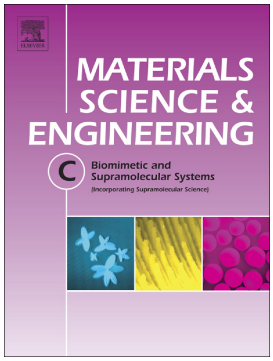

Electrochemical and nonenzymatic glucose biosensor based on MDPA/MWNT/PGE nanocomposite

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Electrochemical and nonenzymatic glucose biosensor based on MDPA/MWNT/PGE nanocomposite

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ABSTRACT

The nonenzymatic detection of glucose has been widely investigated in a variety of fields ranging from biomedical applications to ecological approaches. Among these fields, electrochemical methods have great advantages such as high electrocatalytic ability, high sensitivity, good selectivity and low-cost for the electrooxidation of glucose. Future trends on glucose sensing are nanostructured electrodes depending upon the development of nanotechnology. In this study, an electrochemical and nonenzymatic glucose sensor based on (*E*)-4-((5-methylthiazole-2-yl)diazenyl)-*N*-phenylaniline (MDPA) / multi-walled carbon nanotube (MWNT) / pencil graphite electrode (PGE) was performed. Electrochemical measurements were obtained using cyclic voltammetry and square wave voltammetry techniques, and characterization of surfaces was carried out using scanning electron microscope and electrochemical impedance spectroscopy techniques. The modification of PGE was made using MDPA and MWNT, and 10 cycles coating was used to prepare the

proposed electrode. The effects of scan rate and pH on the peak potential and the peak current were determined. The limit of detection and linear range were calculated using various concentrations of glucose. The interference study was made using coexisting substances including metal ions such as Al^{3+}, Cu^{2+}, Fe^{3+} and ascorbic acid.

Keywords: Nonenzymatic, azo dyes, nanotubes, pencil graphite electrode, glucose.

1. Introduction

Carbon nanotubes (CNTs) consist entirely of carbon and belong to a family of nanomaterials. In this family, multi-walled carbon nanotubes (MWNTs) are multiple layers of superimposed graphite and form a tubular shape rolling on themselves. These cylindrical graphite structures are polymers of pure carbon and can be reacted using the rich chemistry of carbon. This advantage provides opportunity to modify various surfaces allowing innovative applications in optics, electronics, materials, chemical processing and electrochemistry [1]. The structure of MWNTs was represented in Fig. 1, inset (a).

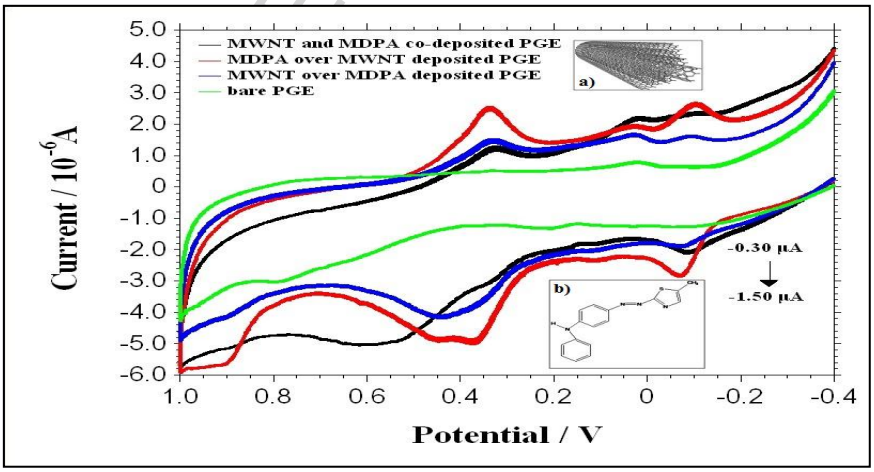

Fig. 1. Cyclic voltammograms of 1.0 mg mL^{-1} MWNT and 1.0 mM MDPA co-deposited PGE, 1.0 mM MDPA over 1.0 mg mL^{-1} MWNT deposited PGE, 1.0 mg mL^{-1} MWNT over 1.0 mM MDPA deposited PGE and bare PGE in BR buffer at pH 3.0 between -0.4 V and +1.0 V vs. Ag/AgCl. Inset: **a)** the structure of MWNTs and **b)** the structure of MDPA.

