



Electrochemical Oxidation of Paracetamol Mediated by MgB₂ Microparticles Modified Glassy Carbon Electrode

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Abstract: A MgB₂ microparticles modified glassy carbon electrode (MgB₂/GCE) was fabricated by adhering microparticles of MgB₂ onto the electrode surface of GCE. It was used as a working electrode for the detection of paracetamol in 0.1 M KH₂PO₄ aqueous solution during cyclic voltammetry. Use of the MgB₂/GCE the oxidation process of paracetamol with a current enhancement significantly by about 2.1 times. The detection limit of this modified electrode was found to be 30 μM. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, supporting electrolyte, temperature and scan rate. The current enhancement observed in different electrolytic media varied in the following order: KH₂PO₄ > KCl > K₂SO₄ > KBr. Interestingly, the oxidation of paracetamol using modified GC electrode remain constant even after 15 cycling. It is therefore evident that the MgB₂ modified GC electrode possesses some degree of stability. A slope of 0.52 dependent of scan rate on current indicates that the system undergoes diffusion-controlled process.

Keywords: MgB₂ microparticles, Modified glassy carbon electrode, Paracetamol, Current enhancement, Cyclic voltammetry

Introduction

Magnesium diboride (MgB₂) is an odourless and brittle compound, exists in the form of powder, crystals and ceramics where the colour varies from one form to the other; black in powder, yellow in crystals and pink in ceramics. It has simple crystal structure with Mg layer alternating with honeycomb B layer¹. It was not discovered 40 years ago due to difficulty in preparation¹. However, recently method of growing MgB₂ such as single crystal²,

powder³ and wires⁴ have been developed. 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 presented⁵⁻⁷. The fabrication of chemically modified electrode (CME) has been widely reported to improve sensitivity and selectivity in determining many amino acids, vitamins, drug, DNA and many more in recent years⁸⁻¹¹. The study of electrochemistry for MgB₂ is still rather lacking. Electrochemical characterization and mediation studies using MgB₂ modified solid electrode has not been reported. In this work, an attempt is made to report the work done using MgB₂ as sensing electrode materials which is mechanically attached to the surface of glassy carbon (GC) working electrode via solid phase voltammetry of microparticles (SPVM).

Experimental

Electrochemical workstations of bioanalytical system Inc. USA: Model BAS 50 W with potentiostat driven by electroanalytical measuring softwares was connected to computer to perform cyclic voltammetry (CV). 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). Unless otherwise stated, the voltammetric experiments were carried out at 25±2 °C using 0.1 M KH₂PO₄ as supporting electrolyte. Solutions were degassed with nitrogen for ten minutes prior to recording of the voltammogram.

Reagents

Magnesium diboride (MgB₂) was obtained from A Johnson Mattney Company, with 99.9% purity. Deionized water by reverse osmosis (RO) via Elken's water filtration system (BIO PURE) was used in the preparation of solutions. Unless otherwise specified, the supporting electrolyte was 0.1 M KH₂PO₄ in aqueous media at room temperature. All solutions were desecrated with oxygen-free nitrogen gas for 15 minutes prior to making the measurement.

Procedures

The solid compound magnesium diboride (MgB₂) was transferred to the surface of the glassy carbon (GC) electrode as followed: Sample amount of 1-3 mg of MgB₂ were placed on a coarse grade filter paper. Glassy carbon was pressed onto the substance and rubbed over the material, causing some compound to adhere to the electrode surface. For electrochemical measurements, the electrode was transferred into the solution. 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 Deionized water by reverse osmosis (RO) via Elken's water filtration system (BIO PURE) was used in the preparation of solutions.

Results and Discussion

Enhancement study

The cyclic voltammograms of 0.1 mM paracetamol in 0.1 M KH₂PO₄ showed two folds increase in the oxidation current enhancement of modified GC electrode with microparticles of MgB₂ as compared to a bare GC electrode as shown in Figure 1. The oxidation current enhancement of paracetamol at the MgB₂/GC electrode was caused by the catalytic effect. The oxidation of paracetamol is reversible during CV.

