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Full Paper

A Promising Enhanced Polymer Modified Voltammetric Sensor for the Quantification of Catechol and Phloroglucinol

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Abstract- In the present paper, poly(Tyrosine) modified graphene paste electrode (PTMGPE) was fabricated by utilizing an electropolymerization technique. Deposition of polymer film at bare graphene paste electrode (BGPE) was characterized by field emission scanning electron microscopy (FE-SEM). The PTMGPE was applied for Voltammetric detection of catechol (CC) and its quantification in phosphate buffer solutions of pH 7.0 (PBS). The detected cyclic voltammetric oxidation current of CC and phloroglucinol (PG) on PTMGPE is nearly 4 times higher with controlled over potential as a contrast to BGPE. This result shows the electrocatalytic effect of the poly (Tyrosine) layer. The differential pulse voltammetry (DPV) results show that CC and PG can be detected instantaneously using PTMGPE with peak separation of 0.300 V between CC and PG. Also, DPV showed two linear current responses in the concentration range of 2×10^{-6} to 1×10^{-5} M and 1.5×10^{-5} to 5×10^{-5} M with a coefficients of correlation 0.9951 and 0.9976 respectively. The detection limit (DL) and quantization limit (QL) were found to be 3.04×10^{-7} and 10×10^{-7} mol L^{-1} respectively. Further, we have also studied real sample analysis in tap water using proposed PTMGPE in the form of recovery studies and the achieved outcomes are found to be excellent agreement with the previous results. The PTMGPE shows exceptional selectivity, good sensitivity, and steadiness, making it as an attractive and alternative sensor for concurrent determination of CC and PG.

Keywords- Catechol; Phloroglucinol; Poly (Tyrosine); Graphene paste electrode; Sensor; Analysis

1. INTRODUCTION

CC (1, 2-dihydroxybenzene) is wildly utilized in organic synthesis. It has excellent applications in the productions of pharmaceuticals and pesticides. Skin contact with catechol causes eczematous dermatitis in humans [1-6]. In humans, the accumulation of CC on the skin leads to an infection resembling that induced by phenolic compounds. Huge dosages of CC can trigger depression of the nervous system and a sustained escalation of blood pressure in animals. Catechol testing in water using low-cost, effective electrochemical sensors is demanding for the protection of the environment [7-14]. Phloroglucinol (PG) is a phenol derivative that shows a cycto protective effect from oxidative damage by enhancing the activity of cellular catalase [15-20]. The concentration levels of CC and PG place an important role in many diseases and disorders. So, for clinical biochemistry, determination of CC concentration is important, therefore much of work has been done for the determination of bioactive molecules. Several analytical techniques such as chromatography, spectrophotometry, and fluorescence are being used to detect these molecules [21–27]. But these strategies are costly, tedious and bulky. Modified sensors can be utilized to conquer the constraints of different strategies. Indeed; they give a simpler convey ability, a quick reaction and highly responsive with a lower limit of detection [28-29]. As of late, there has been expanding enthusiasm for the fabrication of electrode with certain polymers and surfactants, for example, electrochemically incorporated poly (glycine), SDS modification [28-32] to have better electrochemical performance. The electrochemical analysis of CC by differently modified electrodes has been acknowledged by some other research group [33]. In current work, we introduce an effective electrochemical procedure for CC detection based on graphene paste electrode modified with poly (Tyrosine).

2. MATERIALS AND METHODS

2.1. Apparatus and Chemicals

Measurements were performed with a CHI Instrument (CHI-6038E) linked to the private computer for handling and storage of information and experiments was carried out with a three-electrode arrangement. CC (Sisco Research Laboratories Pvt. Ltd., Maharashtra) and Tyrosine (Ty), Phloroglucinol (PG) (Molychem, Mumbai, India), Silicone oil, disodium hydrogen phosphate and monosodium dihydrogen phosphate were obtained from Himedia Chemicals, India. Graphene (5 µm wide, 6-8 nm thickness) was procured TCI Co. limited (Japan). All the chemicals were of A.R grade and used without further refinement. Phosphate buffer solution (PBS) was prepared by intermixing a proper volume of NaH_2PO_4/Na_2HPO_4. The standard CC (25×10^{-4} M), PG (25×10^{-4} M) SDS (25×10^{-3} M) solutions were prepared by dissolving suitable weight in distilled water.

