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Electrochemically Activated Screen Printed Carbon Electrode Decorated with Nickel Nano Particles for the Detection of Glucose in Human Serum and Human Urine Sample

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A simple and sensitive amperometric enzyme-free glucose sensor was developed at the electrochemically activated screen printed carbon electrode (ASPCE) decorated with the nickel nanoparticles (NiNPs). We have applied simple electrochemical methods for the activation of SPCE, and the deposition of NiNPs on the ASPCE surface. The modified electrodes were characterized by the scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and electrochemical impedance spectroscopic methods (EIS). The electrocatalytic behavior of the modified electrode was studied by the cyclic voltammetry (CV), and amperometric method. The modified electrode exhibited good electrocatalytic behavior towards the oxidation of glucose with high oxidized peak current. In addition, the fabricated sensor exhibits the wide range of linearity between 5 µM to 1.5 mM with the high sensitivity of 1.9134 µA µM CM^{-1} and the limit of detection (LOD) is 0.28 µM. The prepared ASPCE/NiNPs electrode shows the good selectivity in the presence of common interfering molecules. The practical feasibility of the sensor exhibited acceptable recoveries in determination of glucose in human blood serum and human urine. Moreover, the fabricated sensor shows good selectivity, reproducibility, and repeatability.

Keywords: Activated screen printed carbon electrode, Nickel nanoparticle, Glucose, Electro catalysis, Electrochemical sensor, Human serum, Human urine.

1. INTRODUCTION

Development of glucose sensor is very much attention owing to its vital roles in different fields, including clinical diagnosis, food industries, environmental monitoring, pharmaceutical analysis and fuel cells [1]. In addition, more than 200 million peoples are affected by diabetes it is becoming a major affection throughout the world [2]. Therefore, the blood glucose needs to be measured with low-cost, high sensitivity and selectivity. Nowadays, glucose oxidase (GOx) immobilized enzyme electrodes have been used for glucose determination due to their high sensitivity and selectivity [3]. However, the enzyme electrodes have many drawbacks such as poor stability, high cost, critical operational temperature and complicated immobilization procedure. Moreover, the catalytic activity of glucose oxidase (GOx) has been affected by temperature and pH [4]. Hence, the non-enzymatic glucose sensor is more considerable one due to the developing, challenging and greatly demanded. So far, the carbon-based nanomaterials modified electrodes are widely used for the non-enzymatic glucose sensor. Especially, the carbon nanotubes modified glassy carbon electrode act as a good electrode material for glucose oxidation. Due to its unique properties, such as high surface area, good conductivity, high electrocatalytic activity and biocompatibility [5, 6, 7]. On the other hand, SPCE has more attraction due to its simplicity, low cost and easy modification with a variety of nanoparticles, requiring no pre-treatment such as electrode polishing [8-12]. Interestingly, the main objective of the enzyme-free modified SPCE was used as a personal glucose sensor by the diabetes patients [13-15]. Besides, for the electrode fabrication they have widely used the noble metals [16], metal alloys [17] and metal nanoparticles [18]. Even though, the metal nanoparticles are an important strategy in the fabrication of non-enzymatic glucose sensors such as Au [19], Ag [20], Pt [21], Ni [22], Cu [23] and Pd [24]. Furthermore, it has been exhibited better electrocatalytic performance towards glucose oxidation. Due to increasing the surface area and enhanced mass transport reaction [25-27]. The electrochemically deposited NiNPs electrode used to construct a high efficient and disposable non-enzymatic glucose sensor [28, 29]. Nickel (Ni) is a ferromagnetic, hard and ductile metal and it is used as a cathode material in fuel-cell. Moreover, it has been used as an alternate metal for expensive noble metals such as Au, Pt, and Ag [30]. In addition, increasing the catalytic activities of NiNPs based glucose sensors due to the agglomeration of NiNPs on the electrode surface. The catalytic process of the NiNPs modified electrodes through the formation of a high -valent oxyhydroxide species (NiOOH) in alkaline medium. The NiNPs modified electrodes have better stability and anti-fouling performance [31]. Y. Zhang et al reported non-enzymatic glucose sensor by RGO/NiNPs modified GCE electrode [33]. Here, we have proposed a non-enzymatic sensor using ASPCE/NiNPs for simple and selective detection of glucose without using carbon-based nanomaterials.

