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ELECTROCHEMICAL DETECTION OF 5-HYDROXYMETHYLFURFURAL WITH BISMUTH OXIDE NANOFLOWER ELECTRODE

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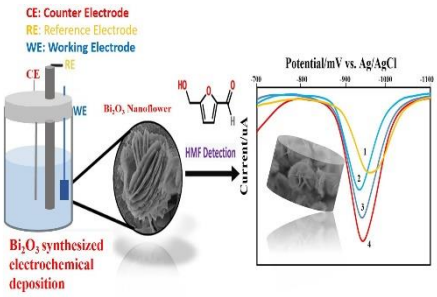
Hydroxymethylfurfural (HMF) is formed when sugary foods are stored at inappropriate temperatures or subjected to high temperature heat treatment during production. The present study reports the electrochemical determination of 5-hydroxymethylfurfural (HMF) using Bi_2O_3 nanoflower electrodes synthesized by the electrodeposition method. The aim of this study is to determine the amount of HMF in honey by using the electrochemical cyclic voltammetry (CV) method, which is a direct and rapid technique, by synthesizing Bi_2O_3 nanoflower-shaped electrodes with high selectivity and large surface area by the electrodeposition method. Highly crystalline bismuth oxide nanoflower films were electrochemically deposited on indium tin oxide (ITO) substrates. The impact of coating duration on the properties, structure, and form of metal oxides produced electrochemically was also investigated. Using potential controlled electrochemical deposition, scanning electron microscopy, X-ray diffraction techniques, X-ray photoelectron spectroscopy spectra analysis, and UV-Vis measurements, a Bi_2O_3 modified metal oxide electrode was successfully produced using an electrochemical method.



INTRODUCTION

Electrochemical sensors and biosensors frequently use nanomaterials such as graphene, bismuth (III) oxide (Bi_2O_3), silver, iridium oxide, titanium oxide (TiO_2), silicon oxide (SiO_2), and fullerenes. These biosensors are reliable and easy to build, and they have been used successfully for sensor preparation. Among all nanomaterials, Bi_2O_3 is thought to be one of the most promising electrode materials for electrochemical sensing devices due to its unique characteristics, including its energy bandgap, large surface area, electrochemical stability, and outstanding catalytic activity applications. It has been shown to have a favorable electrochemical sensor for voltammetric measurement, as well as sensitivity, electrical conductivity, and chemical stability.[1–4] In addition to being biocompatible, bismuth(III) oxide is non-toxic and chemically inert. Compared to macroscale bismuth(III) oxide, nanoscale bismuth(III) oxide has greater advantages and is better suited for biomolecule adsorption due to its larger surface free energy. Additionally, it has emerged as one of the most potent rivals of the most widely used UV-active TiO_2 photocatalyst, particularly Bi_2O_3.[5] Because of its non-toxic oxide forms, bismuth finds utility in active applications such as biosensors,

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functional glasses, and piezoelectric materials.[6–7] According to recent studies on the photocatalytic activity of the various phases of Bi_2O_3, they are non-toxic and photocorrosion-resistant.[8,9]

During food preparation and shelf life, hexose breakdown, caramelization, and the Maillard reaction produce hydroxymethylfurfural (HMF), a cyclic aldehyde.[10] Temperature, sugar type, pH, water activity, and the amount of divalent cations in the medium all affect how HMF forms in food.[11] Overly processed meals like baked, toasted, fried, roasted, and sterilized goods may include it. Additionally, because it may be used to indicate the freshness of food, it is one of the most significant quality indicators. Therefore, sensors capable of detecting trace levels of HMF have been developed.[12] Electrochemical methods offer significant advantages over other sensing technologies in terms of cost, accuracy, and precision. It is essential that electrodes used for the electrochemical detection of HMF exhibit high sensitivity, low cost, and non-toxicity.[13]

