Research Article

Electrochemical Preparation of Polyaniline- Supported Cu-CuO Core-Shell on 316L Stainless Steel Electrodes for Nonenzymatic Glucose Sensor

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In this article, we reported the elaboration of a nonenzymatic glucose sensor based on the polyaniline-supported Cu-CuO core-shell structure prepared on the 316L stainless steel electrode by electrochemical methods. In the first step, polyaniline (PANI) film was electrodeposited on the 316L substrate from a solution of 0.1 M aniline and 0.5 M sulfuric acid in absolute ethanol by the cyclic voltammetry (CV) method. In the second step, the copper particles were electrodeposited on the PANI film from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.01 M precursor prepared in a KCl 0.1 M solution by the CV method. In the third step, Cu particles were partially oxidized to CuO by the CV method in a NaOH 0.1 M electrolyte to form a Cu-CuO core-shell structure supported on the PANI film. The as-prepared electrode (Cu-CuO/PANI/316L) was used to detect glucose in a NaOH 0.1 M solution. The Cu-CuO/PANI/316L sensor exhibited a linear range of 0.1–5 mM ($R^2 = 0.995$) with a detection limit of 0.1 mM ($S/N = 3$) and high sensitivity of ($25.71 \text{ mA} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$). In addition, no significant interference was observed from sucrose, maltose, lactose, and ascorbic acid. The results showed that the polyaniline-supported Cu-CuO core-shell structure has the potential to be applied as an electrode material for the nonenzymatic glucose sensor.

1. Introduction

Nonenzymatic glucose sensor is considered a new generation device in glucose detection. Currently, a nonenzymatic glucose sensor attracted much attention due to its operation based on direct oxidation of glucose without using the enzyme and had a potential to alternative the enzymatic glucose sensor. So far, many metals and their oxide are investigated as the active catalysts for direct oxidation of glucose such as gold [1–5], platinum [6–8], silver [5, 8], nickel [9–11], copper [12–17], palladium [18], and cobalt [19]. We are interested in copper and its oxides because of its potential application in the development of the electrochemical sensors for the selective detection of dopamine [20] and glucose [12–17]. More recently, copper oxide (CuO) has

attracted more interest owing to its easy manufacturing, inexpensive, abundant morphology, and high catalyst activity [12]. To promote catalyst activity, CuO particle hybrid graphene [12, 14], carbon nanotubes (CNTs) [13], and carbon nanofibers [19] have been dedicated in the literature.

Besides, electrically conducting polymers are interested, a representative is polyaniline (PANI), due to their potent properties such as high conductivity, durable, stable, low cost, easy deposition, and control of morphology and thickness [21]. In the enzymatic biosensor, PANI has shown a significant role in detection performance which has improved the detection limit and the sensitivity of the sensor and the sensitivity of the sensor [22–26]. The combination of copper (ion, oxide forms) and PANI has been investigated in several reports. In 2014, Choudhary et al. reported a

nonenzyme glucose sensor based on Cu(I) and PANI which showed an improvement in electrocatalytic activity toward glucose oxidation via the integration of Cu(I) onto PANI [27]. Recently, Zhenget al. reported a highly sensitive nonenzymatic glucose sensor based on the combination of copper nanoparticles, PANI, and graphene (CuNPs/PANI/graphene) [28]; Ghanbari and Babaei synthesized a ternary NiO/CuO/PANI nanocomposite as an effective sensing material for nonenzymatic glucose detection in the alkaline electrolyte [29].

In this paper, for the first time, polyaniline-supported Cu-CuO core-shell structure was prepared on the 316L stainless steel electrode by electrochemical methods for the direct detection of glucose in the alkaline electrolyte. The electrochemical techniques have been used widely in the designing of the glucose sensors [30, 31]. In this work, the use of the electrochemical methods in the development of the sensor makes it possible to control the thickness and morphology of the PANI film as well as the morphology and the structure of the copper-based catalyst contributing to improving the performance of the sensor.