2. EXPERIMENTAL SECTION

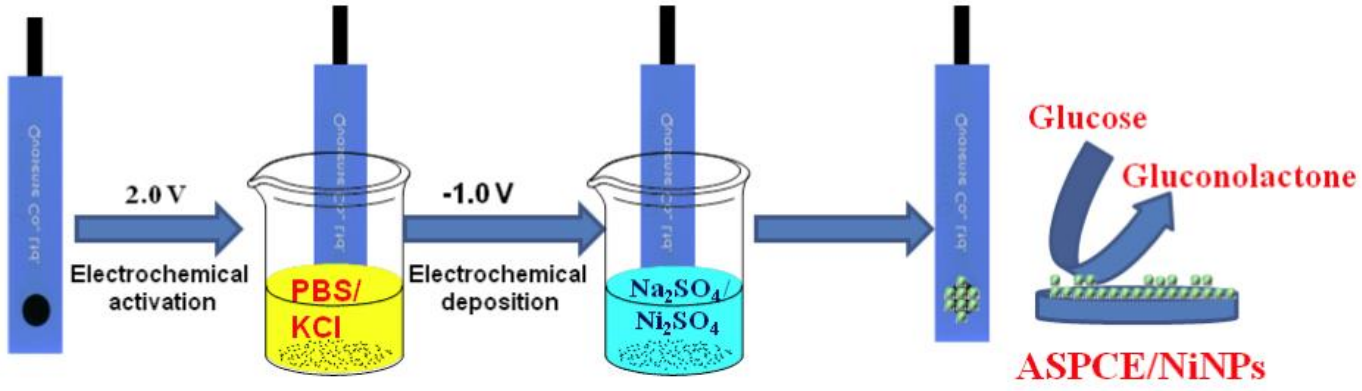
2.1. Materials and methods

Screen printed carbon electrode was purchased from Zensor R&D Co., Ltd. Taiwan. The nickel sulfate ($Ni_2SO_4 \cdot 6H_2O$), sodium sulfate (Na_2SO_4) and sodium hydroxide (NaOH) was purchased from Sigma-Aldrich and used as received. The human blood serum sample was collected from valley

biomedical, Taiwan product & services. Electrochemical experiment was carried out by the cyclic voltammetry (CV) and amperometric technique. Scanning electron microscope (SEM) was performed using Hitachi S-3000H electron microscope. An energy dispersive X-ray (EDX) spectra were recorded using HORIBA EMAX X-ACT attached to Hitachi S-3000H scanning electron microscope. Electrochemical impedance spectra (EIS) carried out by ZAHNER, (Kroanch, Germany) 0.1 Hz to 1 MHz frequency using for the impedance analysis. The atomic force microscope (AFM) images were recorded using a multi mode scanning probe microscope (Bejing, Nano-Instruments CSPM-4000, China). A conventional three electrode system was used for the electrochemical experiment, SPCE was used as a working electrode, platinum wire (0.5 mm) used as a counter electrode and Ag/AgCl (Sat. KCl) as a reference electrodes. Prior to the electrochemical experiments, the electrolyte solution was deoxygenated with purified nitrogen (N_2).

2.2. Fabrication of electrochemically activated screen printed carbon electrode with nickel nano particles (ASPCE/ NiNPs)

The ASPCE was prepared by previously reported methods [32]. In brief, the bare SPCE was first cleaned by bath sonication using ethanol containing water to remove the adsorbed materials on the surface. Then, the cleaned SPCE was transferred into an electrochemical cell containing PBS (pH 7) and KCl, followed by the potential difference was applied between 0 to 2.0 V up to 10 cycles for activation of SPCE (Fig. 1). After the activation, the electrode was dried at room temperature. Then, the ASPCE was transferred into the electrochemical cell containing 0.1 M Na_2SO_4 and 0.02 M Ni_2SO_4 for NiNPs deposition on ASPCE surface. In addition, the constant potential of -1.0 V was applied for 50s to the NiNPs deposition [33, 34]. Finally, the ASPCE/NiNPs (Scheme 1) was used for the detection of glucose without further treatment.



Scheme 1. Schematic presentation of fabrication of ASPCE/NiNPs electrode.

