



# Voltammetric determination of hydroquinone, catechol, and resorcinol by using a glassy carbon electrode modified with electrochemically reduced graphene oxide-poly (Eriochrome black T) and gold nanoparticles

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## Abstract

A nanocomposite consisting of electrochemically reduced graphene oxide, poly(Eriochrome black T) and gold nanoparticles (ERGO-pEBT/AuNPs) was prepared for the simultaneous detection of resorcinol (RC), catechol (CC), and hydroquinone (HQ). The electrochemical oxidation of HQ, CC, and RC was analysed by using cyclic voltammetry and differential pulse voltammetry. Three well-separated potentials were found at 166, 277, and 660 mV (vs. Ag/AgCl) for HQ, CC, and RC, respectively. The linear ranges were 0.52–31.4, 1.44–31.2, and 3.8–72.2  $\mu\text{M}$  for HQ, CC, and RC, respectively. The limits of detections (LODs) for both individual and simultaneous detections are negligibly different are (15, 8, and 39 nM, respectively).

**Keywords** Simultaneous determination · Electroanalysis · Electropolymerization · Differential pulse voltammetry

## Introduction

Resorcinol (RC), catechol (CC), and hydroquinone (HQ) also known as 1,4-dihydroxybenzene, 1,2-dihydroxybenzene, and 1,3-dihydroxybenzene are commonly applied in plastic, pharmaceuticals, rubbers, dyes, and cosmetics industries [1, 2]. According to the Environmental Protection Agency (EPA) and European Union (EU), the phenolic isomers are considered as environmental contaminants and human health risk because of their toxicity [3]. Thus, various analytical techniques such as fluorescence, capillary electrophoresis, and chemiluminescence have been used to detect these phenolic

isomers [4–6]. Although these techniques are accurate, they suffer from time-consuming, complexity of the operation, and expensive. On the other hand, electrochemical approaches are well known for their sensitive detection of organic molecules, low cost as well as accurate and ease of operation [7]. The overlapping of HQ and CC potentials at the non-modified electrode leads to a search for new ways to modify the GCE [8]. In this regard, modified electrodes have been explored to overcome this restriction. For instance, polymerisation of azo-dye eriochrome black T (EBT) on the electrode surface producing an electroactive redox film has been used in the simultaneous detection of uric acid, ascorbic acid, dopamine [9]. Due to catalytic properties of nanoparticles, Xia et al. [7] incorporated gold nanoparticles (AuNPs) into pEBT for simultaneous detection of L-cysteine and L-tyrosine. [10] have also demonstrated that the deposition of AuNPs on MWCNT for simultaneous determination of HQ, CC, and RC and successfully used on-field analysis.

Graphene, an interesting nanomaterial has gained great attention as idealistic electrode material due to its excellent chemical and physical characteristic behaviour. In order to produce graphene, the synthesis process generally contains exfoliation of oxidised graphite to produce graphene oxide (GO) nanosheets, whereas reduced GO (RGO) is obtained

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by chemical, electrochemical or thermal reduction of exfoliated GO [11]. There is always an effort for seeking new materials along with graphene to simultaneously detect HQ, CC, and RC. Moghaddam et al. [12] have studied the addition of chitosan to graphene to enhance graphene properties and used the composite for RC, CC, and HQ analysis. In another study performed by Palanisamy et al. [13] indicated that green synthesized of AuNPs by using *Terminalia chebula* as reducing agent to decorate RGO can be used to detect HQ and CC simultaneously. Immobilization of copper on the reduced graphene oxide (NRCu-rGO/GCE) [14], nitrogen-doped graphene [15] and nafion film containing cerium phosphate nanotubes [16] have also been reported for sensitive simultaneous determination of HQ, CC, and RC.

In this work, ERGO-pEBT/AuNPs was prepared electrochemically for simultaneous determination of HQ, CC, and RC. The electropolymerisation of ERGO-pEBT film was performed in a mixture of EBT and GO. The deposition of AuNPs on ERGO-pEBT has resulted in a modified electrode with a synergistic effect. The modified electrode exhibited three well-separated oxidation peaks with extremely distinct peak potentials as well as enhancement in peak currents when exposed to the three isomers mixture. In addition, ERGO-pEBT/AuNPs/GCE was used for individual selective and simultaneous detection of RC, CC, and HQ with remarkable sensitivity and selectivity.

