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Preparing cuprous oxide nanomaterials by electrochemical method for non-enzymatic glucose biosensor

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Abstract

Cuprous oxide (Cu_2O) nanostructure has been synthesized using an electrochemical method with a two-electrode system. Cu foils were used as electrodes and $NH_2(OH)$ was utilized as the reducing agent. The effects of pH and applied voltages on the morphology of the product were investigated. The morphology and optical properties of Cu_2O particles were characterized using scanning electron microscopy, x-ray diffraction, and diffuse reflectance spectra. The synthesized Cu_2O nanostructures that formed in the vicinity of the anode at 2 V and pH = 11 showed high uniform distribution, small size, and good electrochemical sensing. These Cu_2O nanoparticles were coated on an Indium tin oxide substrate and applied to detect non-enzyme glucose as excellent biosensors. The non-enzyme glucose biosensors exhibited good performance with high response, good selectivity, wide linear detection range, and a low detection limit at 0.4 μM. Synthesized Cu_2O nanostructures are potential materials for a non-enzyme glucose biosensor.

Supplementary material for this article is available online

Keywords: nanostructure, electrochemical, non-enzyme, glucose, Cu_2O

(Some figures may appear in colour only in the online journal)

1. Introduction

Diabetes resulting from high glucose concentration has become a leading cause of death around the world [1]. No treatments are available to prevent or cure diabetes. Therefore, monitoring blood sugar and detecting glucose concentration is important to assuage latent diseases, diminish risk in diagnostic, and enhance treatment efficiency. The development and improvement of fast and reliable methods for accurately and selectively monitoring the concentration of glucose is necessary.

Many strategies for glucose sensing are currently being pursued. These methods include fluorescence, electrochemistry, surface plasmon resonance, capillary zone electrophoresis, and molecular imprinted polymer techniques [2–7]. Among the various detection methods, the electrochemical method is a promising and powerful tool due to its intrinsic simplicity and high sensitivity. Electrochemical methods are analytical techniques that use a measurement of current to determine an analyte's concentration and characterize the analyte's chemical reactivity. Because electrochemical methods are both quantitative and qualitative and have the potential for high accuracy and sensitivity, it has recently received considerable attention from scientists.

Previous publications used noble metals and alloys such as Au, Pt, Pd, Pt–Pd, Pt–Au, and Au–Pd because of their

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strong conductivity and large specific surface. While these metals could be useful for sensing, their high cost is a significant deterring factor [3, 8–11].

The abundance of copper and copper oxides (Cu_2O and CuO) has attracted much interest because of their potential applications to environment, sensors, and energy. In addition, Cu_2O is one of the strongest candidates of electrochemical sensing and may overshadow the use of expensive noble metals in practical applications [12–14]. With of its small band gap of 2.17 eV, Cu_2O has already shown its potential for practical applications from the development of Cu_2O solar cells, photocatalysts, and photoactivated splitting of water and gas sensing [15–19]. Previous work has studied the fabrication of Cu_2O nanoparticles in non-enzyme glucose sensing [3, 20–22]. However, these studies showed that the process is time-consuming, complicated, and inefficient in sensing glucose.

Electrochemical synthesis offers the most attractive approach to preparing micro and nano structural materials at low temperatures [23–25]. In this study, we focused on preparing high quality cuprous oxide (Cu_2O) through a simple electrode method for electrochemical non-enzymatic Glucose sensor. We found that varying pH and applied potential changed both the morphology of the Cu_2O nanoparticles and the amount of CuO that attaches to Cu_2O. This, in turn, varies the band gap of Cu_2O. Lastly, the biosensing capability of Cu_2O towards glucoses was investigated. The proposed glucose sensor has outstanding electrocatalysis, stable, and high repeatability with a low limit of detection (~0.4 μM).

