Facile Synthesis and Electrochemical Performance of Graphene-Modified Cu_2O Nanocomposite for Use in Enzyme-Free Glucose Biosensor

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ABSTRACT: *Graphene-modified Cu_2O nanocomposite was synthesized under facile microwave irradiation of an aqueous solution and has been investigated as an enzyme-free glucose biosensor. Morphology and crystal structure of the graphene-modified Cu_2O nanocomposite were investigated by using electron microscopy and X-Ray Diffraction (XRD) analyses. Also, the electrochemical performance of the graphene-modified Cu_2O nanocomposite for the measurement of glucose concentration in alkaline media was evaluated by using cyclic voltammetry and chronoamperometric measurements. The electrochemical studies revealed that graphene-modified nanocomposite electrode exhibited a high performance for non-enzymatic oxidation of glucose with a desirable sensitivity. Also, the fabricated graphene-modified biosensor exhibited a wide linear response for glucose detection in the concentrations ranges from 2 µM to 12 mM and a desirable detection limit of 2 µM. Also, the graphene-modified Cu_2O nanocomposite provided an appropriate selective response for glucose detection in the presence of high concentrations of ascorbic acid and dopamine.*

KEYWORDS: *Electrochemical biosensor; Non-enzymatic sensors; Graphene; Cu_2O; Glucose.*

INTRODUCTION

Glucose sensors have attracted extensive attention due to increasing demands for fast and reliable detection of glucose in many industries like food industries and clinical diagnostics [1, 2]. Although various techniques such as electrochemical [3], coulometric [4, 5] and optical [6, 7] methods have been developed for glucose monitoring, the amperometric approach has attracted extensive attention due to its advantages such as significant reliability,

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1021-9986/2020/2/1-10 10/$/6.00

appropriate selective response, affordable cost, satisfactory detection limit and also ease of use [8]. The commonly developed amperometric glucose sensors divided into two major classes, including enzymatic and non-enzymatic sensors [9]. The enzymatic glucose sensors are based on glucose oxidase-modified electrode. In these sensors, the glucose oxidase enzyme oxidizes the glucose into gluconic acid via a direct electron transfer in presence of oxygen molecules and would provide a simple blood glucose monitoring with a highly selective response toward glucose detection [10, 11]. However, in presence of enzyme, the environmental conditions such as humidity, temperature, pH and chemical toxicity can easily influence of the electrocatalytic activity of enzymatic biosensors [12]. Also, enzymatic biosensors have several disadvantages such as low stability, need for expensive enzymes and also complicated conditions associated with operating conditions and immobilization of enzyme in a biocompatible matrix [13]. Therefore, development of cost-effective enzyme-free biosensors for fast and reliable detection on glucose is still highly desired. Although several electrode materials including metal alloys [14], noble metal nanoparticles [15] and Carbon NanoTube (CNT) modified nanocomposites [16, 17] have been characterized for development of enzyme-free glucose biosensors, these sensors still suffer from some drawbacks such as low sensitivity, weak selectivity, high cost and chemical poisoning which greatly limited their applications [12].

