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Article

Electrochemical Detection of Acetaminophen in Pharmaceuticals Using Rod-Shaped α - Bi_2O_3 Prepared via Reverse Co-Precipitation

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Abstract: This study employed a novel synthetic approach involving a modified reverse co-precipitation method utilizing glacial acetic acid to synthesize α - Bi_2O_3 . X-ray powder diffraction and scanning and transmission electron microscopy analyses revealed the formation of a rod-like α - Bi_2O_3 microstructure. The prepared material was utilized to modify a glassy carbon paste (GCP) electrode for the development of an electrochemical sensor for acetaminophen (APAP) detection using differential pulse voltammetry (DPV). Cyclic voltammetry studies revealed that the GCP@ Bi_2O_3 electrode exhibited enhanced electrochemical properties compared to the bare GCP. The designed GCP@ Bi_2O_3 sensor detected APAP in the linear concentration range from 0.05 to 12.00 μM , with LOQ and LOD of 36 nM and 10 nM, respectively. Additionally, the developed sensor demonstrated sufficient precision, repeatability, and selectivity toward APAP detection. The recovery values between the declared and found APAP content in a pharmaceutical formulation (Caffetin[®]) displayed the advantageous accuracy, precision, and applicability of the GCP@ Bi_2O_3 sensor and the developed DPV method for real-time APAP detection in pharmaceuticals, with minimal interference from the matrix effect.

Keywords: rod-like α - Bi_2O_3 microstructure; reverse co-precipitation synthesis; electrochemical sensor; acetaminophen detection



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1. Introduction

Acetaminophen, also known as N-acetyl-p-aminophenol (APAP), is a popular and extensively used over-the-counter analgesic and antipyretic drug. It is commonly employed to alleviate mild to moderate pain, fever, and discomfort associated with various conditions, including headaches, muscle aches, menstrual cramps, and cold or influenza symptoms. Its therapeutic effect is achieved through the inhibition of prostaglandin synthesis in the central nervous system and sedation of the hypothalamic center responsible for thermoregulation [1]. Acetaminophen is considered safer than non-steroidal anti-inflammatory drugs for individuals with certain medical conditions, as it does not exhibit significant anti-inflammatory or anticoagulant effects [2,3]. Its popularity stems from its effectiveness in managing pain and fever while being well-tolerated at recommended dosages. However, excessive or prolonged use of acetaminophen may lead to potential hepatotoxicity as a consequence of the accumulation of toxic metabolites [4–6].

It is crucial to detect and accurately quantify APAP in pharmaceutical formulations and biological samples for several reasons: dosage monitoring, quality control in pharmaceuticals, toxicology, and forensics, and bioavailability and pharmacokinetic studies to understand its metabolism and properties for drug development and optimization. The pursuit of developing simple, rapid, accurate, and sensitive analytical methods for determining APAP remains a focus within the scientific community [7]. Numerous techniques have been developed thus far, including liquid chromatography [8–11], spectrophotometry [12–14], chemiluminescence [15–17], titrimetry [18,19], electrophoresis [20–22], spectrofluorimetry [23–25], as well as electrochemical techniques [1,12,26–28]. While some approaches, such as spectrophotometry and chemiluminescence, demand tedious sample preparation, others, like liquid chromatography, can be time-consuming. Electroanalytical techniques stand out among the rest due to their rapidity, selectivity, high sensitivity, simplicity, and cost-effectiveness. Additionally, sample preparation is not required. Since acetaminophen exhibits electroactive properties, electrochemical techniques emerge as the preferred choice for its determination.

Bismuth oxide (Bi_2O_3) is a material of significant interest in modern solid-state technology due to its distinctive structures and functional properties, such as a wide energy band gap, high refractive index, high dielectric permittivity, as well as notable photoconductivity and photoluminescence [29,30]. These remarkable features enable the potential application of Bi_2O_3 in various fields, including sensors [31–35], optical coatings [36,37], photovoltaic cells [38], solid oxide fuel cells [39–41], superconductors [42–44], and catalysts [45–51]. The phase composition of a material is a well-known key factor influencing its functional properties. Also, catalytic activity is closely related to crystalline structure, morphology, and particle size. Therefore, the controlled synthesis of specific Bi_2O_3 phases is of great importance. Bismuth oxide crystallizes in six primary polymorphic forms. Monoclinic ($\alpha\text{-Bi}_2\text{O}_3$) and cubic face-centered ($\delta\text{-Bi}_2\text{O}_3$) forms represent low- and high-temperature stable phases, respectively. In contrast, phases denoted as $\beta\text{-Bi}_2\text{O}_3$ (tetragonal structure), $\gamma\text{-Bi}_2\text{O}_3$ (cubic, body-centered structure), $\varepsilon\text{-Bi}_2\text{O}_3$ (orthorhombic structure), and $\omega\text{-Bi}_2\text{O}_3$ (triclinic structure) are high-temperature metastable phases [52]. The chosen preparation procedures and synthesis conditions influence the transitions between Bi_2O_3 phases. In recent decades, promising catalytic activity has been exhibited in specific Bi_2O_3 structures (rods, wires, tubes, or fibers), attracting scientific interest in developing new synthetic methods to produce novel Bi_2O_3 structures [52–57]. Numerous physical and chemical procedures have been developed for the preparation of Bi_2O_3 , including pulsed laser deposition [58–61], epitaxial growth [62–64], plasma [65,66], magnetron sputtering [67,68], vapor transport method [69,70], co-precipitation [71–74], chemical vapor deposition [75–77], sonochemical [78–81], and hydrothermal [56,82–84]. Chemical preparation methods are the most convenient for large-scale industrial manufacturing. Co-precipitation is a relatively inexpensive and straightforward method. However, the main challenges associated with this procedure are particle size and morphology, which can be highly variable. Nonetheless, these factors can be controlled by carefully selecting synthesis conditions.

In this work, we present the synthesis of $\alpha\text{-Bi}_2\text{O}_3$ rod-like microstructures via reverse co-precipitation, which can potentially be used in catalytic applications. Conventional co-precipitation and reverse co-precipitation routes typically involve the use of nitric acid (HNO_3) to dissolve bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$) as a source of Bi^{3+} ions [72,85,86]. This research describes a modified reverse co-precipitation procedure for synthesizing Bi_2O_3 using glacial acetic acid instead of nitric acid and applying Bi_2O_3 material in the development of an electrochemical sensor. No previous reports exist on preparing Bi_2O_3 rods by reverse co-precipitation using glacial acetic acid. A few structural and morphological characterization techniques confirmed the formation of monoclinic $\alpha\text{-Bi}_2\text{O}_3$ rod-like microstructures. The synthesized $\alpha\text{-Bi}_2\text{O}_3$ material was utilized to modify the glassy carbon paste to produce an electrochemical sensor. Differential pulse voltammetry (DPV) was used as an electroanalytical method for detecting APAP. Subsequently, the proposed electrochemical platform was successfully applied to determine APAP in pharmaceutical formulation.

