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Highly Selective and Sensitive Non-enzymatic Glucose Biosensor Based on Polypyrrole-Borophene Nanocomposite

Gülsen BAYTEMİR*[1]

Abstract

In this study, a non-enzymatic glucose sensor composed of two-dimensional (2D) borophene-decorated polypyrrole (PPy) nanocomposites (NCs) was developed. The PPy-borophene NCs were prepared using a low-cost sonication method. The sensing performance of the PPy-borophene NCs was investigated by the cyclic voltammetry (CV) technique against various biomolecules such as glucose, maltose, lactose, fructose, and urea. According to the electrochemical results, it was observed that in the glucose concentration range of 1.5 to 24 mM within a voltammetric cycle of 1 min, the PPy-based sensor and PPy-borophene NCs-based sensor exhibited sensitivities of 11.88 $\mu AmM^{-1}\ cm^{-2}$ and 213.42 $\mu AmM^{-1}\ cm^{-2}$, respectively. The detection limits of the PPy-based and PPy-borophene NCs-based sensors were determined to be 0.5 µM and 0.04 µM, respectively. Furthermore, selectivity measurement results revealed that the proposed non-enzymatic biosensor has remarkably good sensitivity and high selectivity, indicating that common biomolecules (glucose, maltose, lactose, fructose, and urea) could be captured by the sensor. Consequently, it was proven that the proposed biosensor could be a potential device for diabetes diagnosis.

Keywords: Non-enzymatic electrochemical biosensor, borophene, polypyrrole, glucose.

1. INTRODUCTION

Diabetes is a global health problem that affects millions of people. In 2030, the prevalence of diabetes is estimated to be 4.4% for all age groups worldwide [1, 2]. It is believed that the reasons for the rapid increase in the number of diabetes patients are accelerating obesity, sedentary lifestyles and unhealthy diets. Diabetes is a metabolic disease that occurs when the pancreas is not able to produce enough insulin or the body can not effectively use the insulin it produces. Since the cells cannot absorb the blood sugar (glucose) required for the energy they need due to insulin deficiency, the level of glucose in the blood rises. If not treated or controlled, diabetes can damage blood vessels and cause a variety of complications when glucose concentrations exceed 10–12 mM [2-9]. Therefore, accurate monitoring of glucose concentration is crucial.

Conventional glucose biosensors make use of enzymes such as glucose oxidase and glucose hydrogenase due to their simplicity, high sensitivity and selectivity to glucose. The signal

