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Electrochemical Measurement of Platinum Drug Using Carbon Paste Electrode Modified with Silver Nanoparticles and Modifier

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ABSTRACT

This paper used a carbon paste electrode modified with graphene functionalized with silver nanoparticles and triphenylphosphine to measure the drug Platinol. Raman, Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM) techniques were used to study the behaviour of Platinol. The electrochemical behavior of platinum on a carbon paste electrode modified with silver nanoparticles and 4-Hydroxy-2-(Triphenylphosphine) was analyzed. Differential Pulse Voltammetry (DPV) in the concentration range of 1-120 μM was linearized in two ranges of 1-20 μM and 20-120 μM, and the detection limit of 0.88 μM was obtained. The effects of disturbing on different species were studied to determine the selectivity. The platinum measurement method was used with the mentioned electrode in actual samples.

1. Introduction

cancer start similarly, which is a change in the typical structure of a cell. Abnormal cell division is not controlled, and it is unknown when it stops. A group of abnormal cells is called tonsure.1 Not all tumors are considered cancer. There are two types of tumors: (i) Benign and (ii) Malignant. Benign tumors are not considered cancer, while malignant tumors are cancers that can invade nearby parts of the body and prevent the activity of healthy cells in that area. Malignant tumor cells can spread to other body parts and create a community of abnormal cells away from the original site.2-4 This stage is called metastasis. The human body is made up of millions of cells that together form tissues such as muscles, bones and skin, and each one has a specific function. Cells naturally reproduce by dividing into two cells in a regular and controlled manner, leading to the growth and repair of body tissues. Sometimes, cell division is uncontrolled and abnormal.5 The abnormal and excessive growth of tissue cells is called a tumor. It can be benign or malignant. Benign tumors are usually confined to a small body part and often grow slowly. These tumors cause problems depending on their size and location. After the tumor is treated (usually with surgery), the patient has no further issues. Cancer or malignant tumors start in a confined space but can spread to surrounding tissues and organs6. The bloodstream or lymphatic system may transport cancer cells to distant areas of the body. More than 200 types of cancer are known so far. The types of cancers are (i) Carcinoma includes cancers that form the skin (such as skin cancer) or cover the inner layer of organs (such as lung cancer) or that form glands (such as breast cancer). (ii) Sarcoma includes cancers originating from connective tissues such as cartilage, bone, and muscle. (iii) Leukemia and lymphomas include cancers originating from hematopoietic and immune cells.7 The most common type of cancer in Western countries is skin cancer. Then, there is breast, lung, prostate, colon, bladder, and uterus cancer. Platinol is an anti-cancer drug that prevents cancer cells' growth (spread in the body) or stops or slows down their growth. Platinol is then used to treat bladder, testicular, or ovarian cancers. It may be used alone or in combination with other medications prescribed by a doctor.

2. Materials and methods

An electrochemical analyzer and SEMA 500 software were used in this paper. Electrochemical analyses were performed using three carbon paste electrodes modified with graphene-functionalized silver nanoparticles as the working electrode, saturated calomel electrode as the reference electrode, and graphite electrode as the working electrode. In all stages, a pH meter (Ino lab model, made in Germany) and a personal computer were used to store and analyze the data.

Chemical materials

The chemical materials required for the experiments are:

(1) Platinol produced by Sigma-Aldrich Company.

(2) Triphenylphosphine (HTP) produced by Merck Company.

(3) Silver nitrate (analytical purity-Merck), graphite (99.9% purity-Merck), ascorbic acid (98% purity-Merck), phosphoric acid (98% purity-Merck), sodium hydroxide (97% purity-Merck), sulfuric acid (98% purity-Merck), hydrochloric acid (37% purity-Merck), sodium nitrate (99% purity-Merck), and trisodium citrate (99.99% purity-Merck).

(4) Ether and ethanol solvents

The materials in (2), (3), and (4) clauses were all purchased from Merck Company. In all steps, solutions were used immediately after preparation. Also, pure nitrogen gas (99.99%) was used to remove oxygen from the operating environment.

