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Electrochemical Oxidation of Paracetamol Mediated by Zinc Oxide Modified Glassy Carbon Electrode

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Abstract: Zinc oxide (ZnO) microparticles have been mechanically attached on the surface of a glassy carbon (GC) electrode. The purpose of this paper is to critically examine the modification of GC electrode with Zinc oxide microparticles and the effect on oxidation of paracetamol in 0.1 M KH_2PO_4 electrolyte solution by cyclic voltammetry (CV). Excellent electrocatalytic activity towards the oxidation of paracetamol was observed. Peak potential was observed to shift slightly to less positive value by about 150 mV and current was significantly enhanced by about 1.1 folds as compared to bare GC electrode. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH and scan rate. The variation of scan rate study shows that the system undergoes diffusion-controlled process. In addition, calibration plot reveals linearity from the range 2.0×10^{-5} to 5.0×10^{-3}M with a correlation coefficient of 0.997.

Key words: Zinc oxide Microcrystalline; Modified GCE; Paracetamol; Cyclic Voltammetry

INTRODUCTION

Modification of electrode surface with electroactive materials is an important area of research in electrochemistry for one decade (Hung-Wei, et. al 2008; W. Yantasee, et al 2004). Zinc oxide has been promising applications in catalytic, electrical, optoelectronic, photochemical fields and sensors (S. Ashok Kumar, et al 2009; P.P. Sahay, et.al 2008; P.P. Sahay, et al 2009). Acetaminophenol or paracetamol is one of the most commonly used analgesics in pharmaceutical formulations, for the reduction of fever and also as a painkiller for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain. Acetaminophen is electroactive and voltammetric mechanistic studies for the electrode processes of the acetaminophenol /N-acetyl-p-quinoneimine redox system has been presented (S.-F.Wang et al 2007; Christie, S. Leeds, et.al 1993; R.M.D. Carvalho et.al 2004; M.E. Bosch et.al 2006; N.Wangfuengkanagul, et.al 2002; R. Săndulescu et.al 2000) In this paper, we are reporting the modification of GC electrode with zinc oxide microparticles using various voltammetric techniques. Finally, the electrocatalytic behavior of ZnO/GC electrode was investigated towards oxidation of paracetamol in 0.1 M KH_2P0_4 electrolyte solution.

2. Experimental:

2.1. Instrumentation and Electroanalytical Analysis Methods:

Electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring softwares were connected to computer to perform cyclic voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA). An Ag/AgCl (3 M NaCl) and platinum wire were used as a reference and counter electrodes respectively. The working electrode used in this study was 3 mm diameter glassy carbon (GC). The voltammetric experiments were carried out at 25 ± 2ºC using 0.1 M KH_2P0_4 as supporting electrolyte unless otherwise stated. Solution was degassed with nitrogen for ten minutes prior to recording the voltammogram.

2.2. Chemicals and Reagents:

Zinc oxide was obtained from A Johnson Mattney Company, with 99.9% purity. Paracetamol tablet brand

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named Tempol from, Pharmaceuticals Ltd in (Malaysia) was used. Deionized water from reverse osmosis (RO) water model Elken (BIO PURE) was used. Unless otherwise specified, the supporting electrolyte was 0.1 M KH_2P0_4 in aqueous media at room temperature. All solutions were deaerated with oxygen-free nitrogen gas for 15 minutes prior to making the measurement.

2.3. Procedures:

The pH values of 0.1 M KH_2P0_4, aqueous solution were adjusted using 0.1M KOH or 2M HNO_3.

2.3. Preparation of Zinc Oxide Modified Glassy Carbon Electrode:

The solid compound Zinc oxide (ZnO) was transferred to the surface of glassy carbon (GC) electrode as follows: Sample amounts of 1-3 mg of microcrystalline ZnO were placed on a coarse grade filter paper. The glassy carbon electrode was pressed onto the substance and rubbed over the material, causing some compound to adhere to the electrode surface. The clean glassy carbon surface could be renewed after the measurement by polishing with 0.5 μm alumina slurry, followed by ultrasonic cleaning for about 2-3 minutes, rinsing with distilled water.