2. Materials and Methods

2.1. Chemicals and Solutions

APAP (BioXtra $\geq 99.0\%$), potassium chloride (KCl, 99.9%), potassium hexacyanoferrate(II) trihydrate [$K_4[Fe(CN)_6] \times 3H_2O$, $>98.5\%$], potassium hexacyanoferrate(III) [$K_3[Fe(CN)_6]$, 99%], boric acid (H_3BO_3 , 99.97% trace metals basis), phosphoric acid [H_3PO_4 , ACS reagent, ≥ 85 wt. % in H_2O], acetic acid [CH_3COOH , glacial, ACS reagent, $\geq 99.7\%$], sodium hydroxide (NaOH, ACS reagent, $\geq 97.0\%$), bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \times 5H_2O$, ACS reagent, $\geq 98.0\%$), glassy carbon powder (glassy, spherical powder, 2–12 μm , 99.9% trace metals basis), and mineral oil were supplied by Merck, Darmstadt, Germany.

Merck (Darmstadt, Germany) also delivered chemical compounds used as interfering substances (potassium nitrate (KNO_3 , powder, ACS reagent, $\geq 99.0\%$), sodium sulfate decahydrate ($Na_2SO_4 \times 10H_2O$, powder, ACS reagent, $\geq 99.0\%$), D-glucose (powder, ACS reagent), and caffeine (powder, ReagentPlus[®])).

The Britton–Robinson buffer solution (BRBS) was prepared using a step-by-step process. First, 2.80 mL of H_3PO_4 (≥ 85 wt. % in H_2O) was dissolved, followed by 2.40 mL of CH_3COOH (glacial, $\geq 99.7\%$). Then, 2.48 g of H_3BO_3 was added to the mixture. Finally, the entire solution was dissolved in 1000 mL of deionized water.

The APAP standard solution (0.0050 mol/L) was prepared by dissolving a specific amount of APAP powder ($\geq 99.0\%$) in deionized water.

2.2. Preparation Procedures

2.2.1. Synthesis of Bi_2O_3 Particles

Modified reverse co-precipitation was used to prepare Bi_2O_3 particles [72]. This synthesis starts with the acid-dissolved reactants introduced dropwise into the base solution to form the desired precipitate due to maintaining a high pH value. Glacial acetic acid dissolved $Bi(NO_3)_3 \times 5H_2O$. The final concentration of Bi^{3+} ions was 0.03 M. The obtained solution was added dropwise into the excess NaOH solution (pH ≈ 13). The Bi_2O_3 yellow precipitate was formed, and the suspension was heated at 80 °C for 1 h. The pH of the suspension was about 11. Furthermore, the precipitate was filtered, rinsed three times with deionized water, and dried at ambient temperature for 24 h. The powder was pulverized in an agate mortar and annealed in an electrical furnace with a heating rate of 10 °C/min at 450 °C for 1 h.

2.2.2. Preparation of Working Electrodes

Homogeneous bare glassy carbon paste (GCP) was prepared by hand-mixing 20% mineral oil and 80% glassy carbon powder in a mortar for approximately 20 min. The working electrode was prepared by filling a Teflon tube (with an inner diameter of 2 mm) with the prepared paste. After filling the Teflon tube, the electrode was mechanically polished using weight paper to get a smooth and shiny-looking electrode surface. Subsequently, an electrode was used for electrochemical measurements [87].

The GCP modification was performed by hand-mixing 20% mineral oil, different amounts of Bi_2O_3 modifier (1.0, 2.5, and 5.0%), and glassy carbon powder (up to 80%) in a mortar and pestle for approximately 20 min. The working electrode prepared according to this procedure was labeled GCP@ Bi_2O_3 . The Teflon tube was filled, and the electrode was polished like the bare GCP. All prepared pastes were stored in the fridge at 4 °C [87].

2.2.3. Preparation of Real Samples

Caffetin[®] pharmaceutical formulation (Alkaloid, Skopje, Macedonia) was used as a real sample in this study. Per the manufacturer's instructions, each tablet contains 250 mg of APAP. The detailed content of Caffetin[®] tablets is placed in the Supplementary Material (Addition S1. The detailed content of Caffetin[®] tablets). The content of the target analyte was determined in three tablets taken randomly from the pharmaceutical packaging box. The previously reported procedure was followed to prepare Caffetin[®] tablets, which were

slightly modified [88,89]. Tablets are prepared identically: the whole tablet was crushed in a mortar with a pestle, and the obtained powder was quantitatively transferred to a voltammetric flask of 100 mL, topped up with distilled water, and stirred for 2 h (solution A). Then, 5 mL of solution A was transferred to a 10 mL voltammetric flask and topped with distilled water (solution B). The standard addition method was used to determine APAP content in Caffetin[®] pharmaceutical formulations.

2.3. Methods

2.3.1. Structural Characterization of Material

A Rigaku SmartLab diffractometer was used for the X-ray powder diffraction experiment (XRPD). The diffractometer was equipped with $\text{CuK}_{\alpha 1,2}$ radiation. It used the generator voltage and the generator current of 40 kV and 30 mA, respectively. The recording range between 4 and 90 $2\theta^\circ$ was used in a continuous scan mode with a scanning step size of 0.01 $2\theta^\circ$ and a scan rate of 5 $2\theta^\circ/\text{min}$ by the D/TeX Ultra high-speed detector. The phase composition of the synthesized material, the unit cell parameters, and the size-strain values for $P2_1/c$ polymorph ($\alpha\text{-Bi}_2\text{O}_3$) as well as the phase abundances for $P2_1/c$ polymorph ($\alpha\text{-Bi}_2\text{O}_3$) and $P31c$ polymorph ($\omega\text{-Bi}_2\text{O}_3$), calculated by the relative intensity ratio (RIR) method, were obtained with the use of the PDXL2-integrated X-ray powder diffraction software (Ver. 2.8.4.0; Rigaku Corporation, Tokyo, Japan).

Fourier-transform infrared spectroscopy (FTIR) was recorded on a Nicolet 6700 FTIR instrument (Thermo Scientific, Waltham, MA, USA) in the range of 4000–400 cm^{-1} using the attenuated total reflectance (ATR) technique with a Smart Orbit accessory (diamond crystal).

To gain deeper insight into the morphology and elemental composition of the prepared material, scanning electron microscopy (SEM) (JEOL JSM-6390 LV, JEOL Ltd., Peabody, MA, USA) coupled to electron-dispersive spectroscopy (EDS) (Oxford Instruments X-MaxN, Concord, MA, USA) was used. The accelerating voltage was between 20 and 30 kV. The transmission electron microscopic (TEM) analysis was performed on a JEOL JEM-1400 Plus Electron microscope (JEOL Ltd., Peabody, MA, USA) with a voltage of 120 kV and a LaB_6 filament at a magnification of 1500 \times .

2.3.2. Electrochemical Measurements

All experiments were performed using a *PalmSens4* instrument (Houten, Utrecht, The Netherlands) equipped with PStTrace voltammetric software (Version 5.8). This study used a conventional three-electrode cell (25 mL), with unmodified/modified glassy carbon paste as a working electrode, a platinum sheet electrode (Methrom AG, Herisau, Switzerland) as the auxiliary electrode, and silver/silver chloride (3 mol/L KCl, Ag/AgCl, Methrom, Switzerland) as the reference electrode.

