# A biochar-modified carbon paste electrode

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**Abstract:** The present work examined the use of biochar derived from tea waste as a novel electrode material. For the fabrication of the biochar electrode, suitable amounts of biochar and graphite were mixed with mineral oil for the first time. The electrochemical performance of the biochar-modified carbon paste electrode (BCPE) was measured by various cyclic voltammetric reactions for several redox systems. The factors affecting the electrode kinetics of BCPE surfaces were examined and optimized. The BCPE was applied as transducer in a glucose biosensor. The results reflect the effective properties of composite electrodes and the electrochemical properties of biochar showing that the BCPE could be used for various electrochemical applications.

**Key words:** Biochar-modified carbon paste electrode, composite electrode, glucose biosensor, electrochemical performance

## 1. Introduction

Biosensors are frequently used for the detection of components such as drugs, harmful pathogens, and heavy metals or used for medical diagnostics by converting chemical and biological information together into easily detectable signals.[1−5] The chemical/biological information is provided by electron transfer, which is detected by electrodes. The electrical transfer occurs on the electrode surface supported by electron transfer mediators. There are various approaches to realize high-performance electrodes by developing electron transfer mediators depending on their various applications or motivations.[6−9] A porous solid material as conductive support or transducer is developed and employed to the electrode surface to design the electrical contact between the matrices and the support elements. The support materials immobilize the redox enzymes on electrodes. Recent studies have been reported on support materials integrated with biochar.[10−16]

Biochar is a carbonaceous material derived from biomass by pyrolysis. During the pyrolysis, the biomass feedstock is heated up to the desired temperature in the partial or total absence of oxygen. At that point, the molecules in the biomass as organic waste reorganize to form biochar; the feed stocks carbonize and volatile molecules leave the biomass.

Biochar is a generic term and the characteristics are very variable depending on the composition of the source material biomass and pyrolysis conditions. Biomass is mainly composed of cellulose, hemicellulose, lignin, and small amount of volatiles, which have different thermogravimetric behaviors by pyrolytic decomposition.[17] To this end, biochar from various biomass feedstocks shows different characteristics and physicochemical prop-

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erties such as surface functionalities, cation exchange capacity, porosity, or surface area even if they have similar carbonization ratios.[18,19] Therefore standards have not been established yet for biochar.

The recent interest in biochar has been stimulated by its use in biosensors. Biochar is also used in electroanalysis for special purposes. Especially for the determination of organic and inorganic pollutants in the environment, there are works that report the use of a biochar-modified carbon paste electrode (BCPE). Agustini et al.[10] developed an electrode modified with biochar with the incorporation of bismuth nanostructures. Biochar was produced from castor oil cake and the nanomolar level Pb(II) was determined with this electrode. Since biochar has exhibited high removal capacity of Pb(II) into bismuth nanodots, this promotes the stripping anodic current. It was shown that the detection limit can be enhanced since biochar has high adsorptive capacity.

A BCPE was developed to determine paraquat and bipyridinium contact herbicide via voltammetry.[12,13] The function of biochar derived from castor oil cake was to support the growth of antimony microparticles. The interaction between biochar and paraquat plays a significant role for the progress of biosensors. It was also shown that a BCPE with antimony microparticles could be used as mercury electrode in electroanalytical applications.

Recently, studies have been reported on BCPE with castor oil cake or castor bean. However, no study covering the electroanalytical use of biochar derived from industrial tea waste (BCTW) as BCPE or as biosensor transducer has been found in the literature. The electrochemical performance of BCTW has not been determined before. In the present study, a BCPE was prepared by using BCTW and its electrochemical performance was investigated as a glucose biosensor.

## 2. Results and discussion

### 2.1. Characterization of the biochar

Some physical and chemical properties of the tea waste and biochar are given in Table 1. The ash and moisture contents of the tea waste were 7.20% and 5.03%, respectively. After pyrolysis the carbon content of biomass increases, which is appropriate for electrode applications.[16] A lower H/C ratio was obtained when tea waste biomass was converted to biochar, which suggests that biochar has a more aromatic structure than aliphatic ones such as cellulose. On the other hand, the O/C ratio is indicative for hydrophilicity, with the higher the O/C the higher the hydrophilic structure. Biochar seems to have a less hydrophilic structure. Furthermore, the labile carbon structure in biomass is stabilized by carbonization to form fixed carbon. Labile molecules are destroyed and volatile matter is removed. It is reported that the carbon structure of biochar stays stable for long periods.[24]