## Materials and methods

### Chemicals

Resorcinol (RC), catechol (CC), hydroquinone (HQ), chloroauric acid ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), L-cysteine and sodium chloride were purchased from Sigma Aldrich ([www.sigmaaldrich.com](http://www.sigmaaldrich.com)). EBT, sulfuric acid, nitric acid and glycine were obtained from Fisher Scientific ([www.fishersci.com](http://www.fishersci.com)). GO was received from Graphenea ([www.graphenea.com](http://www.graphenea.com)). Copper (II) sulphate and iron (III) chloride were obtained from Unilab ([www.unilabchem.com](http://www.unilabchem.com)) and Bendosen ([www.johchem.com.my/product/brand-bendosen](http://www.johchem.com.my/product/brand-bendosen)), respectively. Sodium hydroxide NaOH was obtained from Friendemann Schmidt ([www.thermo-line.com](http://www.thermo-line.com)). D (+) glucose was obtained from R&M chemicals ([www.rmchemicals.com](http://www.rmchemicals.com)). Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and potassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4$ ) were obtained from Merck ([www.merckmillipore.com](http://www.merckmillipore.com)) and used for the preparation of phosphate buffer (PB) solution; the pH was regulated with 0.1 M phosphoric acid  $\text{H}_3\text{PO}_4$  (Friendemann Schmidt, [www.thermo-line.com](http://www.thermo-line.com)) or 0.1 M potassium hydroxide KOH (Hmbg chemicals, [www.johchem.com.my/product/brand-hmbg](http://www.johchem.com.my/product/brand-hmbg)). All the chemicals utilised for the experiments were

of pure analytical grade and were used without additional purification. All solutions were prepared with deionised water obtained from the purification system Milli-Q water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ).

### Instrumentation

Potentiostat/galvanostat (Autolab PSTAT204) was utilised to perform the electrochemical measurements i.e. cyclic voltammetry and differential pulse voltammetry. An electrochemical cell connected to three-electrode system arrangement was applied in which the bare GCE or ERGO-pEBT/AuNPs modified GCE was used as working electrode, while Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The validation of samples has been performed using high performance gas chromatography (HPLC) Shimadzu, Model LC 2030C.

### Preparation of ERGO-pEBT/AuNP film modified electrode

Initially, bare GCE was polished to a mirror-like surface using alumina slurry with  $0.05 \mu\text{m}$ . The electrode was then sonicated in 1:1  $\text{HNO}_3$  (v/v) and deionised water for 10 min, respectively. The cleaned GCE was applied for acid treatment in 0.1 M  $\text{H}_2\text{SO}_4$ , followed by NaOH for 15 cycles each. The ERGO-pEBT/AuNPs was prepared as reported in our previous work [17]. Briefly, a mixture of  $0.82 \text{ mg mL}^{-1}$  GO and 0.5 mM EBT was dissolved into 0.1 M PB solution (pH 9.2) and sonicated for 60 min. The pretreated GCE was then cycled in GO-EBT solution for 15 cycles in the range of 1.5 to  $-0.4 \text{ V}$  to obtain ERGO-pEBT. After drying, the modified GCE was immersed into 0.15 mM  $\text{HAuCl}_4$  dispersed in 0.1 M PB solution (pH 9.0) and run for three cycles to obtain ERGO-pEBT/AuNPs/GCE. Other modified electrodes i.e. ERGO/AuNPs/GCE, ERGO-pEBT/GCE, pEBT/AuNPs/GCE, and pEBT/GCE were prepared for comparison. The modified electrodes were used after rinsing with deionised water (DI) and dried at room temperature.

## Results and discussion

### Electropolymerisation mechanism of ERGO-pEBT/AuNPs

The possible interaction between ERGO and pEBT can be deduced from the previous reports. To simplify the mechanism and demonstrate the function of the naphthyl groups in the ERGO-pEBT, the structure of EBT is drawn as A and B (Scheme S1). As discussed by Geng et al. [18], the EBT molecules undergo one-electron oxidation and loss one proton to form radicals. The radicals are stabilised by two molecular

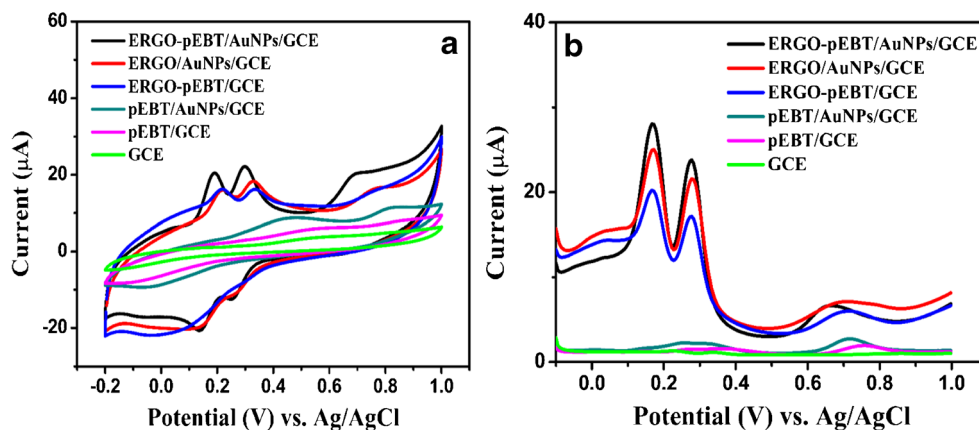
resonances and a positive charge at para-position. The hydroxyl group at ERGO attacks the active para site via one electron–two proton steps, which later undergoes two pathways, I and II. Two polymer structures, C and D are formed. The naphthol B form is less active than the naphthol A due to the presence of withdrawing nitro and sulfonic groups [18]. The final product is capable to interact with AuNPs to form a  $\pi$ - complex [19].

