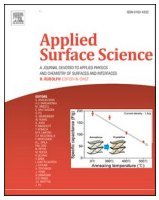
Applied Surface Science 706 (2025) 163588

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc



Full Length Article

Laser-assisted fabrication of new ultrasensitive sensors based on Pd/Graphene/Copper heterogeneous layers for glucose detection

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ARTICLE INFO

Keywords:
Graphene
Palladium Nanoparticles
Glucose
Electrochemical Sensing
Sensitivity
Limit of Detection

ABSTRACT

In this work, we report for the first time a new Palladium (Pd)/Graphene (GR)/Copper (Cu) electrode fabricated with a new way that consists of pulsed liquid laser ablation (PLAL) and drop casting. Pd nanoparticles fabricated by PLAL were dropped into a single layer of graphene and dried at 80 °C. Pd/GR/Cu electrodes were tested towards the detection of glucose using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). With both techniques the detection limit was 0.5 mM and the quantification range was between 0.5 mM to 13.0 mM. The sensitivity values were high, 0.245 $mA.mM^{-1}.cm^{-2}$ by CV and 81.3 $Ohm.mM^{-1}.cm^{-2}$ by EIS. The findings underscore the potential of this novel Pd/GR/Cu electrode as a highly sensitive and stable non-enzymatic sensor for glucose detection, offering significant advancements in biosensing technology.

1. Introduction

During the last decades, enzymatic sensors have shown some disadvantages such as their high fabrication costs, instability, pH reliance, and other drawbacks [1,2]. That's why during the last years non-enzymatic electrochemical sensors have attracted more attention owing to their advantageous properties-over the enzymatic sensors, such as their cost effectiveness, simplicity, stability, and reproducibility [1,3–5].

Graphene (GR) based sensors are widely used in different applications where highly efficiency biosensing is required such as glucose detection. GR is known to have excellent electrical conductivity, excellent stability, wide potential window, and affordability [5–8]. In fact, graphene and its derivatives are extensively employed as the transducer element in fabricating nano-biosensors such as metal/GR [9]. In the last years, evolving electrochemical sensors based on metal/GR, has increased largely, due to its excellent properties. For example, Nugba et al. developed a high-performance Cu-Ni decorated laser-induced GR sensor for nonenzymatic glucose monitoring in sweat[10]. Lu et al. developed mouthguard electrochemical sensor for salivary glucose detection based on Pt metal hydrogel [11]. Kim et al. fabricated a flexible non-enzymatic electrochemical sensor using a Cu nanoparticle/laser-induced GR fiber/porous laser-induced GR network electrode [12]. Dogan et al. synthesized non-enzymatic amperometric detection of glucose on one-pot electrochemical fabricated Palladium (Pd) nanoparticles (NPs)-GR modified electrodes [13]. Although the performance obtained in these sensors, there remain still some drawbacks such as, their high cost, the complex structure of sensors, chemical reagents resulting from the chemical synthesis method, etc. Therefore, there is still a need to overcome these challenges by developing new sensors based on Pd/GR. Given their high electrocatalytic, high reactivity, fast oxidation process, Pd nanostructures have been explored towards different applications, such as sensing, fuel energy storage, catalysis, and hydrogen production via water splitting [13–20]. Pd nanostructures used as sensors, have been improved by combining it with other materials such as GR [5,13,16,21,22]. Pd nanostructures fabricated by physical, top-down approach are of great interest because the synthesized nanostructure surfaces are pure and do not contain reagents and other chemicals, moreover, these nanostructures will be less costly than purchasing or synthesized chemically fabrication of highly sensitive

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https://doi.org/10.1016/j.apsusc.2025.163588
Received 17 February 2025; Received in revised form 24 April 2025; Accepted 20 May 2025
Available online 20 May 2025

sensing devices sensors using Pd nanostructures by chemical methods, such as chemical bath, sol–gel, photo-deposition, and electrodeposition are reported in different studies [16,23–26]. Pd shows an electrocatalytic activity towards the oxidation of several substances including glucose. In literature there are few works regarding the use of pure palladium obtained with Pulsed Laser Ablation in Liquid (PLAL) for applications in electrochemical sensors of glucose. Therefore, in this work we studied the electrocatalytic activity of palladium nanoparticles obtained by PLAL which allows to obtain nanoparticles with a surface free from capping agents and, thus, much more reactive. Furthermore, from a general point of view, non-enzymatic glucose sensors based on 3d series transition metal are low cost, but are unstable because their response depends on the presence of other species and they are sensitive to humidity. Therefore, the future goal of the present work is to realize stable non-enzymatic glucose sensors for self-monitoring or continuous glucose monitoring system applications. This is due to the fact that palladium is well tolerated at the skin level and does not cause allergic reactions. Sensors based on Pd are stable. Furthermore, Pd is a metal that its currently cost is less than half of gold, another element suitable for realizing stable non-enzymatic glucose sensors. However, there is less work using Pd/GR/Cu for glucose detection with Pd fabricated by a physical method especially using PLAL method and drop casting [27–29]. Moreover, the simplicity, easy usage, eco-friendliness and cost effectiveness of the PLAL method disseminate this work than other actual methods. In this work, we designed a sensor that contains different parts: 1-copper as support, 2-single layer graphene as transducers, 3- Pd as highly sensitive materials. In literature there are few works regarding the use of pure palladium obtained with Pulsed Laser Ablation in Liquid (PLAL) for applications in electrochemical sensors of glucose. Therefore, in this work we studied the electrocatalytic activity of palladium nanoparticles obtained by PLAL which allows to obtain nanoparticles with a surface free from capping agents and, thus, much more reactive. The novelty of this work consists of developing new non-enzymatic electrochemical sensing devices using Pd deposited on a single layer of graphene for ultra-sensitive detection of glucose. The graphene layer acts as a good mediator with the copper film support and provides excellent dispersion of electroactive palladium nanoparticles, increases the surface area of active centers, and facilitates electron transfers and diffusion of glucose onto the surface of modified copper electrode. Graphene layer having large surface area enables immobilization of lead nanoparticles and leads to very fast electron transfer between the palladium active centers, glucose and copper film surface. This caused the prepared modified palladium electrode to have high electrical conductivity and stability.