**Table 1.** Properties of tea waste and biochar.

| Property | Moisture (%) | Ash (%) | Surface area (m$^2$/g) | C (%) | H (%) | N (%) | S (%) | O (%) | H/C | O/C |
|---|---|---|---|---|---|---|---|---|---|---|
| Tea waste | 7.20 | 5.03 | 12.7 | 45.4 | 5.7 | 2.9 | 0.0 | 46.0 | 0.13 | 1.01 |
| Biochar | - | - | 3.1 | 63.2 | 3.3 | 3.5 | 0.0 | 30.0 | 0.05 | 0.47 |

It was found in this work that the biochar's surface area is smaller than that of tea waste, which could be due to structure collapse during carbonization. However, the surface has highly carbon–oxygen complexes offering better potential for immobilization of organic and inorganic compounds than activated carbon with a larger surface area.[18] Figure 1 shows the FTIR spectra of tea waste and its biochar form. Generally both

structures are rich in OH groups (broad band at around 3600–3200 cm$^{-1}$). The broad band around 1617–1599 cm$^{-1}$ corresponds to C=O and aromatic C=C stretching. More symmetric bending of CH$_3$ and C–O stretching are observed at around 1454–1446 cm$^{-1}$ and 1234 and 1136 cm$^{-1}$ for tea waste, respectively. The biochar samples contain more –OH, C=O, and C=C than C–H and C–O.[25]
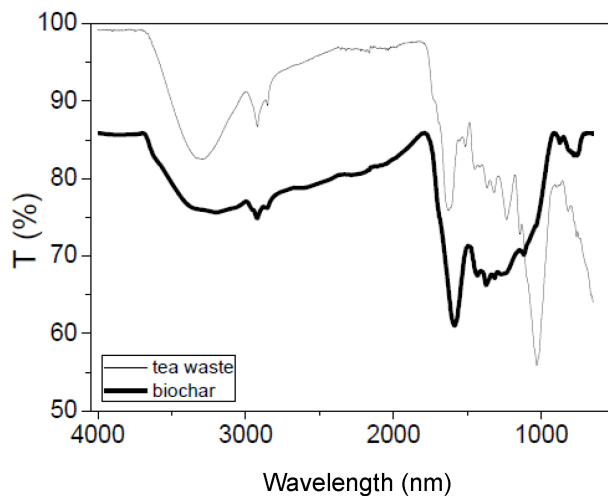


**Figure 1.** FTIR spectra of tea waste and derived biochar.

The SEM and TEM images of tea waste (A) and biochar (B, C) are given in Figure 2. An amorphous and heterogeneous structure is seen for both samples. The SEM images show the morphological changes emerging by converting tea waste to biochar. Torrefaction causes the breaking off of particles. It was discovered by SEM and TEM analyses that the biochar has mostly micro-sized particles.

The physicochemical properties of graphite as an electrode material are already well known and can be found in the literature.[26] Modification of carbon paste electrodes with carbon-based biochar is thought to be effective due to its highly variable and customizable surface chemistry. In the present study, this phenomenon was researched by application of biochar derived from tea waste as glucose transducer. First, the electrochemical performance of the BCPE was determined.

## 2.2. Examination of the electrochemical performance of the BCPE

The composition of the BCPE has a profound effect upon its electrochemical reactivity. The optimum modification ratio was determined. As the first step, pre-experiments were performed to determine the electrochemical performance of the BCPE when solely tea waste biochar was used. However, very low current (55 nA) was observed for the pure biochar electrode while it was around 67 $\mu$A for graphite. The responding potentials for biochar and graphite were also determined and it was found that they respond to similar potential as 0.25 V and 0.23 V, respectively. Then the graphite electrode was modified with biochar with the aim of developing the BCPE. Figure 3 examines the influence of the paste composition upon the separation of the cyclic voltammetric peak potentials and the peak current for K$_3$Fe(CN)$_6$. The current signal increases rapidly at first upon raising the biochar loading 1%, 2%, 4%, 6%, and 8% and then decreases sharply. The optimum ratio for biochar for the BCPE was determined as 2% wt.

In order to examine the effect of introducing biochar into the biosensor, the electrochemical performance was investigated using 1 $\times$ 10$^{-3}$ M K$_3$Fe(CN)$_6$. Then the results obtained were compared with those of a

