

The selectivity and sensitivity of Gr-TiO₂ nanocomposite towards Catechol and Hydroquinone

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Abstract: A novel voltametric sensor based on Graphene-TiO₂ was developed. The graphene-TiO₂ nanocomposite was prepared by the hydrothermal treatment. It provides an efficient and facile approach to yield nanocomposite with TiO₂ nanoparticles uniformly embedded on graphene substrate. The crystallinity and crystalline size were examined by XRD and TEM. The surface morphology of the nanocomposite is examined by SEM. The crystalline size of the as prepared nanocomposite was 17nm. The electrochemical sensor shows excellent selectivity and sensitivity towards CC and HQ.

Keywords: Graphene, Hydrothermal method, Graphene-TiO₂ nano composite, Catechol, Hydroquinone.

1. Introduction

Graphene is a 2D sheet of sp² bonded carbon atoms, densely packed in a honeycomb crystal lattice structure whereby each of these layers is held together by weak Vander Waals forces [1]. The most important property of graphene is its excellent electrical conductivity. The various forms of graphene-based materials include thermally reduced graphene oxide (TRGO), chemically reduced graphene oxide (CRGO), and electrochemically reduced graphene oxide (ERGO), contains oxygen-containing functional groups and certain amounts of defects[2–4]. The rapid electron transfer takes place at the surface of edge planes and defects when compared to the basal planes for the electrochemical sensors fabricated with graphene based materials[5–7]. The presence of these structural defects in the chemically modified graphene can be exploited for electrochemical sensor applications. The presence of oxygen-containing functional groups in the graphene-based materials play a vital role in the electrochemical sensors, which makes the adsorption and preconcentration of the redox species (which is of our analytical interest) and effectively catalyse the redox reactions. In addition, the presence of these functional groups makes an effective functionalization with various biomolecules and polymers for applications[8–10]. The functionalization of these graphene based materials with specific functional groups can enable the use of these excellent materials for electrochemical sensor applications with specific analytes. The functionalized graphene materials also make fast electron transfer by pre-concentrating the target analytes at the electrode surface.

Graphene-based nanocomposites with semiconductor and metal nanoparticles have received increasing attention due to their remarkable electrocatalytic, electrochemical sensing and electrochemical energy conversion properties [11–22]. The remarkable properties of metal nanoparticles incorporated on graphene depicts high electrocatalytic activity, excellent conductivity, and selectivity which makes metal nanostructures decorated on graphene an ideal choice to be used as an active material in electrochemical sensors.

Due to its good biocompatibility and high conductivity, TiO₂ has been widely used in the fabrication of electrochemical biosensors [23–29]. In these biosensors, TiO₂ was employed as support matrix for immobilizing enzymes, which can facilitate the direct electron transfer and enhance the catalytic activity of enzymes.

Catechol (1,2-dihydrobenzene, CC) and hydroquinone (1,4-dihydrobenzene, HQ) are two significant isomers of dihydrobenzene, are widely used in the production of dyes, developer, cosmetics, photostabilizer, plasticizers, pesticides and some pharmaceuticals. These isomers are widely distributed because of their variety sources and they are hazardous to the environment, toxic to humans and very difficult to degrade in the ecological environment. CC and HQ are usually co exist with resorcinol and interferes with each other in their determination because of their similar structure and properties. Simultaneous determination of dihydroxybenzene isomers has turnout to be one of the important topics for environmental evaluation because they have similar systems and properties, and their coexistence in environmental samples.

2. Experimental

2.1. Chemicals

Graphite powder (320 mesh, spectrum pure) was purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium isopropoxide (Ti(OiPr)₄) was obtained from Sigma aldrich. Other chemicals used in this study

were of analytical grade. All solutions were prepared with double distilled water. All the prepared samples were analyzed with PXRD, SEM, Cyclic voltammetry (CV) and differential pulse voltammograms (DPVs) were recorded using CHI 604D electrochemical analyzer, in a conventional three-electrode cell. A platinum wire, Ag/AgCl and a glassy carbon electrode (GCE) modified with the composite were used as counter electrode, reference electrode and working electrode, respectively. All experiments were carried out at room temperature.

