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Preparation and characterization of a novel hybrid hydrogel composite of chitin stabilized graphite: Application for selective and simultaneous electrochemical detection of dihydroxybenzene isomers in water

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Abstract

The development of new and robust sensors for real-time monitoring of environmental pollutants have received much attention. Therefore, in the present work, we have fabricated a simple and robust electrochemical sensor for the simultaneous electrochemical determination of dihydroxybenzene isomers using chitin (CHI) stabilized graphite (GR) hydrogel composite modified electrode. The GR-CHI hydrogel composite was prepared by a simple sonication of raw GR in CHI solution and the as-prepared materials were characterized by range of physicochemical methods. Compared with CHI and GR modified electrodes, the GR-CHI hydrogel composite modified electrode shows an excellent electron transfer ability and enhanced electrocatalytic activity towards hydroquinone (HQ), catechol (CC) and resorcinol (RC). Differential pulse voltammetry was used for the simultaneous determination of HQ, CC and RC. Under optimized conditions, the fabricated electrode detects the HQ, CC and RC in the linear response from 0.2 to 110.6 µM, 0.3 to 110.6 µM and 1.3 to 133.4 µM, respectively. The detection limit for HQ, CC and RC were 0.065 µM, 0.085 µM and 0.35 µM, respectively. The sensor shows its appropriate practicality towards the determination of HQ, CC and RC in different water samples.

Keywords: Graphite; chitin; hydrogel composite, dihydroxybenzene isomers; simultaneous determination; differential pulse voltammetry

1. Introduction

In recent years, development of cost-effective and robust sensors for real-time monitoring of environmental pollutants has received much attention in the scientific community [**1**]. In particular, the simultaneous determination of dihydroxybenzene isomers such as hydroquinone (HQ), catechol (CC) and resorcinol (RC) has received sustainable interest due to their significant role in the industries [**2**]. For example, the HQ, CC and RC has been continually used as important chemicals in various industrial sectors, including pesticide, cosmetics, dyes, medicine, tanning, photography and pharmaceutical applications [**3, 4**]. The U.S. Environmental Protection Agency (EPA) and the European Union (EU) has revealed that HQ, CC and RC as toxic environmental pollutant due to their high toxicity and poor degradability in the biological environment [**2**]. Different analytical methods have been reported so far for the simultaneous determination of HQ, CC and RC [**3, 5–9**]. Compared to high-performance liquid chromatography, spectrometry, fluorescence and chemiluminescence methods, the electrochemical methods are found to be a simple and inexpensive for the simultaneous determination of dihydroxybenzene isomers [**3, 10**]. However, the simultaneous determination of HQ, CC and RC is quite challenging on unmodified carbon electrodes such as glassy and screen-printed carbon due to their poor selectivity and electrode fouling [**11**]. Hence, the chemically modified electrodes have been widely used for simultaneous determination of HQ, CC and RC owing to their high conductivity, high stability and wide potential window [**12**].

Carbon nanomaterials and its composites have received significant interest in the electroanalytical community due to their higher surface area, wide potential window and extreme stability [**13–15**]. For example, carbon nanotubes, graphene oxide and reduced graphene oxide or their composites have been widely used for the simultaneous determination of HQ, CC and RC [**3,**

10, 16–19]. Carbon nanomaterials modified electrodes exhibited good electroanalytical performance Ffor a range of analytes, including dihydroxybenzene isomers, yet the synthesis of carbon nanomaterials is quite-time consuming and expensive. Hence, simple and cost-effective nanomaterials with improved analytical performance for the simultaneous determination of HQ, CC and RC is of interest to the analytical community. Our recent studies revealed that the carbohydrate polymers entrapped graphite (GR) exhibited an enhanced electron transfer ability towards dopamine and the analytical performances have been found analogous to carbohydrate polymers entrapped graphene [**20, 21**].

In the present work, we prepared a highly stable chitin (CHI) stabilized GR hydrogel composite by a simple sonication of GR in CHI solution for the first time. Compared to graphene and other carbon nanomaterials modified electrodes, the GR/CHI hydrogel composite is less expensive, environmentally friendly and can be prepared in a short time (45 min). It is well-known that CHI is a low-cost carbohydrate biopolymer with excellent biocompatibility, biodegradability, low toxicity and high mechanical stability [**22, 23**]. The unique properties of CHI are often more promising in various applications such as protein sorption, water remediation, food wrapping, tissue engineering, wound dressings and drug delivery [**24–26**]. To the best of our knowledge, we have for the first time, we have prepared GR-CHI hydrogel composite and its potential application in electroanalysis. As a proof, the as-prepared GR-CHI hydrogel composite is used for the simultaneous determination of HQ, CC and RC and the analytical characteristics were compared with graphene-CHI hydrogel composite modified electrode. The strong hydrogen bonding between dihydroxybenzene isomers with CHI and large edge plane defects of exfoliated GR sheets in the composite result in the enhanced electrocatalytic activity of dihydroxybenzene isomers. The electrochemical behavior of HQ, CC and RC was studied and the analytical performance of the

GR/CHI hydrogel composite modified electrode was compared with previously reported carbon nanomaterials modified electrodes (see **Table 1**). Furthermore, the analytical features (limit of detection and linear response range) of the developed sensor were comparable with previously reported graphene and carbon nanotubes modified composite electrodes.

2. Experimental details

2.1. Materials and method

Chitin (from crab shells) and raw graphite powder (average diameter >20 μm) were purchased from Sigma Aldrich and used without purification. Hydroquinone, catechol and resorcinol were obtained from Wako Pure Chemical Industries, Ltd and used as received. Phosphate buffer with pH 7 (PBS) was used as a supporting electrolyte, and prepared using 0.1 M Na_2HPO_4 and NaH_2PO_4. The chemical solutions were prepared using Millipore water without purification.

CHI 750a Electrochemical analyzer (CH instruments) was used for the cyclic voltammetry and differential pulse voltammetry (DPV) measurements. The DPV was operated under the pulse width = 0.05 s, sampling width = 0.0167 s, amplitude = 0.05 V, and pulse period = 0.2 s. Hitachi S-3000 H scanning electron microscope was used to evaluate the surface morphological studies. Thermo SCIENTIFIC Nicolet iS10 instrument was used for the Fourier transform infrared spectroscopy (FTIR) measurements. Electrochemical impedance spectroscopy (EIS) was performed using IM6ex ZAHNER (Kronach, Germany). Typical three electrode system was used for electrochemical experiments, in which modified glassy carbon electrode (GCE), Sat. Ag/AgCl and platinum wire were used as a working, reference and counter electrodes, respectively. The electrochemical measurements were carried out at room temperature in absence of oxygen.

2.2. Preparation of GR-CHI hydrogel

To prepare GR-CHI hydrogel, first the CHI solution was prepared by dissolving 20 mg of CHI into the 5% acetic acid for 30 min sonication. Then, the raw GR (5 mg mL^{-1}) was added into the CHI solution and sonicated continuously for 45 min. After the successful sonication, the clear GR-CHI hydrogel was obtained. The schematic representation of the preparation of GR-CHI hydrogel composite is shown in **Scheme 1**.

<**Please inset Scheme 1 here**>

About 8 μL of the GR-CHI hydrogel (optimum concentration) composite was drop casted on the pre-cleaned GCE and dried at room temperature. The obtained GR-CHI hydrogel composite modified electrode was further used for electrochemical experiments. The CHI modified electrode was prepared by drop coating of CHI solution without GR. Consequently, the GR modified electrode was prepared without CHI and GR dispersion was prepared by similar procedure as reported previously [**21**]. For comparison, the graphene-CHI hydrogel composite was prepared by similar method using graphene instead of GR. The modified electrodes were stored at room temperature under dry condition when not in use.

