



Preparation and characterization of copper nanoparticles/zinc oxide composite modified electrode and its application to glucose sensing

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ABSTRACT

We report a new method for selective detection of D(+)-glucose using a copper nanoparticles (Cu-NPs) attached zinc oxide (ZnO) film coated electrode. The ZnO and Cu-NPs were electrochemically deposited onto indium tin oxide (ITO) coated glass electrode and glassy carbon electrode (GCE) by layer-by-layer. In result, Cu-NPs/ZnO composite film topography was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. SEM and AFM confirmed the presence of nanometer sized Cu-NPs/ZnO composite particles on the electrode surface. In addition, X-ray diffraction pattern revealed that Cu-NPs and ZnO films were attached onto the electrode surface. Indeed, the Cu-NPs/ZnO composite modified electrode showed excellent electrocatalytic activity for glucose oxidation in alkaline (0.1 M NaOH) solution. Further, we utilized the Cu-NPs/ZnO composite modified electrode as an electrochemical sensor for detection of glucose. This glucose sensor showed a linear relationship in the range from 1×10^{-6} M to 1.53×10^{-3} M and the detection limit ($S/N=3$) was found to be 2×10^{-7} M. The Cu-NPs/ZnO composite as a non-enzymatic glucose sensor presents a number of attractive features such as high sensitivity, stability, reproducibility, selectivity and fast response. The applicability of the proposed method to the determination of glucose in human urine samples was demonstrated with satisfactory results.

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1. Introduction

Electrochemical methods have potential application in the detection of D(+)-glucose in blood samples [1] and also in bio-fuel cells [2]. Glucose oxidase (GOD) is one of the most extensively studied enzyme and has been successfully employed for preparing glucose biosensors. The development of glucose biosensors utilizing GOD is an active research area [3–6]. A majority of glucose sensors, especially those used in in-vivo application are based on the electrochemical oxidation of hydrogen peroxide which is formed in the course of the enzyme-catalyzed oxidation of glucose by dissolved oxygen. Recently, excellent review articles have been published and discussed about the principles of electrochemical glucose biosensors and key challenges in their further development and use [7,8].

Over the past decades, a number of studies have been conducted to alleviate the drawbacks of enzymatic glucose sensors. The most common and serious problem is insufficient stability originated from the nature of the enzymes which is hardly overcome. Although GOD is quite stable compared with other enzymes, the glucose sensors based on GOD are always exposed to the possible thermal and chemical

deformation during fabrication, storage or use. Further, GOD quickly loses its activity below pH 2 and above pH 8 and temperature above 40 °C can cause fatal damages [9]. Ionic detergents also deactivate GOD as well. To overcome the above obstacles, non-enzymatic glucose sensors have been developed and kept coming closer to practical applications. A review by Park et al. discussed about the merits and mechanism of glucose oxidation on non-enzymatic sensors [10]. Nanostructured particles have attracted extensive scientific and industrial interest due to their unique electronic, optical and catalytic properties. Nanoparticles can display four unique advantages over macroelectrodes when used for electroanalysis. These are: enhancement of mass transport, catalysis, high effective surface area and control over electrode microenvironment [11].

Electrochemical deposition of copper nanoparticles (Cu-NPs) and their applications in electrocatalysis is an active research area [11,12]. Though, the Cu-NPs were prepared in several matrixes by several researchers, no effort has been made to prepare Cu-NPs embedded in functional matrix material like zinc oxide (ZnO). In the present paper, for the first time, we have deposited Cu-NPs onto ZnO film using electrochemical technique. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) studies revealed that Cu-NPs were uniformly implanted on the ZnO film. X-ray diffraction study (XRD) confirmed the presence of Cu-NPs and ZnO films on the electrode surface. Electrochemical and electrocatalytic properties of a Cu-NPs/ZnO film coated electrode were reported. In addition,

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electrocatalytic oxidation and amperometric determination of glucose was demonstrated using the Cu-NPs/ZnO composite coated electrode.

2. Experimental

2.1. Reagents and apparatus

All chemicals and reagents used in this work were of analytical grade and used as received without further purification. These were: uric acid, fructose, sucrose, maltose, mannose, lactose and galactose and were purchased from Sigma-Aldrich (St. Louis, MO, USA). D(+)-Glucose, potassium perchlorate and sodium hydroxide were purchased from Wako pure chemicals (Osaka, Japan). Ascorbic acid, sodium acetate, potassium nitrate, zinc nitrate and sodium dihydrogen phosphate were received from E-Merck (Darmstadt, Germany). Copper sulfate pentahydrate was received from Ishizu Seiyaku Ltd. The aqueous solutions were prepared by using doubly distilled deionized water and before each experiment the solutions were deoxygenated by purging with pre-purified nitrogen gas.

