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Coal Tar Pitch / Graphene / Polyglycine Modified Pencil Graphite Electrode for Simultaneous Electrochemical Detection of Guanine and Adenine

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Abstract

In this study, a coal tar pitch / graphene / polyglycine modified pencil graphite electrode sensor was developed for the quantitative detection of guanine and adenine, two of the most important components of DNA and RNA. Therefore, the determination of guanine and adenine is of great significance. The coal tar pitch / graphene / polyglycine modified pencil graphite electrode was characterized by scanning electron microscope. Cyclic voltammetry, electrochemical impedance spectroscopy, linear sweep voltammetry, and square wave voltammetry techniques were employed to analyze the behavior of guanine and adenine on coal tar pitch/ graphene/ polyglycine modified pencil graphite electrode in 0.1 M of H_2SO_4*. Under the optimal conditions, electrical signals were linear over the concentration ranges from 1.0 to 25 μM and 10.0 to 140 μM for simultaneous determination of guanine and adenine with the detection limit as low as 0.6 μM and 6 μM, respectively. As a candidate for developing electrochemical sensors, the coal tar pitch/ graphene/ polyglycine modified pencil graphite electrode sensor presented here has a wide range of potential applications.*

Keywords: *Adenine, Guanine, Cyclic voltammetry, Square wave voltammetry, Pencil graphite electrode, Polyglycine.*

1. INRODUCTION

Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) in genetic information storage as well as in protein synthesis are two biological molecules that play an essential role [1]. Determination of DNA and amino acids is also essential in many areas, particularly in pharmacogenetics, genetics, criminology, and pathology [2]. The four primary bases in DNA are guanine (GU) and adenine (AD) purines along with thymine and cytosine pyrimidines [3, 4, 5]. The abnormal changes in the concentration ratios of these compounds are indicative of DNA abnormalities and mutations resulting from certain diseases such as cancer, epilepsy, HIV, etc. such as cancer, epilepsy, HIV, etc. [6]. Adenine or guanine concentration levels have been linked to genetic diseases including hepatocellular carcinoma (adenine) and Lesch-Nyhan syndrome (guanine) [7, 8, 9, 10].

Several known analytical methods have been developed for the determination of guanine and adenine, such as high-performance liquid chromatography (HPLC) [11], flow injection chemiluminescence (CL) [12], fluorescence [13], ion-pairing liquid chromatography (IPIC) [14], electrospray ionization mass spectrometry (ESI MS) [15]. However, these techniques can have excellent accuracy, sensitivity, and selectivity. On the other hand, some disadvantages such as high costs, specialized equipment, time-consumption portability, and difficult sample preparation procedures may harm these techniques. Modification of various surfaces with layers provides great advantages to provide desired functionality or features. Due to their stability, usefulness, speed, low equipment, chemical inertness, low background current, and low cost, electrochemical modification techniques have received a lot of attention among other modification methods [16, 17, 18, 19]. Various materials can be employed in the development of electrochemical sensors for the determination of adenine and guanine, such as multi-walled carbon nanotubes (MWCNTs) [20, 21], graphene [22], graphite sparked screen-printed electrode [23] and graphene oxide (GO) [24]. A variety of electroanalytical techniques has been employed for guanine and adenine detection such as differential pulse voltammetry (DPV) [25], cyclic voltammetry (CV) [26], and square wave voltammetry (SWV) [27].

The main purpose of this work was to demonstrate coal tar pitch (CTP), graphene (GR), and Polyglycine (POLYGLY) based modified pencil graphite sensor electrode (PGE) for the determination of AD and GU using electrochemical techniques. With this aim, this study was performed (i) to electrochemically polymerization glycine (GLY) onto the PGE/CTP/GR electrode surface using CV, (ii) to characterize POLYGLY-modified PGE/CTP/GR electrode by CV and electrochemical impedance spectroscopy (EIS), (iii) to check whether the molecule is bound to the PGE/CTP/GR electrode surface as diffusion controlled, (iv) to investigate whether the new surface obtained is sensitive to GU and AD through SWV technique.

2. MATERIALS AND METHODS

2.1. Chemicals and Reagents

Guanine, adenine, and other chemicals were purchased from Sigma-Aldrich, Merck, Fluka, and Riedel and were of the analytical reagent grade. None of the chemicals were purified before usage. Guanine and adenine were prepared as a stock solution by dissolving them in 0.1 M H_2SO_4 due to their weak aqueous solubility and strong hydrophobic properties. When not in use, the working solutions are kept at 4°C.

2.2. Electrochemical Equipment and Apparatus

In our experiments, all electrochemical and spectroelectrochemical studies were performed using a conventional three-electrode cell system. The GAMRY Reference 600+ potentiostat/galvanostat/ZRA from (Gamry instruments, USA) electrochemical analyzer from GAMRY Instruments (PA, USA) was utilized in all experiments. Reference electrodes included Ag/Ag^+ (10 mM $AgNO_3$) (BAS Model MF-2042) for non-aqueous media and Ag/AgCl/3 M KCl (BAS Model MF-2063, USA) for aqueous media. Pt wire (BAS Model MW-1033) was used as the counter electrode. Software PHE200 Physical Electro-chemistry and EIS300 Electrochemical Impedance Spectroscopy were used to apply the CV and EIS techniques, respectively. SWV was used with PV220 Pulse Voltammetry Software.

