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Application of Glassy Carbon Electrode modified with Chitosan and ZnO nanoparticles as Enzymatic Glucose Biosensor

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In this study, the modified chitosan/ZnO electrode was applied to electrochemical determination of glucose. ZnO nanoparticles (ZnO NPs) was synthesized through the hydrothermal treatment and applied to modification of glassy carbon electrode (GCE). The chitosan was immobilized on ZnO NPs/GCE electrode. TEM and XRD analysis were applied to structural studies of synthesized ZnO NPs. Cyclic voltammetry and amperometry analysis were used to electrochemical sensing properties of Chit/ZnO NPs/GCE. The electrochemical studies exhibited the modified electrode had fast response, selective and stable in determining glucose. The wide linear range and detection limit of sensor were estimated 10 to 90 mM and 0.9 µM, respectively. The sensor response was studied to determine glucose content in grape juice as real sample.

Keywords: Glucose; Electrochemical sensor; ZnO nanoparticles; Chitosan/ZnO/glassy carbon electrode

1. INTRODUCTION

High levels of glucose in the blood can lead to diabetes and metabolic disorders that cause death and disability in humans [1]. The complications of diabetes are many, containing higher risks of blindness, kidney failure, or heart disease which can be reduced by careful control of blood glucose [2]. The management and diagnosis of diabetes mellitus thus it is necessary to have a precise measurement of blood glucose levels. Therefore, it is necessary to study and develop the sensing tools and techniques for determination of glucose. Various techniques, such as near infrared spectroscopy, photoacoustic and optoacoustic, Raman spectroscopy, sonophoresis, thermal emission and electrochemical methods [3-6]. Some of these techniques are sensitive and precise but they are costly and need a professional operator [7]. Electrochemical techniques are fast response and inexpensive to monitor glucose concentration [8, 9]. The electrochemical techniques must be developed through modification of electrodes to promote the biosensor performance. Recently, the nanostructure were applied to optimize the sensors and biosensors because of the high surface chemical and catalytic activates [10, 11]. Among nanostructures, metallic and semiconductors nanostructures such as Ni, Mn, Fe, ZnO lead to excellent sensing properties due to high stability and high electron transfer rate [12].

ZnO based materials are beneficial structures and tools in fabrication of very important systems such as solar cell, ultra-violet laser diodes, ceramic industry, cigarette filters and corrosion prevention in nuclear reactors [13, 14]. In considering the introduction of nanotechnology, synthesis, and properties of ZnO nanostructures are showing the most promising characterization in applications in many fields of industry and researches. For example, fabrication of chemical and biosensors based ZnO nanostructures exhibited excellent properties such as biocompatibility, nontoxicity, high stability in chemical and photochemical properties, high specific surface area, supreme electrochemical activities, high electron transfer mediators [15]. Thus, ZnO nanostructures are considered interesting materials and many types of researches are focusing on the synthesis of different morphologies and nano-scale structures in zero, one and two dimensions. Nano-wires, nano-ribbons, nano-belts, nano-combs, nano-rings, nano-cages, nano-bowls, nano-spheres, nano-fibers, and nano-tetrapods are most common of ZnO nanostructures that many researchers had performed in recent decades [16, 17].

By considering the ZnO properties, many types of researches were focused on improving ZnO physical and electrochemical properties by doping and immobilization with more electrocatalyst materials [18, 19]. This modification can improve the sensitivity of the electrode in electrochemical studies. Chitosan is low cost and the natural polymer product that is applied for immobilization of enzyme in electrode surface to study the electrochemical properties of enzymes. Moreover, Chitosan shows high permeability, biodegradability, nontoxicity, and biocompatibility properties that lead to its usage for the modification the electrode surfaces in biological studies [20, 21]. Morphologies of structures on surface and its biopolymeric network are the important factors for immobilization of enzyme in electrode surface. Hence, modification of surface with nanostructure and chitosan can provide the beneficial surface for biological analytes.

In this study, Chit/ZnO NPs/GCE was applied for the determination of glucose. First, ZnO NPs were synthesized and applied to modify the GCE. Then, the structural properties of synthesized ZnO NPs were studied by TEM and XRD analyses. Finally, electrochemical techniques were applied to determine glucose.