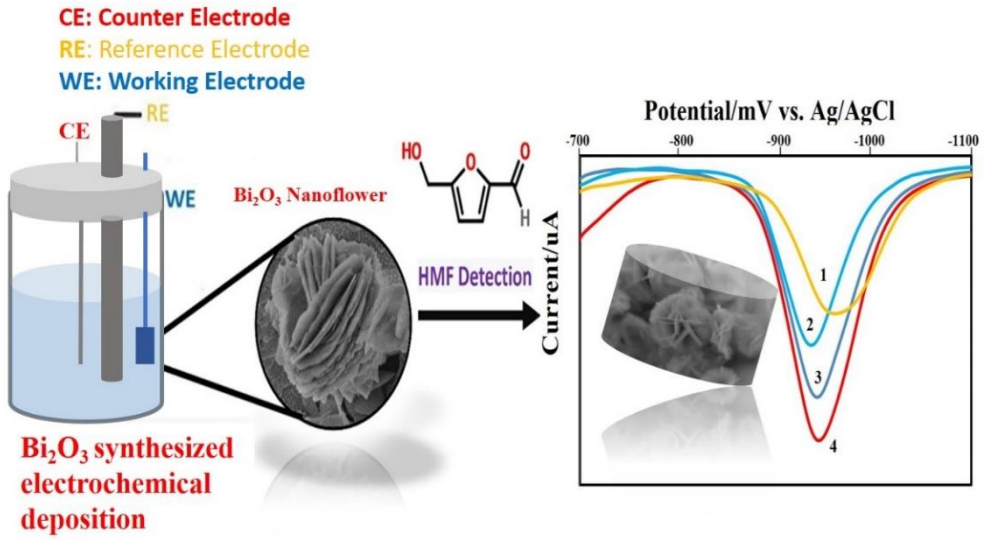

Fig. 1 – Systematic demonstration of HMF detection with Bi_2O_3 nanostructure electrodes.

MATERIAL AND METHOD

Using a BAS 100B/W electrochemical workstation coupled to a three-electrode cell (C3 Cell Stand, BAS), electrochemical tests were carried out at room temperature. For optical measurements, the working electrode was a quartz substrate covered with indium tin oxide (ITO) (working electrode area 1.0 cm^2) and having a sheet resistance of 10 Ω cm^{-2}. Platinum wire served as the counter electrode in all electrochemical tests, while Ag/AgCl (3 M NaCl) served as the reference electrode. In every experiment, deionized water (*i.e.*, >18 MΩ) was utilized. Electrochemical deposition was carried out at room temperature in a solution containing dissolved O_2 gas, 1 mM $Bi(NO_3)_3$ and pH 1.5. Electrochemical deposition of Bi_2O_3 nanostructures was carried out at ambient temperature. The voltage was kept at +300 mV for 30 minutes. After drying the Bi_2O_3 working electrode at room temperature, the film was cured with O_2 gas for about a minute. The density (ρ) and molecular weight (M) of Bi_2O_3 are 8.9 g·cm^{-3} and 465.96 g·mol^{-1}, respectively, and the surface area of the working electrode is 1 cm^2. At pH 1.5, six electrons are transferred during the electrochemical formation of Bi_2O_3 (n = 6), meaning that six equivalent charges are required to produce 1 mol of Bi_2O_3. Based on an average deposition time of 30 minutes, the thickness of the electrochemically deposited ternary Bi_2O_3 semiconductor films was estimated to be approximately 904 nm. To guarantee that the surfaces produced by the potential controlled electrolysis process of nanostructured Bi_2O_3 films on ITO substrates at a constant voltage (+300 mV) had a high surface area, the Bi_2O_3 modification was applied electrochemically (Fig. 1). Using a Zeiss Sigma 300 apparatus, scanning electron microscopy (SEM) measurements were carried out under ambient circumstances for the study. A Hitachi 5100N equipment was used for AFM imaging in the air to capture 3D pictures and surface topography. An analytical Pyrean was used to get X-ray diffraction patterns. A Shimadzu UV-3101 UV-Vis-nearIR spectrometer was used to assess absorption at ambient temperature. The elements'

composition, chemical makeup, and electronic structure were measured using a Speca-Flex type XPS instrument.