Synthesis of graphene

In this experiment, 50 mL of concentrated H_2SO_4 solution was added to a 2 L Erlenmeyer flask, cooled to 0 °C in an ice bath, and graphite powder (1g) and $NaNO_3$ (5g) were gradually added to the flask under magnetic stirring. Then, 100 mL of distilled water was added to the mix, and its temperature reached 90 °C within 30 min, and it was diluted with distilled water until it turned dark brown. Next, the mixture was cooled to 50°C for 30 min. Then, 50 mL of concentrated hydrogen peroxide was added to the mix to produce a yellowish-green mix. During this time, the heating was stopped, and the produced precipitation (yellow-brown) was washed

with 100 mL of 5% hydrochloric acid solution until the pH of the washed precipitation reached 7. 50 mL of ascorbic acid solution (20%) was added to prepared graphene oxide to darken it. Then 50 mL of distilled water was added, and the sample was kept for 12 hours. In the next step, it was washed with distilled water to reach a pH of 7. Finally, the sample was dried at 50 °C, and the FTIR spectrums were obtained, per previous reports.

The SEM images of the synthesized graphene surface

The SEM images of the synthesized graphene surface presented in Figure 1.

[Insert Figure 1 near here]

FTIR spectrum for graphene

The FTIR spectrums were recorded to evaluate the structure of the synthesized grapheme (Figure 2).

[Insert Figure 2 near here]

Interpretation of FTIR spectrum of graphene

As shown, a degree of irregularity and disturbance is observed at the region (wavenumber) of 1550 cm^{-1}, which can be attributed to flake graphite. The wavenumber of 1640 cm^{-1} can be attributed to the vibrational structure of non-oxidized graphite (alkene).

Raman spectrum of synthesis of graphene and GO

Raman spectrums were recorded to confirm the structure of synthesized GO and graphene.

[Insert Figure 3 near here]

Figure 3a shows the Raman spectrum of GO. As shown, there is a relatively intense band in the region of 1340 cm^{-1}, a band in the region of 1570 cm^{-1}, and a weak band in the region of 2690 cm^{-1}. Figure 3b shows the Raman spectrum of graphene. The spectrums of a and b for GO and grapheme were consistent with the previous reports.

Synthesis of silver nanoparticles

To synthesize silver nanoparticles, 0.5% trisodium citrate was added to the boiling solution of 5×10^{-3} M $AgNO_3$. Heating was continued slowly until a color change appeared. Then it was cooled to room temperature. To stabilize silver nanoparticles on the surface of graphene, 1 gram of graphene powder was added to 25 mL of silver nanoparticles solution, and the beaker contents were stirred for 20 min. Then the solution was purified and dried at room temperature. The size of the particles after stabilization (immobilization) on the graphene surface was 60-80 nm, and graphite was also stabilized (immobilized) on the surface. A morphological examination was done with SEM.

SEM image of silver nanoparticles on the surface of graphene

SEM images were recorded to evaluate the morphology of synthesized graphene and the size of silver nanoparticles stabilized on the surface of the grapheme (Figure 4).

[Insert Figure 4 near here]

Preparation of electrode modified with graphene functionalized with silver nanoparticles and modifier

100.0 mg of graphite powder, 0.5 mg of functionalized graphene with silver nanoparticles, and 0.5 mg of modifier were mixed to prepare the modified carbon paste electrode. Then, by adding paraffin, the mix was made into a paste. With a spoon, we attached it to the end of the plastic tube with a depth of 10 mm and a diameter of 4 mm and smoothed the surface of the dough. An electrical connection was achieved by inserting a copper wire into the compressed paste tube. Fig. 5. Cyclic voltammetry of (a) modified carbon paste electrode with graphene functionalized with silver nanoparticles and modifier, (c) modified carbon paste electrode with graphene and modifier, (e) modified carbon paste electrode with the modifier, (g) modified carbon paste electrode with graphene functionalized with silver nanoparticles, (i) modified carbon paste electrode with graphene, and (k) carbon paste electrode, in 0.1 M sodium perchlorate buffer solution in the presence of 0.1 M chloride ion at pH of 7 with a scanning speed of 50 mVs^{-1}. Voltammetry (a), (c), (e), (g), (i), and (k) are the same as (b), (d), (f), (h), (j), and (l) in the presence of 0.1 mM cisplatin. The appendix clearly shows graphs (k) and (l).

[Insert Figure 5 near here]

Figure 5 shows the average peak current changes in all four repeated measurements based on the platinum concentration of 2.0, 8.0, 14.0, and 18.0 μM. The slope of the calibration curve and the correlation coefficient confirm the repeatability (reproducibility) at low concentrations. The following equation was used to find the detection limit of platinum on the surface of the carbon paste electrode modified with graphene functionalized with silver nanoparticles and modifier.