2.2. Preparation of GR/TiO₂ nanocomposite

Graphene oxide was synthesized from graphite powder by the improved Hummers method [13]. Suitable amount of graphite powder was taken in a RB flask. To this required quantity of cold concentrated mixture of H₂SO₄ and orthophosphoric acid was added. The mixture was stirred for about 2 hours at room temperature. After the stirring, add KMnO₄ very slowly under stirring kept the temperature of the mixture below 20°C. Then the reaction was heated to 50°C and kept under stirring for 6 hours. Then it was cooled and poured into ice containing 30% H₂O₂. The mixture was then centrifuged, washed and dried. Graphene was prepared by the thermal exfoliation of graphene oxide. Hydrothermal preparation of GR/TiO₂ nanocomposite was carried out by the following procedure. Titanium isopropoxide (0.2 mL) was mixed with graphene (50 mg) in a 25mL Teflon-sealed autoclave, and H₂SO₄ (1 M, 2mL) was then added. The resultant mixture was ultrasonicated for 10 min, and then the autoclave was kept in oven maintained at 170 °C for 24 h. The final product was isolated by filtration, rinsed thoroughly with deionized water and methanol, and dried in vacuum. The GR/TiO₂ nanocomposite was obtained in the form of black powder.

2.3. Preparation of Modified electrode

The as Prepared Gr-TiO₂ nanocomposite(1.5mg) was dispersed in 1 ml DMF to form a homogenous suspension. The Gr-TiO₂ modified GCE was prepared by dropping 7microL of the suspension on the surface of freshly polished GCE and dried.

3. Results and Discussion

3.1. Characterization of Graphite oxide and Reduced Graphene oxide

Figure 3.1.1 shows the XRD patterns of Graphene oxide prepared by the Modified Hummers method [13]. Figure 3.1.2 depicts the XRD pattern of Graphene prepared by the thermal exfoliation of graphene oxide.

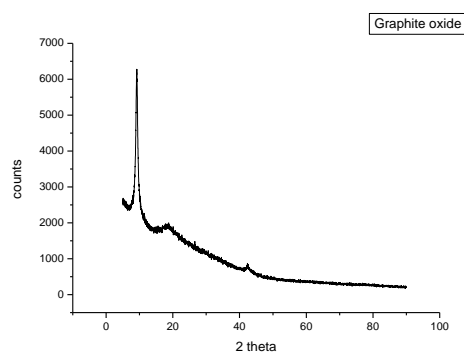


Fig 3.1.1: XRD of Graphene Oxide

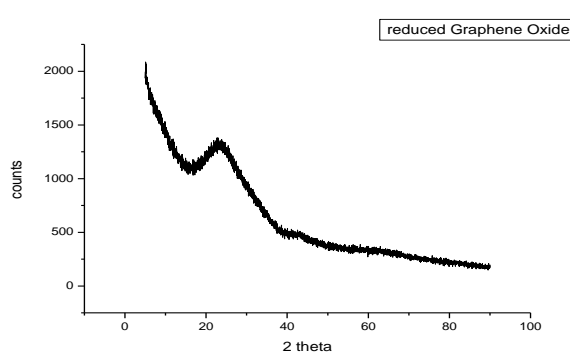
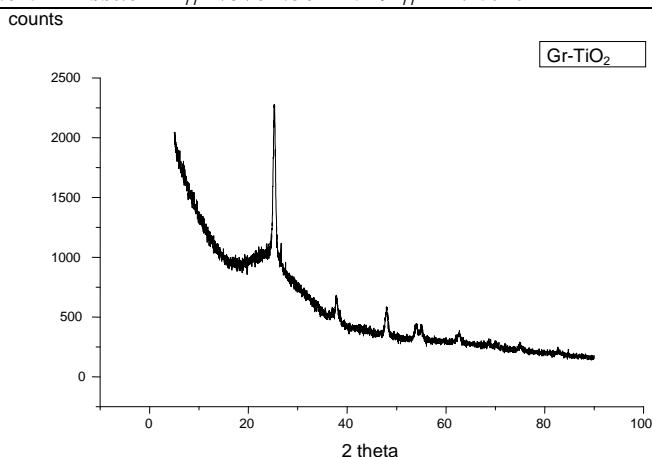


