

Electrocatalytic activity of Cu₂O nanocubes-based electrode for glucose oxidation

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MS received 8 July 2013; revised 14 October 2013; accepted 13 November 2013

Abstract. A direct electrocatalytic activity of glucose oxidation on cuprous oxide modified glassy carbon electrode is reported. Cu₂O nanocubes were synthesized by a simple wet chemical route in the absence of surfactants. Purity, shape and morphology of Cu₂O are characterized by XRD, SEM, XPS and DRS-UV. The Cu₂O nanocubes-modified glassy carbon electrode (GCE) exhibited high electrocatalytic activity towards glucose oxidation compared with bare GCE electrode. At an applied potential of +0.60 V, the Cu₂O electrode presented a high sensitivity of 121.7 μA/mM. A linear response was obtained from 0 to 500 μM, a response time less than 5 s and a detection limit of 38 μM (signal/noise=3). The Cu₂O nanocubes-modified electrode was stable towards interfering molecules like uric acid (UA), ascorbic acid (AA) and dopamine (DA). In short, a facile chemical preparation process of cuprous oxide nanocubes, and the fabricated modified electrode allow highly sensitive, selective, and fast amperometric sensing of glucose, which is promising for the future development of non-enzymatic glucose sensors.

Keywords. Cuprous oxide nanocubes; electrocatalysis; non-enzymatic glucose sensor; amperometric sensing.

1. Introduction

Glucose detection is extremely important in food analysis, textile industry, environmental monitoring and medical diagnosis.^{1–5} Sensitive and accurate detection of glucose has many applications because the concentration of glucose is an informal indicator in many diseases such as diabetics and other endocrine metabolic disorder. Especially in clinical diagnosis, diabetes is the worldwide public health problem, which occurs due to the metabolic disorder resulting from insulin deficiency.^{6–9} Treatment has been a far more sophisticated science, with self-testing becoming more compact and hence accurate determination requires a close monitoring of blood glucose levels.^{10,11} Many effective methods have been developed for the measurement of glucose like electrochemical,¹²

electrochemiluminescence,¹³ optical,¹⁴ and fluorescent technologies.¹⁵ Among them, electrochemical glucose sensors have attracted much attention because of their high sensitivity, easy operation and low cost.^{16,17} In general, electrochemical glucose sensors are classified into two types viz. non-enzymatic and enzymatic sensors. In the fabrication of non-enzymatic biosensors, the electrocatalytic activity of the material for glucose oxidation is crucial. For electrochemical sensing, conductive nanostructures immobilized on electrodes enhance electrocatalytic behaviour due to quantum confinement and exhibit unique properties including more favourable faradaic-to-capacitive current densities, and faster mass transport by convergent diffusion than their larger micro/macro electrode counterparts. Numerous nanomaterials like ZnO nanoparticles,¹⁸ Au nanowires,¹⁹ NiO nanofibres,²⁰ flake like Pt-Pd,²¹ and CuO micro fibres,²² have been used for non-enzymatic electrochemical glucose sensors. Among the various materials, transition metal oxide based electrodes are

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more advantageous due to their higher sensitivity, specificity, low cost and absence of interference by other electroactive species such as ascorbic acid (AA), dopamine (DA) and uric acid (UA).

The electrochemical sensors based on Cu materials possess fast amperometric current response, low detection limit and wide linear range due to their greater ability to promote electron transfer reactions.^{23,24} Previous studies reveal that the catalytic property of the sensor based on Cu materials strongly depends on size, distribution and shape.²⁵ In the present paper, cuprous oxide nanocubes were successfully synthesized by one-pot wet-chemical route using L-ascorbic acid as a reducing agent. The Cu₂O biosensor integrated advanced properties of the nanomaterial and exhibited excellent detection range, high selectivity, sensitivity and stability. The preparation method and properties of biosensor based on Cu₂O nanocubes are presented and discussed in detail.