### Electrocatalytic performance of HQ, CC and RC

The electrocatalytic activity of the ERGO-pEBT/AuNPs/GCE was tested in the individual solution of 0.5 mM HQ, CC, and RC in 0.1 M PB solution (pH 6.0) in comparison to other modified electrodes using cyclic voltammogram (CV) at a scan rate of 100 mV.s<sup>-1</sup>. As shown in Fig. S1 (a-c), there is a rise in the peak currents when pEBT was deposited on GCE, while pEBT/AuNPs/GCE gives remarkable higher peak currents due to the accelerated electron transfer that attributed to the presence of AuNPs. While ERGO-pEBT/GCE and ERGO/AuNPs/GCE give rises in the peaks current for the dihydroxybenzene isomers as a result of the higher surface area of ERGO. A prominent enhancement in redox peak currents at ERGO-pEBT/AuNPs/GCE are achieved for HQ (Fig. S1a), CC (Fig. S1b), and RC (Fig. S1c). These results indicate the excellent electrocatalytic activity of ERGO-pEBT/AuNPs/GCE with respect to the oxidation of HQ, CC, and RC. Thus, ERGO-pEBT/AuNPs/GCE with a unique catalytic activity, large surface area and excellent conductivity can promote the separation of RC, CC and HQ during the voltammetry which furnishes the potential determination of HQ, CC, and RC simultaneously. Fig. S1(d) shows the overlaid potential oxidations of the three dihydroxybenzene isomers at the ERGO-pEBT/AuNPs/GCE. The peak potentials for the three isomers are clearly seen and positioned at different potentials. Thus, ERGO-pEBT/AuNPs/GCE has good electrocatalytic behaviour with respect to the determination of HQ, CC, and RC.

This work aims to detect HQ, CC, and RC simultaneously in their ternary mixture. Thus, CVs and differential pulse voltammograms (DPVs) were conducted to examine the electrochemical behaviour of the three dihydroxybenzene isomers at different modified electrodes. Figure 1a demonstrates the CVs of different modified electrodes in a solution containing a mixture of HQ, CC, and RC at a scan rate of 100 mV.s<sup>-1</sup>. It is observed that only one broad oxidation peak is obtained at bare GCE, implying overlapping of HQ, CC, and RC. The unresolved oxidation peaks at the non-modified GCE may be assigned to the slow electron kinetics, electrode fouling and limited diffusion of HQ, CC and RC [20, 21]. In contrast, pEBT/GCE and pEBT/AuNPs/GCE show different behaviour towards RC, CC, and HQ which exhibits two overlapped oxidation peaks of HQ and CC, and one oxidation peak of RC. However, when ERGO-pEBT/GCE is used, three oxidation peaks can be observed that assigned to HQ (217 mV), CC (337 mV) and RC (759 mV). The ERGO/AuNPs modified GCE reveals a slight increase in currents compared to ERGO-pEBT/GCE. Interestingly, when ERGO-pEBT/AuNPs/GCE is exposed to HQ, CC, and RC solution, three well-defined separated oxidation potential peaks with higher peak currents are observed identifying HQ (185 mV), CC (300 mV), and RC (688 mV). The peak to peak separations are 115 and 388 mV for HQ-CC and CC-RC, respectively, which promotes the simultaneous determination of the three isomers. Differential pulse voltammetric measurements were also performed for the determination of dihydroxybenzene isomers. As shown in Fig. 1b, pEBT/AuNPs/GCE, pEBT/GCE, and GCE reveal weakened and broad peaks, implying the difficulty of detection of RC, CC, and HQ at these electrodes. While better peak currents and good separation for the three analytes are observed at ERGO-pEBT/GCE and ERGO/AuNPs/GCE. On the other hand, three well-defined isolated peaks with enlarged peak currents at ERGO-pEBT/AuNPs/GCE indicating oxidation of HQ, CC, and RC. The peak currents are observed at 14.82, 13.57, and 2.87  $\mu$ A for HQ (166 mV), CC (277 mV), and RC (660 mV), respectively.

**Fig. 1** a CVs and b DPVs of 200  $\mu$ M mixture of HQ, CC and RC at different modified electrodes in 0.1 M PB solution (pH 6.0), scan rate 100 mV.s<sup>-1</sup>



The peak separations between RC-CC and CC-HQ are found to be 111 and 383 mV, respectively. This remarkable enhancement is due to the high surface area of ERGO which possesses more active sites that enhance the electron transfer between the electrode and analytes [22] and AuNPs favour the electron movement due to its excellent conductivity [23]. The pEBT plays an important role as a stabilising agent which prevent AuNPs from aggregation [24]. Thus, the synergistic effect of each material at ERGO-pEBT/AuNPs/GCE has resulted in well-separated peaks and enhanced peak currents.