Fig 3.1.2: XRD of Graphene

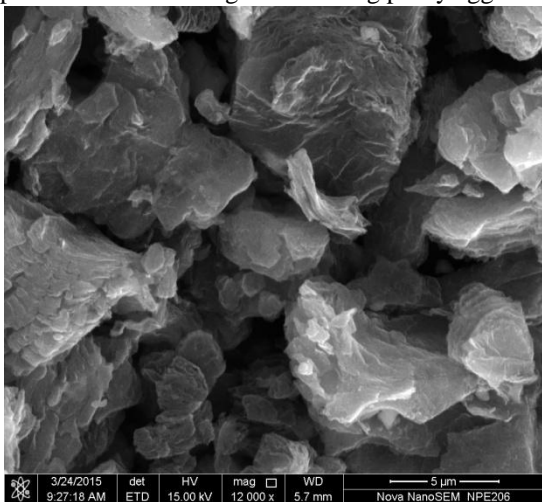
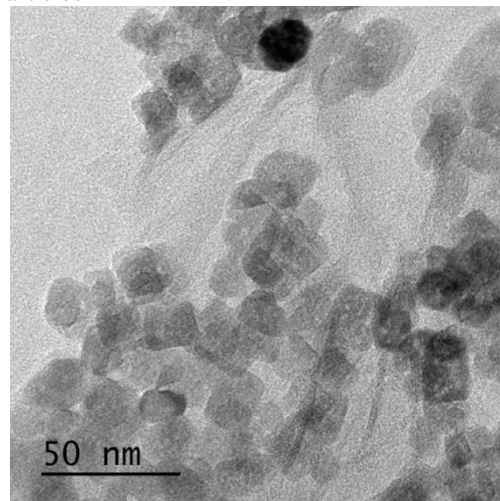
3.2. Characterization of Graphene-TiO₂ nano composite

The crystalline phase of TiO₂-graphene nanocomposite was determined by powder X-ray diffraction (XRD). As shown in Fig.3.2.1, the XRD patterns can be indexed to the anatase TiO₂ phase (JCPDS file no. 89-4921), suggesting the complete formation of anatase TiO₂ during the hydrothermal process. The high intensity and the small width at the half height of the diffraction peaks indicate the big crystallized portion of the TiO₂ particles on the surface of graphene. However, the diffraction peaks of graphene are not distinguishable in XRD patterns of the nanocomposite, which might be ascribed to their low diffraction intensity and shielding of the graphene peaks by those of TiO₂.

Fig 3.2.1: XRD of Graphene-TiO₂ nano composite

The SEM image of the TiO₂-graphene is given in Fig 3.2.2. It can be seen that TiO₂ was formed in a highly faceted morphology on the substrates of graphene with ca. 50–100nm diameter for the clusters. The structure characterization results suggest that hydrothermal reaction proceeded with efficient crystallization of TiO₂ in anatase phase and their in situ immobilization on graphene substrate.

TEM analysis revealed a homogeneous distribution of TiO₂ nano particles at the surface of grapheme shown in figure 3.2.3. From the images we can observe that graphene is composed of well dispersed TiO₂ nano particles with dark regions showing partly agglomerated nano particles

Fig 3.2.2: SEM images of Graphene-TiO₂ nano compositeFig 3.2.3: TEM images of Graphene-TiO₂ nano composite

3.3. Electrochemical response of Catechol and hydroquinone Towards Modified electrodes

The electrochemical response of CC and HQ were examined by cyclic voltammetry. Cyclic Voltammograms were recorded in 0.1M PBS (pH 7) at the Bare GCE, GR/GCE and GR-TiO₂/GCE at a scan rate of 100mV/s. The electrochemical response of CC and HQ in Gr-TiO₂/GCE and with that of bare GCE is shown in the figures 5.2A and B. 0.375 mM CC and HQ in 0.1M PBS at pH 7 were used for the electrochemical responses. A well defined oxidation and reduction peak is observed for CC and HQ on Gr-TiO₂/GCE compared to those of bare GCE.