RESULTS AND DISCUSSION

Following the electrochemical deposition of Bi_2O_3 nanoflowers, Figure 2 displays the SEM image of the Bi_2O_3 nanostructures that were electrodeposited on ITO electrodes. This finding demonstrates that the concentration and deposition potential (+300 mV), which have a major impact on the morphology-controlled synthesis of Bi_2O_3 nanostructures, maintain a steady Bi_2O_3 level during the electrochemical treatment. These findings also demonstrate that coating the Bi_2O_3 films increases their surface area.[14]

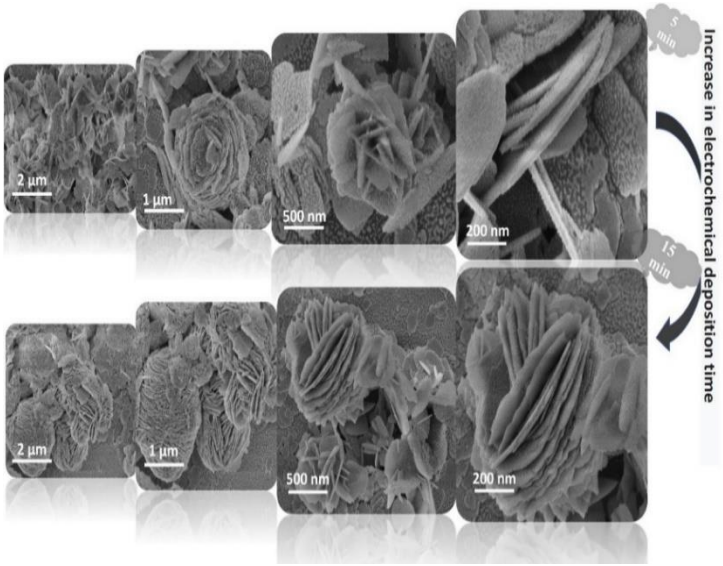

Fig. 2 – SEM images of Bi_2O_3 nanostructures obtained at different deposition times on the ITO electrodes for 5 min and 15 min.

The Bi_2O_3 phase exhibits a preferred electrochemical growth orientation, as evidenced by the detection of a single, extremely strong (212) peak. The XRD diffractogram of electrodeposited Bi_2O_3 clearly shows the peaks of the ITO substrate used as the working electrode at $2\theta = 11.56°$, 40.09° (212), and 55.02° (421). The Bi_2O_3 phase exhibits a favored electrochemical growth orientation, as evidenced by the discovery of a single, extremely strong (212) peak.[15] The XRD spectra make it evident that as the deposition time increases, so do the peak intensities of Bi_2O_3. Figure 3 shows the Bi_2O_3 AFM results. In the AFM data, Bi_2O_3 exhibits morphological characteristics similar to a nanoflower, and thin films are uniformly and fully deposited on the ITO electrodes, as seen in the 3D images.

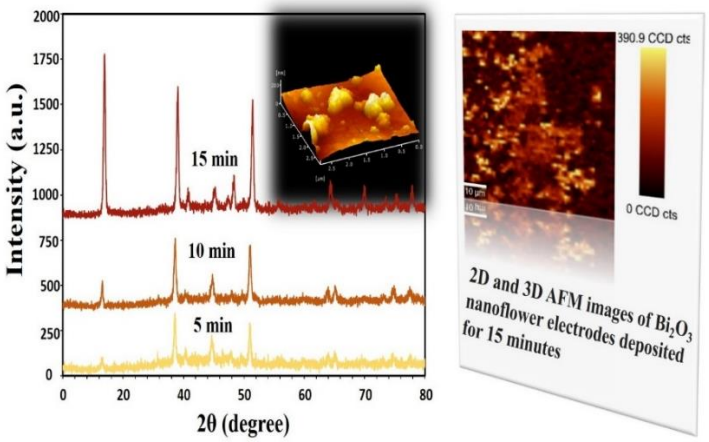

Fig. 3 – X-ray diffractions of Bi2O3 nanostructured films obtained as a result of electrodeposition on ITO electrodes for 5, 10, 15 min. Radiation source:Cu-Kα and 2D and 3D AFM images of Bi2O3 nanoflower electrodes deposited for a) 5 min, b) 10 min and c) 15 min.