Electrochemical measurements were performed using a CH Instruments (Model: 750A). Indium tin oxide-coated glass electrode (ITO) was purchased from Merck Display Technologies Ltd. and glassy carbon electrode (GCE) was purchased from Bioanalytical System Company. Platinum wire is used as the counter electrode. All the cell potentials were measured with respect to an Ag/AgCl [KCl (sat)] reference electrode. The AFM images were recorded with a multimode scanning probe microscope system operated in tapping mode (Being Nano-Instruments, CSPM-4000, Ben Yuan Ltd.). X'Pert PRO Diffractometer (PANalytical, ALMELO) was used for X-ray diffraction analysis. Hitachi Scientific Instruments (London, UK) Model S-3000H SEM was used for surface image measurements. Electrochemical impedance measurements (EIS) were performed using an impedance measurement unit, IM6ex ZAHNER, Messsysteme (Kroanach, Germany).

2.2. Cu-NPs/ZnO composite sensor preparation

ITO substrates were cleaned by using detergent, diluted hydrochloric acid and then finally rinsed with distilled water. GCE was polished with alumina paste (0.05 μm) on a soft polishing cloth (Buehler) and sonicated in absolute ethanol and then in water for 5 min. Thereafter, GCE was treated with cyclic scanning in the potential range of -0.5 to 1.2 V at a scan rate of 100 mV s^{-1} in 0.1 M H_2SO_4 until the stable cyclic voltammograms (CVs) were obtained. Transparent ZnO films have been cathodically deposited onto conductive ITO glasses or GCE from a simple aqueous zinc nitrate electrolyte bath kept at 335 K [13]. Electrodeposition of ZnO film was carried out potentiostatically (-0.7 V for 20 min) using a potentiogalvanostat without stirring. ZnO-modified ITO and GCE were rinsed with distilled water to remove unbounded materials from the electrode surface and then dried by nitrogen gas.

Next, Cu-NPs were deposited onto a ZnO film coated ITO or GCE from the solutions of 0.01 M $\text{CuSO}_4 + 0.1$ M KClO_4 under fixed applied potential of -0.9 V (vs. Ag/AgCl) for 3 min [14]. For comparative studies, Cu-NPs were deposited onto an unmodified ITO or GCE as described above. Finally, the Cu-NPs/ZnO composite modified electrode was thoroughly washed with doubly distilled water to remove unbounded materials from the electrode surface and then dried in air for 30 min before use.

3. Results and discussion

3.1. Characterization of the Cu-NPs/ZnO modified electrode

Fig. 1 (a) shows the SEM image of the Cu-NPs/ZnO film modified electrode which clearly indicated that nanoparticles were attached onto the electrode surface. The particle sizes were observed in the range from

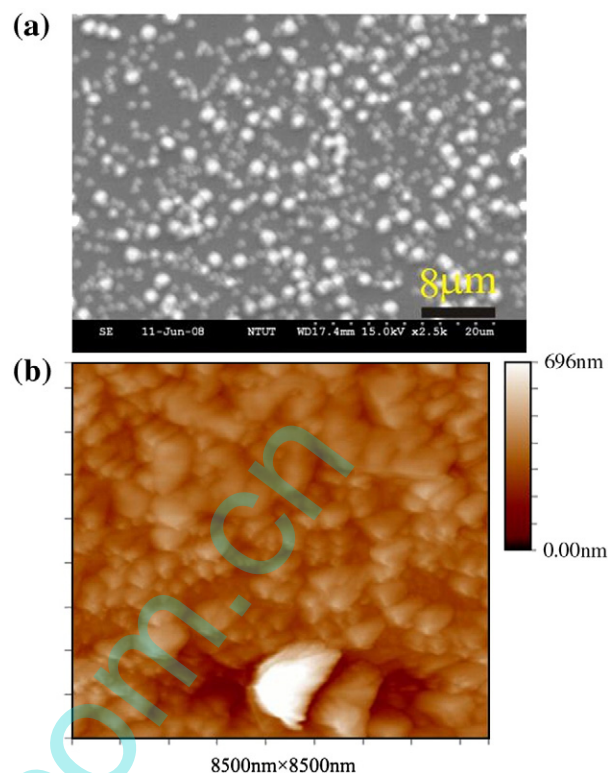


Fig. 1. (a) SEM and (b) AFM images of Cu-NPs/ZnO composite modified electrode.