Organic dyes, especially azo dyes can combine with MWNTs with strong π-π interactions to form stable hybrids [2]. Various applications of MWNTs with azo dyes have been already reported [3–5]. Electrocatalytic activity of these combinations gains great advantages such as high mechanical stability and sensitivity for different electrochemical techniques possessing excellent responses to various substances such as as redox proteins [6], drugs [7], small biomolecules [8], hormones [9], and so on. (*E*)-4-((5-methylthiazole-2-yl)diazenyl)-*N*-phenylaniline (MDPA) is a novel azo dye that can be synthesized by a coupling reaction in two stages: dinitration and coupling. Therefore, MDPA was selected as a new modification mediator in line with MWNT. The structure of MDPA (molecular weight, MW = 294.09 g mol^{-1}) was represented in Fig. 1, inset (b).

A number of studies have been used to monitor glucose levels in blood [10–12]. Among these studies, electrochemical and optical methods have been developed extensively. Glucose oxidase based electrochemical biosensors are widely preferred with the ability of high selectivity. However, these techniques can be affected by enzyme immobilization, pH and temperature [13]. Therefore, enzyme-free techniques are necessary on the direct electrochemical oxidation of glucose. The electrochemical and nonenzymatic detection of glucose is a cost-effective, rapid, sensitive and stable approach. In recent years, noble metals and alloys are used to fabricate nonenzymatic glucose sensors, but their applications are limited because of high cost [14]. Also, a large scale of platinum-based materials are commercially applied as nonenzymatic glucose sensors. However, their use is restricted by poor stability and high cost [15]. Therefore, various nanomaterials have been developed as excellent nanocatalysts to provide new surfaces on the fabrication of novel nonenzymatic glucose sensors. Among these materials, CNTs show unique physical and chemical properties, so they are widely used to fabricate enzyme-free glucose sensors. The first study

was reported by Ye et al. using CNT modified electrode [16] and since then, researchers continue to develop novel CNT composites as nonenzymatic glucose sensors.

In this work, the strong noncovalent adsorption by π-π interactions of novel synthesized MDPA on the surface of MWNT/PGE was performed electrochemically, and the prepared stable, uniform and sensitive film (MDPA/MWNT/PGE) was used for direct determination of glucose for the first time. The improvement of electrooxidation response of glucose was completed using MDPA/MWNT/PGE nanocomposite. The surfaces of modified electrodes were characterized using scanning electron microscope and electrochemical impedance spectroscopy techniques. The effects of scan rate and pH on the peak potential and the peak current of glucose signal were determined. Interference studies were made to determine the selectivity of MDPA/MWNT/PGE for glucose.

2. Material and methods

2.1. Chemicals

COOH functionalized MWNTs from Nanografi (>95%, OD: 20-30 nm) were dissolved in water and the concentration of solution was adjusted to 1.00 mg mL^{-1}. MDPA was prepared as 1.00 mM in water. D-(+)-glucose (minimum 99.50 %) from Sigma was dissolved in 0.10 M NaOH from Merck and the concentration was adjusted to 5.00 mM. Boric acid, phosphoric acid and acetic acid from Merck were used to prepare 0.20 M Britton-Robinson (BR) buffer solution and pH was adjusted to 3.00 by using 1.00 M HCl and 1.00 M NaOH from Merck. 0.10 M phosphate buffer solution (PBS) at pH 7.00 was prepared from pellet dissolving in 100.00 mL water. $K_4Fe(CN)_6$ from AnalaR Analytical Reagents, $K_3Fe(CN)_6$ from the Fischer Scientific Company and KCl from Merck were used to prepare a 0.10 M redox solution for electrochemical impedance spectroscopy. Metal ions containing $CuCl_2.2H_2O$, $Fe(NO_3)_3$ and $AlCl_3.6H_2O$ from Merck were used 275-folds concentrated as 0.25 g mL^{-1}. L (+)-ascorbic acid

from Merck was used 132-folds concentrated as 0.12 g mL^{-1}. Other reagents were in analytical grade. In all analysis, pure N_2 gas was passed from all solutions for sufficient period of time to remove oxygen.

2.2. Instruments

Electrochemical experiments were performed on *CH Instruments CHI660C* model potentiostat with a conventional three electrode system which consisted of pencil graphite working electrode (PGE), silver/silver chloride reference electrode (Ag/AgCl) and platinum counter electrode. PGE was prepared using mechanical pencil *Model T 0.50* (Rotring, Germany) as a holder for pencil lead (Tombo, Japan) which was purchased from a local bookstore and a metallic wire was wrapped around the metallic part of the pencil to provide electrical contact to the lead. All leads had a total length of 60.00 mm and a diameter of 0.50 mm. A total of 10.00 mm of lead was immersed in solution per measurement. Surface area of PGE in such a length was 15.90 mm^2. SEM images of the modified surfaces were obtained using a *Zeiss Evo 60 EP-SEM* scanning electron microscope.