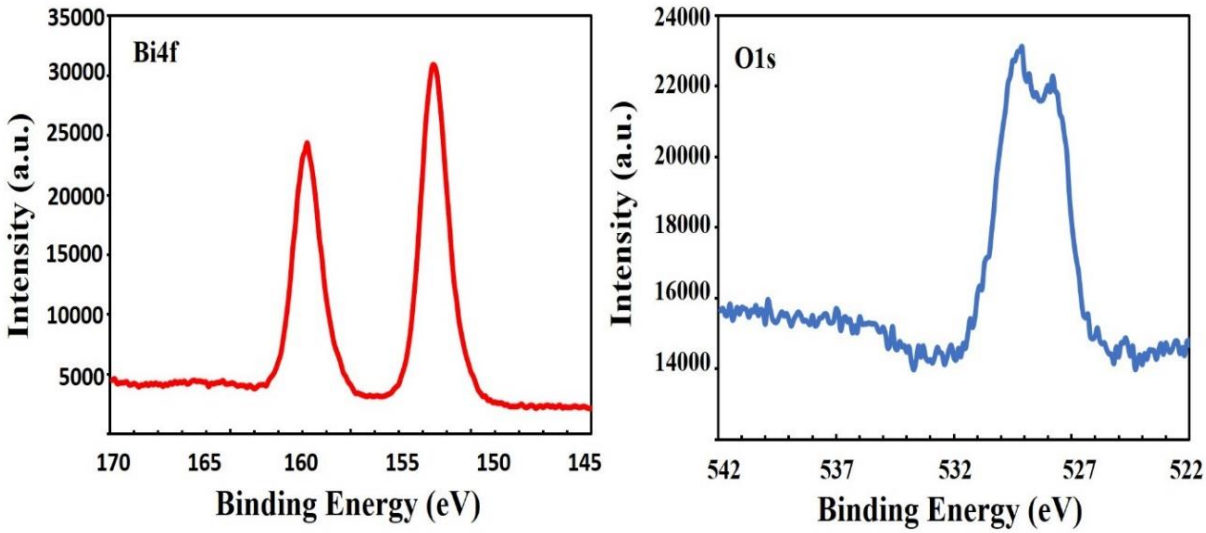

Fig. 4 – High-resolution X-ray photoelectron spectroscopy (XPS) spectra of Bi_2O_3 nanoflower thin film: a) Bi 4f7/2-Bi 4f5/2 (145–170 eV); b) O 1s (522–542 eV).

Only Bi and O elements are visible on the Bi_2O_3 nanoflower electrodes, according to X-ray photoelectron spectroscopy (XPS) spectrum data in Fig. 4. This is in good agreement with the findings of X-ray diffraction analysis. This translates to binding energies of 159.1 and 164.4 eV at the Bi 4f 7/2 and Bi 4f 5/2 levels, respectively, for elemental Bi in the form of Bi_2O_3, as shown in Fig. 4.[16,17] In Bi_2O_3, the existence of oxygen species is shown by the O 1s peaks at 530.3 and 532.0 eV.

