERIMENTAL

2.1. Apparatus

The cyclic voltammetry measurements were carried out with a model 660c (CH Instruments). A conventional three electrode electrochemical system was used for all electrochemical experiments, which consists of bare carbon paste electrode (BCPE), ZnO modified CPE (CPE/ZnO), CPE/TX-100, CPE/ZnO/TX-100, CPE/CTAB, CPE/ZnO/CTAB, CPE/PG and CPE/ZnO/PG as the working electrode. An aqueous saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode.
2.2. Materials

Uric acid, cetyltrimethyl ammonium bromide, triton X-100, glycine, disodium hydrogen phosphate (Na2HPO4), sodium dihydrogen orthophosphate (NaH2PO4), and silicone oil were purchased from Himedia chemicals. The graphite powder, potassium ferrocyanide, KCl and NaOH procured from Merk chemicals. Stock solution of UA was prepared in 0.1 M NaOH solution, phosphate buffer of pH 7.4 (0.2 M) and all aqueous solution were prepared with double distilled water.

2.3. Preparation of bare carbon paste electrode

The bare carbon paste electrode (BCPE) was prepared by mixing of graphite powder and silicone oil at a ratio of 70:30 (w/w) in an agate mortar until a homogeneous paste was obtained, the mixture was then packed into a homemade Teflon cavity and polished using smooth paper.

2.4. Preparation of modified carbon paste electrode

In the preparation of ZnO/MCPE the ZnO (10, 20, 30, 40 and 50 mg) powder was mixed with graphite powder (0.24 g) and silicone oil (0.05 mL), the mixing and packing is same as that of BCPE. ZnO/TX-100 or ZnO/CTAB MCPE was prepared by immobilizing 10 μL solution of 25 mM TX-100 or CTAB on the CPE/ZnO and incubated for 5 min. For TX-100 and CTAB MCPE same procedure was followed, instead of CPE/ZnO the BCPE was used. ZnO/PG MCPE was prepared by electrochemical polymerization of glycine at the CPE/ZnO and was carried out by using cyclic voltammetric method in aqueous solution containing 0.04 M glycine in 0.2 M acetate buffer (pH 5.8). Electropolymerization was accomplished by the formation of film that grew between -0.5 V and 1.8 V at a scan rate of a 0.1 Vs⁻¹ for a 10 cycles using cyclic voltammetry [28]. In preparing PG MCPE, the same procedure was followed, instead of CPE/ZnO only BCPE was used.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical behavior of potassium ferrocyanide at ZnO MCPE

Fig. 1A shows the cyclic voltammograms of 0.1 mM K₄[Fe(CN)₆] in 1 M KCl at the different concentration of ZnO MCPE at a scan rate of 0.1 Vs⁻¹. Fig. 1B the graph of the anodic peak current versus the different concentration of (10, 20, 30, 40, and 50 mg) ZnO used in the modification of electrodes and shows the 30 mg ZnO MCPE is response to the maximum current, and this optimized concentration is maintained during further investigation of K₄[Fe(CN)₆].
Fig. 2a shows the cyclic voltammograms of BCPE (dotted line) and ZnO MCPE (solid line) in 1 M KCl containing 0.1 mM K₄[Fe(CN)₆], this illustrate a good electrochemical activity of the ZnO MCPE contrast with the BCPE. Due to increase in the peak current, the MCPE possess the good electrocatlytic activity.