2.3. Deposition and surface morphologies of PGE

PGE surfaces were modified in 1.0 mM MDPA and 1.0 mg mL^{-1} MWNT solutions using 10 cycles coating by cyclic voltammetry (CV) between -1.0 V and +1.0 V vs. Ag/AgCl. The order of depositions was determined comparing the current enhancements of co-deposited, MDPA deposited and MWNT deposited PGEs in PBS at pH 7.0. The surface morphologies of PGEs were compared using scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS) techniques. The superiority of MDPA over MWNT was accepted and the surface was titled as MDPA/MWNT/PGE.

2.4. Detection of glucose

The detection of glucose in 5.0 mM glucose/0.1 M NaOH solution was performed using square wave voltammetry (SWV) between -0.8 V and 0.0 V vs. Ag/AgCl. The detection limit and linear range of glucose were calculated and the effects of co-existing substances including metal ions and ascorbic acid were determined.

3. Results and discussion

3.1. The amount of deposition thickness

The coverage of deposition is an important parameter for electrochemistry because it can influence the surface area and possible interactions between substances [17–19]. High accumulation with increase number of cycle can decrease the current enhancement. Therefore, the optimum thickness for co-deposition and single depositions of MDPA and MWNT was determined using various number of cycles (5 – 20) between -1.0 V and +1.0 V vs. Ag/AgCl, and the current responses were compared in PBS at pH 7.0. As could be seen from Table 1, maximum current enhancements were obtained using 10 cycles (red colored) in all surfaces and the experiments were performed in this condition.

Table 1. The effect of depositon cycles on the peak currents.

Number of cycles	**MWNT and MDPA co-deposited PGE Current (10^{-7} A)**	**MDPA deposited PGE Current (10^{-7} A)**	**MWNT deposited PGE Current (10^{-7} A)**
5	3.85	3.38	-18.12
10	9.25	6.01	-20.25
15	5.40	3.85	-5.93
20	6.98	3.66	-15.79

3.2. The order of deposition

The order of deposition of the carbon nanotubes and azo dyes, as well as their amounts of thickness, can influence the performance characteristic to behave as sensors. The best sensor performance and the best synergistic effect can vary with the order of deposition. If MDPA is deposited initially, the entry of MWNT to the pores of MDPA will be influenced by the degree of porosity. If MWNT is deposited first, the speed of movement of MDPA within the nanopores of MWNT during electropolymerization will be affected by polymer growth depending on size, geometry and ease of nucleation [20–22]. Therefore, cyclic voltammograms of 1.0 mg mL^{-1} MWNT and 1.0 mM MDPA co-deposited PGE, 1.0 mM MDPA over 1.0 mg mL^{-1} MWNT deposited PGE, 1.0 mg mL^{-1} MWNT over 1.0 mM MDPA deposited PGE and bare PGE in BR buffer at pH 3.0 between -0.4 V and +1.0 V vs. Ag/AgCl were compared in Fig. 1. The superiority of MDPA over MWNT deposited PGE (red line) was proved observing the current response of MDPA over MWNT as 5-folds higher than bare PGE (green line).

3.3. Surface morphologies of PGE

3.3.1. Characterization by EIS technique

EIS technique was performed to investigate the electron transfer capacities of 1.00 mg mL^{-1} MWNT and 1.00 mM MDPA co-deposited PGE, 1.00 mM MDPA over 1.00 mg mL^{-1} MWNT deposited PGE, 1.00 mg mL^{-1} MWNT over 1.00 mM MDPA deposited PGE and bare PGE. The impedance spectrum was obtained at +0.15 V vs. Ag/AgCl in 5.00 mM $Fe(CN)_6^{4-/3-}$ redox probe containing 0.10 M KCl. As could be seen from Fig. 2-a, in the presence of redox probe, all modified surfaces had a semi-circle in the high frequency region as a difference from bare PGE (green line) due to the charge transfer process, increase the porosity of the electrode surfaces and the active sides where faradaic reactions could occur [23]. The

semicircle diameter equals to the electron transfer resistance, R_{ct} which controls the electron transfer kinetics of the redox probe at the electrode interface (Fig. 2-g) and the order of R_{ct} was arranged as MDPA over MWNT deposited PGE (1296 Ω) > MWNT over MDPA deposited PGE (847.3 Ω) > MWNT and MDPA co-deposited PGE (546.8 Ω) > bare PGE (32.3 Ω), respectively. The highest R_{ct} at high frequency resulted in the best electrochemical architecture as in MDPA over MWNT deposited PGE (red line) [24]. The long linear portion at low frequency was obtained at bare PGE (green line) suggesting a small impedance at the surface. The CV results in Fig. 2-b were obtained between -1.00 V and +1.00 V vs. Ag/AgCl in 5.00 mM $Fe(CN)_6^{4-/3-}$ redox probe containing 0.10 M KCl. The highest peak enhancement occured at bare PGE (green line) and the lowest at MDPA over MWNT deposited PGE (red line), because PGE surface was interacted well using MDPA over MWNT decreasing the peak current.