3. Results and discussion

3.1. Characterizations

The surface morphology of the as-prepared materials was characterized by SEM. **Fig. 1** shows the SEM images of GR (A), CHI (B) and GR-CHI hydrogel composite in lower (C) and higher (D) magnification. The SEM image of GR shows flake sheet morphology with the association of bundle of micro graphitic sheets. The SEM of CHI shows the dense pore structure morphology where CHI microfibers are interlinked each other. Whereas, the uniform distribution of CHI in GR layers was observed in the SEM image of GR-CHI hydrogel composite. The strong interaction between CHI and GR sheets resulted in the formation of GR-CHI hydrogel composite and excellent dispersion ability (**Scheme 1**) of GR in CHI solution.

<**Please inset Figure 1 here**>

<**Please inset Figure 2 here**>

The formation of GR-CHI hydrogel composite was confirmed by FTIR, and the corresponding FTIR spectra of GR, CHI and GR-CHI hydrogel is shown in **Fig. 2**. It can be seen that the FTIR spectrum of GR (green profile) is found featureless in the fingerprint region. While, the GR-CHI hydrogel composite (red profile) shows three distinct bands at 3466, 3258, and 3122 cm^{-1}, which are characteristic peaks for O–H, N–H (asymmetric), and N–H (symmetric) stretching vibrations of CHI [**22, 27**]. In addition, two new bands were observed at 1683 and 1580 cm^{-1}, which are associated to the characteristic amine II and III bonds of CHI [**27**]. In addition, similar FTIR bands were observed for FTIR spectrum of CHI (blue profile), and confirms the presence of CHI in GR-CHI hydrogel composite. It is interesting to see that the FTIR spectrum of GR-CHI does not show any characteristic new bands when compared with CHI and GR, which indicates that the composite was formed by strong interaction between GR and CHI. The result confirms the formation of GR-CHI hydrogel composite.

<**Please inset Figure 3 here**>

EIS of Nyquist plot was used to monitor the electrochemical impedance changes at the different modified GCEs. **Fig. 3** shows the EIS of GR (a), bare (b) and GR/CHI hydrogel composite (c) modified GCEs in PBS containing 5 mM $Fe(CN)_6^{3-/4-}$. Inset of **Fig. 3** shows the Randles equivalent circuit model. The bare GCE shows larger semicircle with an electron transfer resistance (R_{ct}) value of 132 Ω when compared to GR modified GCE (97 Ω). The result indicates that GR modified electrode has fast electron transfer than bare GCE. On the other hand, GR/CHI hydrogel composite modified GCE showed a depressed semicircle with R_{ct} value of 11.6 Ω, which indicates the high conductivity and fast electron transfer ability towards the electrode surface. The fast electron transfer of the hydrogel composite modified electrode is due to the strong interaction of CHI with GR, and result into the exfoliation and activation of the edges of GR. The above results indicate the GR/CHI hydrogel composite modified electrode has fast electron transfer towards electrode surface than other modified electrodes.

3.2. Electrochemical behaviors of HQ, CC and RC

To evaluate the electrochemical behavior CC, cyclic voltammetry was carried out for the detection of HQ, CC and RC using different modified electrodes. **Fig. 4A** shows the cyclic voltammetric response of bare (a), CHI (b), GR (c) and GR-CHI (d) modified electrodes for 50 µM of HQ, CC and RC containing N_2 saturated PBS. The scan rate was 50 mV/s. The un-modified electrode did not show any obvious response to the presence of HQ, CC and RC. A quasi-reversible redox couple was observed for CC with the oxidation peak at 0.382 V at CHI modified electrode. However, no significant response was observed on CHI modified electrode for HQ and RC. From the above results, we can conclude that the bare and CHI modified electrodes are not suitable for the simultaneous detection of HQ, CC and RC. A weak quasi redox couple and oxidation peak was observed for HQ and RC at GR modified electrode. The oxidation peaks of HQ and RC were located at 0.116 and 0.216 V. However, the GR modified electrode did not show the oxidation peak response to CC. The result clears that the GR modified electrode is not suitable for simultaneous detection of HQ, CC and RC. A well-defined redox couple appeared at GR-CHI hydrogel composite modified electrode for HQ and CC, which is due to the reversible electrochemical behavior of hydroxyl- benzene isomer to benzoquinone. The oxidation peak of HQ and CC appeared at 0.1 and 0.217 V for the GR-CHI hydrogel composite, which was 3.5 and

4 folds higher than those observed for the GR modified electrode. In addition, the observed redox couple of HQ and CC was 4 folds higher than the GR modified electrode, which indicates that the electrochemical redox behavior of HQ and CC was greatly enhanced in the composite electrode. A sharp oxidation peak was also observed for CC along with the two redox couple, and the oxidation peak was appeared at 0.580 V. It was worthy to note that the oxidation peak of RC was not observed for the CHI and GR modified electrodes. The above results clear that the GR-CHI hydrogel composite modified electrode is more suitable for simultaneous electrochemical determination of HQ, CC and CC. The strong hydrogen bonding between dihydroxybenzene isomers with CHI and large edge plane defects of exfoliated GR sheets are resulted in the enhanced electrocatalytic activity towards HQ, CC and RC.

<**Please inset Figure 4 here**>

We have also evaluated the electrochemical activity of GR-CHI hydrogel composite in the absence and presence of HQ, CC and RC and the results are shown in **Fig. 4B**. The GR-CHI hydrogel composite did not show any significant peak response for HQ, CC and RC in the absence of dihydroxybenzene isomers (curve a), which indicates that the hydrogel composite modified electrode is electrochemically inactive in this particular potential window although, a sharp response was observed in the presence dihydroxybenzene isomers. The result clears that the redox peaks and oxidation peak at GR-CHI hydrogel composite are associated to the presence of dihydroxybenzene isomers. As we stated in the introduction, graphene based composites are widely used for simultaneous detection of dihydroxybenzene isomers. Hence, the performance of our composite modified electrode need to be compared with graphene-CHI hydrogel composite modified electrode. The comparative cyclic voltammetry results are shown in **Fig. 4C**. It can be seen that the GR-CHI hydrogel composite modified electrode (curve b) exhibits an equal electrochemical activity to graphene-CHI hydrogel composite modified electrode (curve a) for the detection of HQ, CC and RC. In fact, the GR-CHI hydrogel composite modified electrode shows an enhanced electrochemical behavior to HQ, CC and RC than graphene-CHI hydrogel composite. The result authenticates that the as-prepared GR-CHI hydrogel composite modified electrode can be used as a sensitive and alternative probe for graphene-CHI hydrogel composite.

<**Please inset Figure 5 here**>

Fig. 5 shows cyclic voltammetry response of GR-CHI hydrogel composite modified electrode in PBS containing 50 µM HQ, CC and RC at different scan rates. The scan rates were used from 20 to 200 mV/s. The redox peak current of HQ and CC and the oxidation peak current of RC increases with increasing the scan rates, and the redox peak and oxidation peak current of HQ, CC and RC have a linear dependence with the square root of scan rates from 20 to 200 mV/s, as shown in **Fig. 5A inset**. The linear regression equations for anodic peak of HQ, CC and RC were expressed as: I_{pa} (µA) = -1.8501+0.4118 $(\nu)^{1/2}$ $(mV/s)^{1/2}$ (R^2 = 0.9961), I_{pa} (µA) = -2.5478+4.8721 $(\nu)^{1/2}$ $(mV/s)^{1/2}$ (R^2 = 0.9741) and I_{pa} (µA) = -1.0774+1.8422 $(\nu)^{1/2}$ $(mV/s)^{1/2}$ (R^2 = 0.991), respectively. The linear regression equations for cathodic peak of HQ and CC were expressed as: I_{pc} (µA) = 1.2335-0.2808 $(\nu)^{1/2}$ $(mV/s)^{1/2}$ (R^2 = 0.9944) and I_{pc} (µA) = 1.1724-2.1322 $(\nu)^{1/2}$ $(mV/s)^{1/2}$ (R^2 = 0.9847), respectively. The result indicates that the electrochemical behavior of HQ, CC and RC at GR-CHI hydrogel composite modified electrode is a typical diffusion controlled electrochemical process [**19**].