2. MATERIALS AND METHOD

All the needed materials were purchased from Sigma-Aldrich (Chemicals CO., USA). A 0.5 M aqueous NaOH solution was added drop-wise to an aqueous 0.6 M ZnCl2 solution (1:1 (v/v)) in the presence of 150 ppm hexamethylenetetramine at 25°C. White zinc hydroxide precipitates were instantaneously formed. This suspension was retained at room temperature at 10 cycles/min and 75% sonication output power for 20 minutes. The resulting precipitate was separated by decantation and then washed several times with deionized (DI) water. The suspension of obtained precipitates in DI water was hydrothermally treated into a Teflon-coated microwave and irradiated for 10 minutes. The radiation power and frequency were 1.0 kW and3.0 GHz, respectively. The resulting irradiated suspension was again subjected to ultra-sonication at 9 cycles/min and 75% sonication output power for 15 min. The obtained product was separated by decantation, washed by DI water several times and dried at 80°C for 10 hours.

The surface of GCE was cleaned using DI water and polished with 0.1 μm alumina slurry. For preparation of ZnO NPs/GCE, 5 mg of ZnO NPs was dispersed in 10 mL DI water and ultra-sonicated for about 30 min. This suspension (20 μL) was coated on the GCE surface and dried at room temperature.

The chitosan (Sigma Aldrich, Q8 UK) solution was prepared by dissolving 0.5 g of chitosan flakes in 10 ml of 0.05 M acetate buffer solution. For immobilization chitosan, ZnO NPs/ GCE were immersed into transparent chitosan solution for 20 minutes at room temperature. Finally, modified ZnO NPs/GCE was washed with deionized water.

The morphology of synthesized ZnO NPs was analyzed by transmission electron microscopy (LEO system, model 912 AB). Crystal structure of ZnO NPs was investigated with Xpert Pro X-ray diffractometer with 1.5404 Å (Cu Kα) in wavelength and 40KV/30 mA power.

Electrochemical studies were performed in the three-electrode cell which contains Ag/AgCl/(sat KCl) as reference electrode, a Pt wire as the counter electrode and Chit/ZnO NPs/ GCE as the working electrode. Voltammetry on the working electrode was conducted in the buffers without the chitosan molecule. Autolab modular electrochemical system (Eco ChemieUltecht) was used for electrochemical studies. The 0.1 M phosphate buffer solutions were provided from H_3PO_4 and NaH_2PO_4. The pH of the phosphate buffer solution was adjusted by applying HCl and NaOH solution to the phosphate buffer solution.

Fresh grape were purchased from the market, peeled, washed with water and squeezed to obtain juices (SJ3000, Braun, Germany). The prepared grape juice was passed through a filter. The obtained transparent and pure solution of apricot was added into a 0.1 M phosphate buffer solution (1:1, v/v) at pH 7.0.

3. RESULTS AND DISCUSSION

Figure 1a shows TEM micrographs of ZnO NPs synthesized through the hydrothermal treatment. TEM image shows that the ZnO NPs are both in uniform nanocrystalline spherical and hexagonal shapes. The average diameter of nanoparticles are ~ 25 nm.

Figure 1b shows the XRD patterns of synthesized ZnO NPs. The diffraction peaks at 31.79˚, 34.48˚, 36.41˚, 47.59˚ and 56.637˚corresponds to (100), (002), (101), (102) and (110), respectively, which reflects that the hexagonal wurtzite structure of ZnO are in good agreement with standard JCPDF data reference (No. 89-1397). The XRD results indicate ZnO NPs oriented along the c-axis [22, 23].