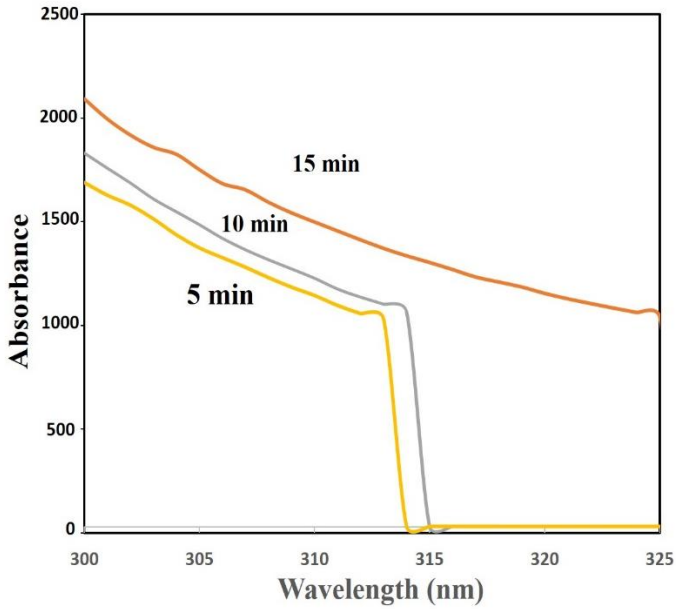

Fig. 5 – Absorption spectra of Bi_2O_3 nanostructured films obtained as a result of electrodeposition on ITO electrodes for 5, 10, 15 min.

Spectroscopic examination was carried out using UV-Vis spectroscopy techniques. Figure 5 shows UV spectra Bi_2O_3 nanostructured electrodes at different deposition times. Depending on the increase in deposition time, Bi_2O_3 nanoflower films obtained by electrodeposition for 5, 10 and 15 minutes show absorption in the light region from approximately 312 nm to 314 nm as the deposition time increases.

Voltammograms of HMF were plotted under the same circumstances in order to determine the redox couple A2/C2 (Fig. 6).[18–20] Only the electroreduction of the 2,5 Diformylfuran (DFF) produced two cathodic peaks towards –0.9 and –1.6 V, which

coincided with peaks C2 and C1, respectively, according to an analysis of these findings. To provide a high-quality analytical signal, the potential scan was restricted to 0–2 V. Under various experimental conditions, the cathodic peak C1 was examined.To determine the process that limits the reduction reaction of 1.26 g L^{-1} HMF at pH = 7 on the Bi_2O_3 electrode, voltammograms were plotted at different potential scan rates between 100 and 300 mV s^{-1} (Fig. 6). The current of the peak C1 increased with the potential scan rate. As clearly shown in Fig. 6, indium tin oxide (ITO) electrodes, when used as substrates, exhibit limited electrochemical sensitivity on their own. However, this sensitivity increases significantly when their surfaces are coated with metal oxides. Upon electrochemical modification of the ITO surface with Bi_2O_3, the active surface area of the electrode was substantially enhanced, the electron transfer kinetics were improved, and the interaction between the analyte and the electrode surface was strengthened.[21,22]

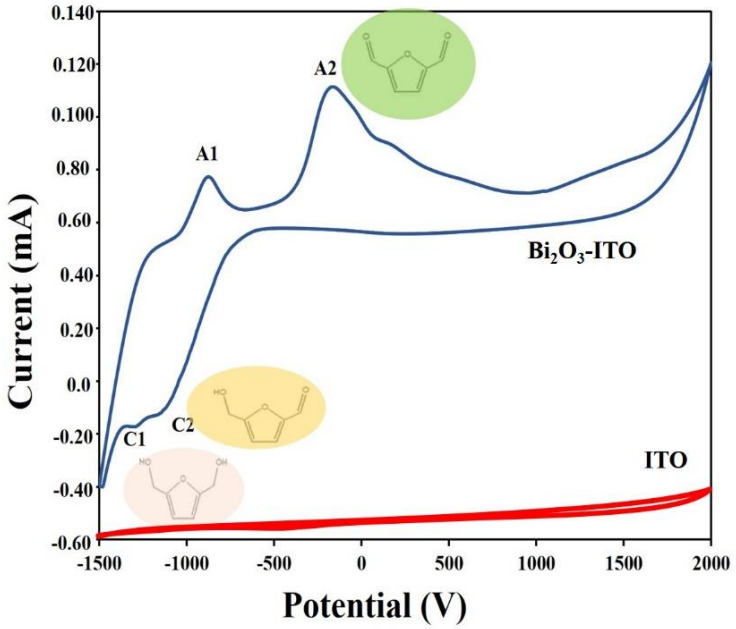

Fig. 6 – Cyclic voltammograms of the Bi_2O_3-ITO electrode and unmodified ITO in 0.016 M Na_2SO_4 solution containing 0.14 g L^{-1} 5-hydroxymethylfurfural. pH:7, v = 100 mV s^{-1} T = 25 °C.