3. Results and Discussion

3.1. Structural and Morphological Characterization of Bi_2O_3 Material

The XRPD results confirmed the presence of Bi_2O_3 , predominantly composed of $P2_1/c$ polymorph ($\alpha\text{-Bi}_2\text{O}_3$) modification (96.3(1)%), as shown in Figure 1A. The obtained unit cell parameters were close to the reference values (PDF # 01-070-8243) (Table S1). The other polymorph modification of $\omega\text{-Bi}_2\text{O}_3$ ($P31c$) was found in the minority (3.7(1)%), so the calculation of unit cell and microstructural parameters could not be determined with a good confidence level. The presence of Bi_2O_3 ($P2_1/c$, PDF # 01-080-2589) and Bi_6O_7 ($I4/mmm$, PDF # 03-065-5490) near the limit of detection might be possible.

FTIR spectroscopy was used to confirm the identification of the bismuth oxide phases given by the XRPD pattern. Figure 1B shows the FTIR spectrum of the synthesized material. The band at 1389.0 cm^{-1} originates from the vibration of the $-\text{NO}_3$ group, which indicates the existence of nitrate residues attached to the Bi_2O_3 surface [90,91]. The sharp peak at 846.7 cm^{-1} can be attributed to the Bi-O-Bi vibration modes [92,93]. A strong absorption band at 503.7 cm^{-1} is due to the Bi-O stretching mode [51,94].

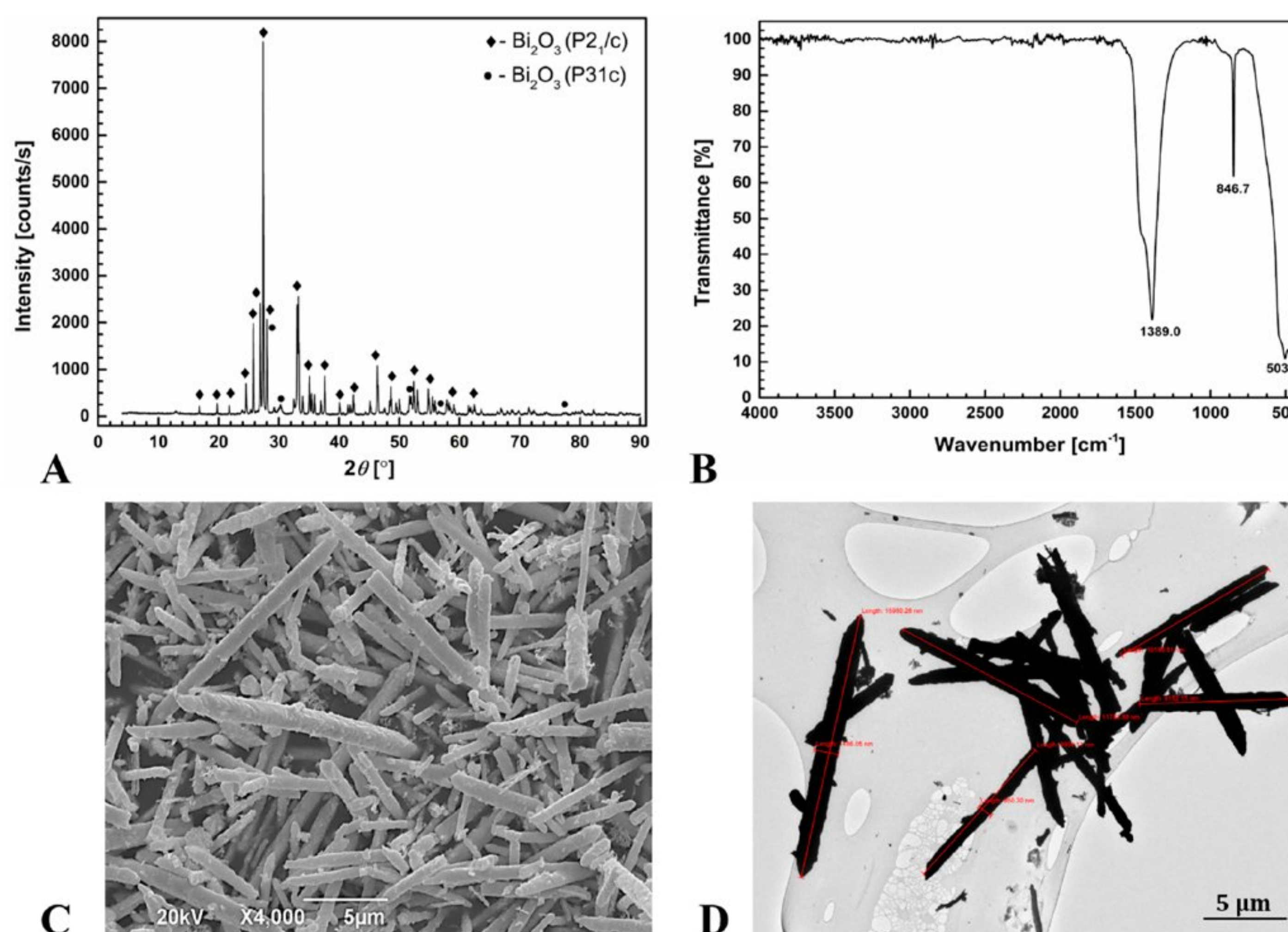


Figure 1. (A) X-ray powder pattern of the synthesized Bi_2O_3 , (B) FTIR spectrum of the synthesized Bi_2O_3 , (C) SEM, and (D) TEM micrographs of the synthesized Bi_2O_3 .

The SEM results are presented in Figure 1C. The Bi_2O_3 particles predominantly exhibited a rod-shaped morphology. Other observed morphologies can be attributed to minor phases identified by XRPD analysis. Additionally, this can be attributed to the presence of amorphous, unorganized $\alpha\text{-Bi}_2\text{O}_3$ particles. EDS confirmed the high purity level of the obtained sample (Figure S1). Mitsunori et al. also obtained rod-like $\alpha\text{-Bi}_2\text{O}_3$ particles in the micrometric range using a co-precipitation route at 80°C reaction mixture temperature with a nitric acid solution [95]. Notably, they obtained particles with lengths of several tens of micrometers. In the present work, the Bi_2O_3 particles prepared by a modified reverse co-precipitation route combined with calcination are smaller in size.

The TEM micrograph (Figure 1D) confirmed the presence of long rod-shaped particles in the micrometer range. Most particles were approximately $10\ \mu\text{m}$ or longer and had a width of around $1\ \mu\text{m}$.

3.2. Electrochemical Characterization of Working Electrodes

Cyclic voltammetric and electrochemical impedance spectroscopic analysis. Electrochemical behavior of APAP over a $\text{GCP@Bi}_2\text{O}_3$ sensor.