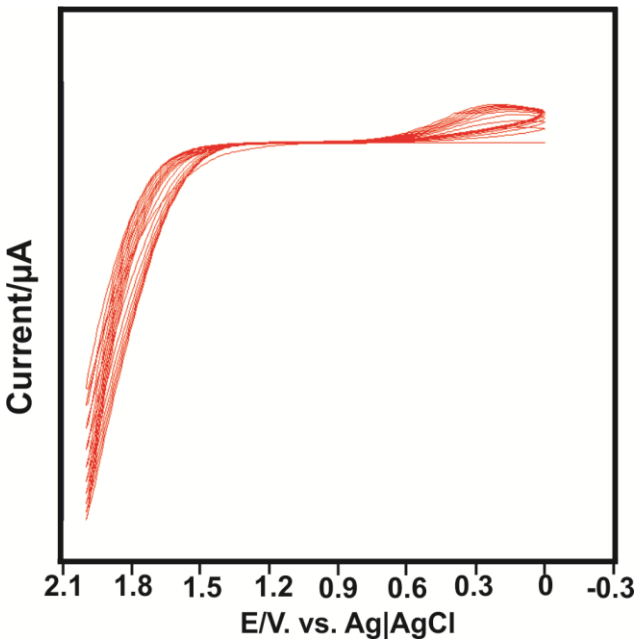


Figure 1. CV of electro chemically activated screen-printed carbon electrode

3. RESULT AND DISCUSSION

3.1. Characterization

Surface morphological studies were carried out by the scanning electron microscope (SEM). Fig. 2 shows the SEM image of bare SPCE (A), ASPCE (B), ASPCE/NiNPs (C, D) with different magnifications. The SEM image of ASPCE exhibits the more cracked surface along with large defects than that of the bare SPCE. It is confirmed that the electrochemical activation greatly affects the surface morphology of SPCE. Fig. 2Cand 2D exhibit the SEM image of ASPCE/NiNPs. It can be seen that the small ball like NiNPs equally distributed over the ASPCE surface with the average size range of 70 nm. The fabricated ASPCE/NiNPs was confirmed by the EDX spectral analysis shown in Fig 3A that observed the presence of Ni on the surface of ASPCE. The elemental mapping was used to investigate the elemental composition and distribution of the fabricated ASPCE/NiNPs electrode. Fig. 3B, C and D exhibit the elemental mapping of C, O and Ni respectively. The corresponding elemental mapping further confirms that the NiNPs present on the ASPCE surface.

EIS was used to investigate the impedance of the different modified electrodes at the electrode and electrolyte interfaces. Fig. 4 exhibit the EIS spectra of bare SPCE (a), ASPCE (b) and ASPCE/NiNPs (c) modified electrodes in PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1M KCl. Fig. 4 inset shows the Randles equivalent circuit model, whereas, the R_{ct}, C_{dl} and Z_w represents the charge transfer resistance, double layer capacitance and Warburg impedance respectively. The electron transfer kinetics of the modified electrode was calculated by the semicircle of the impedance spectra. Furthermore, the semicircle obtained from the parallel combination of electron transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) of the electrode. The bare SPCE shows a large semi circle with R_{ct} of 589 Ω, however the ASPCE with R_{ct} of 97.6 Ω was obtained. It revealed that the well electron transfer behavior of ASPCE, due to the electrochemical activation the charge transfer resistance was

decreased. On the other hand, the Ni nano particles deposited on the ASPCE (ASPCE/NiNPs) show the small semicircle with (R_{ct}) value 23.87 Ω compare with aforementioned electrodes. It clearly shows that NiNPs increase the surface area as well as enhance the electron transfer kinetics. This result exhibited that the ASPCE/NiNPs electrode has a higher electron transfer kinetics compared with other modified electrodes.

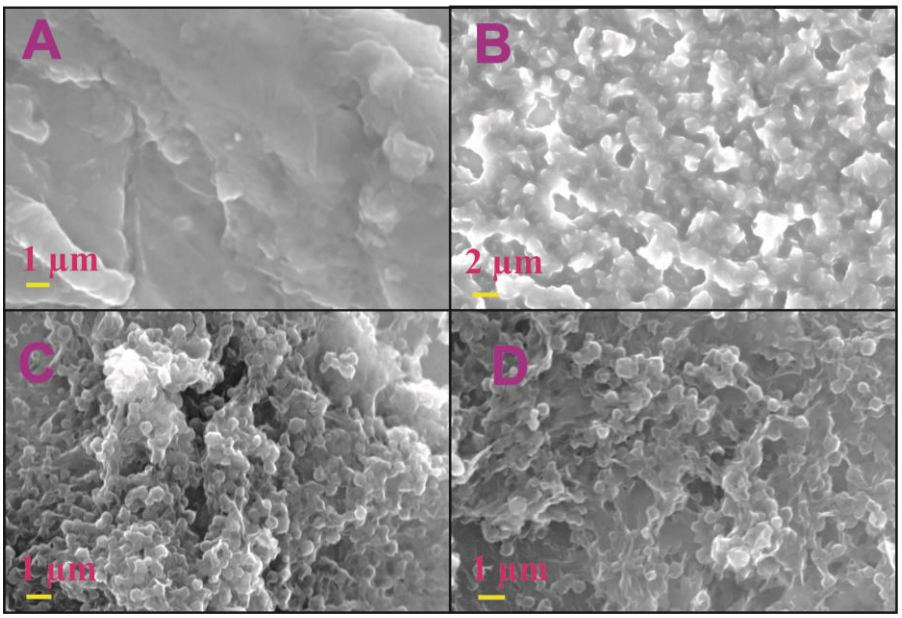


Figure 2. SEM image of bare SPCE (A), ASPCE (B), ASPCE/NiNPs (C, D)