$C_m = S_b/m3$

The obtained detection limit (0.49 μM) was improved for platinum on the surface of the carbon paste electrode modified with graphene functionalized with silver nanoparticles and modifier. The method's repeatability was evaluated with ten repeated measurements at a concentration of 18.0 μM, and the corrected average current was 1.83 (± 0.012). The coefficient of variance of 0.014% indicates the accuracy of the method

(Figure 6).

[Insert Figure 6 near here]

3.Results and Conclusions

Studying the effect of possible disturbing of foreign species

To study the selectivity and efficiency of the proposed method in different matrices, the effect of species disturbing in urine and blood serum samples (which can be present together with platinum in these samples) was investigated. For this purpose, the species were investigated in 0.1 M sodium perchlorate buffer solution in the presence of 0.1 M chloride ion at a pH of 7. The results of this study are listed in Tables 1-3. This Table confirms the possibility of using the proposed method in platinum quantitative measurements.

[Insert Table 1 near here]

Table 1 shows that glucose had the least disturbing while ascorbic acid had the most disturbing.

The use of carbon paste electrode modified with graphene functionalized with silver nanoparticles and modifier in determining the amount of platinum in urine and serum samples

The modified electrode was used in actual samples. A urine sample was collected from people who did not inject platinum. After filtration, the sample was diluted 50 times using 0.1 M sodium perchlorate buffer solution in the presence of 0.1 M chloride ion with a pH of 7. Different amounts of platinum standard solution were added to this sample. Table 2-6 shows a summary of the results. According to the values of relative standard deviations and recovery (%), the proposed method for determining the amount of platinum in urine sample is effective and efficient.

[Insert Tables 2 and 3 near here]

Conclusions

Based on the results of this paper, the detection of platinum using a carbon paste electrode modified with graphene functionalized with silver nanoparticles and modifier led to a decrease of 410 mV in the anodic oxidation potential. The possibility of measuring platinum using the DPV technique was investigated. The slope of the calibration curve was close to the graph of the average peak current changes for four repeated measurements based on platinum concentration. Therefore, the slope of the calibration curve and the correlation coefficient confirmed the repeatability even at low concentrations, and it is necessary to conduct more extensive studies for more detailed research. Also, the desired method was used to measure platinum in urine and serum samples, and acceptable results were obtained.

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Tables

Table 1. The effect of studied species in determining the quantity of platinum using a carbon paste electrode modified with graphene functionalized with silver nanoparticles and a modifier.

Foreign species	Molar ratio
Glucose	950
Triglyceride	840
Certain	800
Urea	460
Uric acid	50
Ascorbic acid	<1

Table 2. Quantitative determination of platinum in urine sample by DPV method.

Relative standard deviation (%)	Recovery(%)	Gained *(µM)	Added (µM)	**Sample**
1/1	**95/6**	**19/1 ± 0/2**	**20**	
/95	**102/9**	**61/8 ± 0/6**	**60**	
1/1	**102/6**	**82/1 ± 0/5**	**80**	**Urine**
1/1	**101/9**	**101/9 ± 0/1**	**100**	

* Average of three measurements

Table 3. Quantitative determination of platinum in serum sample by DPV method.

Relative standard deviation (%)	Recovery(%)	Gained *(µM)	Added (µM)	S**ample**
0/9	105/1	19/0 ± 0/2	20/0	
1/0	103/3	62/0 ± 0/6	60/0	**Serum**
1/0	98/5	78/8 ± 0/8	80/0	
1/0	99/0	99/0 ± 0/1	100/0	