In the preparations of all aqueous solutions and glassware washing, ultra-pure quality water with a resistance of 18.2 M cm (MP MINIPURE purification system, DEST UP, USA) was used. All electrochemical experiments were performed at room temperature (25±1°C).

2.3. Electrode Characterizations

Surface characterizations after the modification process were performed by CV, LSV, and EIS. 1 mM ferrocene solution in 100 mM NBu_4BF_4 was used in the characterizations with CV, at a scan rate of 100 mV s^{-1} and a potential range of 0.1 V to 0.6 V in non-aqueous media. EIS was used to evaluate impedance in a 1 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ mixture (in 100 mM KCl) over the frequency range of 100.000 Hz to 0.05 Hz, and Nyquist plots were recorded.

2.4. Preparation of Working Electrodes

According to the literature, working electrodes were prepared [28, 29]. SEM was applied for the characterization of PGE/CTP/GR/POLYGLY layers deposited on the PGE/CTP/GR electrode surface in Figure 1.

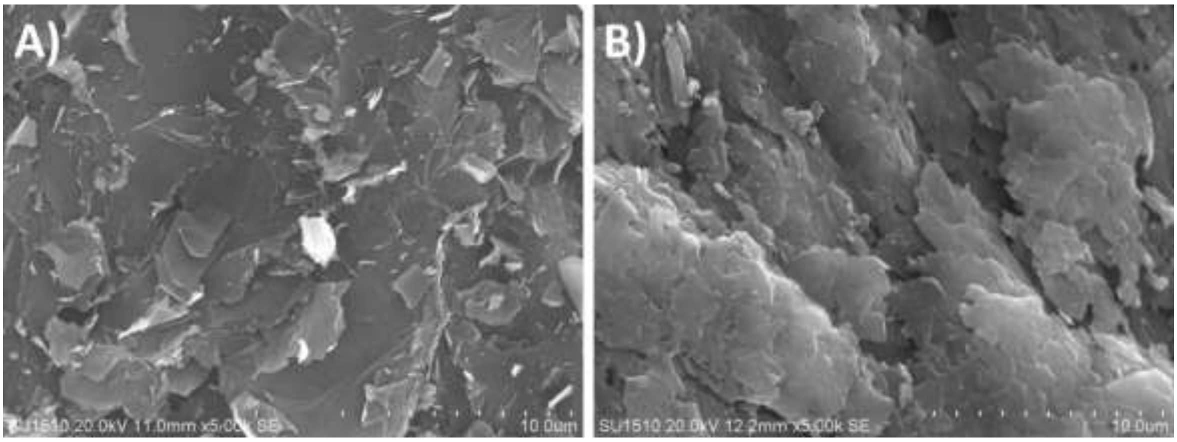


Figure 1. *SEM images of PGE/CTP/GR (a) and PGE/CTP/GR/POLYGLY electrode (b).*

3. RESULTS

3.1. Fabrication and Optimization of PGE/CTP/GR/POLYGLY Electrode

As a result of the electropolymerizing of amino acids onto nanomaterials, stable surfaces with good electrochemical properties, biocompatibility, and bioactivity, can be produced quickly and easily just in one step [26].

For fabricating polymer-based modified electrodes, electrochemical or chemical methods are usually used. In this work, CTP, GR, and POLYGLY-based modified PGE was fabricated using the electrochemical method in 0.1 M Phosphate buffer solution (PBS) with pH 7.2 containing 1mM glycine by CV technique between -0.5 V and +1.8 V at scan rate of 0.1 V s^{-1} [30].

Figure 2 shows the electropolymerization of glycine on the PGE/CTP/GR surface after 10 cycles. After the electrode film was deposited, it was wiped with demineralized water to remove unreacted materials physically adsorbed.

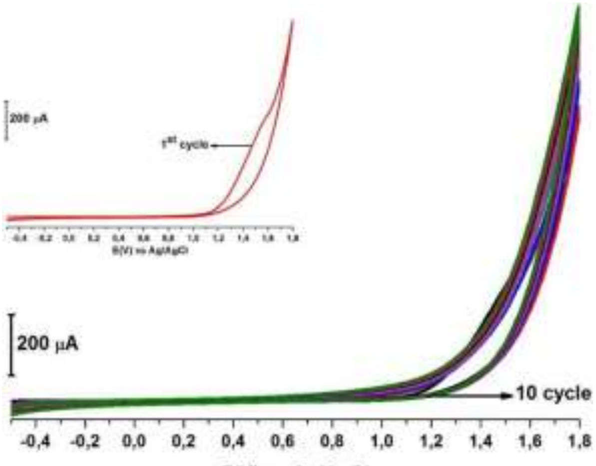


***Figure 2**. Cyclic voltammograms of preparation POLYGLY modified PGE/CTP/GR electrode. 1 mM aqueous solution of Glycine was taken in 0.1 M PBS with pH 7.2 at 10 cycles with a scan rate of 0.1 V s^{-1}.*

3.2. Surface Characterization of PGE/CTP/GR/POLYGLY Electrode

The newly prepared ferrocene was used as an electrochemical probe to study the electrocatalytic activity of the designed sensor through CV and EIS techniques.