2. Experiments

2.1 Preparation of Cu₂O nanocubes

Cuprous oxide nanocubes were synthesized according to an earlier report.²⁶ In brief, 0.1 M CuCl₂·2H₂O and 0.2 M NaOH was added into 500 mL de-ionized water under continuous stirring. After 5 min, with the addition of 0.1 M L-ascorbic acid, the colour changed from blue to green, yellow and finally brick red. The solution was further stirred for another 30 min and centrifuged, washed with DI water and ethanol thrice to remove the unwanted impurities. The final compound was dried at 50°C to obtain cuprous oxide powder.

2.2 Fabrication of sensor element

Prior to use, the bare glassy carbon electrode surface (GCE, 3 mm diameter) with geometric area of 0.071 cm² was polished with 0.05 micron alumina slurry, rinsed with DI water, sonicated in ethanol and double distilled water and then dried at room temperature. The catalyst ink was prepared by suspending 3 mg of the prepared cuprous oxide powder in 150 μL (5 wt%) Nafion solution under sonication for 15 min. 3 μL of cuprous oxide/Nafion homogeneous solution was dropped onto the glassy carbon electrode surface and was allowed to dry in room temperature for 1 h. The thickness of the resulting coated film calculated from the mass and surface area of the casted film assuming a dry Nafion density of 1.98 g/cm³ was about 3 μm.²⁷ All

measurements were carried out in 0.1 M NaOH, pH 13 at room temperature.

2.3 Electrochemical measurements

The electrochemical measurements were performed with a computer-controlled CHI 660 C electrochemical workstation to study the electrochemical behaviour of the synthesized samples for the detection of glucose. Bare or modified glassy carbon electrode (Cu₂O/Nafion/GC), Pt-wire and Ag/AgCl electrode (1 M KCl) were used as the working, counter and reference electrodes, respectively. The cyclic voltammetry measurements were performed at various scan rates in the potential window 0.0 V to 0.8 V. Electrochemical impedance measurements were carried out in the wide frequency range of 0.1 Hz to 100 Hz with an AC amplitude of 5 mV and a bias potential of 0.1 V. The impedance *Z* was expressed in terms of a real (*Z'*) and an imaginary (*Z''*) component.

3. Results and discussion

3.1 Material characterization and analysis

The crystallinity of the prepared Cu₂O nanocubes were examined by powder X-ray diffraction as shown in figure 1. The major peaks at 2θ = 38°, 43°, 62° and 74°, correspond to (111), (200), (220) and (311) planes, which match well with cubic Cu₂O phase (JCPDS file: 77-0199).^{28–30} The diffraction peaks of the synthesized cuprous oxide sample belongs to cubic structure with a space group of pn3m. Figure 2(a–d) show the FE-SEM micrograph of the as-obtained product at different magnifications. It can be seen that the as-synthesized Cu₂O nanocrystals exhibit uniform cubic shape with an average dimension ranging between 420 and 450 nm. The SEM images show that the grown Cu₂O nanocubes were uniform and homogeneous. UV-Vis spectroscopy was recorded to reveal the energy structures and optical absorption properties of the Cu₂O nanocubes (figure S1). An absorbance maximum was observed at 530 nm, which is in perfect agreement with the standard report.³¹ From the observed DRS-UV graph, the band gap of Cu₂O nanocubes were calculated according to the classical Tauc approach as per the equation given below.

$$\alpha h\nu = A(h\nu - E_g)^{n/2}, \quad (1)$$

where α is the absorption coefficient, ν is the frequency of photons, A is proportionality constant and $n = 1$ for direct transitions. An interesting aspect observed is that the band gap of the Cu₂O nanocubes (2.2 eV) is larger than the reported band gap of bulk Cu₂O (2 eV).³²