* Average of three measurements

Figures

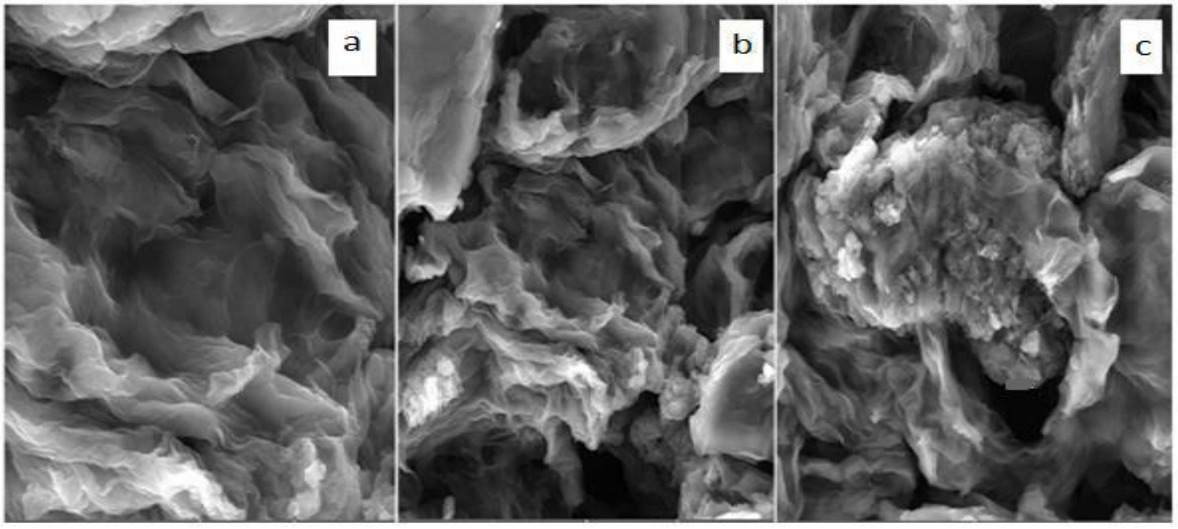

Figure 1. The SEM images of the synthesized graphene surface.

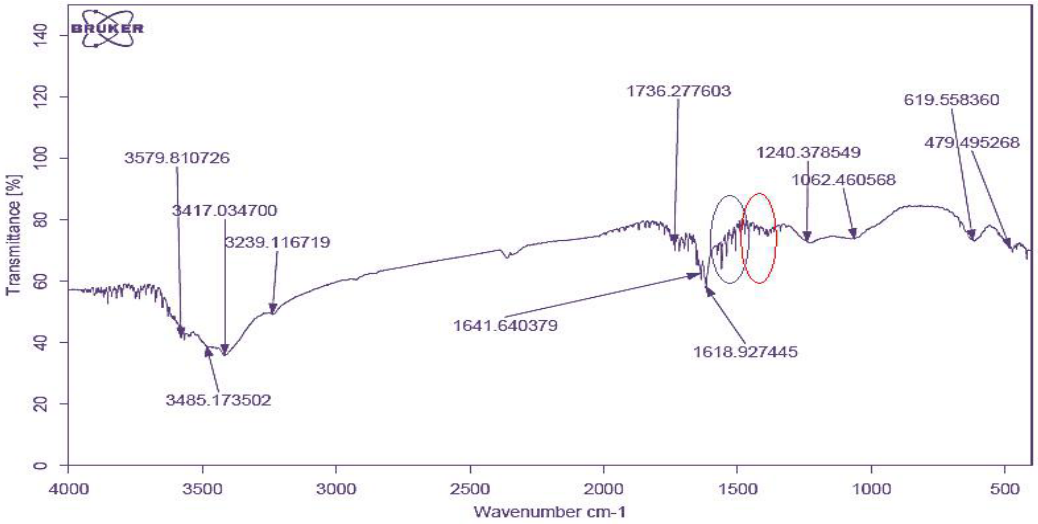

Figure 2. FTIR spectrum for grapheme.

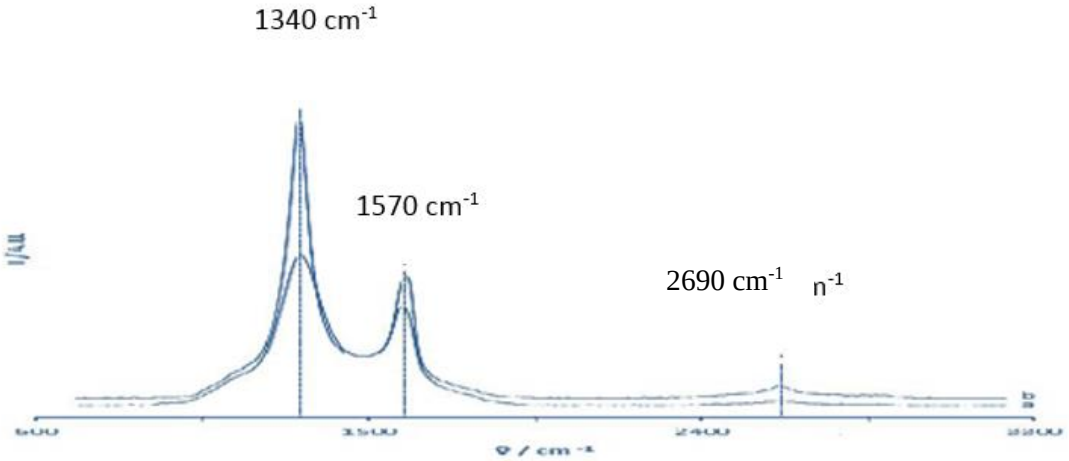

Figure 3. Spectrums of a and b attributed to GO and graphene.

