

Fast monitoring of sucrose using CuO/MWCNTs nanocomposite modified glassy carbon electrode

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Abstract- An electrochemical sensor was fabricated for sucrose using glassy carbon electrode modified with cupric oxide (CuO)/multiwall carbon nanotubes (MWCNTs) nanocomposite. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the morphology and structure of the nanocomposite. The electrochemical characterization of CuO/MWCNTs nanocomposite modified glassy carbon (GC) electrode was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Synergistic effect of CuO/MWCNTs/GC electrode led to a selective oxidation of sucrose in an alkaline medium. The electrode was applied to measure sucrose in sugar beet juices, demonstrating its potential as a sucrose sensor.

Keywords- sucrose determination, sugar beet juices, sensor, voltammetry, nanocomposite.

I. INTRODUCTION

Sucrose commonly known as table sugar comes from plant sources. Sugar beets and sugarcane are the two important sugar crops in which sugar can account for 12-20% of the plants dry weight. Several methods including colorimetry, fluorometry, calorimetry, polarimetry, spectrophotometry, gas chromatography–mass spectrometry and high performance liquid chromatography have been developed for the determination of sucrose. These methods, however, are expensive, time consuming and sometimes require highly qualified technicians [1-5].

Oxide electrodes are likely to be suitable for carbohydrate oxidation because the molecules are expected to get easily adsorbed on the oxide layer by the formation of hydrogen bonds via the –OH groups, which facilitate electron transfer [6-8]. A range of electrodes such as platinum, gold, silver, nickel, cobalt, and copper have been explored for direct electro-oxidation of carbohydrates. However, most of them have such drawbacks as low sensitivity and poor selectivity due to poisoning/fouling of the electrode surface [9-15].

In recent years, nanomaterials with special physical and chemical properties have been widely applied in electrochemical sensors [16-19]. Carbon

nanotubes (CNTs) have become an attractive material of electroanalysis due to their high electrical conductivity, chemical stability, large surface area, high surface/volume ratio, high mechanical strength, and chemically modifiable surface [2021]. On the other hand, as a p-type semiconductor with a narrow band gap of 1.2 eV, copper oxide (CuO) is of particular interest due to its application in heterogeneous catalysts for the oxidation of carbohydrates, methanol, carbon monoxide and nitric oxide. There have been several efforts on the determination of carbohydrates using nanostructured CuO. Other efforts have been made to fabricate nanosensors using CNTs with metals/metal oxides and employing various fabrication techniques [22-26].

This paper focuses on the use of CuO nanoparticles and multiwall carbon nanotubes (MWCNTs) to modify glassy carbon (GC) electrode and improve their electroactivity and selectivity for the detection of sucrose. The modified electrode is sensitive to glucose. The sensor was successfully applied to determine of sucrose in sugar beet juices.

II. EXPERIMENTA

A. Chemicals

All chemicals used were of analytical reagent grade.

Multiwall carbon nanotubes (> 90% MWCNT basis, $d \times l = (110 - 70 \text{ nm}) \times (5 - 9 \text{ }\mu\text{m})$) was purchased from Aldrich–Sigma. To eliminate any metal oxide within the multiwall carbon nanotubes, they were refluxed in a mixture of $3.0 \text{ mol L}^{-1} \text{ HNO}_3$ and $2.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (3:1, v/v) for 22 h; then, they were washed several times with distilled water to neutrality, and dried at room temperature.

Sucrose, glucose, fructose, raffinose, kestose, copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), ammoniac (NH_4OH (25%, w/w)), and sodium hydroxide were purchased from Merck and used without further purification.

A fresh solution of the chosen carbohydrate in NaOH (0.50 mol L^{-1}) was prepared daily.

B. Apparatus

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) were performed in an analytical system in which Autolab PGSTAT 12, potentiostat/galvanostat has been connected to a three-electrode cell, Metrohm Model 663 VA stand. The system was run on a PC using GPES and FRA 4.9 software package (Eco Chemie, The Netherlands). A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode was used. The working electrode was prepared as CuO/MWCNTs/GC electrode. For impedance measurements, a frequency range of 100 kHz to 0.01 Hz was employed. The AC voltage amplitude used was 5mV. The prepared electrode was characterized by scanning electron microscopy (SEM), a XLC Philips.