### Effect of the pH value

Considering the effect of pH on the electrochemical reactions, there is no doubt electrolyte acidity has a crucial role in the redox of phenolic isomers. The effectiveness of the pH of the solution on the oxidation peak currents and potentials of HQ, CC, and RC were measured using differential pulse voltammetry between pH 4.0 and 8.0 at the ERGO-pEBT/AuNPs/GCE. The peak currents of HQ and CC drop when pH is changed from 4.0 to 5.0 as demonstrated in Fig. 2a, and then increase to the maximum reading at pH 6.0 followed by a decrease in current. It was reported that EBT has  $pK_a$  values of 6.6 and 11.6 [25]. The  $pK_a$  values of CC, RC and HQ are 9.4, 9.4 and 9.85, respectively. When the pH is between 4.0 and 6.0, the hydroxy group in the ERGO-pEBT/AuNPs and dihydroxybenzene isomers will be undissociated. At higher pH, there will be more ions of hydroxyl in the medium which can reduce the adsorption capacity [26]. The variation of the RC signal is not clearly observed with the increase in pH. However, it gives a slightly higher signal at pH 6.0 and at higher pH, the currents remain steady. Based on these results, pH 6 is the optimum pH for determination of RC, CC, and HQ.

A relationship between the potential oxidation peak and pH is shown in Fig. 2b, with linear regression equations of  $E(V) = 0.446 - 0.056 \text{ pH}$  ( $R^2 = 0.997$ ) for HQ,  $E(V) = 0.552 - 0.057 \text{ pH}$  ( $R^2 = 0.995$ ) for CC and  $E(V) = 1.013 - 0.063 \text{ pH}$

( $R^2 = 0.994$ ) for RC. The slopes are near to Nernst value revealing that both of the electrons and protons participate in the redox reaction of RC, CC, and HQ [27]. In accordance with the above-mentioned results, the preferred reactions of these isomers at ERGO-pEBT/AuNPs/GCE can be suggested as follows (Scheme 1) [28]:

### Effect of scan rate

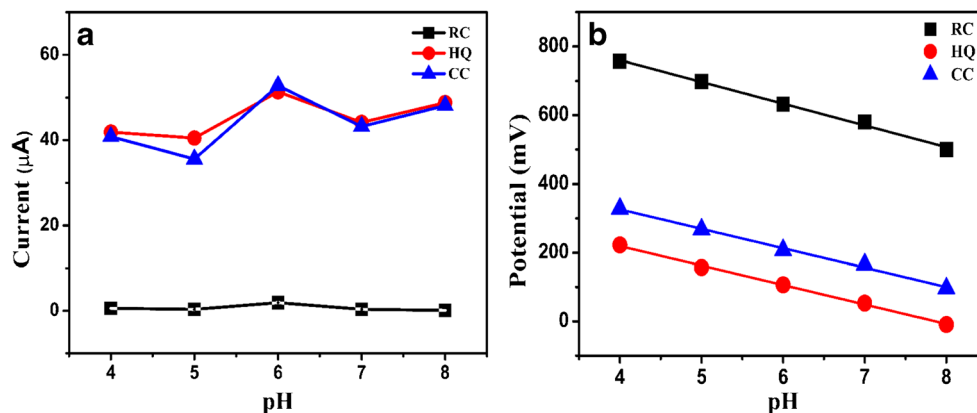
Figure 3a shows the CVs of ternary mixtures of 200  $\mu\text{M}$  HQ, CC, and RC in 0.1 M PB solution (pH 6.0) at the scan rates of 0.01 to 0.1  $\text{V}\cdot\text{s}^{-1}$ . The progressive increase in scan rate has resulted in increasing of redox peak currents. As seen in Fig. 3b, the log peak currents of the CVs for all three analytes are linearly proportional to the log of scan rate ( $\nu$ ) and the slope is close to 0.5, implying a process of diffusion controlled [29]. From Fig. 4b, the regression equation of HQ is  $I_{pa} (\mu\text{A}) = -0.27 + 0.38 \nu^{1/2} (\text{mV}\cdot\text{s}^{-1})^{1/2}$  ( $R^2 = 0.986$ ), while CC is  $I_{pa} (\mu\text{A}) = -0.16 + 0.30 \nu^{1/2} (\text{mV}\cdot\text{s}^{-1})^{1/2}$  ( $R^2 = 0.998$ ), and for RC is  $I_{pa} (\mu\text{A}) = 0.23 + 0.08 \nu^{1/2} (\text{mV}\cdot\text{s}^{-1})^{1/2}$  ( $R^2 = 0.959$ ).