2.2. Development of polymer modified graphene paste electrode

Graphene material was mixed with silicon oil with a quantity of 60:40 (w/w) systematically in an agate mortar to get the uniform paste. The obtained paste was firmly filled into the hole of Teflon rod (3 mm in diameter) and to reinforce the effectiveness of surface and improve its activity, the bare carbon paste electrode was pre-treated in step with a method reportable by Manjunatha [34]. The electrochemical treatment of BGPE was performed within the mixture of Tyrosine and buffer solution (0.1 M) using cyclic voltammetry (CV) in between 0.3 V and 1.2 V, with a voltage scan rate of 0.1 Vs^{-1} for 10 scans shown in Fig. 1.

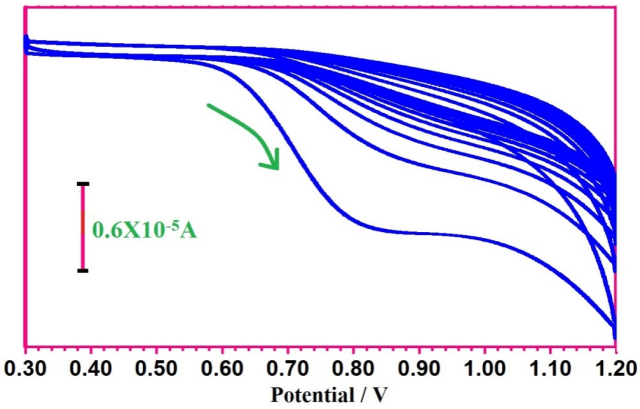


Fig. 1. Cyclic voltammograms of Poly (Tyrosine) on BGPE in 0.1 M buffer solution in the potential range from 0.3 V to 1.2 V, with a potential sweep rate of 0.1 Vs^{-1}

3. RESULTS AND DISCUSSION

3.1. Surface analysis by FESEM

To evaluate the surface nature of the PTMGPE and BGPE surface, the FESEM analysis was employed (Fig. 2a and b). As represented in Figures the surface characterization portrays the formation of polymer film.

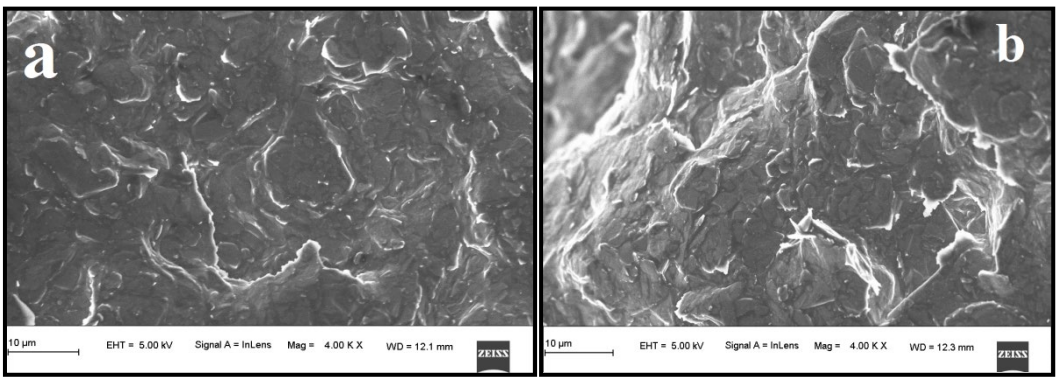


Fig. 2. FESEM characteristics of BGPE (a) and PTMGPE (b)

It is noticeable that there is a significant difference in surface arrangement of BGPE and PTMGPE which confirms formation of dense polymer film. This result shows that the electrode surface was coated with poly(tyrosine) film. The active surface area of the PTMGPE electrode was improved by the formation of polymer layer [31].