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is obtained from the oxidation of hydrogen peroxide produced as a result of the reaction of these enzymes. However, although the development of enzyme-modified electrodes has advanced considerably, these enzymatic sensors often suffer from stability issues due to the nature of enzymes. In order to overcome this problem, it is attractive to produce non-enzymatic sensors that can directly oxidize glucose at the electrode surface [10-15]. In general, metal/metaloxides [16-21] such as platinum (Pt), gold (Au), platinum-lead (Pt-Pb), nickel (Ni), copper (Cu), nickel-titanium (Ni-Ti), nickel-copper (Ni-Cu), transition metal oxides [22-26] such as tricobalt tetroxide (Co_3O_4), nickel oxide (NiO), nickel hydroxide ($Ni(OH)_2$), and copper hydroxide ($Cu(OH)_2$) etc.,can be used as sensing materials for the detection of glucose sensor. However, these electrodes have some disadvantages, such as low sensitivity, poor selectivity, and poisoning by chloride ions. Carbon and carbon-based nanomaterials (carbon nanotubes, carbon fibers, carbon dots, and graphene) have recently received increasing attention due to their unique physical and chemical properties. In particular, graphene, which is a two-dimensional (2D) material, attracts attention as a glucose sensing material due to its high surface area, chemical stability, and biocompatibility [27-29]. In addition, since conductive polymers such as polypyrrole (PPy) [30], polyaniline (PANI) [31], poly-o-aminophenol (POAP) [32] have similar electrical and optical properties to metal or inorganic semiconductor materials, they are of interest for chemical sensor, biosensor, and supercapacitor studies. In particular, PPy has been reported as being suitable for the design of various sensors since it is a good substrate for the immobilization of nanomaterials. For instance, the electrochemical sensor fabricated for the determination of D-glucose using a polypyrrole-N-phenylboronic acid modified Pt electrode has been reported to exhibit a low detection limit [33]. In another study, glucose was detected over a wide dynamic detection range of 0.001-4.863 mM using overoxidized polypyrrole nanowire electrodes (nf-Ni(OH)2@oPPyNW) modified with nickel hydroxide nanoflakes. The proposed electrode exhibits a low detection limit of 0.3 μM, making it suitable for a sensitive, selective, and stable electrochemical sensor [34]. In another study, it has been shown that the limit of detection of the hybrid NF/$NiCo_2O_4$@Ppy electrochemical sensor created by fabricating $NiCo_2O_4$@polypyrrole nanowires on a nickel foam (NF) substrate for glucose sensing was 0.22 μM [35]. An enzyme-free sensor developed for glucose detection based on chemical oxidative polymerization of pyrrole monomers on the surface of $CuFe_2O_4$ nanoparticles exhibited a limit detection of 0.1 μM for low glucose concentrations and 0.47 μM for high glucose concentrations [36]. In a study examining an enzyme-free biosensor modified with cobalt(II) phthalocyanine tetrasulfonate (CoPcTS)-based on the electrodeposition of over-oxidized polypyrrole nanofiber on a pencil graphite electrode, excellent performance was observed for glucose sensing with a wide linear range (0.25–20 mM) and highly reproducible response. In addition, the calculated limit of detection was 0.1 mM [37]. Li et al. worked on an enzyme-free glucose biosensor based on Au nanoparticles (Au/PPyNFs) supporting polypyrrole nanofibers. It has been shown that with a non-enzymatic glucose sensor based on Au/PPyNFs, 0.2-13 mM of glucose can be detected [38].

In recent years, borophene as a two-dimensional nanomaterial has been the subject of many studies due to its unique physical, chemical, and electronic properties. In 2015, in the first theoretical studies of borophene, its chemical stability at room temperature was reported. As of 2018, borophene has started to be prepared by wet chemical methods, but there are still a limited number of papers. In these studies, it is reported that the performance of supercapacitors and sensors is improved with the addition of prepared borophene to conductive polymers [39-44]. Here, the addition of borophene to conductive polymers increases the electrical conductivity of conductive polymer-borophene

nanocomposite-based devices. Therefore, it can be predicted that the PPy-borophene NCs obtained with the addition of borophene will improve the redox interaction between glucose and the nanocomposite in a non-enzymatic electrochemical sensor.

In this study, PPy-based and PPy-borophene NCs-based non-enzymatic sensors were prepared and their glucose sensing properties were investigated. It was demonstrated that borophene improves the glucose sensing properties of the sensor. The novelty of this work is that the glucose sensing mechanism of the PPy-borophene NCs-based electrochemical sensor has been reported for the first time. In addition, the prepared sensors have been tested to detect urea, fructose, lactose, and maltose, and it has been shown that the sensors are more selective towards glucose.

2. EXPERIMENTAL

Borophene nanosheets were prepared by physical exfoliation of boron microparticles (1.5 μm particle size) in dimethylformamide (DMF) as previously described [45-47]. High resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) techniques were performed to elucidate the crystalline structure and morphology of the borophene. Then, PPy and borophene were mixed at a ratio of 1:1, and the solution was sonicated at 200 W for 15 min. Scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) analysis of the PPy-borophene NCs were performed.