<**Please inset Figure 6 here**>

Fig. 6 depicts the electrochemical redox behavior of 50 µM HQ, CC and RC in different pH (pH 3, 5, 7 and 9) for the GR-CHI hydrogel composite modified electrode. The scan rate was 50 mV/s. The anodic (E_{pa}) and cathodic peak (E_{pc}) potential of HQ and CC shifted towards negative

direction upon increasing the pH from 3 to 9. In addition, the E_{pa} of RC shifted towards negative potential upon increasing the pH. The result indicates that the protons are involved in the oxidation of HQ, CC and RC. We have obtained a linear plot (**Fig. 6 inset**) for the anodic and cathodic peak potential of HQ and CC vs. pH; and the anodic peak potential of RC vs. pH. The linear regression was found for HQ, CC and RC as E_{pa} (mV) = -0.0557 pH + 0.5927 (R^2 = 0.9913), E_{pa} (mV) = -0.0555 pH + 0.5927 (R^2 = 0.9981) and E_{pa} (mV) = -0.0558 pH + 1.0338 (R^2 = 0.9938), respectively. The obtained slope values of HQ (-55.7 mV/pH), CC (-55.5 mV/pH) and RC (-55.8 mV/pH) are nearly close to the theoretical value (–59.6 mV/pH) of Nernstian equation for equal number of protons and electrons transfer redox electrochemical process [**19**]. In addition, a maximum anodic peak current response of HQ, CC and RC was appeared at pH 7 than other pH. Hence, pH 7 was selected as an optimal for the simultaneous determination of HQ, CC and RC.

3.3. Simultaneous and selective determination of HQ, CC and RC

DPV was used for the simultaneous electrochemical detection of HQ, CC and RC using GR-CHI hydrogel composite modified electrode, since DPV has high sensitivity than other voltammetric methods. **Fig. 7A** shows the DPV response of GR-CHI hydrogel composite modified electrode for the simultaneous addition of different concentration of HQ (0.2–133.4 µM), CC (0.3–133.4 µM) and RC (1.3–133.4 µM) into the PBS. It can be seen that the DPV shows notable three peaks at 0.079, 0.176 and 0.588 V for each addition of HQ, CC and RC into the PBS, which are corresponding to the oxidation of HQ, CC and RC. In addition, the DPV also shows a sharp peak at -0.09 V which is due to presence of CHI hydrogel in the GR/CHI composite. DPV response increases with increasing the concentration of HQ, CC and RC. The DPV response was found linear over the concentration ranging from 0.2 to 110.6 µM, 0.3 to 110.6 µM and 1.3 to 133.4 µM for HQ, CC and RC (**Fig. 7A inset**). The limit of detection (LOD) was calculated as 0.065 µM, 0.085 µM and 0.35 µM for HQ, CC and RC respectively, based on S/N=3. In order to evaluate the analytical advantages of the sensor, the LOD and linear response range of the sensor was compared with previously reported carbon nanomaterials modified electrodes and the comparison results are shown in **Table 1**. Comparative results clearly reveal that the GR-CHI hydrogel composite has an appropriate analytical performance to the previously reported carbon nanomaterials based electrodes for the simultaneous determination of dihydroxybenzene isomers [**3, 9, 11–13, 17–19, 27, 30–33**]. Hence, the as-prepared GR-CHI hydrogel composite modified electrode can be used as an alternative electrode material for the simultaneous determination of dihydroxybenzene isomers.

<**Please inset Figure 7 here**>

<**Please inset Table 1 here**>

The selectivity of the electrode is more important in order to access the modified electrode for real time applications. Hence, the cross-reactivity of each dihydroxybenzene isomers were examined in the presence of other two isomers by DPV under the same experimental conditions. **Fig. 7B** shows the DPV response of GR-CHI composite modified electrode for the different concentration additions of HQ (0.2–133.4 µM) in the presence of 10 µM CC and 25 µM RC containing N_2 saturated PBS. It was observed that the DPV response of HQ was not affected by the response of CC and RC, which indicates that HQ did not have a cross-reactivity with CC and RC. The similar phenomenon has been found for the selective detection of CC (**Fig. 7C**) and RC (**Fig. 7D**) in the presence of HQ and RC; and HQ and CC. The result clearly indicates that the GR-CHI hydrogel composite modified electrode can be used for selective determination of HQ, CC and RC in the presence of other dihydroxybenzene isomers.

We have also studied the selectivity of the as-prepared GR-CHI hydrogel composite modified electrode in the presence of potentially active phenolic compounds (100 µM) and common metal ions (500 µM) for the simultaneous detection of 10 µM HQ, CC and 25 µM RC by using DPV. The obtained results tabulated in **Table 2**. **Table 2** evident that a 100 µM addition of inorganic metal ions had less effect (< 2 %) on the simultaneous detection of HQ, CC and RC. On the other hand, 100 µM addition of phenolic compounds show little effect (< 2.7 %) on the simultaneous detection of HQ, CC and RC. However, 100 µM addition of dopamine shows a more effect (3.65–4.21 %) on the oxidation peak current response of the detection of HQ and CC due to the close oxidation potential of dopamine where HQ and CC was oxidized. The result clearly indicates that GR-CHI hydrogel composite modified electrode has appropriate selectivity in the presence of phenolic compounds and common metal ions for the simultaneous detection of HQ, CC and RC.

<**Please inset Table 2 here**>

The storage stability of the sensor was examined periodically to the response of 10 µM concentration of HQ, CC and RC by DPV (not shown) with the same experimental conditions to **Fig. 7A**. The GR-CHI hydrogel composite modified electrode retains its initial sensitivity about 92.6 %, 93.6 % and 91.7 % for HQ, CC and RC after 14 days storage in PBS. The result indicates the fabricated sensor has an appropriate storage stability towards the detection of HQ, CC and RC. The repeatability and reproducibility of the sensor was evaluated by cyclic voltammetry and the experimental conditions are similar to **Fig. 4A**. Under the optimum conditions, the relative standard deviation (RSD %) of 2.1 %, 3.6 % and 3.3 % was found for 10 successive measurements of 50 µM of HQ, CC and RC using a single sensor. The RSD of 4.1 %, 4.5 % and 3.7 % was observed for 5 different sensor electrodes towards the detection of 50 µM of HQ, CC and RC. The obtained results revealed that the GR-CHI hydrogel composite modified electrode has appropriate repeatability and reproducibility towards the detection of HQ, CC and RC.

3.4. Determination of HQ, CC and RC in water samples

The practicality of the sensor is more important to further access the modified electrode for real-time sensing in real samples. Hence, the GR-CHI hydrogel composite modified electrode was used for the simultaneous determination of HQ, CC and RC in different water samples. We have chosen the tap, pond and drinking water samples for real sample analysis. DPV was used to evaluate the practicality of the sensor and the recoveries of HQ, CC and RC were calculated using the standard addition method, as reported previously [**19, 29**]. The DPV working experimental conditions are same as to **Fig. 7A**. The obtained recoveries of HQ, CC and RC in different water samples are tabulated in **Table 3**. The **Table 3** clearly revealed that the fabricated sensor is able to detect HQ, CC and RC in the tap, pond and drinking water samples with an average recovery of 97.7, 99.0 and 98.7%, respectively. The above results clearly validate that the as-prepared GR-CHI hydrogel composite modified electrode can be used for the simultaneous determination of HQ, CC and RC in the investigated water samples.