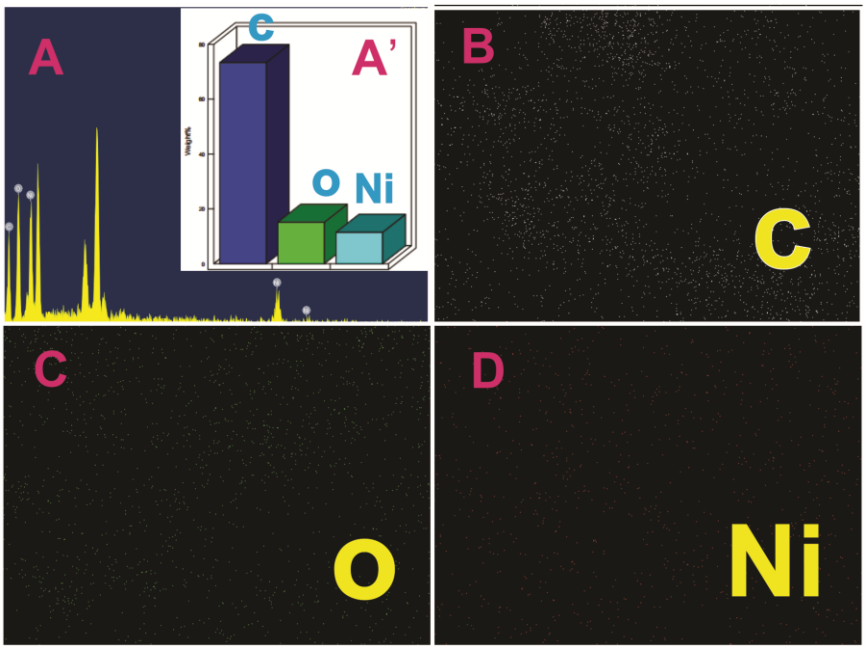


Figure 3. (A) shows the EDX spectrum of ASPCE/NiNPs. 3 (B), 3(C) and 3(D) shows the elemental mapping of Carbon, Oxygen and Nickel on the fabricated ASPCE/NiNPs electrode

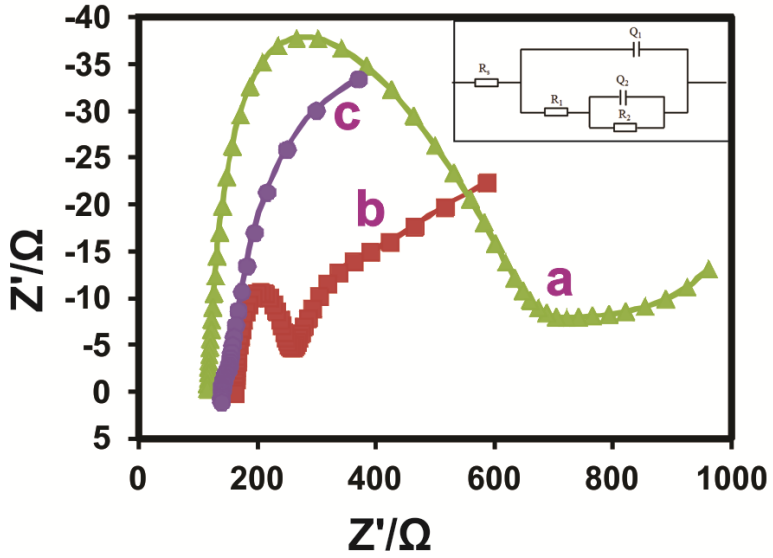


Figure 4. EIS of bare SPCE (a), ASPCE (b), ASPCE/NiNPs (c) modified electrodes in PBS containing 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl. Inset shows the Randles equivalent circuit model used for EIS analysis