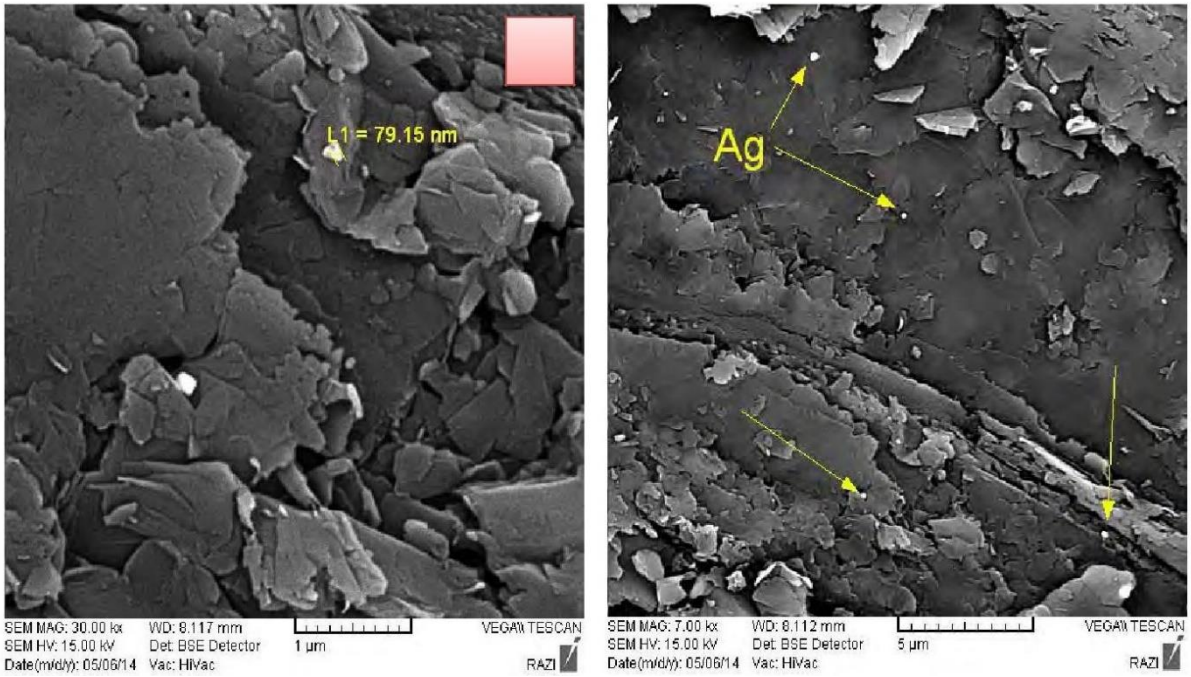

Figure 4. The SEM images of silver nanoparticles on the surface of grapheme.