Cyclic voltammetry was used to investigate the electrochemical characteristics of bare GCP and GCP modified with Bi_2O_3 particles ($\text{GCP@Bi}_2\text{O}_3$). In this study, GCP was modified with 2.5% Bi_2O_3 particles. Cyclic voltammetric measurements were applied in the potential range of $-1.0\ \text{V}$ to $1.0\ \text{V}$. Five millimolar $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in $0.1\ \text{M}$ KCl was used as the tested analyte. Figure 2A depicts the cyclic voltammetric response of bare GCP and $\text{GCP@Bi}_2\text{O}_3$ in $0.1\ \text{M}$ KCl containing $5\ \text{mM}$ $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ with a scan rate of $50\ \text{mV/s}$. Both working electrodes allowed well-defined redox peaks in the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system. The $\text{GCP@Bi}_2\text{O}_3$ electrode showed a higher current intensity of oxidation ($I_{p(\text{ox})}$) and reduction peaks ($I_{p(\text{red})}$) and better reversibility of the redox probe (different between oxidation peak potential ($E_{p(\text{ox})}$) and reduction peak potential ($E_{p(\text{red})}$), ΔE) compared to bare GCP (for $\text{GCP@Bi}_2\text{O}_3$: $I_{p(\text{ox})} = 29.5\ \mu\text{A}$, $I_{p(\text{red})} = -22.4\ \mu\text{A}$, $\Delta E = 0.633\ \text{V}$; for bare GCP: $I_{p(\text{ox})} = 24.4\ \mu\text{A}$, $I_{p(\text{red})} = -19.3\ \mu\text{A}$, $\Delta E = 0.687\ \text{V}$). A similar trend to cyclic voltammetric measurements was noticed during the EIS analysis. Figure 2B represents Nyquist plots of bare GCP and $\text{GCP@Bi}_2\text{O}_3$ electrodes. The obtained Nyquist

plots are characterized by a semicircular diameter and a linear part. The charge transfer resistance (R_{ct}) at the surface of working electrodes can be determined from the semicircular diameter by extrapolation. The conductivity on the electrode surface can be defined based on the obtained R_{ct} values (R_{ct} is inversely proportional to conductivity). The linear part of the Nyquist plot refers to the diffusion of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ analyte [87,96]. Bare GCP was defined with an R_{ct} of 37.4 k Ω . On the contrary, the GCP@Bi₂O₃ electrode provided an R_{ct} of 26.8 k Ω , indicating a positive influence on the conductivity on the electrode surface after introducing the Bi₂O₃ modifier.

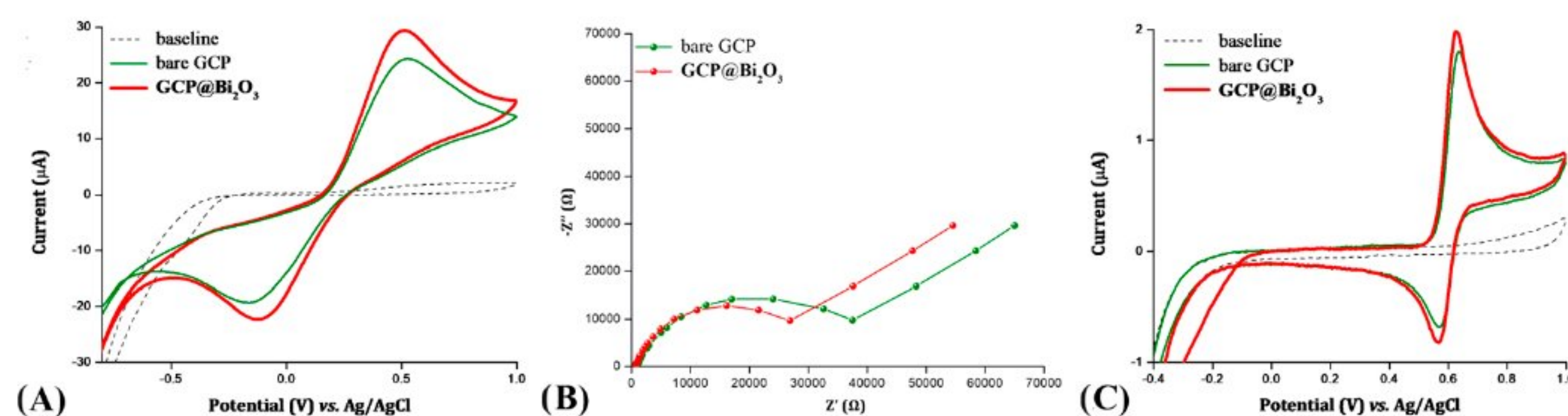


Figure 2. (A) Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M KCl at bare GCP and GCP@Bi₂O₃ electrode; a scan rate of 50 mV/s. (B) EIS spectra in the form of Nyquist plots at bare GCP and GCP@Bi₂O₃ electrodes in 0.1 M KCl containing 5 mM $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$. (C) Cyclic voltammetric profile of 10 μM APAP in BRBS pH = 3 recorded by bare GCP and GCP@Bi₂O₃ electrode; a scan rate of 50 mV/s.

The electrode surface area (ESA) and heterogeneous rate constant (k^0) of working electrodes were calculated using Equation (1) [87] and Equation (2) [97], respectively, as follows:

$$I_p = 2.69 \times 10^5 A n^{\frac{3}{2}} C D^{\frac{1}{2}} \nu^{\frac{1}{2}} \quad (1)$$

where I_p —the peak current (A), n —the number of electrons ($n = 1$), A —the electrode surface area (cm^2), D —the diffusion coefficient ($6 \times 10^{-6} \text{ cm}^2/\text{s}$ for the redox probe), C —the concentration of the redox probe (mol/mL), and ν —the scan rate (V/s).

$$\Delta E = 201.39 \log\left(\frac{\nu}{k^0}\right) - 301.78 \quad (2)$$

where ΔE —the difference between $E_{p(ox)}$ and $E_{p(red)}$ (V) and ν —the scan rate (V/s).

The ESA for bare GCP and GCP@Bi₂O₃ were 0.033 cm^2 and 0.040 cm^2 , respectively, indicating an increase in the electroactive sites on the electrode surface after GCP was modified with Bi₂O₃ material. The k^0 was calculated at $15.742 \times 10^{-4} \text{ 1/s}$ for bare GCP and $15.752 \times 10^{-4} \text{ 1/s}$ for GCP@Bi₂O₃ electrode. These results show a higher electron transfer rate at the surface of the GCP@Bi₂O₃ electrode than bare GCP.

Glassy carbon powder is characterized by high conductivity [98], while Bi₂O₃ material is exemplified by catalytic activity and a high surface area [52–57,99]. The synergistic effect of glassy carbon powder and Bi₂O₃ particles can be attributed to an increase in the current intensity of the redox peaks, better reversibility, favorable conductivity at the electrode surface, a higher ESA, and a higher k^0 recorded by the GCP@Bi₂O₃ electrode. By introducing a Bi₂O₃ modifier in carbon paste electrodes, improvements in the electrochemical performances were noticed in several research papers [97,100,101].

Cyclic voltammetry was also used to investigate the electrochemical response of bare GCP and GCP@Bi₂O₃ electrodes toward the main analyte. Figure 2C represents the cyclic voltammetric profile of working electrodes in BRBS pH = 3, containing 10 mM APAP, with a scan rate of 50 mV/s. Both working electrodes provided oxidation and reduction of APAP under both experimental and instrumental conditions. APAP oxidation occurred at around 0.63 V, while the APAP reduction peak was at around -0.57 V . Additionally, more intense APAP redox peaks ($I_{p(ox)} = 1.95 \mu\text{A}$, $I_{p(red)} = -1.28 \mu\text{A}$) were recorded with the GCP@Bi₂O₃ electrode compared to bare GCP ($I_{p(ox)} = 1.67 \mu\text{A}$, $I_{p(red)} = -0.99 \mu\text{A}$). These

results additionally demonstrated improvement in the electrochemical response of the CPE after introducing the Bi_2O_3 material into a glassy carbon paste.