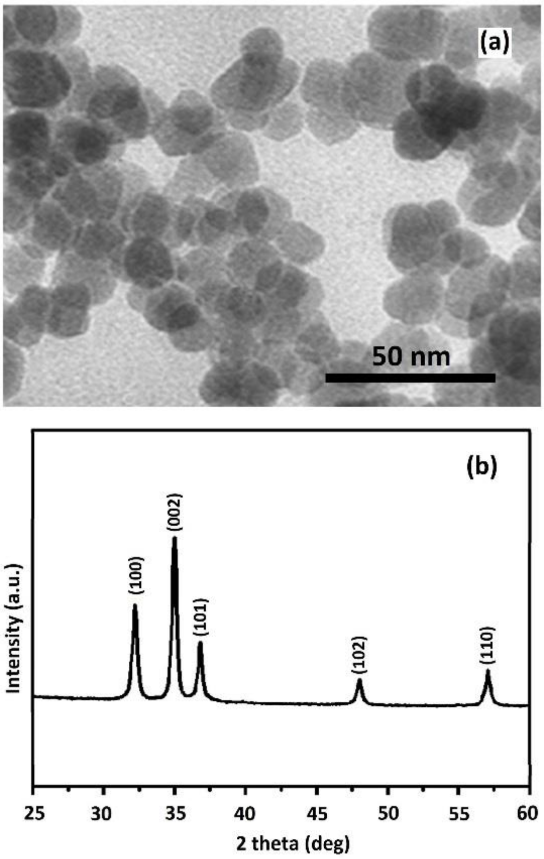

Figure 1. (a) TEM image and (b) XRD pattern of synthesized ZnO NPs

All CV studies of electrodes were carried out in 0.1 M phosphate buffer solution with pH 7.0 at a scan rate of 10 mV s^{-1} in the potential range of -0.50 to 1.0 V. In order to study the adsorption of chitosan on GCE and ZnO NPs/GCE surfaces, the electrodes were immersed in chitosan solution for 20 minutes, then the electrodes were washed by diluted water. The stability of the chitosan on both electrode surfaces were evaluated by continuous recorded CVs. Figure 2a shows no redox peaks for GCE after being immersed in chitosan solution and also the background current had changed. As seen, after 100 successive CVs, the background current was decreased more than 77%. Therefore, chitosan was not adsorbed stably on GCE. Figure 2b shows the well-defined redox peaks for Chit/ZnO NPs/GCE electrode in 0.15 V and 0.30 V because of the reduction and oxidation of chitosan, respectively. As seen, the change in peak current was less than 6% after 100 successive cycles for Chit/ZnO NPs/GCE that refers to the stability of chitosan on ZnO NPs. This stability in an aqueous solution was related to the chemical and mechanical stability of the ZnO NPs and the strong adsorption of chitosan on the nanoparticles because of the high aspect ratio and the high active sites on ZnO nanostructure surface [24]. Electrochemical reversibility and the high electron transfer rate of ZnO NPs demonstrate the potential for these nanoparticles as mediators for electron transferring between analytes and electrode surface in electro-catalysis activities.

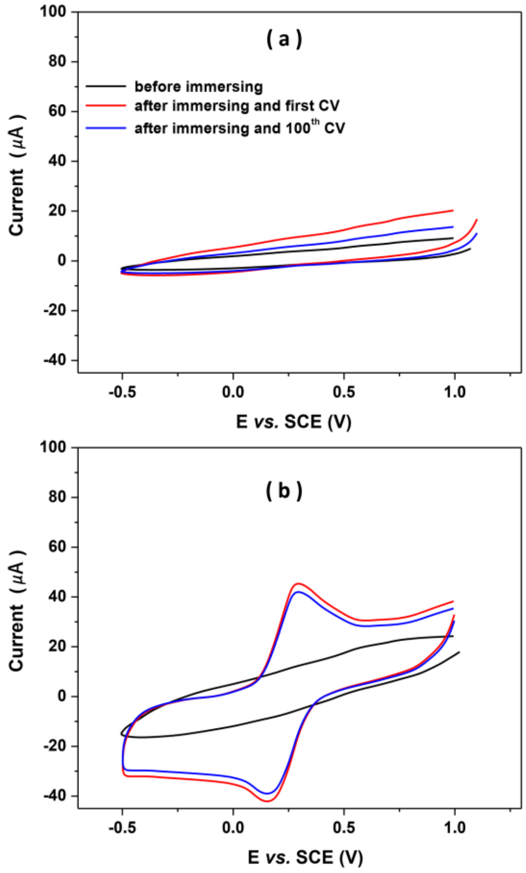

Figure 2. Recorded CVs of (a) GCE and (b) ZnO NPs/GCE before immersing (black), after immersing electrodes chitosan in first (red) and 100th (blue) cycles in 0.1 M phosphate buffer solution pH 7.0 and the scan rate of 10 mV s^{-1}.