RESULTS AND DISCUSSION

3.1. Enhancement Study:

The cyclic voltammograms of 0.1 mM paracetamol in 0.1 M KH_2P0_4 showed 1.1 fold increase in the oxidation current enhancement of modified GC electrode with microparticles of ZnO as compared to a bare GC electrode as shown in Fig. 1. While at the modified GC electrode, peak shift of 150 mV towards less positive region was observed for ZnO/GC with a slight current increase as compared to those of an unmodified electrode. The oxidation current enhancement of paracetamol at the ZnO/GC electrode was caused by the catalytic effect and is irreversible during CV.

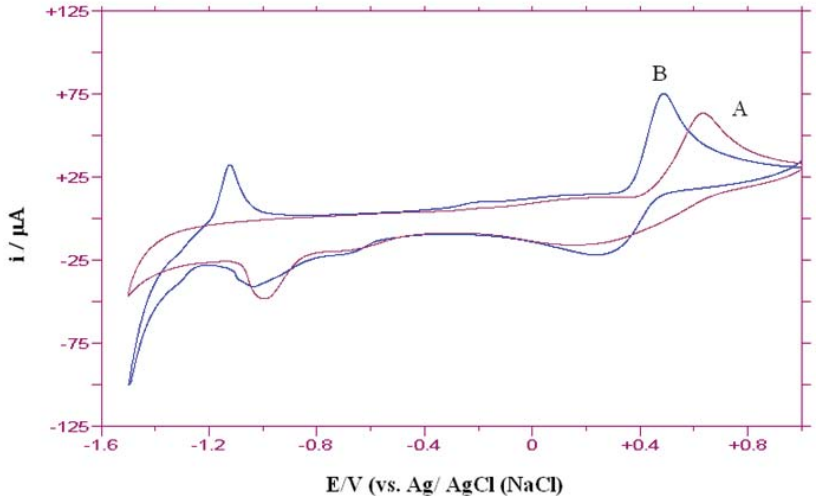


Fig. 1: Cyclic voltammograms for oxidation of 0.1 mM paracetamol obtained at (a) bare GC electrode and (b) ZnO/GC in 0.1M KH_2P0_4 at a scan rate of 100mV/s at 25°C and pH 4.5

3.2. Effect of pH:

The pH was varied from pH 3.0 to 10.0 to determine its effect on the catalytic oxidation of 0.1 mM paracetamol at the ZnO/GC modified electrode. Fig. 2 shows that the oxidation current of 0.1 mM paracetamol increases with maximum current enhancement at pH 4.5. The current slowly decreased from pH 4.5 to pH 10.0. As can be seen, the peak potential for paracetamol oxidation varies linearly with pH and is shifted to more negative potentials with increase in pH.

3.3. Effect of Temperature:

Effect of temperature on the oxidation process of paracetamol was studied. The current increased gradually at the temperature of $25C^0$ to $80C^0$ using ZnO/GC composite mechanically attached to a 3 mm GCE in the presence of 0.1 mM paracetamol using CV (Fig. Voltammogram is not shown). The plot of log oxidation

