Voltammetric determination of Sudan I in food samples based on platinum nanoparticles decorated on graphene-β-cyclodextrin modified electrode

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Abstract

In the present work, we report a sensitive and low level electrochemical detection of Sudan I in food samples using platinum nanoparticles (PtNPs) decorated graphene-β-cyclodextrin (graphene/β-CD) modified electrode for the first time. Cyclic voltammetry was used to evaluate the electrochemical behavior of different modified electrodes towards Sudan I. Cyclic voltammetry results reveal that graphene/β-CD/PtNPs composite modified electrode has high electrocatalytic activity towards Sudan I than other modified electrodes. Under optimum conditions, the graphene/β-CD/PtNPs composite modified electrode detects the Sudan I in the linear response ranging from 0.005 to 66.68 µM with a lower limit of detection of 1.6 nM. As a proof of concept, the graphene/β-CD/PtNPs composite modified was used for the determination of Sudan I in chili powder, chili sauce, tomato sauce and ketchup and found satisfactory recovery of Sudan I. Therefore, the fabricated sensor can be used for the detection of Sudan I in adulterated food samples.

Keywords: Sudan I; Graphene; β-cyclodextrin; Platinum nanoparticles; Modified electrode; Food analysis

1. Introduction

The accurate and sensitive detection of contaminants in food samples has received much attention in the analytical and food chemistry. In particular, Sudan I (1-Phenylazo-2-naphthol) is a synthetic azo-colorant dye, has commonly been found in the adulterated chili powder, curry products and sauces [1, 2]. Sudan I has been widely used for coloring of various foodstuffs, however it has been strictly banned by many countries including European Union due to its high carcinogenic nature as reported by the International Agency for Research on Cancer [3, 4]. Regrettably, the use of Sudan I is inevitable in foodstuffs due to its intense color and low cost [4]. Furthermore, Sudan I still has been widely used in food stuffs by some countries. Hence, a sensitive and low level detection of Sudan I in foodstuffs is of great interest. Till date, different analytical methods have been reported for accurate determination of Sudan I, such as high performance liquid chromatography [5], high performance liquid chromatography combined mass spectrometry [6], mass spectrometry [7] and electrochemical methods [8]. Notwithstanding, the electrochemical methods are found simple and inexpensive, has provide high sensitivity, selectivity and reproducibility than chromatographic and capillary electrophoresis methods [9]. Over the past decades, different chemically modified electrodes have been reported for the electrochemical determination of Sudan I, such as carbon nanomaterials [9–12], metal nanoparticles [4], metal oxides [13], ionic liquids [14] and metal porphyrins [15]. However, the carbon nanomaterials such as carbon nanotubes and graphene-based composites have been widely used for the sensitive determination of Sudan I due their high surface area and extreme chemical stability. Compared with other carbon nanoforms, graphene has been widely applied for the electrode modifications due to its large specific surface area and excellent conductivity [16, 17]. However, graphene has poor dispersion ability in aqueous solutions due to the strong π-π stacking between individual

graphene sheets, hence the surfactants or supramolecular adducts have been used to enhance the dispersion ability of carbon nanomaterials in aqueous solutions [**18, 19**]. Recently, we have dispersed the graphene in β-cyclodextrin (β-CD) aqueous solution via strong guest-host supramolecular chemistry, and the resulting graphene/β-CD composite has showed excellent electrochemical activity than pristine graphene [**20**]. In addition, the decoration of metal nanoparticles on the graphene/β-CD composite could further enhanced the surface area and active sites of the graphene/β-CD composite. Compared with other metal and metal alloy nanoparticles, platinum nanoparticles (PtNPs) has large surface area and high stability [**21, 22**]. Hence, in the present study, for the first time we have decorated PtNPs on graphene/β-CD composite and used as a sensitive probe for low-level electrochemical detection of Sudan I. To the best of knowledge, either graphene/β-CD or graphene/β-CD/PtNPs composite modified electrodes have not been used yet for electrochemical detection of Sudan I and its analogous. In addition, the graphene/β-CD/PtNPs nanocomposite can detects the Sudan I in sub micromolar range, and the observed limit of detection was much lower than previously reported modified electrodes for the determination of Sudan I (see Table 1).

In the present study, we report a sensitive and low-level electrochemical detection of Sudan I using graphene/β-CD/PtNPs nanocomposite. The fabricated nanocomposite modified electrode not only increase the analytical sensitivity of Sudan I, and also enhanced the linear response range of the sensor. The sensor also applied for the determination of Sudan I in food samples and the results are discussed in detail.

2. Experimental

2.1. Material

Sudan I and potassium hexachloroplatinate (IV) (≥99.9% trace metals basis) were purchased from Sigma Aldrich and used as received. Graphene 8 nm nanoflakes (product number UR-GRAPHENE) was purchased from UniRegion Bio-Tech, Taiwan. The supporting electrolyte pH 7.0 was prepared using 0.1 M Na_2PO_4 and NaH_2PO_4 in doubly distilled water and the pH was adjusted using 0.1 M H_2SO_4 or 0.1 M NaOH. All other chemicals used in this work were of analytical grade and used without any further purifications. Food samples such as Red chili powder, chili sauce and tomato sauce were purchased from local store from Taipei, Taiwan.

2.2. Methods

Cyclic voltammetry and differential voltammetry (DPV) experiments were performed using computerized CHI750A electrochemical work station from CH instruments. A conventional three-electrode system consisting of a modified glassy carbon electrode (GCE) as a working electrode, platinum wire and Ag/AgCl electrode as a counter and reference electrodes, respectively. Scanning electron microscopy (SEM) images of the as-prepared materials were taken using Hitachi S-3000H SEM. Elemental analysis (EDS) of the composite modified electrode was performed using Hitachi S-3000H SEM attached HORIBA EMAX X-ACT analyzer. Fourier transform infrared spectroscopy (FTIR) studies were acquired using JASCO FT/IR-6600 FTIR spectrometer.