Figure 4 displays the CVs of GCE, ZnO NPs/GCE and Chit/ZnO NPs/GCE. It is observed that no oxidation or reduction peaks were recorded for the GCE and ZnO NPs/GCE in the absence and the presence of glucose in the electrolyte solution. Addition of glucose solution to the electrochemical cell led to an increase in the background current for both of GCE and ZnO NPs/GCE. Figure 4(c) shows the well-defined redox peaks for Chit/ZnO NPs/GCE electrode related to the oxidation and reduction of chitosan in the absence of glucose in the electrolyte, respectively [25]. When 10 mM of glucose solution was added into the electrolyte, recorded CVs showed a sharp oxidation peak at 0.30 V for Chit/ZnO NPs/GCE. Figure 4(c) demonstrates addition of glucose lead to an increase in the oxidation peak of Chit/ZnO NPs/GCE. It can be considered that the chitosan had catalyzed the oxidation of glucose. High current of oxidation peak refers to the higher sensitivity response in determining glucose.

The stability response of all electrodes were studied for oxidation behavior of glucose. Therefore, the successive CVs of all electrodes were recorded after the injection of 10 mM of glucose in 0.1 M phosphate buffer solution. Figure 3 shows the first and 100th recorded CVs. As seen, the background currents changes for GCE and ZnO NPs/GCE are more than 35% and 60%, respectively. Moreover, the oxidation current of Chit/ZnO NPs/GCE change is less than 9%. In addition, Chit/ZnO NPs/GCE exhibits a more stable and sensitive response to the electrochemical determination of glucose. Therefore, Chit/ZnO NPs/GCE is selected for more electrochemical study in this work.