Many studies have been conducted [18] to prepare enzyme-free glucose biosensors by using nonprecious transition-metal compounds such as ZnO [19, 20], CuO [21, 22], Cu_2O [23, 24], NiO [25, 26] and Fe_3O_4 [27]. Among these, cuprous oxide (Cu_2O) nanomaterials have been proposed as promising candidate for development of enzyme-free glucose detection due to their characteristics such as high specific surface area, good electrochemical activity, cost-effective preparation and the possibility of high electrocatalytic activity for enzyme-free detection. In addition, Cu_2O has attracted more and more research attentions for its important applications in hydrogen production, solar energy conversion, catalysis, gas sensors and also electrochemical biosensors [28-30]. In this regard, cupreous oxide has been used as L-Tyrosine sensor [31, 32]. Also, Cu_2O/MWCNTs nanocomposite has been fabricated and characterized as an enzyme-free glucose sensor [33]. In addition, thin film of cuprous oxide has been proposed as a novel NO_2 gas sensor [34]. However, the use of cuprous oxide nanomaterials for non-enzymatic glucose sensors is still a new topic and need more investigation. The performance of an electrochemical glucose sensor is mainly characterized by properties such as fast and highly selective detection, low detection limit and also high sensitivity. These features are significantly influenced by physicochemical properties such as structure and chemical composition of the electrode materials, conductivity, size and also distribution of electroactive sites over the electrode surface. The sensing performance could be substantially enhanced through addition of suitable additive materials. In the last decade, various allotropes of carbon nanomaterials have been developed and utilized for enhancement of electrocatalytic performance of active materials for applications such as fuel cells and electrochemical biosensors [35-42]. Graphene, which is an allotrope of carbon, has recently attracted extensive attentions as a promising electrode material due to its extraordinary properties such as unique two dimensional structures, large surface area, superior electrical conductivity, high mechanical strength and also appropriate stability [17, 41, 43, 44]. Graphene-based materials exhibited a promising potential for gas sensor and biosensor applications [22, 45-47]. Also, studies have exhibited that the use of graphene as co-catalyst in the electrode structure would result in high sensitivity and low detection limit because of its unique properties. In this regard, *Foroughi et al.* [22] have shown that graphene-modified CuO nanocomposite have much better electrochemical performance toward glucose oxidation as compared to CuO nanoparticles. *Zhang et al.* [48] have synthesized Cu_2O/graphene nanocomposite under hydrothermal condition. They have reported that the prepared nanocomposite exhibited a good electrocatalytic performance for determination of dopamine. Also, *Yu-Wei Hsu et al.* [2] have prepared a CuO/graphene nanocomposite under hydrothermal condition and reported that the prepared nanocomposite exhibited a promising performance for use in non-enzymatic detection of glucose. In addition, *Kim et al.* [49] have reported that incorporation of graphene in electrode material can enhance selective measurement of dopamine in the presence of ascorbic acid [49].

In addition to reasonable selection of electrode materials, it is of prime importance to apply a satisfactory preparation technique. The use of microwave heating for materials synthesis can provide several advantages in comparison with conventional heating methods [50-54]. It is a quick, simple, homogeneous, cost-effective and efficient method. Since microwave irradiation generates uniform heat through synthesis reactor, it can lead to a homogeneous nucleation and short crystallization time and thereby results in formation of nanoparticles with relatively uniform particle size distribution [50, 52]. To the best of our knowledge there has been no report on the performance of a graphene-modified Cu_2O nanocomposite as an amperometric glucose sensor. In this study, we aim to prepare a graphene-modified Cu_2O nanocomposite and investigate the effect of graphene particles on the performance of the prepared nanocomposite for the enzyme-free glucose sensor.

EXPERIMENTAL SECTION

Materials

Cupric Acetate ($Cu(OAC)_2.H_2O$), Ethylene Glycol (EG) and polyvinylpyrrolidone (PVP) with average molecular weight of MW=58000 were supplied by Acros Chemicals. Cetyltrimethylammonium bromide (CTAB) (99%), sodium hydroxide (NaOH) (95%) and Nafion (5 wt%) were obtained from Merck. D-(+)-glucose, Ascorbic Acid (AA) and dopamine (DA) were purchased from Sigma Aldrich and also commercial available few-layered graphene particles were prepared from Angstron Materials (N002-PDR). The chemicals used in this study were of analytical grade.