<**Please inset Table 3 here**>

4. Conclusions

A simple and robust electrochemical sensor was developed for the simultaneous electrochemical determination of HQ, CC and RC using GR-CHI hydrogel composite modified electrode for the first time. The SEM and FTIR observations confirmed the formation GR-CHI hydrogel composite. The as-prepared GR-CHI hydrogel composite can selectively detect the HQ, CC and RC without cross reactivity of each other. The fabricated sensor exhibited many analytical advantages for simultaneous determination of HQ, CC and RC, such as wider linear response, high sensitivity and low LOD. The good practicality of the sensors revealed that the as-prepared GR-CHI hydrogel composite can be used for the selective and simultaneous electrochemical determination dihydroxybenzene isomers in the investigated water samples.

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Table. 1 Comparison of analytical performance of the as-prepared GR/CHI hydrogel composite modified electrode with the previously reported modified electrodes for the simultaneous determination of HQ, CC and RC.

Electrode	**Linear response range (μM)**			**LOD (μM)**			**Ref.**
	HQ	**CC**	**RC**	**HQ**	**CC**	**RC**	
GR/CHI/GCE	1.0–400.0	1.0–550.0	1.0–300.0	0.75	0.75	0.75	[**3**]
Poly-*p*-ABSA/GCE	1.2–600.0	2.0–900.0	NR	0.4	0.5	NR	[**9**]
GR–La(OH)$_3$/GCE	5.0–300.0	5.0–300.0	NR	0.05	0.01	NR	[**11**]
CNF/GCE	6.0–200.0	2.0–200.0	NR	0.25	0.1	NR	[**12**]
MOF/CHI-ERGO/GCE	5.0–400.0	2.0–200.0	1.0–200.0	0.41	0.44	0.33	[**13**]
MWNTs-IL/GCE	0.2–35.0	0.18–35.0	NR	0.07	0.06	NR	[**17**]
ERGO/GCE	6.0–200.0	1.0–200.0	NR	0.2	0.1	NR	[**18**]
RGO-CuNPs/GCE	3.0–350.0	3.0–350.0	12.0–200.0	0.03	0.03	0.09	[**19**]
CdSe nanosheets/GCE	0.6–1500.0	0.2–300.0	NR	0.011	0.06	NR	[**27**]
Fe$_3$O$_4$/NH$_2$-CNTs/FTO	1.0–260.0	NR	NR	0.5	NR	NR	[**30**]
PANI/MnO$_2$/GCE	0.2–100.0	0.2–100.0	0.2–100.0	0.13	0.16	0.09	[**31**]
ECF-CPE	1.0–200.0	1.0–200.0	NR	0.4	0.2	NR	[**32**]
NCNT@CNF/GCE	0.1–425.0	0.08–350.0	NR	0.05	0.02	NR	[**33**]
GR/CHI/GCE	0.2–110.6	0.2–110.6	1.3–133.4	0.065	0.085	0.35	This work

Abbreviations:

LOD – limit of detection; GR – graphene; CHI – chitosan; GCE – glassy carbon electrode; Poly-*p*-ABSA – poly (p-aminobenzoic acid); NR – not reported; CNF – carbon nano-fragment; MOF – metal organic framework; ERGO – electrochemically reduced graphene oxide; MWCNTs – multiwalled carbon nanotubes; IL – ionic liquid; CNTs – carbon nanotubes; FTO – fluorine-doped tin oxide; PANI – polyaniline; ECF – electrospun carbon nanofiber; CPE – carbon paste electrode; NCNT – N-doped carbon nanotube; CNF – electrospun carbon nano-fiber.

Table 2 Effect of potentially active phenolic compounds and common metal ions on the simultaneous determination of 10 µM HQ, CC and 25 µM RC at GR/CHI hydrogel composite modified electrode

Interfering substance	**Relative error (%)**			**Interfering substance**	**Relative error (%)**		
	HQ	**CC**	**RC**		**HQ**	**CC**	**RC**
Phenol	0.36	0.62	1.62	Na^+	-0.41	-0.32	0.06
p-Acetamidophenol	-0.41	1.32	2.11	K^+	0.26	-0.08	-0.72
o-Acetamidophenol	0.99	0.12	2.61	Ca^{2+}	0.06	0.45	0.01
m-Acetamidophenol	1.21	0.33	-0.77	NH_4^+	0.19	0.09	-0.45
p-Aminophenol	-0.06	1.33	0.11	Al^{3+}	0.44	0.21	0.13
Dopamine	3.65	4.21	-0.12	Cu^{2+}	1.91	1.15	0.79
m-Nitrophenol	2.03	0.77	0.19	Mg^{2+}	-1.01	0.08	0.71
Gallic acid	-0.75	-0.19	0.06	Zn^{2+}	0.25	0.93	0.02
o-Nitrophenol	0.61	-2.21	0.13	Fe^{2+}	0.62	0.63	-0.21

Table 3. Simultaneous determination of HQ, CC and RC in different water samples using GR-CHI hydrogel composite modified electrode. (n=5)

Sample labeled	**Added**			**Found**			**Recovery (%)**		
	HQ	**CC**	**RC**	**HQ**	**CC**	**RC**	**HQ**	**CC**	**RC**
Drinking water	–	–	–	–	–	–	–	–	–
	5.0	5.0	15.0	4.92	4.96	14.86	98.4	99.2	99.1
Tap water	–	–	–	–	–	–	–	-	-
	5.0	5.0	15.0	4.96	4.97	14.95	99.2	99.4	99.7
Pond water	–	–	–	–	–	–	–	–	–
	5.0	5.0	15.0	4.78	4.92	14.61	95.6	98.4	97.4

Figure captions

Scheme 1. Schematic representation for the preparation of GR–CHI hydrogel composite.

Figure 1. SEM images of GR (A), CHI (B), GR-CHI hydrogel composite in lower (C) and higher (D) magnification.

Figure 2. FTIR spectra of GR, CHI and GR-CHI hydrogel composite.

Figure 3. EIS of GR (a), bare (b) and GR/CHI hydrogel composite (c) modified GCEs in PBS containing 5 mM $Fe(CN)_6^{3-/4-}$. Inset is the Randles equivalent circuit model.

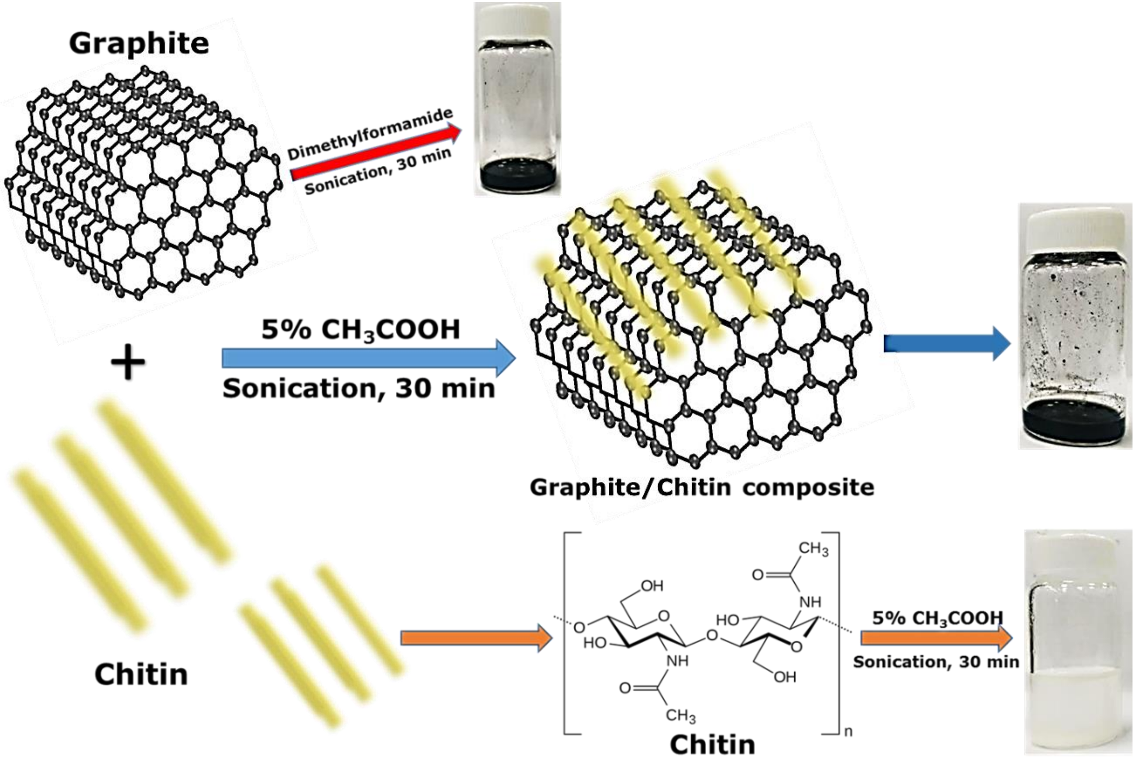
Figure 4. A) Cyclic voltammetry response of bare (a), CHI (b), GR (c) and GR-CHI hydrogel composite (d) modified electrodes in the presence of 50 µM HQ, CC and RC containing N_2 saturated PBS at a scan rate of 50 mV/s. B) At similar conditions, CV response of GR-CHI hydrogel composite modified electrode in the absence (a) and presence of 50 µM HQ, CC and RC (b). C) Cyclic voltammetry response of GR-CHI (a) and graphene-CHI hydrogel composite (b) modified electrodes in the presence of 50 µM HQ, CC and RC containing N_2 saturated PBS at a scan rate of 50 mV/s.