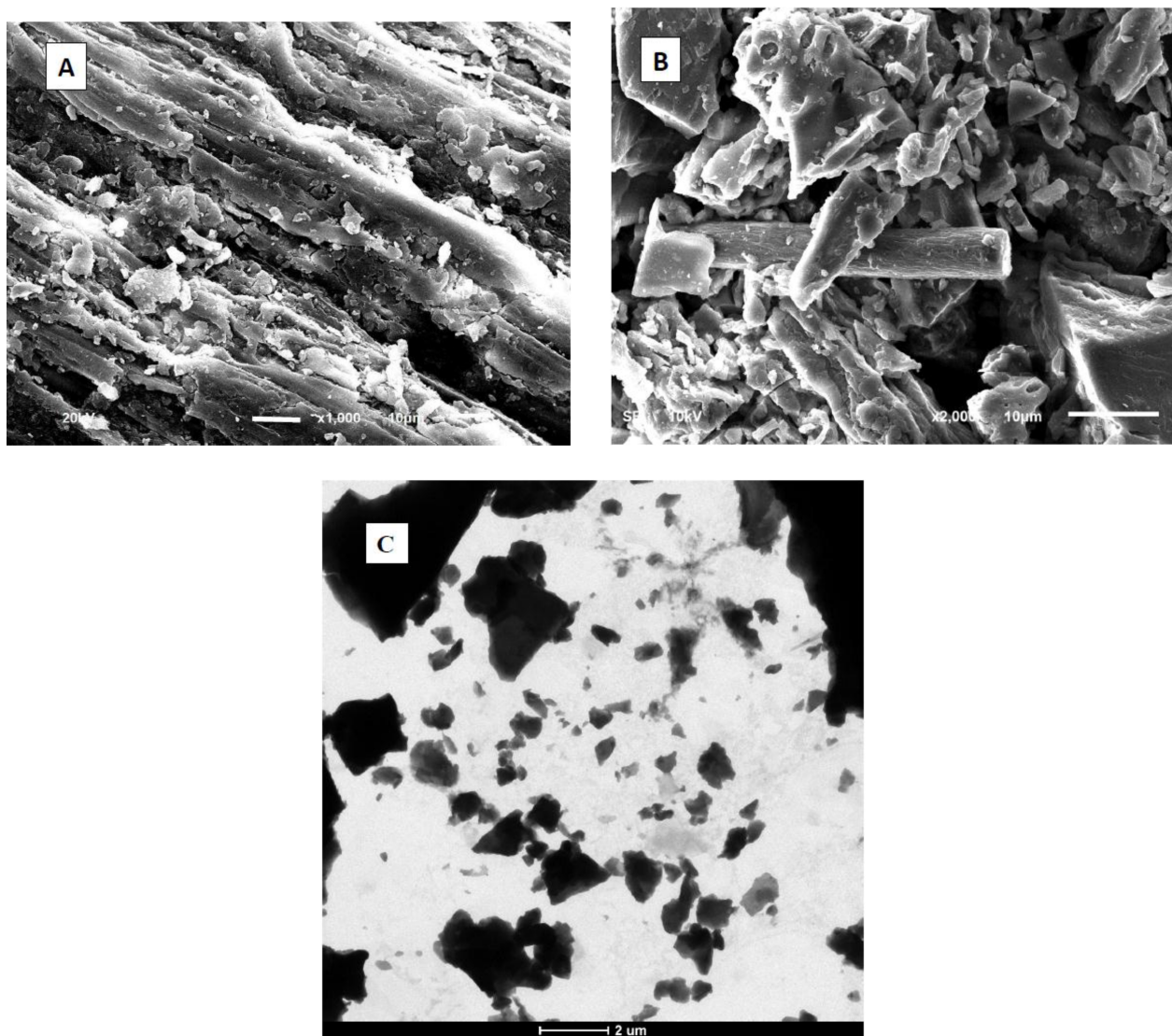**Figure 2.** (A) SEM images of tea waste ($\times 1000$, 10 $\mu$m) and (B) biochar ($\times 5000$, 5 $\mu$m); (C) TEM image of biochar (2 $\mu$m).

plain carbon paste electrode (CPE). Figure 4 displays cyclic voltammograms obtained at 100 mV/s for (a) $1 \times 10^{-3}$ M ferricyanide, (b) $1 \times 10^{-3}$ M catechol, and (c) $1 \times 10^{-3}$ M $Ru(NH_3)_6^{3+}$ at the BCPE (CPE includes 2% wt biochar) (A) and CPE (B). The BCPE indicates sharper and larger voltammetric peaks for all three redox systems, which shows that modification of the CPE with biochar enhances the electron transfer rate. The current values for the corresponding figures are given in Table 2.

On the other hand, it can be seen from the voltammograms for the BCPE and CPE that all three chemicals display a quasireversible response. The voltammetric parameters are summarized in Table 3. It is observed that the reversibility is better for catechol (with the larger current peak) and ferricyanide systems than the hexaammine ruthenium (III) chloride one, since the peaks separate gradually. However, diffusion rate is higher for hexaammine ruthenium (III) chloride with lower $\Delta E_p$ around 59 mV.