### Selective and simultaneous determination of HQ, CC, and RC

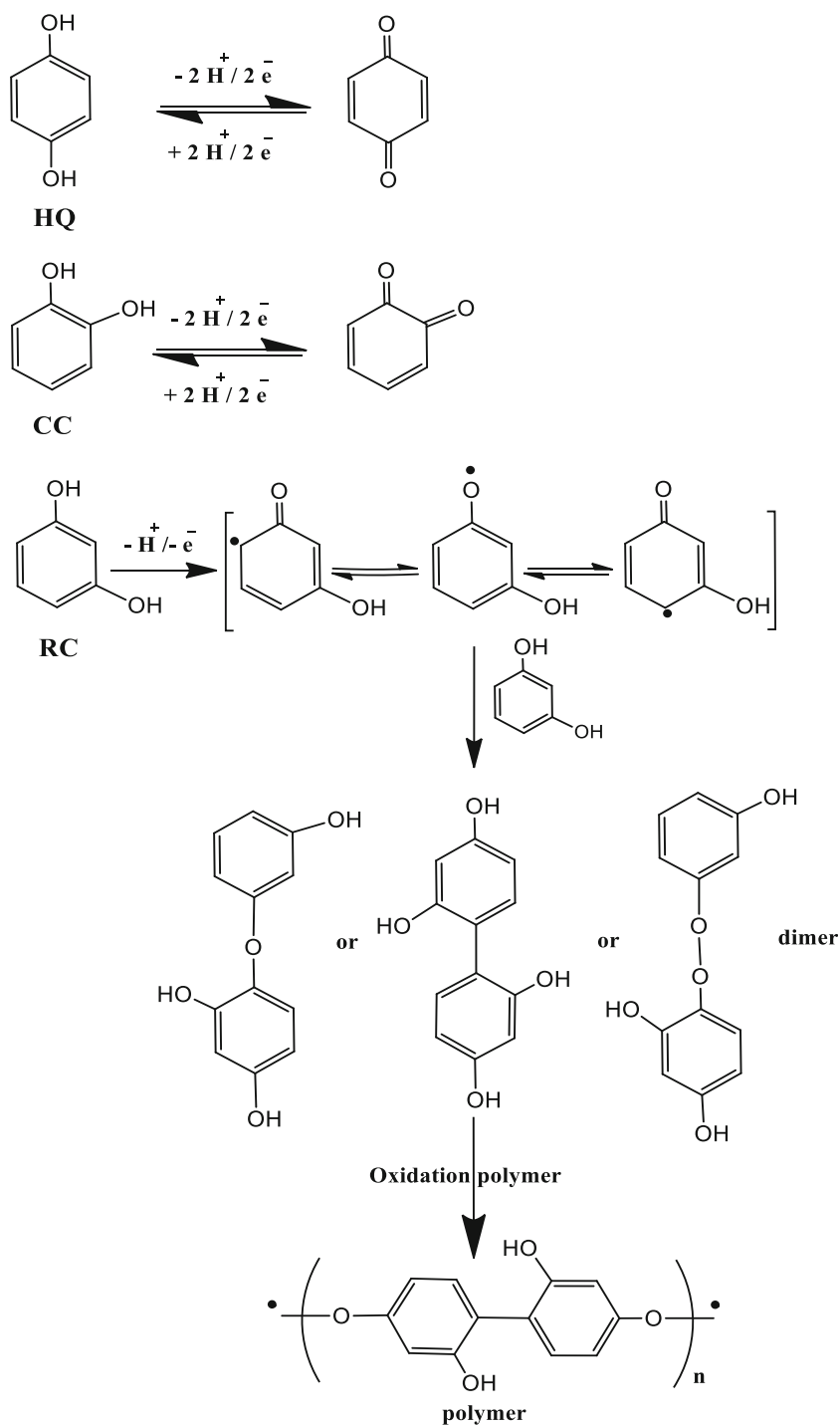
Both selective and simultaneous determination of HQ, CC, and RC were performed at ERGO-pEBT/AuNPs/GCE at optimised conditions using DPV. The selective determination of dihydroxybenzene isomers was carried out by changing each isomer concentration individually. Fig. 4a-c shows the variation of HQ, CC, and RC concentration in the range of 1.4–31.2, 1.5–31.2, and 8.5–41.7  $\mu\text{M}$ , respectively. The regression equations are presented below, with the limit of detections (LODs) of 3, 4, and 22 nM for HQ, CC, and RC, respectively.

$$I_{p,\text{HQ}} (\mu\text{A}) = 2.80 + 0.48 \text{ HQ} (\mu\text{M}) \quad (R^2 = 0.989) \quad (1)$$

**Fig. 2** Influence of pH on the (a) peak current and (b) peak potential of 500  $\mu\text{M}$  HQ, CC, and RC in 0.1 M PB solution



**Scheme 1** Electrochemical redox reactions of HQ, CC, and RC at ERGO-pEBT/AuNPs



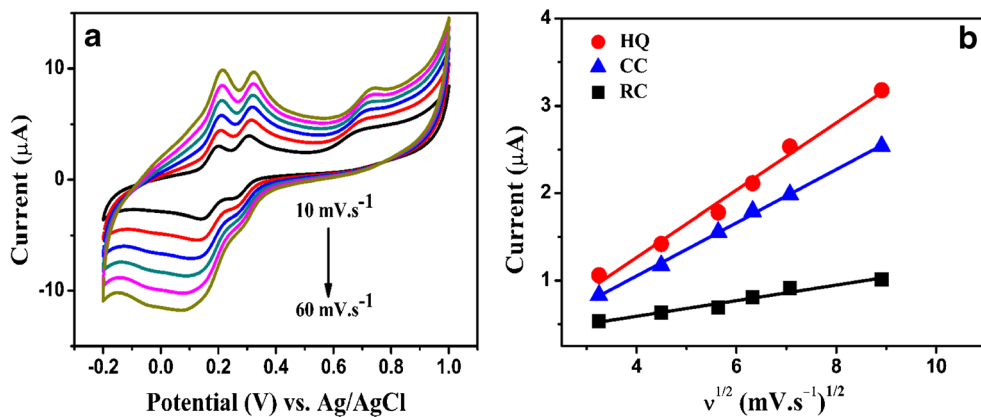
$$I_{p,CC} (\mu\text{A}) = 0.47 + 0.35 \text{CC} (\mu\text{M}) \quad (R^2 = 0.990) \quad (2)$$