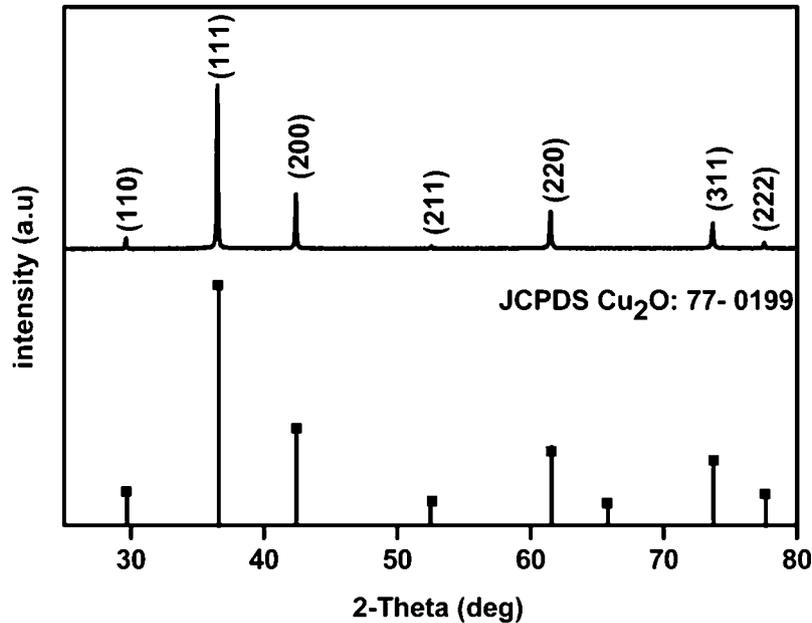


Figure 1. X-ray diffraction pattern of cuprous oxide.

This might be caused by the quantum size effect of the grown nanostructures with the appearance of blue shift as reported in the literature.³³ In small particles the charge carriers like electron and hole are important to split the energy levels with effective band gap.^{34,35}

In order to further investigate the purity and composition of the samples, XPS measurement was carried out as shown in figures S2 and S3. An overall spectrum of the Cu_2O samples as seen from figure S2 shows the presence of C1s peak at 284.6 eV, Cu peak at 932.5 eV

and O1s peak at 530.1 eV. The high resolution spectrum of Cu 2p can be fitted into two peaks, which is attributed to the Cu^+ of Cu_2O .³⁶ The Cu 2p_{3/2} and Cu 2p_{1/2} spin orbital photoelectrons were located at binding energies of 932.5 eV and 952.4 eV, respectively, which are in good agreement with the reported values of Cu_2O . Thus, the synthesized nanocubes were Cu_2O rather than CuO in accordance with the XRD data. Figure S3(b) displays the deconvoluted O1s spectra, the high band energy component at 530.1 eV indicates the formation

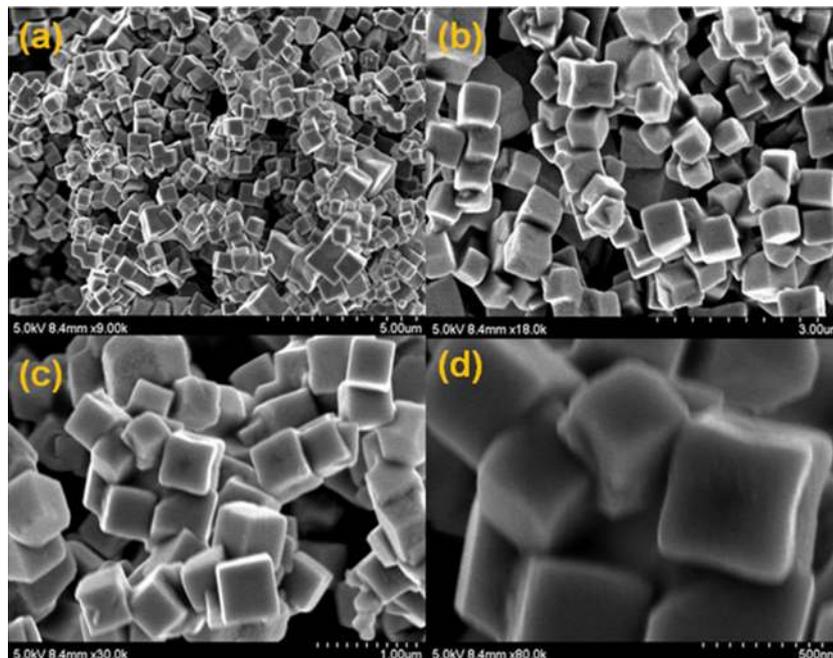


Figure 2. FE-SEM images of cuprous oxide nanostructures at different magnifications.