3.2. Electrochemical oxidation of CC at PTMGPE

The cyclic voltammograms at BGPE and PTMGPE in a PBS (0.1 M, pH 7.0) comprising 1×10^{-4} M CC was obtained. At PTMGPE the redox peak currents of CC obviously increased with decrease of Ep (0.292 V and 0.439 V), which is due to the high active surface area of PTMGPE leading to an upsurge in the electron exchange between the analyte and the sensor material, demonstrating that the rapid electron transfer rate was obtained on the PTMGPE (Fig. 3). The improved kinetics of electron transfer on the PTMGPE might due the excellent electronic conductivity of graphene.

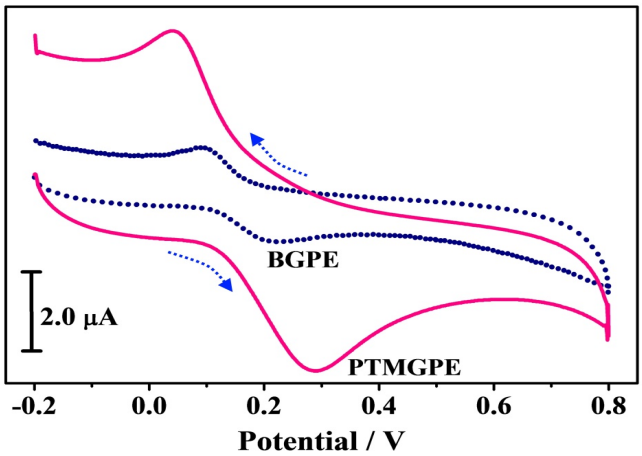


Fig. 3. Cyclic voltammograms of 0.1 mM CC at PTMGPE and BGPE in PBS solution (0.1 M, pH 7.0) between the potential window -0.2 V and 0.8 V, with a sweep rate of 0.100 Vs^{-1}

Fig. 4 illustrates the DPV responses at BGPE and PTMGPE in PBS solution (0.1 M, pH 7.0) in the presence and absence of 0.1 mM CC. No peak was detected at PTMGPE in blank PBS, demonstrating that the PTMGPE is stable in the selected potential region without any interference. For the BGPE, a voltammetric signal of CC was appeared with the peak current (I_p) of 0.977 µA and the peak potential of 0.140 V. On the other hand, at PTMGPE, the peak current was 2.41 µA and the peak potential was 0.149 V. These modifications in the peak current and potential specified that PTMGPE showed a catalytic effect towards the CC oxidation. The results indicates that the presence of poly (Tyrosine) layer at electrode surface had substantial enhancement for the electrochemical response, which was partly due to outstanding features of graphene such as high electrical conductivity, mechanical stability and effective surface area.

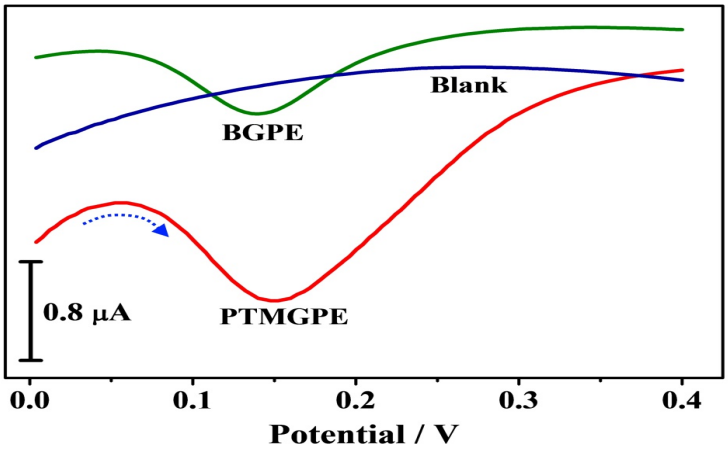


Fig. 4. Differential pulse voltammograms of 0.1 mM CC (Presence and absence) at PTMGPE and BGPE in PBS solution (0.1 M, pH 7.0) having the potential between 0.0 V to 0.4 V

3.3. The voltammetric response of CC at different pH

The influence of pH is well known to have a major effect on the electrochemical response of bioactive compounds. This parameter was studied to calibrate pH for electrochemical detection CC at PTMGPE.