100 nm to 1.5 μm . Fig. 1 (b) shows an AFM image (8500 $\text{nm} \times 8500$ nm) of the Cu-NPs/ZnO composite modified electrode. The important parameters of the Cu-NPs/ZnO composite modified electrode were extracted from the AFM image analyzer such as surface roughness (31.3 nm), particle sizes (100 nm to 1.5 μm) and film thickness (696 nm). From SEM and AFM studies, it was confirmed that composite particles were attached onto the electrode surface.

Fig. 2 shows the XRD pattern of the Cu-NPs/ZnO composite films. XRD patterns revealed that copper peaks along with the peaks correspond to ZnO. Part of the peaks in XRD patterns (Fig. 2) can be

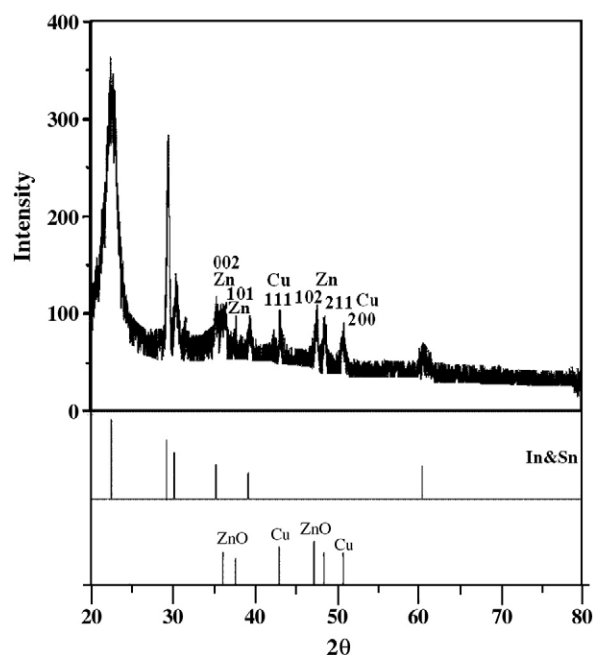


Fig. 2. XRD pattern of Cu-NPs/ZnO composite films.

well matched to the standard diffraction pattern of wurtzite ZnO [15] which demonstrates the formation of wurtzite ZnO films. Characteristic peaks of ZnO at 31.8, 34.48, 36.28 and 47.5 corresponded to [1 0 0], [0 0 2], [1 0 1] and [1 0 2] diffraction peaks of the wurtzite form which indicates that ZnO shell possesses a polycrystalline hexagonal crystal structure. Further, the diffraction pattern clearly shows two major peaks at 43.50 and 50.50° in the range of 10 to 80° which can be assigned to the diffraction from the [111] and [200] planes, respectively, of the face-centered cubic lattice of Cu(0) [16]. The XRD results clearly indicated that the layers of Cu-NPs and ZnO films were attached onto the electrode surface by electrodeposition.

Fig. 3a shows CVs of a bare ITO, ZnO-modified ITO and Cu-NPs/ZnO film modified ITO recorded in 0.1 M NaOH containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at a scan rate of 50 mV s^{-1} . Quasi-reversible one-electron redox behavior of ferricyanide/ferrocyanide was observed on the bare ITO (Fig. 3a, line b) with a peak separation (ΔE_p) of 659 mV. After the electrode was modified with ZnO, the lowest peak current (I_p) and the largest ΔE_p were observed (Fig. 3a, line a). According to the zero-point charge (zpc) of ZnO ($\text{pH}_{\text{zpc}} = 9.0$), ZnO is negatively charged at higher pH [17], so it hinders the diffusion of ferricyanide/ferrocyanide ions toward the electrode surface. As expected, at the Cu-NPs/ZnO composite modified electrode (Fig. 3a, line c), I_p was increased and ΔE_p was decreased compared with that of the bare ITO and ZnO-modified electrode which indicated that Cu-NPs played a role in the increase of electroactive surface area and promoted electron transfer process.