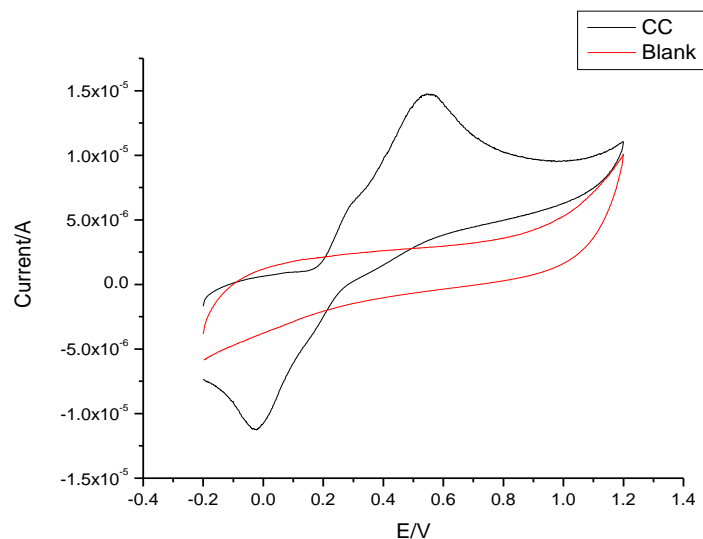


Fig. 3.3.1. Cyclic Voltammograms of Catechol 0.375 mM CC in 0.1M PBS at pH 7

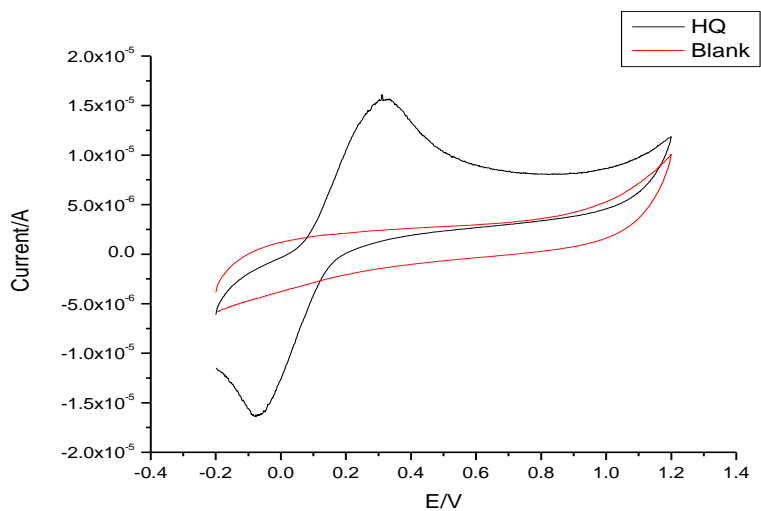


Fig. 3.3.2. Cyclic Voltammograms of Hydroquinone 0.375 mM CC in 0.1M PBS at pH 7

3.4 Electrochemical response of Catechol -- hydroquinone mixture Towards Modified electrodes

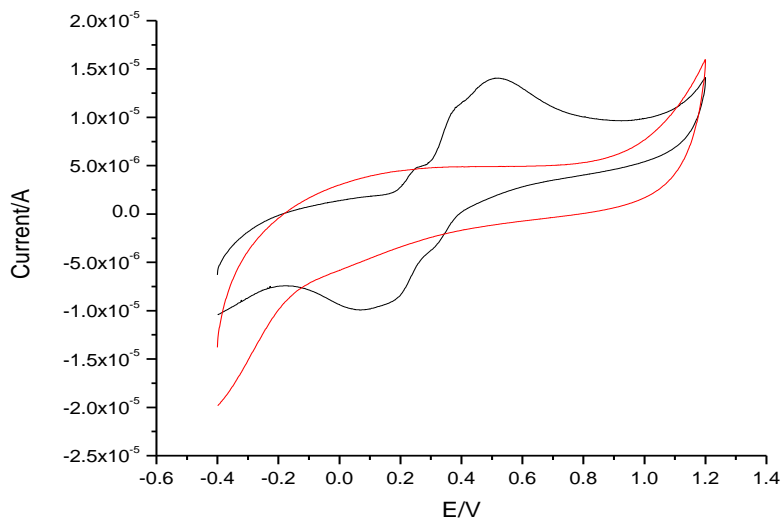


Fig. 3.4.1. Cyclic Voltammograms of CC and HQ mixture (0.3 mM) in 0.1M PBS at pH 7

This figure 3.4.1 shows the electrochemical response of the simultaneous determination of the mixture of CC and HQ, both at 0.3mM concentration in 0.1M PBS (pH 7) on bare GCE and Gr-TiO₂/GCE. Compared to GCE two distinguishable peaks are observed for CC and HQ on Gr-TiO₂/GCE.