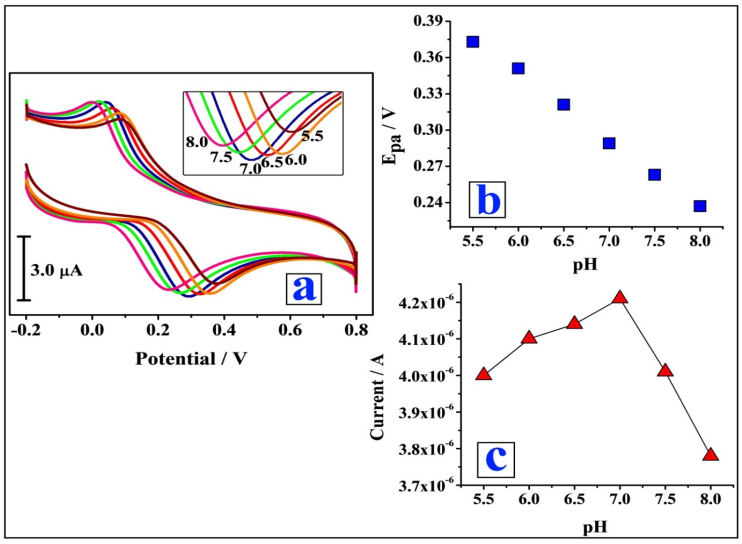


Fig. 5. (a) Cyclic voltammograms of 0.1 mM CC at PTMGPE in different pH of PBS having the potential range from 0.3 V and 1.2 V, with a sweep rate of 0.100 Vs^{-1}; (b) Plot of pH vs. anodic peak potential; (c) Plot of pH vs. oxidation peak current

In order to determine this, the cyclic voltammetric response of CC was obtained in solutions with different pH from 5.5 to 8.0 (Fig. 5a) at PTMGPE. The linear connection between the oxidation peak potential (E_{pa}) and pH is given by Eq. (1). E_{pa} (V) = −0.055pH + 0.682, r^2 = 0.998 [34]. Result confirms that the potential (E_p) of CC oxidation was pH

dependent, with a slope of – 0.055 V/pH (Fig. 5b) unit which was equal to the Nernstian value (0.059) for a two electrons, two protons electrochemical reaction (Scheme 1)). It can be seen that extreme peak current was obtained at pH 7.0 (Fig. 5c), so this pH value was optimized for further measurements.

3.4. Impact of potential sweep rate

The influence of variation of voltage scan rate on I_{pa} of CC was studied at PTMGPE. Fig. 6a illustrates the cyclic voltammograms of 1 × 10^{-4} M of CC at various scan rates (V s^{-1}): 0.100, 0.125, 0.150, 0.175, 0.200, 0.225 and 0.250 at PTMGPE. I_{pa} showed a linear correlation with sweep rate in the range 0.100– 0.250 V s^{-1}, as represented in inset of Fig. 6b. The linear regression equation for this range of scan rate is I_{pa} (μA) = 715.4 v (Vs^{-1}) – 47.26 (r^2 = 0.997). This implies that the CC oxidation at PTMGPE is controlled by adsorption [33]. The oxidation peak potential moves to more positive potential with the rise in scan rate.