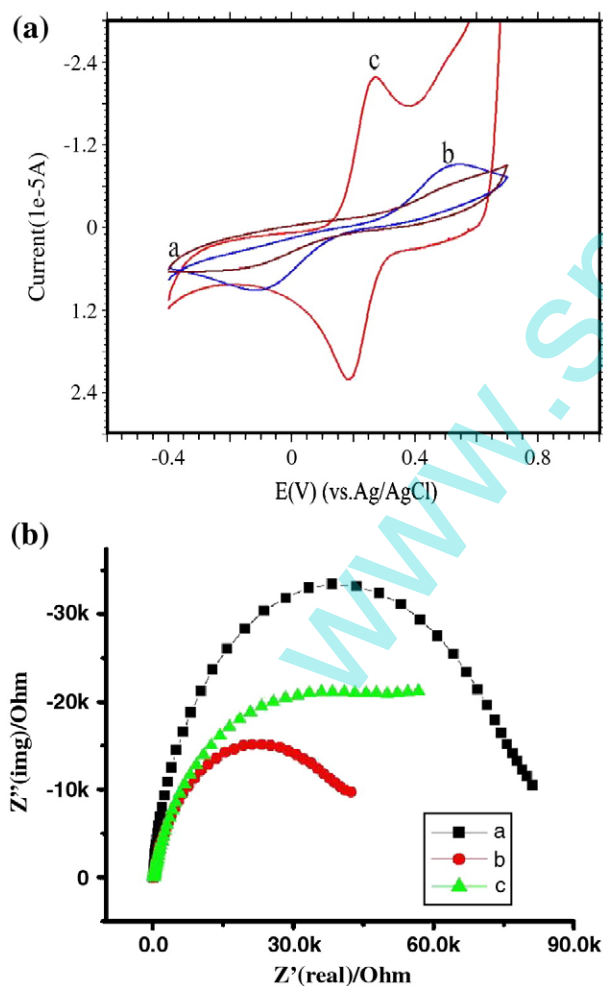


Fig. 3. (a) The cyclic voltammograms (CVs) of a bare ITO (b), ZnO/ITO (a) and Cu-NPs/ZnO/ITO (c) recorded in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1 M NaOH at 50 mV s^{-1} . (b) EIS results of a bare ITO (curve a), Cu-NPs/ZnO/ITO (curve b) and ZnO/ITO (curve c) in the presence of equimolar $[\text{Fe}(\text{CN})_6]^{3-/4-}$ + 0.1 M NaOH.

Further, CVs show that the Cu-NPs/ZnO composite film was effectively immobilized on ITO surface and provided necessary conduction pathways in promoting the electron transfer between the interface of redox probe and electrode just like a nanoscale electrode.

EIS was applied to monitor the whole process of the electrode modification. EIS can give useful information of the impedance changes on the electrode surface between each step. Fig. 3b shows the results of EIS for a bare ITO and other two modified electrodes in the presence of equimolar $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M NaOH. The EIS includes a semicircular part and a linear part. The semicircular part at higher frequencies corresponds to the electron transfer limited process and the diameter is equivalent to the electron transfer resistance (R_{ct}). The linear part at lower frequencies corresponds to the diffusion process. During the fabrication, significant differences were observed. R_{ct} of a bare ITO is 81.533 k Ω (Fig. 3b, line a). As reported [18], bare ITO is negatively charged so it hinders the diffusion of ferricyanide ions towards the electrode surface. For this reason higher R_{ct} value was observed for bare ITO. After, the ITO was modified with ZnO, R_{ct} value was decreased markedly to 56.533 k Ω (Fig. 3b, line c). EIS results for the electrode modified with the Cu-NPs/ZnO composite are shown in Fig. 3b (line b) and R_{ct} was considerably decreased to 42.333 k Ω . These results confirmed that the Cu-NPs/ZnO film was successfully immobilized on the ITO surface and the results are consistent with CVs (Fig. 3a). From these observations, we can conclude that the Cu-NPs/ZnO composite films were highly conductive and expected as a good platform for sensing applications.

3.2. Electrochemical properties

Fig. 4 shows the CVs of (a) the Cu-NPs/ZnO/ITO electrode and (b) the Cu-NPs/ITO recorded at a scan rate of 50 mV s^{-1} in 0.1 M NaOH solution. In both cases, the CVs indicated the evidence of Cu-NPs oxidation and reduction states. The anodic waves labeled a_1 and a_2 correspond to the formation of Cu(I) and Cu(II) while the cathodic peaks marked c_1 and c_2 represent the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0), respectively. These observations are consistent with the CVs of a bare Cu electrode as previously reported in strongly alkaline solutions [19].