Figure 3A shows descriptive CVs of 1 mM Ferrocene on PGE, PGE/CTP, PGE/CTP/GR, and PGE/CTP/GR/POLYGLY electrodes at a scan rate of 0.1 V s^{-1}.

The Nyquist plots and charge transfer resistance values of the redox couples 1 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 0.1 M KCl on the same electrodes are shown in Figure 4.

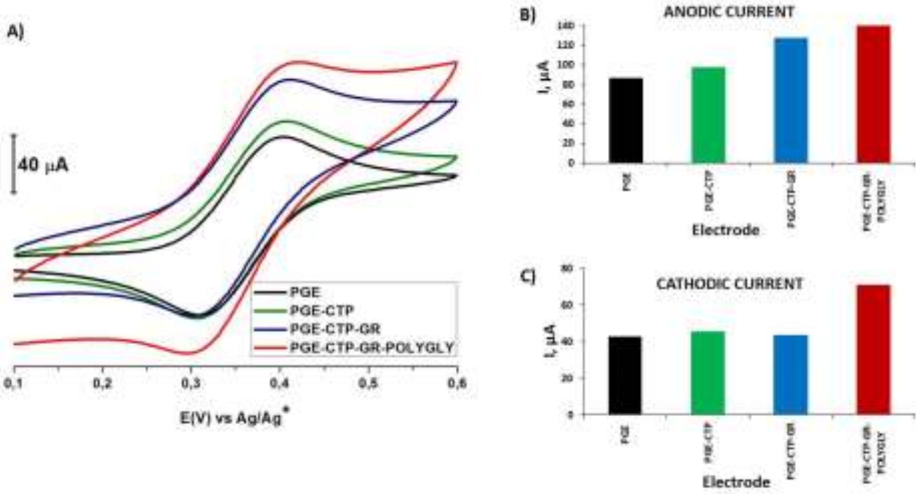


***Figure 3**.Overlaying the PGE, PGE/CTP, PGE/CTP/GR, and PGE/CTP/GR/POLYGLY electrode voltammograms at 1 mM ferrocene redox probe solution vs. Ag/Ag$^+$ (10 mM) in CH_3CN+ 0.1 M NBu_4BF_4 using 0.1 V s^{-1} scanning rate (A). Anodic current values for each electrode' s response (B). Cathodic current values for each electrode's response (C).*

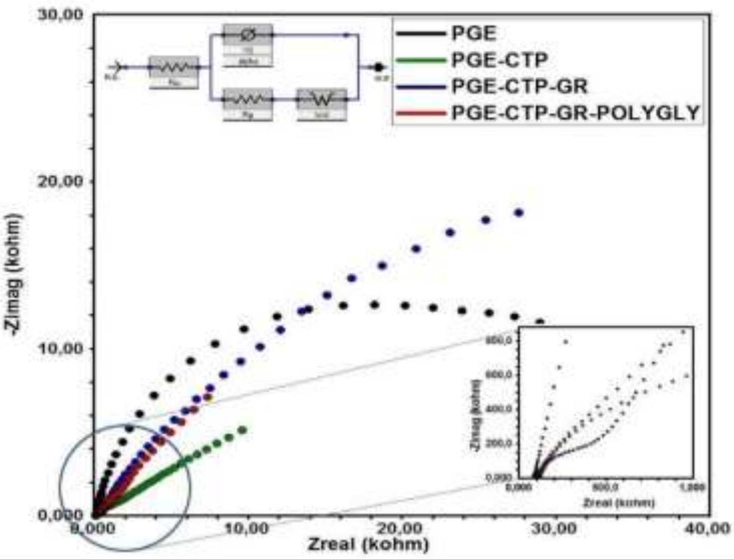


***Figure 4.** Nyquist plot for electrochemical impedance spectra of 1 mM $Fe(CN)_6{}^{3-/4-}$ redox couple solution in 0.1 M KCl in the frequency range of 100 000–0.05 Hz at 10 mV wave amplitude.*

Based on Warburg's diffusion-controlled equivalent circuit modeling, the Nyquist plot was evaluated [31]. As shown in Figure 4, the redox probe had the lowest charge transfer resistance at the surface of the PGE/CTP/GR/POLYGLY electrode, which is in agreement with the CV results.

From Figures 3 and 4, compared with other electrodes, the electron transfer rate of the redox couples on the surface of the PGE/CTP/GR/POLYGLY electrode is increased. The increase of redox current on the modified surface indicates a higher electron transfer rate and better conductivity.

3.3. Investigation of Binding Type

Diffusion-controlled processes are expected to modify the molecule onto the electrode surface in CV modification. A smooth and better electrode surface is produced as a result of this preference, as well as easy molecule binding to the surface. Various scanning rates were used to bind the molecule to the electrode surface to understand whether the modification process is diffusional controlled or not. By diffusion-controlled process, a molecule binds to the electrode surface under two conditions. The first is to plot log I_p against log υ and have the slope be 0.5. Second, the linear plot should be obtained when $\sqrt{\upsilon}$ is plotted against the peak current, I_p. A plot of log I_p versus log υ was used according to the Randles-Sevcik equation. From Figure 5D, it was obtained a slope of 0.66 which is very close to 0.5. This result concluded that the POLYGLY is mostly moved onto the electrode surface via diffusion control.