2. Experimental section

2.1. Reagent and chemicals

Hydroxylamine ($NH_2OH . HCL$, Sigma-Aldrich, 99%) and copper foil (0.05 mm, 99.8%) were purchased from Sigma Aldrich. Sodium Hydroxide (NaOH, 98%), and Sodium Nitrate ($NaNO_3$, 98%) were purchased from Alfa Asera. All chemicals were used as received without further purification. Deionized water was used for all solution preparation.

2.2. Characterization

The morphological, optical, and structural properties of fabricated structures were investigated by field emission scanning electron microscopy (SEM, MIRA-II LMH, Tescan, US), transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan), x-ray diffraction (XRD, Panalytical, Netherlands), UV–vis-NIR spectroscopy (Jasco V670, Japan), Fourier transform infrared spectroscopy (FT-IR 6300, Jasco, Japan). Cyclic voltammetry (CV) was performed by a galvanostat (VSP Instruments, EC Lab Version 9.41, Bio-logic science Instruments).

2.3. Cu_2O particles synthesis

A facile procedure for the preparation of Cu_2O particles was set up in the following steps: firstly, the electrolyte solution was made up of $NaNO_3$ (0.1 M) and NH_2OH (0.1 M). Next, NaOH powder was used to adjust the pH of the electrolyte solution. Then, two polished copper foils (50 mm × 5 mm × 5 mm) were used as the anode and the cathode. These electrodes were placed 2 cm apart and immersed in the electrolyte solution. The resulting electrochemical reaction was performed at different applied potentials. When the potential was applied across the electrodes, yellow dispersed Cu_2O particles appeared immediately in the vicinity of the anode and then precipitated from the solution. The dispersed product was collected over a period of 0.5, 1, 3, 5 and 7 min. This product was washed with deionized water and ethanol and then dried at 60 °C for 12 h in a vacuum oven.

2.4. Preparation of Cu_2O /Nafion/ITO

ITO was polished and rinsed thoroughly in distilled water and ethanol several times. The Cu_2O (10 mg) was dispersed in a mixture of 0.1 ml Nafion and 0.9 ml ethanol, followed by homogenizing with a ultrasonic homogenizer for 10 min. The Cu_2O suspension (50 μl) was then dropped on the surface of electrode, and the electrode was dried in air at room temperature.

2.5. Electrochemical procedures

For the electrochemical detection of Glucose, the measurements were performed on the three-electrode chemical analyzer model controlled by a computer, Cu_2O containing ITO as a working electrode, Ag/AgCl (Sat. NaCl) as a reference electrode, and Platinum wire as a counter electrode. While the reference electrode allowed measuring the applied potential of the working electrode without passing current through it, the counter electrode allowed passing current. The CV and current response using chronoamperometry (CA) measurements were conducted in 0.1 M NaOH electrolyte solution. The experiments were carried out with a constant applied scanning potential in the range of (-1.0)–$(+1.0)$ (V) at a scan rate of 20 mV s^{-1}. Once the current obtained a baseline in the absence of glucose, glucose was added every 30 s thereafter. All measurements were carried out at room temperature.

3. Results and discussions

3.1. Material synthesis and characterization

In this work, the resultant Cu_2O particles were prepared via the two-step reaction mechanism involving the anodic dissolution of Cu to generate Cu^{2+}, followed by the reduction of Cu^{2+} in an alkaline solution of NH_2OH and $NaNO_3$ to produce Cu_2O. The reaction scheme is as follows [26, 27]:

$$Cu - 2e^- \rightarrow Cu^{2+} \quad (1)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad (2)$$