**Fig. 1.** (A) Cyclic voltammograms of 0.1 mM K₄[Fe(CN)₆] at different concentration of ZnO in a carbon paste electrode in 1 M KCl at a scan rate of 0.1 V s⁻¹; (B) Graph of the anodic peak current (Iₚₐ) vs. the concentration of ZnO in carbon paste electrode

**Fig. 2.** (a) Cyclic voltammograms of 0.1 mM K₄[Fe(CN)₆] at bare CPE(dashed line) and at ZnO modified CPE (solid line) in 1 M KCl as Supporting electrolyte at scan rate 0.1 V s⁻¹; (b) Graph of anodic peak current versus square root of scan rate at bare CPE and CPE/ZnO in 1 M KCl containing 0.1 mM K₄[Fe(CN)₆]
3.2. Effect of scan rate on the peak current of potassium ferrocyanide

The effect of scan rate for 0.1 mM K₄[Fe(CN)₆] in 1 M KCl was studied by cyclic voltammetry at the BCPE and MCPE. The graph as in Fig. 2b shows an increase in the scan rate (0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 Vs⁻¹) the peak current also increases for both BCPE and ZnO MCPE. The graph obtained for anodic peak current versus square root of scan rate (ν¹/²) exhibits good linearity for both BCPE and CPE/ZnO with correlation coefficient (0.9997 and 0.9998) which indicates, in both electrodes the electron transfer reaction was diffusion-controlled process. The surface area available for the electron transfer to species in solution can be estimated by the Randles-Sevcik equation (1) [27]. This equation relates the peak current for an electron transfer controlled process with square root of the scan rate as follows.

\[
\text{i}_p = (2.69 \times 10^5) \ n^{3/2} \ A \ D^{1/2} \ C_0 \ \nu^{1/2}
\]  

(1)

Where \text{i}_p is the peak current, \text{n} is the number of exchanged electron, \text{A} is the electroactive surface area (cm²), \text{D} is the diffusion co-efficient (cm² s⁻¹) which is obtained from slope of \text{I}_{pa} versus \nu^{1/2}, \text{C}_0 is the concentration of the electroactive species (mol cm⁻¹) and \text{v} is the scan rate (V s⁻¹). From equation (1) the surface area of BCPE and MCPE in 0.1 mM K₄[Fe(CN)₆] at scan rate 0.15 Vs⁻¹ was calculated and were found be 0.039±0.0012 cm² and 0.0428±0.0015 cm². Compared with BCPE, the ZnO MCPE exhibits enhanced electrode surface area. Thus the high surface area of the MCPE enhanced the electrode contact area of K₄[Fe(CN)₆].

![Graph](image_url)

**Fig. 3.** (a) Cyclic voltammograms of different concentration ((A)0.1 mM, (B)0.15 mM, (C)0.2 mM, (D)0.25 mM, (E)0.3 mM, (F)0.35 mM, (G)0.4 mM, (H)0.45 mM, (I)0.5 mM) of
K₄[Fe(CN)₆] at ZnO modified CPE in 1 M KCl at the scan rate of 0.1 Vs⁻¹; (b) Graph of anodic peak current versus concentration of potassium ferrocyanide

3.3. Effect of concentration of K₄[Fe(CN)₆]

The effect of concentration of K₄[Fe(CN)₆] in 1 M KCl at the scan rate 0.1 Vs⁻¹ was studied at CPE/ZnO. Fig. 3a shows voltammetric response of different concentration K₄[Fe(CN)₆] at ZnO MCPE, the peak current increases with increase in concentration of (0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 mM) K₄[Fe(CN)₆]. The graph of the anodic peak current versus the concentration of K₄[Fe(CN)₆] exhibits good linearity as shown in Fig.3b.

3.4. Electrochemical response of K₄[Fe(CN)₆] at the ZnO/TX-100 and ZnO/CTAB MCPE

Fig. 4A shows the cyclic voltammograms of 0.1 mM K₄[Fe(CN)₆] in 1 M KCl and scan rate of 0.1 Vs⁻¹ at bare CPE (dashed line), CPE/TX-100(a) and CPE/ZnO/TX-100(b). The anodic peak current of bare CPE will smaller than CPE/TX-100 and CPE/ZnO/TX-100. Among them CPE/ZnO/TX-100 have higher anodic peak current, therefore CPE/ZnO modified with TX-100 shows good electrocatalytic activity towards K₄[Fe(CN)₆]. Similarly in Fig. 4B the anodic peak current of BCPE lesser than the CPE/CTAB and CPE/ZnO/CTAB. However, the voltammetric response is apparently enhanced at CPE/CTAB modified carbon paste electrode, reflected by the enlargement of the peak currents compare to the CPE/ZnO/CTAB.