2. Experimental

2.1. Chemicals and Materials. D-(+)-Glucose, sucrose (99.7%), D-(+)-mannose (99%), D-(+)-lactose, and L-ascorbic acid (99%) were purchased from Across Organics. Sodium hydroxide (99%), aniline, ethanol, sulfuric acid (96%), and potassium chloride (99.5%) were purchased from Merck company. Copper (II) chloride dihydrate (99%) was purchased from Fisher Scientific (UK). AISI-type 316L stainless steel (316L) of analyzed chemical composition (wt.%) 0.1037 Si, 1.553 Mn, 0.0015 P, 0.00069 S, 7.686 Ni, 19.39 Cr, 0.4790 Mo, 0.1957 Cu, 69.19 Fe, 0.1281 V, 0.262 Co, and 1.01 others was used as a metallic substrate.

2.2. Electrochemical Cell and Electrochemical Equipment. A conventional single-compartment three-electrode cell was used for the electrodeposition process. 316L rods were used as the working electrode. Rods with a diameter of 0.9 cm were embedded in epoxy resin, and the working surface area of samples was equal to 0.63 cm². A platinum mesh was used as an auxiliary electrode. All the potentials were measured versus an Ag/AgCl (3 M KCl) reference electrode. All the experiments were carried out using the Biologic MPG2 electrochemical equipment controlled by the EC-Lab software.

2.3. Electrodeposition of PANI Films. Before electrodeposition, working electrodes were wet mechanically and polished successively with 400, 600, 800, 1200, and 2000 abrasive paper. Afterward, the electrode was rinsed with doubly distilled water and degreased in acetone to remove impurities using an ultrasonic cleaner and finally dried at room temperature. The PANI films were synthesized electrochemically from 0.1 M aniline containing solutions of 0.5 M sulfuric acid in absolute ethanol. The deposition of PANI on 316L electrodes was carried out using cyclic voltammetry

(CV) technique for a potential range between −0.2 and 1.2 V for 26 cycles with a scan rate of 30 mV/s. After 26 CV cycles, the PANI-coated 316L (PANI/316L) was rinsed with deionized water to remove the adsorbed electrolyte, monomer, and the soluble oligomers and then dried for 1 h at room temperature. The thickness (*d*) of the PANI film was calculated using the following equation [32, 33]:

$$d = \frac{QM_w}{zFS\rho}, \quad (1)$$

where *Q* is the amount of charge calculated from the final scan form of the CV electrodeposition; *M_w* is the molecular weight of the aniline monomer; *z* is the number of electrons per monomer unit (*z* = 0.5); *S* is the surface area of the working electrode; *ρ* is the specific density of aniline; and *F* is Faraday's constant.

2.4. Electrodeposition of the Cu-CuO Core-Shell onto the PANI Film. Cu-CuO core-shell structure was prepared on the surface of the PANI film via a two-step protocol [34]: in the first step, Cu particles were electrodeposited onto the PANI/316L electrode from CuCl₂·2H₂O 0.01 M precursor in KCl 0.1 M electrolyte by the CV method in a potential range of −0.6–0 V at a scan rate of 100 mVs^{−1} for three cycles. In the second step, the received Cu/PANI/316L electrode from the first step was then immersed in NaOH 0.1 M to partially oxidize Cu into CuO by the CV method with the potential range from −0.5 to 0.8 V at a scan rate of 100 mVs^{−1} for 20 cycles (second step) to get the Cu-CuO/PANI/316L electrode.

2.5. Structural Characterization. The PANI film deposited on the 316L electrode was scrapped off and characterized by Fourier transform infrared spectrometer (FTIR) using a Bruker Vertex 70 and KBr pellets of solid samples. The morphology and chemical composition of the polyaniline-supported Cu-CuO core-shell sample were analyzed by FESEM/EDX technique using a Hitachi S-4800 instrument. The structure of the Cu-CuO core-shell was further analyzed on Bruker D8 advance powder X-ray diffractometer with Cu Kα (*λ* = 1.54178 Å) as the incident radiation.

2.6. Characterization of the Cu-CuO/PANI/316L Nonenzymatic Glucose Sensor. Electrocatalytic properties of the Cu-CuO/PANI/316L electrode were examined by CV measurements in 0.1 M NaOH solution containing 5 mM glucose within the potential range of 0–0.8 V at a scan rate of 100 mVs^{−1}. The sensing performance of the fabricated electrode-based nonenzymatic glucose sensor was studied by the chronoamperometry (CA) method at an applied potential of 0.63 V in 0.1 M NaOH electrolyte under constant stirring and successive addition of glucose in the range of 0 and 15 mM. The anti-interference of the sensor was analyzed by the sequential addition of 1 mM of sucrose, maltose, lactose, ascorbic acid, and glucose into a solution of 1 mM glucose in NaOH 0.1 M solution at a constant applied potential of 0.63 V.