2.3. Fabrication of graphene/β-CD/PtNPs nanocomposite modified electrode

The graphene/β-CD composite was prepared by our previous reported method [**20**]. Briefly, the β-CD aqueous solution was prepared by dispersing of β-CD (1 mg mL^{-1}) into the distilled water by ultra-sonication for 10 min. Then, 10 mg of graphene was added into the as-prepared β-CD solution and sonicated for 30 min at room temperature. The resulting graphene/β-CD composite was centrifuged and re-dispersed (1 mg mL^{-1}) in water by sonication for 15 min. Then,

about 8 µL of graphene/β-CD composite was drop coated on the pre-cleaned GCE and dried at room temperature. The graphene/β-CD modified electrode was transformed into the electrochemical cell containing 0.5 mM K_2PtCl_6 solution with 1 mM KCl and applied a constant applied potential of −1.4 V for 90 s [23]. The schematic representation for the fabrication of graphene/β-CD/PtNPs composite is shown in **Fig. 1**. The resulting graphene/β-CD/PtNPs composite modified electrode was gently rinsed with water and dried at room temperature. The PtNPs modified electrode was independently prepared by similar method without graphene/β-CD composite. The graphene modified electrode was prepared by drop coating of 8 µL of graphene dispersion on pre-cleaned GCE, and was prepared by dispersing of graphene (1 mg mL^{-1}) in dimethylformamide by ultra-sonication for 30 min. All modified electrodes were stored under dry conditions unless otherwise stated.

<**Please inset Figure 1 here**>

3. Results and discussion

3.1. SEM, EDS and FTIR

The surface morphology of as-prepared materials was characterized by SEM and the results are shown in **Fig. 2A-C**. The SEM image of PtNPs (**Fig. 2A**) shows that the uniform electrodeposition of spherical PtNPs with an average diameter of 70 ± 5 nm on the electrode surface. The SEM image of graphene/β-CD (**Fig. 2B**) shows typical crumbled morphology, where the graphene nanoflakes were entrapped by β-CD, which is due to the strong interaction between the polar hydroxyl groups of β-CD with the edge planes of graphene. The observed morphology of graphene/β-CD composite is similar to our previous reports [**20**]. On the other hand, the SEM image of graphene/β-CD/PtNPs composite (**Fig. 2C**) shows that the spherical PtNPs are clearly visible and decorated uniformly on graphene/β-CD composite. In addition, the observed diameter

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of electrodeposited PtNPs on graphene/β-CD/PtNPs composite is more consistent with the diameter of PtNPs (**Fig. 2A**). The presence of graphene and PtNPs was confirmed by EDS and the corresponding results are shown in **Fig. 2D**. It can be seen that the graphene/β-CD/PtNPs composite shows the distinct signals for C and Pt which are due the presence of graphene and PtNPs. The SEM and EDS results confirmed the presence of PtNPs on graphene/β-CD/PtNPs composite.

<**Please inset Figure 2 here**>

FTIR spectroscopy is further used for the characterization of graphene, β-CD and graphene/β-CD composite, since it is widely used to confirm the functional groups and study the interaction between the compounds. **Fig. 3** shows the FTIR spectra of graphene (black profile), β-CD (blue profile) and graphene/β-CD composite (red profile). The FTIR spectrum of graphene did not show any obvious bands in the fingerprint region. While, the graphene/β-CD composite shows three distinct bands were observed at 3382, 2965 and 1015 cm^{-1}, which are corresponding to the O–H (from water), C–H stretching vibration and C–O–C groups of β-CD on the composite [24]. The similar characteristic bands were observed for the FTIR spectrum of β-CD. The result confirms that graphene is firmly attached on the β-CD, which is due to the strong interactions between the polar hydroxyl groups of β-CD and graphene [20].

<**Please inset Figure 3 here**>

3.2. Optimizations

The optimization of the modified electrode is more important and can be directly affect the sensitivity of the electrode. Hence, we have evaluated the optimization of effect of loading of graphene/β-CD composite and effect of deposition time of PtNPs using cyclic voltammetry for the detection of 10 μM Sudan I. The optimization results are shown in **Fig. 4A and 4B**. It

can be seen that an optimum sensitivity for Sudan I was found for 8 µL drop coated graphene/β-CD composite and 90 s electrodeposited PtNPs on the graphene/β-CD/PtNPs composite. Hence, 8 µL drop coated graphene/β-CD composite and 90 s electrodeposited PtNPs was used as an optimum.

<Please inset Figure 4 here>

3.3. Electrochemical behavior of Sudan I

To investigate the electrochemical behavior of Sudan I, cyclic voltammetry was used for detection of 10 µM Sudan I using different modified electrodes. **Fig. 4C** shows typical cyclic voltammetry response of graphene (a), PtNPs (b), graphene/β-CD (c) and graphene/β-CD/PtNPs (d) modified electrodes in 10 µM Sudan I containing pH 7 at a scan rate of 50 mV/s. It can be seen that graphene and PtNPs modified electrodes show a weak oxidation peak at 0.778 and 0.678 V for Sudan I. This is due to the irreversible electro-oxidation of –OH group in Sudan I, as reported previously [25]. The result indicates that graphene and PtNPs has similar electrochemical oxidation ability towards Sudan I. On the other hand, graphene/β-CD composite modified electrode shows an enhanced oxidation peak current response at 0.672 V for the presence of Sudan I. The enhancement effect of oxidation peak current of Sudan I is due to the combined unique properties of graphene and β-CD. However, graphene/β-CD composite modified electrode did not show the obvious redox couple for Sudan I, which indicates the irreversible electrochemical behavior of Sudan I. The graphene/β-CD/PtNPs modified electrode shows a well-defined redox couple for Sudan I. The anodic and cathodic peaks were appeared at 0.674 and 0.636 V with the peak-to-peak separation of 38 mV. The decoration of Pt nanoparticles on the graphene/β-CD composite provides a more active sites for the adsorption of Sudan I and effectively accelerate the electron transfer between the electrode surface and Sudan I. This could