3.2. Electrocatalytic behaviors of different modified electrodes

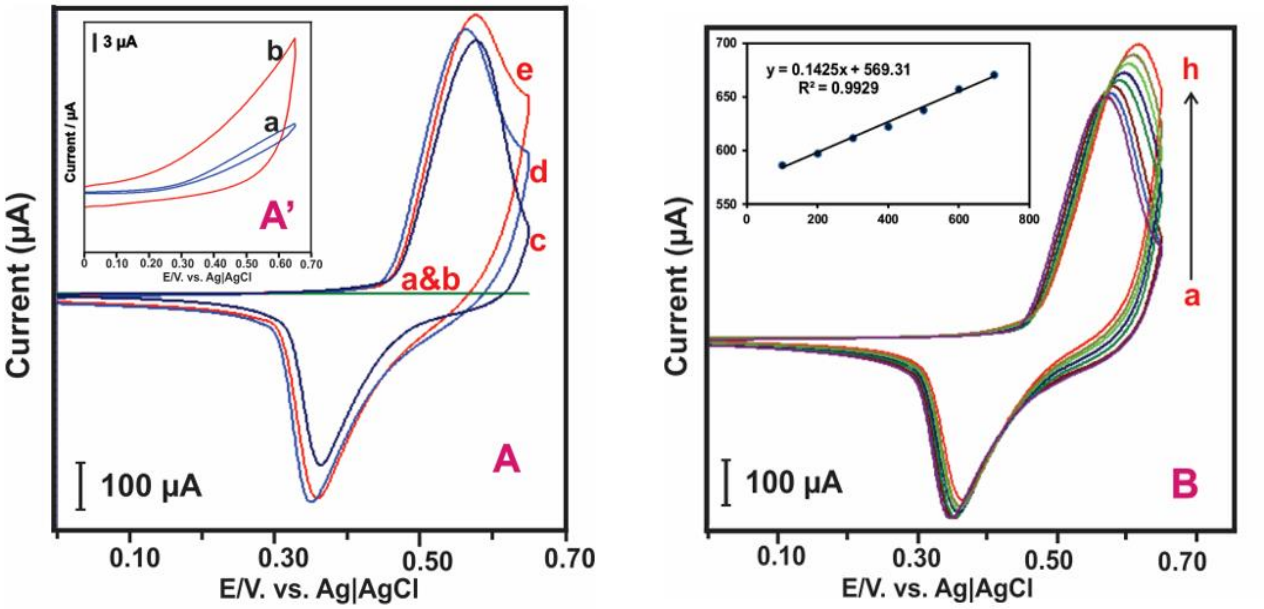


Figure 5. (A) CVs obtained at bare SPCE (a), ASPCE (b) SPCE/NiNPs (c) ASPCE/NiNPs (e) film modified electrodes in 0.1 M NaOH containing 200 µM glucose and ASPCE/NiNPs (d) in the absence of glucose at the scan rate 50 mV s^{-1} and 5 (A') Inset shows the bare SPCE (a), ASPCE (b) in 0.1 M NaOH containing 1mM glucose. Figure 5B shows CVs obtained at the ASPCE/NiNPs fabricated electrode in the absence (a) and presence (b–h) of each 200 µM glucose addition in 0.1 M NaOH at scan rate 50 mVs^{-1}.

The electrocatalytic behavior of the modified electrodes was examined, towards the electrocatalytic oxidation of 200 µM glucose in nitrogen saturated 0.1 M NaOH solution at a scan rate of 50 mVs^{-1} by CV. Fig. 5A shows the CVs of SPCE (a), ASPCE (b), SPCE/NiNPs (c), ASPCE/NiNPs (e) in the presence of glucose and the ASPCE/NiNPs (d) shows absence of glucose. For comparison, the CVs of SPCE (a) and ASPCE (b) have been compared and the results are shown in Fig. 5A' (inset). Compare to bare SPCE, the ASPCE exhibited high capacitance and more catalytic activity towards the oxidation of glucose. The enhanced capacitance of ASPCE is resulting from the high surface area of ASPCE. On the other hand, a well-defined redox pair peak was observed at ASPCE-NiNPs (d) without the addition of glucose. This is due to the oxidation and reduction of Ni in alkaline medium whereas the redox peak corresponds to $Ni^{(III)}$ / $Ni^{(II)}$. After the addition of 1mM glucose, the anodic peak current was increased. In addition, compare to SPCE/NiNPs (c), the ASPCE/NiNPs (e) shows higher oxidation peak current at low oxidation potential of 0.52 V. It revealed, the ASPCE/NiNPs exhibited a better electrocatalytic activity due to the high surface area of the modified electrode by activating the SPCE and therefore enhancing the deposition of NiNPs on its surface. Hence, we activated the SPCE for preparing the non-enzymatic glucose sensor. The electrocatalytic activity of the modified electrode was evaluated by CV at different scan rate from 10 to 100 mV in nitrogen saturated 0.1M NaOH. Fig. 6A exhibited the CVs of glucose oxidation at ASPCE/NiNPs modified electrode in the presence of 200 µM glucose. Herein, both anodic (I_{pa}) and cathodic (I_{pc}) peaks are increased linearly with increasing the scan rate. Fig. 6B shows the anodic and cathodic peak current response Vs square root of scan rate exhibited the linear relationship. It can be seen that the glucose oxidation at ASPCE/NiNPs fabricated electrode as a diffusion controlled process.