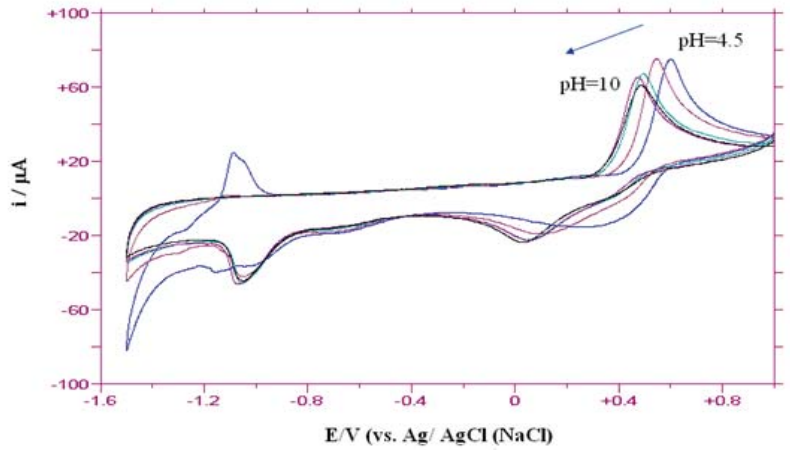


Fig. 2: Effect of varying pH on the oxidation of 0.1 mM paracetamol in 0.1 M KH_2P0_4 using ZnO/GC electrode, and a scan rate of 100 mV/s.

current of paracetamol versus reciprocal of temperature was found to be fairly linear in agreement with thermodynamic expectation of Equations 1 and 2 given below.

$$\sigma = \sigma^0 \text{ Exp } (- E_a / RT) \quad (1)$$

$$D = D^\circ \exp (- E_a / RT) \quad (2)$$

Where σ /D are conductivity/diffusion coefficient and σ^0/D° are standard conductivity of the initial diffusibility. However while use at elevated temperature, it can give an increase in current, in nanoparticle sense application need to be continued close to ambient temperature.

3.4. Effect of Varying Paracetamol Concentrations:

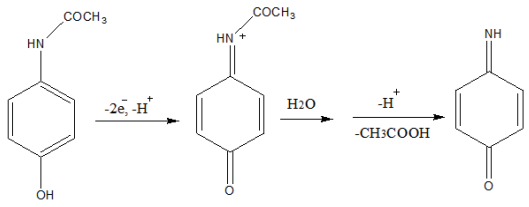
Linear current dependent on paracetamol concentration between 2.0×10^{-5} and 5.0×10^{-3} M, which showed excellent correlation of 0.997 R^2 value. The slope of 46.78 $mALmMol^{-1}$

Showed a good sensitivity response is readily obtained using ZnO/GC modified electrode.

3.5. Effect of Varying Scan Rate:

The effect of varying scan rates (*v*) on the cyclic voltammograms of 0.1 mM paracetamol using modified ZnO/GC as working electrode in 0.1 M KH_2P0_4 supporting electrolyte was studied over 5 – 100 mV/s. The oxidation peak current of zinc oxide increase with scan of the electrode potential between -1.3 and - 0.6 V. and also the oxidation current of paracetamol were observed to increase with scan rate due to heterogeneous kinetics.

Based on a plot of log (peak current) versus log (scan rate, v) for reduction current of the first cycle, a straight line was obtained fulfilling the equation y = 0.55 x + 0.239 with R^2=0.99. A slope of 0.55 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process. From this study, approximately two protons were transferred in the reaction. Paracetamol oxidation is a two-electron two-proton process in Equations 3 given below. This result is consistent with that reported in the literature by Xiaodong ShangGuan *et. al.* (2008).



(3)