$$I_{p,RC} (\mu\text{A}) = 0.34 + 0.07 \text{RC} (\mu\text{M}) \quad (R^2 = 0.983) \quad (3)$$

The assessments were performed by varying one isomer concentration while the other two isomers were fixed as depicted in Fig. S2 (a-c). When the concentration of each isomer is changed, the oxidation currents increase with the

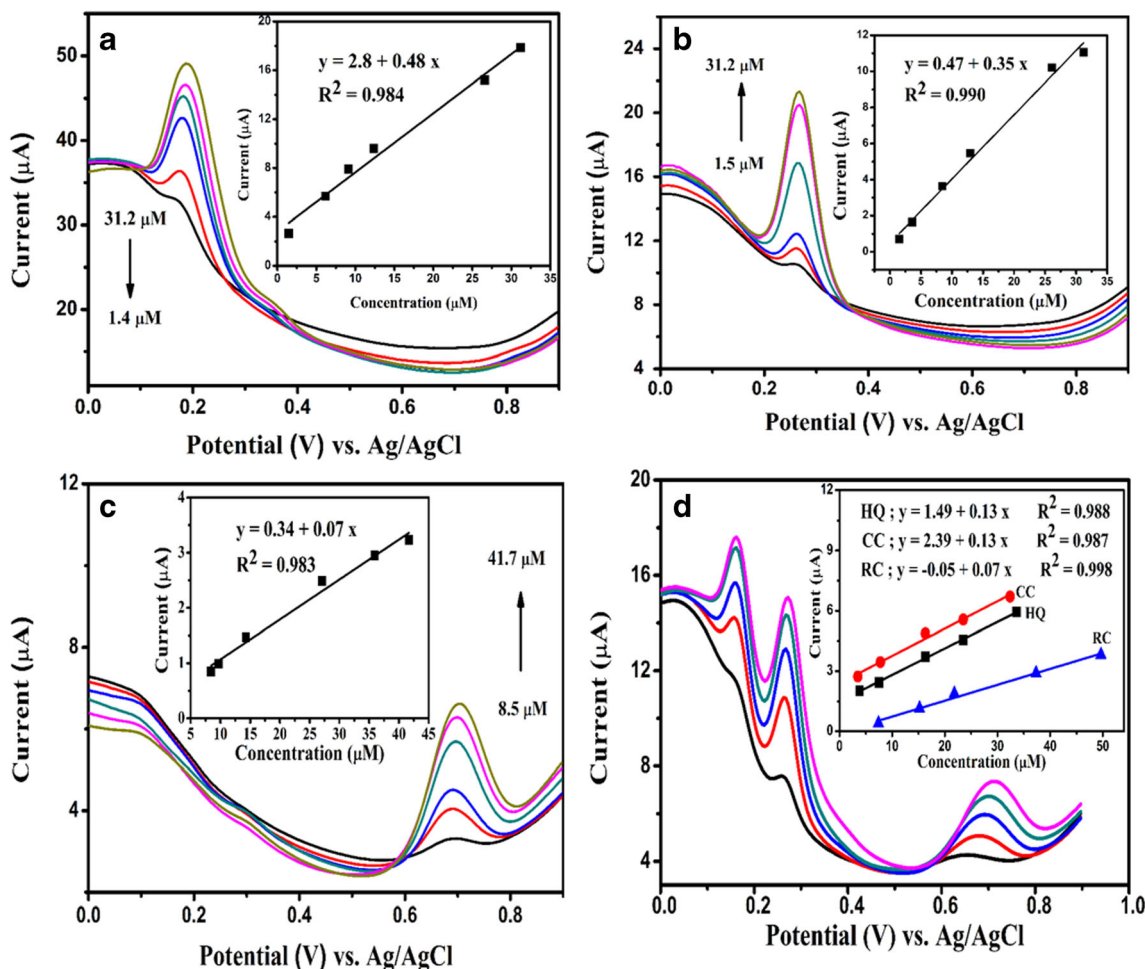
concentration and the peak potentials remain relatively constant. Fig. S2a exhibits DPVs of various concentrations of HQ in 0.1 M PB solution (pH 6.0) at a fixed 10.2  $\mu\text{M}$  CC and 50.6  $\mu\text{M}$  RC. The results reveal that the oxidation peak currents are related to the increment in HQ concentration whereas the peak currents of CC and RC approximately remain steady. The linear range of HQ is 0.52–31.4  $\mu\text{M}$  with a regression