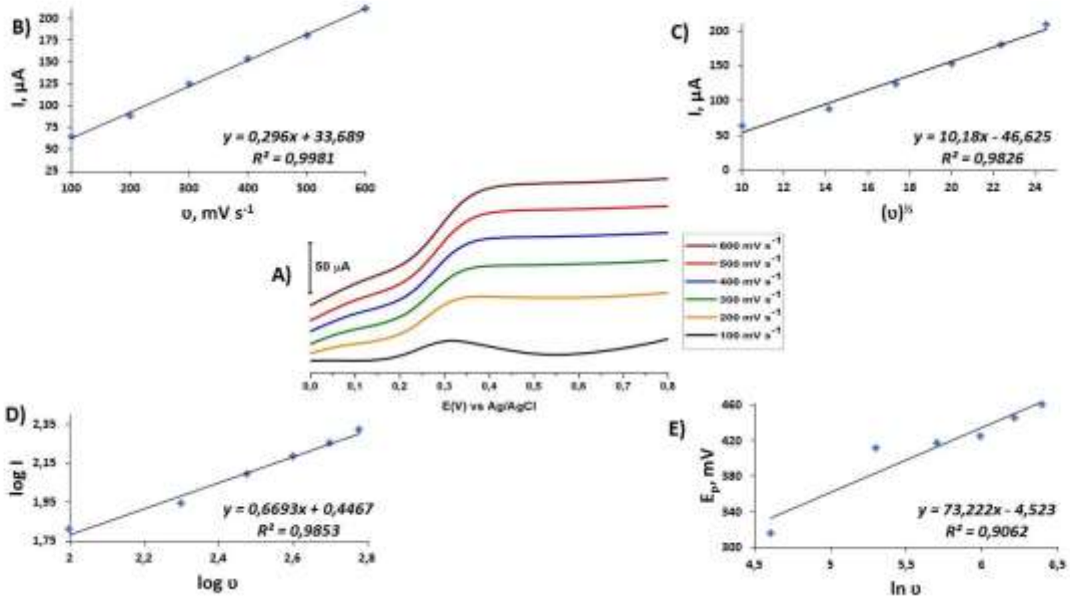


Figure 5. *LSV voltammograms were obtained at PGE in 0.1 M of PBS with pH 7.2 containing 1.0 mM glycine at various scan rates (100-600 mV* s^{-1}*) (A). Shows the plot of the anodic peak current versus scan rate (B). Calibration plot of the redox peak currents vs. square root of scan rate (C). Relation between log scan rate and log peak current (D). Plot of variation of* E_p*, mV versus ln* υ*, mV* s^{-1} *(E).*

3.4. Electrochemical Performance

After POLYGLY modification and ferrocene testing, it was found that the electrode surface was completely covered with a POLYGLY. PGE, PGE/CTP, PGE/CTP/GR, and PGE/CTP/GR/ POLYGLY electrodes were investigated electrochemically SWV.

Figure 6 shows the SWV voltammograms of the PGE/CTP/GR/POLYGLY electrode in the absence and presence of GU and AD.

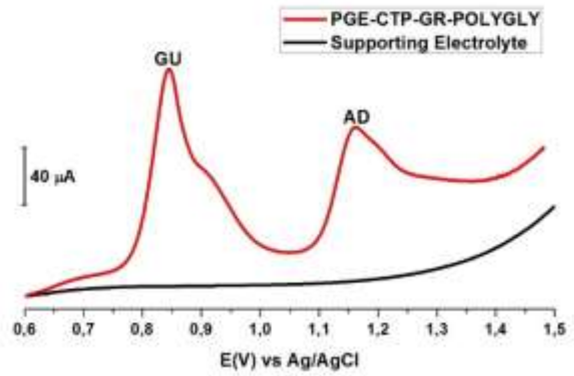


Figure 6. *SWV voltammograms of PGE/CTP/GR/POLYGLY electrode in the absence and presence of GU and AD*

From Figure 6, there are no electrochemical signals in the absence of GU and AD in H_2SO_4 (0.1 M) on the PGE/CTP/GR/POLYGLY electrode. However, the two oxidation peaks in the PGE/CTP/GR/POLYGLY electrode in the presence of 1 mM of Gu and 1 mM of AD are significantly improved.

The voltammetric response of the new sensor electrode to GU and AD was evaluated on unmodified PGE, PGE/CTP, PGE/CTP/GR, and PGE/CTP/GR/POLYGLY electrodes compared by using SWV for 1 mM GU and 1 mM AD solutions in 0.1 M H_2SO_4. Figure 7A shows SWV voltammograms for 1 mM AD and 1 mM GU solution in 0.1 M H_2SO_4 on PGE, PGE/CTP, PGE/CTP/GR, and PGE/CTP/GR/POLYGLY electrodes at a scan rate of 0.1 V s^{-1}.