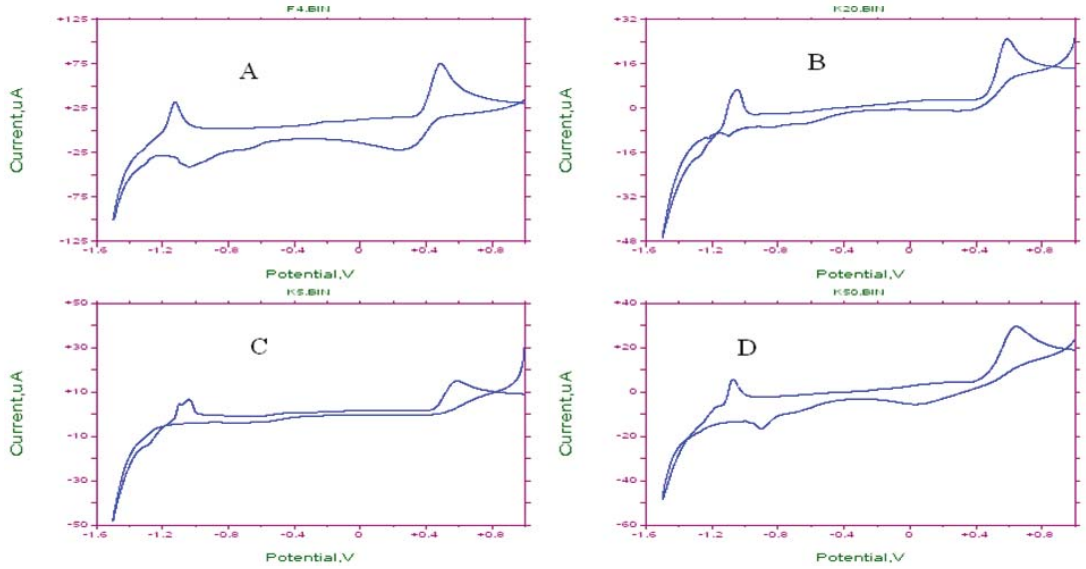


Fig. 3: Cyclic voltammograms obtained for the oxidation of microcrystal ZnO mechanically attached to a glassy carbon electrode and 0.1 mM paracetamol in 0.1 M KH_2P0_4 at pH4.5 using a scan rate of (a) 5mV, (b)20mV, (c)50mV,(d)100mV.

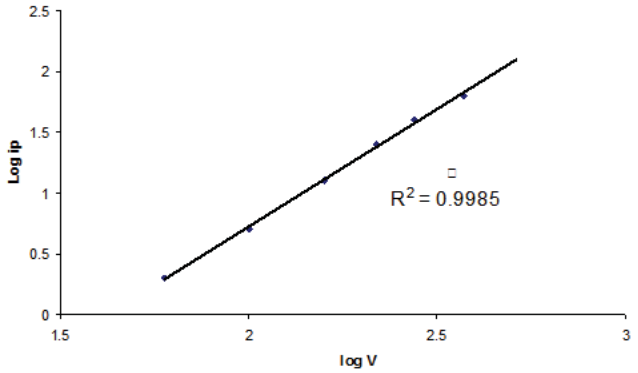


Fig. 4: Plot of log Ip_a versus log *v*. Effect of varying scan rates of 0.1 mM paracetamol using ZnO/GC electrode in 0.1 M KH_2P0_4 at pH4.5

3.6. Effect of Potential Cycling:

The stability of the ZnO/GC modified electrode was studied for the reversible process in 0.1 M KH_2P0_4 aqueous electrolyte using a 100 mV/s scan rate by CV. The result in Figure 4 shows that the peak of oxidation current of paracetamol remained virtually constant throughout the 10 potential cycles, reflecting the stability of the ZnO/GC composite modified GCE. On the other hand, the anodic peak of Zn decreased gradually until 10 cycles[17], while the peak of cathodic current of Zn remains unchanged when the electrode was modified with ZnO/GC. The above explanation is shown as follows (Equation 4):

$$Zn^0 + e^- \rightleftharpoons Zn^{II} \quad (4)$$

3.7. Scanning Electron Microscopy:

Figure 6. Scanning electron micrographs of ZnO mechanically attached to a basal graphite electrode (5 mm diameter) and immersed in 1.0M KH_2PO_4 electrolyte (a) before electrolysis (b) after electrolysis with an enlargement of 3000 times.