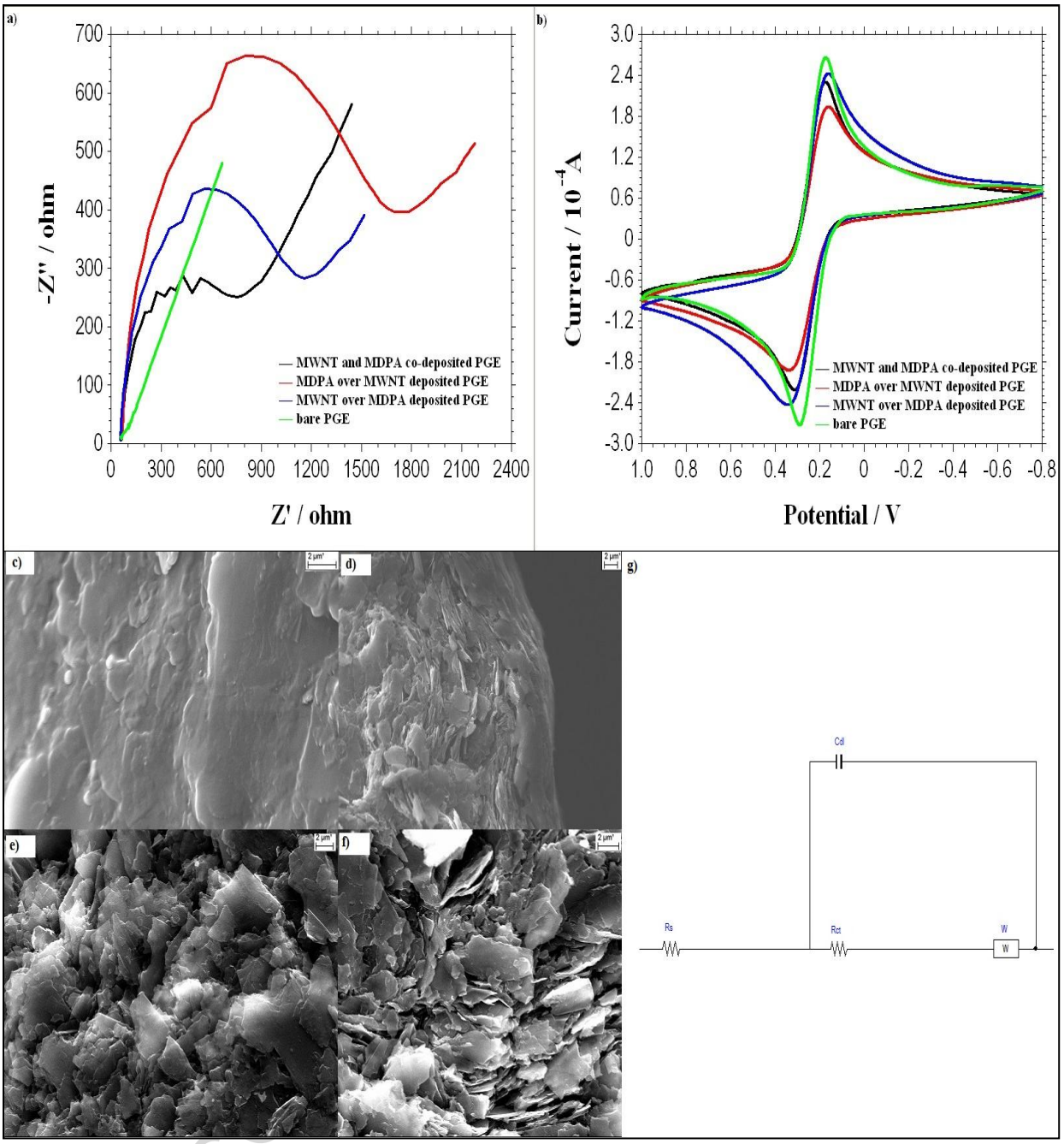

Fig. 2. a) EIS plots at +0.15 V vs. Ag/AgCl, **b)** cyclic voltammograms between -1.00 V and +1.00 V vs. Ag/AgCl of 1.00 mg mL^{-1} MWNT and 1.00 mM MDPA co-deposited PGE, 1.00 mM MDPA over 1.00 mg mL^{-1} MWNT deposited PGE, 1.00 mg mL^{-1} MWNT over 1.00 mM MDPA deposited PGE and bare PGE in 5.00 mM $Fe(CN)_6^{4-/3-}$ redox probe containing 0.10 M KCl and SEM images of **c)** bare PGE, **d)** MDPA/PGE, **e)** MWNT/PGE, **f)** MDPA/MWNT/PGE and **g)** equivalence circuit for EIS plots.