$$2Cu(OH)_2 \xrightarrow{NH_2OH\ .\ HCl} Cu_2O + H_2O + 2OH^-. \quad (3)$$

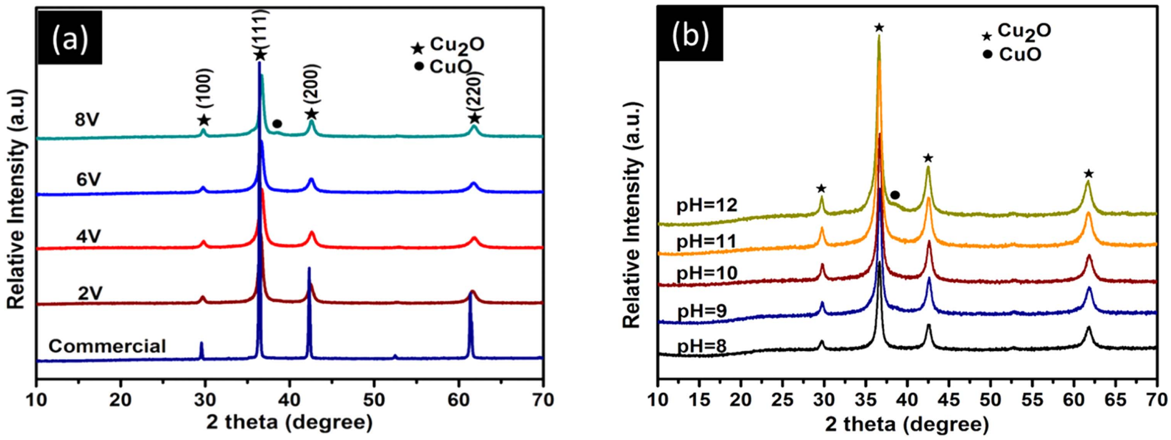

Figure 1. XRD patterns of the fabricated materials obtained for 5 min (a) at pH = 11. In the applied potential range 2–8 V and (b) pH range = 8–12 at applied potential of 2 V.

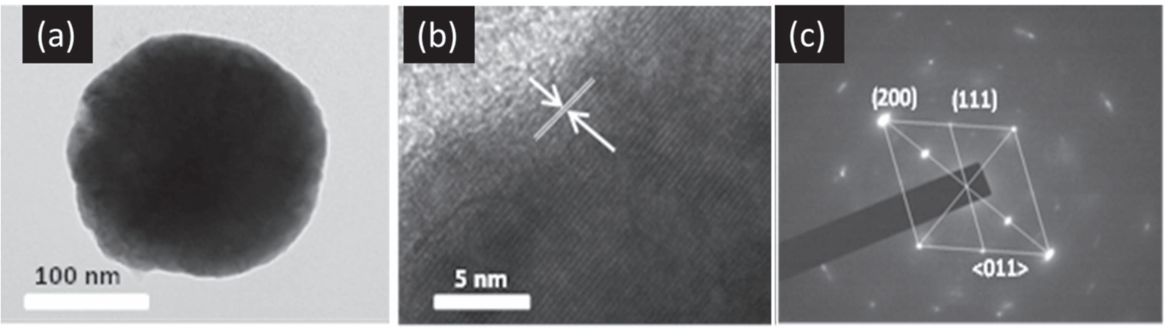

Figure 2. TEM images (a), with high-magnification (b), and SAED patterns (c) of cubic Cu_2O.

In our procedure, we used two parameters, pH values and applied potentials, to control the formation of Cu_2O microstructures through electrochemical method. To measure the effects of the applied potentials, the XRD patterns of the synthesized Cu_2O samples were obtained and matched up with the International Center of Diffraction Data card (JCPDF No. 05-0667) (figure 1(a)). The diffraction peaks of the samples were indexed to the cubic phase of Cu_2O, which are located at the 2θ values of 29.5, 36.4. 42.3, and 61.3° corresponding to the (110), (111), (200), and (220) lattice planes of the crystalline Cu_2O, respectively. At low applied potentials, no other characteristic diffraction peaks from any other impurities, including Cu and CuO, were detected in these prepared samples (figure 1(a)). However, a weak peak at ~37° appeared (remarked as black circles in figure 1(a)) when the highest potential (8 V) was applied across the electrodes. This is presumably due to a small amount of CuO that formed. These results suggest that Cu_2O was the dominant substance in the samples at the applied low potentials (<8 V).