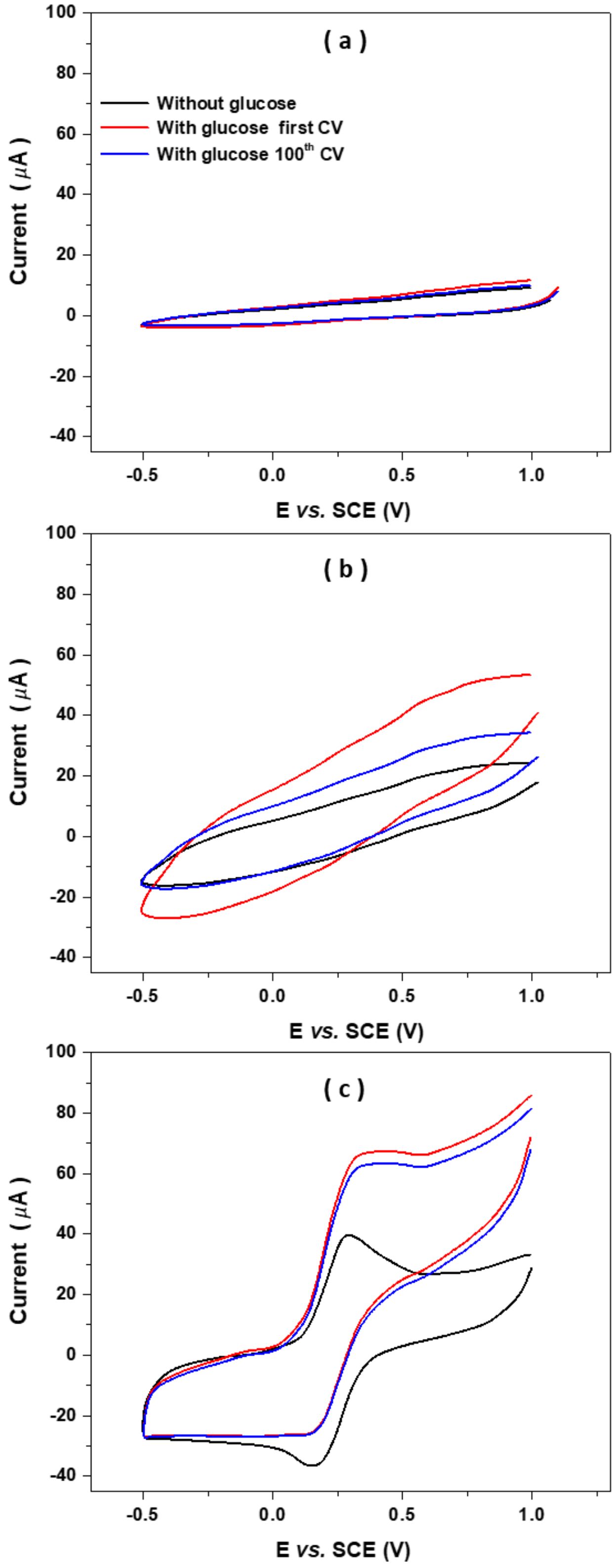

Figure 3. Recorded CVs of (a) GCE, (b) ZnO NPs/GCE and (c) Chit/ZnO NPs/GCE in absent (black), first present (red) and 100th present (blue) of 10 mM glucose solution.

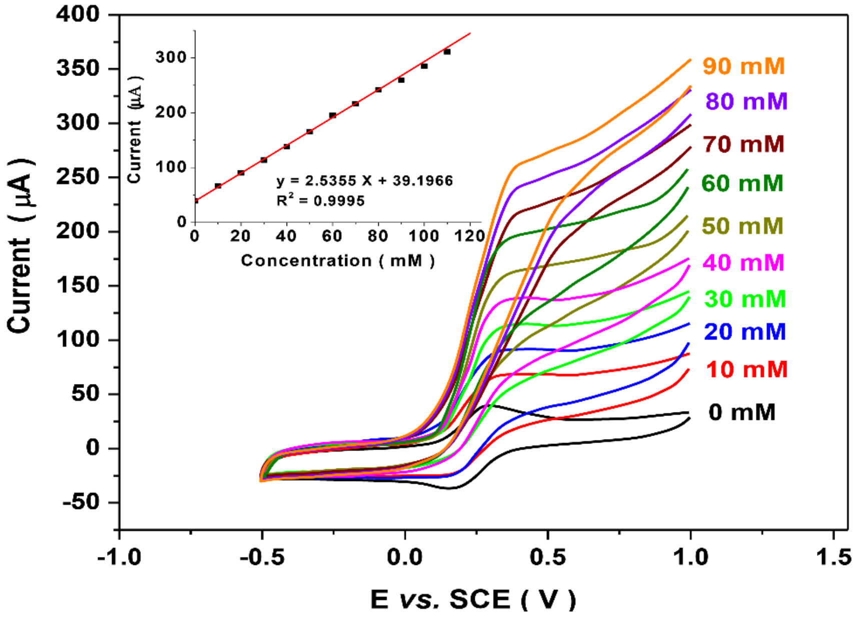

Figure 4. The recorded CVs of Chit/ZnO NPs/GCE in 0.1 M phosphate buffer solution in successive additions of 10 mM glucose solution; inset is plot of calibration graphs.

There is a clear positive synergistic effect when chitosan and ZnO NPs are combined as modifiers in the same electroanalytical platform. The electro-catalytic properties, sensitivity and magnitude can be dramatically enhanced when the ZnO NPs are decorated with other materials [26, 27]. These characteristics justify the different cyclic voltammograms shown in figure 3. As can be seen, ZnO NPs/GCE presents a larger currents in comparison to unmodified GCE, probably due to the expansion of the surface area provided by the functionalized nanostructures [28]. Such effect is also observed for Chit/ZnO NPs/GCE, but in the latter case the performance is even higher, confirming the advantages obtained when the modifiers are used in association. Furthermore, these data also shows that the deposited chitosan on ZnO NPs/GCE films can potentiates the advantages observed for the isolated ZnO NPs.