Preparation of Graphene-modified Cu_2O Particles

Graphene-modified Cu_2O nanoparticles were prepared by microwave heating of an aqueous solution of Cu precursors in the presence of graphene particles. In a typical experiment, 20 mL of cupric acetate aqueous solution (0.02 M) and 30 mL of PVP aqueous solution (0.13 M) were added into a round-bottomed flask. Then 3.56 mg of graphene particles were mixed with the reaction solution and treated ultrasonically for 30 min. At the next step, 100 mL of EG solution containing 0.08 M NaOH and 0.05 M CTAB were added to the flask solution. The molar ratio of $Cu(OAC)_2.H_2O$:NaOH:PVP were adjust to be 1:2:10. Then, solution was heated in a household microwave oven (Butan, 900 W, 2450 MHZ) with a heating procedure of 120 s on and 30 s pause and the cycle was repeated for 4 times. A dark brown colloid solution was obtained and the flask was cooled down to room temperature. Finally, the graphene-modified Cu_2O nanoparticles were collected by centrifugation at 4000 rpm for 30 min and washed with ethanol for several times. The obtained graphene-modified Cu_2O powders were dried at room temperature. The loading of graphene particles was 10%. Cu_2O nanoparticles were also prepared by the same method.

Materials Characterization

An X-ray diffractometere (Philips X'pert diffractometer) using the Cu k_α as the radiation source was used to identify the crystalline structure of the materials. Also, transmission electron microscopy (TEM) and scanning electron microscopy (model Cambridge-360) were used to investigate the morphology and size of the nanoparticles.

Preparation of Modified Electrodes and Electrochemical Measurements

An Autolab potentiostat/galvanostat (model type 3) was used for electrochemical experiments. The measurements were conducted in a three electrode cell system consisting of an Ag/AgCl (3.5 M KCl) reference electrode and a platinum wire as counter electrode. The working electrode was a thin layer of Nafion-bonded powder ink casted on a glassy carbon electrode (5 mm in diameter). For preparation of the Nafion-bonded powder ink, 5 mg of the prepared graphene-modified Cu_2O powder, 700 µL of ethanol and 60 µL of the 5 wt% Nafion were mixed under ultrasonication to form a homogeneous ink. Then, 30 µL of this ink was dropped on the surface of a well cleaned and polished glassy carbon electrode. Cyclic voltammetry and chronoamperometric measurements were used to characterize the glucose sensing performance of the prepared graphene-modified Cu_2O nanocomposite in 0.1 M NaOH and 0.1 M KOH solutions. All potentials reported in this study are versus Ag/AgCl (3.5 M KCl) reference electrode.

RESULTS AND DISCUSSION

Morphology and Microstructure of the Cu_2O and Graphene-modified Cu_2O Powders

The TEM image of the graphene particles is shown in Fig. 1. As shown, the graphene species exhibited tangled

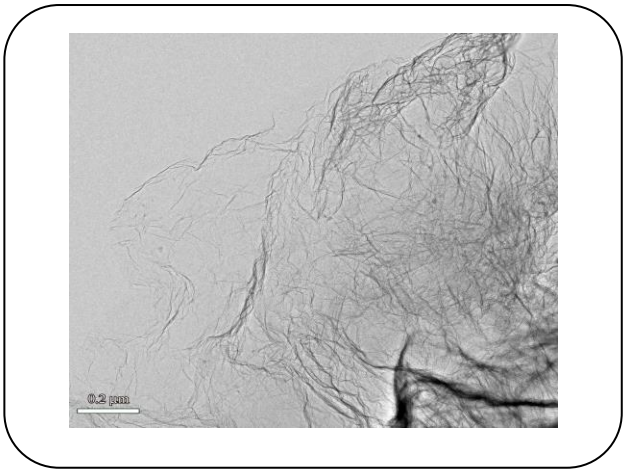

Fig. 1: TEM image of the graphene particles.