The XRD results indicated that the applied potentials play an important role in the formation of copper oxide. The relatively broader diffraction peaks suggest that the fabricated material possessed small crystallite size. XRD measurements were also conducted to verify the effect of pH values on the formation of the Cu_2O crystal (with applied voltage = 2 V) (figure 1(b)). The results confirm that Cu_2O nanostructures with cubic phase were successfully prepared in the pH range of 8–11. However, at higher pH values, a minor amount of CuO formed (figure 1(b)).

The morphology of obtained Cu_2O samples was examined by SEM (figure S1—supplementary materials is available online at stacks.iop.org/NANO/29/205501/mmedia). The SEM images demonstrated that Cu_2O particles possess a porous spherical form. The magnified SEM images also exhibit a large number of nanopores that appear on the surface after the evolution from $Cu(OH)_2$ to Cu_2O in the presence of NH_2OH. Each of the Cu_2O nanoparticles with porosities on its surface was caused by shrinking during the growth process. Therefore, in addition to the presence of NH_2OH, the applied potential also played a crucial role in the formation of the porous structure.

To further determine the structure's material, TEM analyses were conducted. Figure 2 exhibits TEM images of the as-synthesized Cu_2O (for 5 min reaction time). The interplanar distance measured at 2.42 Å could be indexed to the {111} plane for a cubic Cu_2O lattice (figure 2(b)). The selected area of electron diffraction pattern shows the characteristic polycrystalline rings consisting of a number of diffraction spots which arise from the Bragg reflection of an individual crystalline (figure 2(c)). These results confirmed that the cubic Cu_2O containing the {111} crystal facet exhibits a lattice structure.

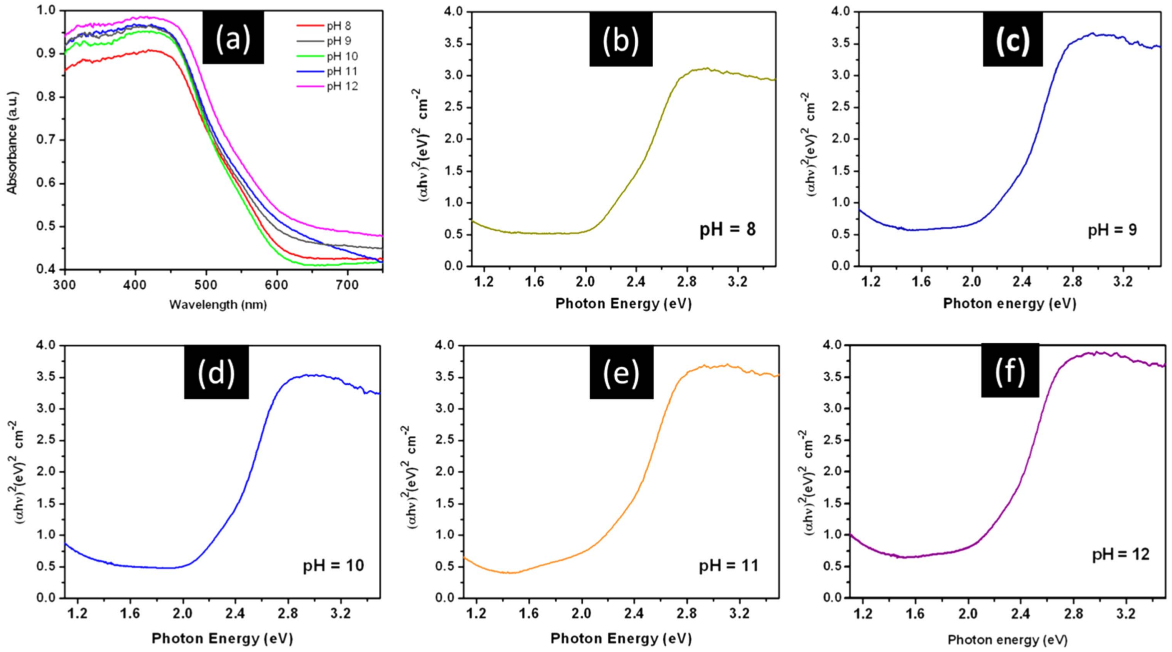

Figure 3. (a) Effect of pH value on the absorption spectra of the samples; plot defining Tauc's region of the materials prepared at different pH values: (b) 8, (c) 9, (d) 10, (e) 11, and (f) 12.