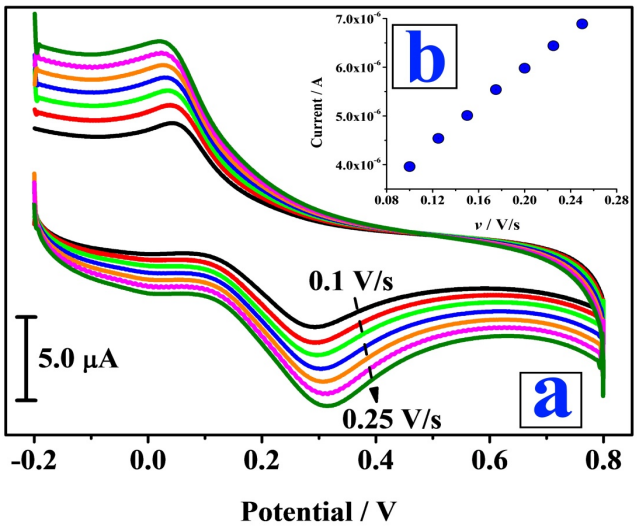
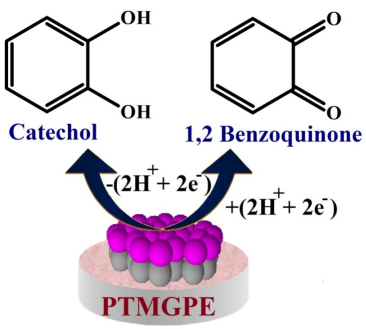


Fig. 6. (a) Cyclic voltammograms of 0.1 mM CC at PTMGPE in PBS having the potential window from -0.2 V to 0.8 V, with a voltage sweep rates in the range from 0.100 to 0.250 V/s; (b) Plot of scan rate vs. anodic peak current



Scheme 1. Redox reaction mechanism of CC on PTMGPE

3.5. Simultaneously determination of CC and PG

CC and PG coexist in many samples. Therefore, the next study was reserved to simultaneous resolution of the target molecules. The planned method has been thus adopted for instantaneous separation of CC and PG. The DPVs of mixture at PTMGPE as depicted in Fig. 7 showed two magnified peak potentials at 0.138 and 0.544 V relating to the oxidation of CC and PG respectively. The peak to peak separation is 0.406 V. The enhanced response and resolution of CC and PG peaks at PTMGPE, clearly indicates that the prepared sensor can be effectively applied for the simultaneous trace level determination of CC with other molecules.

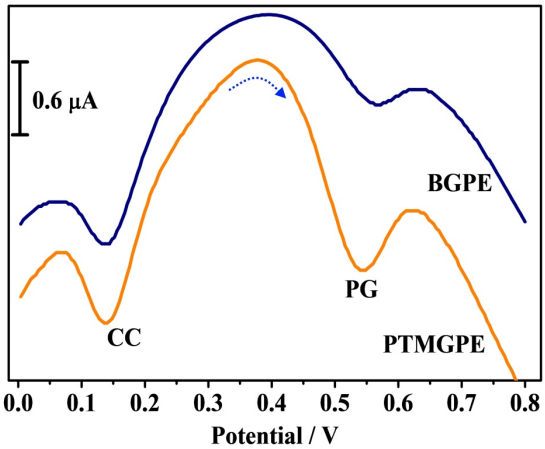


Fig. 7. DPVs of 0.1 mM CC and 0.1 mM PG at BGPE and PTMGPE in PBS having the potential range from 0.0 V to 0.8 V

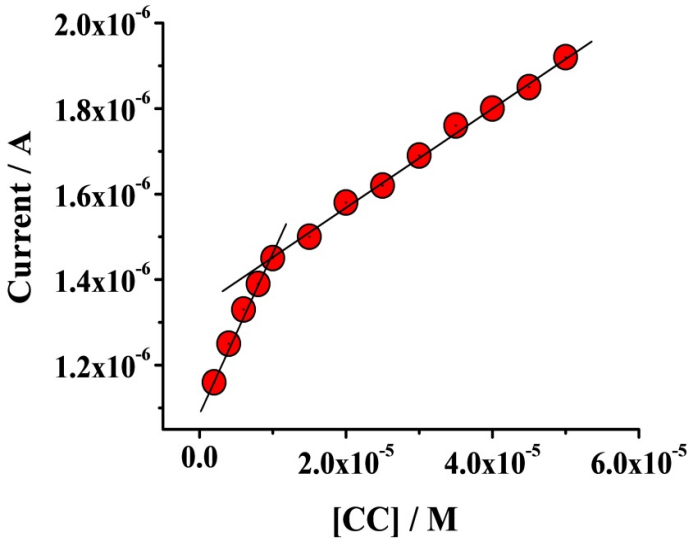


Fig. 8. Calibration plot of different concentrations of CC v/s peak currents of CC