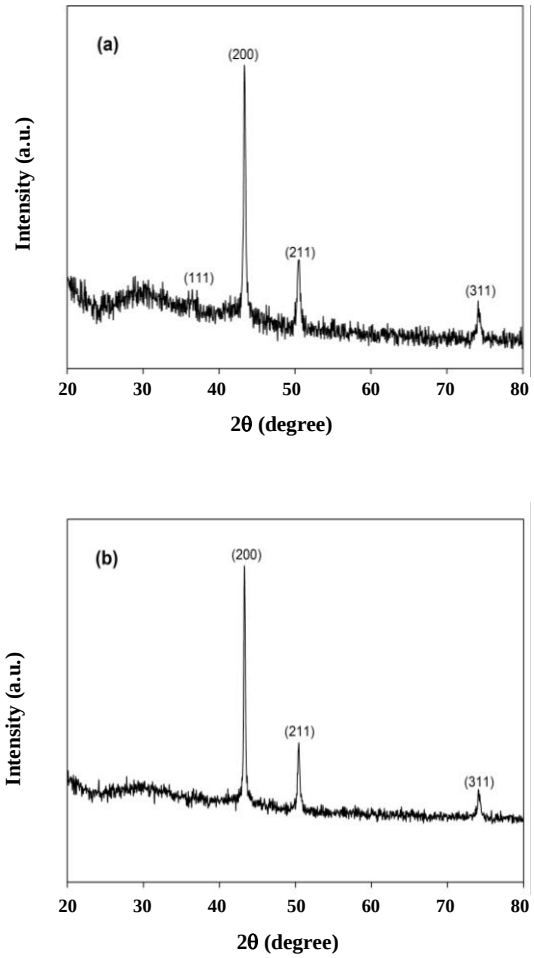

Fig. 2: XRD pattern of (a) Cu_2O nanoparticles and (b) graphene-modified Cu_2O nanocomposite.

thread-like morphology. Typical XRD patterns of the prepared Cu_2O and graphene-modified Cu_2O powders are shown in Fig. 2. As can be seen, three diffraction peaks at angles (2Ɵ) of 43.2953, 51.4363 and 74.0895 correspond to (200), (211) and (311) diffraction peaks of Cu_2O structure, respectively. According to the results of XRD analysis, the diffraction patterns of Cu_2O and graphene-modified Cu_2O nanopowders were corresponded to diffraction pattern of Cu_2O with cubic crystalline structure.

Fig. 3 displays the SEM micrographs of the graphene-modified Cu_2O powders. It can be seen that Cu_2O nanoparticles graphene-modified Cu_2O sample exhibited a spherical morphology with a mean particle size of 150 nm. Also, according to Fig. 3 the graphene particles were dispersed in the graphene-modified Cu_2O composite specimen.

Glucose Sensing Performance of the Cu_2O and Graphene-modified Cu_2O Powders

Cyclic voltammetry and chronoamperometric measurements were conducted to characterize the glucose sensing performance of the prepared Cu_2O and graphene-modified Cu_2O powders. Fig. 4a shows the cyclic voltammograms of the Cu_2O electrodes in absence and presence of various concentrations of glucose. As shown, in the presence of glucose, an oxidation peak was appeared with a maximum at about 0.65 V and onset potential of 0.41 V. It was observed that current of glucose oxidation peak (ip) increased with increasing glucose concentration. Also, as shown in Fig. 4b, the plot of glucose peak maximum current vs. glucose concentration revealed a linear relationship in the concentration range of 0-12 mM with the correlation coefficient of R=0.9863.

The cyclic voltammograms of graphene-modified Cu_2O composite electrodes in the absence and presence of various concentrations of glucose in a 0.1 M NaOH solution are shown in Fig. 5a. As can been seen, upon addition of glucose, the graphene-modified Cu_2O composite electrode exhibited a glucose oxidation peak with a maximum peak potential of 0.6 V and the onset potential of 0.31 V. The negative shift of the glucose oxidation peak potential revealed a better electrocatalytic activity for glucose oxidation as compared to that of pure Cu_2O electrode. The superior electrocatalytic activity

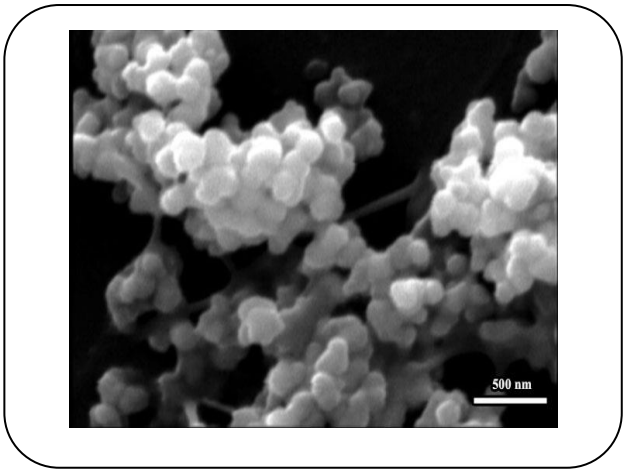

Fig. 3: SEM image of the graphene-modified Cu_2O powder.