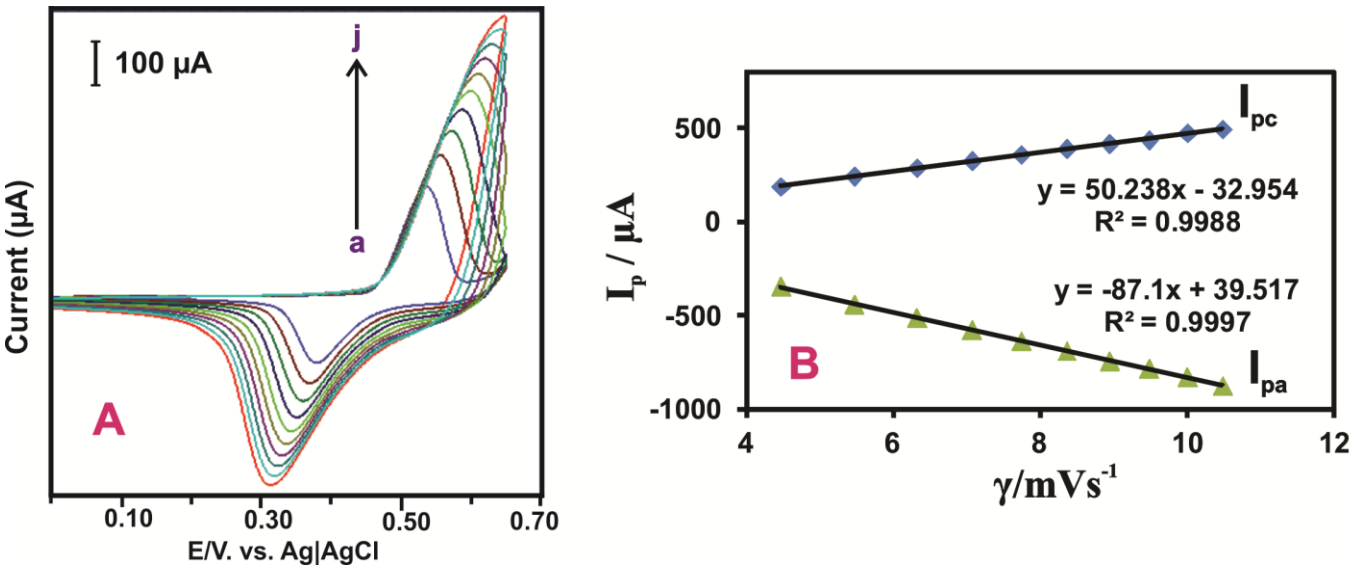


Figure 6. (A) The cyclic voltammetric response of ASPCE/NiNPs in 0.1M NaOH containing 200 µM glucose at different scan rate from 0.01 to 0.1 V s-1 (a-j). 6 (B) Linear plot for I_{pa} vs square root of scan rate.

3.3. Electrocatalytic oxidation of glucose at ASPCE/NiNPs modified electrode

The electrocatalytic oxidation of glucose at ASPCE/NiNPs modified electrode was studied varying the concentration of glucose 200 to 800 µM in deoxygenated 0.1M NaOH. The obtained CV results were displayed in Fig. 5B. The anodic peak current response was increased linearly with increasing the concentration of glucose from 200 to 800 µM. In addition, the absence of glucose in 0.1M NaOH solution, the ASPCE/NiNPs modified electrode exhibited a pair of redox peaks, which is due to the oxidation of (Ni^{III}) and reduction of (Ni^{II}) of Ni in alkaline medium [35, 28]. When the Ni is immersed in alkaline solutions it forms $Ni(OH)_2$, due to the dissolution of the metal [36]. In the absence of glucose, the oxidation and reduction peaks of the modified electrode correspond to the oxidation of $Ni(OH)_2$ to NiOOH and the reduction of NiOOH to $Ni(OH)_2$ vice versa. In addition, when the glucose was added, a catalytic reaction was performed thus leads to increase the anodic peak current. The anodic peak potential was shifted to positive side during the positive scan and suggests that the high-valent NiOOH oxidizes the glucose into gluconolactone. This can be explained by the following mechanism,

$$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^- \quad (1)$$

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \quad (2)$$

$$NiOOH + \text{glucose} \rightarrow Ni(OH)_2 + \text{glucolactone} \quad (3)$$

From the results, the glucose molecules were adsorbed and oxidized on the surface of $Ni(OH)_2$ in ASPCE/NiNPs modified electrode parallel to the oxidation of Ni $^{(II)}$ to Ni $^{(III)}$. In addition, the oxidation of $Ni(OH)_2$ to NiOOH decreasing the glucose absorption with the poisoning effect of the intermediates. Therefore, the anodic peak shifts occurred at the ASPCE/NiNPs modified electrode during the glucose oxidation [29, 33, 37].

3.4. Amperometric determination of glucose

The amperometric response of the glucose at ASPCE/NiNPs modified electrode was performed in nitrogen saturated 0.1M NaOH with the continuous stirring at 1500 RPM. Fig. 7 shows the amperometric response of the glucose with the sequential addition for each 50 seconds and the applied electrode potential was held at 0.5 V. The sharp amperometric response was observed for addition of 2.5 µM glucose up to 1.5 mM. The modified electrode ASPCE/NiNPs shows the wide linearity ranging from 5 µM to 1.5 mM. A calibration plot was made between the concentration of glucose and the peak current; the corresponding linear regression equation can be expressed as (4)

$$I_p(\mu A) = 0.269\ [\text{glucose}](\mu A\ mM^{-1}) + 15.07\ (\mu A),\ R^2=0.992 \quad (4)$$

The sensitivity of the fabricated sensor was calculated to be 1.9134 µA μM^{-1}, and the limit of detection (LOD) was 0.28 µM based on the $3\sigma/s$ formula. Here, σ is the standard deviation and s is the slope

value. The fabricated sensor in this work shows better performance compared with the previously reported other glucose sensors. Moreover, the comparison results are shown in Table1.