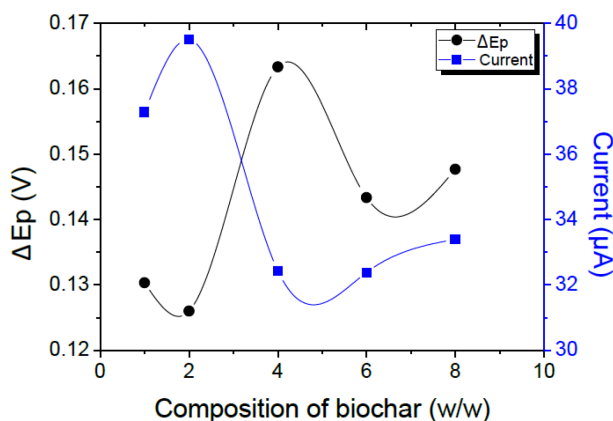The reversibility is also a function of electrode surface as well as the type of redox couple. The similar

**Figure 3.** The effect of the paste composition on the peak potential separation ($\Delta$Ep) and (B) Peak current for $1 \times 10^{-3}$ M $K_3Fe(CN)_6$. Compositions: 1%/69%/30%, 2%/68%/30%, 4%/66%/30%, 6%/64%/30%, 8%/625/30% (biochar/carbon paste/mineral oil). Electrolyte, 0.2 M phosphate buffer (pH 6.8).

**Table 2.** Current values of the BCPE (containing 2% biochar) and the CPE at 100 mV/s for (a) $1 \times 10^{-3}$ M ferricyanide, (b) $1 \times 10^{-3}$ M catechol, and (c) $1 \times 10^{-3}$ M $Ru(NH_3)_6^{3+}$ for the corresponding figures given in Figure 4.

| Marker | BCPE | | CPE | |
|---|---|---|---|---|
| | $I_a$ | $I_c$ | $I_a$ | $I_c$ |
| Ferricyanide | 39.51 | 37.08 | 30.61 | 29.19 |
| Catechol | 88.99 | 94.36 | 69.11 | 71.89 |
| Hexaammine ruthenium (III) chloride | 42.03 | 25.26 | 38.63 | 20.53 |

$I_a$: Anodic current, $I_c$: Cathodic current

**Table 3.** Summary of cyclic voltammetric data for several redox systems at the CPE and BCPE.

| Marker | | BCPE | CPE |
|---|---|---|---|
| Ferricyanide | $\Delta E_p*$ (mV) | 126 | 148 |
| | $E^{0'}$ (mV) | 220 | 223 |
| Catechol | $\Delta E_p$ (mV) | 183 | 205 |
| | $E^{0'}$ (mV) | 223 | 224 |
| Hexaammine ruthenium (III) chloride | $\Delta E_p$ (mV) | 59 | 58 |
| | $E^{0'}$ (mV) | −203 | −210 |

$$\Delta E_p = |-E_P^A - E_P^C|, E^{0'} = \left(E_P^A + E_P^C\right)/2$$

potential for the BCPE and CPE for the hexaammine ruthenium (III) chloride system could be a result of surface characteristics or porosity of the electrode. Since biochar from tea waste has a fibrous structure, there could be insulated regions rather than sphere surfaces.[20]