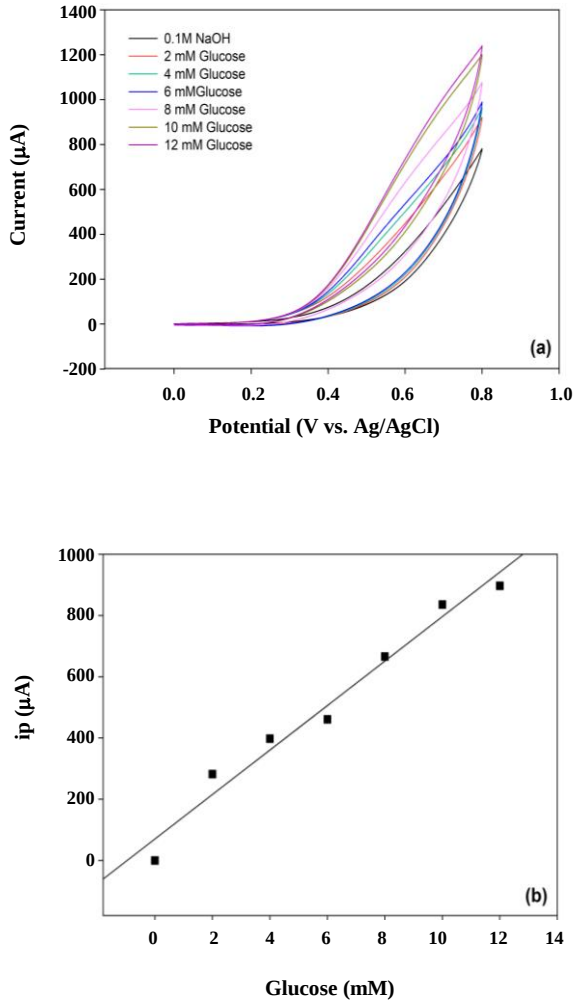

Fig. 4: (a) CV curves and (b) maximum peak current (ip) of the Cu_2O modified electrode at different glucose concentration at the scan rate of 50 mV/s.

of the graphene-modified Cu_2O composite electrode could be attributed to the synergistic interaction between Cu_2O and graphene species in the composite electrode. As shown in Fig. 5b, a linear relationship between the peak maximum current (ip) and glucose concentration was observed in the concentration range of 0 to 12 mM for graphene-modified Cu_2O composite electrode. The corresponding linear regression equation is given by i(µA)=78.321c(mM)+395.5 and the linear correlation coefficient was calculated to be R=0.9980 which was close to unity and verify the validity of linear relationship. Since the normal glucose level in human blood is 4.4 to 6.1 mM, this method covers the range very well for practical clinical applications.

Also, the Cu_2O electrode exhibited a linear relationship in the concentration range of 0 to 12 mM with the linear equation of i(µA)=72.625c(mM)+69.964 and the correlation factor of 0.9863 which revealed the better linearity of the graphene-modified Cu_2O composite electrode. It was observed that Cu_2O and graphene-modified Cu_2O composite electrodes exhibited the detection limits of 5.5 and 2 µM, respectively. Also, the glucose sensing sensitivities of the Cu_2O and graphene-modified Cu_2O electrodes were calculated to be 371 $\mu AmM^{-1}cm^{-2}$ and 400 $\mu AmM^{-1}cm^{-2}$, respectively, which confirmed the superior sensitivity of the graphene-modified Cu_2O electrode. According to cyclic voltammetry measurements it was revealed that the graphene-modified Cu_2O composite electrode exhibited a superior glucose sensing performance. The cyclic voltammograms of the Cu_2O and graphene-modified Cu_2O composite electrodes in a 0.1 M NaOH solution containing 6 mM of glucose were compared in Fig. 6. According to Figs. 4 and 5, the presence of graphene species in graphene-modified Cu_2O composite electrode resulted in a significant increase of the peak maximum current and thereby enhancement of the electrode sensitivity. The superior sensitivity of the composite electrode could be attributed to the better electrocatalytic activity of the graphene-modified Cu_2O particles and also the presence of a large number of electroactive sites over the electrode surface which is due to the unique characteristic features of the graphene species such as high conductivity and large specific surface area. Also, presence of graphene species during the microwave synthesis of the Cu_2O particles leads to a large number of