3.5 The influence of pH on the electrolytic response of Catechol – hydroquinone mixture

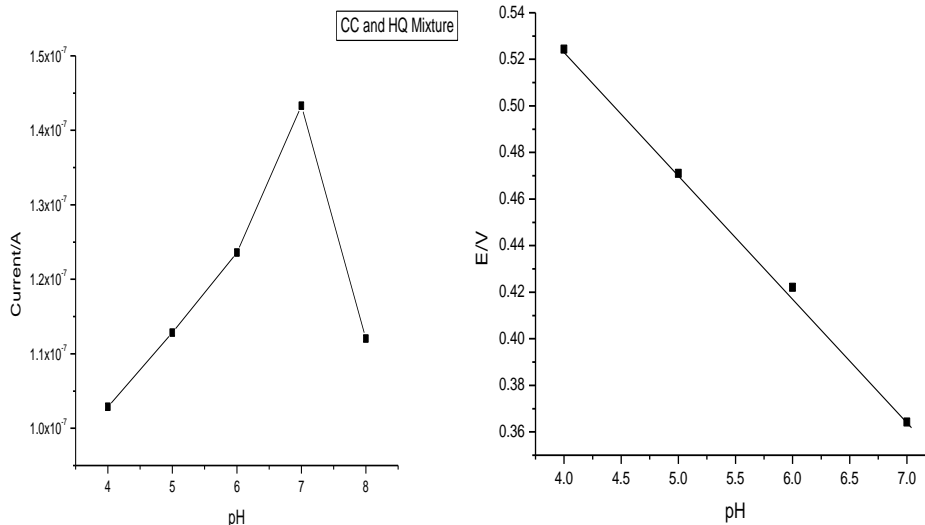


Fig 3.5.1 : Cyclic Voltammograms of CC and HQ mixture at different pH

Figure 3.5.1 depicts the effect of pH on the current response of CC and HQ mixture on the GR-TiO₂/GCE electrode. The oxidation peak current gradually increased with increase of pH values from 4 to 7. Therefore considering the sensitivity the physiological pH 7 was taken for the subsequent experiments.

3.6 Effect of scan rate on the detection of catechol – hydroquinone mixture at modified electrode

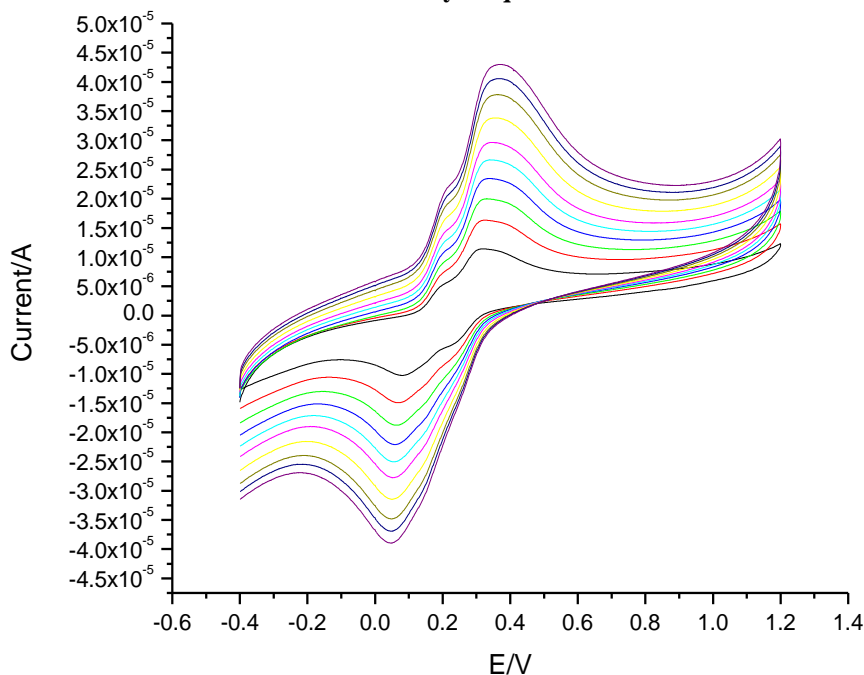


Fig. 3.6.1 Variation of peak current of CC and HQ mixture with different Scan rates from 10mV/s to 1000mV/s