The BCPE surface has more oxygen-containing groups than the CPE, which could affect the attraction or repulsion of chemicals in redox systems, resulting in lower separation of peaks.[27] The possible interactions could be a result of covalent or ionic ones since all three redox systems have polar and apolar sites.[28] Xie et al.[18] noted that the surface of biochar could be charged negatively and thus positively charged ions could interact with biochar easily.
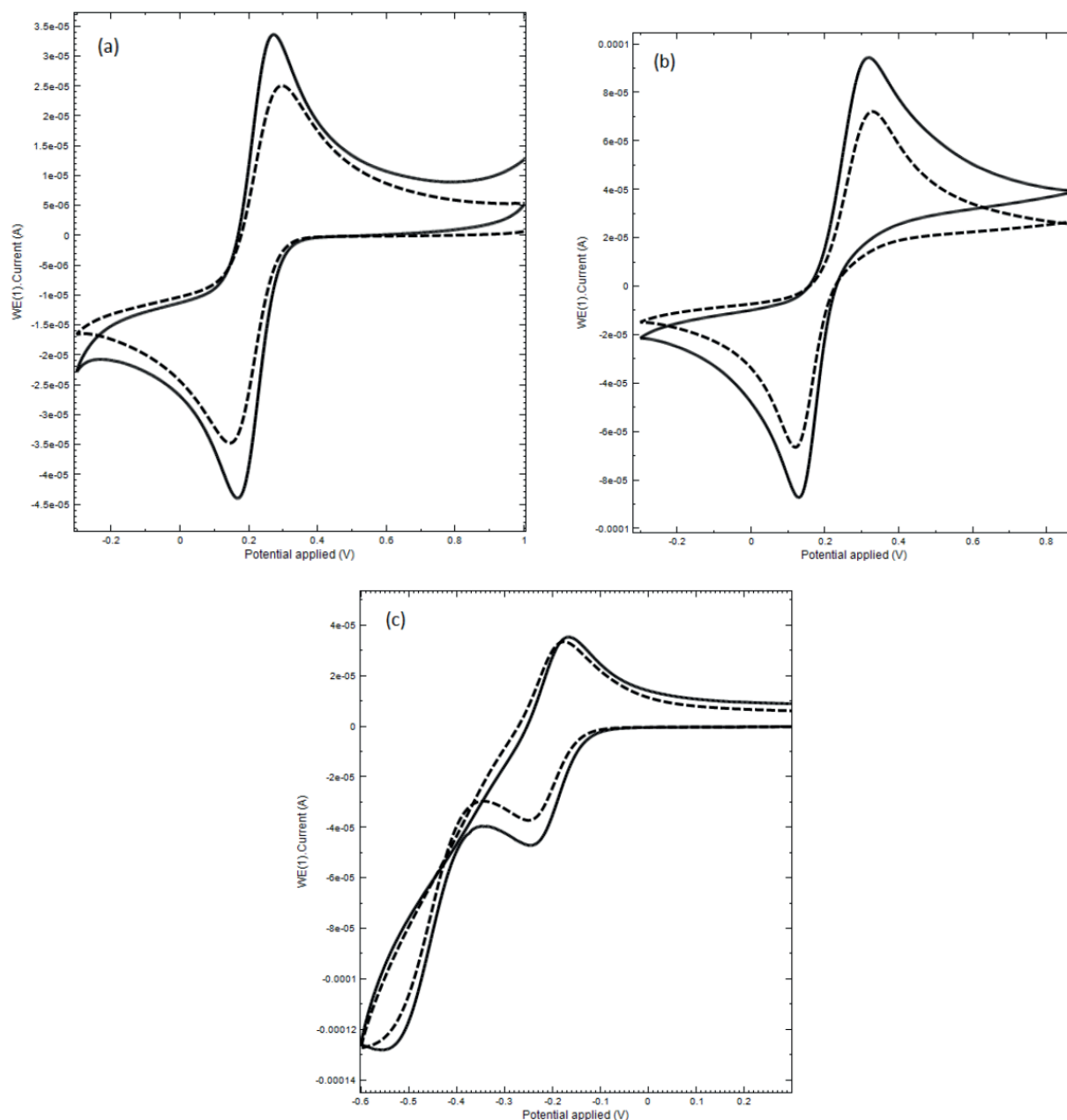
**Figure 4.** Cyclic voltammograms for a) $1 \times 10^{-3}$ M $K_3 Fe(CN)_6$, b) $1 \times 10^{-3}$ M catechol, c) $1 \times 10^{-3}$ $Ru(NH_3)_6^{3+}$. Straight line: BCPE (Biochar/graphite/oil ratio of 2/68/30 (w/w) %), dashed line: CPE (graphite/oil 70/30 (w/w) %).

The effect of polishing time on the electrode was assumed to be very low. The same polishing time was applied for both electrodes and the biochar-modified electrode provides better results.

## 2.3. Biochar-modified CPE as a glucose biosensor transducer

CPEs have been widely used for the design of amperometric enzyme electrodes. [29−31] Biochar-enzyme electrodes combine the spectacular advantages of biocomposite electrodes with improved amperometric detection. BCPE has a potential to become a more effective transducer as the operating potential increases as shown in this

study. The repeatability of both electrodes to GOx enzyme was almost the same, while the BCPE indicated simply higher current values with lower peak potentials compared to the CPE.

The analytical characteristics of a BCPE-based biosensor were compared with a plain CPE-based biosensor. Amperometric linear ranges for the biosensors were obtained as follows: for the BCPE, a linear range was obtained in the concentration range for glucose between 25 $\mu$M and 600 $\mu$M with the equation y = 0.0004x + 0.012 ($R^2$ = 0.99). The relative standard deviation (RSD) (n = 3 for 50 $\mu$M glucose) and limit of detection (LOD) values were 3.07% and 1.59 $\mu$M, respectively. The chronoamperometric response and calibration graph for the BCPE biosensor is given in Figure 5. The linear range of the CPE glucose biosensor was obtained between 25 $\mu$M and 600 $\mu$M with the equation y = 0.0003x + 0.029 ($R^2$ = 0.98). The RSD (n = 3 for 50 $\mu$M glucose) and LOD values were 6.04% and 2.83 $\mu$M, respectively. The chronoamperometric response and calibration curve for the CPE is given in Figure 6. The characteristics show that the BCPE is more sensitive along with high reproducibility. The values are given in Table 4. Comparison of analytical parameters of the present biosensor with the previously reported studies is summarized in Table 5. As seen, the BCPE glucose biosensor electrode's performance is comparable with that of the graphene-based nanocomposites biosensor.