Glucose analytes with 1.5 mM, 3 mM, 6 mM, 12 mM and 24 mM concentrations were prepared in phosphate buffer solution (PBS). PPy and PPy-borophene solutions were coated on the gold (Au) electrochemical transducers by drop casting and dried at 40 ^{0}C to obtain the sensors. Measurements for each glucose concentration were carried out by the 3-electrode cyclic voltammetry method. In addition, I-V characteristics of the sensor for each glucose concentration in the range of [-1, +1] V were obtained in real-time measurements. Since the current response is based on the reduction and oxidation reactions, the sensitivities of the sensors were thus determined.

3. RESULT AND DISCUSSION

The HRTEM images and XRD pattern of borophene were given in Figure 1. The HRTEM micrographs of the borophene show that borophene, prepared using the ultrasonic method, has excellent structural morphology. As seen in Figure 1-a, borophene has a uniform nanosheet structure with hexagonal boron crystals. The nanosheets have a crystalline structure with a 0.41 nm stripe pitch, and this matches the characteristics of a β-rhombohedral boron structure [48]. Moreover, the Fast Fourier Transform (FFT) diffraction pattern of an individual borophene nanosheet is also given in the inset of Figure 1-b. The XRD pattern given in Figure 1-c, in which the phase and crystallinity of the nanosheets were examined, corresponds to the centrosymmetric (0001) plane of β- rhombohedra borophene (0001) plane (unit cell parameters: a=10.925Â, b=10.925Â and c=23.814Â). The XRD pattern was indexed to the crystal system of the β-borophene was R-3 m (166) [49]. The results of HRTEM and XRD techniques are compatible with each other.

The surface morphology of the ultrasonically prepared PPy-borophene NCs was also identified. SEM images of borophene and PPy-borophene NCs are given in Figure 2 (a-b). The SEM image of the PPy-borophene NCs at higher magnification is also given in the inset of Figure 2-b. According to the experimental results of the PPy-borophene NCs, it has a random nanofringe structure. The results of the FTIR used to determine the chemical functional groups of borophene and PPy-borophene NCs are presented in Figure 2-c. In the previous studies of our group, it was reported that the characteristic peaks of borophene were observed at 3479 cm^{-1} (O-H), 2929 cm^{-1} (B-B), 2861 cm^{-1} (B-H), 1653 cm^{-1} (C=O), 1496 cm^{-1} (B-H), 1385 cm^{-1} (B-O), 1255 cm^{-1} (B-O), and 1091 cm^{-1} (B – O – B vibrations), 865 cm^{-1} (B–

OH stretching vibration), and 659 (B–O–B stretching vibration) [31]. The characteristic peaks of the prepared PPy-borophene NCs were observed at 3272 cm^{-1} (O–H vibrational stretching), 1634 cm^{-1} (C=C stretching), 1126 cm^{-1} (C–H in-plane bending vibration), and 1037 cm^{-1} (–C–O–C) [50]. According to the FTIR results, it was concluded that borophene sheets were encapsulated in the polymer matrix (PPy).