To further investigate the electrochemical kinetics at the composite electrode, CV's were recorded at various scan rates. Both anodic and cathodic peak currents increase with scan rate. The voltametric peak currents increases with increase of square root of scan rate, ie peak current proportional to $v^{1/2}$ indicates that the electron transfer at the electrode is controlled by diffusion which is ideal condition for a qualitative analysis and

peak appears begins to increase with increase in scan rate indicating a quazi reversible reaction. Figure 3.6.1 shows the CV curves with scan rates of 20, 20, 60, 80, 100, 120, 150, 180, 200 and 220 mV/s resp. The oxidation peak current increased gradually with the scan rate.

3.7 Simultaneous detection of Catechol and Hydroquinone by using Dpv

3.7.1 Electrochemical determination of CC and HQ mixture at different concentrations

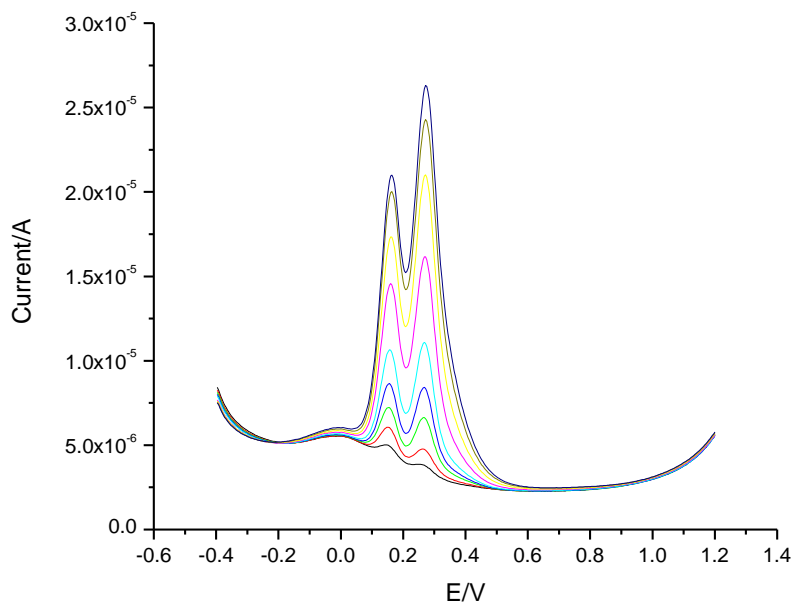


Fig. 3.7.1A: DPV of CC and HQ 5, 10, 20, 30, 50, 100, 150, 200, 250 μM concentrations at 50mVs

Differential pulse voltammetry is used to investigate the simultaneous and quantitative determination CC and HQ mixture on Gr-TiO₂/GCE because of its high sensitivity towards current and its good resolution. 5, 10, 20, 30, 50, 100, 150, 200 and 250 μM CC and HQ concentrations at 50mVs was carried out in DPV. The peak currents increased linearly with increase in concentrations of the mixture which is shown in the figure 3.7.1.