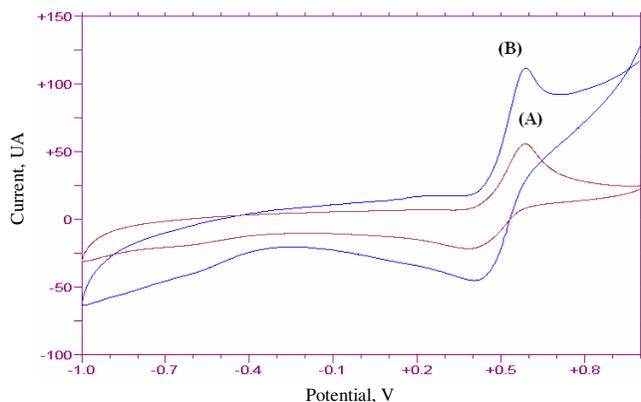


Figure 1. Cyclic voltammograms for oxidation of 0.1 mM paracetamol obtained in 0.1 M KH_2PO_4 (pH 6.0), with potential scanning in the positive direction from -1000 to +1000 mV vs. Ag/AgCl at a scan rate of 100 mV/s at 25 °C at (a) bare GC electrode and (b) modified MgB_2/GC

Effect of pH

The pH was varied from pH 3.0 to 11.0 to determine its effect on the catalytic oxidation of 0.1 mM paracetamol at the MgB_2/GC modified electrode. Figure 2 shows that the oxidation current of 0.1 mM paracetamol increases with an increase in pH between 3.0 to 6.0 with maximum current enhancement at pH 6. The current slowly decreased from pH 6 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.

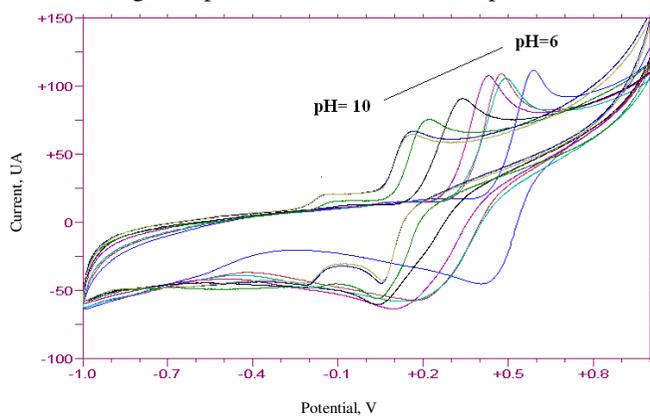


Figure 2. Cyclic voltammograms with varying pH levels for GC electrode modified with modified MgB_2/GC in 0.1 M KH_2PO_4 . potential scanning in the positive direction from -1000 to +1000 mV vs. Ag/AgCl at a scan rate of 100 mV/s .

Effect of temperature

Effect of temperature on the oxidation process of paracetamol was studied. The current increases gradually from 20 to 80 °C. The plot of log oxidation current of paracetamol versus reciprocal of temperature was found to be fairly linear in agreement with thermodynamic

expectation of Equations 1 and 2. The conductivity of the MgB₂ microparticles with the increase in temperature also played a significant influence on the activation energy for diffusion of the substrate of interest, E_a as described by the Arrhenius equation (Eqs.1 and 2) given below.

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

$$D = D^0 \text{exp} (- E_a / RT) \quad (2)$$

Where σ/D are conductivity/diffusibility and σ^0/D^0 are standard conductivity the initial diffusibility. However while use at elevated temperature, it can result to an increase in current, in microparactical sense application needs to be continued close to ambient temperature.

Effect of varying paracetamol concentrations

Voltammograms in Figure 3 show peak current of paracetamol increases rapidly and linearly with increasing concentration from (5.0×10^{-7} to 2.0×10^{-3} mol/L), as described by Equations $y = 21.28x + 0.65$, which showed excellent correlation of 0.995 R² value. Based on the slope, m of the linear graph, a good sensitivity response of 21.22 $\mu\text{A}/\text{mM}$ was obtained.