3.3.2. Characterization by SEM technique

The surface morphologies of bare PGE, MDPA/PGE, MWNT/PGE and MDPA/MWNT/PGE were investigated by SEM technique and the results were represented in Fig. 2. The coated nanoparticles were observed on MWNT/PGE (Fig. 2-e), but the MDPA/MWNT/PGE (Fig. 5-f) surface was more uniform and compact because of the covering of thin MDPA film on the surface of nanotubes. The nanopores as a different from both bare PGE (Fig. 2-c) and MDPA/PGE (Fig. 2-d) were seen obviously allowing the free entry of substrates such as glucose.

3.4. Detection of glucose

3.4.1. Electrochemical behaviors of glucose on different electrodes

Electrocatalytic performance of the modified surfaces towards the oxidation of glucose was investigated by SWV between -0.8 V and 0.0 V vs. Ag/AgCl in 0.1 M NaOH solution containing 5.0 mM glucose. SWVs of 1.0 mg mL^{-1} MWNT and 1.0 mM MDPA co-deposited PGE, 1.0 mM MDPA over 1.0 mg mL^{-1} MWNT deposited PGE, 1.0 mg mL^{-1} MWNT over 1.0 mM MDPA deposited PGE and bare PGE were represented in Fig. 3-a. Oxidation process of glucose started at -0.8 V following two oxidation peaks at -0.6 V and -0.4 V vs. Ag/AgCl. The results indicated that the modification improved the electrocatalytic activity towards the oxidation of glucose. The former peak was oxidation of glucose to glucolactone and the other was originated from consequent oxidation of glucolactone [25–26]. The main differentiation of MDPA over MWNT deposited PGE (red line) was obtained at -0.6 V vs. Ag/AgCl observing 5-folds higher current enhancements than bare PGE (green line) and the proposed surface was titled as MDPA/MWNT/PGE.