![Fig. 4. Cyclic voltammograms of 0.1 mM K₄[Fe(CN)₆] (A) Bare CPE(dashed line), CPE/TX-100 (a), CPE/ZnO/TX-100 (b);(B) Bare CPE(dashed line), CPE/CTAB(a), CPE/ZnO/CTAB(b) in 1 M KCl at the scan rate of 0.1 Vs⁻¹](image)
Because the electrochemical characterization of cationic surfactant (CTAB) MCPE mechanism illustrate adsorptive behavior of CTAB on carbon paste electrode. They revealed that CTAB formed a compact monolayer on the electrode surface with elevated density of positive charges bounded outside of the electrode [26,29].

In CPE/ZnO/CTAB there may possibility for capping of CTAB on ZnO and therefore the expose of positive charge (CTAB) on surface of electrode may be lesser than the CPE/CTAB and therefore the peak current of CPE/ZnO/CTAB is lesser than the CPE/CTAB.

### 3.5. Electrochemical response of UA at ZnO MCPE

Fig. 5A shows the cyclic voltammograms of 0.1 mM UA at the different weight of ZnO MCPE at a scan rate of 0.1Vs⁻¹ in 0.2 M phosphate buffer (pH 7.4), Fig. 5B the graph of the anodic peak current versus the different concentration of (10, 20, 30, 40, and 50 mg) ZnO used in the modified electrodes and shows the 30 mg ZnO MCPE is response to the maximum current, and this optimized concentration is maintained during further investigation of UA.

The cyclic voltammograms of 0.1 mM UA in 0.2 M phosphate buffer and scan rate of 0.1 Vs⁻¹ at BCPE (dashed line) and ZnO MCPE (solid line) was obtained, however a sharp oxidation and a small re-reduction peak was appeared [30] as shown in the Fig. 6 and the ZnO MCPE illustrate an increase in anodic peak current and there is an refusal change in cathodic peak current compare to BCPE. This indicates the CPE/ZnO was exhibit good electrocatalytic activity than BCPE.

![Fig. 5.](image_url)

**Fig. 5.** (A) Cyclic voltammograms of 0.1 mM UA at different concentration of ZnO in carbon paste electrode in presence of 0.2 M phosphate buffer solution (pH 7.4) and scan rate 0.1 Vs⁻¹; (B) Graph of the anodic peak current (IPA) vs. the different concentration of ZnO in carbon paste electrode
Fig. 6. Cyclic voltammograms of 0.1 mM UA in 0.2 M phosphate buffer solution (pH 7.4) and scan rate 0.1 Vs⁻¹ at bare CPE (dashed line) and ZnO MCPE (solid line)

3.6. Effect of scan rate

The effect of scan rate for 0.1 mM UA in phosphate buffer (pH 7.4) was studied by cyclic voltammetry at ZnO MCPE. The cyclic voltammograms of UA as in Fig.7a shows an increase in the anodic and cathodic peak current by increasing the scan rate (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 Vs⁻¹). In Fig.7b, the graph of anodic peak current (I_{pa}) versus the scan rate (ν) shows a good linearity and correlation coefficient (0.9997), which indicates an adsorption controlled reaction [31,32].

Fig. 7. (a) Cyclic voltammograms of 0.1 mM UA at CPE/ZnO in 0.2 M phosphate buffer solution (pH 7.4) at scan rates of: (A) 0.05 Vs⁻¹, (B) 0.1 Vs⁻¹, (C) 0.2 Vs⁻¹, (D) 0.3 Vs⁻¹, (E) 0.4 Vs⁻¹ and (F) 0.5 Vs⁻¹.; (b) Plot of the anodic peak current versus the scan rate
3.7. Effect of concentration of UA

The electrocatalytic oxidation of UA was carried out by varying the concentration of UA at ZnO MCPE. Fig. 8a shows the cyclic voltammograms of UA at phosphate buffer solution (pH 7.4). As the concentration of UA increases from 0.1 mM to 0.8 mM the electrochemical anodic peak current also increases and $E_{pa}$ values shifts towards more positive side, and the cathodic peak current remains same [25]. The graph of the anodic peak current versus the concentration of UA exhibits good linearity as shown in Fig. 8b.