Figure 5. Cyclic voltammograms obtained at GR-CHI hydrogel composite modified electrode in 50 µM HQ, CC and RC containing PBS at different scan rates (20 to 200 mV/s). Inset: square root of scan rates vs. anodic and cathodic peak current of HQ and CC, and square root of scan rates vs. anodic peak current of RC (RSD = 2.6 %).

Figure 6. Cyclic voltammetry response of GR-CHI hydrogel composite modified electrode in 50 µM HQ, CC and RC containing different pH (pH 3, 5, 7 and 9) at a scan rate of 50 mV/s. Inset: pH vs. formal potential of HQ, CC and anodic peak potential of RC (RSD = 1.9 %).

Figure 7. A) DPV response of GR-CHI hydrogel composite modified electrode for the simultaneous addition of different concentration of HQ (0.2–133.4 µM), CC (0.3–133.4 µM) and

RC (1.3–133.4 µM) into the PBS. Inset is the calibration plot for current response vs. [HQ], [CC] and [RC]. B) DPV response of GR-CHI hydrogel composite modified electrode for the different concentration additions of HQ (0.2–133.4 µM) in the presence of 10 µM CC and 25 µM RC containing N_2 saturated PBS. C) At the same conditions, DPV response of GR-CHI hydrogel composite modified electrode for different concentration additions of CC (0.3–133.4 µM) in the presence of 10 µM HQ and 25 µM RC. D) At the same conditions, DPV response of GR-CHI hydrogel composite modified electrode for different concentration additions of RC (1.3–133.4 µM) in the presence of 10 µM HQ and 10 µM CC.


Graphite
Dimethylformamide
Sonication, 30 min
5% CH3COOH
Sonication, 30 min
Graphite/Chitin composite
Chitin
OH
O
HO
NH
O
CH3
HO
NH
O
CH3
OH
Chitin
n
5% CH3COOH
Sonication, 30 min