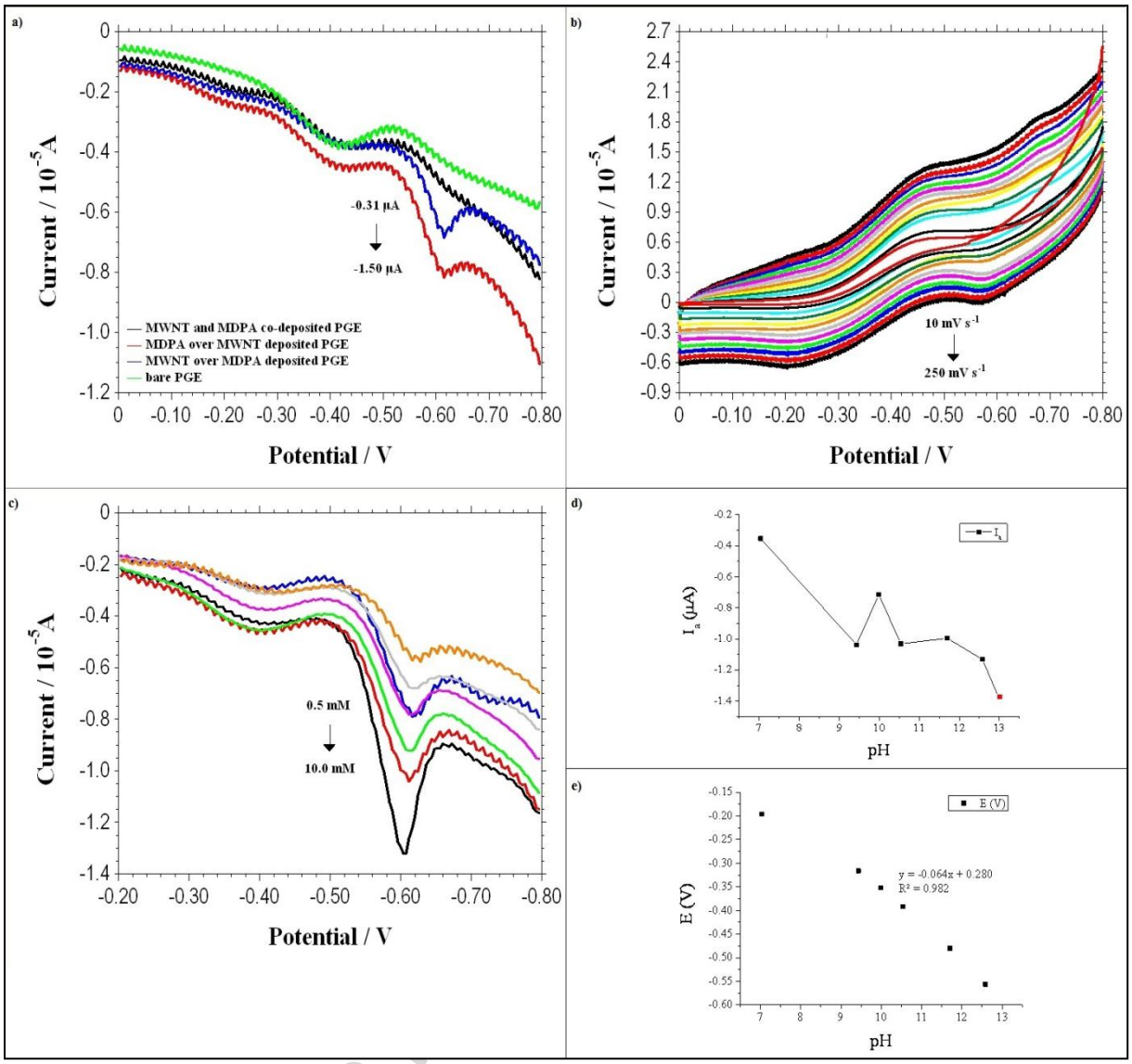

Fig. 3. a) Square wave voltammograms of 1.0 mg mL^{-1} MWNT and 1.0 mM MDPA co-deposited PGE, 1.0 mM MDPA over 1.0 mg mL^{-1} MWNT deposited PGE, 1.0 mg mL^{-1} MWNT over 1.0 mM MDPA deposited PGE and bare PGE between -0.8 V and 0.0 V vs. Ag/AgCl in 0.1 M NaOH solution containing 5.0 mM glucose, **b)** cyclic voltammograms of MDPA/MWNT/PGE between -0.8 V and 0.0 V vs. Ag/AgCl in 0.1 M NaOH solution containing 5.0 mM glucose in various scan rates between 10 and 250 mV s^{-1}, **c)** SWV response of glucose on MDPA/MWNT/PGE between -0.8 V and -0.2 V vs. Ag/AgCl in 0.1 M NaOH with successive addition of various concentrations of glucose and the plots of **d)** the anodic peak current (µA) vs. pH and **e)** the anodic peak potential (V) vs. pH.

3.4.2. Influence of scan rate

The influence of scan rate on the peak current and the peak potential was studied between -0.8 V and 0.0 V vs. Ag/AgCl in 0.1 M NaOH solution containing 5.0 mM glucose in various scan rates between 10 and 250 mV s^{-1}. As could be seen from Fig. 3-b, the anodic peak currents increased in negative side and the anodic peak potentials slided to more positive side with the increase scan rate.

The plots of the anodic peak current (μA) vs. scan rate [v (V s^{-1})] and the anodic peak potential (V) vs. natural logarithm of scan rate [ln (v / V s^{-1})] were given in Fig. 4. In Fig. 4-a, linear response of the peak current to scan rate between 10 and 250 mV s^{-1}, decrease the anodic peak current (I_a) with the increase scan rate and linear regression equation expression as I_a = –6.653 v – 0.580, R^2 = 0.993 suggested that the oxidation process of glucose at MDPA/MWNT/PGE was adsorption controlled. In Fig. 4-b, the oxidation peak potential (E_a) shifted to more positive side with the increase scan rate, had a linear relationship with ln v and the linear regression equation was E_a = 0.005 ln v – 0.573, R^2 = 0.985. The following Laviron's equation can be used for irreversible reactions [27]:

$$E_a = E^0 + (RT/\alpha nF) \ln (RTk^0/\alpha nF) + (RT/\alpha nF) \ln v \quad \textbf{(1)}$$

Where α is the electron transfer coefficient (0.5 for irreversible process), F is the Faraday constant (96485 C mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the Kelvin temperature (298 K), and n is the number of electron transferred. Therefore, the slope of Eq. 1 is equal to $RT/\alpha nF$. In this way, the electron transfer number (n) was calculated to be 10 suggesting that the electrooxidation of glucose at MDPA/MWNT/PGE was a ten-electron transfer mechanism.