The performance of the sensors was evaluated towards the glucose detection using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The Pd/GR/Cu sensors showed high sensitivity of 245 $\mu A.mM^{-1}.cm^{-2}$ by CV and 81.3 $Ohm.mM^{-1}.cm^{-2}$ by EIS. The detection limit of 0.5 mM, and detection range of concentration was 0.5–13.0 mM. These results obtained from the sensors, with their cost-effective, eco-environmental, and simplicity, open the ways for glucose's real monitoring applications.

2. Experimental section

2.1. Characterization methods

Scanning electron microscopy (SEM) was used to study the samples surface morphology using a Zeiss FEG-SEM Supra 25 Microscope operating at 5 kV. A confocal Raman microscope (LabRAM HR800, Horiba Scientific, Villeneuve-D'Ascq, France) was used in a backscattering geometry with a spectral resolution of 0.23 cm^{-1} at ambient temperature to record Raman spectra. A He-Ne Laser of $\lambda = 632.8$ nm with an output power of 2 mW, an objective of 50X and a grating of 1800 L/mm were used for the Raman measurement. An Instrument Gamry potentiostat/galvanostat/ZRA Reference 600 having software v7 has been used for electrochemical cyclic voltammetry and impedance measurements. The three-electrode cell used consists of: 1) reference electrode (saturated silver − silver chloride electrodes (sat. Ag/AgCl)), 2) counter electrode (platinum wire 0.5 mm), and 3) a working electrode (Pd/graphene/copper film (Pd/GR/Cu), with area of 1 cm^2, mounted on a silver wire (1 mm)) to maintain electrical connection with the potentiostat. A 0.5 M NaOH solution was employed as an electrolyte. For the impedance measurement, a sinusoidal voltage perturbation of amplitude 10 mV rms (potentiostatic mode) was applied in the frequency range 100 kHz–0.1 Hz with 10 points/decade. Chemicals: Glucose ≥99.5 % and NaOH ≥ 98 % were purchased from Sigma-Aldrich. In a typical electrochemical measurement experiment, a glucose stock solution (1 M) was prepared by dissolving 1.8015 gm of glucose in 10 ml deionized water. Then aliquot of 0.02 ml up to 0.25 ml of the glucose stock solution was added to 20 ml NaOH (0.5 M) in order to obtain the glucose analyte solution ranging from 0.999 mM to 12.34 mM.

2.2. Fabrication

Dispersion of Pd (NPs) was produced by the laser ablation of a corresponding metallic target held in liquid (Fig. 1). A target of Pd plate with purity of 99,9 % was used as a target (from Quorum Technologies). In particular, a pulsed Nd: Yttrium Aluminum Garnet YAG Laser (Quanta-ray PRO-Series pulsed Nd:YAG laser) operating at $\lambda = 1064$ nm, with a 10 ns duration of the pulse, at repetition rate of 10 Hz, with 6 W of power and fluence of 5 J/cm^2 was used to perform the laser ablation process. The beam laser was focused, perpendicularly aligned, to the Pd target by means of 20 cm focal length a lens. The Pd target was placed at the bottom of a Teflon vessel filled with 8 mL of deionized Milli-Q water (resistivity 18MΩ cm). During the irradiation of the target, the solution's color becomes brown. The irradiation time was 12 min to obtain highly concentrated nanoparticles dispersions.

The target has been weighed before and after the ablation process using a micro analytical balance in order to estimate the total amount of the ablated material released in the solution resulting in a Pd concentration of $\sim 11 \times 10^{-2}$ gram/liter. All the solutions have been kept in the fridge at 3 °C to prevent the nanoparticles' agglomeration.

Graphene substrates, synthesized via the chemical vapor deposition method, were delivered from Graphene Laboratories (NY, USA, graphene-supermarket.com). Single layer graphene was grown directly on copper foil. A continuous single-layer graphene film is deposited across copper surface steps and grain boundaries.

To fabricate the Pd nanoparticles/Graphene electrodes, a drop (20 μL) of the nanoparticle dispersion was cast on the GR/Gu foil (onto the

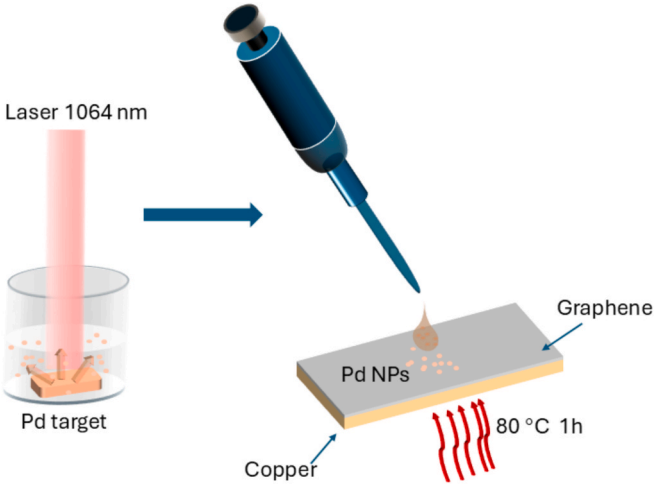

Fig. 1. Schematic representation of the fabrication process Pd/GR/Cu electrode.

graphene side) and dried on a hot plate at 80 °C for 1 h (Fig. 2). This temperature was optimized to have a sufficiently slow evaporation of the solvent from the drop and resulting in an homogeneous dispersion of separated Pd nanoparticles on the graphene surface and avoiding formation of aggregates of Pd nanoparticles. In addition, the deposition of Pd nanoparticles onto graphene was preceded by an ultrasonic dispersion process, on the colloidal suspension, in order to further avoid the agglomeration of Pd nanoparticles. This process results in a single layer of Pd NPs over the graphene surface. We think that the adhesion of the Pd NPs on the graphene surface is high enough to guarantee the electrode reusability. In fact, the sensor was tested for multiple usage obtaining the same results till, at least, ~10 times. Possibly, this strength of the Pd NPs adhesion is determined by the microscopic Pd-C bonding, by the 80 °C temperature during the drying of the Pd NPs colloidal solution drop on the Graphene/Cu surface and by the roughness of the Cu surface on which the graphene is supported.