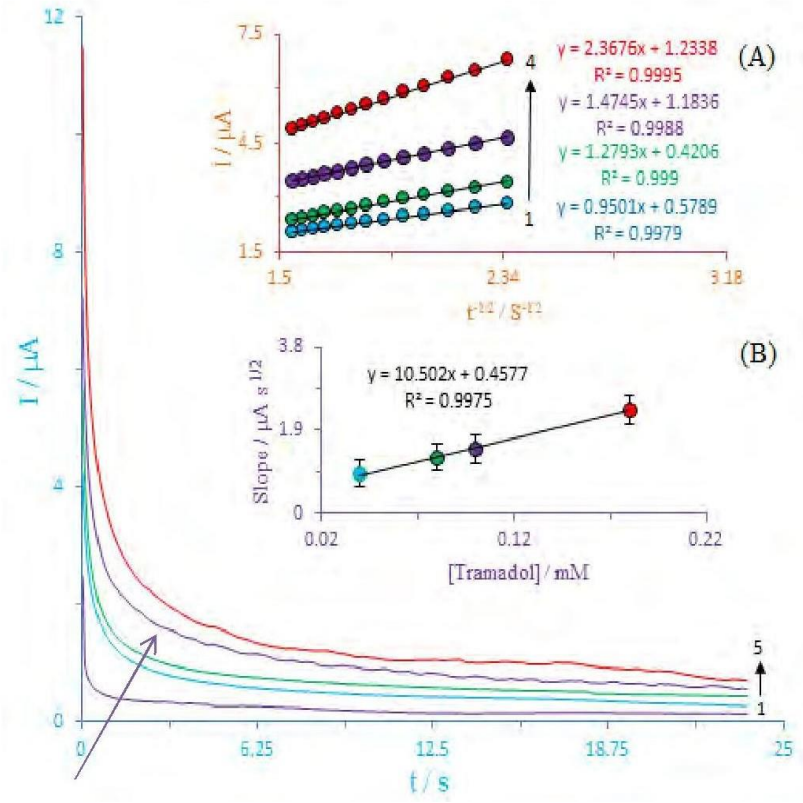

Figure 5. The average peak current changes in all four repeated measurements based on the platinum concentration of 2.0, 8.0, 14.0, and 18.0 µM.

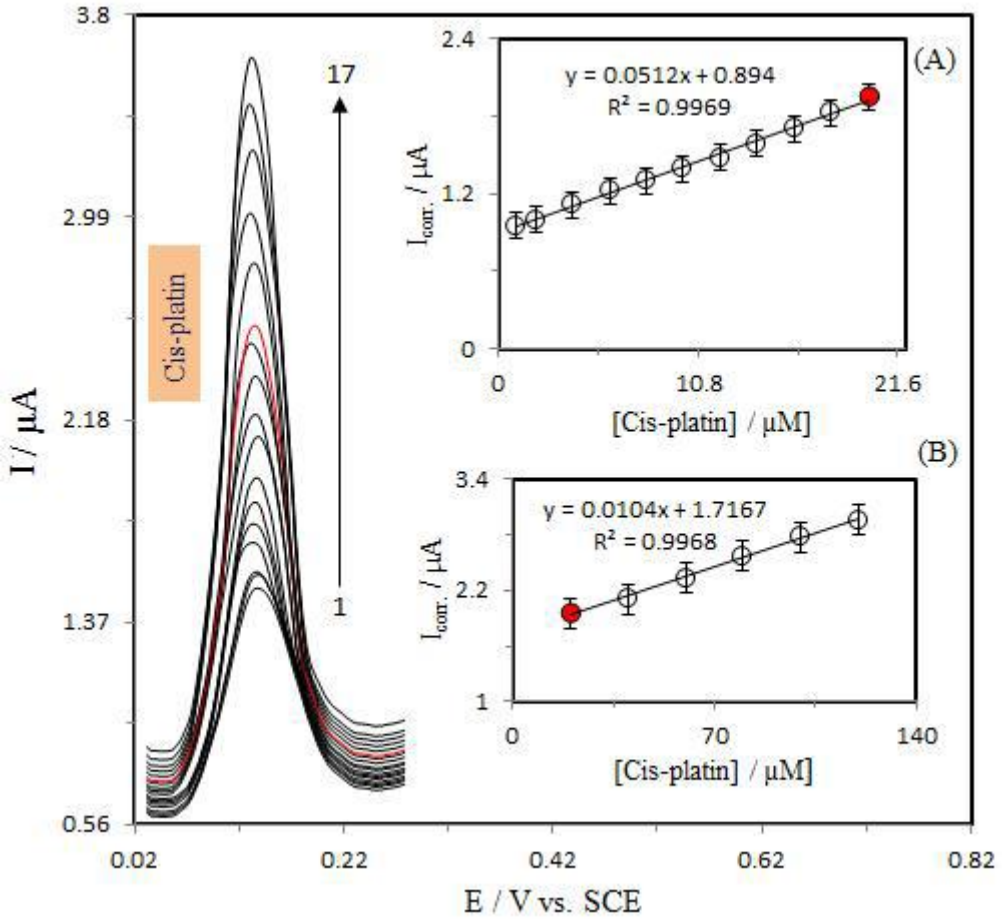

Figure 6. The DPV curve for carbon paste electrode modified with graphene functionalized with silver nanoparticles and modifier in 0.1 M sodium perchlorate buffer solution in the presence of 0.1 M chloride ion at pH=7, and containing different concentrations of cisplatin. Appendix A is for the concentration range of 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, and 20.0 M. Appendix B is for the concentration range of 20.0, 40.0, 60.0, 80.0, 100.0, and 120.0 M.

Figure captions

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