**Table 4.** LOD values and calibration constants.

|  | LOD | RSD | Slope | Intercept | $R^2$ | Concentration range |
|---|---|---|---|---|---|---|
| Biochar | 1.59 $\mu$M | 3.07% | $4.03 \times 10^{-4}$ | 0.012 | 0.99 | 25–600 $\mu$M |
| Graphite | 2.83 $\mu$M | 6.04% | $3.32 \times 10^{-4}$ | 0.029 | 0.98 | 25–600 $\mu$M |

[LOD = 3 × (std deviation of blank)/(slope of calibration)], std deviation of blank was calculated for 3 measurements].[29]

[RSD % = [(std deviation of 50 $\mu$M glucose)/(mean of current measurements)] × 100, std deviation of 50 $\mu$M glucose was calculated for 3 measurements]

**Table 5.** Comparison of present work with recently reported similar glucose biosensors.

| Sensing matrix | Linear range | LOD ($\mu$M) | Reference |
|---|---|---|---|
| Pt/PPy/GOx | 0.25 mM to 20 mM | 250 | 30 |
| PGA/GCE/GOx | 0.5 mM to 5.5 mM | 120 | 31 |
| PPG/GOx | 0 mM to 7.5 mM | 30 | 32 |
| Ru-RP/GOx | 0 mM to 10 mM | 290 | 33 |
| Au/PPy/GOx | 50 mg/dL to 400 mg/dL | nr | 34 |
| ITO/ZnO/AuNPs/GOx | 0.2 mM to 13 mM | nr | 35 |
| GC/Graphene-CuNPs/GOx | 25 $\mu$M to 400 $\mu$M | 2.87 | 21 |
| BCPE /GOx | 25 $\mu$M to 600 $\mu$M | 1.59 | This work |

nr – not reported

In the present study, biochar obtained from tea waste was applied as an electrochemical electrode material. The electrochemical performances of the developed biosensor were examined using chemical solutions. The practicability of the biosensor was determined by applying it as a glucose transducer in model solution. Introducing biochar into the carbon-paste electrode structure increased the CPE's sensitivity and enhanced the electrochemical responses. Biochar modification offers higher electrochemical reactivity. The current was enhanced around 25% by modifying the CPE using 2% biochar. Such enhancements are worthwhile in regards to lowering the biosensor cost, assessing biomass resources as added value products, or even for material flow management.
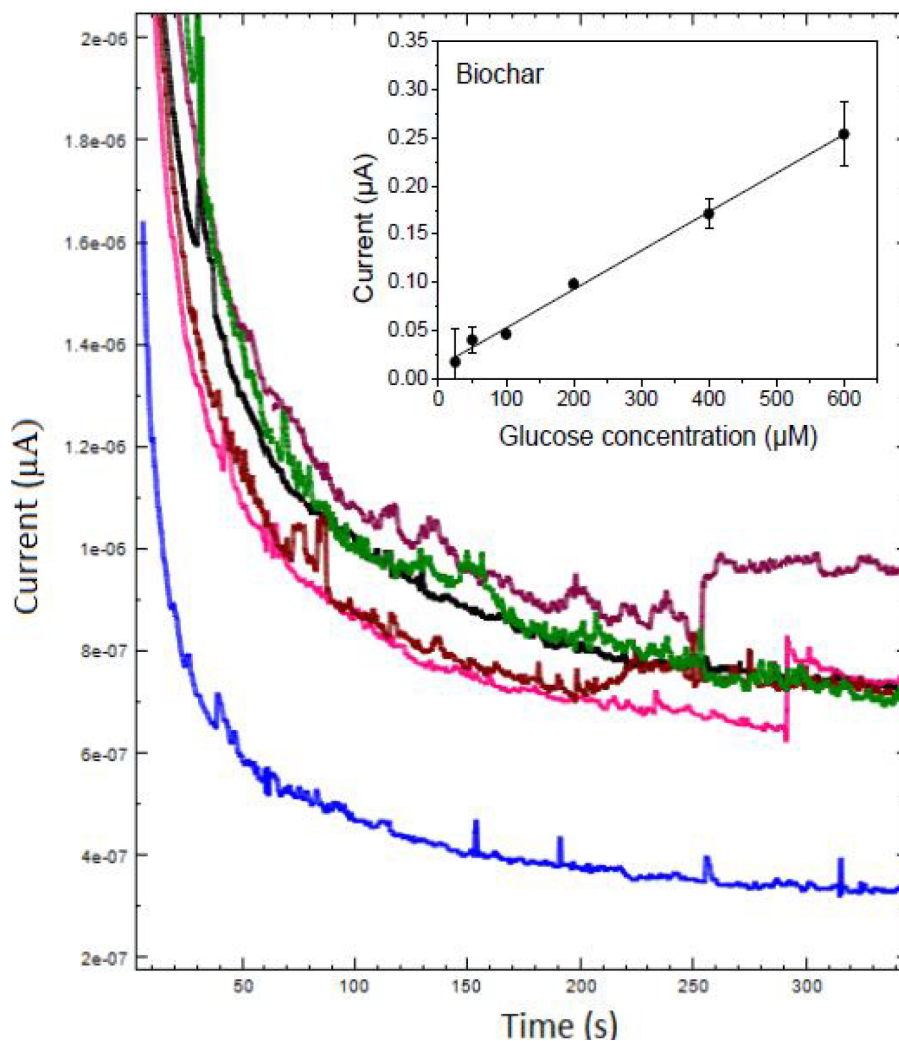
**Figure 5.** Chronoamperometric response and calibration graph at the BCPE containing 55.7 unit GOx enzyme and 2% biochar, in 50 mM pH 7.4 phosphate buffer solution, at +900 mV potential, 25 °C (biochar/carbon paste/GOx enzyme/mineral oil (2:65:3:30 (%)). (Black curve 25 $\mu$M, blue curve 50 $\mu$M, green curve 100 $\mu$M, maroon curve 200 $\mu$M, pink curve 400 $\mu$M, purple curve 600 $\mu$M).