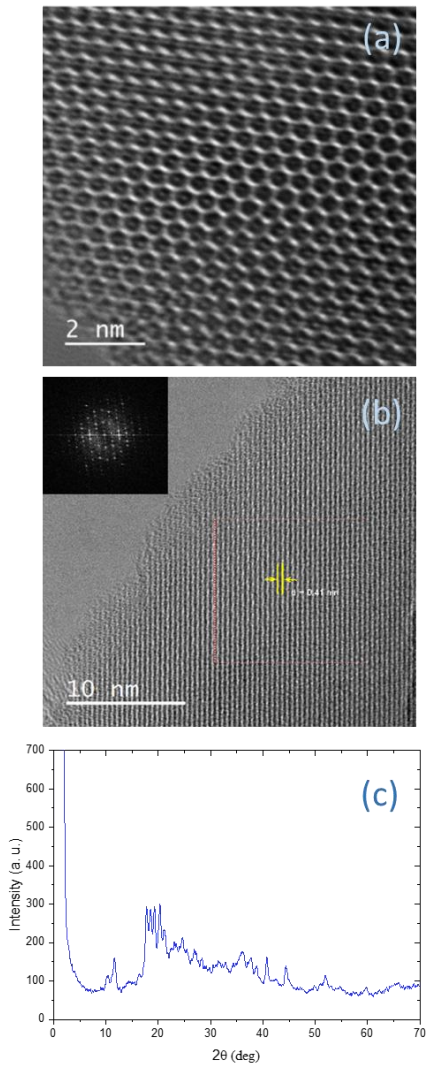

Figure 1 HRTEM images of the β-rhombohedral borophene at (a) high magnification, (b) low magnification. The inset of (b) is the FFT diffraction pattern of an individual borophene nanosheet. (c) XRD pattern of the β-rhombohedral borophene.

Electrochemical measurements of the PPy and PPy-borophene NCs based biosensors were carried out in the [−1, +1] V range with a 50 mV/s scan rate. The sensors were tested to detect glucose in the 1.5-24 mM concentration range. The measurements started with 1.5 mM glucose concentration, and the glucose was added continually to 24 mM. The current density-voltage graphs of the sensors for each glucose concentration were presented in Figure 3 a-b. The peak current measured during voltammetry varied depending on the analyte concentration. The response of the sensors to the changes in the glucose concentrations is represented by an increase in the output current.

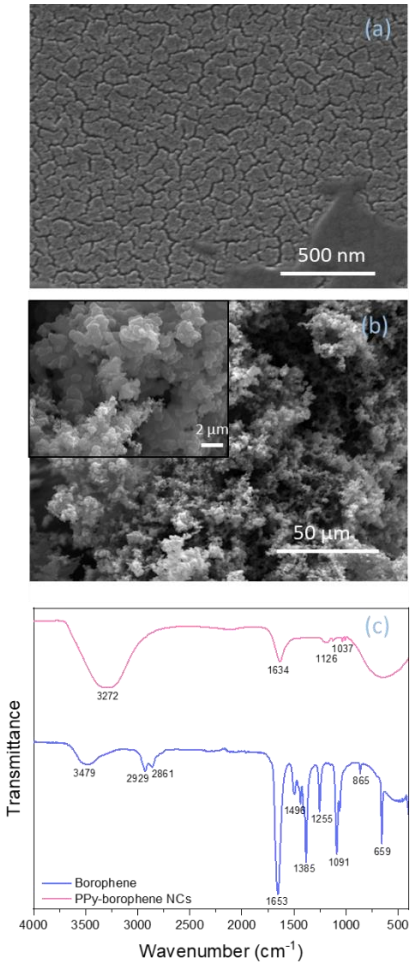

Figure 2 SEM images of (a) borophene, (b) PPy-borophene NCs. (Higher magnification is given as inset) (c) FTIR analysis of the borophene and PPy-borophene NCs.

The current peaks arise from redox reactions of glucose with the PPy and PPy-borophene NCs. The current density-voltage curves of the PPy-borophene NCs-based sensor indicated a highly prominent redox peak for the 1.5-24 mM glucose concentration range. The results show that the PPy-borophene nanocomposite-based sensor detects glucose with higher sensitivity due to the enhanced redox mechanism resulting from the borophene additive. The sensitivities of the PPy and PPy-borophene NCs based sensors were obtained by calculating the slope of the current density versus glucose concentration curves shown in Figure 3-c. PPy-based and PPy-borophene NCs-based sensors detected glucose in 1.5-24 mM concentration range with a sensitivity of 11.88 $\mu AmM^{-1} cm^{-2}$ and 213.42 $\mu AmM^{-1} cm^{-2}$ within 1 min voltammetric cycle, respectively (Figure 3-c).

The detection limit of the sensors were calculated by the

$$LOD = 3S_{y/x}/b$$

equation where $S_{y/x}$ is the standard deviation of the background current and b is the slope of the calibration curve [51]. PPy-based sensor was calculated as 0.5 μM, while that of the PPy-borophene NCs-based sensor was calculated as 0.04 μM. Table 1 shows the characteristics of the non-enzymatic, nanomaterial-modified PPy electrochemical biosensors used for glucose detection and their limit of detection values.