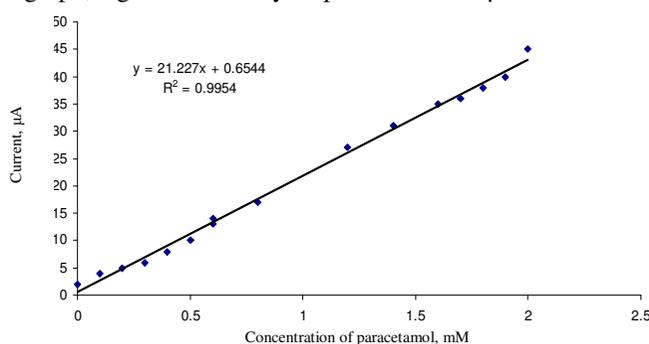
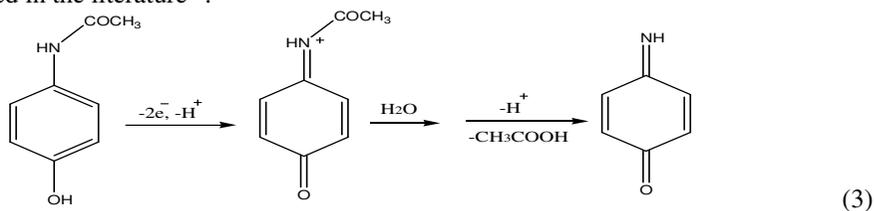


Figure 3. A plot showing the dependence of the oxidation current on different concentration of paracetamol MgB₂/GC in 0.1 M KH₂PO₄ solution with a scan rate of 100 mV/s.

Effect of varying scan rate

The effect of varying scan rates (ν) on the cyclic voltammograms of 0.1 mM paracetamol using modified MgB₂/GC as working electrode in 0.1 M KH₂PO₄ supporting electrolyte was studied over 5-1000 mV/s. Oxidation currents of ascorbic acid was observed to increase with scan rate due to heterogeneous kinetics. Figure 4 shows the plot of log (peak current) *versus* log (scan rate, ν) for oxidation current of the first cycle, a straight line was obtained fulfilling the equation $y = 0.516x - 5.687$ with R²=0.969. A slope of 0.5, which is comparable with theoretical slope of 0.5 for diffusion-controlled process, was obtained. 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. A conclusion that is consistent with that reported in the literature¹¹.



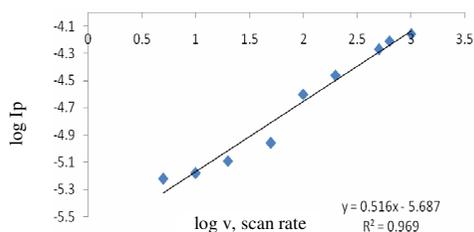


Figure 4. Plot of $\log I_{p_a}$ versus $\log v$. Effect of varying scan rates of 0.1 mM paracetamol using MgB_2/GC electrode in 0.1 M KH_2PO_4 (pH 6.0) at a scan rate rang from 5-1000 mV/s

Effect of potential cycling

The potential cycling of the oxidation of paracetamol solution, 0.1 mM paracetamol was carried out at the electrode surface of a glassy carbon electrode (3 mm diameter) modified with MgB_2 microparticles during cyclic voltammetry. Continuous potential cycling to Continuous potential cycling did seem to affect the oxidation peak of paracetamol at magnesium diboride modified GC electrode since the faradaic activity appears reproducible even after 15 cycles reflecting the the oxidation peak of paracetamol remained high; consequently , its can stability of the MgB_2 coat/film at the surface of GC electrode.