A pH = 7-adjusted 0.016 M Na_2SO_4 solution containing 0.14 g L^{-1} HMF was used to test the impact of temperature on the Bi_2O_3 electrode response at various temperatures. Figure 7 displays an overlay of cyclic voltammograms at a scan rate of 100mVs^{-1}. It is evident that the CV currents rise as the temperature rises.[23] When the temperature rises from 25 to 50 degrees Celsius, the current is amplified by a factor of 2.01. The considerable solubility and sophisticated mass/charge transport of reactive species across the electrode surface at high temperatures are responsible for this notable catalytic action.

The HMF concentration in the honey samples was determined using the polarograms produced with a borate medium. Sample contents for Differential Pulse Polarography (DPP): In the: sample 1 – 0.9260 g honey, 10 mL boric acid solution (pH 9.1)(Natural honey); sample 2 – 0.9260 g honey, 10 mL pH: 9.1 boric acid in 1.8 ppm HMF; sample 3 – 0.9260 g honey, 10 mL pH: 9.1 boric acid in 3.6 ppm HMF and sample 4 – 0.9260 g honey, 10 mL pH: 9.1 boric acid in 4.2 ppm HMF were prepared. As HMF concentration decreased between the honey samples, measurement ambiguity increased, which derives from the low ambiguity in measuring high currents and the high ambiguity in measuring low currents. Polarograms of samples 1–4 recorded in borate medium clearly show well-defined HMF signals with increasing current density (Fig. 8).[24] The polarogram of Sample 1 (Fig. 8) showed a lower current density signal for HMF from natural honey and the HMF concentration values were determined to be in the range of 0.85–1.35 ppm based on the evaluation of the standard solutions (Samples 2–4).