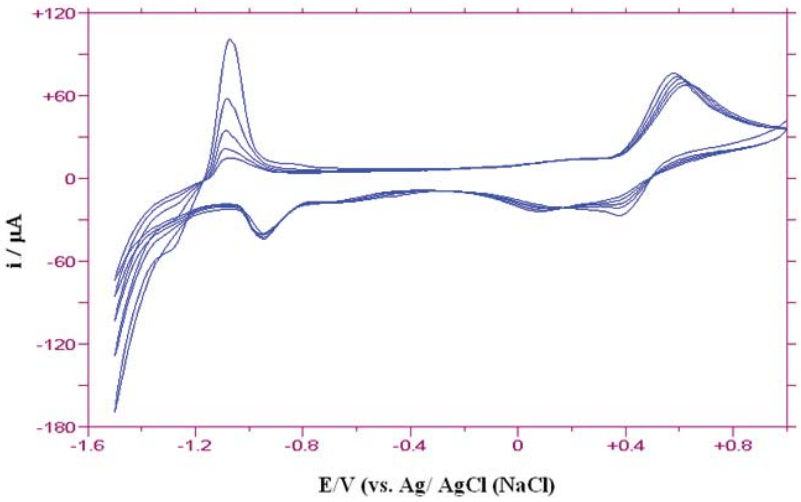


Fig. 5: Multiple Cycle voltammetry of 0.1 mM paracetamol in 0.1 M KH_2P0_4 at pH 4.5, for the ZnO/GC modified electrode.

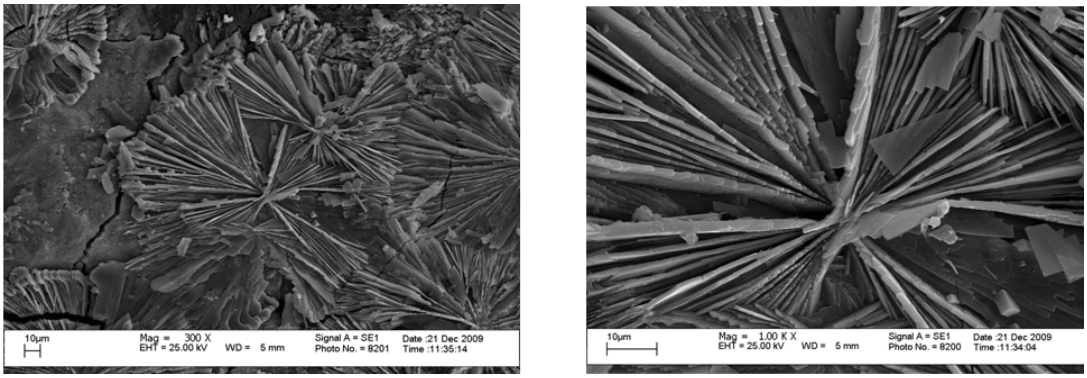


Fig. 6:

The morphology of ZnO/GC electrodes was characterized using scanning electron microscopy (SEM). (a) Before electrolysis and (b) after electrolysis with immersed in 0.1 M KH_2PO_4 electrolyte and an enlargement of 3000 times. Fig. 6 shows the change in of ZnO mechanically attached at carbon electrode. Before electrolysis, the appearance of ZnO samples are flower-like structures composed of ZnO tiny rods. Each of the rods has one end outside and another end bound to other rods at the centre. The flowerlike ZnO has larger surface area leading to increased crystallite diameter after electrolysis with the magnification of 3000 times.

4. Conclusions:

The glassy carbon electrode surface modified with ZnO/GC showed good electrocatalytic response for the oxidation of paracetamol. The oxidation current of paracetamol at ZnO/GC modified electrode appeared with enhancement of 1.1 times compared to bare GC electrode. The variation of scan rate study shows that the system undergoes diffusion-controlled process. Calibration plot reveals linearity from the range $5.0x10^{-7}$ to $1.5x10^{-3}$ M with a correlation coefficient of 0.997. The flowerlike ZnO shows synergistic effect and the modified GC electrode gives an enhanced electrocatalytic activity towards of the oxidation of paracetamol.

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