![Graph showing the effect of concentration on anodic peak current](image)

**Fig. 8.** (a) Cyclic voltammograms of different concentration (0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.6 mM and 0.8 mM) of UA at ZnO modified CPE in 0.2 M phosphate buffer solution (pH 7.4) at the scan rate of 0.1 Vs$^{-1}$.; (b) Graph of anodic peak current versus concentration of UA

3.8. Electrochemical response of UA at different modified carbon paste electrodes

Fig. 9 shows the cyclic voltammograms of 0.1 mM UA in presence of phosphate buffer (pH 7.4) and scan rate 0.1 Vs$^{-1}$ at BCPE (dashed line), CPE/TX-100 (a) and CPE/ZnO/TX-100 (b). In CPE/TX-100 and CPE/ZnO/TX-100 both have shown increase in anodic peak current. Fig. 10 shows the cyclic voltammograms of 0.1 mM UA in the presence of phosphate buffer solution (pH 7.4) and scan rate of 0.1 Vs$^{-1}$ at BCPE (dashed line), CPE/CTAB (a) and CPE/ZnO/CTAB (b). Among them CPE/CTAB have shown the higher anodic peak current. The Fig. 11 shows the cyclic voltammograms for BCPE (dashed line), CPE/PG (a) and CPE/ZnO/PG (b). The Fig. 12 shows the graph of anodic peak current ($I_{pa}$) as a function of bare and different modified CPE in 0.1 mM UA in the presence of phosphate buffer (pH 7.4) and scan rate of 0.1 Vs$^{-1}$. CPE/ZnO/PG modified electrode shows 15-fold excess anodic peak.
current than the BCPE and incredibly maximum anodic peak current judging against other electrodes which are used in the present work. This shows CPE/ZnO/PG modified electrode exhibits good electrochemical response towards uric acid.

**Fig. 9.** Cyclic voltammograms obtained for the electrochemical response of 0.1 mM of UA in bare CPE (dashed line), CPE/TX-100 (a) and CPE/ZnO/TX-100 (b) in 0.2 M phosphate buffer solution (pH 7.4), at a scan rate of 0.1Vs\(^{-1}\)

**Fig. 10.** Cyclic voltammograms obtained for the electrochemical response of 0.1 mM of UA in bare CPE (dashed line), CPE/CTAB (a) and CPE/ZnO/CTAB (b) in a 0.2 M phosphate buffer solution (pH 7.4), at a scan rate of 0.1Vs\(^{-1}\)
**4. CONCLUSIONS**

In the present work the synthesized ZnO used as a modifier for the electrochemical studies towards UA. The ZnO modified carbon paste electrode exhibits stable enhanced electrocatalytic activity, sensitivity and higher linear range for potassium ferrocyanide in KCl solution. In CPE/TX-100 and CPE/ZnO/TX-100, the CPE/ZnO/TX-100 electrode and in CPE/CTAB and CPE/ZnO/CTAB, the CPE/CTAB electrode shows good electrochemical
sensitivity towards potassium ferrocyanide. However similar to K₄[Fe(CN)₆], for the detection of UA in phosphate buffer solution (pH 7.4), ZnO MCPE shows good electrochemical response. The ZnO/surfactant (TX-100 and CTAB) based CPE will shows inferior electrocatalytic activity than surfactant based CPE. The CPE/ZnO/PG electrode shows extremely good electrochemical response towards UA than all other electrode used in the present work and it could hold great application in the field of biosensors.

REFERENCES