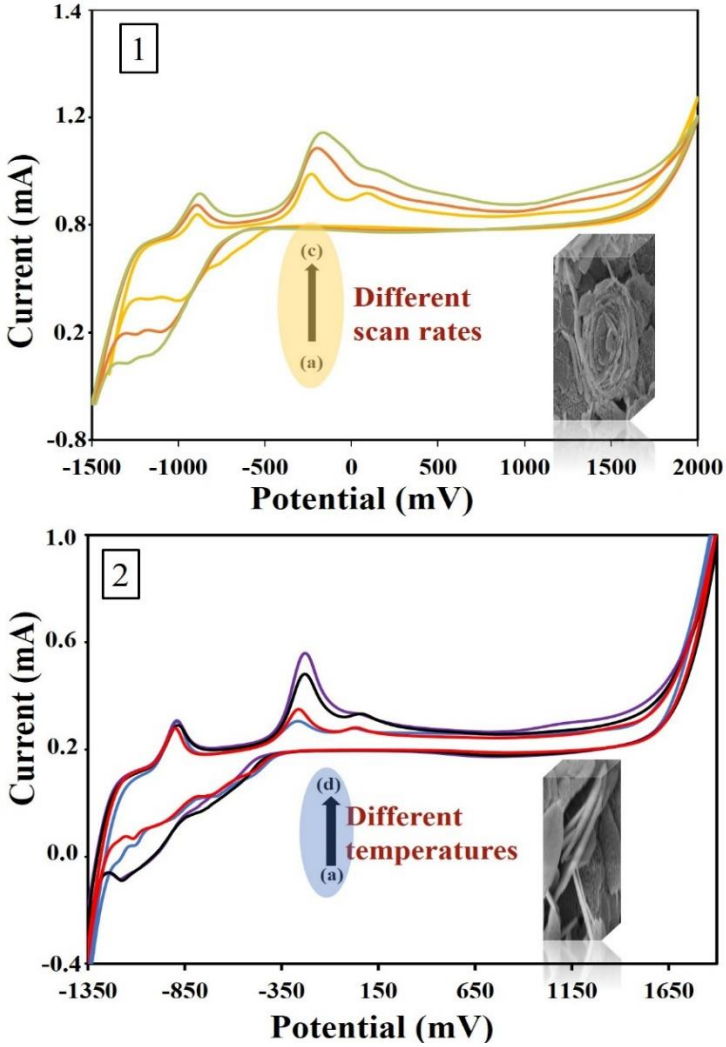

Fig. 7 – 1) Cyclic voltammograms of Bi_2O_3 electrode in 0.016 M Na_2SO_4 solution containing 1.4 g L^{-1} 5 hydroxymethylfurfural recorded at different scan rates: a) 100; b) 200; c) 300; T = 25 °C and 2) Cyclic voltammograms of Bi_2O_3 electrode in 0.016 M Na_2SO_4 solution containing 0.14 g L^{-1} 5-hydroxymethylfurfural recorded at different temperatures: a) 25; b) 35; c) 50°C and v = 100 mV s^{-1}.

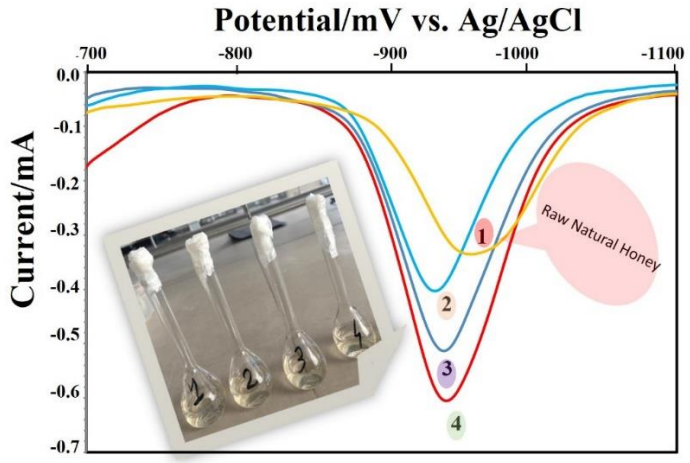

Fig. 8 – Sample 4 polarograms using Differential Puls Polarography (DPP) and standard addition method with Bi_2O_3 electrode. Ep: –1100mV DPP, Pulse amplitude: 100 mV; sweep rate: 2 mV s; drop life time: 1.5 s. Curve 1: 10 mL of 0.5 M borate solution (pH 9.1) plus 1 mL Sample 1 solution (0.9260 g honey); curves 2 to 4: successive HMF standard additions; final standard molar concentration (HMF).

The amount of HMF was determined as 1.35 ± 0.85 ppm (CV = 63.0%) by the electrochemical method using a Bi_2O_3 electrode with Differential Pulse Polarography (DPP), 1.50 ± 1.20 ppm (CV = 80.0%) by the HPLC method, and 1.20 ± 1.44 ppm (CV = 120.0%) by the GC method. The obtained results indicate that the Bi_2O_3 electrode-based DPP technique exhibits a lower coefficient of variation (CV) compared to both HPLC and GC methods. This finding demonstrates that the electrochemical method provides higher precision and better measurement repeatability.

Although HPLC and GC techniques are considered important standards in analytical chemistry due to their high separation efficiency and accuracy, the higher SD and CV values observed in Table 1 suggest that, especially at low concentrations (ppm level), signal-to-noise ratio and sample preparation-related errors may negatively affect measurement sensitivity. In contrast, the large active surface area and fast electron transfer kinetics of the Bi_2O_3 electrode may allow HMF molecules to generate more stable signals on the electrode surface.