As an example, Fig. 2 reports a SEM image of the produced and Pd nanoparticles drop-casted on the graphene/Cu substrate.

3. Results and discussions

3.1. Structural analysis

Fig. 2 shows in (a) a SEM micrograph of the GR/Cu surface after the deposition of the Pd Nanoparticles on the grapheme surface. These nanoparticles can be recognized as the circular bright spots in the images, indicating their three-dimensional spherical shape. Fig. 2b reports a magnification of a single Pd particle. The morphology, structure and composition of these nanoparticles were characterized in detail using scanning electron microscopy, transmission electron microscopy, selected area electron diffraction, X-ray diffraction and energy dispersive X-ray measurements. The results were reported elsewhere. [29]. Here, we summarize the basic results and characteristics: the Pd nanoparticles have spherical shape with a Gaussian diameters distribution and a mean diameter value of 12 nm (and good agreement was found by comparing transmission and scanning electron microscopes analyses and analyses of the X-ray diffraction spectra by using the Debye–-Scherrer) and a standard deviation of 3 nm. In addition, both X-ray diffraction analyses and selected area electron diffraction (performed during the transmission electron microscopy characterizations) show that these nanoparticles are single crystals. Finally, energy dispersive X-ray analysis (performed during the scanning electron microscopy characterizations) and high-angle annular dark field scanning transmission electron microscopy analysis resulted in no detectable contaminations for the nanoparticles. Overall, therefore, these are spherical, pure, single-crystals Pd nanoparticles with diameter of 12 ± 3 nm. To evaluate the size distribution, in particular the TEM analyses were greatly useful. The SEM images allow to evaluate the spatial distribution of the Pd nanoparticles over the graphene surface, however, due to the limited SEM spatial resolution, the smaller NPs are not recognizable from the SEM images. They were, correctly, imaged and counted by the TEM images and they resulted as the major part of the NPs determining the 12 nm mean value. It was our aim to perform a cross-section SEM image: however, on the graphene/Cu surface there is only a single layer of Pd nanoparticles, not a thick film. So, due to the limited SEM spatial resolution and the very low amount of Pd nanoparticles, it was impossible to image the Pd nanoparticles by cross-sectional SEM analyses. However, the transmission electron microscope analysis [29] shows that the single Pd nanoparticle has a spherical shape.

3.2. Raman

Fig. 3a shows the Raman spectrum of Gr/Cu substrate. The two modes of graphene belonging to D band and 2 G bands are clearly observed. The 2D/G band intensity ratio is 2.35. This value confirms the presence of a single graphene layer. Fig. 3b shows the Raman spectra taken from different positions of the electrode Pd/GR/Cu after multiple electrochemical measurements using glucose. The measurements were performed after 6 months of the electrochemical measurements. The Raman spectra were scanned within the spectral range (0, 3000 cm^{-1}) to identify the presence of glucose or by products. No Raman bands belonging to glucose/by products were observed in the spectra [30–32], however, some bands located at 523 and 620 cm^{-1} were clearly detected in some positions that could be due to the formation of metal oxide such as a thick layer of PdO [33,34]. The non-presence of glucose or by products after EIS and CV studies confirmed the performance of the electrodes.

3.3. Electrochemical studies

Fig. 4 reports the electrocatalytic activity of Pd/GR/Cu cast on glassy carbon electrode, investigated using cyclic voltammetry (CV) in a 0.5 M NaOH solution, in absence of glucose. Three oxidation peaks (A1, A2 and A3) and four reduction peaks (B1, B2, B3 and B4) within the potential range (−1.0 to +1.0 V vs. Ag/AgCl) are present. Table 1 reports the potential and current measured for each observed peak. One redox couple (A1/B3) was due electroactivity of Pd or adsorption of OH^- onto the surface; another redox couple (A3/B4) which is greatly affected by the presence of glucose is assigned to due to oxygen evolution reaction.

The anodic A1 peak was due to the adsorption of OH^- on Pd/GR/Cu electrode, the A2 peak was due to the oxidation of palladium, to palladium oxides. Also present a weak shoulder peak A3, due to the oxygen evolution reaction (onset potential at 0.6 V). This peak becomes overwhelmed with the much higher current peak due to glucose oxidation if glucose is added to the solution. The shape of voltammogram is analogous to the previous reports for palladium-based nanomaterials [35,36]. B1 and B2 peaks can be related to the stripping of hydroxyl anion from the electrode surface. The voltammograms measured in the presence of glucose in the concentration range 0.99 mM to 12.34 mM, at a scan rate of 50 mVs^{-1}, in the potential range of −1.0 to +1.0 V and −0.5 to +0.8 V