In order to study the glucose concentration effect, CV responses of Chit/ZnO NPs/GCE were recorded. Figure 4 shows the CV responses in successive injections of 10 mM glucose solution. The calibration graphs in Figure 4 exhibits the equation current (μA) = 2.5255 [concentration of glucose (mM)] (μA/ mM) + 39.1966 (μA) with a correlation coefficient of 0.9995. It can be evaluated that the broad linear range and sensitivity values are 10 to 90 mM and 2.5255 μA/ mM, respectively.

Amperometry technique is applied to study the detection limit, sensitivity, and selectivity of electrochemical sensor in 0.1 M phosphate buffer solution pH 7.0 at 0.7 V. Figure 5 shows the amperometric response of Chit/ZnO NPs/GCE in successive injections of 10 μM glucose solution. The inset of Figure 5 shows the calibration graphs as equation current (μA) = 0.04153 [concentration of glucose (μM)] (μA/ μM) + 0.01468 (μA) with a correlation coefficient of 0.99994. Therefore, the sensitivity and detection limit values are estimated 0.04153 μA/ μM and 0.9 μM, respectively by amperometric technique. In addition, the electrochemical sensor is a very fast response. Chit/ZnO NPs/GCE electrode showed a well-defined step response. Increasing the chitosan loading in the multilayered assembly did not present any improvement in property and the linear range narrowed. The excellent electrochemical behavior for Chit/ZnO NPs/GCE can be explained by the chitosan dispersion and surface properties. The porous structure derived from the Chit/ZnO NPs facilitated the dispersion of NPs into the matrix, which increased the specific area of these materials and improved catalytic efficiency [29, 30]. Also, due to the high electronic conductivity of the ZnO NPs, charge was able to be transmitted along the chains towards the dispersed metals where the electrocatalytic reaction occurred [31].

A comparison in the performance of glucose electrochemical sensors is shown in Table 1. The results illustrate the calculated detection limit of Chit/ZnO NPs/GCE is better than other sensors. It can be considered that the Chit/ZnO NPs/GCE can be applied for a study in low concentration of glucose for example in fruit juices. A wide linear range is seen for this work. It can be concluded that the ZnO nanoparticles have high porosity and more sensitive site on electrode surface [32]. Therefore, the saturation of site had happened in a high concentration (> 90000 μM) in comparison with the other glucose sensors.

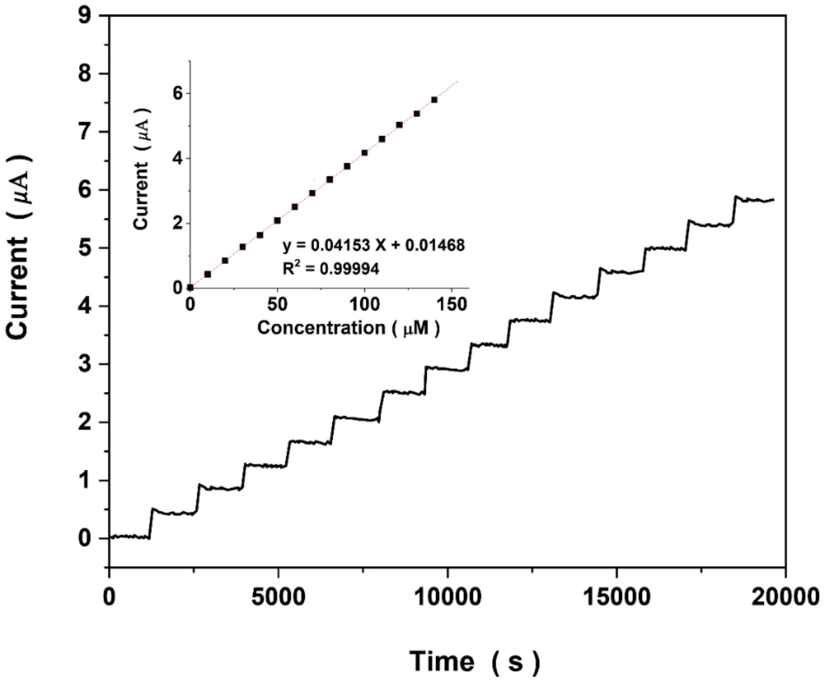

Figure 5. The amperometric response of Chit/ZnO NPs/GCE in 0.1 M phosphate buffer solution in successive additions of 10 μM glucose solution; inset is the plots of calibration graphs.