Scheme 1

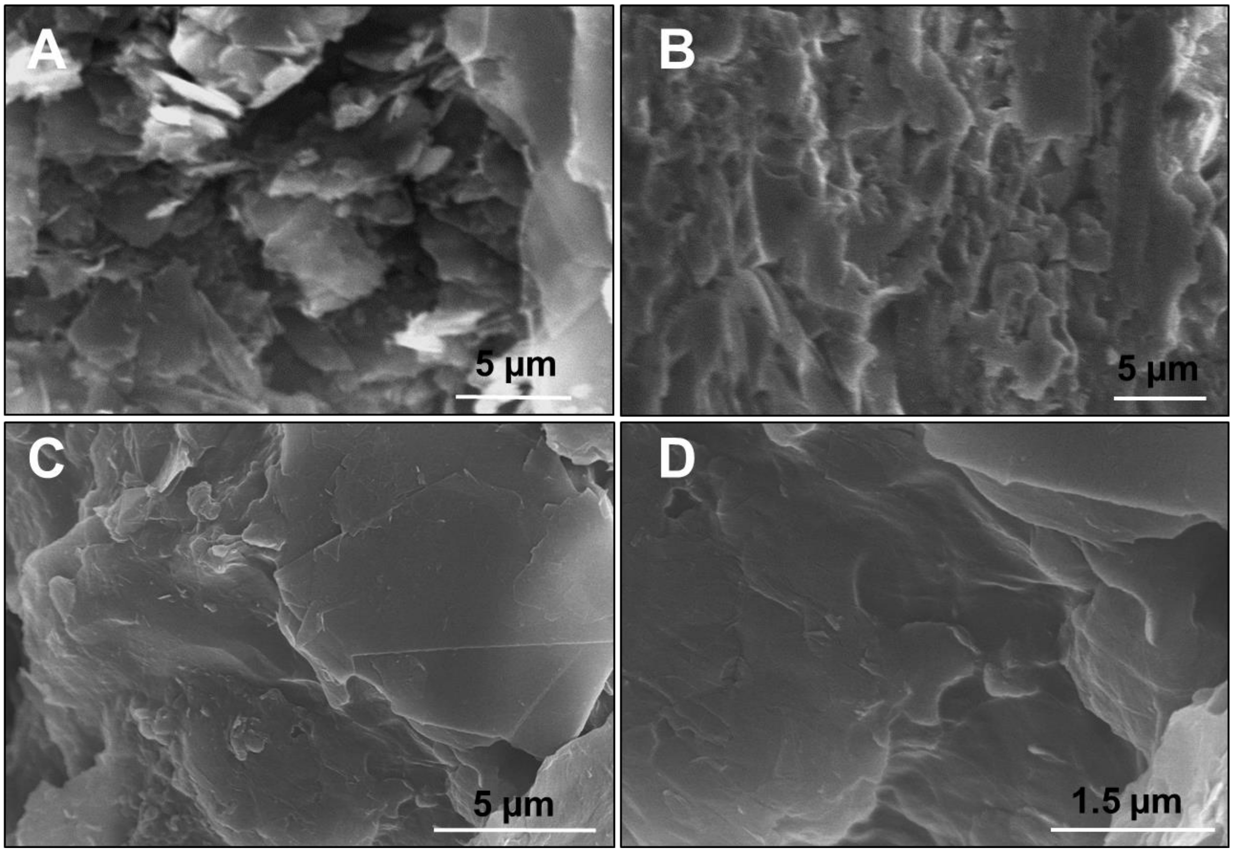


Figure 1

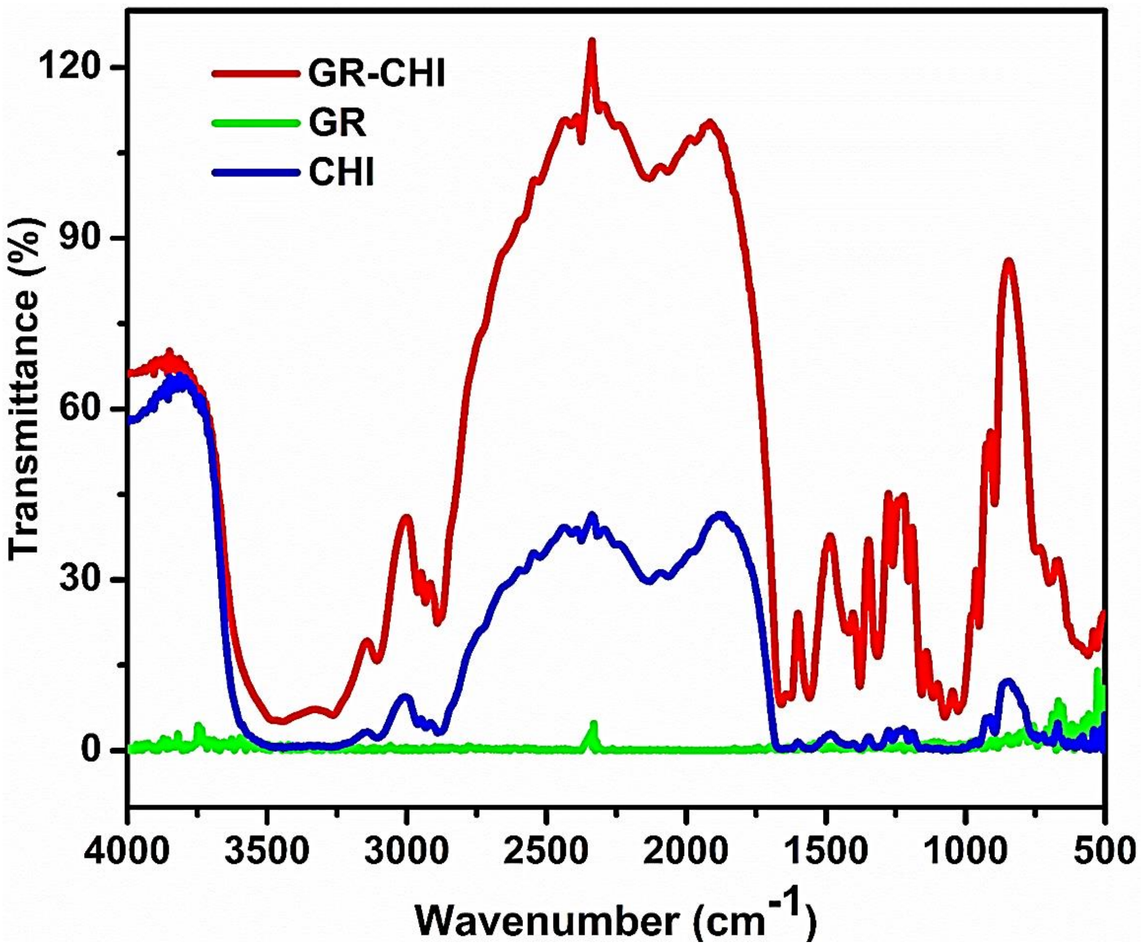

GR-CHI
GR
CHI
Transmittance (%)
120
90
60