3.6. Calibration curve

Fig. 8 illustrates the effect of concentration variation of CC at the surface of PTMGPE. As it is obtained, the peak current is directly related to concentration of CC in the range from 2×10^{-6} to 1×10^{-5} M and 1.5×10^{-5} to 5×10^{-5} M with an r^2 of 0.9951 and 0.9976 respectively. The DL and QL was calculated as DL = $3S_b/m$, QL = $10S_b/m$, here S_b is equal to standard deviation for the blank measurements (n = 5) and m is the slope of the calibration plot [32] and are determined to be 3.04×10^{-7} and 10×10^{-7}mol L^{-1} respectively. Table 1 shows DL comparison with several previously reported sensors [35-43].

Table 1. Comparison of PTMGPE with previously reported sensor for CC estimation

Detection technique	Working electrode	DL (µM)	Reference
DPV	RGO–MWNTs	1.8	[35]
CV	MWCNT–NF–PMG/GCE	31.0	[36]
DPV	[Cu(Sal-β-Ala) (3,5-DMPz)2]/SWCNTs/GCE	3.5	[37]
LSV	CNx/GCE	2.71	[38]
CV	TX-100/CPE	0.59	[39]
CV	PNMCPE	0.31	[40]
CV	Poly(glycine) MGPE	0.87	[41]
CV	Poly(methionine) MCPE	55.6	[42]
DPV	PGE/MWCNTS	0.7	[43]
DPV	PFHSAAC/GCE	0.42	[44]
DPV	PTMGPE	0.30	This work

DPV- differential pulse voltammetry, RGO- reduced graphene oxide, MWNTs- multiwalled carbon nanotubes, CV- cyclic voltammetry, [Cu(Sal-β-Ala)(3,5-DMPz)2]/SWCNTs/GCE- (copper(II) complex [Cu(Sal-β-Ala) (3,5-DMPz)2] (Sal = salicylaldehyde, β-Ala = β-alanine, 3,5-DMPz = 3,5-dimethylpyrazole) and single-walled carbon nanotubes (SWCNTs)), CNx- nitrogen-doped carbon nanotubes, GCE- glassy carbon electrode, CPE- carbon paste electrode, TX-100 - triton X 100, PGE- pencil graphite electrode, PFHSAAC- perilla frutescens activated carbon PNMCPE- poly(niacinamide) modified carbon paste electrode, MGPE- modified graphene paste electrode

3.7. Analytical applications

CC was estimated in tap water sample by applying standard addition manner. Recoveries were found between 99.72–101.64 %. The reproducibility of the PTMGPE was examined; the relative standard deviations for CC determination, based on the three replicates of analysis was 2.68 %. The repeatability and stability of PTMGPE was examined by the CV. When using seven new analyte solution, the RSD was 2.48 %. When the electrode was stored

in the laboratory, the modified electrode (PTMGPE) retains 95 % of its original response even after two weeks and 92 % after 50 days. These results indicate that PTMGPE is stable and reproducible sensor for CC.

4. CONCLUSION

In conclusion, effective PTMGPE sensor has been equipped for CC detection at lower concentrations. The electrode was made-up with simple electropolymerization approach. The results indicated that the PTMGPE sensor shows superior or comparable analytical performance in terms of excellent current, extensive linear range, high sensitivity and selectivity. In addition, the use of graphene as starting material suggests fast electron transfer and economic feature of proposed sensor. The electropolymerization expand their applicability and performance in the field of sensors and biosensors for real-time applications.

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Conflict of interest

The authors declare there is no conflict of interest.

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