Additionally, the influence of the modifier amount in the GCP on the electrochemical behavior of APAP was examined by cyclic voltammetry. The electrochemical response of the $\text{GCP@Bi}_2\text{O}_3$ electrodes (where GCP was modified with 1.0, 2.5, and 5.0% of Bi_2O_3) was followed in BRBS pH = 3 containing 10 μM APAP under a scan rate of 50 mV/s. The GCP with a 2.5% modifier provided the most intense APAP redox peaks. Therefore, GCP modified with 2.5% Bi_2O_3 was used for further experiments.

3.2.1. Effect of pH

The effect of the pH of the BRBS on the electrochemical response of the $\text{GCP@Bi}_2\text{O}_3$ sensor towards APAP was investigated using cyclic voltammetry. Figure 3A depicts the cyclic voltammetric profile of 10 μM APAP in BRBS at various pH values (from pH = 2 to pH = 8) over the $\text{GCP@Bi}_2\text{O}_3$ electrode (at a scan rate of 50 mV/s). Each pH examined provided the target analyte's oxidation and reduction peak (Figure 3A). Compared to the appearance of the peaks, the favorable shape of the redox peaks of APAP was registered in BRBS pH = 6 (Figure 3A). Therefore, BRBS pH = 6 was selected as the most convenient, and this supporting electrolyte was used in further electrochemical analysis.

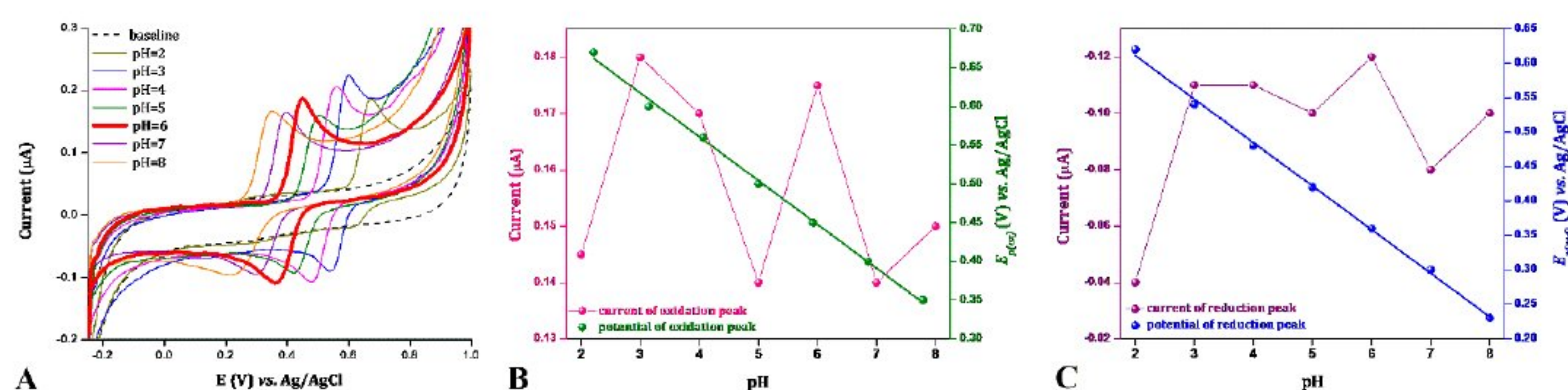


Figure 3. (A) Cyclic voltammetric profile of 10 μM APAP in BRBS at different pH values recorded using the $\text{GCP@Bi}_2\text{O}_3$ sensor with a scan rate of 50 mV/s. (B) Linear plot of oxidation peak current (μA) and $E_{p(ox)}$ vs. pH at the $\text{GCP@Bi}_2\text{O}_3$ electrode in the presence of 10 μM APAP. (C) Linear plot of reduction peak current (μA) and $E_{p(red)}$ vs. pH at the $\text{GCP@Bi}_2\text{O}_3$ electrode in the presence of 10 μM APAP.

In addition, increasing the pH leads to shifts in APAP oxidation and a reduction in peak potentials to negative potential values. In BRBS pH = 2, the oxidation and reduction peaks of the analyte occur at 0.67 V and -0.02 V; at pH = 8, these peaks are shifted to 0.17 V and -0.10 V, respectively (Figure 3A). The plots of $E_{p(ox)}$ vs. pH (Figure 3B) and $E_{p(red)}$ vs. pH (Figure 3C) show high linearity for APAP redox peaks. These linearities can be expressed by Equations (3) and (4):

$$E_{p(ox)}(\text{V}) = 0.767 - 0.054 \text{ pH} \quad (r = -0.999) \quad (3)$$

$$E_{p(red)}(\text{V}) = 0.738 - 0.063 \text{ pH} \quad (r = -0.999) \quad (4)$$

The obtained slopes of -54 mV/pH (for the oxidation peak) and -63 mV/pH (for the reduction peak) indicated an equal number of electrons and protons involved in the oxidation and reduction processes of APAP at the surface of the $\text{GCP@Bi}_2\text{O}_3$ sensor since the slope values are very close to the Nernstian theoretical value (-59 mV/pH).

Tafel patterns were analyzed to discover the potential redox mechanism of APAP at the surface of the $\text{GCP@Bi}_2\text{O}_3$ electrode. The Tafel region refers to the linearly increasing segment in the electrode's voltammetric response (current, I (A) vs. potential, E (V)) toward the analyte affected by electron transfer kinetics between the analyte and the electrode surface [87]. Figure S2A shows the cyclic voltammetric response of the $\text{GCP@Bi}_2\text{O}_3$ electrode toward 10 μM APAP in BRBS pH = 6 at a scan rate of 50 mV/s. Red- and orange-colored dots demonstrate Tafel regions for APAP oxidation and reduction peaks (Figure S2A). The number of electrons participating in redox processes can be calculated based on the slope

obtained from the E (V) vs. $\log I$ (A) linear dependence. Figures S2B and S2C depict the Tafel plot of E (V) vs. $\log I$ (A) for APAP oxidation and APAP reduction peaks, respectively. Slopes of 133 mV/A (for the oxidation peak) and 118 mV/A (for the reduction peak) indicated two electrons (the theoretical value of 59 mV/A corresponds to one-electron exchange in the reaction [87]) participating in the oxidation, that is, the reduction of APAP at the electrode surface. Figure S3 gives the potential sensing mechanism of APAP at the GCP@Bi₂O₃ electrode, based on: (i) pH measurement, which concluded that an equal number of protons and electrons participate in APAP redox processes, and (ii) the Tafel plot of E (V) vs. $\log I$ (A), which indicated two electrons in the oxidation, that is, the reduction process at the electrode surface.