3.2. Band gap study

Previous studies showed the significant effect of NH_2OH . HCl as the reductant. In this study, various pH values were applied as a synthesized parameter. It was suggested that the reductant possessed an important role in maintaining the morphology of Cu_2O. The UV–vis absorbance properties of the Cu_2O samples were also studied using UV–vis NIR, (figure 3(a)). The absorbance of the samples was strong in the UV region and declined gradually in range of 460–600 nm. To characterize the optical band gap, Tauc's equation was used [27]

$$ah\nu = C_1(h\nu - E_g)^n,$$

where C_1 is a proportionality constant, $h\nu$ is the photo energy, E_g is the allowed energy gap, $n = 1/2$ got allowed direct transition, $n = 2$ for allowed indirect transition, and a is the linear absorption coefficient of the material. The values of the band gaps can be obtained from the tangent line of the Tauc plot by using the Kubelka-Munk equation $[F(R_0)h\nu]^2$ (or $(ah\nu)^2$) [28]:

$$[F(Ro)hv]^2 = C_2(hv - E_g). \tag{4}$$

Figures 3(b)–(f) displayed the relationship between $(ahv)^2$ and photon energy of the samples, which were synthesized at the different pH values of 8, 9, 10, 11, and 12. The band gaps of these samples were calculated to be 2.10, 2.08, 2.12, 2.07 and 2.05, respectively. These values are lower than that of the bulk Cu_2O (2.14–2.60 eV) [29, 30]. It is well known that the band gap correlates well with the amount of oxidized Cu^{2+} in the sample because CuO has a band gap of about 1.4 eV [31]. The obtained values decreased significantly with a corresponding increasing amount of CuO. This explains why they absorb more visible light [32].

3.3. Mechanism of the evolution of Cu_2O

To understand the growth mechanism of this novel architecture, the samples were analyzed by SEM at different growth states (figure S2). It can be seen that the sample at various stages of the growth process changed dramatically. The hollow hexagonal structures were observed to grow after 1 min (figure S2(a)), and the surface and morphology of Cu_2O were gradually rounded and also made smoother and less hollow after 3 min of reaction time (figure S2(b)). The formation of Cu_2O crystals was completed with a homogenous spherical shape after 5 min (figure S2(c)). Many previous articles have demonstrated that NH_2OH . HCl is necessary for the growth of Cu_2O powder because the reductant that could directly affect the evolution of Cu_2O depends on reaction time [33].

In addition, the crystal growth of Cu_2O at the beginning of the growth process is exhibited by the yellowing of the anode solution. The effect of the reaction time could be shown clearly by the changing of the Cu_2O morphology. The evolution of Cu_2O particles can be explained as follows: first, Cu_2O nanocrystal seeds were generated in the vicinity of anode during the electrochemical process. This was followed by the growth of the nanocrystals in solution to form the microporous particles. Finally, the formation of Cu_2O crystals was completed with a homogenous spherical shape.

3.4. Application in glucose sensing

In order to evaluate the synthesized Cu_2O sample as an electrode material for sensing applications, we fabricated a non-enzyme glucose sensor by the deposition of the Cu_2O powder on an ITO surface with working area of 5 mm × 5 mm.