30
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Figure 2

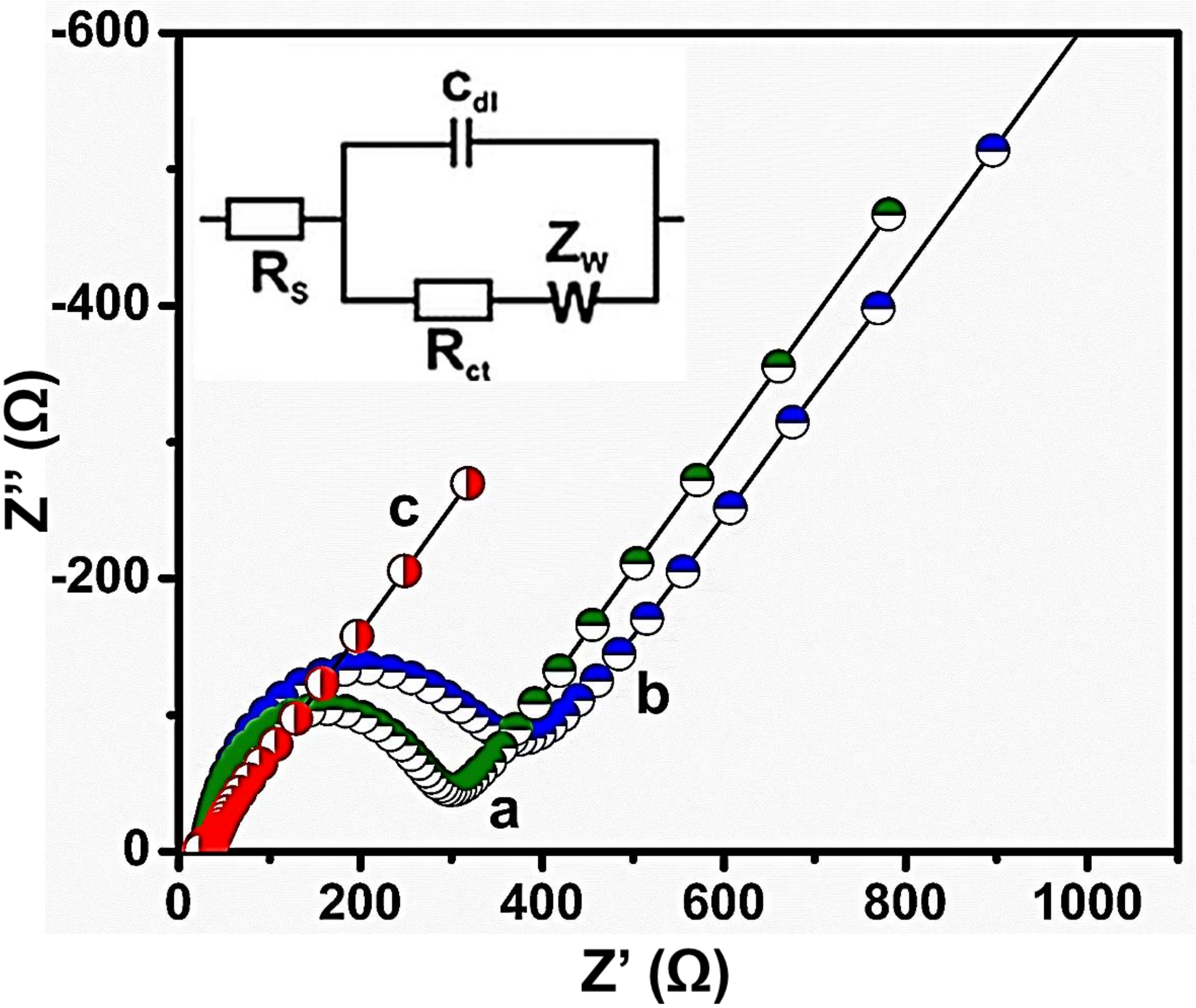
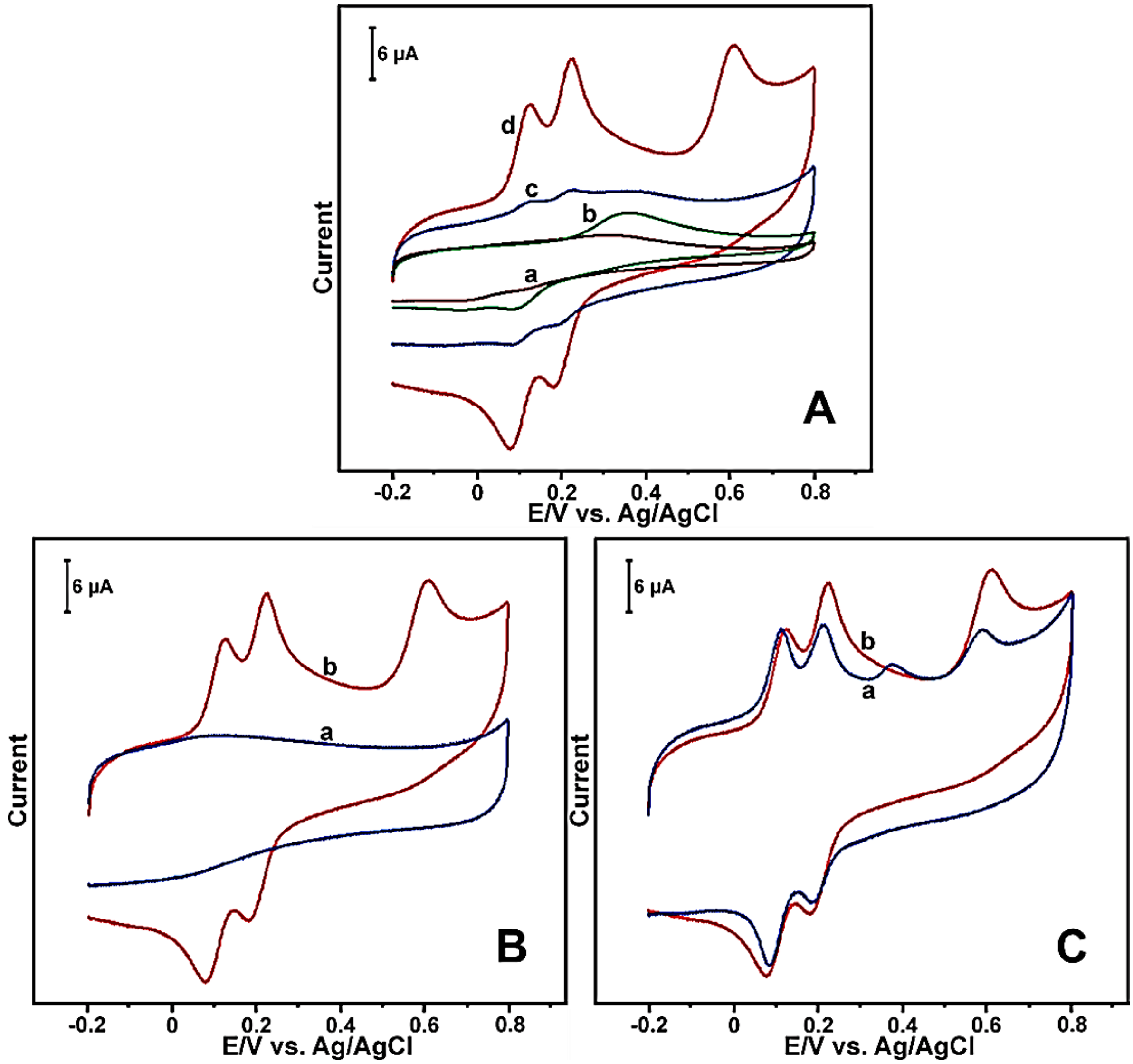