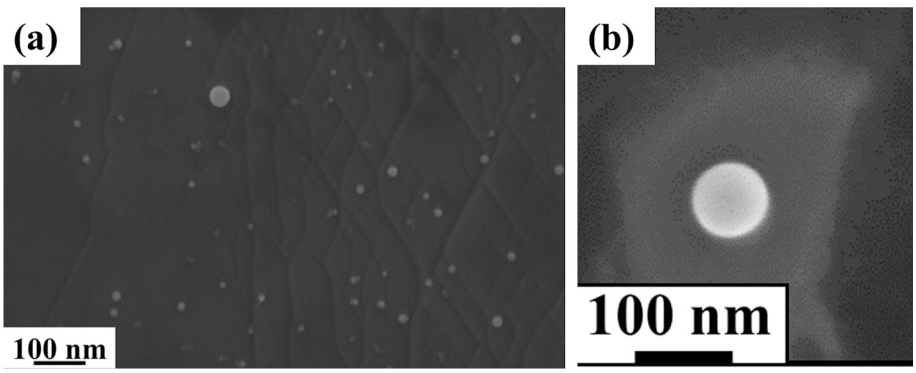

Fig. 2. (a) SEM image of Pd nanoparticles on the GR/Cu substrate. (b) Magnification of a single Pd nanoparticle.

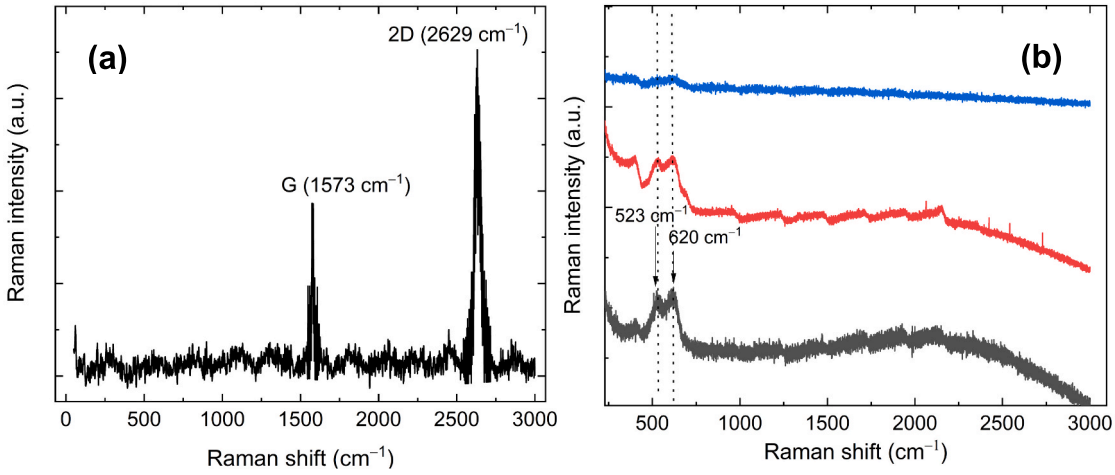

Fig. 3. (a) Raman spectrum of GR/Cu substrate. (b) Raman spectra of Pd/GR/Cu electrode after multiple electrochemical measurements in glucose, blue, red, and black curves represent the three positions where Raman spectra were recorded.

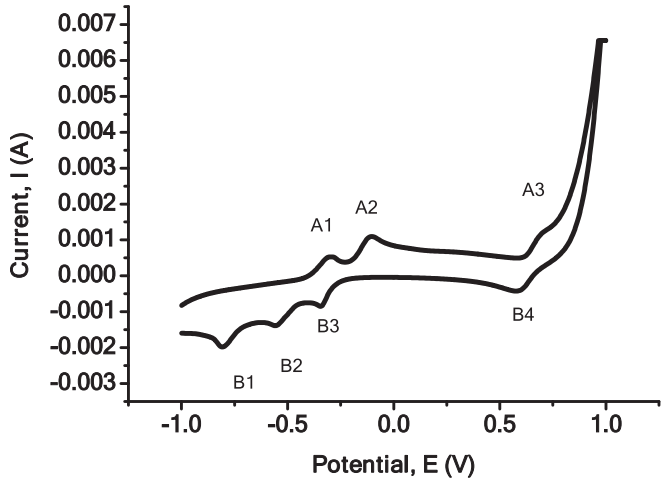

Fig. 4. Cyclic voltammogram in 0.5 M NaOH of Pd/GR/Cu electrode at a scan rate 50 mV s^{-1}, measured in absence of glucose.

vs. Ag/AgCl, are shown in Fig. 5a and 5c, respectively. When glucose is present, the current of the anodic peak A2 slightly increased while the current of the anodic peak A3 at 0.7 V increased noticeably with increase in glucose concentration, suggesting that Pd nanoparticles had strong electrocatalytic activity for glucose oxidation for scan range −1.0 to +1.0 V (Fig. 5a) and for scan range −0.5 to +0.8 V (Fig. 5c) [37]. The glucose was proposed to be oxidized by PdO to gluconolactone [24].

Thus, Fig. 5 a) indicated that during the forward anodic scan, three oxidation peaks were observed: peak A1 at −0.308 V due to the chemisorption of hydroxide ion OH^- onto the palladium surface, peak A2 at −0.0796 V due to the formation of palladium oxide PdO accompanied by a shoulder at 0.123 V due to further oxidation of electrodes surface [38], peak A3 at 0.745 V due to glucose oxidation reaction which increases with glucose concentration increase. While during the backward cathodic scan, four reductions peaks were observed: B4 peak at 0.587 V due to reduction of glucose oxidation products, B3 peak at 0.393 V related to PdO reduction, B2 peak at – 0.557 V caused by OH^- desorption and finally B1 peak at – 0.818 V related to hydrogen desorption from the electrode surface [39].

The electroactive species in Pd/GR/Cu electrode, where the graphitic matrix contains uniformly dispersed palladium nanoparticles ranging in size from 50 to 100 nm (Fig. 2). Therefore, the electrode demonstrated improved electrocatalysis and maintained a large surface area for interaction with glucose.