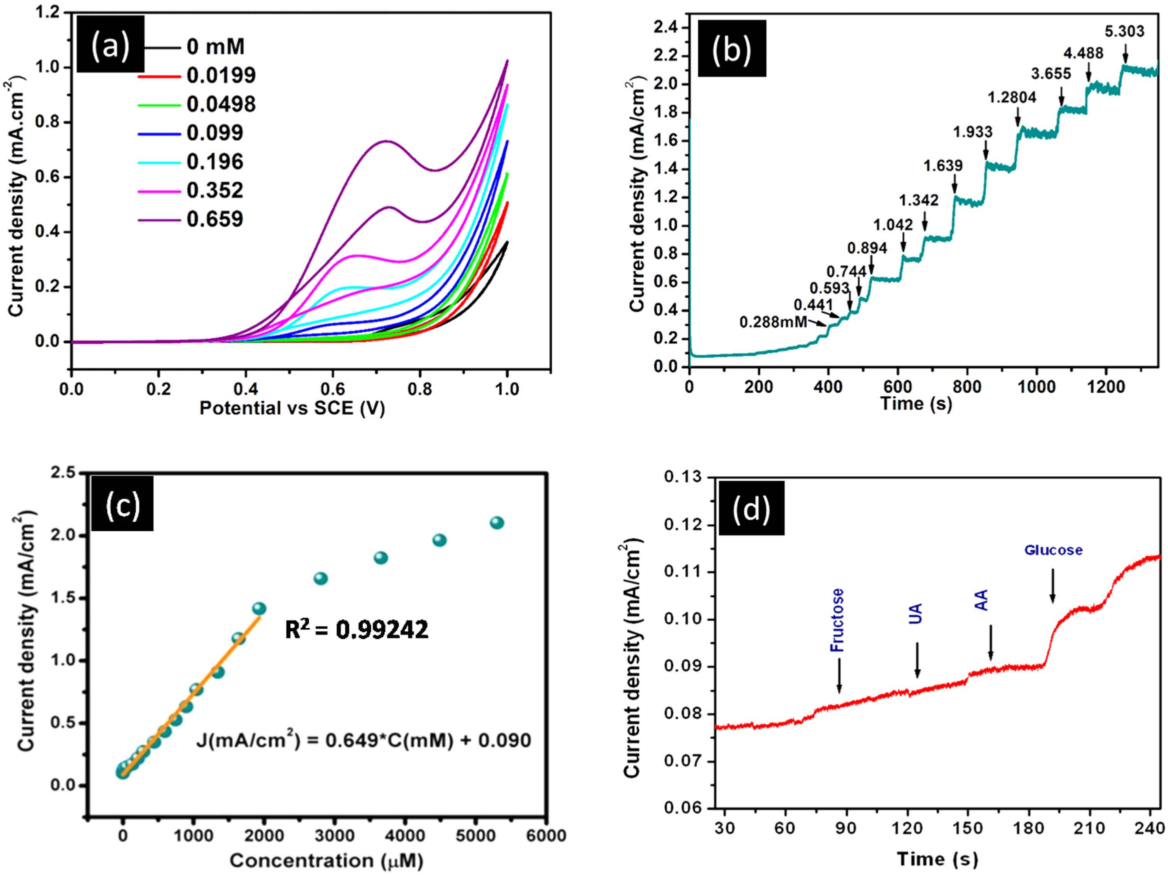

Figure 4. (a) Linear sweep voltammograms collected for the as-prepared Cu_2O/Nafion/ITO in range of glucose concentrations between 0 and 0.659 mM, (b) Current–time response of the Cu_2O/Nafion/ITO electrode with successive addition of different amounts of glucose at applied potential of +0,65 V versus Ag/AgCl, (c) Dependence of steady-state current density on the glucose concentration for the Cu_2O/Nafion/ITO electrode with successive addition of different amounts of glucose from (b), and (d) interference tests of synthesized Cu_2O/Nafion/ITO with successive addition of interferences, and glucose in 0.1 M NaOH at applied potential of +0.65 V versus Ag/AgCl.