of Cu_2O phase. The other peaks at 531.4 eV and 533 eV can be attributed to the presence of hydroxyl group and molecular water adsorbed on the surface, respectively.³⁷ All these results indicate that the samples are Cu_2O and the XPS survey spectra show that no obvious impurities could be detected in the samples.

3.2 Electrochemical analysis

To understand the nature of the modified electrode, cyclic voltammetry was carried out in 2 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ / 0.1 M KCl in figure 3a. The observed redox peaks are due to the electrochemical reduction of Cu_2O . The cathodic peak corresponds to the reduction of $\text{CuO}/\text{Cu}_2\text{O}$ redox couple, and the anodic peak from the formation of CuO layer.³⁸ As can be seen from figure 3b, the peak current (I_p) increased linearly with square root of scan rate both in the anodic and cathodic directions implying that the electrochemical oxidation of glucose on the modified electrode is a diffusion controlled process. Before probing the electrocatalytic property of the modified electrode towards glucose oxidation, the electrode was tested to know its resistance/impedance. EIS spectrum of the bare GCE and $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode based electrode was recorded in the frequency range 0.1 Hz to 100 Hz in 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl solution (figure 4). The EIS spectra include two segments; first segment at higher frequency range, seen as circular portion is due to an electron transfer limited process. The second segment at lower frequency range linear portion is due to the diffusion controlled process. The corresponding Randle's equivalent circuit (inset figure 4) contains constant phase element (Q), electrolyte solution resistance (R1), charge-transfer resistance (R2), Warburg impedance (W) and adsorption resistance (R3). The R_{CT}

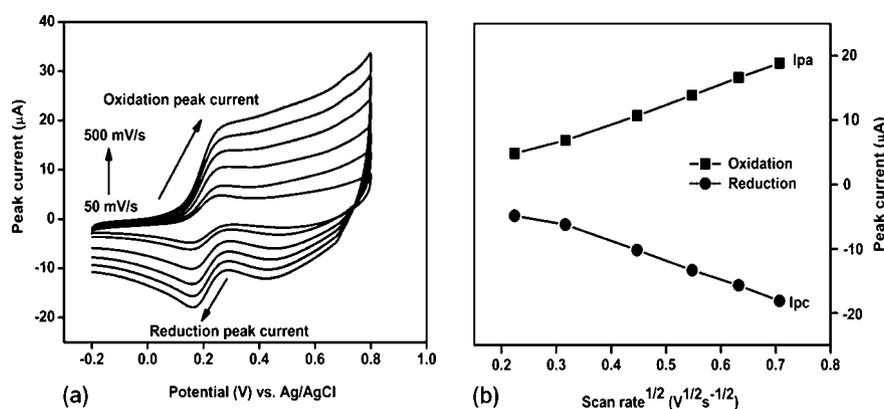


Figure 3. (a) Cyclic voltammograms of $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode in 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.1 M KCl solution at various scan rates. (b) Plots of anodic and cathodic peak currents vs. scan rate (I_p vs. $\nu^{1/2}$).