Table 1

Comparison of electrochemical and chromatographic methods for the determination of 5-hydroxymethylfurfural

Method	Average (ppm)	SD (ppm)	CV (%)	Sensitivity Comment
Bi_2O_3 (DPP)	1.35	0.85	63.0	Most sensitive, good repeatability
HPLC	1.50	1.20	80.0	Medium sensitivity requires high precision
GC	1.20	1.44	120.0	Lowest sensitivity, sensitive to sample preparation

In conclusion, the Bi_2O_3 electrode-based electrochemical method demonstrates high repeatability and strong sensitivity potential for HMF detection. However, for validation in terms of accuracy and selectivity, the electrochemical results should be statistically compared with HPLC and GC data, as presented in Table 1. The electrochemical approach could offer a low-cost, rapid, and sensitive alternative for HMF monitoring in complex matrices.[25,26]

Table 2

Comparison of analytical performance for HMF determination using different methods

Method	Electrode/ Stationary Phase	Linear Range (ppm)	Sensitivity ($\mu A \cdot ppm^{-1}$ or $AU \cdot ppm^{-1}$)	Detection Limit (LOD, ppm)	R^2	Reference
Electrochemical (This work)	Bi_2O_3 modified electrode (DPP)	0.5 – 10.0	0.89 $\mu A \cdot ppm^{-1}$	0.25	0.996	This study
HPLC–UV	C18 column (λ = 284 nm)	1.0 – 50.0	0.62 $AU \cdot ppm^{-1}$	0.40	0.992	[27]
GC–MS	DB-5 capillary column	0.8 – 40.0	0.55 $AU \cdot ppm^{-1}$	0.35	0.991	[28]
DPV (Glassy carbon)	Unmodified GCE	1.0 – 20.0	0.45 $\mu A \cdot ppm^{-1}$	0.50	0.988	[29]

The analytical performance of the proposed Bi_2O_3-modified electrode for the determination of 5-hydroxymethylfurfural (HMF) using Differential Pulse Polarography (DPP) exhibits a wider linear response range (0.5–10.0 ppm) and higher sensitivity (0.89 $\mu A \cdot ppm^{-1}$) compared to conventional chromatographic techniques. The limit of detection (LOD = 0.25 ppm) achieved with the Bi_2O_3-modified electrode is lower than those obtained by HPLC (0.40 ppm) and GC (0.35 ppm),

indicating a superior analytical capability for detecting trace levels of HMF. The coefficient of determination (R^2 = 0.996) confirms an excellent linear correlation between current response and analyte concentration, thereby demonstrating the reproducibility and reliability of the developed electrode. The enhanced sensitivity can be attributed to the large electroactive surface area, improved electron-transfer kinetics, and the specific adsorption affinity of HMF molecules on the Bi_2O_3-modified surface. Furthermore, the electrochemical method eliminates complex sample preparation procedures and significantly reduces analysis time compared to chromatographic methods. In conclusion, the comparison summarized in Table 2 clearly demonstrates that the Bi_2O_3-modified electrode provides a rapid, cost-effective, and highly sensitive analytical alternative for HMF determination. This electrochemical approach represents a promising technique for on-site or real-time monitoring of HMF in complex food and environmental matrices, highlighting its potential as both a fast and reliable detection method.

CONCLUSION

For the detection of hydroxymethylfurfural (HMF), a straightforward and sensitive electrochemical sensor based on Bi_2O_3 nanoflowers deposited onto an ITO electrode was developed. In comparison to the bare ITO electrode, it was shown that the bismuth film electrode significantly increased the electron transfer rate and demonstrated superior electrochemical activity for the oxidation of HMF. Temperature, scan rate, and HMF concentration all had an impact on how well Bi_2O_3 responded to HMF detection. Regulations have severely limited the amount of HMF in food because of its harmful health consequences, hence it is crucial to create quick and easy analytical techniques for HMF identification. The electrochemical sensor based on Bi_2O_3 was found to have improved sensitivity and opened the door for precise and reproducible measurements for HMF detection. An economical method for the electrochemical detection of HMF is the Bi_2O_3-based electrochemical sensor. As a result, it is thought that the electrochemical sensor based on Bi_2O_3 nanoflowers may be used for various food samples and will serve as a substitute technique for HMF detection in the future.

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