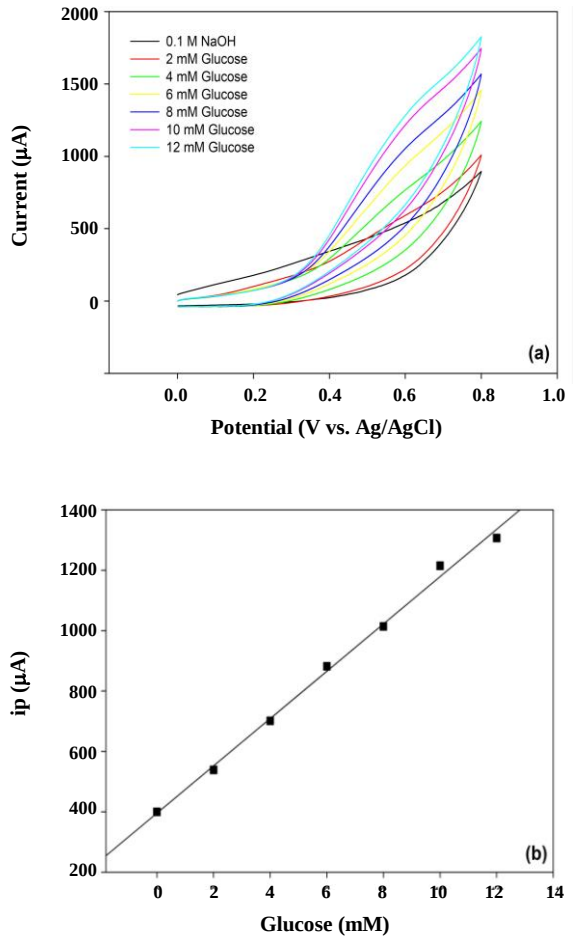

Fig. 5: (a) CV curves and (b) maximum peak current (ip) of the graphene-modified Cu_2O electrode at different glucose concentration at the scan rate of 50 mV/s.

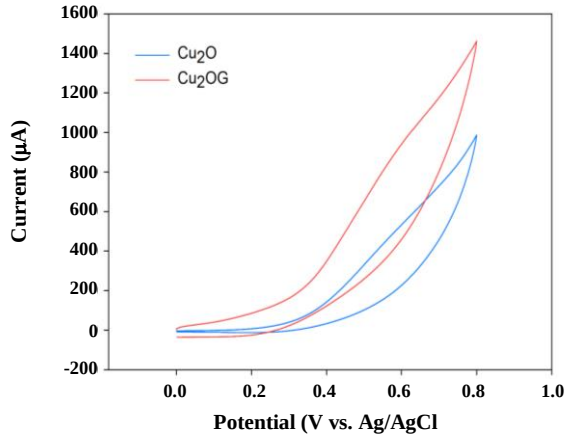

Fig. 6: CV curves of the Cu_2O and graphene-modified Cu_2O composite electrodes in 0.1 M NaOH solution containing 6 mM of glucose at the scan rate of 50 mV/s.

heterogeneous nucleation sites for the preferred nucleation of Cu_2O nanoparticles which in turn causes a better utilization and enhanced electrical contact between electroactive sites and the external electrical circuit.