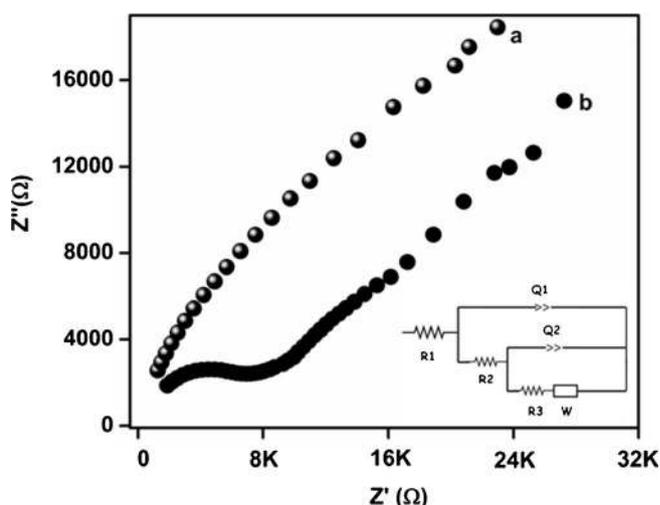


Figure 4. EIS spectrum of the (a) bare GCE and (b) $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ based electrode and its equivalent circuit (inset).

at the modified electrode surface as quantified by the diameter of the semicircle in EIS spectrum is $5 \text{ K}\Omega$ which is lower than that of bare GCE ($R_{CT} 18 \text{ K}\Omega$). From the analysis, it could be seen that the resistance of the modified electrode is typically low indicating that it could be utilized for electrocatalytic applications.

The electrocatalytic property of Cu_2O nanocubes modified electrode was investigated by cyclic voltammetry over a potential range from 0 to 0.8 V. Figure 5 shows the CV of the $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode in 0.1 M NaOH, in the absence and presence of glucose at various concentrations at a scan rate of 0.1 mV/s. No significant oxidation current was observed in the absence of glucose for the modified electrode. In the presence of glucose, the oxidation started at approximately +0.30 V and a gradual increase in current was observed around +0.60 V, suggesting

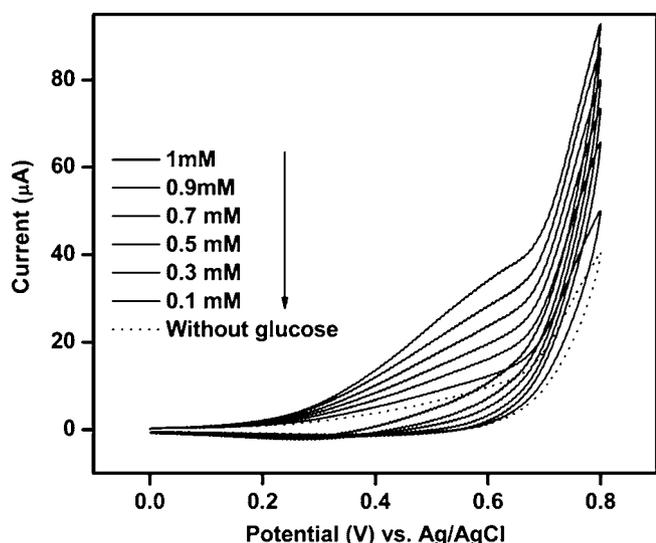


Figure 5. (a) Cyclic voltammety of $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode in the absence and presence of different concentration of glucose (0.1 mM to 1 mM).

that Cu_2O nanocubes have greatly improved the performance of the electrode and increased the electrocatalytic ability towards glucose oxidation. The oxidation of glucose to gluconolactone occurs in the potential range of 0.2 V to 0.7 V, where the oxidation is catalysed by Cu(II) to Cu(III) conversion.^{38,39} This shows that Cu_2O enabled the electron transfer between glucose and GCE electrode, catalysed by Cu(III) species, which acted as an electron transfer mediator.⁴⁰ Upon addition of $200\ \mu\text{M}$ glucose, the currents of the electrocatalytic oxidation peaks at +0.60 V increased in 0.1 M NaOH medium. Hence, these experiments strongly support the fact that Cu_2O has good electrocatalytic activity

Table 1. Electrochemical characteristics of the $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode.