X-ray powder diffraction (XRD) measurement was performed on an X'pert X-ray diffractometer (Philips) with graphite monochromatized Cu K α radiation ($\lambda = 0.15418$ nm) and nickel filter.

C. Preparation of CuO/MWCNTs composite

CuO/MWCNTs composite was prepared by the method developed by Wang et al. [27]. Cu(CH₃COO)₂·H₂O was used as copper source. At first, 16 mg Cu(CH₃COO)₂·H₂O was dissolved in 5.0 mL deionized water. Then, 0.10 mL NH₄OH (25.0 wt%) solution was slowly added into the above solution under continuous stirring to form the precursor solution and 10 mg MWCNTs were soaked in the solution for 17 h. Subsequently, the MWCNTs were centrifugally separated from the solution, dried at 70 °C in vacuum, giving the intermediate products. Finally, the intermediate products were calcined at 300 °C in the presence of N₂ for 2 h and the CuO/MWCNTs composite was obtained.

D. Preparation of the modified electrode

GC electrode was polished before each experiment with 0.05 μ m alumina powder, rinsed thoroughly with distilled water, ultrasonicated in ethanol for 5 min, and allowed to dry at room temperature. CuO/MWCNTs powder was dispersed in ethanol and ultrasonicated for 5 min. Then, 10 μ L of the mixture was dropped onto the surface of the GCE and followed by the evaporation of ethanol. This electrode (CuO/MWCNTs/GCE) was used as the working electrode and for further characterization.

III. RESULTS AND DISCUSSION

A. Characterization of the CuO/MWCNTs nanocomposite

Direct observation of the morphology of the prepared CuO/MWCNTs nanocomposite was achieved by SEM. "Fig. 1" shows that CuO

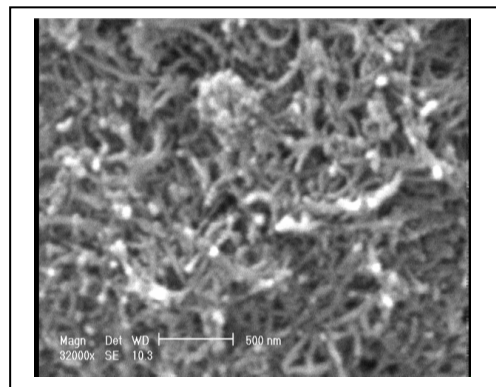


Figure 1. SEM image of CuO/MWCNTs nanocomposite

nanoparticles are homogeneously coated on the surface of MWCNTs. The particle size distributions of CuO nanoparticles are mainly around 50 nm.

To confirm the structure and the phase composition of the as-prepared nanocomposite, XRD analysis was also carried out ("Fig. 2"). The diffraction peaks confirm that the prepared nanocomposite consists of both MWCNTs and CuO. The diffraction peaks with 2θ 33.52, 35.47, 38.52, 48.87, 57.57, 61.77, 66.57, and 68.17° can be assigned to the (110), (-111), (111), (-202), (202), (-113), (-311), and (220) planes of crystalline CuO, respectively (JCPDS 80-1916) and the peaks with 2θ of 26.32, 43.32, 43.92, and 53.42° may be related to the diffraction from the (002), (100), (101), and (004) planes, respectively, corresponding to MWCNTs. No other peak is observed that would belong to the impurities, indicating the high purity of the prepared nanocomposite. The size of the CuO particles was calculated from the (-111) diffraction peak using the Debye-Scherrer equation:

$$L = k\lambda/\beta\cos\theta \quad (1)$$

where L is the average size of the particle, λ is the X-ray wavelength (0.154 nm), k is equal to 0.89, β is the peak broadening, and θ is the angle of the peak maximum. The calculated average size of the CuO particles in the composite was 10.42 nm. Thus, the CuO particles of about 50 nm in size were observed from the SEM image and considered as nanoclusters of nanocrystalline CuO.