The palladium oxide PdO was formed in the anodic scan as a result of adsorption of OH^- on Pd to form Pd-OH_{ads} followed by reaction of OH^- with Pd-OH_{ads}. However, during the cathodic scan, PdO was reduced back to Pd which then reform Pd-OH_{ads} during the forward anodic scan. The Pd-OH_{ads} is the electroactive species in the glucose oxidation reaction that produces gluconolactone, water and palladium [39,40].

Cyclic voltammetry (CV) is a crucial tool for assessing electrocatalyst's efficiency because they can be monitored in relation to the concentration of glucose. Fig. 5b and 5d shows the calibration curves obtained considering the intensity of A3 peak as function of glucose concentration, at different potential scan ranges. The curve was fitted linearly with a correlation coefficient of 0.9721. The slope, that represents the sensitivity, was found equal to 0.240 mA.mM^{-1}.cm^{-2} and 0.245 mA.mM^{-1}.cm^{-2} (Fig. 5d). The limit of detection of glucose was experimentally found to be equal to 0.5 mM. Since the method used in the preparation of electrode involved fixation of palladium nanoparticles on graphene layer using drop-casting method. There was no observable loss of active material palladium catalyst during the electrochemistry experiment.

The electrochemical impedance spectra (EIS) for a Pd/GR/Cu modified electrode with a broad range of glucose concentrations were investigated in order to further confirm the feasibility of developing a glucose sensor. The electrical equivalent circuit (EEC) (Fig. 6), fits the Nyquist plots quite well (Fig. 7a). Two-time constants were present in

Table 1
Cyclic voltammetry data peak currents and (potentials) for electrode Pd/GR/Cu in 0.5 M NaOH, scan range from −1.0 V to +1.0 V with as 50 mV/s scan rate.

	Anodic peaks Current, mA (potential, mV)			Cathodic peaks Current, mA (potential, mV)		
Peaks	A1	A2	A3	B1	B2	B4
Electrode Pd/GR/Cu	0.422 (−311.4)	1.091 (−91.68)	1.303 (711.7)	−2.075 (−823)	−1.595 (−567.1)	−0.304 (+595.8)

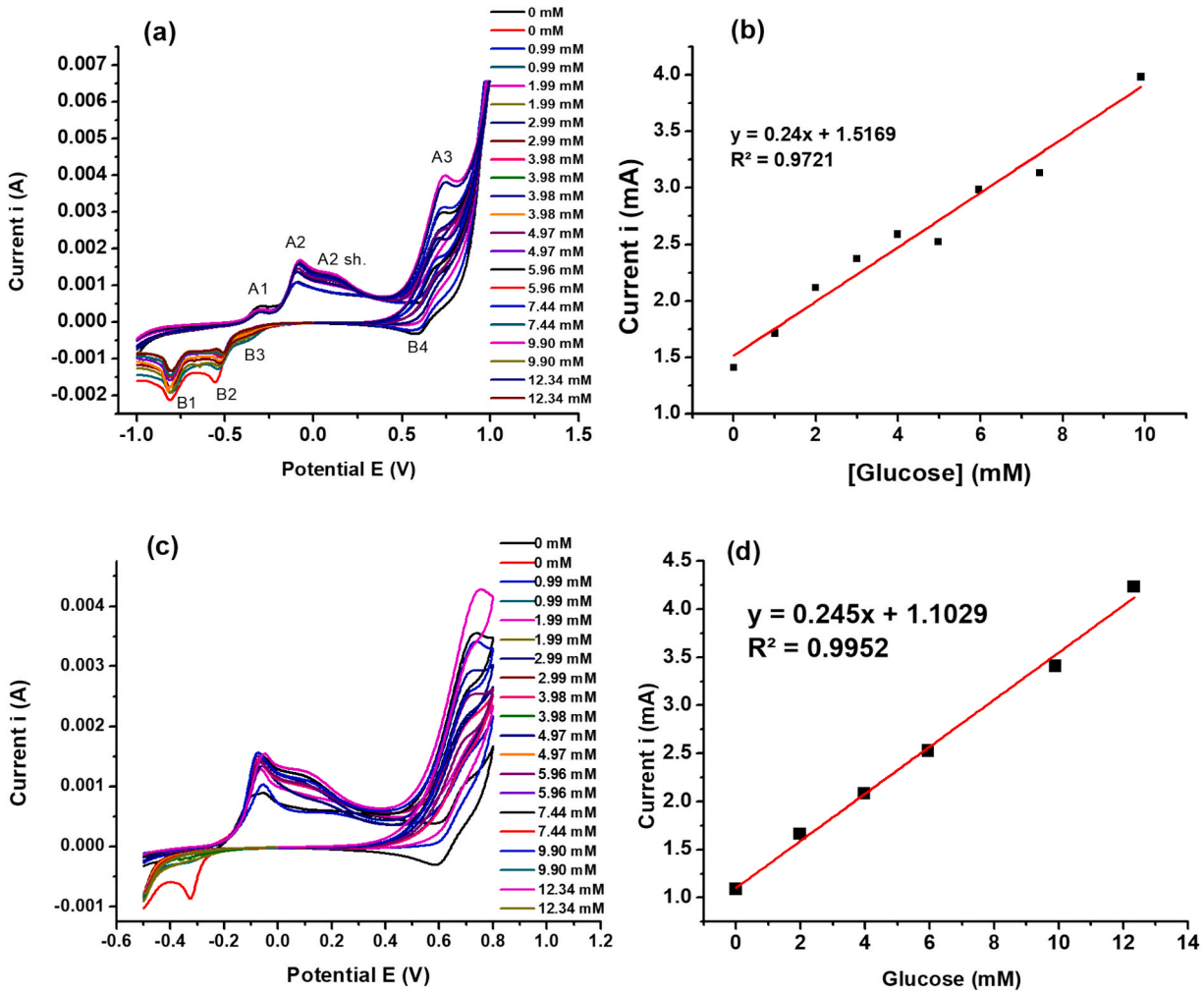

Fig. 5. (a) Cyclic voltammogram in presence of different glucose concentrations (mM) and (b) the related calibration curve in the range −1.0 to +1.0 V; (c) cyclic voltammograms and (d) the related calibration curve in the range −0.5 to +0.8 V using electrode Pd/GR/Cu at a scan rate of 50 mVs^{-1} in 0.5 M NaOH solution.