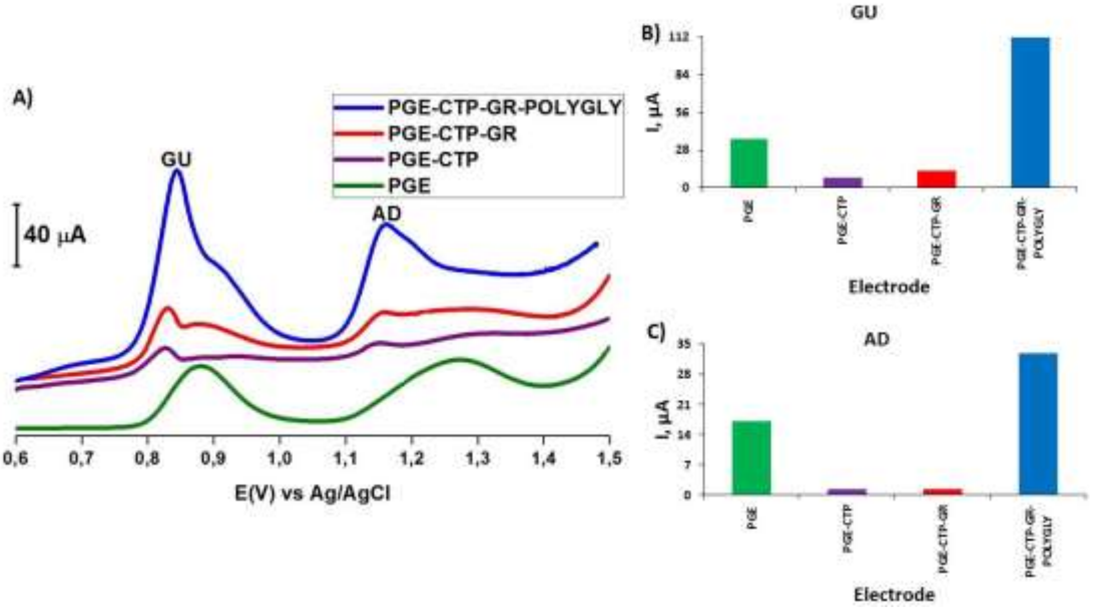


Figure 7. *SWV voltammograms for 1 mM AD and 1 mM GU solution in 0.1 M H_2SO_4 on PGE, PGE/CTP, PGE/CTP/GR, and PGE/CTP/GR/POLYGLY electrodes at a scan rate of 0.1 V s^{-1} (A). GU current values for each electrode's response (B). AD current values for each electrode's response (C).*

Relative to GU and AD-purine bases, the PGE/CTP/GR/POLYGLY electrode showed bigger and better peak currents than PGE, PGE/CTP, and PGE/CTP/GR electrodes. These voltammetric responses mean that the newly fabricated PGE/CTP/GR/POLYGLY electrode exhibits better detection performance in the determination of AD and GU. Furthermore, the POLYGLY-modified PGE/CTP/GR sensor was about 3.1, 6.0, and 2.9 times more sensitive to GU than PGE, PGE/CTP, and PGE/CTP/GR electrodes, respectively. On the other hand, the PGE/CTP/GR/POLYGLY sensor was about 1.9, 60.0, and 58.7 times more sensitive to AD than PGE, PGE/CTP, and PGE/CTP/GR electrodes, respectively (Figure 7B). Therefore, the PGE/CTP/GR/POLYGLY sensor exhibits more attractive voltammetric sensing properties compared with other bare electrodes and modified electrodes.

It can be concluded that the improved sensor performance is due to the formation of conductive POLYGLY film on the PGE/CTP/GR surface area in the system. In addition, the peak oxidation potentials of GU-AD were 0.880-1.274 V and 0.845-1.162 V for PGE and PGE/CTP/GR/ POLYGLY electrodes, respectively. According to these changes in peak potential, the oxidation of adenine and guanine-purine bases on the PGE/CTP/GR/POLYGLY electrode was simpler at lower potentials. The peak separation (ΔE_p) between GU and AD was 317 mV, which allowed simultaneous differentiation of GU and AD.

3.5. Effect of Scan Rates

To investigate the reaction kinetics of GU and AD oxidation on the surface of modified electrodes, LSV was used LSV to examine the relationship between anodic peak currents and scan rates. Fig. 8A shows the LSV voltammograms for 1 mM GU and 1 mM AD solution in 0.1 m H_2SO_4 on PGE/CTP/GR/POLYGLY electrodes at different scan rates of 100, 300, 500, 700 and 900 mV s^{-1}. Throughout the studied range from 100 mV s^{-1} to 900 mV s^{-1}, the anodic peaks continuously elevated and the peak potentials moved in a positive direction. The oxidation peak currents of GU and AD increased linearly with the increase in scan rates (Figure 8B). The linear equations between peak currents for GU and AD and scan rates can be written as:

$$\boldsymbol{I_{pa\,GU}(\mu A) = 123.9 + 0.3089\,\upsilon\ (mV\,s^{-1}),\ R^2 = 0.9949}$$

and

$$\boldsymbol{I_{pa\,AD}(\mu A) = 161.26 + 0.3183\,\upsilon\ (mV\,s^{-1}),\ R^2 = 0.9953},$$

referring that the electrochemical oxidation prosses of GU and AD at the PGE/CTP/GR/POLYGLY electrode's surface were adsorption-controlled process [32, 33].