**Fig. 3** a CVs of 200  $\mu\text{M}$  HQ, CC, and HQ, CC, RC in 0.1 M PB (pH 6.0) at ERGO-pEBT/AuNPs/GCE at different scan rates (0.01  $\text{V}\cdot\text{s}^{-1}$  to 0.06  $\text{V}\cdot\text{s}^{-1}$ ) (b) square root of scan rate versus anodic peak current



equation of  $I_{pa, HQ} (\mu\text{A}) = 0.04 + 0.10 HQ (\mu\text{M})$  ( $R^2 = 0.998$ ). The DPVs of variation of CC concentrations from 1.44–31.2  $\mu\text{M}$  at a constant concentration of 10.2  $\mu\text{M}$  HQ and

RC 50.6  $\mu\text{M}$  are displayed in Fig. S2b. The regression equation can be expressed as  $I_{pa, CC} (\mu\text{A}) = 0.78 + 0.18 CC (\mu\text{M})$  ( $R^2 = 0.996$ ). Similarly, DPVs of various RC concentrations



**Fig. 4** DPVs of ERGO-pEBT/AuNPs/GCE in (a) HQ (1.4, 6.1, 9.1, 12.4, 26.6, 31.2  $\mu\text{M}$ ); (b) CC (1.5, 3.6, 8.4, 12.8, 26.1, 31.2  $\mu\text{M}$ ); (c) RC (8.5, 9.7, 14.3, 27.1, 35.9, 41.7  $\mu\text{M}$ ) and (d) various concentrations of HQ and

CC (3.52, 7.52, 16.3, 23.5, 33.6  $\mu\text{M}$ ) and RC (7.4, 15.2, 21.8, 37.2, 49.7  $\mu\text{M}$ ). The inset shows the calibration plots. DPV conditions: pulse amplitude: 50 mV, pulse width: 50 ms, scan rate: 20  $\text{mV}\cdot\text{s}^{-1}$

from 3.8–72.2  $\mu\text{M}$  with a linear relation of  $I_{\text{pa, RC}} (\mu\text{A}) = 0.15 + 0.04 \text{ RC } (\mu\text{M})$  ( $R^2 = 0.990$ ) is presented in Fig. S2c. The LODs calculated using Eq. 4 for HQ, CC, and RC and are found to be 15, 8 and 39  $\mu\text{M}$  (signal-to-noise ratio (S/N) = 3), respectively.

$$\text{LOD} = 3S/M \quad (4)$$

where, S is referring to the standard deviation of the blank and M is the slope.

As depicted in Fig. S2 (a-c), there is a progressive increment in peak current with an increase in one analyte concentration, this indicates that the coexistence of other two isomers does not affect the oxidation of HQ, CC, and RC at the ERGO-pEBT/AuNPs/GCE. The measurements of RC, CC, and HQ have been established by varying their concentrations simultaneously. As depicted in Fig. 4d, the anodic peak potentials of the three isomers are clearly separated from each other, while their oxidation peak currents increase linearly with their respective concentrations as displayed in calibration plots (inset Fig. 4d). The regression equations for HQ, CC, and RC are  $I_{\text{p, HQ}} (\mu\text{A}) = 1.49 + 0.13 \text{ HQ } (\mu\text{M})$  ( $R^2 = 0.988$ ),  $I_{\text{p, CC}} (\mu\text{A}) = 2.39 + 0.13 \text{ CC } (\mu\text{M})$  ( $R^2 = 0.987$ ), and  $I_{\text{p, RC}} (\mu\text{A}) = -0.05 + 0.07 \text{ RC } (\mu\text{M})$  ( $R^2 = 0.998$ ), respectively. The LODs are found to be 12, 12, and 22 nM for HQ, CC, and RC respectively. Apparently, there is no such difference in linear ranges and LODs between the selective and simultaneous detection of RC, CC, and HQ. Therefore, both sensitive and simultaneous determination of HQ, CC, and RC are favoured without valid interference between them. As displayed in Table 1, the performance of the ERGO-pEBT/AuNPs modified GCE is comparable to other modified electrodes.

## Interference study

Selectivity of the ERGO-pEBT/AuNPs/GCE was tested, where a specific amount of interferent was added to a solution containing 100  $\mu\text{M}$  RC, CC, and HQ in 0.1 M PB solution (pH 6.0). From the results, it is found that the presence of 2000-fold  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , 100-fold of  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , 50-fold uric acid, 5-fold 2,4-dinitrophenol and chlorophenol do not produce any apparent change in the oxidation current response (current signal changed <5%). On the other hand, phenol as interferent affects the DPV signal. Thus, it is suggested during the analysis of the real sample, phenol should be eliminated. The analysis of the results confirmed that the modified electrode ERGO-pEBT/AuNPs has outstanding selectivity.