Figure 3



6 μA
d
c
b
a
Current
A
-0.2
0
0.2
0.4
0.6
0.8
E/V vs. Ag/AgCl
6 μA
b
a
Current
B
-0.2
0
0.2
0.4
0.6
0.8
E/V vs. Ag/AgCl
6 μA
b
a
Current
C
-0.2
0
0.2
0.4
0.6
0.8
E/V vs. Ag/AgCl

Figure 4

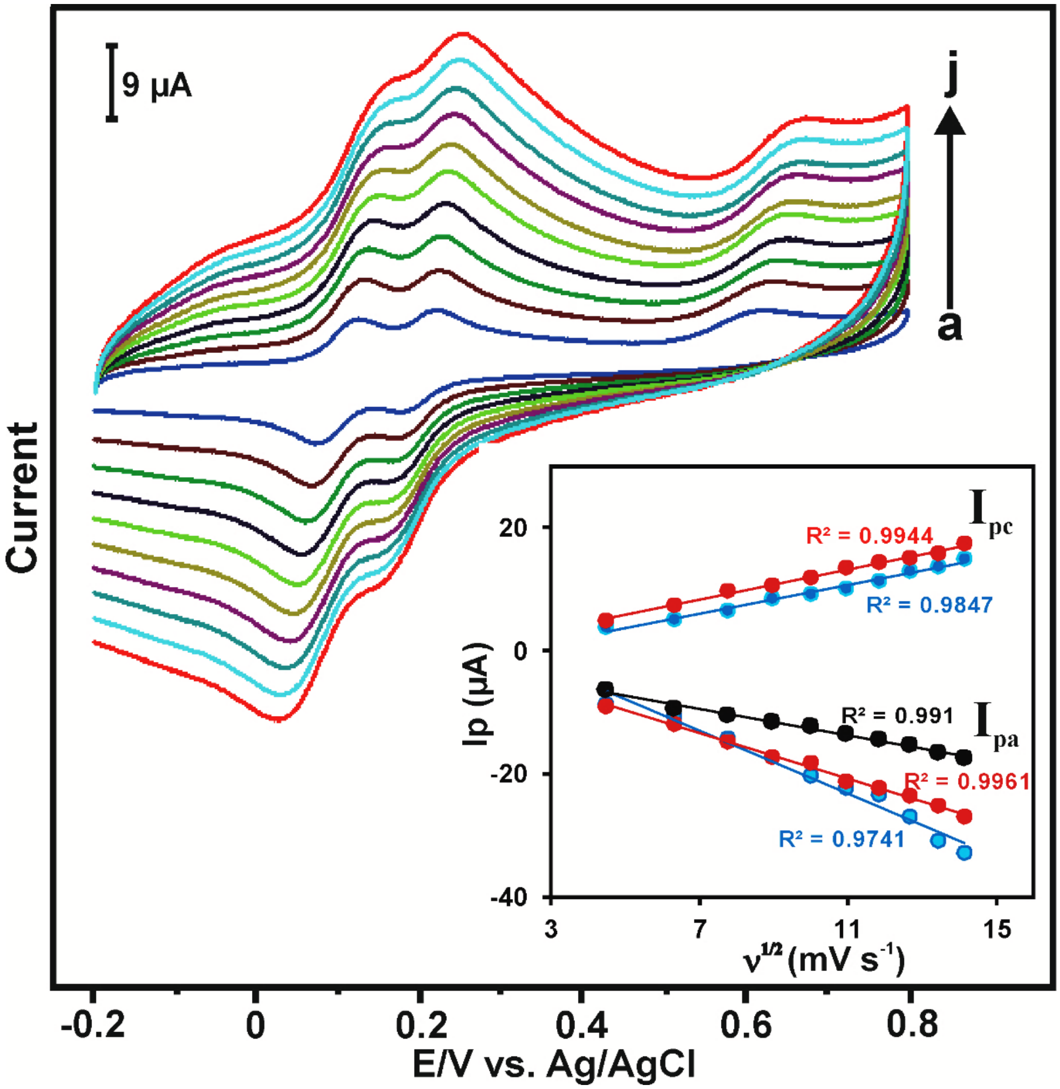
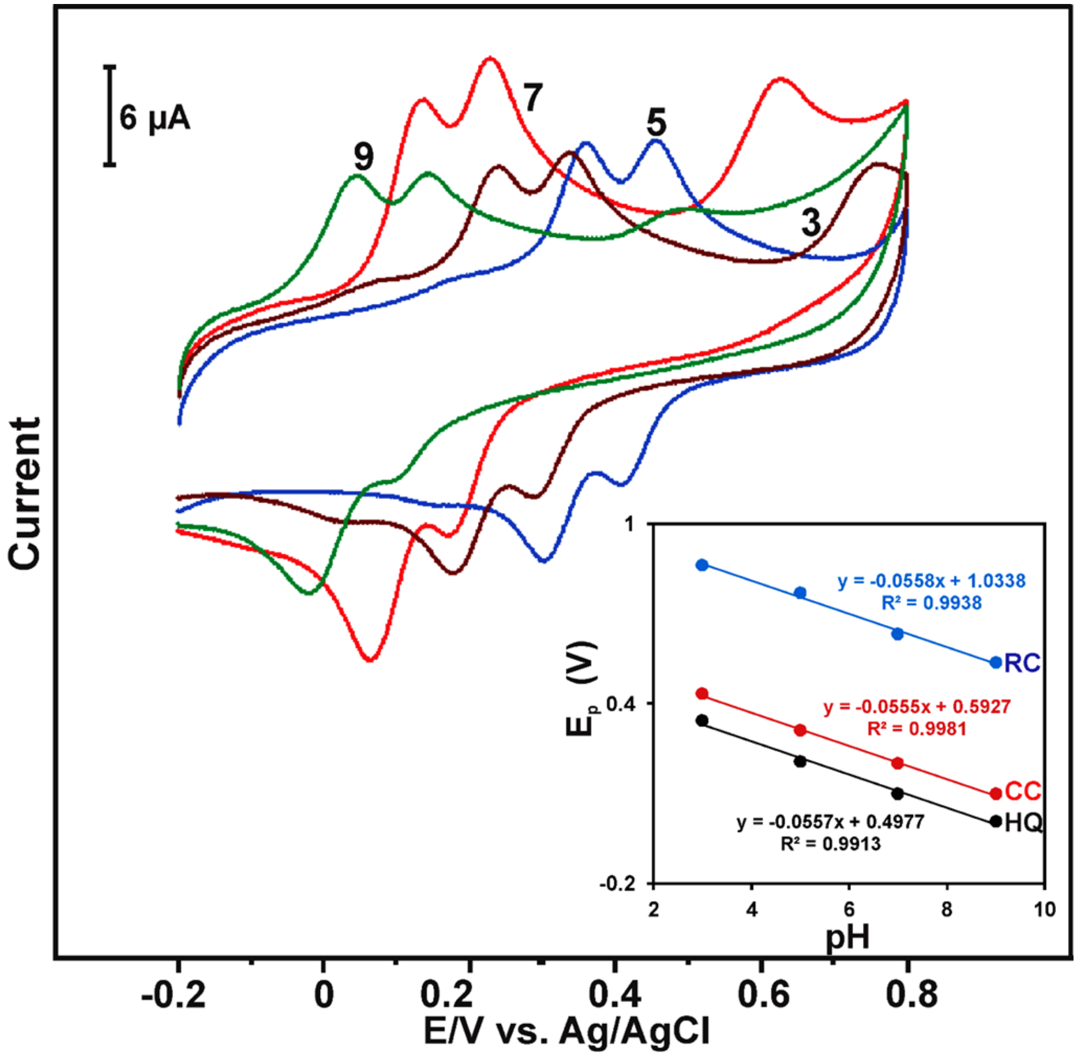
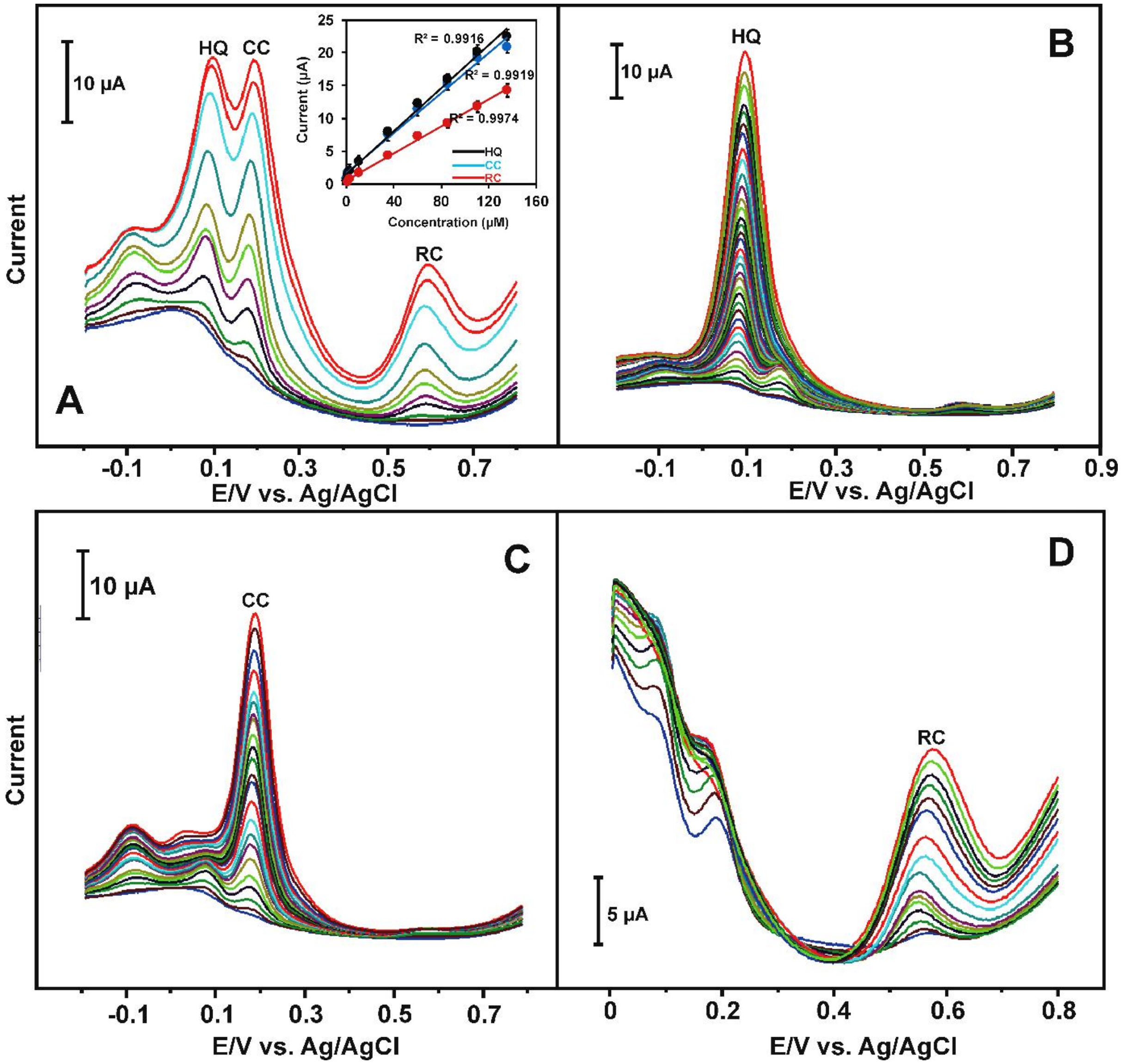

9 µA
j
a
Current
-0.2
0
0.2
0.4
0.6
0.8
E/V vs. Ag/AgCl
Ip (µA)
20
0
-20
-40
3
7
11
15
$\nu^{1/2}$ (mV s^{-1})
I_{pc}
R² = 0.9944
R² = 0.9847
I_{pa}
R² = 0.991
R² = 0.9961
R² = 0.9741

Figure 5



6 μA
9
7
5
3
Current
-0.2
0
0.2
0.4
0.6
0.8
E/V vs. Ag/AgCl
1
0.4
-0.2
E_p (V)
2
4
6
8
10
pH
y = -0.0558x + 1.0338
R² = 0.9938
RC
y = -0.0555x + 0.5927
R² = 0.9981
CC
y = -0.0557x + 0.4977
R² = 0.9913
HQ

Figure 6



A
10 μA
HQ
CC
RC
Current
-0.1
0.1
0.3
0.5
0.7
E/V vs. Ag/AgCl
R² = 0.9916
R² = 0.9919
R² = 0.9974
Current (μA)
25
20
15
10
5
0
0
40
80
120
160
Concentration (μM)
HQ
CC
RC
B
10 μA
HQ
-0.1
0.1
0.3
0.5
0.7
0.9
E/V vs. Ag/AgCl
C
10 μA
CC
Current
-0.1
0.1
0.3
0.5
0.7
E/V vs. Ag/AgCl
D
RC
5 μA
0
0.2
0.4
0.6
0.8
E/V vs. Ag/AgCl

Figure 7

Research highlights and TOC