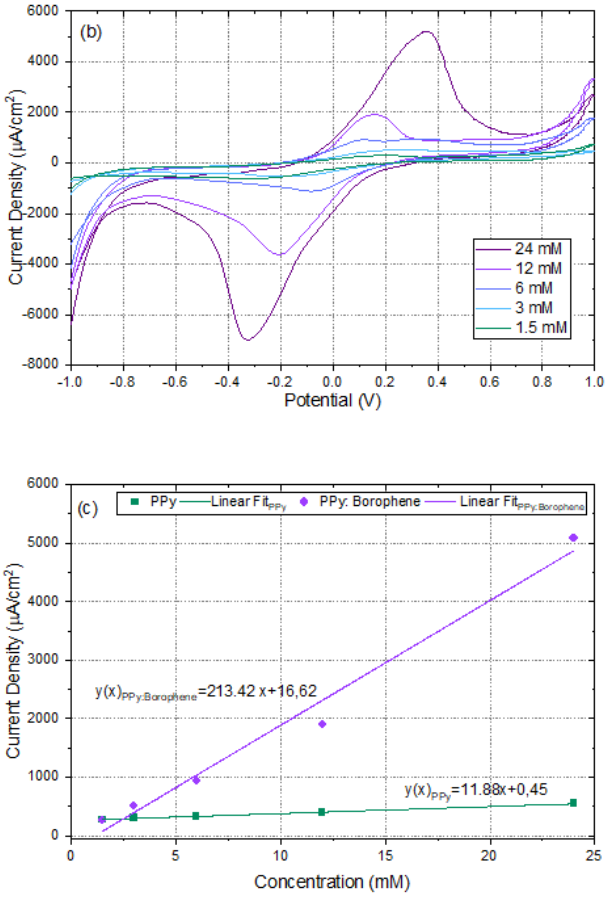

Figure 3 (a) Current density-voltage graph of PPy-based sensor against glucose, (b) PPy-borophene NCs-based sensor for varying glucose concentration, (c) The sensitivities of the sensors

Furthermore, Figure 4 shows the comparison of current density-voltage curves of PPy and PPy-borophene NCs-based sensors for glucose, maltose, lactose, fructose, and urea at 24 mM concentration. According to the results given in Figure 4 a-b, both of the sensors are remarkably selective for glucose. In the literature, there is no report on the PPy-borophene NCs-based glucose sensor. This is the first report on the preparation, structural characterization, and measurements of the PPy-borophene NCs-based glucose sensor. The measurements were performed 3 times, and obtaining similar results shows that the sensor has repeatability and stability. In light of the above, it can be said that the sensor is a potential device for rapid, cost-effective, selective, and sensitive diagnosis of diabetes

Table 1 The performances of various nanomaterials modified PPy non-enzymatic biosensors for glucose detection

Electrode	Concentration Range	Limit of Detection	Detection method	Ref.
PPy–phenylboronic acid	0.05–0.52 mM	80 µM	Voltammetry	[33]
Over-oxidized PPy nanowires modified with $Ni(OH)_2$ nanoflakes	0.001-4.863 mM	0.3 µM	Amperometry	[34]
$NiCo_2O_4$@PPy nanowires on nickel foam substrate	0.001–20 mM	0.22 µM	Voltammetry	[35]
Core-shell–$CuFe_2O_4$ /PPy nanocompo	20 µM-5.6 mM	0.1 µM for low concentrations 0.47 µM for high concentrations	Voltammetry	[36]
Overoxidized PPy nanofiber electrode modified with CoPc tetrasulfonate	0.25–20 mM	0.1 mM	Amperometry	[37]
PPy nanofibers supporting Au nanoparticles (Au/PPyNFs)	0.2–13 mM	0.2 mM	Amperometry	[38]
PPy PPy-borophene NCs	1.5-24 mM	0.5 µM 0.04 µM	Voltammetry	This work