the EEC in addition to the solution resistance R_s. The first time constant has a double-layer capacitor Cdl and a film resistance R_f. While, the second one has a constant-phase element CPE, a charge transfer resistance R_{CT}, and a Warburg impedance W. The ratio of solution resistance R_s/R_{s0} is proportional to glucose concentration up to 12.34 mM with a sensitivity of 0.0207 mM^{-1} for Pd/GR/Cu electrode (Fig. 7b) [41].

Additionally, Bode plots demonstrated that the complex impedance represented by logZ (ohms) increases systemically at a frequency of 0.2 Hz, (Fig. 8a) with the increase in glucose concentration. As a result, the change in the complex impedance at a particular frequency can be used to create calibration curves (Fig. 8b). The obtained sensitivity of the electrode for glucose is equal to 81.34 Ohm.mM^{-1}.cm^{-2}. The limit of detections using the resistance method was 3 mM, while it was 0.5 mM for the single frequency method. An alternate method for determining how the charge-transfer resistance R_{ct} changes as concentration rises is the single-frequency approach [42]. As the equivalent circuit must be adequately fitted to acquire the resistance values involved in the circuit, the results show that while Rs variations as a function of glucose

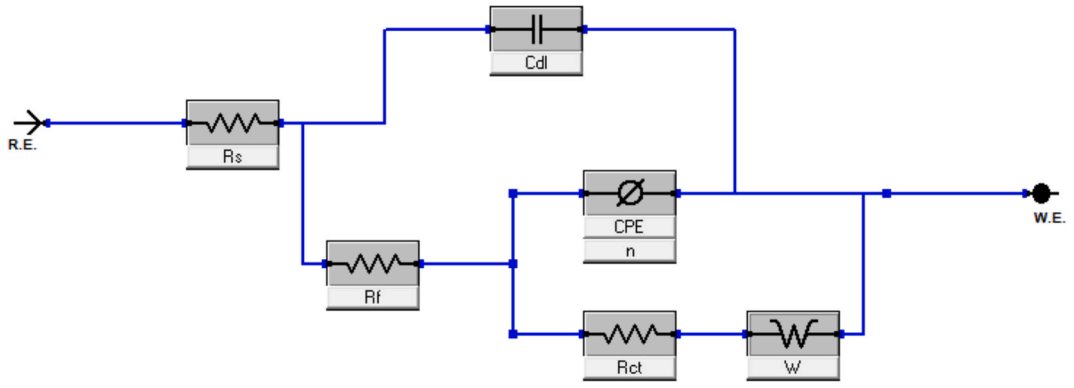

Fig. 6. The best-fitted equivalent electrical circuit Model for electrode Pd/GR/Cu.

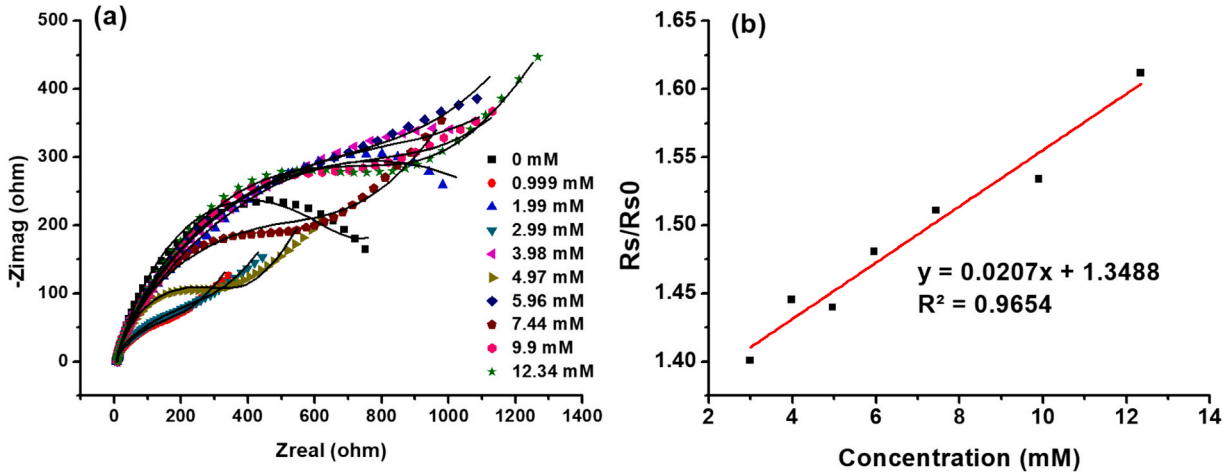

Fig. 7. (a) Nyquist plot of EIS recorded at different glucose concentration in 0.5 M NaOH solution. The EIS were fitted using the equivalent circuit Model described in Fig. 6. (b) Calibration curves obtained at different concentrations of glucose (mM) in 0.5 M NaOH for electrode Pd/GR/Cu from the normalized Rs by fitting the data of Nyquist plot with equivalent circuit model of Fig. 6.