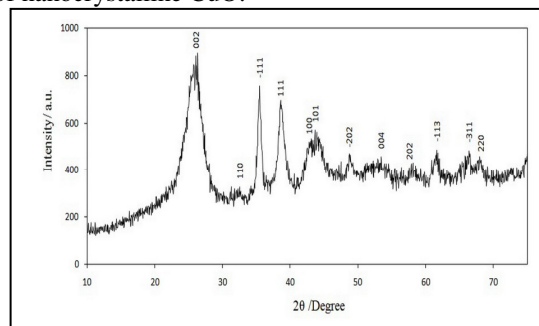


Figure 2. XRD pattern of CuO/MWCNTs nanocomposite

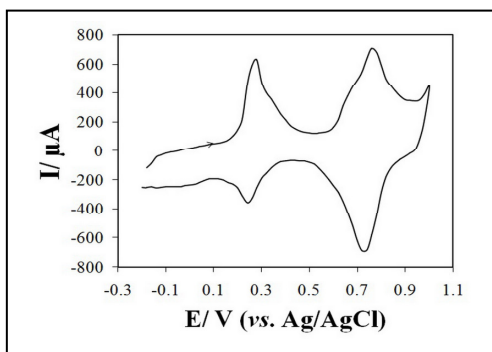


Figure 3. Cyclic voltammograms of CuO/MWCNTs/GC electrode in $0.50 \text{ mmol L}^{-1} \text{K}_3[\text{Fe}(\text{CN})_6]$ plus $1.0 \text{ mol L}^{-1} \text{KCl}$

B. Electrochemical characteristics of the modified electrode

To estimate the active area of CuO/MWCNTs/GC electrode, a solution of $0.50 \text{ mmol L}^{-1} \text{K}_3[\text{Fe}(\text{CN})_6]$ with $1.0 \text{ mol L}^{-1} \text{KCl}$ was used. "Fig. 3" shows a typical cyclic voltammogram of CuO/MWCNTs GC electrode at a scan rate of 50 mV s^{-1} at the surface of CuO/MWCNTs/GC electrode. A pair of the anodic and cathodic peaks, due to the redox reactions of $\text{Fe}(\text{CN})_6^{3-}$, were found between $+0.20$ and $+0.30 \text{ V}$, indicating that the redox reaction is quasi-reversible at the modified electrode. Another pair of anodic and cathodic peaks was found between $+0.70$ and $+0.80 \text{ V}$, which is due to redox reactions of CuO.

The active surface area of the modified electrode was estimated according to the slope of the I_p vs. $v^{1/2}$ plot, which is based on the Randles-Sevcik equation:

$$I_p = 0.4463 n^{3/2} F^{3/2} A C_0 (vD/RT)^{1/2} \quad (2)$$

Where I_p is the anodic peak current (A), n is the electron transfer number ($= 1$), A is the surface area of the electrode (cm^2), F is the Faraday constant in C mol^{-1} , R is the gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), D_R is the diffusion coefficient ($0.76 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), T is the temperature in $^\circ\text{K}$, C_0 is the concentration of the electro active species $\text{K}_3\text{Fe}(\text{CN})_6$, in mol L^{-1} , and v is the scan rate (V s^{-1}). The calculated values of the surface area were found as 0.00034 and 0.56 cm^2 for the bare GCE and CuO/MWCNTs/GC electrode respectively at $25 \text{ }^\circ\text{C}$, based on the redox peaks of $[\text{Fe}(\text{CN})_6]^{3-}$. These results obviously show that the CuO/MWCNTs nanocomposite increases the active surface of the electrode.

Electrochemical impedance spectroscopy (EIS) was also used to study the characteristics of the modified electrode. In the EIS, The semicircle diameter of Nyquist plot corresponds to the electron transfer limited process and the diameter is equivalent to the electron transfer resistance (R_{ct}). "Fig. 4" shows the results of EIS on a bare GC electrode (a) and CuO/MWCNTs/GC electrode (b) in an electrolyte of $0.1 \text{ mol L}^{-1} \text{KCl}$ and equimolar of $[\text{Fe}(\text{CN})_6]^{3-}$. In the equivalent circuit from the inset of Figure 2B, R_s , C_1 , R_{ct} and Z_w represent the resistance of the electrolyte solution, the capacitance,