For comparative studies, Cu-NPs were deposited onto a bare ITO electrode and the CVs of Cu-NPs/ITO are shown in Fig. 4, curve b. The area of the electrode used for the modification was 0.5 cm^2 . The principal difference between Cu-NPs/ZnO/ITO and Cu-NPs/ITO film

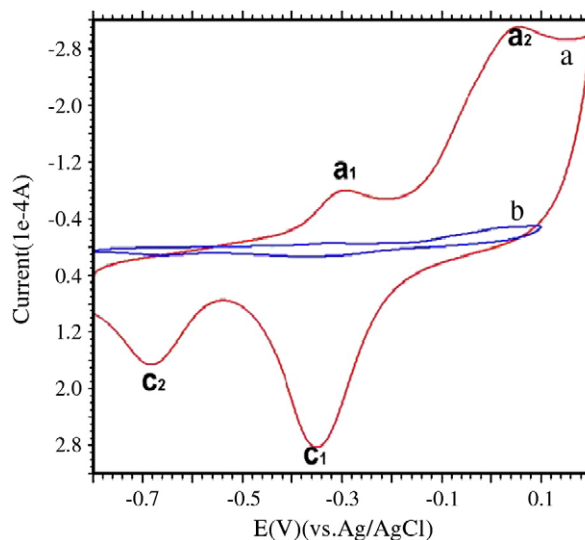


Fig. 4. The electrochemical behaviors of (a) a Cu-NPs/ZnO/ITO electrode and (b) Cu-NPs/ITO by sweeping the potential between -0.8 and 0.2 V at a scan rate of 50 mV s^{-1} in 0.1 M NaOH solution.

modified electrodes can be seen in their peak currents. In particular, the principal cathodic and anodic peak currents were increased dramatically at the Cu-NPs/ZnO/ITO than the Cu-NPs/ITO modified electrode. It is suggested that the ZnO film influenced the electrochemical deposition of Cu-NPs and served as host matrix for incorporation of Cu-NPs. These observations are also supported by previous reports where ZnO film worked as a good matrix for other inorganic nanoparticles such as germanium [20] and nickel [21]. We also tested the stability of both modified electrodes by continuous potential sweeping between -0.8 and 0.1 V at a scan rate of 50 mV s^{-1} . After the 100th cycle, the peak currents were decreased as 2% and 28% for Cu-NPs/ZnO/ITO and Cu-NPs/ITO, respectively. As stated earlier [15,20,21], ZnO film is a good host material for inorganic nanoparticles and this might be the reason for high stability of composite electrode in alkaline solution. The anodic and cathodic peaks of Cu-NPs/ZnO/ITO were ascribed to the intrinsic characteristics of Cu-NPs immobilized on the electrode surface [19,22–24].

3.3. Electrocatalytic oxidation of glucose

Fig. 5 shows CVs of the Cu-NPs/ZnO composite modified electrode recorded in 0.1 M NaOH in the absence (curve a) and presence (curve b) of 5 mM glucose at a scan rate of 20 mV s^{-1} . It exhibited a single oxidation peak around 0.8 V vs. Ag/AgCl, but no corresponding reduction peak was seen under the conditions employed. This indicated that glucose could be irreversibly oxidized at the composite modified electrode. Fig. 5 (curves d and e) shows CVs obtained for glucose at an unmodified electrode (curve d) and a ZnO-modified electrode (curve e). These electrodes did not exhibit a single oxidation peak around 0.8 V under the condition employed. This indicated that glucose could be only irreversibly oxidized at the Cu-NPs/ZnO modified electrode. In this case, required detection potential for glucose with the Cu-NPs/ZnO/ITO electrode could not be lower than 0.8 V vs. Ag/AgCl in order to obtain enough sensitivity. Although, Cu-NPs/ITO electrode showed the oxidation peak current for glucose like the Cu-NPs/ZnO composite modified electrode (Fig. 5 curve c), the catalytic (oxidation) current was two orders smaller than observed at the Cu-NPs/ZnO composite electrode. As shown in Fig. 5 curve b, enhancement of glucose oxidation current was observed on the Cu-NPs/ZnO composite modified electrode which is due to the presence of high amount of Cu-NPs active centers. These observations indicated that the ZnO film worked as a good

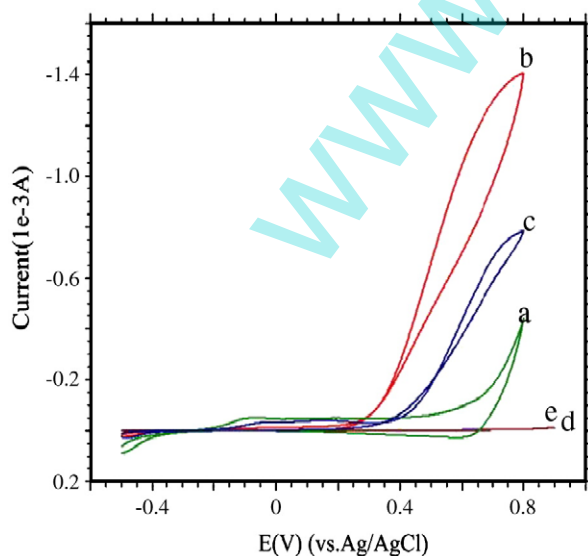


Fig. 5. The CVs of a Cu-NPs/ZnO composite modified electrode in 0.1 M NaOH in the absence (curve a) and presence of 5 mM glucose (curve b). The CVs of a Cu-NPs/ITO (curve c), ZnO/ITO (curve d) and bare ITO (curve e) in 5 mM glucose at a scan rate of 20 mV s^{-1} .