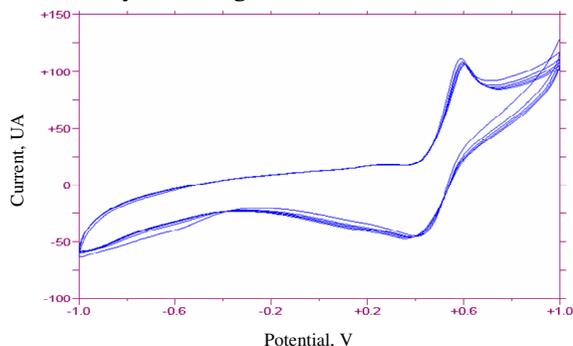
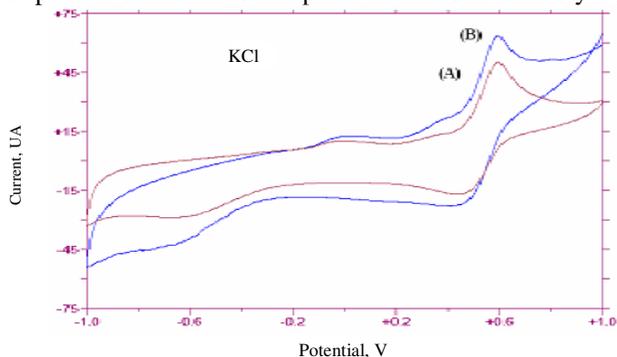


Figure 5. Cyclic voltammogram of potential cycling for the oxidation of paracetamol at the MgB_2/GCE in 0.1 M KH_2PO_4 (pH 6.0). potential scanning in the positive direction from -1000 to +1000 mV vs. $Ag/AgCl$ at a scan rate of 100 mV/s for 10 cycles

Effect of varying supporting electrolyte

Based on the pH study, different types of 0.1 M aqueous supporting electrolytes with neutral conditions were studied. In the presence of $H_2PO_4^-$ in electrolyte, paracetamol peak currents were increase the peak of oxidation as compared to others in electrolyte solution (Figure 6).