3. Results and Discussion

3.1. Electrodeposition of PANI on 316L. Figure 1 represents the successive voltammograms recorded during the growth of PANI films deposited from ethanol and aqueous solutions of 0.1 M aniline and 0.5 M sulfuric acid by cycling the potential from -0.2 to 1.2 V at a scan rate of 30 mV/s. During the subsequent scans for PANI, anodic peaks at 0.4 V (A) and 0.9 V (B) were attributed to the alteration of PANI from the reduced leucoemeraldine (LE) state to the partially oxidized emeraldine (EM) state and transformation of emeraldine to the fully oxidized pernigraniline (PE) structure, respectively. The rate of electrodeposition initiated slowly in the first five cycles and then returned more rapidly over the next 15–26 cycles. An increase in the current of peaks A and B shows that the deposition thickness increases with cycles. This characteristic of CV curves has been reported on another nonmetallic substrate, such as indium tin oxide (ITO) [35]. Finally, it was seen that the surface of the 316L substrates was covered with brilliant green of the emeraldine salt (ES) state of the polymer layer. The thickness of polymer coatings was estimated by using equation (1) which is about $0.3\text{ }\mu\text{m}$.

FT-IR spectra of PANI synthesis on the 316L SS electrode in the ethanol medium are shown in Figure 2. Characteristic peaks of PANI appear at wavenumbers of 1477 cm^{-1} (benzenoid ring vibration), 1561 cm^{-1} (C-C stretching mode for the quinoid rings), 3421 cm^{-1} (N-H vibration), 1302 cm^{-1} (C-N stretching vibration), 1248 cm^{-1} (C-N⁺ stretching vibration), 1653 cm^{-1} (C=N vibration), 2922 and 2853 cm^{-1} (C-H stretching vibration), 802 cm^{-1} (C-H bending vibration), and 2375 cm^{-1} ($\text{C}_6\text{H}_5\text{-N=N}^+$ vibration) demonstrating existence of the head-head PANI mode [36, 37]. In addition, there is the presence of SO_4^{2-} radical in production at 1108 cm^{-1} [38].

In order to obtain information concerning the morphology of the PANI film, SEM measurements were performed on the 316L electrode before and after deposited with the PANI film. It can be seen from Figure 3 that the PANI film showed “cauliflower” morphology and formed a dense layer on the 316L substrate [39], which was attributed to the slower growth rate in ethanol media. The adhesion of the PANI coating on the 316L was verified by the sellotape test, which consisted of applying with a thumbnail pressure on the whole surface, which was removed by slow peeling with a back pull of the tape [40]. Results showed that the PANI film had been successfully deposited on 316L from an ethanol solution by the CV method. The obtained coating is thin, very adherent to the stainless steel substrate, and reveals compact and uniform morphology.

3.2. Preparation of the Cu-CuO Core-Shell on the PANI/316L Electrode. Figure 4 shows the CVs for electrodeposition of Cu onto the PANI/316L electrode and formation of the CuO shell on the surface of Cu (core) to form the Cu-CuO core-shell structure.

It can be seen from Figure 4(a) that a reduction peak at about -0.35 V is associated with the reduction of Cu(II) to Cu(0). The intensity of the reduction peak decreased with the

FIGURE 1: CVs recorded during electrodeposition of polyaniline onto the 316L electrode from ethanol solution containing 0.1 M aniline and 0.5 M H_2SO_4 at scan rate 30 mV/s.

FIGURE 2: FT-IR spectra of PANI synthesis on the 316L electrode.

proceeding of the potential scan which was attributed to the formation of CuO on the surface of Cu due to the electro-oxidation of Cu in the reverse scan at the potential around -0.1 V [34]. To completely oxidize Cu on the surface of Cu particles, a repetitive CV (20 cycles) was performed on the Cu/PANI/316L in 0.1 M NaOH electrolyte. The appearance of an anode peak at around 0.5 V on the first cycle was attributed to the oxidation of Cu(0) to CuO [34]. The disappearance of this anode peak during successive cycles indicated that the surface of Cu particles was oxidized to CuO, which formed a Cu-CuO core-shell structure (Figure 4(b)).