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be reason for low peak-to-peak separation of Sudan I than the expected standard redox value of 59 mV. Since, the electro-oxidation of Sudan I is totally irreversible at graphene/β-CD/PtNPs modified electrode. The result confirms that graphene/β-CD/PtNPs modified electrode has enhanced electrochemical behavior towards Sudan I than other modified electrodes. In addition, the oxidation peak current response of Sudan I at graphene/β-CD/PtNPs modified electrode is 3 folds higher than those observed at other modified electrodes, which is due to combined unique properties of graphene/β-CD and PtNPs. **Fig. 4D** shows that the graphene/β-CD/PtNPs modified electrode did not show any obvious response in the absence (curve a) of Sudan I. While, a well-defined redox couple was observed in the presence (b) of 10 µM Sudan I. The result further indicates that the graphene/β-CD/PtNPs composite is electrochemically inactive in pH 7. The plausible electrochemical mechanism for the redox behavior of Sudan I at graphene/β-CD/PtNPs modified electrode is shown in **Fig. 5**. The high surface area of graphene and more active sites PtNPs could provide more adsorption sites for the interaction of Sudan I on the composite electrode, thus result into the enhanced sensitivity and well-defined redox behavior of Sudan I. Hence, graphene/β-CD/PtNPs modified electrode is more suitable for the sensitive quantification of Sudan I than other modified electrodes.

<Please inset Figure 5 here>

3.4. Effect of scan rate and pH

Fig. 6A shows the effect of scan rate on the cyclic voltammetric response of graphene/β-CD/PtNPs modified electrode for detection of 10 µM Sudan I in pH 7. It can be seen that the anodic and cathodic peak currents of Sudan I increases with increasing the scan rate from 10 to 200 mV/s. As shown in **Fig. 6B**, the anodic and cathodic peak current of Sudan I had a linear dependence with the square root of scan rates with the correlation coefficient of 0.9965 and

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0.9915. The result suggests that the electrochemical redox behavior Sudan I is a typical diffusion controlled electrochemical process [25]. The result also validates that the Sudan I first adsorbed and then diffused on the composite electrode surface. The obtained results are in good agreement with the previous literature [25]. In addition, the number of transferred electrons (n) in the oxidation of Sudan I was obtained from the Bard and Faulkner equation, as $\alpha n = 47.7/(E_p-E_{p/2})$. Where α = electron transfer coefficient and $(E_p-E_p)_{/2}$ = the peak potential of $E_{pa}-E_{pc}$ (46.6 mV) in cyclic voltammogram of Fig. 6A at a scan rate of 50 mV/s. The αn was calculated as 1.023, in which the αn is assumed to be 0.5 for an irreversible electrochemical process. The n in the oxidation of Sudan I was calculated as 2.046, which is equal to two electron and proton transferred electrochemical reaction in the oxidation of Sudan I at GR/β-CD/PtNPs modified electrode. We have also studied the effect of pH on the electrochemical oxidation of 10 µM Sudan I by cyclic voltammetry. The obtained results are shown in **Fig. 6C**. It can be seen that a maximum sensitivity for Sudan I was appeared at pH 7 than other pH. This is may be due to the high electrocatalytic activity of the composite in pH 7 than other pH. Hence, pH 7 was used as an optimum for further studies.

<Please inset Figure 6 here>

3.5. Determination of Sudan I

It is well-known that DPV has high sensitivity and better resolution than other voltammetric methods [26], hence DPV was used for the determination of Sudan I. **Fig. 7** displays the DPV response of graphene/β-CD/PtNPs modified electrode for different concentration (0.005–73.688 µM) additions of Sudan I into the pH 7. Under the optimized conditions, the DPV response of Sudan I is linearly proportional to the concentration in the ranging from 0.005 to 68.68 µM (**Fig. 7 inset**). The linear regression equation for DPV peak current response vs. [Sudan I] was

expressed as I_{pa} (μA) = 0.4563C (μM) + 1.2935 with the correlation coefficient (R^2) of 0.9911. The detection limit (LOD) was estimated as 1.6 nM based on S/N=3. The sensitivity was estimated as 2.82 μAμM^{-1} cm^{-2} and was calculated from the slope/electrochemically active surface area (ESCA) of the modified electrode. The ESCA of the graphene/β-CD and graphene/β-CD/PtNPs modified electrodes were 0.126 and 0.162 cm^2 and were calculated from the cyclic voltammetric response of graphene/β-CD and graphene/β-CD/PtNPs modified electrodes in 1 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl using Randles–Sevcik equation [26].

<**Please inset Figure 7 here**>

<**Please inset Table 1 here**>

To evaluate the superiority and advancement of the sensor, we have made the comparison table for the analytical performance of our graphene/β-CD/PtNPs modified electrode with previously reported composite modified electrodes for the determination of Sudan I and the comparison results are shown in **Table 1**. The comparative results clearly reveal that the LOD (1.6 nM) of our sensor is much lower than previously reported graphene and carbon nanotubes based composite modified electrodes. The sensitivity (2.82 μAμM^{-1} cm^{-2}) of the sensor is comparable with those reported graphene and carbon nanotubes composite modified electrodes [**10, 12, 13, 25, 27–30**]. The result clearly indicates the superiority of the graphene/β-CD/PtNPs modified electrode for determination of Sudan I.

3.6. Real samples determination

The graphene/β-CD/PtNPs composite modified electrode is further used for the determination of Sudan I in chili powder, chili sauce, tomato sauce and ketchup samples. All real samples were used without any further pretreatment (only dilutions made). The chili powder, chili sauce, tomato sauce and ketchup stock solutions were prepared using pH 7. The real samples were

tested and are Sudan I free, then a known concentration of Sudan I was added into the samples and was determined by DPV. The experimental conditions are similar as of in **Fig. 7**. The standard addition method was used for the determination of Sudan I in real samples. The optimized conditions were used for the determination of Sudan I in real samples and the obtained recoveries are summarized in **Table 2**. It can be seen that graphene/β-CD/PtNPs composite modified electrode can able to detect the Sudan I with the average recovery of 98.5, 98.2, 97.2 and 97.7 % in chili powder, chili sauce, tomato sauce and ketchup samples. The result indicates that the as-prepared graphene/β-CD/PtNPs composite modified electrode has appropriate recovery towards the determination of Sudan I in food samples. Usually much natural pigments are present in chili powder, including beta-carotene, cryptoxanthin and capsanthin. However, the recovery of Sudan I was not affected by these compounds using graphene/β-CD/PtNPs composite, which indicates the high selectivity of the proposed method for the determination of Sudan I.