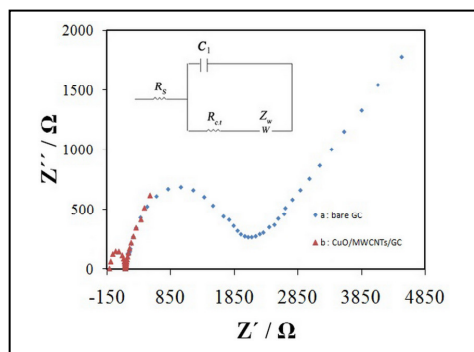


Figure 4. EIS of (a) bare GC electrode, and (b) CuO/MWCNTs/GC electrode. Inset is the equivalent circuit. R_s , C_1 , R_{ct} and Z_w . The frequency range is from 0.01 Hz to 100 kHz .

the charge-transfer resistance and the warburg impedance, respectively. The charge transfer resistance (R_{ct}) of the bare GC electrode was $2000 \text{ } \Omega$. After GC electrode was modified with CuO/MWCNTs nanocomposite, R_{ct} was decreased markedly to $140 \text{ } \Omega$. The results show that the CuO/MWCNTs nanocomposite is successfully immobilized on the GC electrode surface and acts as a powerful electron mediator.

C. Electrocatalysis of sucrose at CuO/MWCNTs/GC electrode

The electrocatalytic activity of the bare GC and CuO/MWCNTs/GC electrodes towards the oxidation of sucrose in an alkaline solution was demonstrated by CVs. "Fig. 5" displays the CVs of the bare GC and CuO/MWCNTs/GC electrodes in $0.5 \text{ mol L}^{-1} \text{NaOH}$ solution in the absence and presence of 10.0 mmol L^{-1} sucrose. As shown in "Fig. 5" (curve a), only a small background current was observed at the bare GC electrode in the NaOH solution, while an obvious increase of current was observed when the CuO/MWCNTs/GC electrode was used ("Fig. 3", curve c). This indicates that CuO/MWCNTs nanocomposite greatly improves the performance of the electrode. This may be attributed to the large surface area and the active sites, owing to the CuO/MWCNTs nanocomposite. Upon addition of sucrose, any forward wave was observed for GC electrode (curve b), while a single forward oxidative wave, corresponding to the irreversible sucrose oxidation, was observed for the CuO/MWCNTs/GC electrode (curve d). As depicted in "Fig. 5" (curves b and d), CuO/MWCNTs/GC electrode displays an oxidation of sucrose starting at approximately $+0.20 \text{ V}$ and an oxidation peak centered at $+0.49 \text{ V}$. All these show that the synergistic effect performance towards the oxidation of sucrose has been greatly improved by the immobilization of CuO/MWCNTs nanocomposite onto the surface of GC electrode.

The CVs of sucrose solution at different scan rates are shown in Fig. 6. The anodic peak current of the sucrose oxidation is proportional to the scan rate.

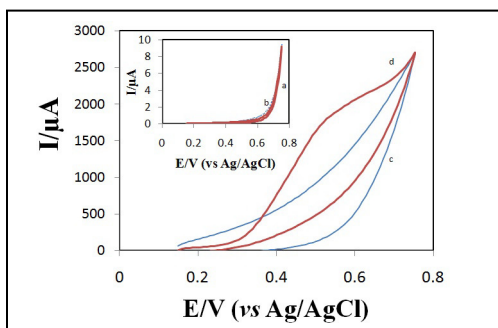


Figure 5. CVs of GC (a and b) and CuO/MWCNTs/GC (c and d) electrodes in the absence (a and c) and presence (b and d) of 10.0 mmol L⁻¹ sucrose in 0.50 mol L⁻¹ NaOH at 50 mV s⁻¹.

A good linearity was obtained as indicated in the inset of Fig. 6. The linear regression equation $I/\mu\text{A} = 0.009\mu\text{A} + 0.526 v/\mu\text{A}(\text{mV s}^{-1})^{-1}$, with the correlation coefficient (R) of 0.996, was obtained. The results indicate that the electrochemical kinetics is controlled by the adsorption of sucrose on the surface of electrode. It can also be noted that the peak potential for the oxidation of sucrose shifts positively with the increasing scan rate.

It is well known that an alkaline medium is required to enhance synergistic effect of CuO for the oxidation of carbohydrates. In this study, the effect of NaOH concentration on sucrose oxidation (10.0 mmol L⁻¹) at CuO/MWCNTs/GC electrode was also investigated. The concentrations of NaOH were 0.10, 0.25, 0.50, 0.75, 1.00 mol L⁻¹. As shown in Fig. 7, with increasing NaOH concentration, the oxidative current is enhanced and the oxidative potential negatively shifts until NaOH concentration reaches 0.50 mol L⁻¹; then, with the further increase in NaOH concentration, the oxidative current is decreased. Higher NaOH concentrations would unstable the electrode materials. Thus, 0.50 mol L⁻¹ NaOH was selected as the optimal concentration to obtain the highest sucrose oxidation current at low potential.