The formation of the Cu-CuO core-shell structure on the surface of the PANI film was further investigated by SEM/EDX and XRD techniques. It can be seen clearly from the SEM image of the Cu-CuO/PANI/316L electrode that Cu-CuO clusters are present on the surface of the PANI film. The corresponding EDX spectrum has semi-quantitatively confirmed the presence (atom %) of C (88.35%), N (6.07%), O (2.21%), and Cu (3.37%). The Cu/O atomic ratio is about 1.5, which indicates the presence of the Cu-CuO core-shell structure (Figure 5). The XRD pattern of the Cu-CuO/PANI/

FIGURE 3: SEM images of the 316L electrode before (a) and after (b) modified with the PANI film.

FIGURE 4: CVs recorded during electrodeposition of Cu onto the PANI/316L electrode from 0.01 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ precursor in 0.1 M KCl solution (a) and partially oxidize Cu into CuO in 0.1 M NaOH electrolyte (b), with the scan rate of 100 mVs^{-1} .

FIGURE 5: SEM images (a) and EDX (b) of the Cu-CuO/PANI/316L electrode.

316L sample showed two distinct diffraction peaks at 2θ values of 43.7° and 50.7° , which correspond to the (200) and (112) crystalline planes of the fcc structure of copper (JCPDS

04-0836). In addition, the appearance of two weak diffraction peaks at 2θ values of 25° and 75.5° assigned to the (021) and (004) planes of CuO (JCPDS 005-0661),

FIGURE 6: XRD pattern of the Cu-CuO/PANI/316L electrode.

FIGURE 7: Comparison of CV curves of 316L (a), PANI/316L (b), and Cu-CuO/PANI/316L (c) electrodes measured in 5 mM glucose in 0.1 M NaOH solution with scan rate 100 mV/s.

FIGURE 8: Calibration curve of the glucose concentration versus current for the Cu-CuO/PANI/316L nonenzymatic glucose sensor at an applied potential of 0.63 V in 0.1 M NaOH.

FIGURE 9: Interference examined in the Cu-CuO/PANI/316L sensor in 0.1 M NaOH solution with 1 mM glucose and 1 mM of interferences (sucrose, maltose, lactose, and ascorbic acid).

characteristics of a thin structure of the CuO shell (Figure 6). Overall, polyaniline-supported Cu-CuO core-shell structure had been successfully prepared on the 316L substrate.

3.3. Electrocatalytic Properties of Glucose at the Cu-CuO/PANI/316L Electrode. Electrocatalytic properties of the Cu-CuO/PANI/316L electrode to glucose oxidation were examined by comparison with bare 316L and PANI/316L electrodes by CV measurements in 0.1 M NaOH solution containing 5 mM glucose within the potential range of 0–0.8 V at a scan rate of 100 mV s⁻¹. As shown in Figure 7, in the same solution, only the Cu-CuO/PANI/316L electrode exhibited an anode peak at around 0.63 V which is attributed to the direct oxidation of glucose in alkaline media.

Cu-CuO catalysis oxidation of glucose can be explained following the mechanics [12, 19].

3.4. Sensing Performance of Glucose at the Cu-CuO/PANI/316L Electrode. The sensing performance of the Cu-CuO/PANI/316L sensor was studied by the chronoamperometry (CA) method at an applied potential of 0.63 V in 0.1 M NaOH electrolyte under constant stirring and successive addition of glucose in the range of 0 and 15 mM. It can be found in Figure 8 that the Cu-CuO/PANI/316L sensor

exhibited a linear range of 0.1–5 mM ($R^2=0.995$) with a detection limit of 0.1 mM (S/N = 3) and high sensitivity of 25.71 mA·mM⁻¹·cm⁻².

The anti-interference property of the Cu-CuO/PANI/316L nonenzymatic sensor has been examined with other organic substances that can be oxidized at the same potential as glucose. The results received showed that there was no significant interference observed from sucrose, maltose, lactose, and ascorbic acid (Figure 9).

4. Conclusion

316L electrode has been successfully modified by the polyaniline-supported Cu-CuO core-shell structure. The Cu-CuO/PANI/316L electrode exhibited good electrocatalytic activity to the direct oxidation of glucose and was used as a nonenzymatic glucose sensor. The as-prepared sensor exhibited high sensitivity and selectivity with a linear range of 0.1–5 mM. The polyaniline-supported Cu-CuO core-shell structure has the potential to be applied as an electrode material for the nonenzymatic glucose sensor.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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