## Reproducibility, repeatability and stability

The reproducibility of ERGO-pEBT/AuNPs/GCE was evaluated using five different modified electrodes with a solution containing 100  $\mu\text{M}$  of RC, CC, and HQ. The relative standard deviations (RSDs) are 1.39%, 0.83%, and 2.34% for HQ, CC and RC, respectively. The repeatability of the modified electrode was carried out for ten measurements (Fig. S3a and b) in a solution containing 100  $\mu\text{M}$  of HQ, CC, and RC in 0.1 M PB solution (pH 6.0) and the RSDs are 4.31%, 5.03%, and 2.90%, respectively. The stability of the modified electrode was tested over a period of 10 days immersed in PB solution (pH 6.0). The oxidation peak currents for RC, CC and HQ are maintained as 93.9%, 95.5%, and 96.1%, respectively. These results reveal that ERGO-pEBT/AuNPs/GCE has good reproducibility, repeatability and stability performance.

**Table 1** Comparison of ERGO-pEBT/AuNPs/GCE and other electrodes for simultaneous determination of RC, CC, and HQ

Electrode	Linear Range ( $\mu\text{M}$ )			LOD (nM)			Ref.
	HQ	CC	RC	HQ	CC	RC	
Gr-CS/GCE	1–300	1–400	1–550	750	750	750	[12]
rGO/Au-NPs/GCE	3–90	3–300	15–150	150	120	780	[13]
NRCu/rGO/GCE	0.13–131.5	0.13–131.5	0.13–131.5	49	52	60	[14]
ERNGO-GCE	0.05–1	0.05–1	0.05–1	15	13	13	[15]
CePO <sub>4</sub> @GCE	0.23–5500	0.23–5500	0.23–5500	140	140	140	[16]
1D PEDOT-Gr/GCE	5–250	2–400	1–250	60	80	160	[30]
Au-PdNF/rGO/GCE	1.6–100	2.5–100	2–100	500	800	700	[31]
P-rGO/GCE	5–90	5–120	5–90	80	180	2620	[32]
ERGO-pEBT/AuNPs/GCE	0.52–31.7	0.44–31.2	3.8–72.7	15	8	39	This work

Gr, graphene; CS, chitosan; NRCu, nanoraspberry-like copper; ERNGO, nitrogen-doped graphene; CePO<sub>4</sub>, cerium phosphate nanotubes; 1D, one-dimensional, PEDOT: poly(3,4-ethylenedioxythiophene); NF, nanoflower; P, porous; rGO, reduced graphene oxide

**Table 2** Analysis of HQ, CC, and RC in tap water samples by the ERGO-pEBT/AuNPs/GCE and HPLC method ( $n = 5$ )

Sample	Analyte	ERGO-pEBT/AuNPs/GCE			HPLC method		
		Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)
Tap water 1	HQ	1.39	1.29 $\pm$ 0.03	92.8	1.39	1.38 $\pm$ 0.03	99.28
	CC	0.86	0.90 $\pm$ 0.03	104.6	0.86	0.91 $\pm$ 0.03	105.8
	RC	0.73	0.69 $\pm$ 0.02	94.5	0.73	0.66 $\pm$ 0.02	90.41
Tap water 2	HQ	2.76	2.80 $\pm$ 0.03	100.4	2.76	2.77 $\pm$ 0.04	100.3
	CC	1.01	0.94 $\pm$ 0.02	93.1	1.01	0.95 $\pm$ 0.04	94.05
	RC	1.30	1.38 $\pm$ 0.03	106.2	1.30	1.37 $\pm$ 0.03	105.4
Tap water 3	HQ	4.15	4.18 $\pm$ 0.04	100.7	4.15	4.20 $\pm$ 0.04	101.2
	CC	1.52	1.60 $\pm$ 0.03	105.3	1.52	1.46 $\pm$ 0.04	96.05
	RC	1.56	1.64 $\pm$ 0.05	105.1	1.56	1.58 $\pm$ 0.03	101.3

### Measurement of RC, CC, and HQ in synthetic wastewater

To study the effectiveness of ERGO-pEBT/AuNPs/GCE for measuring HQ, CC and RC for practical applications, tap water was used as a test sample. The dihydroxybenzene isomers with different concentrations have been added to the tap water to form artificial waste water and their contents and recoveries were calculated. The results presented in Table 2 show that the recoveries of the measurements are between 92.8% and 107.4%. The obtained results are validated by high-performance liquid chromatography (HPLC) [33]. Fig. S4 shows a typical chromatograph of water sample spiked with HQ, CC, and RC. Statistical analysis ( $t$ -test) indicates that there are no significant differences between the two methods at 95% confidence level.

### Conclusion

Simultaneous determination of dihydroxybenzene isomers was successfully performed using the ERGO-pEBT/AuNPs/GCE nanocomposite. Improvement in peak currents and oxidation potentials in comparison to other modified electrodes has been achieved due to the superior properties of the nanocomposite sensor. The results have shown the capability of ERGO-pEBT/AuNPs/GCE to detect and resolve the dihydroxybenzene isomers potentials with high sensitivity, selectivity, and remarkable stability. The nanocomposite sensor revealed a promising application to detect HQ, CC, and RC in artificial water samples.

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