<**Please inset Figure 7 here**>

<**Please inset Table 2 here**>

The repeatability and reproducibility of the graphene/β-CD/PtNPs modified electrode for the detection of Sudan I was evaluated by CV and the experimental conditions are similar to those in **Fig. 4C**. The relative standard deviation (RSD) about 3.1 % was found for a single graphene/β-CD/PtNPs modified electrode for 10 successive measurements to the detection of 10 μM Sudan I. Meanwhile, 8 independently prepared graphene/β-CD/PtNPs modified electrode were applied to the detection of 10 μM Sudan I and shows the RSD about 2.6 %. The result confirmed that the graphene/β-CD/PtNPs modified electrode has good repeatability and reproducibility for the detection of Sudan I, and can be used for the accurate detection of Sudan I in food samples.

4. Conclusions

In conclusion, a sensitive and reliable sensor has been developed for trace level detection of Sudan I in food samples using graphene/β-CD/PtNPs nanocomposite modified electrode for the first time. Graphene/β-CD/PtNPs nanocomposite modified electrode shows a well-defined redox electrochemical behavior with enhanced oxidation current response towards Sudan I than that of other modified electrodes. Compared with previously carbon nanomaterials modified electrodes, the graphene/β-CD/PtNPs composite modified electrode exhibited an appropriate sensitivity (2.82 μAμM^{-1} cm^{-2}) and very low LOD (1.6 nM) for the detection of Sudan I. The appropriate recovery of Sudan I in food samples authenticates the potential practical ability of the graphene/β-CD/PtNPs composite. However, the selectivity of the graphene/β-CD/PtNPs composite modified electrode in the presence of other Sudan analogues are not studied, and these compounds may interfere the oxidation peak current response of Sudan I.

Conflict of interest

We declare that we have no conflict of interest.

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Table 1 Comparison of the analytical performance of graphene/β-CD/PtNPs modified electrode with previously reported carbon nanomaterials and metal nanoparticles modified electrodes for the determination of Sudan I.

Modified electrode	Detection method	LOD[1] (nM)	Sensitivity ($\mu A \mu M^{-1} cm^{-2}$)	Ref.
MWCNT[2]/GCE[3]	Amperometry	34.6	0.00215	[12]
AgNPs[4]@GO[5]/GCE	Amperometry	1140.0	0.00683	[27]
rGO[6]/AuNPs[7]/GCE	DPV[8]	1.0	1.34	[24]
Fe_3O_4/GCE	DPV	1.0	0.32	[13]
GR[9]/GCE	CV[10]	40.0	3.46	[26]
ERGO[11]/GCE	LSV[12]	10.0	3.68	[10]
MWCNT/GCE	SWV[13]	20.02	–	[28]
MIP[14]/AuNPs/GCE	LSV	2.0	–	[29]
Graphene/β-CD/PtNPs/GCE	DPV	1.6	2.82	**This work**

[1]Limit of detection; [2]Multiwalled carbon nanotubes; [3]Glassy carbon electrode; [4]Silver nanoparticles; [5]Graphene oxide; [6]Reduced graphene oxide; [7]Gold nanoparticles; [8]Difffrential pulse voltammetry; [9]Graphene; [10]Cyclic voltammetry; [11]Electrochemically reduced graphene oxide; [12]Linear sweep voltammetry; [13]Squre wave voltammetry; [14]Molecular imprinted polymers

Table 2 Determination of Sudan I in food samples using graphene/β-CD/PtNPs modified electrode by DPV. The RSD is relative to 6 measurements.

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Chili powder	1.0	0.98	98.0	1.9
	3.0	2.97	99.0	2.0
Chili sauce	1.0	0.97	97.0	2.3
	3.0	2.98	99.3	2.1
Tomato sauce	1.0	0.96	96.0	2.9
	3.0	2.95	98.3	2.6
Ketchup	1.0	0.98	98.0	1.6
	3.0	2.92	97.3	2.3

Figure captions

Figure 1 Schematic representation of the fabrication of graphene-β-CD/PtNPs composite.

Figure 2 SEM images of PtNPs (A), graphene/β-CD (B) and graphene/β-CD/PtNPs composite (C). D) The corresponding EDS of graphene/β-CD/PtNPs composite. Scale bar = 0.5 μm.

Figure 3 FTIR spectra of graphene (black line), graphene/β-CD (red line) and β-CD (blue line).

Figure 4 The effect of loading of graphene/β-CD (A) and effect of PtNPs deposition time (B) on graphene/β-CD/PtNPs composite towards the cyclic voltammetric oxidation peak current of 10 μM Sudan containing pH 7; scan rate is 50 mV/s. C) Typical cyclic voltammetry response of the graphene (a), PtNPs (b), graphene/β-CD (c) and graphene/β-CD/PtNPs (d) modified electrodes in 10 μM Sudan I containing pH 7 at a scan rate of 50 mV/s. D) At same conditions, cyclic voltammetry response of graphene/β-CD/PtNPs modified electrode in the absence (a) and presence (b) of 10 μM Sudan I.

Figure 5 Schematic representation for the electrochemical mechanism of redox behavior of Sudan I on graphene/β-CD/PtNPs composite.

Figure 6 A) cyclic voltammetry response of graphene/β-CD/PtNPs modified electrode in 10 μM Sudan I containing pH 7 at different scan rates from 10 to 200 mV/s. B) Linear plot for square root of scan rate vs. oxidation peak current of Sudan I. C) Effect of pH vs. oxidation peak current of Sudan I.