Table 1. Comparison of analytical performance of ASPCE/NiNPs electrode with other reports for the detection of glucose.

Electrode	Linear range	Limit of detection (µM)	References
NiONPs	0.01 mM -2.14 mM	1.7	[38]
Ni NPs/TiO_2NTs	0.004 mM -4.8 mM	2	[39]
NiNPs/GCE	5 µM-1.155 mM	1	[40]
GNs/ZnO/GOx	0.3 mM -4.5 mM	70	[41]
MSN/Ni-Co/GCE	0.00 1 mM -5.0 mM	0.39	[30]
GOD–CS–HRP/AgNTs/GCE	0.01 mM -1.5 mM	0.69	[42]
Tio_2/Polyaniline	0.02 mM to 6.0 mM	18	[43]
GOD/HFs/GCE	0.05 to 1.0 mM	5	[44]
CuNPs/N-GO	0.004-4.5 mM	1.3	[45]
TCS-TiO2/GOx	5.0 µM to 1.3 mM	2.0	[46]
GOx/PtNPs/PAMAM-Sil-rGO/GCE	10 µM to 8.1 mM	0.8	[47]
RGO/AuNPs	1 to 8 mM	10	[48]
Au–Ni coaxial nanorad array	27.5 µM–27.5 mM	5.5	[49]
MOSF/ GOx	50 to 1950 µM,	4.2	[50]
CNT–Ni	5 µM–2 mM	2	[51]
GR–CNT–ZnO–GOx	10 µM to 6.5 mM	4.5	[52]
ASPCE/NiNPs	2.5 µM -1.5 mM	0.28	This work

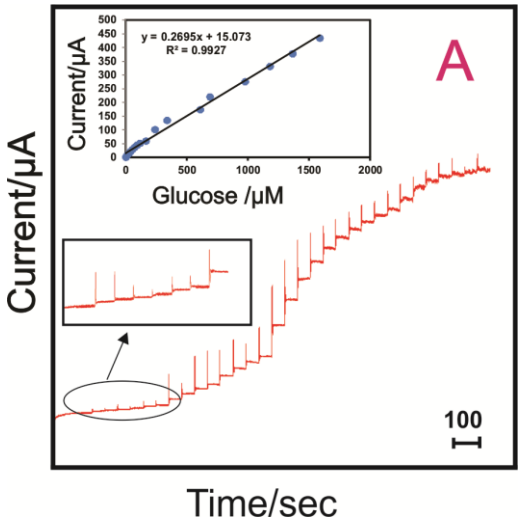


Figure 7. Amperometric response obtained at the ASPCE/NiNPs modified electrode into continuously stirred 0.1M NaOH, applied potential 0.5 V.

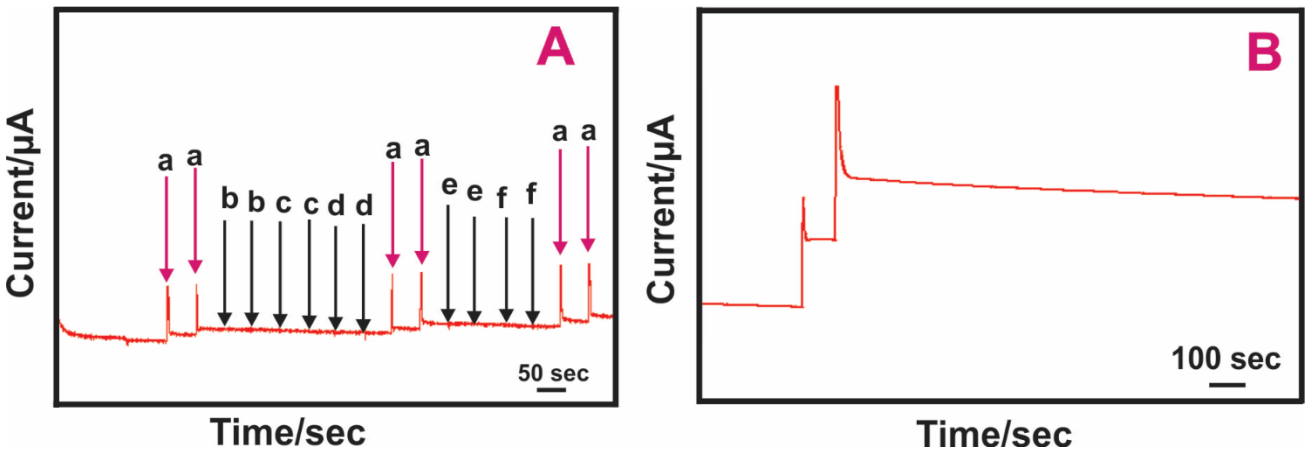


Figure 8. (A) Amperometric response of ASPCE/NiNPs modified electrode upon addition of 500 µM glucose (a) and 5 mM concentration of ascorbic acid (b), uric acid (c), dopamine (d). **(B)**Amperometric stability studies ASPCE/NiNPs fabricated electrode into continuously