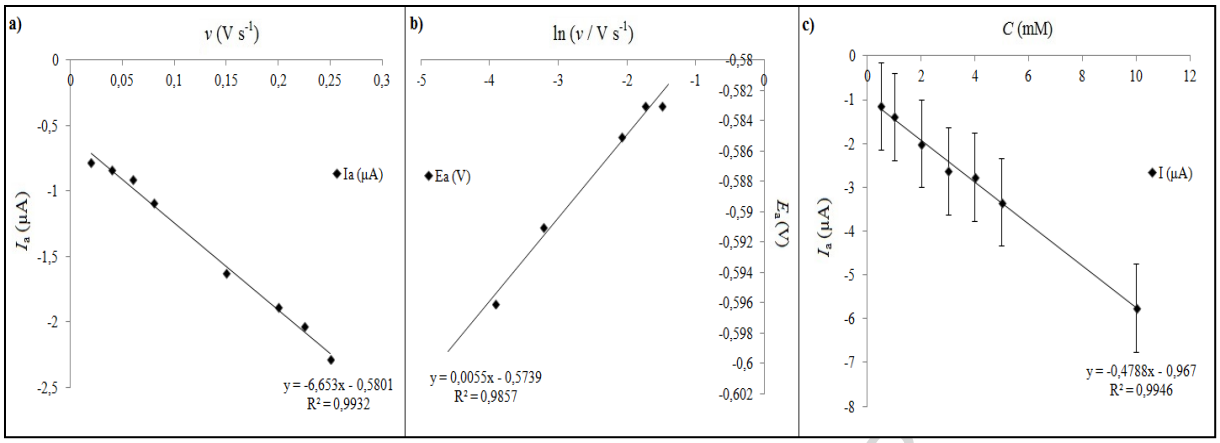

Fig. 4. The plots of **a)** the anodic peak current (µA) vs. scan rate [v (V s^{-1})], **b)** the anodic peak potential (V) vs. natural logarithm of scan rate [ln (v / V s^{-1})] and **c)** current (µA) vs. concentration (mM).

3.4.3. Influence of pH

It is generally accepted that chemisorption of hydroxide ions (OH^-) reduces the activation energy for the oxidation of glucose and facilates a stronger interaction between glucose and surface. Therefore, the effects of the peak current and the peak potential on pH were investigated in 0.1 M NaOH solution containing 5.0 mM glucose and the plots were represented in Fig. 3. The peak potential shifted to right as more negative side and the peak current increased negatively increasing pH. Nonenzymatic glucose detection is a pH-dependent reaction and an alkaline environment is beneficial to it, so higher sensitivity of nonenzymatic glucose detection is commonly observed in a higher pH environment. In this study, maximum current enhancement was observed at pH = 13 (red filled in Fig. 3-d) and the slope of graph (0.064 V pH^{-1}) in Fig. 3-e was near to Nernstian value (0.059 V pH^{-1}) signifying an equal number of protons and electrons involved in the electrochemical process for electrooxidation of glucose to glucolactone [28–29]. Also, glucose responses at lower pH values near to neutral were observed and will be improved to apply in human serum solution for the construction of biologically compatible sensors.

3.4.4. Determination of glucose on MDPA/MWNT/PGE

The response of glucose on MDPA/MWNT/PGE between -0.8 V and -0.2 V vs. Ag/AgCl in 0.1 M NaOH with the successive addition of various concentrations of glucose was determined by SWV and the results were given in Fig. 3-c.

The plot of current (μA) vs. concentration (mM) with error bars was represented in Fig. 4-c. The current response exhibited a linear relationship with the concentration of glucose in the range between 0.5 and 10.0 mM.

The linear regression equation was I (μA) = -0.478 C (mM) - 0.967, R = 0.994 and limit of detection (LOD) = 0.125 mM (S/N = 3). As parameters of various techniques and electrodes were compared in Table 2, MDPA/MWNT/PGE had an average LOD value. The mean normal blood glucose level in humans is about 5.5 mM, so the proposed technique can be applied in humans as 44-folds lower level using simple and rapid SWV technique.

Table 2. Comparison of parameters with previously studied techniques.

Electrode	**Linear Range (M)**	**Technique**	**LOD (μM)**	**Reference**
PtAg/MWCNT	$(1.0 – 2.4) \times 10^{-3}$	DPV	600.0	[30]
Porous Au	$2.0 \times 10^{-3} – 1.0 \times 10^{-2}$	Amperometry	5.0	[31]
Pt-Pb/CNT	Up to 1.1×10^{-2}	Amperometry	1.8	[32]
GNP/MWNT/CR	$5.0 \times 10^{-6} – 37.0 \times 10^{-3}$	Amperometry	0.5	[33]
MDPA/MWNT/PGE	$(0.5 – 10.0) \times 10^{-3}$	SWV	125.0	This work

3.5. Effect of co-existing substances

To evaluate the selectivity of proposed sensor, an interfering biomolecule such as ascorbic acid which co-exists with glucose in real samples and metal ions such as Al^{3+}, Cu^{2+} and Fe^{3+} were examined [34]. The effect of co-existing substances on the response of glucose was represented in Table 3. The relative error between 9 – 18 % indicated that 91 – 72 % current response of glucose was saved. Therefore, the selectivity was improved by negligible interference.