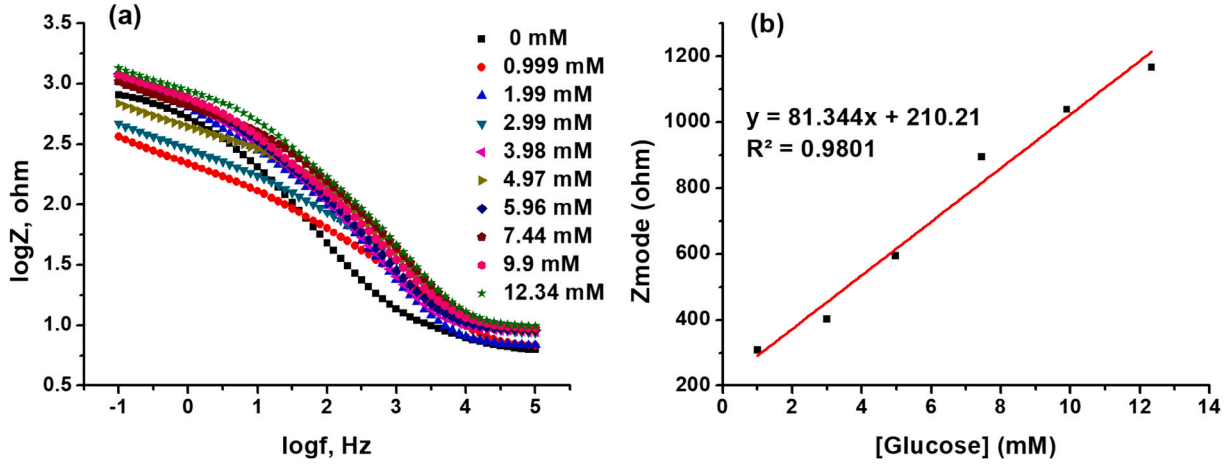

Fig. 8. (a) Bode plot for electrode Pd/GR/Cu in NaOH (0.5 M) at different glucose concentration (mM) and (b) Calibration curves obtained at different concentrations of glucose (mM) in 0.5 M NaOH for electrode Pd/GR/Cu from Bode plot of the complex impedance at a frequency of 0.2 Hz.

concentration could be used to quantify fructose, it is a difficult and time-consuming operation.

In the cyclic voltammetry method (CV), the current (mA) was measured and was dependent on the glucose concentration, while in the second method Zmode (ohm) from Bode plot was measured and was found dependent on the glucose concentration. Since the correlation coefficient of the calibration curve in the first case was higher than that of the second method, the first CV method is more reliable based on the experimental conditions used.

Therefore, Pd/GR/Cu was deployed as an electrochemical biosensor of glucose. It showed good electrocatalysis toward glucose using different glucose concentrations, from 0.5 to 13 mM, which covers the levels of blood glucose for both normal and diabetic persons.

Finally, a comparison of some important parameters between the sensor in our work and the other prepared non-enzymatic glucose sensors is presented in Table 2. The parameters compared were detection range, sensitivity and limit of detection (LOD). It was found that the electrode sensitivity of nano-palladium/graphene/copper (Pd/GR/Cu) was greater than graphene-copper oxide nanoparticles (CuO/GR) [43], glucose oxidase immobilized onto a glassy carbon electrode modified with reduced graphene oxide/palladium nanocomposite (GCE–R-GO–Pd–Gox) [24], nickel and palladium particles on silicon nanowire

Table 2
Comparison of the present electrochemical glucose sensor with others reported in the literature.

Electrode	Detection technique	Detection range (mM)	Sensitivity ($\mu A.mM^{-1}.cm^{-2}$)	Limit of detection (LOD, mM)	Reference
CuO/Gr	Cyclic voltammetric	5–14	37.63	0.005	[43]
(GCE–RGO–Pd–Gox)	Cyclic voltammetric	2–10	41.3	–	[24]
Pd–Ni/SiNW	Amperometric	2–20	190.72	$2.88x10^{-3}$	[47]
Pt-NTAE/AAM	Amperometric	2–14	0.1	1	[44]
Pd/MWCNTs	Cyclic voltammetric	1–22	1275	0.2×10^{-3}	[45]
4-NTP/u-7.5 nm/Gr/Cu	Cyclic voltammetric	1–29	420.8	0.5	[46]
Pd/GR/Cu Nanopalladium/graphene/copper	Cyclic voltammetric	0.5–13	245	0.5	Present work

Pd–Ni/SiNW [36], highly ordered platinum-nanotubule array in 3-aminopropyltrimethoxysilane-modified alumina membrane [44]. However, the sensitivity of Pd/GR/Cu electrode was less than Palladium nanoparticles decorated functionalized multiwall carbon nanotubes (Pd/MWCNTs) [45] and (4-Nitrothiophenol)-nanogold/graphene/copper (4-NTP/Au-7.5 nm/GR/Cu) [46]. The detection limit of the nano-palladium/graphene/copper (Pd/GR/Cu) sensor is indeed higher than certain previously reported sensors, such as Pd/MWCNTs. This difference in sensitivity can be attributed to several factors. First, the interaction between palladium nanoparticles and the graphene layer in the Pd/GR/Cu electrode may not be optimized, resulting in a less efficient electron transfer mechanism. Second, the surface area of the electrode might be lower compared to multiwall carbon nanotube-based systems, potentially limiting the adsorption of target molecules. Improvement in sensitivity could be achieved by refining the synthesis process to enhance the uniform dispersion of palladium nanoparticles and optimize their interaction with graphene. Additionally, incorporating higher-surface-area nanomaterials or creating hybrid composite structures might further improve the electrochemical properties. Investigating other functionalization techniques to tailor the electrode surface for better target analyte recognition could also be a promising avenue for enhancing sensitivity.

For a healthy person, the glucose concentration varies between 4 and 6 mM and above 7.0 mM for diabetics, and the sensitive glucose response by Pd/Gr/Cu electrode was in the concentration range 0.5 mM to 13 mM, this promotes the present modified palladium electrode to be ideal for determining blood sugar concentration.