Table 1. Comparison of Chit/ZnO NPs/GCE sensor performance with other glucose sensors.

Electrodes	Technique	detection limit (μM)	Linear range (μM)	Sensitivity (μA/μM)	Ref.
Poly(diallyldimethylammonium chloride)–cellulose nanocrystal/Au nanohybrids	Amperometry	2.4	4–6500	0.0628	[33]

Platinum Nanoflowers Decorated Multiwalled Carbon Nanotubes-Graphene Hybrid	Amperometry	387	1000-7000	0.0111	[34]
Lamellar ridge–Au	Amperometry	0.87	2–23000	0.029	[35]
porous $NiMn_2O_4$ nanosheet arrays on nickel foam	Amperometry	0.24	115–661	12.2	[36]
polynorepinephrine /glucose oxidase/Au NPs	Amperometry	1.76	3-8044	59170	[37]
Glucose Oxidase Encapsulated Chitosan Modified Glassy Carbon Electrode	Amperometry	100	600-2800	233	[38]
Chit/ZnO NPs/GCE	Amperometry	0.9	10000 – 90000	0.04153	This work

In order to study the selectivity and interference response of Chit/ZnO NPs/GCE as glucose sensor, the amperometric study was performed in the presence of different analytes. Figure 6 displays the amperometric response of Chit/ZnO NPs/GCE in 0.1 M phosphate buffer solution pH 7.0. As shown, two successive additions of 0.2 mM glucose solution followed by successive additions of 2 mM of uric acid, ascorbic acid, tyrosine, galactose, glycine, fructose, chlorpromazine and gemfibrozil analytes, and then two successive additions of 0.2 mM glucose solution. The results illustrate that the modified electrode showed a clear response to all additions of glucose solution. The modified electrode did not show any significant response for the additions of other analytes. In addition, the modified Chit/ZnO NPs/GCE showed a selective response to glucose in the presence of the above analytes and the above analytes did not interfere with the determination of glucose on Chit/ZnO NPs/GCE surface.

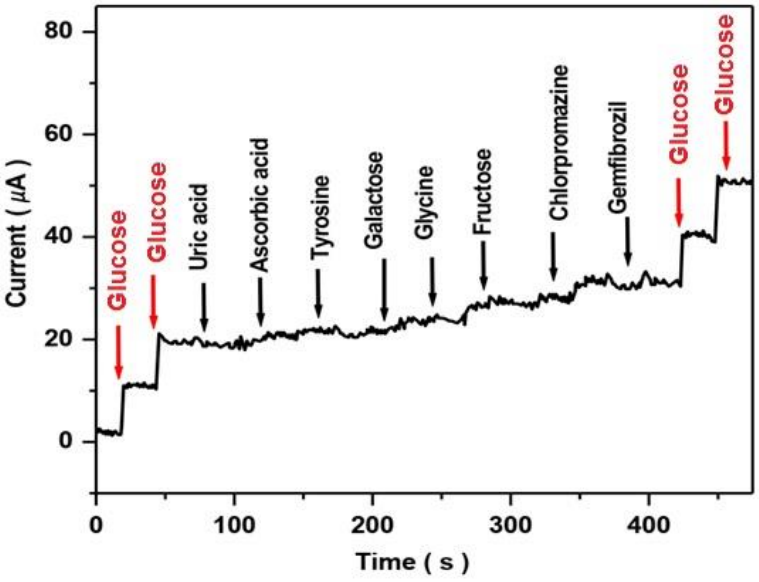

Figure 6. The amperometric response of Chit/ZnO NPs/GCE electrode in 0.1 M phosphate buffer solution for 0.2 mM addition of glucose and 2 mM addition of uric acid, ascorbic acid, tyrosine, galactose, glycine, fructose, chlorpromazine and gemfibrozil solutions.