Table 3. The effect of co-existing substances on the response of glucose.

Co-existing Substance	Current (µA)	% Relative Error
Cu^{2+}	-1.224	+18.400
Fe^{3+}	-1.685	-12.300
Al^{3+}	-1.648	-9.900
ascorbic acid	-1.285	+14.300
ion-free	-1.500	theoretical value

4. Conclusions

In this study, a rapid, simple, low cost and convenient electrochemical method was developed to detect glucose based on MDPA/MWNT/PGE nanocomposite. The modification of film was applied using performance characteristics such as the amounts of thickness and the order of depositon, and the surfaces were illuminated using EIS and SEM techniques. The produced MDPA/MWNT/PGE sensor displayed a novel and competitive modification technique, an average limit of detection and high electrocatalytic activity towards glucose using square wave voltammetry differently from amperometry and literature. The results were satisfied to detect glucose levels in human serum adjusting neutral pH medium for biocompatibility.

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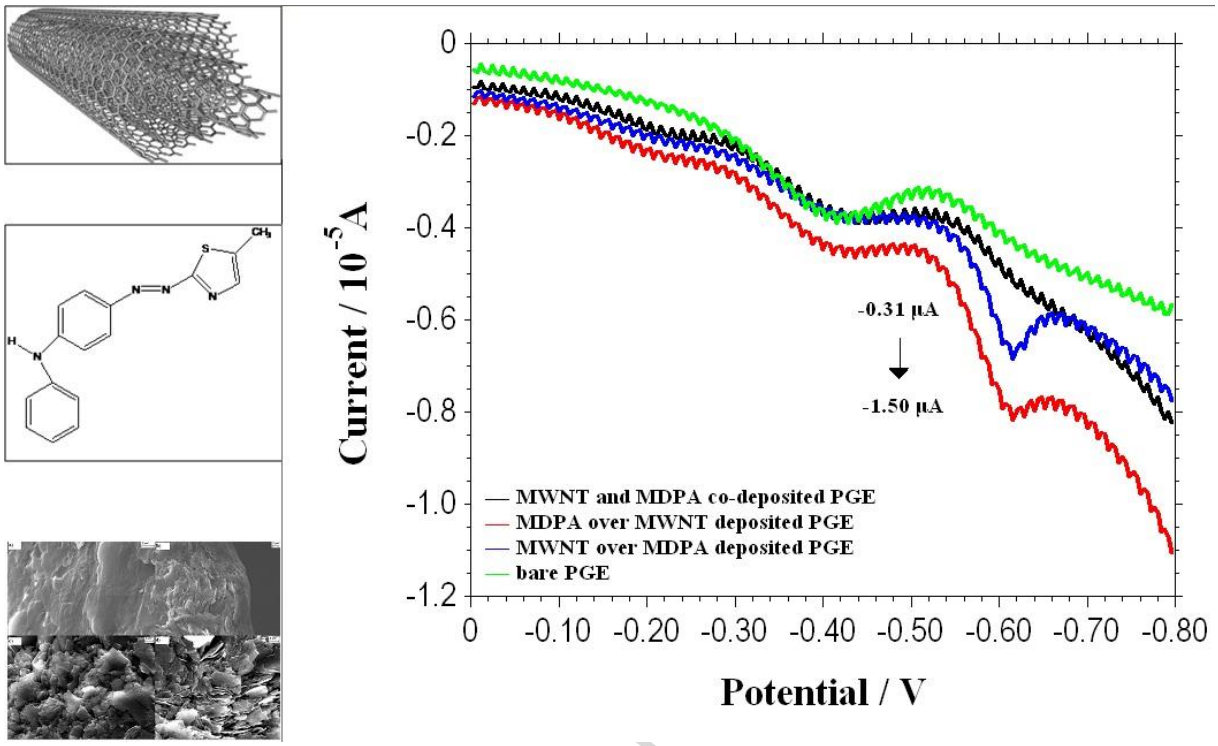
Graphical abstract



Highlights

- (*E*)-4-((5-methylthiazole-2-yl)diazenyl)-*N*-phenylaniline (MDPA) was a new azo dye.
- Electrochemical and nonenzymatic glucose sensor was obtained.
- The electrooxidation of glucose was determined on proposed composite.
- The effects of scan rate and pH were determined.
- Interference studies were performed to determine the selectivity.