While Table 2 highlights that certain sensors, such as Pd/MWCNTs, exhibit higher sensitivity compared to the nano-palladium/graphene/copper (Pd/GR/Cu) sensor developed in this study, there are notable trade-offs that make our sensor advantageous: The fabrication process for Pd/GR/Cu involves relatively cost-effective materials and techniques compared to multiwall carbon nanotube-based systems, which often require specialized synthesis steps or functionalization that can increase overall costs. The Pd/GR/Cu sensor benefits from a simpler and more scalable fabrication process, making it more suitable for mass production. In contrast, sensors like Pd/MWCNTs often involve intricate procedures for ensuring uniform dispersion and functionalization of nanoparticles within the nanotubes, which may limit production scalability. The Pd/GR/Cu sensor demonstrates robust structural stability and consistent performance over time, whereas some higher-sensitivity sensors may exhibit challenges such as degradation or diminished reproducibility under certain operating conditions. In summary, while the Pd/GR/Cu sensor may have a higher detection limit, its advantages in terms of cost-effectiveness, ease of fabrication, and durability make it a promising candidate for practical applications, especially in scenarios where these factors are critical.

The following points highlight the study's utility and underscore its contribution to the field of sensor development. The innovative use of pulsed liquid laser ablation (PLAL) and drop-casting for fabricating Pd/GR/Cu electrodes marks a significant improvement over traditional method. This opens avenues for producing highly sensitive non-enzymatic glucose sensors with enhanced stability and reproducibility. The combined properties of palladium, graphene, and copper enhance the electrode's stability, electrical conductivity, and rapid electron transfer capabilities. Indeed, the Pd/GR/Cu electrode exhibited high sensitivity for glucose detection, with values of 0.245 $mA.mM^{-1}.cm^{-2}$ by CV and 81.3 $Ohm.mM^{-1}.cm^{-2}$ by EIS and the detection range (0.5 mM to 13 mM) makes it suitable for monitoring glucose levels across both healthy individuals and diabetic patients, providing potential for medical diagnostics. This makes the Pd/GR/Cu sensor a promising candidate for next generation sensing devices. While this study focuses on glucose, the electrode's robust design and sensitivity could be extended to detect other biomolecules or analytes, broadening its scope for use in medical, environmental, and industrial applications. The scalable fabrication method and impressive performance metrics make the Pd/GR/Cu electrode suitable for mass production, paving the way for cost-effective, high-performance non-enzymatic glucose sensors in the market.

The following highlight the future scope that could emerge from the present innovative work: a) additional refinement of the pulsed liquid laser ablation (PLAL) and drop-casting method could improve the stability, reproducibility, and scalability of Pd/GR/Cu electrodes for commercial applications, b) further research could aim to lower the detection limit and expand the quantification range of glucose sensing, making these sensors more suitable for real-time monitoring in medical or biochemical applications c) the sensing capabilities of Pd/GR/Cu electrodes could be extended to detect other biomolecules or environmental pollutants, broadening their applicability, d) valuating the long-term performance and durability of the Pd/GR/Cu electrodes in varied conditions could enhance their reliability for practical use, and incorporating these electrodes into wearable or portable glucose monitoring devices could revolutionize point-of-care diagnostics.

4. Conclusion

PLAL was used to produce dispersion of Pd NPs (12 nm in average diameter) which were, then, used to decorate single layer graphene supported on Cu foil. The Pd NPs/GR/Cu stack was exploited for ultrasensitive electrochemical detection of glucose, also for multiple usage. In particular, CV and EIS studies showed high values of sensitivity for glucose detection: 0.245 $mA.mM^{-1}.cm^{-2}$ by CV and 81.3 $Ohm.mM^{-1}.cm^{-2}$ by EIS respectively. The lowest detection limit (LOD) was 0.5 mM and the range of concentration was 0.5–13.0 mM in both techniques. The immobilization of the NPs and the rapid electron transport between the Pd, glucose, and copper film surface are made possible by the graphene layers with high surface area. As a result, the developed modified palladium electrode exhibited good stability and electrical conductivity. The highly sensitive glucose response by the Pd/GR/Cu electrode in the range 0.5 to 13 mM cover both healthy individual and diabetics. This makes the current modified palladium electrode ideal for measuring blood sugar levels which is the next future step of this work. Building on these findings, future work could focus on optimizing the fabrication process for enhanced reproducibility and scalability of the Pd/GR/Cu electrodes. Additionally, extending the sensing capabilities to other biomolecules or environmental analytes could broaden the application scope. Research into integrating the electrodes into wearable or portable devices may advance point-of-care diagnostics. Finally, long-term stability studies under varied conditions could provide insights into improving durability for real-world applications. These avenues present exciting opportunities for further development and innovation. These results improve the abilities of laser-based synthesis approach towards sensing applications [48,49]

CRediT authorship contribution statement

Chawki Awada: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Hassan H. Hammud:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Waleed A. Aljamhi:** Writing – review & editing, Writing – original draft, Investigation, Data curation. **Stefano Boscarino:** Writing – review & editing, Writing – original draft, Investigation, Data curation. **Antonino Scandurra:** Writing – review & editing, Writing – original draft, Investigation, Data curation. **Francesco Ruffino:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Funding

This work was supported by the Deanship of Scientific Research, Vice Presidency for Graduate Studies and Scientific Research, King Faisal University, Saudi Arabia [Grant No. KFU250188].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

F. R., S. B., A. S. thank the MUR-PNRR project SAMOTHRACE (Grant No. ECS00000022). F. R. thanks, also, the PNRR MUR project PE0000023-NQSTI the PNRR – NQSTI "National Quantum Science and Technology Institute" Spoke 7 and the project "Multifunctional Hybrid Nanomaterials for Cancer Diagnosis and Personalized Target Therapy" through Programma di Ricerca di Ateneo UNICT 2024-26 linea 1.

Data availability

Data will be made available on request.

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