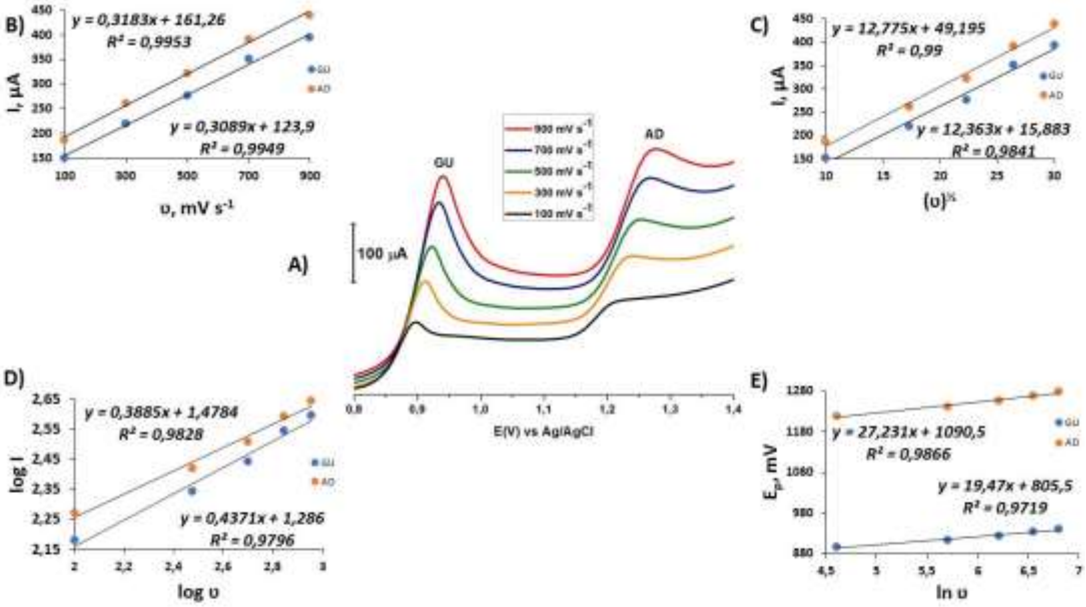


Figure 8. *Impact of scan rate on 1 mM GU and 1 mM AD in 0.1 M H_2SO_4 solution at PGE/CTP/GR/POLYGLY electrode from 100-900 mV s^{-1}(A). shows the plot of the anodic peak current for GU and AD versus scan rate (B). Calibration plot of the redox peak currents vs. square root of scan rate (C). Relation between log scan rate and log peak current. E) Plot of variation of E_p, mV versus ln υ, mV s^{-1} (D).*

As shown in Figure 8D, plotting the log of scan rate (log υ) against the log of the anodic peak current of GU and AD (log I_{pa}) yielded a slope of 0.437 ($R^2 = 0.9796$) for GU and slope of 0.388 ($R^2 = 0.9828$) for AD. According to this finding, electrode kinetics are maintained by diffusion [34]. Figure 8C shows the plot of the square root of scan rate ($\upsilon^{1/2}$) versus oxidation peak current (I_{pa}) for GU and AD. In addition to providing good linearity, the established plot confirms the validity of the electrode reaction. The anodic peak potential (E_{pa}) and ln υ. The corresponding linear equation is

$$\mathbf{E_{pa,\,GU}(mV)=19.47\ ln\ \upsilon\ \left(mV\ s^{-1}\right)+805.5;\ R^2=0.9719}\ \text{and}$$

$$\mathbf{E_{pa,\,AD}(mV)=27.231\ ln\ \upsilon\ \left(mV\ s^{-1}\right)+1090.5;\ R^2=0.9866}$$

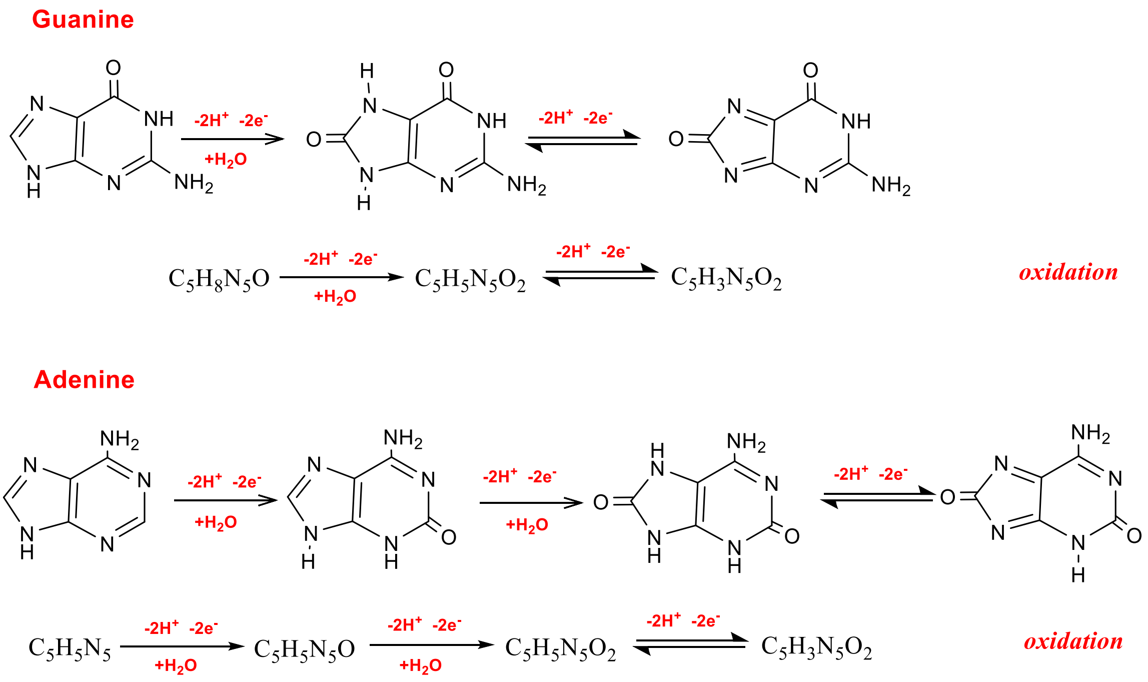
According to Laviron's equation: [35]