CuO/MWCNTs/GC electrode responds to the changes in sucrose concentration. Differential pulse

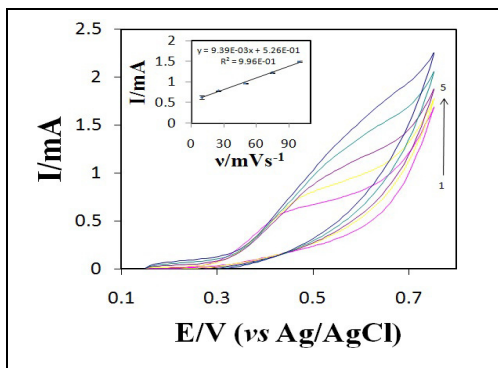


Figure 6. CVs of CuO/MWCNTs/GC electrode in 0.5 mol L⁻¹ NaOH solution containing 10.0 mmol L⁻¹ sucrose at scan rates of (1 to 5) 10, 25, 50, 75, 100 mVs⁻¹. Inset shows the oxidation peak current vs. scan rate

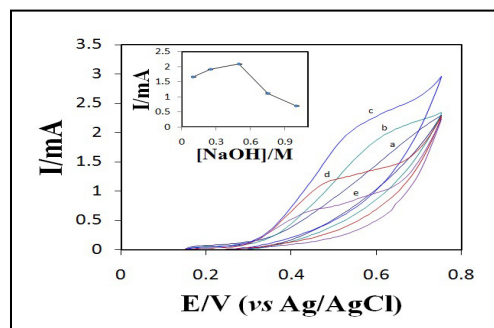


Figure 7. Effect of NaOH concentrations on the peak current of 10.0 mmol L⁻¹ sucrose at CuO/MWCNTs/GCE. a-e: 0.10, 0.25, 0.50, 0.75, 1.00 mol L⁻¹, respectively.

voltammetry (DPV), from 0.00 V to 0.70 V, (using pulse amplitude of 50 mV, a modulation time of 0.05 s, and a step potential of 8 mV) was used to determine the concentration of sucrose because of its better sensitivity. The corresponding calibration curve is presented in Fig. 8. The results show that the currents were linearly increased with the sucrose concentration in the low range of 0.1 – 10.0 and 10.0 – 40.0 mmol L⁻¹ with regression equations of $I (\mu\text{A}) = 3.467C (\text{mmol L}^{-1}) + 3.396$ ($R^2 = 0.981$) and $I (\mu\text{A}) = 0.758C (\text{mmol L}^{-1}) + 29.9$ ($R^2 = 0.987$), respectively. The response is then saturated at the higher sucrose concentration of about 50 mmol L⁻¹. The limit of detection based on $S/N=3$ was 0.03 mmol L⁻¹ sucrose.

The high sensitivity, low detection limit and fast response of this electrode can be attributed to the fact that CuO/MWCNTs nanocomposite can form a network to shuttle electron between sucrose and the working electrode, facilitating high catalytic activity towards sucrose and large active surface area.

D. Reproducibility, stability and specificity of CuO/MWCNTs/GC electrode

The reproducibility and stability of the sensor were investigated by CV measurements. Five CuO/MCNTs/GC electrodes were fabricated under the same conditions and their current responses to

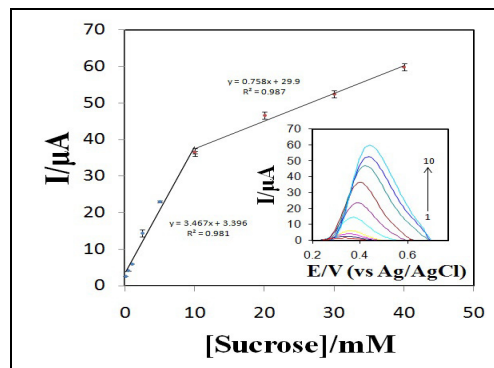


Figure 8. Calibration curve for sucrose determination using CuO/MWCNTs/GC electrode. Inset is the differential pulse voltammograms of sucrose concentrations (1 to 10) 0.1, 0.5, 1.0, 2.5, 5.0, 10.0, 20.0, 30.0, and 40.0 mmol L⁻¹.