The glucose sensing performance of the graphene-modified Cu_2O nanocomposite was further investigated by amperometric measurement. Fig. 7 displays the amperometric response of the graphene-modified Cu_2O nanocomposite electrode after subsequent addition of 10 µM glucose in a 0.1 M KOH solution at the fixed potential of 0.6 V. As shown, after successive addition of glucose, the nanocomposite electrode exhibited a step-style increase in current which quickly reaches a steady state current within 5 s. These indicate the linear response and rapid electrocatalytic oxidation of glucose on the surface of graphene-modified Cu_2O nanocomposite.

Since dopamine (DA) and ascorbic acid (AA) are important compounds of human physiological fluids, they coexist with glucose in human serum samples and may cause interference effect for the enzyme-free detection of glucose. The amperometric response of the graphene-modified Cu_2O nanocomposite electrode for the glucose oxidation in the presence of DA and AA species is shown in Fig. 8. It was revealed that the graphene-modified Cu_2O nanocomposite exhibited a satisfactory selectivity for glucose detection and the addition of DA and AA had an inconsiderable effect on the amperometric response of the glucose at the fixed potential of 0.6 V.

CONCLUSIONS

Graphene-modified Cu_2O nanocomposite and Cu_2O nanoparticles were successfully prepared under microwave irradiation. The graphene-modified Cu_2O composite electrode exhibited a higher peak current at the same glucose concentration as compared to that of Cu_2O electrodes. The graphene-modified Cu_2O nanocomposite electrode displayed a high sensitivity (400 µAm/M.cm^2) for detection of glucose concentration with a low detection limit of 2 µM. Also, the fabricated sensor exhibited a good selectivity for glucose in the presence of high concentrations of DA and AA. It could be concluded that the graphene-modified Cu_2O nanocomposite can be proposed as a promising electrode material for the determination of glucose concentration in clinical applications.

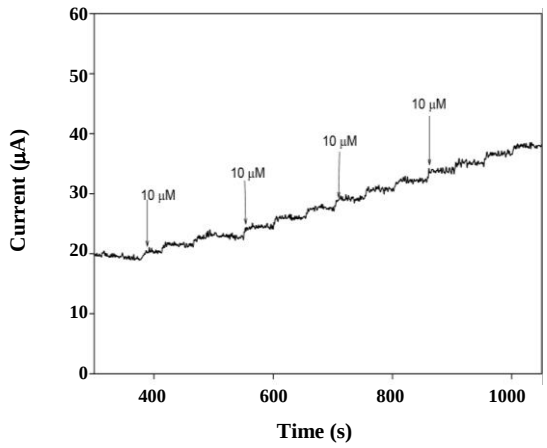

Fig. 7: Amperometric responses of the graphene-modified Cu_2O composite with subsequent addition of glucose concentration in a 0.1 M KOH at 0.6 V.

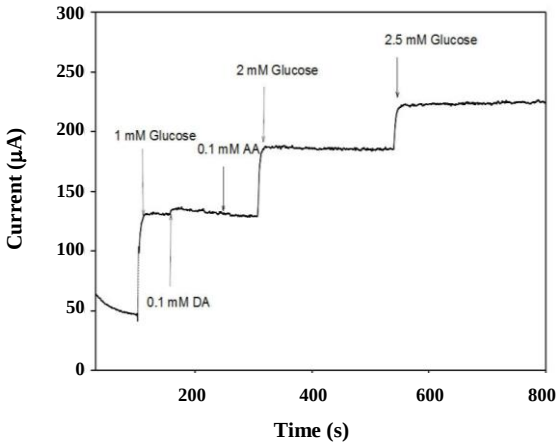

Fig. 8: Amperometric response of the graphene-modified Cu_2O composite with subsequent addition of 1 mM glucose, 0.1 mM DA and 0.1 mM AA in a 0.1 M NaOH at 0.6 V.

Acknowledgments

Authors gratefully appreciate Shiraz University for the financial support of this research work.

Received : Aug. 9, 2018 ; Accepted : Nov. 19, 2018

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