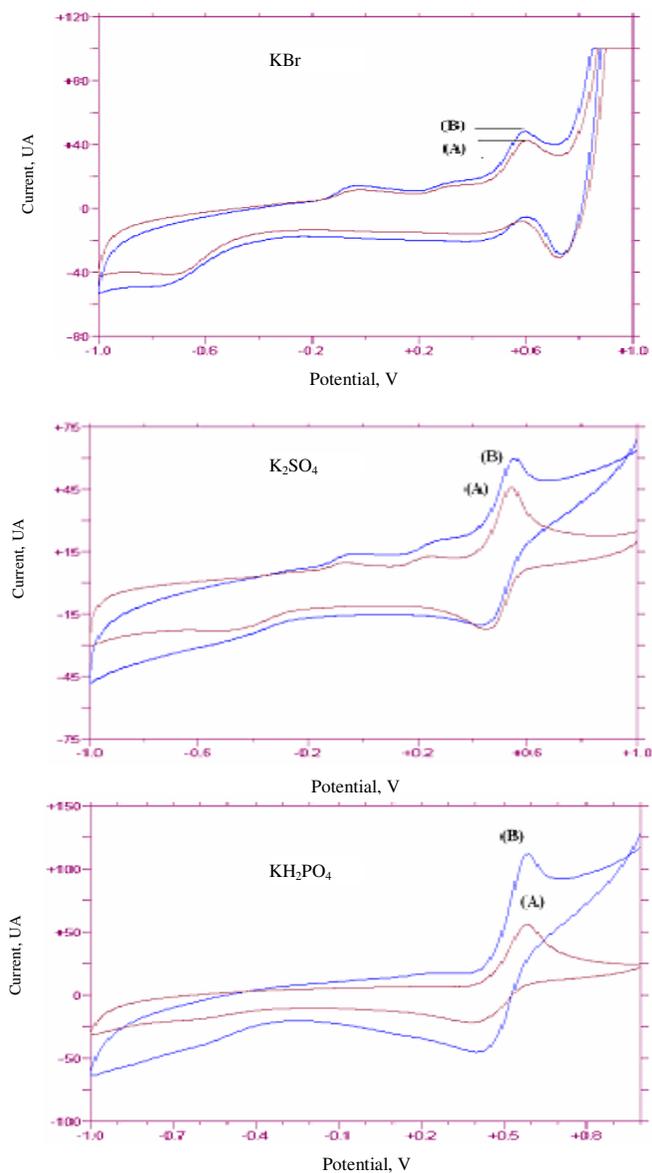


Figure 6. Tile graph (background subtracted) of the oxidation current of paracetamol at the in different supporting electrolytes at (a) bare GC electrode and (b) modified MgB₂/GC with a scan rate of 100 mV/ s

In noncomplexing solutions (Table 1), most of the aqueous solutions observed showed no distinct changes. Similar potential ranges were obtained using electrolytes solutions of KCl>K₂SO₄>KBr. However, the oxidation peak of paracetamol show that the greatest enhancement effect is obtained when potassium dihydrogen phosphate is used as electrolyte. In general, degree of current enhancement in varying electrolyte varies in the following order KH₂PO₄ > KCl > K₂SO₄> KBr (Table 1).

Table 1. Effect of varying supporting electrolytes of 1mM paracetamol, during cyclic voltammetry using at MgB₂/GCE with a scan rate of 100 mV/s

Solution	Oxidation current / μM		Enhancement
	Without MgB ₂	With MgB ₂	
Potassium bromide	39	41	1.05
0.1 Potassium dihydrogen orthophosphate	55	115	2.0
0.1 Potassium chloride	45	59	1.3
Potassium sulfate	43	61	1.4

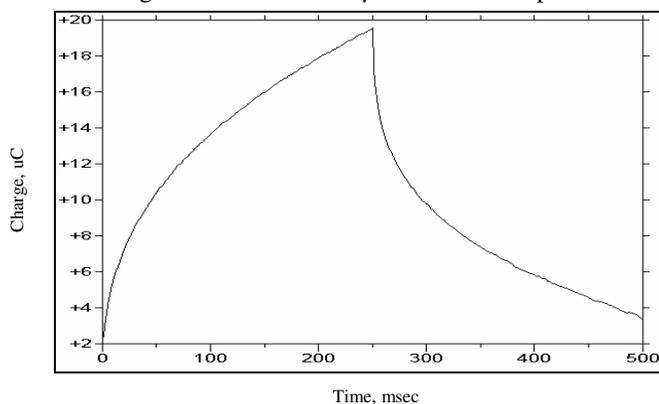
Chronocoulometry study

Chronocoulometry (CC) is the integral analogs of the corresponding chronoamperometry approaches. The integral of the Cottrell equation gives the cumulative charge passed in reducing or oxidizing the diffused component [12]:

$$Q = 2nFAD^{1/2}C_0\sqrt{\pi t} \quad (4)$$

Where Q = Charge and the other parameters have its usual meanings. The analysis of chronocoulometry (CC) data is based on the Anson equation above (Eq. 4), which defines the charge-time dependence for linear diffusion control. The Anson plot shows linear dependency of Q upon $t^{1/2}$ (Figure 7) indicating that the process involved is diffusion controlled.

Based on Anson's plot of the above, surface charge can be calculated by taking the difference between two intercepts of forward and reverse steps at $t=0$. It was found that the MgB₂/GC has a total charge transferred of 3.0 μC when 1 mM paracetamol was reduced.

**Figure 7.** Chronoamperogram of paracetamol at the MgB₂/GCE in 0.1 M KH₂PO₄ at (pH6.0)

Conclusion

Among the various solid electrodes used GC electrode by far a better choice of solid state electrode to be modified with MgB₂ microparticle mediates the oxidation process of paracetamol during cyclic voltammetry. Resulted in the optimization of the oxidation current, which appeared to be 2 times more enhanced compared to bare GC electrode. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, electrolyte and scan rate. Some physical constants such as diffusion coefficient, MgB₂ film appearances of well defined edges remain intact, even after 20 potential cycling.

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