platform for incorporation of Cu-NPs. Bi-layer film of ZnO and Cu-NPs increased the oxidation current and sensitivity of the proposed method (Fig. 5 curve b). Moreover, the proposed Cu-NPs/ZnO composite electrode had high stability and showed higher catalytic current for glucose. Electrocatalytic oxidation of glucose in alkaline media occurred at the Cu-NPs/ZnO modified electrode as reported by other researchers [16]. Cu(III) species have been proposed to act as an electron transfer mediator. As shown in Fig. 5 curve b, the oxidation of glucose occurs in the potential range of 0.40 to 0.8 V like other Cu-NPs modified electrodes [16,25].

3.4. Amperometric determination of glucose

The determination of glucose concentration using the Cu-NPs/ZnO composite modified glassy carbon disk electrode was performed with amperometry. The oxidation current of glucose was monitored in 0.1 M NaOH ($\text{pH} = 13$) at an applied potential of 0.8 V and plotted against the bulk concentration of glucose after subtraction of background current (Fig. 6). The dependence of response currents on the concentration of glucose is a linear relationship in the range of $1 \times 10^{-6} \text{ M}$ to $1.53 \times 10^{-3} \text{ M}$ (inset of Fig. 6). The linear regression equation is expressed as $i_p (\mu\text{A}) = -0.1042x - 3.543$ ($r^2 = 0.9973$). The detection limit ($S/N=3$) was $2 \times 10^{-7} \text{ M}$. The relative standard deviation of eight successive scans is 2.7% for $5 \times 10^{-4} \text{ M}$ glucose which indicates that the Cu-NPs/ZnO composite modified electrode had an excellent reproducibility. The Cu-NPs/ZnO composite modified electrode responds with each addition of glucose within 3 s. The sensitivity of the Cu-NPs/ZnO modified electrode for glucose was found to be 0.16 ± 0.02 ($n = 6$) $\mu\text{A } \mu\text{M}^{-1}$. This higher sensitivity might be due to the high electrocatalytic active centers on the composite modified electrode. The sensitivity of the proposed sensor is higher than that of the other modified electrodes such as copper nanocluster/multi walled carbon nanotubes (MWCNTs) ($17.16 \mu\text{A mM}^{-1}$) [16], oil/MWCNTs/Cu-NPs composite (59.2 nA mM^{-1}) [25], multilayer films containing chitosan/MWCNTs/GOD ($0.45 \mu\text{A/mM}$) [26], layer-by-layer (LBL) self-assembly of MWCNTs, gold nanoparticles and GOD on the Pt electrode ($2.527 \mu\text{A/mM}$) [27], palladium nanoparticles/poly (3,4-ethylenedioxythiophene) nanofibers/GCE ($1.6 \text{ mA M}^{-1} \text{ cm}^{-2}$) [28] and alternative layers of a nanocomposite comprising of MWCNTs/Au nanoparticles/thiol functionalized polyaniline/GOD ($3.97 \mu\text{A/mM}$) [29].

The linear range and detection limit of the proposed method were compared with the other methods of glucose determination in Table 1. From the data presented in Table 1, our proposed method

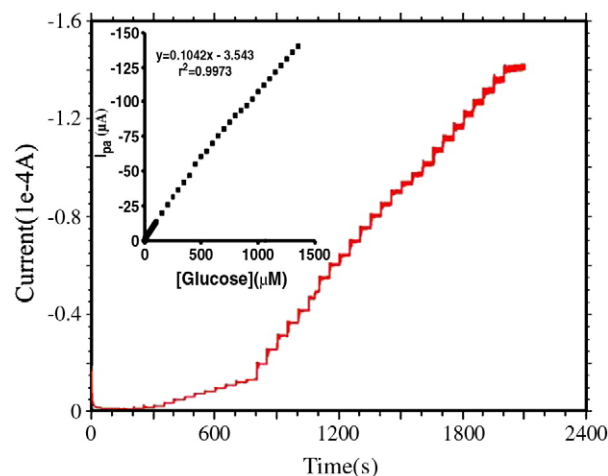


Fig. 6. The amperometric determination of glucose using a Cu-NPs/ZnO composite modified electrode in 0.1 M NaOH . Applied potential = 0.8 V . The concentrations of glucose were added from $1 \times 10^{-6} \text{ M}$ to $1.53 \times 10^{-3} \text{ M}$.