To address the availability of application of the synthesized Cu_2O sample, we investigated the electrocatalytic activity of Cu_2O towards glucose deposited on the ITO surface. We conducted a controlled study to examine the catalytic activity of the modified Cu_2O/Nafion/ITO in the presence of glucose. A change of current was observed with the addition of glucose (figure 4(a)). The signal increased dramatically with increasing glucose concentration from 0 to 0.659 mM over the potential range 0–1.0 V and reached peaks of +0.7 V in 0.1 M NaOH solution. The obtained current signals indicate the significant catalytic activity of Cu_2O/Nafion/ITO to response to glucose. This demonstrates that the synthesized Cu_2O/Nafion/ITO could act as a promoter to enhance the analytical sensing ability of glucose.

The CA method was conducted to measure the current response to glucose at a fixed potential for use in amperometric sensing applications. Figure 4(b) displays the current–time response plot of the synthesized Cu_2O/Nafion/ITO modified electrode with successive stepwise changes of the glucose concentration in 0.1 M NaOH solution. As expected, the modified Cu_2O/Nafion/ITO showed linearly increasing responses towards linearly increasing glucose concentration and showed a steady-state signal for 30 s. To guarantee a homogeneous glucose concentration and electrolyte, the solution was slightly stirred over time. The modified-Cu_2O/Nafion/ITO electrode responded immediately to the glucose, and the current increased instantly before reaching a stable value.

As expected from the data, the modified electrode showed good linear response to the changes in glucose concentration and generated steady-state signals within 30 s. The modified Cu_2O/Nafion/ITO electrode gives a linear dependence with good correlation ($R^2 = 0.99242$) in range of glucose concentration between 1.2 μM and 2.0 mM (figure 4(c)). The modified Cu_2O/Nafion/ITO demonstrated a detection limit of 0.4 μM and a sensitivity of 1050 μA mM^{-1} cm^{-2} for glucose (figure 4(d)). This value is much lower than the normal blood glucose range of 80–120 mg dl^{-1} (4.4–6.6 mM) [34]. In fact, the content of glucose in normal human blood is at least 20–30 times greater than those of ascorbic acid (AA), uric acid (UA), and other carbohydrate compounds [35, 36]. The anti-interference against AA, UA, and fructose in the detection of glucose was investigated by the successive addition of 0.4 mM of glucose, 0.04 mM of AA, UA, and fructose. The results showed that the anodic current of AA, UA, and fructose were weaker than that of glucose and had no effect on the steady-state amperometric detection of glucose (figure 4(d)). This result testified that the prepared sensing material possessed high selectivity in trace detection of glucose with negligible interference from AA, UA, and fructose.

Table 1. Analytical performance of the prepared Cu_2O/Nafion/ITO in comparison with other reports.

Electrode materials	Sensitivity (μA μM^{-1} cm^{-2})	Limit of detection (μM)	Linear range (μM)	References
Cu_2O spherical microstructure	0.697	0.4	1.2–2000	This work
Octahedral Cu_2O	0.241	128	300–4100	[37]
Cu_2O hollow nanocubes	0.053	0.87	1–1700	[38]
Cu_2O NPs	0.190	47.2	50–1100	[39]
Cu_2O/GNs	0.285	3.3	300–3300	[2]
GO/CuO/GCE	0.262	0.7	—	[40]
CuO/Cu_2O NFs electrode	0.830	0.7	—	[20]
Porous Cu_2O microcube	0.011	1.3	2–350	[41]

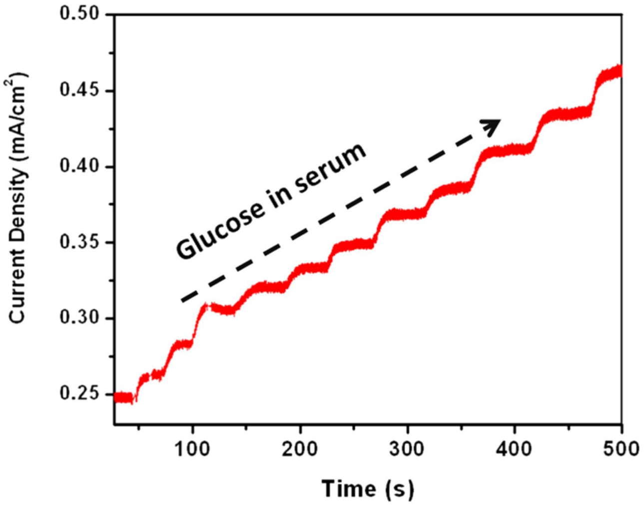

Figure 5. Real sample test—Typical amperometric response of Cu_2O/Nafion/ITO electrode to the successive addition glucose to 0.1 M NaOH solution.