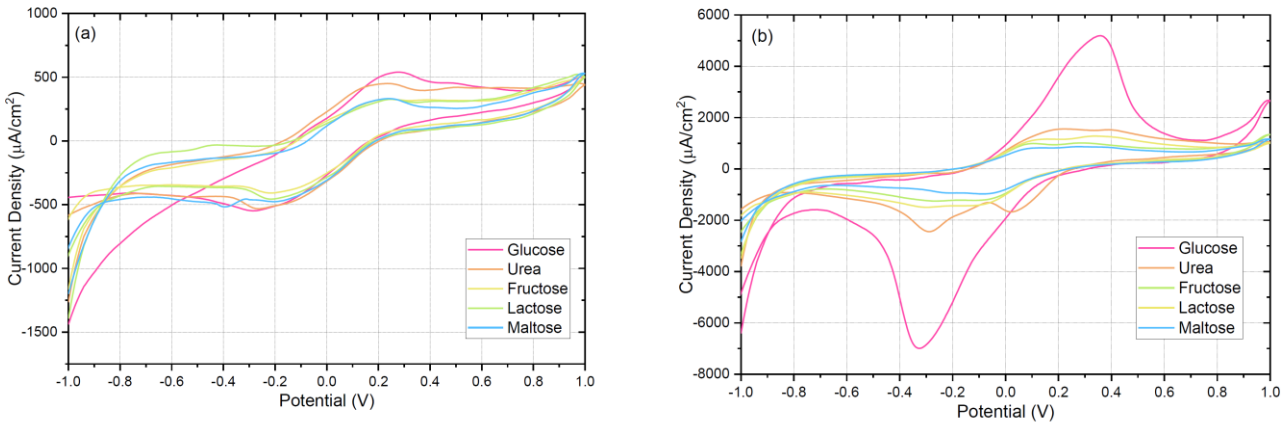

Figure 4 Selectivity of (a) PPy-based sensor (b) PPy-borophene NCs -based sensor.

4. CONCLUSION

Borophene with a uniform transparent nanosheet structure and PPy-borophene NCs with a random nanofringe structure were prepared by the ultrasonic method. After that, PPy and PPy-borophene NCs-based non-enzymatic electrochemical sensors were prepared to investigate glucose detection and the selectivity of

the sensors to glucose, maltose, lactose, fructose, and urea. In the 1.5 to 24 mM glucose concentration range, the sensitivity of the PPy-based sensor was 11.88 $\mu AmM^{-1} cm^{-2}$ and the sensitivity of the PPy-borophene NCs-based sensor was 213.42 $\mu AmM^{-1} cm^{-2}$. The detection limits of the PPy-based and PPy-borophene NCs-based sensors were determined to be 0.5 μM and 0.04 μM, respectively. These results revealed that both of the sensors were remarkably selective for glucose. The PPy-borophene NCs-based sensor detected glucose with higher sensitivity and lower detection limit due to the enhanced redox mechanism arising from the borophene additive. Moreover, current density-voltage curves of PPy and PPy-borophene NCs-based sensors for glucose, maltose, lactose, fructose, and urea at 24 mM concentration show that both of the sensors are remarkably selective for glucose. In addition, the measurements were performed 3 times and similar results were observed. In the light of the above, it can be concluded that the PPy-borophene NCs-based sensor has high sensitivity, high selectivity, and stability. Since this is the first report on the preparation, structural characterization, and measurements of the the PPy-borophene NCs-based glucose sensor it could be further developed in the future as a potential device for the diagnosis of diabetes.

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Authors' Contribution
The author confirms sole responsibility for the following: study conception, data collection, interpretation of results, and manuscript preparation.

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The author of the paper declares that there are no competing financial and non-financial interest.

The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics
The author of the paper declares that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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