Biochar as an additive to CPEs could be attractive for composite electrode materials because of its practicability and low cost, which could lead to this electrode being marketed for use in various real electrochemical applications. Modified BCPEs with biochar derived from different biomass resources should be investigated to discover the effect of BCTW. Further research should be performed to determine the practical feasibility of biochar-modified biosensors in real solutions to find out the interference effects.

## 3. Experimental

### 3.1. Apparatus

Chronoamperometric and cyclic voltammetric measurements were carried out with the AUTOLAB PGSTAT 101 electrochemical measurement system driven by NOVA 1.10 software using a three-electrode system (the measuring range is between 10 nA and 1 A). The BCPE served as working electrode for the glucose biosensor
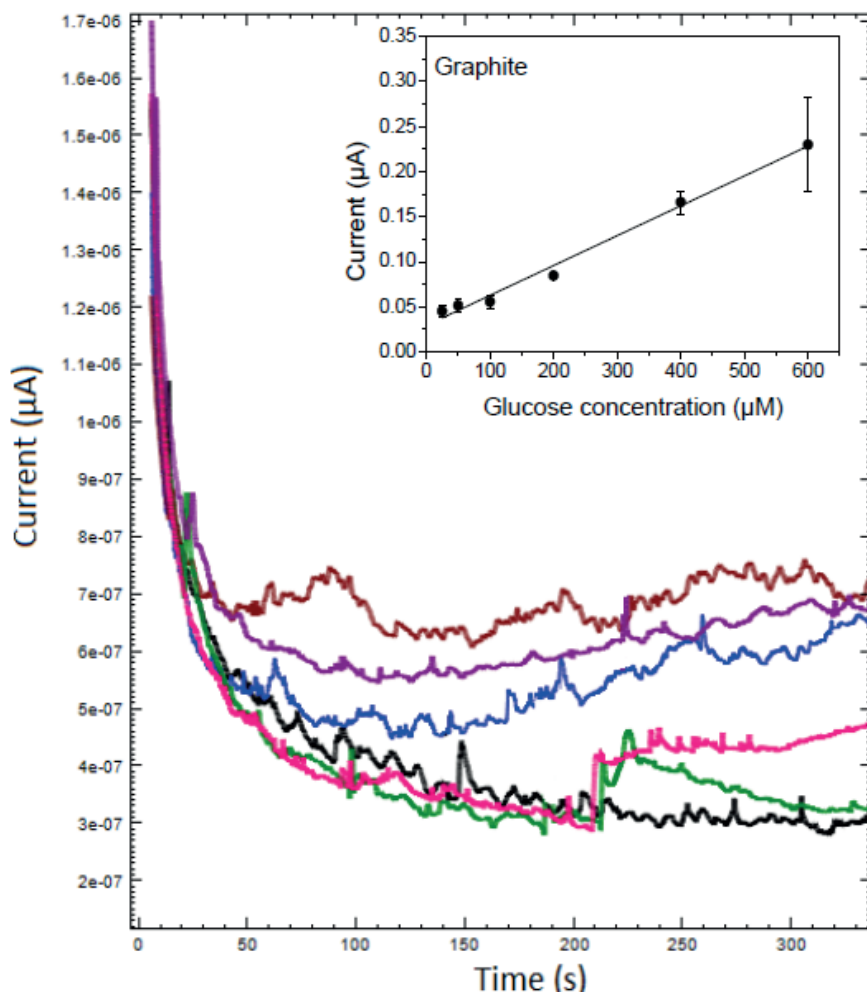
**Figure 6.** Chronoamperometric response and calibration graph at the CPE containing 55.7 unit GOx enzyme and 67% carbon paste, (carbon paste/GOx enzyme/mineral oil (67:3:30 (%)).(Black curve 25 $\mu$M, blue curve 50 $\mu$M, green curve 100 $\mu$M, maroon curve 200 $\mu$M, pink curve 400 $\mu$M, purple curve 600 $\mu$M).