10.0mmol L⁻¹ sucrose in 0.5 mol L⁻¹ NaOH had a relative standard deviation (RSD) of 2.5%, confirming that the fabrication method was highly reproducible. Seven measurements of 10.0mmol L⁻¹ sucrose at CuO/MWCNTs/GC electrode yielded an RSD of 1.9%, demonstrating that the sensor was stable. The electrode was not deactivated by the oxidation process and could be used repeatedly (several times) for the detection of sucrose. The stability of CuO/MWCNTs/GC electrode was also investigated by adding 0.10 mol L⁻¹ NaCl in the supporting electrolyte. The linear response for sucrose at CuO/MWCNTs/GC electrode remains almost constant (data not shown), indicating that the electrode can be used in the presence of chloride ions.

To verify the specificity of the fabricated sensor towards sucrose, compounds existing in sugar beet juices with similar structure to sucrose including raffinose, kestose, glucose, and fructose were added into the sucrose solution. The result solution was then analyzed to find the sucrose, using the proposed method. The results showed that 10-fold of glucose and fructose had no interference, which is due to their less OH groups and thus less electron transfer. Comparatively 5-fold of raffinose and kestose had no interferences effect, which may be explained by the fact that these compounds have more OH groups and more electron transfer. Therefore, the proposed method is highly recommended as a selective sensor for measuring sucrose in sugar beet juices.

The influence of various substances co-existing with sucrose in sugar beet juices as potential interferences compounds on the determination of sucrose was studied under the optimum conditions. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than $\pm 5\%$ for determination of sucrose. 100-fold of them were added to a sample solution containing sucrose. The results showed that 100-fold of real concentrations of hydrochloric acid, sulfuric acid, citric acid, oxalic acid, formic acid, lactic acid, acetic acid, NaCl, KNO₃, CaCO₃, and ammonia; and 10-fold of real concentrations of glycine, alanine, valine, aspartic acid, leucine, lysine and glutamic acid in sugar beet juices had no influence on the response of CuO/MWCNTs/GC electrode to sucrose.

E. Real sample analysis

The CuO/MWCNTs/GC electrode was applied for the determination of sucrose in real samples. Raw juice, thin juice, thick juice, and molasses obtained from sugar beet were used after dilution with 0.5 mol L⁻¹ NaOH solution without any more preparations steps. The samples were spiked with different amounts of standard sucrose solution, and then the sensor measured the total amount of sucrose. The corresponding results are given in Table 1. The results are in agreement with those determined by HPLC method. The results show that the sensor has

TABLE 1. DETERMINATION OF SUCROSE IN SUGAR BEET JUICE SAMPLES.

Real samples	Added (mmol L ⁻¹)	Found by the sensor* (mmol L ⁻¹)	Recovery (%)	HPLC method (mmol L ⁻¹)
Raw Juice	—	0.42(±0.05)	—	0.44
	1.96	2.26(±0.60)	94	—
	2.91	3.30(±0.12)	98	—
Thin Juice	—	0.83(±0.04)	—	0.80
	2.91	3.62(±0.67)	96	—
	3.84	4.90(±0.32)	106	—
Thick Juice	—	1.79(±0.02)	—	1.75
	2.91	4.61(±0.54)	97	—
	3.84	5.82(±0.62)	105	—
Molasses	—	1.27(±0.01)	—	1.23
	0.99	2.25(±0.44)	99	—
	1.96	3.19(±0.62)	98	—

*. In 1000-fold diluted sample.

capability in determination of sucrose in sugar beet juices.”

IV. CONCLUSIONS

CuO/MWCNTs/GC electrode presents several attractive analytical features such as excellent synergistic effect, good reproducibility, strong stability, and high selectivity as well as quick response to sucrose. The electrode was successfully applied to measure sucrose in sugar beet juices. The sucrose sensor developed is in good agreement with those from HPLC method for the sucrose detection, demonstrating that the developed sensor has a great potential for the practical usage for sugar beet juices.

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