In order to study the Chit/ZnO NPs/GCE for the determination of glucose in real samples, the concentration of glucose in the grape juice was measured. The standard injection of glucose was applied to determine the glucose in the sample. Figure 7 shows the amperometric response of Chit/ZnO NPs/GCE prepared sample of grape juice in successive injections of 0.01 mM glucose solution. The inset of Figure 7 shows the calibration curve as the current (µA) = 27.03 [concentration of glucose (mM)] (µA/ mM) + 8.917 (µA) with a correlation coefficient of 0.99674. Therefore, the concentration of glucose was estimated 0.329±0.005 mM in 0.1 M phosphate buffer solution and 0.167 ±0.005 mM in pure grape juice which was very close to the results of Krzyczmonik et al.[39]. The results show that Chit/ZnO NPs/GCE can be considered as biosensor for glucose measurement in food samples.

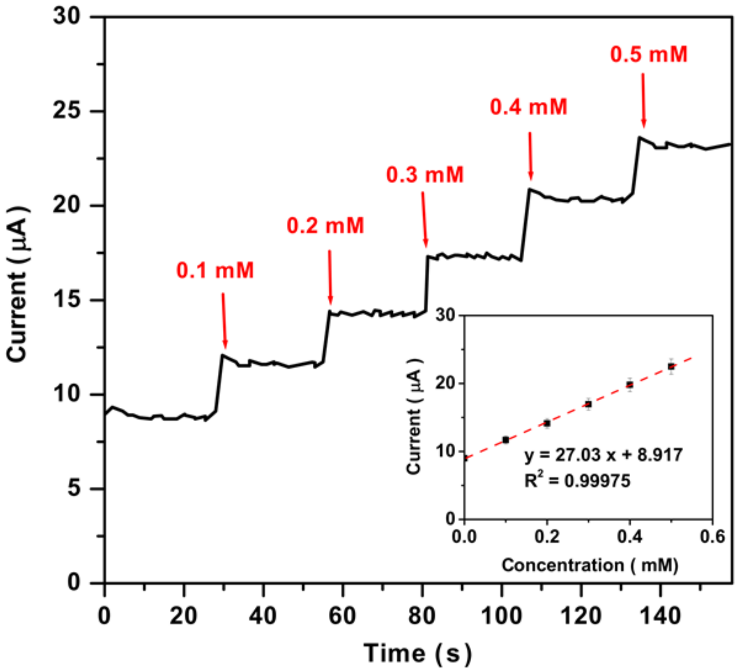

Figure 7. The amperometric response of Chit/ZnO NPs/GCE in 0.1 M phosphate buffer solution in addition of different concentrations of glucose in a real sample; inset is plot of calibration curve.

4. CONCLUSIONS

The Electrochemical characterization of chitosan/ZnO/GCE electrode for enzymatic glucose biosensor was performed by CV and amperometry techniques. The ZnO NPs were synthesized through the hydrothermal method and used for modification of GCE. The structural properties of synthesized ZnO NPs were studied by TEM and XRD analyses. The results of the structural studies showed that high aspect ratio of ZnO NPs were synthesized in hexagonal wurtzite structure. Chitosan was immobilized on ZnO NPs/GCE surface. The electrochemical studies of Chit/ZnO NPs/GCE showed an oxidation sharp and stable peak in at 0.30 V for glucose. Amperometry studied showed Chit/ZnO NPs/GCE was fast response, sensitive, selective and stable in determination of glucose. The wide linear range, sensitivity, and detection limit of sensor were estimated 10 to 90 mM, 0.04153 µA/ µM and 0.9 µM, respectively. The results showed the modified electrode was successfully applied to glucose detection in grape juice as a real sample. Furthermore, investigation of the interfere effect showed that the uric acid, ascorbic acid, tyrosine, galactose, glycine, fructose, chlorpromazine and gemfibrozil analytes did not interfere with determination of glucose on Chit/ZnO NPs/GCE electrode.

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