transducer. A Ag/AgCl electrode (containing 3.0 M KCl) and a platinum electrode were used as reference and counter electrode, respectively (CHI 111 reference electrode). The electrodes were inserted into the cell through the Teflon cover. The morphology of the samples was scanned by scanning electron microscope (SEM, JEOL/JSM-6610) and transmission electron microscope (TEM, FEI Tecnai G2 Spirit BioTwin CTEM). C, H, N, and S contents of feedstock and biochar samples were determined using an elemental analyzer (LECO CHNS 932) according to ASTM D3176-89. Surface areas were measured by Quantachrome Autosorb 1 C.

### 3.2. Reagents

Graphite powder, mineral oil, potassium chloride (KCl), sodium hydroxide (NaOH), and glucose oxidase ($GO_x$) from *Aspergillus niger* (174.9 units/mg solid) were purchased from Sigma-Aldrich. D (+)-glucose monohydrate and potassium dihydrogen phosphate ($KH_2PO_4$) were purchased from Merck. Hexaammine ruthenium (III) chloride ($Ru(NH_3)_6Cl_3$) and potassium ferricyanide (III) ($K_3Fe(CN)_6$) were obtained from Aldrich and catechol ($C_6H_4$-1,2-$(OH)_2$) was from Sigma. The chemicals have more than 99% purity. Solutions were prepared

with double distilled water. pH was buffered with phosphate buffer solution (supporting electrolyte). The optimum pH values and working potentials had already been determined in previous studies and were applied here as described in those studies.[20, 21]

### 3.3. Electrode preparation

BCPEs were prepared by mixing of graphite powder with enzyme, biochar, and mineral oil (70:30 (w/w). The amount of $GO_x$ was optimized in our previous study as 0.3 mg.[22] A portion of the resulting paste was then packed firmly into the Delrin rod's electrode cavity (cell dimensions are 3.0 mm diameter and 5.0 mm depth, filled with electrode material) and the electrode's surface was polished using a weighing paper. Electrical contact was established via a copper wire.

### 3.4. Biochar preparation

Tea manufacturing waste was provided by a tea processing plant located in Rize, Turkey, in the form of straw ($< 2.36$ mm). Tea waste is a useless end product coming from tea processing that was used in our experiments as received without any grinding or pretreatment. The biochar was produced by dry pyrolysis (torrefaction). The experiment was carried out in a vertical reactor (V = 1 L) under nitrogen atmosphere at 400 $^\circ$C with a reaction time of 30 min. A detailed description of the experimental procedures can be found in the literature.[23] The resulting biochar was pulverized at 600 rpm for 1.5 min (Fritsch Pulverisette 9) and then sieved through a 25-$\mu$m sized sieve. This biochar sample was used in all experiments.

### 3.5. Procedure

Cyclic voltammetric measurements were conducted using the markers $Ru(NH_3)_6^{3+}$, ($C_6H_4$-1,2-$(OH)_2$), and $K_3Fe(CN)_6$ in the potential range of –600 to +1000 mV at 100 mV/s scan rate. The pH was adjusted to 6.8 with 0.2 M phosphate buffer solution.[20]

Chronoamperometric measurements were carried out in 10 mL of 50 mM phosphate buffer medium under the operating potential of +900 mV while the solution was stirred. The pH value was adjusted to 7.4.[21] The three electrodes (working electrode, platinum electrode, and reference electrode) were immersed into the electrochemical cell. In that potential, the evolution of $H_2O_2$ was monitored according to the enzymatic reaction as shown in Eq. (1).

$$Glucose + O_2 Gluconic acid + H_2O_2 \tag{1}$$
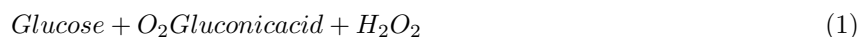
The duration of each analysis was 600 s and the transient current decreased to a steady-state value after 200 s in the presence of supporting electrolyte. The electrode surface was renewed before every single measurement. All experiments were performed at room temperature and repeated 3 times. The repeatability was as high as 95%.

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