has wide linear range [30–32] and lower detection limit [30–33] than earlier reports. The performance of the Cu-NPs/ZnO composite electrode was comparable with the Ni powder/sol–gel derived ceramic graphite composite electrode [34]. In addition, our proposed electrochemical sensor shows a wide linear range and the lowest detection limit for glucose than the enzyme modified electrode [35]. However, gold nanoparticles/chitosan composite and gold nanotube array electrodes have shown wide linear range for glucose determination than the proposed method [36–38] (Table 1). Based on these observations, we conclude that the proposed electrochemical sensor can be employed for detection of glucose.

The reproducibility and storage stability of the Cu-NPs/ZnO composite modified electrode were also examined. The relative standard deviation (RSD) of the sensor response to 2.0 mM glucose was 2.9% for 10 successive measurements. The electrode fabrication reproducibility was tested by measuring 2.0 mM glucose using freshly prepared five Cu-NPs/ZnO composite modified electrodes and the RSD was 3.2%. The Cu-NPs/ZnO composite modified electrode was stored at room temperature and used to measure its catalytic current at intervals of 1 week, it retained about 86% of its original sensitivity after 6 weeks. These observations indicated that the Cu-NPs/ZnO composite modified electrode possesses considerable shelf-life and reproducible results can be obtained.

3.5. Effect of interferences on analytical response

The effect of common interfering species on Cu-NPs/ZnO composite modified electrode was examined. Fig. 7 shows amperometric response of the Cu-NPs/ZnO composite modified electrode with interfering species including ascorbic acid, uric acid, fructose, sucrose, maltose, mannose, lactose and galactose at an applied potential of 0.8 V. The injection of 1.0 mM glucose caused an immediate increase of the oxidation current, while subsequent injection of ascorbic acid (a) and galactose (h) shows 1% response current compared to glucose. However, uric acid (b), fructose (c), sucrose (d), maltose (e), mannose (f) and lactose (g) did not show any effect on the current response. The reason for reducing interference on the Cu-NPs/ZnO composite modified electrode can be explained as follows. ZnO ($pH_{zpc} = 9.0$) is a negatively charged matrix in higher pH [17], so it is able to reduce the interferences caused by some substances such as ascorbic acid and uric acid since they present as anions [16,17]. Moreover, the high selectivity towards glucose was obtained on Cu-NPs/ZnO composite film than other carbohydrates which was early observed for other copper based electrode materials [39]. The reason for this selectivity is not yet explored and further studies are invited to explore this phenomenon. Thus, highly selective response to glucose was obtained at the Cu-NPs/ZnO composite modified electrode. This was an ad-

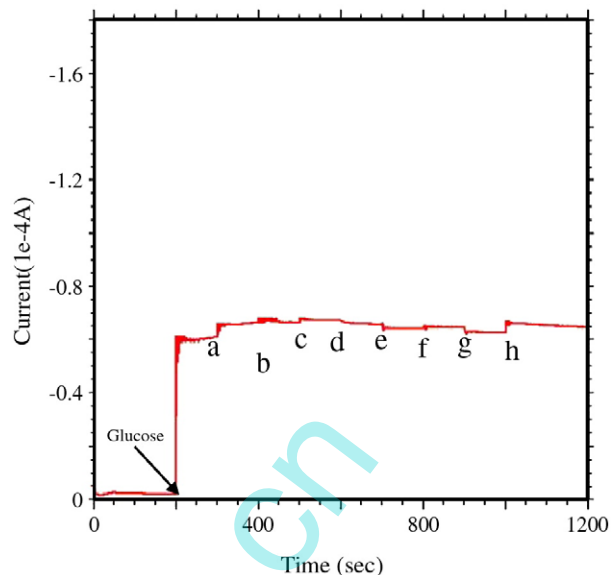


Fig. 7. The amperometric response of 1 mM glucose, ascorbic acid (a), uric acid (b), fructose (c), sucrose (d), maltose (e), mannose (f), lactose (g) and galactose (h) at a detection potential of 0.8 V. Concentration of each substance (from ascorbic acid to galactose) was 5 mM.

vantage of the proposed modified electrode as an electrochemical sensor for glucose [16,19,23,25].