3.5. Repeatability, reproducibility and stability of the proposed sensor

The repeatability and reproducibility of the proposed sensor were carried out by the CV. The ASPCE/NiNPs modified electrode exhibited the acceptable repeatability with the RSD of 2.35 % for ten successive repeated measurements in a single modified electrode. In addition, the fabricated sensor shows excellent reproducibility with an RSD of 2.51 % for five individual measurements carried out at five different modified electrodes. Moreover, the storage stability of the modified electrode was carried out by the CV technique. The ASPCE/NiNPs has retained 96.21 % of its initial current after one-month storage revealing its appreciable storage stability. The Figure 8B shows the investigation of operational stability to the ASPCE/NiNPs modified electrode in the presence of 5 mM glucose at 1500 RPM into continuously stirred 0.1M NaOH for 1000 Sec. The stability studies reveal that only 6 % current was decrease from the initial current continuously operated ASPCE/NiNPs modified electrode. It is indicating that the excellent operational stability of the ASPCE/NiNPs modified electrode.

3.6. Determination of glucose in blood serum and urine sample

The practicality of the ASPCE/NiNPs modified electrode has been carried out for the glucose determination in the human blood, serum and urine sample. The human blood serum and the urine sample was collected from the healthy man. The collected human blood sample was allowed to clot and the clot was removed by centrifugation for 15 min at the speed of 1500 RPM. The blood serum sample was separated and stored at the -20 °C. Furthermore, the collected urine sample was filtered with Whatman filter paper and diluted in the ratio of 1: 50 with the addition of 0.1 M NaOH (37). An amperometric method (i-t) was used for the real sample analysis and the experimental condition was similar to the section 3.3. It can be seen from the table 2 and 3 the appreciable recovery (93.5 % and 91.9 %) was obtained for the glucose detection. Moreover, the obtained results are good agreement

with the commercial sensor. Therefore, the ASPCE/NiNPs can be used as a suitable electrode material for the detection of glucose in any unknown biological samples.

Table 2. The electrochemical detection of glucose in human blood serum at ASPCE/NiNPs fabricated electrode

Sample	Glucose added (µM)	Glucose found (µM)	Recovery (%)	RSD (%)
1	10	9.2	92	3.18
2	20	18.7	93.5	2.36
3	30	28.5	95	2.40

Table 3. The electrochemical detection of glucose in human urine sample at ASPCE/NiNPs fabricated electrode.

Sample	Glucose added (µM)	Glucose found (µM)	Recovery (%)	RSD (%)
1	10	8.7	87	2.92
2	20	18.3	91.5	3.62
3	30	29.2	97.3	3.45

3.7. Selectivity of the ASPCE/NiNPs modified sensor

The selectivity of the ASPCE/NiNPs modified electrode was evaluated by the amperometric method. The electro active molecules are co-existed with human blood and their oxidized potential is similar to the glucose oxidized potential. Therefore, the selectivity of ASPCE/NiNPs fabricated electrode is the most important one. Fig. 8A shows the amperometric response of the ASPCE/NiNPs modified electrode upon the addition of 500 µM glucose (a) and 5 mM of common interfering molecules such as ascorbic acid (b), uric acid (c), dopamine (d). A stable and notable amperometric response was obtained for the addition of 500 µM glucose and there is no peak appeared for the addition of other interfering molecules. These results are confirmed that the ASPCE/NiNPs modified electrode have high selectivity for the detection of glucose even in the presence of interfering molecules.

4. CONCLUSION

For the first time, we have fabricated the non enzymatic glucose sensor without using carbon nanomaterials. The fabricated ASPCE/NiNPs electrode exhibited good electrocatalytic behaviour towards oxidation of glucose in 0.1 M NaOH. The prepared non-enzymatic glucose sensor shows good analytical response such as wide linearity 5 µM to 1.5 mM with the high sensitivity of 1.9134 µA µM CM^{-1} and the limit of detection (LOD) 0.28 µM. In addition, the fabricated sensor shows good

selectivity towards detection of glucose in the presence of common interfering molecules. The fabricated sensor shows good recoveries for real sample studies in human blood and urine samples. The ASPCE/NiNPs exhibited the good repeatability, reproducibility, and stability towards the glucose determination.

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