3.2.2. Effect of Scan Rate

Cyclic voltammetry was used to examine the effect of the scan rate on the electrochemical behavior of the working electrode in the presence of the target analyte. This experiment was performed in triplicate. The electrochemical response of the GCP@Bi₂O₃ electrode in BRBS pH = 6 towards 10 μ M APAP at different scan rates (ν) is represented in Figure 4A. The current intensity of the APAP redox peaks increased continuously with the applied scan rate (Figure 4A). In addition, the peak potential of the oxidation peak shifted towards the positive potential side. In contrast, the potential of the reduction peak moved to negative potential values. Figure 4B depicts that the $I_{p(ox)}$ and $I_{p(red)}$ of APAP are linearly dependent on the square root of the scan rate ($\nu^{1/2}$), indicating a diffusion-controlled process responsible for the APAP redox processes at the electrode surface [102]. Plots of $\log I_{p(ox)}$ vs. $\log \nu$ and $\log I_{p(red)}$ vs. $\log \nu$ were constructed to confirm the process on the electrode surface. Figure 4C,D show plots of $I_{p(ox)}$ vs. $\log \nu$ and $I_{p(red)}$ and $\log \nu$, where linear dependences can be expressed by Equations (5) and (6), respectively, as follows:

$$\log I_{p(ox)}(A) = 0.51 \log \nu (mV/s) - 7.60 \quad (r = 0.998) \quad (5)$$

$$\log I_{p(red)}(A) = 0.57 \log \nu (mV/s) - 7.84 \quad (r = -0.998) \quad (6)$$

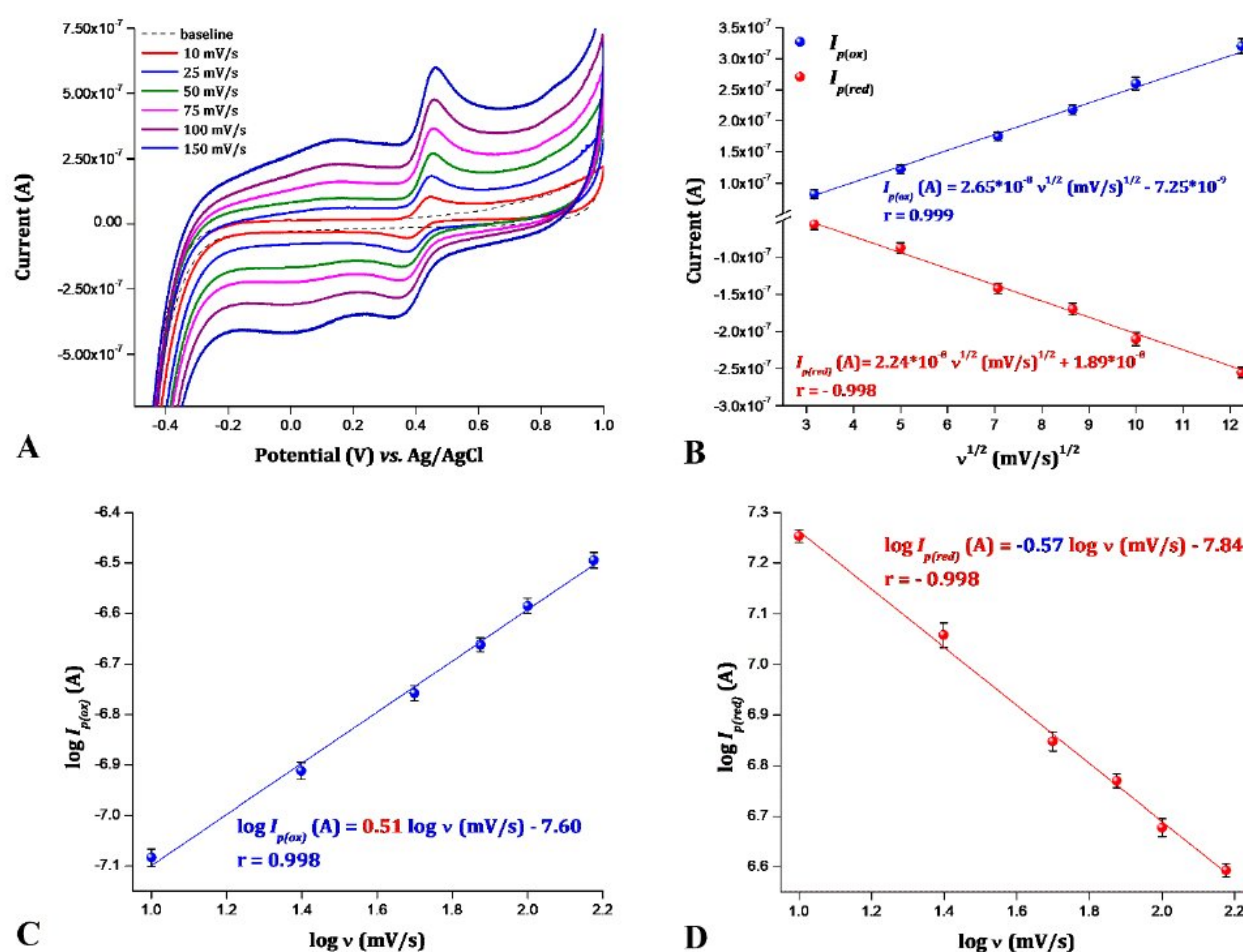


Figure 4. (A) Cyclic voltammetric profile of 10 μ M APAP recorded at the GCP@Bi₂O₃ sensor in BRBS pH = 6 at different scan rates (10–150 mV/s). (B) Linear plot of I_p vs. $\nu^{1/2}$ for APAP redox peaks; (C) Linear plot of $\log I_{p(ox)}$ vs. $\log \nu$. (D) Linear plot of $\log I_{p(red)}$ vs. $\log \nu$. (B–D) show error bars representing the standard deviation between measurements ($n = 3$).

The slope of 0.51 (in the case of $I_{p(ox)}$ vs. $\log v$) and 0.57 (for $I_{p(red)}$ vs. $\log v$ dependence) confirms that the diffusion-controlled process is answerable for the oxidation and reduction of APAP on the surface of the GCP@Bi₂O₃ electrode due to the close values of the obtained slopes to the theoretical value of 0.5 [102]. These results comply with previously reported findings, where the authors described that the diffusion-controlled process is responsible for APAP oxidation at modified CPEs [88,89,103,104].

3.3. Voltametric Detection of the APAP at the GCP@Bi₂O₃ Sensor

An electroanalytical method for APAP detection was developed using DPV. APAP's oxidation peak was evaluated for this experiment. First, the influence of the amplitude of the DPV method on the electrochemical response of the GCP@Bi₂O₃ electrode toward the target analyte was investigated. The DPV profile of the GCP@Bi₂O₃ electrode in BRBS pH = 6 containing 5 μ M APAP at different applied amplitudes (from 5 to 45 mV) is depicted in Figure S4A. Figure S4B shows an increase in $I_{p(ox)}$ with an applied amplitude up to 40 mV. A further increase in the amplitude decreases the intensity of the current signal and widens the oxidation peak (Figure S4B). Consequently, the amplitude of 40 mV was selected as optimal, and this value was used for further measurements.

The electroanalytical parameters were examined, such as the linear concentration range, the limit of detection (LOD), and the limit of quantification (LOQ). The electrochemical behavior of the GCP@Bi₂O₃ electrode was followed after successive additions of APAP standard solution (0.0050 M) in BRBS pH = 6 under the DPV method (amplitude of 40 mV, a pulse width of 0.2 s, a sampling width of 0.02 s, and a pulse period of 0.5 s). The developed sensor detected APAP in a wide concentration range from 0.05 to 12 μ M (Figure 5A). The calibration was performed in triplicate. The corresponding calibration curve is depicted in Figure 5B, where error bars correspond to the standard deviation between measurements ($n = 3$). The linearity between $I_{p(ox)}$ and APAP concentration (C_{APAP}) is described by the equation: $I_{p(ox)} (A) = 0.0055 C_{APAP} (M) - 2.14 \times 10^{-10}$, with Pearson's coefficient (r) of 0.9996. LOQ and LOD were determined from the calibration curve as $S/N = 10$ and $S/N = 3$, respectively. LOQ was 36 nM, while LOD was calculated to be 10 nM.