The primary requirement for it to be utilized as an effective sensor is the reproducibility of the electrode. The stability and reproducibility were also explored. Successive voltammograms did not show any decrease in peak current, confirming the efficient stability of the electrode. The relative standard deviation (RSD) of the amperometric response versus Ag/AgCl in 10 μM glucose at the applied potential of 0.65 V is 3.21% for 10 cycles. The reproducibility as a critical factor for further real application was investigated through periodic measures of the sensor response to 10 μM of glucose. The RSD value was calculated to be about 2.5%, which confirmed that this modified electrode is highly reproducible. The repeatability of the prepared sensor was investigated. The RSD of 4.7% was obtained to 10 μM glucose from four different modified electrodes. These data indicates that Cu_2O synthesized by electrochemical method and used for making the modified Cu_2O/Nafion/ITO displays an excellent response to glucose in alkaline solutions at a low limit of detection.

The reliability of the proposed sensor for practical applications was primary evaluated to determine glucose in human serum samples. The human serum sample was diluted 50 times by 0.1 M NaOH before testing. The amperometric measurements were taken when analyte was spiked into the cell. The addition of glucose was accompanied with an obvious increase in the current of glucose (figure 5). This observation suggests that the proposed sensor can be used for practical applications after further studies in analytical performance.

The exact mechanism for the electrocatalytic oxidation of glucoses at Cu_2O/Nafion/ITO electrode is not understood completely. Briefly, the possible redox processes on the surface of the electrode in the presence of glucose may be summarized as follows [20]:

$$\mathrm{Cu(I)} - e \rightarrow \mathrm{Cu(II)} \tag{5}$$

$$\mathrm{Cu(II)} - e \rightarrow \mathrm{Cu(III)} \tag{6}$$

$$\mathrm{Cu(III)} + \text{glucose} \rightarrow \mathrm{Cu(II)} + \text{gluconic acid} \tag{7}$$

$$\text{or glucose} - e \rightarrow \text{gluconic acid} \tag{8}$$

$$\mathrm{Cu(II)} + \text{glucose} \rightarrow \mathrm{Cu(I)} + \text{gluconic acid.} \tag{9}$$

The reactions (7)–(9) are related to the oxidation of glucose during the electrocatalytic process. The conversion of Cu(III) to Cu(II) could cause the high oxidation peaks at about +0.7 V (figure 4(a)), which suggests a strong electrocatalytic ability towards the oxidation of glucose in alkaline solutions [20]. The LOD and sensitivities of this modified Cu_2O/Nafion/ITO electrode are comparable or relatively better than other non-enzymatic sensors fabricated from Cu_2O and other materials (table 1). The significant electrocatalytic performance of the material is ascribed to the specific surface area of Cu_2O and the homogeneous distributions of the Cu_2O microstructure with Nafion on ITO glass.

4. Conclusion

In summary, we had successfully fabricated Cu_2O microstructures through an electrochemical method for electrochemical non-enzymatic glucose sensor. The effect of the pH, the effect of potential, the reaction times, and the evolution process of Cu_2O crystal in the presence of the reductant NH_2OH were investigated. This is a simple and efficient method to prepare Cu_2O with simple equipment. The prepared Cu_2O/Nafion/ITO electrode displayed high electrocatalytic ability towards the oxidation of glucose in alkaline solution and showed good limit of detection (up to 0.4 μM). This work would open up new approach in exploring practically non-enzymatic electrochemical sensors.

Acknowledgments

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