3.7.2 Electrochemical response of CC with varying concentrations by keeping constant HQ concentration

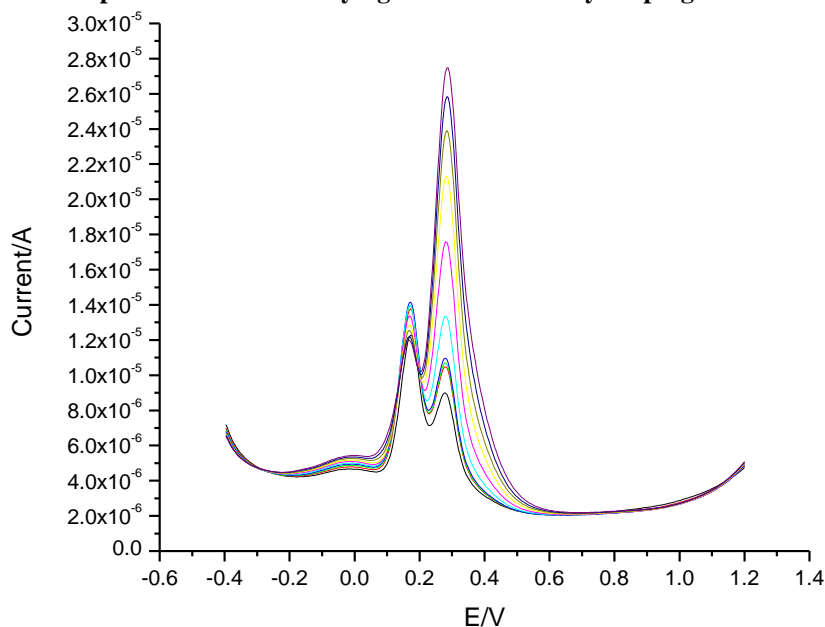


Fig. 3.7.2 DPV of HQ (50 μM) and CC at 5, 10, 15, 25, 50, 100, 150, 200, 250 and 300 μM concentrations

The individual response of CC and HQ in their mixtures is carried out on Gr-TiO₂/GCE by keeping the concentration of one species kept constant. In this CC at 5, 10, 15, 25, 50, 100, 150, 200 and 250 μM concentrations were used in DPV on Gr-TiO₂/GCE by keeping the concentration of HQ at 50 μM . The peaks of CC are increasing linearly with the increase in concentration, which is shown in the figure 3.7.2

3.7.3 Electrochemical response of HQ with varying concentrations by keeping constant CC concentration

In this 5, 10, 15, 25, 50, 75, 100, 125 and 150 μM HQ concentrations were used to carry out DPV on Gr-TiO₂/GCE by keeping the CC concentration at 10 μM . The HQ peak current increases linearly with the increase in concentration of HQ.

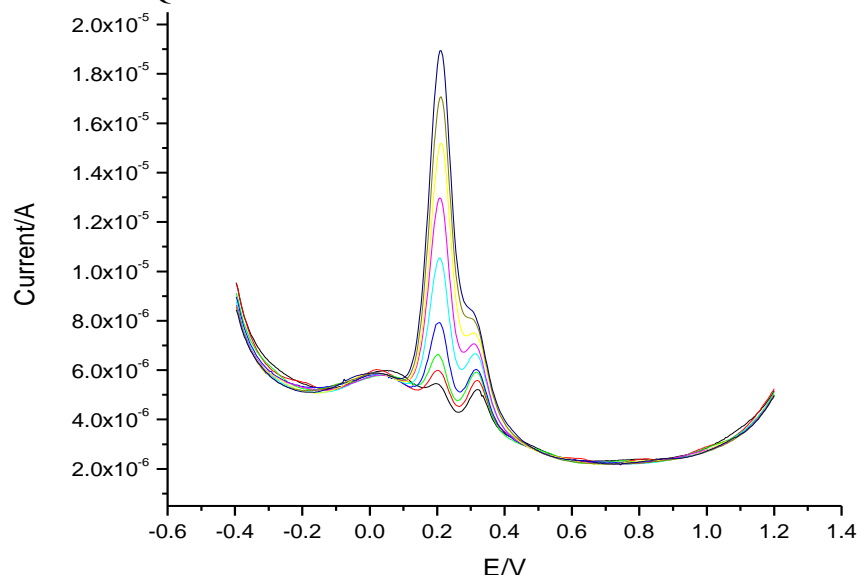


Fig.3.7.3 DPV of CC (10 μM), HQ 5, 10, 15, 25, 50, 75, 100, 125, 150 μM concentrations

4. Conclusions

The electrochemical sensor shows excellent selectivity and sensitivity towards CC and HQ. The significant increase of peak currents was obtained at the Gr-TiO₂/GCE which clearly indicates that Gr-TiO₂ could be used as an efficient promoter to enhance the kinetics of the electrochemical process of CC and HQ. The Gr-TiO₂ composite shows excellent selectivity and no interference between CC and HQ. We successfully synthesised the graphene-TiO₂ nanocomposite by the hydrothermal treatment. The crystallinity and crystalline size were examined by XRD and TEM. The surface morphology of the nanocomposite is examined by SEM. The crystalline size of the as prepared nanocomposite was 17nm.

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