$$E_{pa} = E^{\circ} + \frac{RT}{(1-\alpha)nF} ln\upsilon$$

where E° is the standard potential (V); n is the number of transition electrons in the rate-determining step; R is the universal gas constant, T is the temperature (298 K), F is Faraday's constant (96,485 $Cmol^{-1}$) and α is the charge transfer coefficient for completely irreversible electrode process. In the irreversible process, the value of α is 0.5 [36].

GU and AD can be directly electrochemically oxidized by 2.63 and 1.89 electrons, respectively, based on the slope of the E_{pa} versus ln υ curve. GU and AD were oxidized in a multistep mechanism on the surface of the PGE/CTP/GR/POLYGLY electrode, with the first two-electron step determining the rate [37, 38, 39].

Considering these results, it might be possible that the mechanisms of electro-oxidation of GU and AD at PGE/CTP/GR/POLYGLY electrode are as illustrated in scheme 1. which is in agreement with the literature [21, 40, 41, 42, 43].



Scheme 1. *Oxidation mechanism of GU and AD.*

3.6. Simultaneous Determination of Guanine and Adenine Using SWV

It is important to measure a sensor's sensitivity based on its concentration range and limit of detection (LOD).

PGE/CTP/GR/POLYGLY electrode was used to detect GU and AD simultaneously using the SWV technique between 0.7 and 1.3 V vs Ag/AgCl (1 M KCl). To test adenine or guanine in a separate concentration range, they were mixed GU and AD (one amount is unchanged, the other is changed). GU and AD electrochemically oxidize at 0.844 and 1.162 V, respectively, as shown in Figure 6.

With the addition of the two analytes, the two anodic peaks increased progressively. According to Figures 9B and 10B, the calibration curves for GU and AD are plotted using their peak current densities, demonstrating linear responses when the concentration increases.

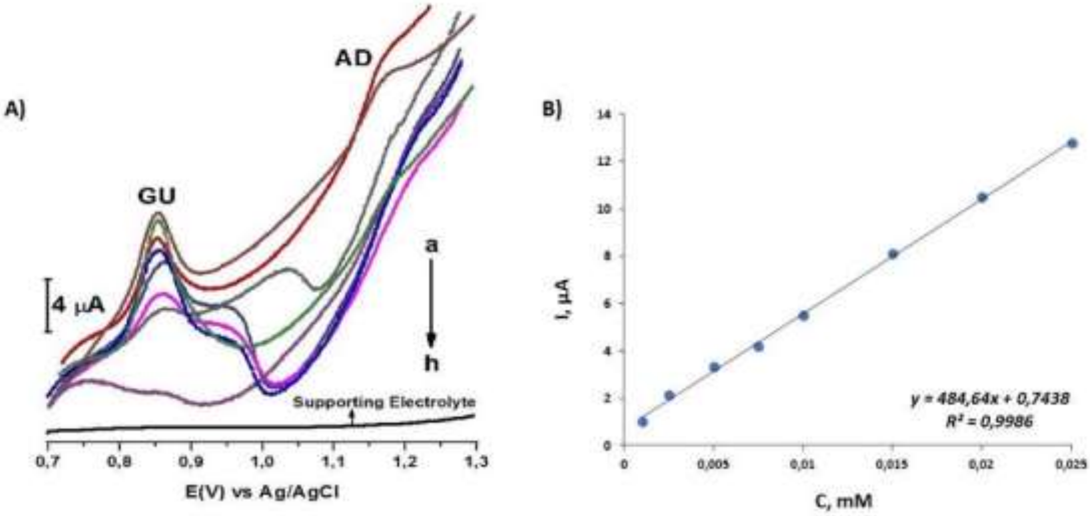


Figure 9. *SWV curves of GU in the presence of AD (10 µM) in 0.1 M H_2SO_4. GU concentrations: a) 2.5 × 10^{-5} M b) 2.0 × 10^{-5} M, c) 1.5 × 10^{-5} M, d) 1.0 × 10^{-5} M, e) 7.5 × 10^{-6} M, f) 5.0 × 10^{-6} M, g) 2.5 × 10^{-6} M, h) 1.0 × 10^{-6} M (A), and the plot of I_{pa} versus concentration of GU (B).*