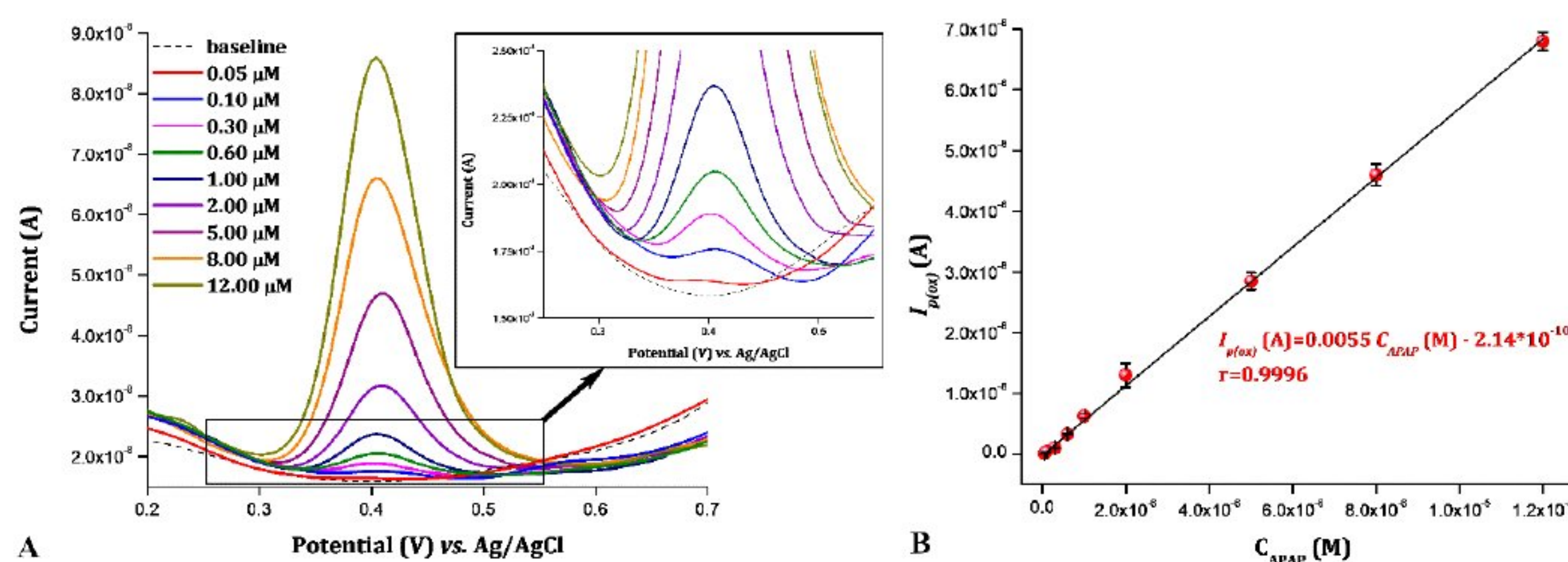


Figure 5. (A) DPV profiles of the GCP@Bi₂O₃ electrode for different APAP concentrations (0.05 to 12 μ M) recorded in BRBS pH = 6 (DPV parameters: amplitude of 40 mV, pulse width of 0.2 s, sampling width of 0.02 s, and pulse period of 0.5 s). (B) Plot of $I_{p(ox)}$ vs. C_{APAP} with corresponding error bars ($n = 3$).

The precision and repeatability of the developed DPV method were examined using the GCP@Bi₂O₃ sensor. All measurements were performed in BRBS pH = 6. The sensor's precision was investigated by measuring the 1.0 μ M APAP with three independently prepared GCP@Bi₂O₃ electrodes. The relative standard deviation (RSD) between measurements was 2.95%. The sensor's repeatability was studied by measuring three different APAP concentrations with the same GCP@Bi₂O₃ electrode in five consecutive measurements. The RSD between repetitions for APAP concentrations of 0.3 μ M, 1.0 μ M, and 5.0 μ M were 1.75%, 1.03%, and 0.87%, respectively. These results indicated good

precision and repeatability of the proposed GCP@Bi₂O₃ sensor and the developed DPV method toward the electrochemical determination of APAP. In addition, the stability of the developed sensor was examined in BRBS pH = 6 containing 1.0 μM APAP under the optimized DPV method. This test started the same day when the modified paste was prepared. The identical measurements were conducted with the same paste over 30 days (the paste was stored in the fridge at 4 °C). The APAP current signal was measured every 5 days. The changes in the current signal were not above 4%, indicating the excellent stability of the GCP@Bi₂O₃ sensor.

The electroanalytical parameters (LOD, LOQ, and linear concentration range) acquired with the GCP@Bi₂O₃ sensor were compared with identical parameters obtained with previously published carbon paste-based electrochemical sensors for APAP detection. Table 1 shows that the proposed GCP@Bi₂O₃ sensor and developed DPV method provided similar or superior properties for the given electroanalytical parameters. The advantages of the proposed electrochemical platform for APAP detection are reflected through the low-cost precursors for Bi₂O₃ synthesis, the simple and rapid synthesis of the Bi₂O₃ material, and the simple preparation of the working electrode. Additionally, the GCP@Bi₂O₃ sensor provided adequate precision, repeatability, and selectivity (see Section 3.4. Selectivity of the Developed GCP@Bi₂O₃ Sensor) toward APAP detection, indicating that the results provided by this electrochemical platform are appropriate and comparable to those previously reported.

Table 1. Comparison of electroanalytical parameters of different electrochemical sensors based on carbon paste modification with different materials previously published for APAP detection with this study.

Electrode	Technique	Linear Concentration Range (μM)	LOQ (nM)	LOD (nM)	Literature
CPE/NiZ/GO	DPV	0.026–0.795	26	7.8	[88]
CPE/safranin	CV	10–100	1580	470	[105]
CPE/GR-CoFe ₂ O ₄	SWV	0.03–12.00	83	25	[89]
CPE/carbon	DPV	0.1–1000.0	n.g.	15	[103]
CPE/nevirapine	DPV	2–12	n.g.	770	[106]
CPE/GO/poly(Val)	DPV	5–60	960	290	[107]
CPE/SSW	SWV	80–1000	n.g.	5.54	[108]
CPE/RGO	SWV	1.2–220.0	930	310	[109]
CPE/MoO ₃	SWV	1–15	n.g.	140	[110]
CPE/La ₂ O ₃	SWAdV	0.99–19.00	n.g.	20	[111]
GCP/ILC	DPV	0–120	n.g.	2800	[112]
GCP/MMTK ₁₀	DPV	1–15	n.g.	460	[113]
GCP@Bi ₂ O ₃	DPV	0.05–12.00	36	10	This work

CPE—carbon paste electrode; CV—cyclic voltammetry; DPV—differential pulse voltammetry; GO—graphene oxide; GR—graphene; ILC—ionic liquid crystal; MMTK₁₀—potassium montmorillonite (MMTK₁₀)clay; NiZ—mesoporous natural zeolite with the introduced Ni²⁺; poly(Val)—electropolymerized L-Valine; RGO—reduced graphene oxide; SSW—shrimp shell waste; SWAdV—square wave adsorptive voltammetry; SWV—square wave voltammetry.