Recently, using LBL technique, indium tin oxide-(poly(vinylsulfonate))/polyamidoamine-Au₃/cobalt hexacyanoferrate/GOD biosensor was proposed for detection of glucose at 0.0 V vs. SCE. In this study, cobalt hexacyanoferrate functioned as a redox mediator [40]. Also, a bienzymatic sensor based on periodate-oxidized glucose oxidase and horseradish peroxidase on controlled multilayer films of sulfonate-capped gold nanoparticles/thionine film was reported for glucose detection at -180 mV [41]. These two biosensors can be applied for detection of glucose at lower potential and good electrocatalytic effects were observed for glucose. However, when compared to the above biosensors, the proposed non-enzymatic sensor (Cu-NPs/ZnO composite film) shows comparable and good analytical data such as wide linear range, lower detection limit and fast response for glucose detection (Table 1). In addition, proposed electrode materials have several advantages such as easy fabrication, enzyme-free (thermally stable and pH independent), good stability, lower interference, less cost etc. We hope that the Cu-NPs/ZnO composite film modified electrode can be employed as a non-enzymatic electrochemical sensor for detection of glucose.

Table 1

Analytical data of the proposed method and other reports of glucose determination.

Electrode	Matrix	Catalyst used	pH	E_{app} (V)	Linear range	Detection limit	Reference
GCE	SWCNT/Nafion	Cu-NPs	12	0.65	250 nM to 500 μ M	0.25 μ M	[30]
Au	ZnO nanowire	GOD	7.4	0.8	1 μ M to 0.76 mM	1 μ M	[31]
Basal plane pyrolytic graphite electrode	–	CuO nanorod agglomerates	13	0.6	Upto 1 mM	1.2 μ M	[32]
PET/Ti/Au	–	ZnO:Co/GOD	7.4	0.55	0 to 4 mM	20 μ M	[33]
Sol–gel derived ceramic graphite composite	Sol–gel	Ni powder	13	0.45	0.5 μ M to 5 mM	0.1 μ M	[34]
GCE	Chitosan–gold nanoparticles	GOD	7.4	0.7	50 μ M to 1.3 mM	50 μ M	[35]
GCE	Chitosan	Gold nanoparticles nanocomposite	0.1 M NaOH	–	0.4 mM to 10.07 mM	0.37 mM	[36]
Pt	Chitosan/laponite nanocomposite	GOD	6.5	0.6	1 to 50 μ M	0.3 μ M	[37]
Gold substrate	Porous anodic alumina	Gold nanotube array electrode	7.4	0.25	1 mM–42.5 mM	10 μ M	[38]
GCE	ZnO	Cu-NPs	13	0.8	1 μ M to 1.53 mM	0.2 μ M	Proposed method

GCE: Glassy carbon electrode, SWCNT: single walled carbon nanotubes, PET/Ti/Au: poly(ethylene terephthalate)/titanium/gold film, GOD: glucose oxidase, and Pt: platinum electrode.

Table 2
Determination of glucose in urine samples.

Labels	Spiked (mM)	Found (mM)	RSD ^a (%)	Recovery (%)
Sample-A	1.0	1.030	2.41	103
Sample-B	1.0	0.982	2.97	98.2

^aThere are six measurements.

3.6. Determination of glucose in urine samples

Glucose was spiked into the urine samples and the spiked samples were analyzed using the Cu-NPs/ZnO composite modified electrode. Urine samples were obtained from a normal healthy man. The urine samples were diluted with 0.1 M NaOH in the ratio of 1:100. Amperometric studies were performed before and after addition of glucose into urine samples using the Cu-NPs/ZnO composite modified electrode. Table 2 shows the comparison of the determined values and the spiked values. Analytical recoveries of the added glucose into the urine samples were from 98.2 to 103.0%.

4. Conclusions

This study has indicated that the Cu-NPs/ZnO composite modified electrode exhibits higher electrocatalytic activity towards glucose oxidation. The obtained results revealed that determination of glucose can be easily performed using the Cu-NPs/ZnO composite films and the modified electrode had dramatically enhanced electrocatalytic activity towards glucose with high stability in its solution. Further, Cu-NPs/ZnO composite films were characterized by SEM, AFM, EIS and CV. The newly developed non-enzymatic glucose sensor presents a number of attractive features such as high sensitivity, stability, reproducibility, selectivity and fast response. The applicability of the method to the determination of glucose in human urine samples was demonstrated. This new Cu-NPs/ZnO composite modified electrode provides opportunity as an electrochemical sensing platform for glucose and thus it is expected to have potential applications in real sample analysis.

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