Figure 7 DPV response of graphene/β-CD/PtNPs composite modified electrode for different concentration (0.005–73.688 μM) additions of Sudan I into the pH 7. The DPV parameters are the pulse amplitude = 50 mV, pulse width = 0.05 s, pulse period = 0.2 s. Inset shows the linear plot for DPV current response vs. [Sudan I).
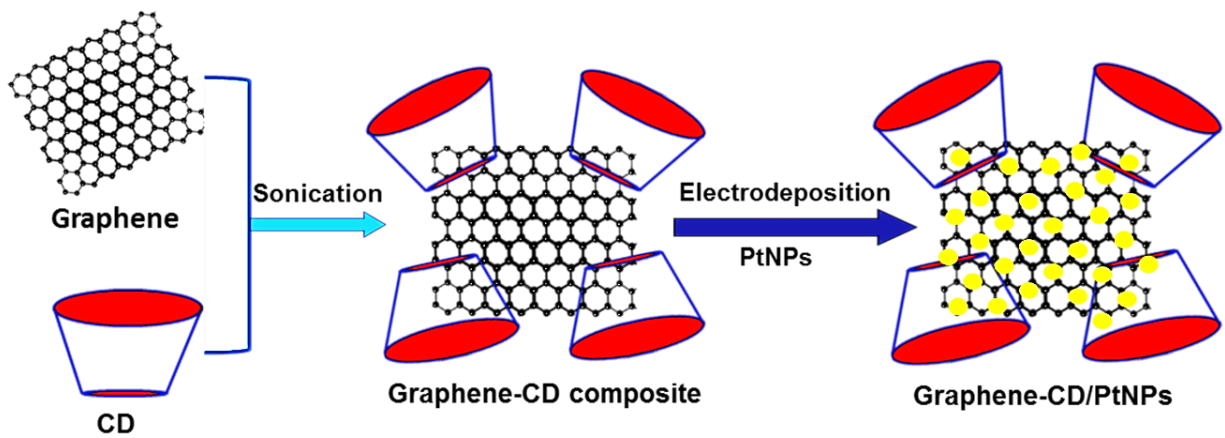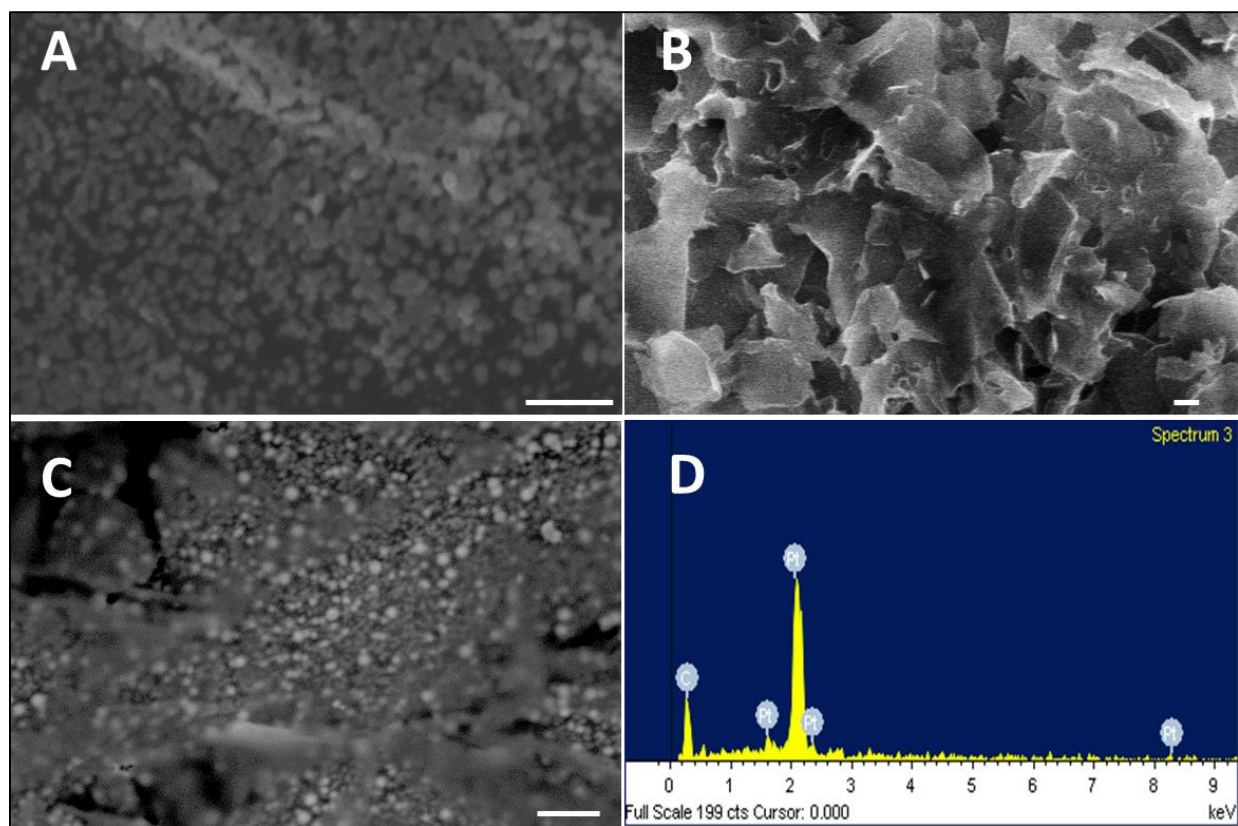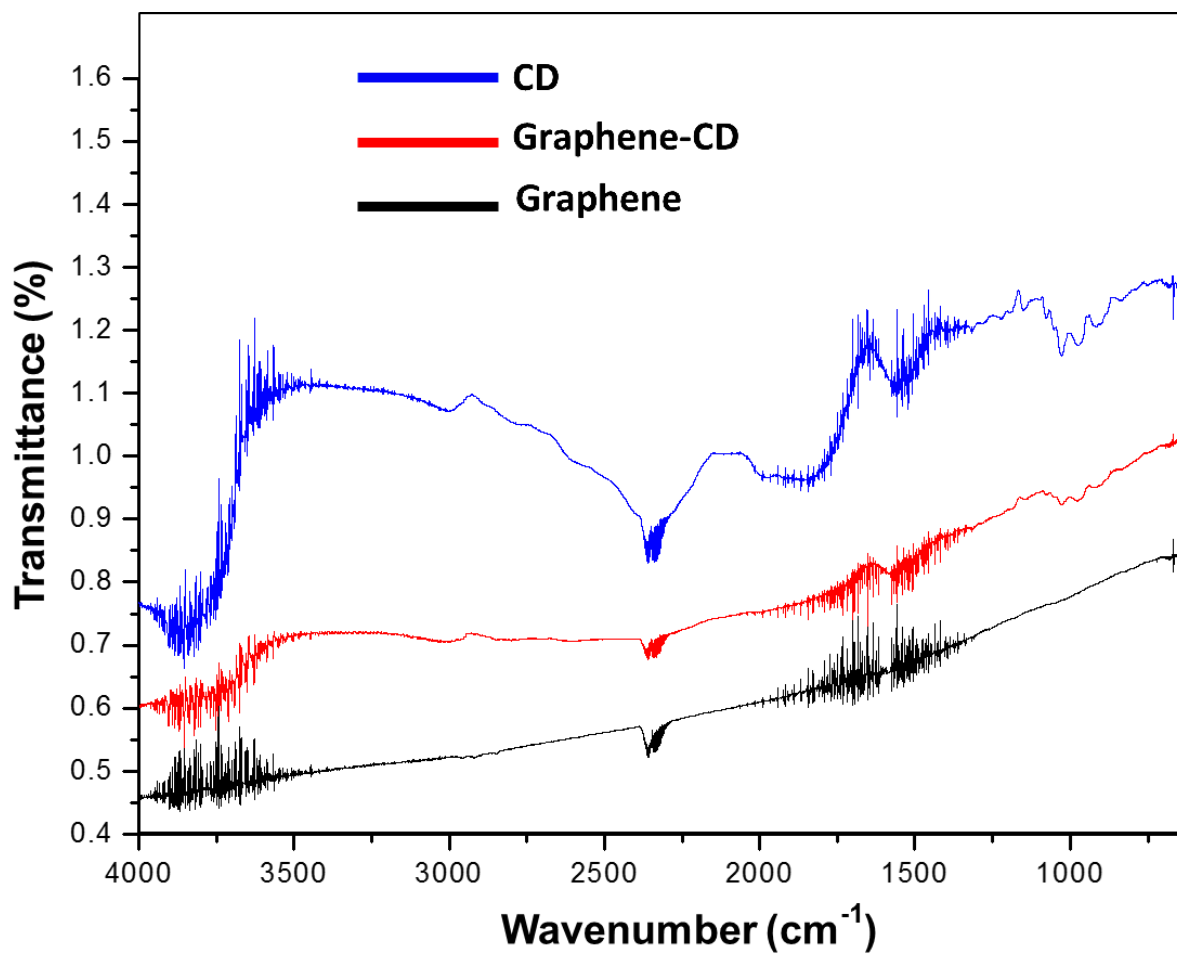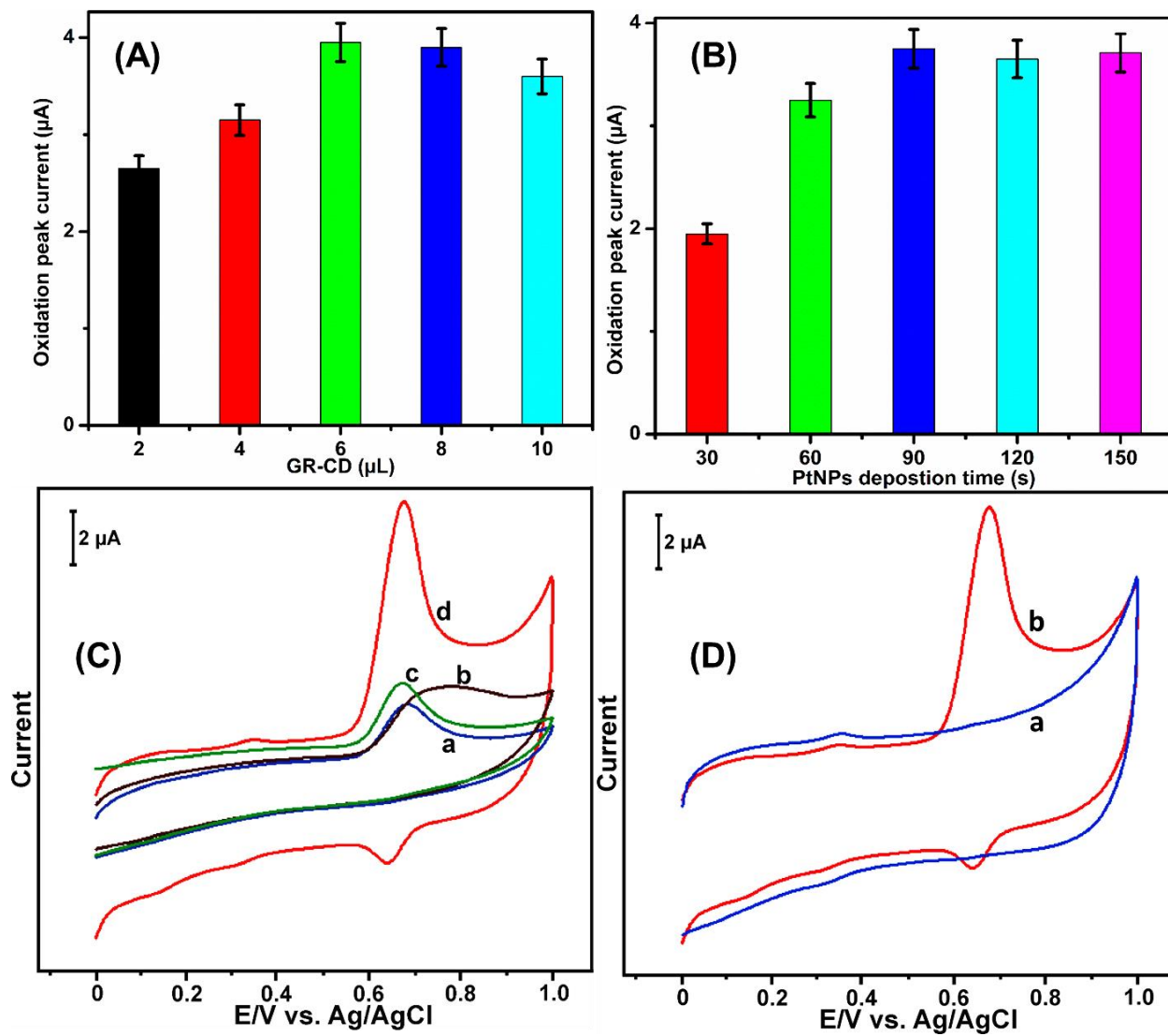
Figure 1