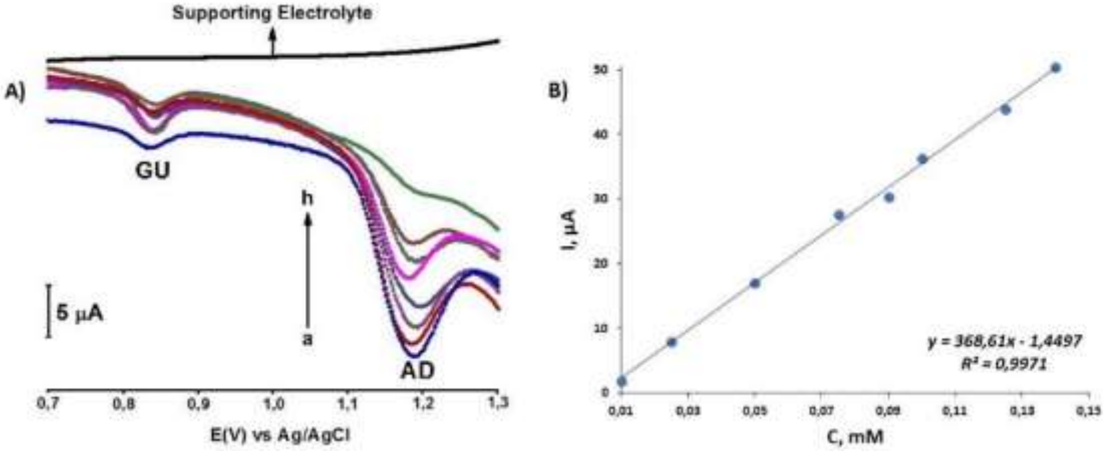


Figure 10. *SWV curves of AD in the presence of GU (10 µM) in 0.1 M H_2SO_4. AD concentrations: a) 1.4 × 10^{-4} M b) 1.25 × 10^{-4} M, c) 1.0 × 10^{-4} M, d) 9.0 × 10^{-5} M, e) 7.5 × 10^{-5} M, f) 5.0 × 10^{-5} M, g) 2.5 × 10^{-5} M, h) 1.0 × 10^{-5} M (A), and the plot of I_{pa} versus concentration of AD (B).*

In Figure 9A, 9B, when the concentration of GU varies between 1.0 and 25 µM by keeping the concentration of AD unchanged (10 µM), the linear equation is

$$\boldsymbol{I_{pa\,GU}(\mu A) = 484.64\, mM \times [GU] + 0.7438}$$

$$\boldsymbol{R^2 = 0.9986}$$

and LOD is 0.6 μM.

In Figure 10A, 10B, when the AD concentration varies between 10 and 140 μM by keeping the GU concentration unchanged (10 μM), the linear equation is

$$\boldsymbol{I_{pa\,AD}(\mu A) = 368.61\, mM \times [AD] - 1.4497}$$

$$\boldsymbol{R^2 = 0.9971}$$

and LOD is 6 μM.

Linear current responses for both GU and AD were gained over the concentration ranges of 1.0-25 and 10-140 μM (Figure 9A, 10A). The detection limits of GU and AD were 0.6 and 6 μM, respectively.

4. DISCUSSION

In Table I, the detection performance of the developed electrochemical sensor is compared with other modified electrodes for simultaneous detection of GU and AD. It can be seen that the PGE/CTP/GR/POLYGLY electrode has a relatively wider linear range or lower detection limit. This excellent electrochemical performance may be due to the large folded structure of the PGE/CTP/GR electrode that can provide a large surface area to accommodate a large amount of POLYGLY, resulting in good electrical conductivity and electrocatalytic activity. Therefore, the developed PGE/CTP/GR/POLYGLY electrode is a promising nanomaterial for the individual and simultaneous detection of GU and AD.

Table 1. *Comparison of different modified electrodes for the determination of GU and AD.*

Electrode type	**Modified materials**	**GU Linear range (μM)**	**GU LOD (μM)**	**AD Linear range (μM)**	**AD LOD (μM)**	**Ref**
CPE	MWCNT-Fe_2O_3@PDA-Ag	8.0–130	4.80	10–120	2.90	[44]
Graphite	Au-rGO/MWCNTs	15–185	3.70	13–165	3.30	[45]
GCE	polyaniline/MnO_2	10-100	4.8	10-100	2.9	[46]
GCE	Cu^{II}TPTAPc	5-70	1.66	5-70	2.53	[47]
GCE	PANI-MnO_2	10–240	4.8	10-150	2.9	[46]
GCE	pAHNSA	10–250	0.93	10–250	6.2	[48]
GCE	CNT–PNF	10–1800	18.2	20–3000	8.6	[49]
CPE	TAN-gNPPANF	0.01–15.0	3.0	0.08–25	2.8	[50]
GCE	CB	4–60	1.64	4–80	4.96	[51]
PGE	CTP/GR/POLYGLY	1.0 - 25	0.6	10-140	6	This work

5. CONCLUSION

A simplistic and new developer graphite pencil electrode sensor was synthesized by graphene nanoparticles and electropolymerization with glycine. The sensor has several attractive properties, such as easy electrode fabrication, low cost, and relatively large reactive surface area. Kinetic analyses were performed to complement the nature of the electrode process and were found to be adsorption and diffusion-controlled. The modulated sensor successfully lowered detection and quantitation limits and effectively resolved the overlapping peaks of AD and GU into two well-segregated anodic peaks.

ACKNOWLEDGEMENT

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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