3.4. Selectivity of the Developed GCP@Bi₂O₃ Sensor

A selectivity study is required to successfully apply the electrochemical sensor to real samples. Therefore, the selectivity of the developed GCP@Bi₂O₃ sensor was evaluated in the presence of different interferences that are regularly present in real samples. This experiment was performed using the optimized DPV method. The electrochemical behavior of the GCP@Bi₂O₃ electrode toward 1 μM APAP (oxidation peak was evaluated) in BRBS pH = 6 was followed in the absence and, then, the presence (successive addition) of different ions (K⁺, Na⁺, NO₃[−], and SO₄^{2−}), glucose (Glu), and caffeine (Caff). These compounds were selected due to the practical application of the sensor in pharmaceuticals. K⁺ and Na⁺ ions were applied in a concentration of 200 μM, while a concentration of NO₃[−] and SO₄^{2−} was 100 μM. The concentrations of Glu and Caff in this experiment were 100 μM and 16 μM, respectively. Figure S5 depicts the peak current change (%) in the presence of a 16- to 200-fold higher concentration of interfering compounds (compared to the target

analyte), where the current signal change was less than 10%. These results indicated satisfactory selectivity of the GCP@Bi₂O₃ sensor toward APAP determination. On the other hand, the selectivity of the developed sensor toward APAP is not investigated in the presence of compounds structurally analogous to APAP.

3.5. Real Sample Analysis

The practical application of the proposed GCP@Bi₂O₃ sensor and developed DPV method were examined in pharmaceuticals. The standard addition method determined APAP in three independent tablets of the Caffetin[®] pharmaceutical formulation. According to the manufacturer, each tablet contains 250 mg of APAP. The preparation of Caffetin[®] tablets is described in Section 2.2.3. Preparation of Real Samples. During electrochemical analysis, a certain amount of solution B was added to 25 mL of BRBS pH = 6, whereby the GCP@Bi₂O₃ sensor, under optimized DPV parameters, recorded the presence of APAP in the analyzed system. Further analysis was based on adding different amounts of APAP standard solution (0.0050 M) into the electrochemical cell. The final concentration of standard additions was 3.00 μM, 6.00 μM, and 8.00 μM. The APAP detection in the Caffetin[®] pharmaceutical formulation was performed in triplicate. Figure S6A shows the DPV responses of the GCP@Bi₂O₃ sensor during APAP detection in the pharmaceutical formulation using the standard addition method. The DP voltammograms in Figure S6A refer to the APAP analysis in tablet 2, where the final spike (sample) concentration was 1.0 μM (found value was 1.022 μM). Figure S6B provides a corresponding plot of I_{p(ox)} vs. C_{APAP}. The recalculated results are summarized in Table 2. The recovery obtained between the declared APAP content and the found APAP content (Table 2) indicated favorable accuracy, precision, and applicability of the GCP@Bi₂O₃ sensor and the developed DPV method for real-time APAP detection in pharmaceuticals, with minimal influence of the matrix effect.

Table 2. Results for APAP determination in pharmaceutical formulation Caffetin[®] using GCP@Bi₂O₃ sensor and developed DPV method; comparison with declared value.

Pharmaceutical Formulation	Declared APAP Content (mg) ¹	Found APAP Content (mg) ² ± SD ³	Recovery (%) ⁴
Tablet 1	250	262 ± 2	105
Tablet 2	250	257 ± 2	103
Tablet 3	250	260 ± 2	104

¹ prescribed by the manufacturer. ² found by the proposed GCP@Bi₂O₃ sensor and the developed DPV method. ³ SD—standard deviation between repetitions (*n* = 3). ⁴ Recovery (%) was calculated as (C_{APAP} found/C_{APAP} declared) × 100.

4. Conclusions

A novel approach for synthesizing the α-Bi₂O₃ structure was employed, involving a modified reverse co-precipitation method that utilized glacial acetic acid instead of the conventionally used nitric acid. Structural and morphological characterization techniques confirmed the formation of α-Bi₂O₃ microstructure with a rod-like morphology. The synthesized α-Bi₂O₃ material was used to modify a GCP electrode to develop an electrochemical sensor to detect APAP using the DPV technique. Cyclic voltammetry studies demonstrated that the GCP@Bi₂O₃ sensor exhibited enhanced redox peak currents of APAP in BRBS pH = 3, improved reversibility, favorable conductivity at the electrode surface, increased electroactive surface area, and a higher heterogeneous electron transfer rate constant compared to the bare GCP. The favorable electrochemical performances of the GCP@Bi₂O₃ sensor toward APAP were provided in BRBS pH = 6. The scan rate study displayed a diffusion-controlled process responsible for APAP redox processes at the surface of the developed sensor. The DPV measurements showed that the GCP@Bi₂O₃ sensor detected APAP in a wide linear concentration range (0.05 to 12 μM). The LOQ and LOD of the developed electroanalytical method were 36 nM and 10 nM, respectively, indicating that the obtained findings are reliable, comparable, and/or superior to previously reported

studies. The developed sensor offered adequate precision, repeatability, and selectivity toward APAP detection. The recovery tests indicated that α - Bi_2O_3 material can be used as a highly functional carbon paste modifier for real-time APAP detection in pharmaceuticals.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemosensors12070122/s1>, Addition S1. The detailed content of Caffetin[®] tablets; Figure S1: EDS results of the synthesized Bi_2O_3 ; Figure S2: (A) Cyclic voltammetric response of the GCP@ Bi_2O_3 electrode in BRBS pH = 6 containing 10 μM APAP. Scan rate of 50 mV/s. Red- and orange-colored dots demonstrate Tafel regions for APAP oxidation and reduction peak; (B) Tafel plot (E (V) vs. $\log I_{p(\text{ox})}$ (A)) for APAP oxidation peak; (C) Tafel plot (E (V) vs. $\log I_{p(\text{red})}$ (A)) for APAP reduction peak; Figure S3: Proposed redox mechanism of APAP; Figure S4: (A) DPV records of the GCP@ Bi_2O_3 electrode for 5 μM APAP in BRBS pH = 6 at different amplitudes (5 to 45 mV). The other DPV parameters were a pulse width of 0.2 s, a sampling width of 0.02 s, and a pulse period of 0.5 s; (B) Plot of $I_{p(\text{ox})}$ vs. applied amplitude with corresponding error bars ($n = 3$); Figure S5: Change in the APAP peak current after successive addition of investigated interferences; and Figure S6: APAP detection in Caffetin[®] tablet 2 using the standard addition method. (A) DPV records of the GCP@ Bi_2O_3 sensor in BRBS pH = 6 for APAP detection in the pharmaceutical formulation: the concentration of the spike sample was 1.0 μM ; the concentration of the first standard addition was 3.0 μM ; the concentration of the second standard addition was 6.0 μM ; and the concentration of the third standard addition was 8.0 μM . DPV parameters were amplitude of 40 mV, pulse width of 0.2 s, sampling width of 0.02 s, and pulse period of 0.5 s; (B) Appropriate plot of $I_{p(\text{ox})}$ vs. C_{APAP} with corresponding error bars ($n = 3$); Table S1: The phase composition, unit cell, and microstructural parameters for the synthesized Bi_2O_3 .

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