Figure 2

Figure 3

Figure 4

Sudan I

Graphene-CD/PtNPs

Oxidized form of Sudan I

Figure 5

Figure 6

The figure shows a differential pulse voltammetry plot with Current on the y-axis (scale bar: 5 µA) and E/V vs. Ag/AgCl on the x-axis ranging from 0 to 1.0. The inset shows a calibration plot of Current (µA) vs. C (µM) with the equation:
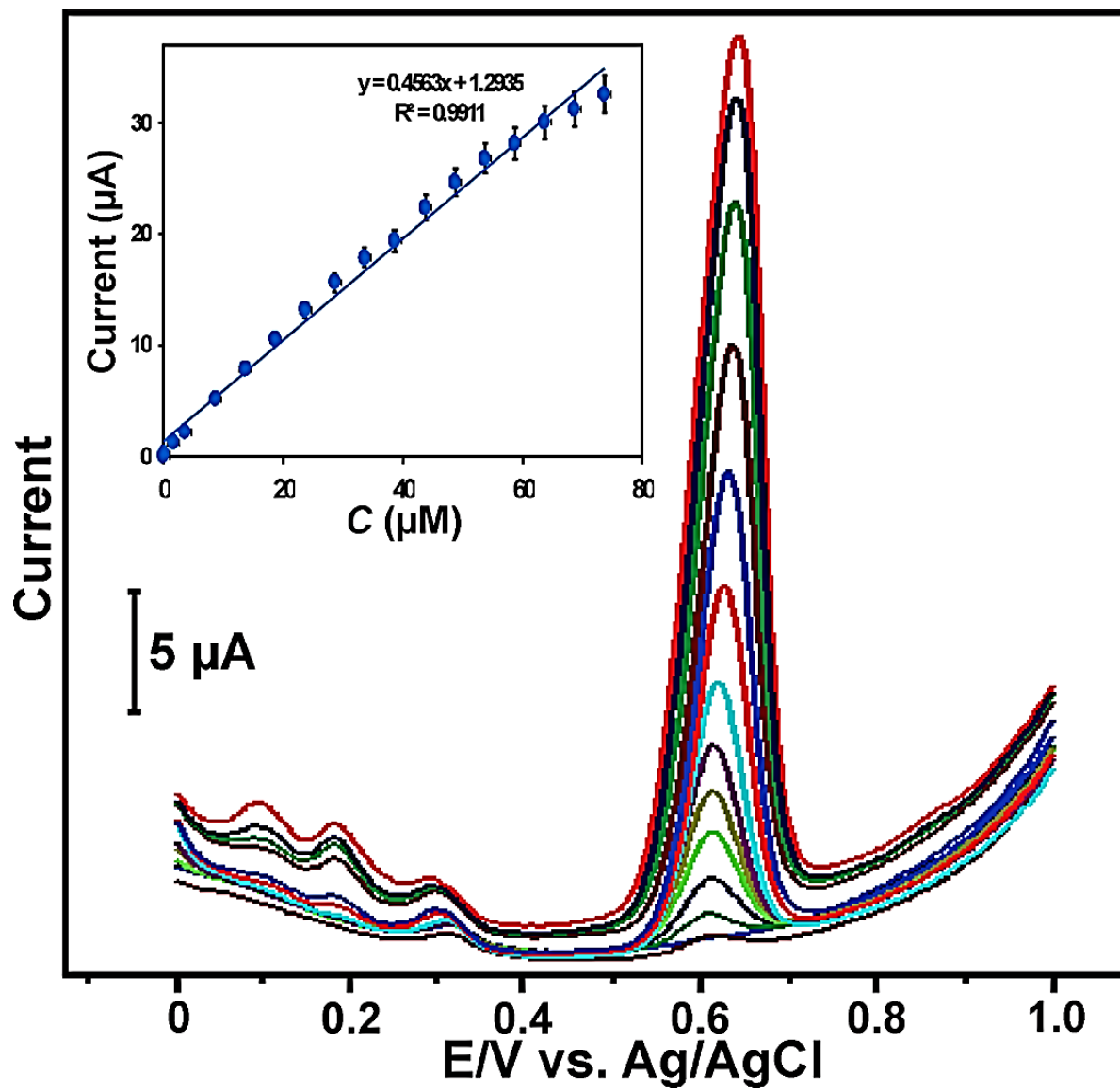
$$y = 0.4563x + 1.2935$$
$$R^2 = 0.9911$$
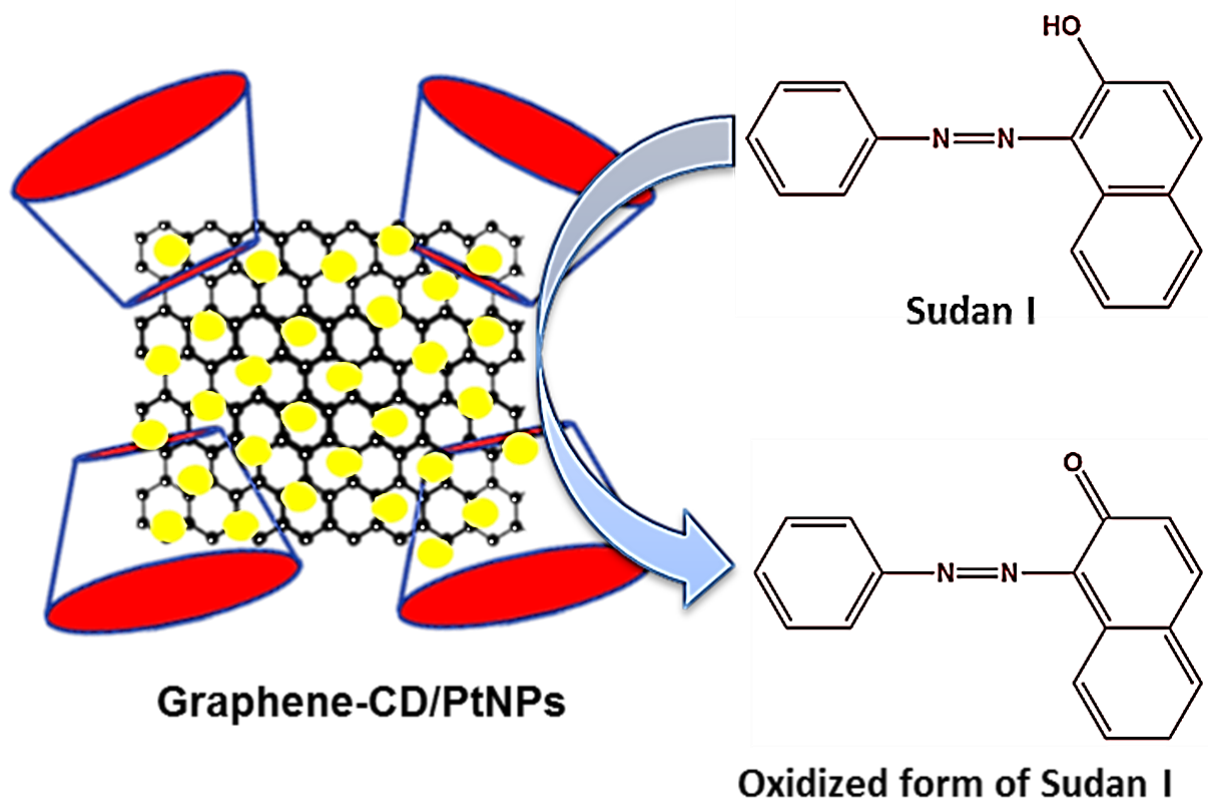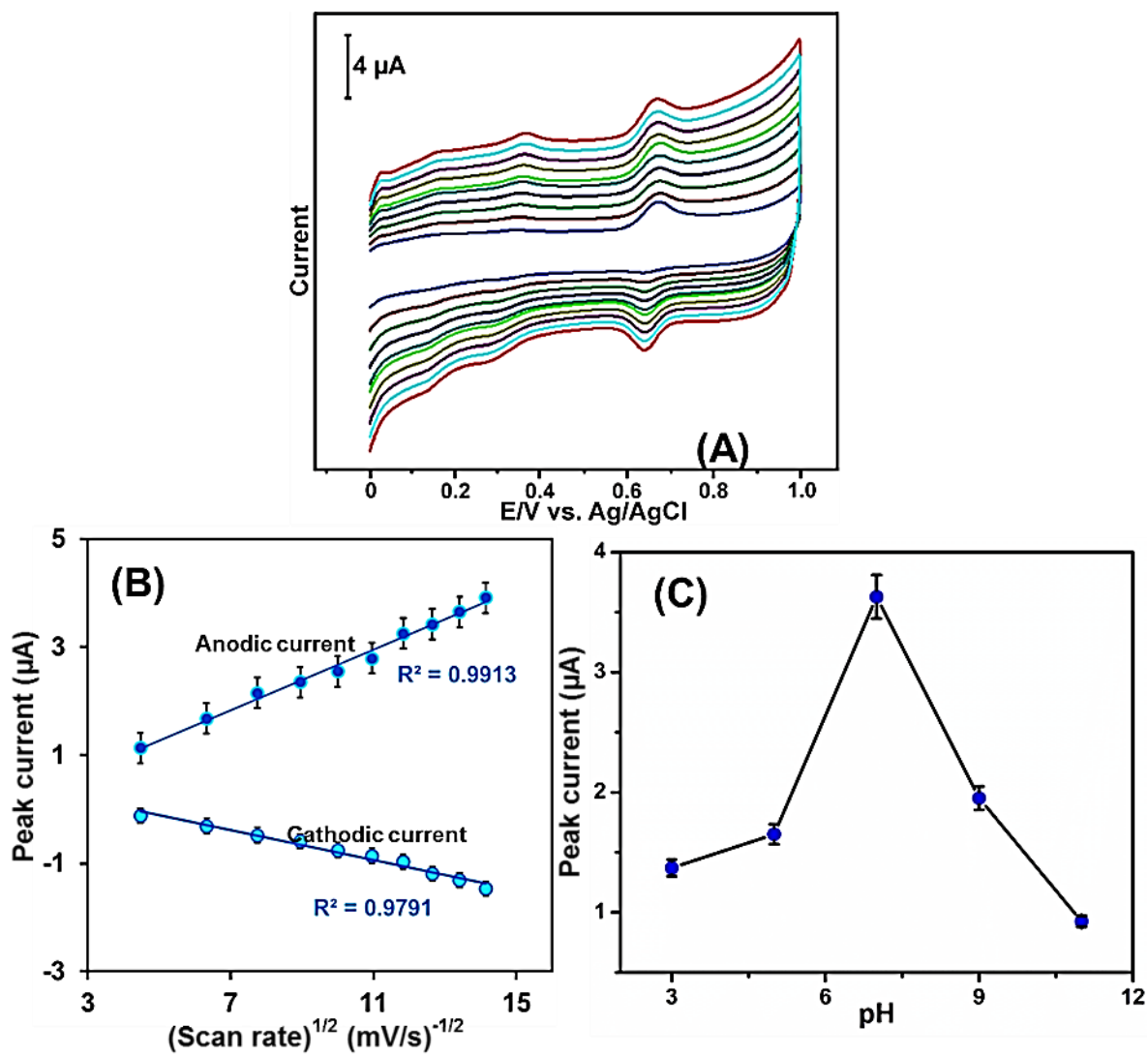
Figure 7

TOC and highlights

Graphene-CD/PtNPs

Sudan I

Oxidized form of Sudan I