Parameters	Results
Sensitivity	$121.7\ \mu\text{A}\ \text{mM}^{-1}$
Linearity	0–500 μM
Response time	<5 s
Detection limit	38 μM
Stability	15 days

towards the oxidation of glucose. The electrochemical oxidation of glucose in NaOH medium at GCE surface modified with cuprous oxide ($\text{Cu}_2\text{O} + \text{Nafion}$) undergoes oxidation in several steps.⁴¹ Here, Cu(I) is electrochemically oxidized to Cu(II) species viz. Cu(OH)_2 . Glucose is electrochemically oxidized to gluconic acid by the formed Cu(II) species, which can be further oxidized into CuO(OH) on the surface of the electrode. The formation of this Cu(III) species leads to high catalytic current towards glucose oxidation.

The high electrocatalytic performance of the $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode suggests that the modified electrode act as an excellent electrochemical sensing platform for amperometric determination of glucose. For amperometric glucose sensing application, electrodes are generally evaluated by measuring current with standard addition of glucose. The chronoamperometric current response of the fabricated electrode was measured in 0.1 M NaOH solution with an addition of glucose at a step of four segments ($10\ \mu\text{M}$, $20\ \mu\text{M}$, $50\ \mu\text{M}$ and $100\ \mu\text{M}$) under constant stirring (figure 6a). A well-defined stable and fast amperometric response could be observed at 0.6 V with successive addition of glucose into 0.1 M NaOH. The as-prepared cuprous oxide

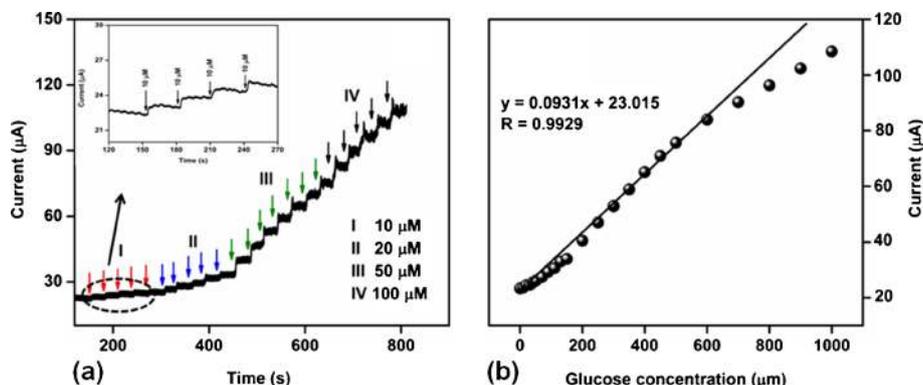


Figure 6. (a) Amperometric steady state current time response obtained at $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode upon successive additions of glucose into 0.1 M NaOH solution. The upper left inset shows the enlarged view at low concentrations of glucose. (b) The linear plot of amperometric current vs. glucose concentrations.

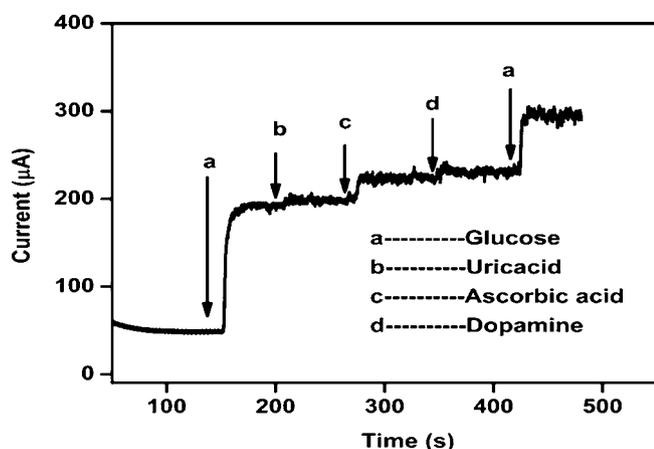


Figure 7. Interference test of $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode modified electrode in 0.1 M NaOH at 0.6 V with $300\mu\text{M}$ glucose in the presence of $300\mu\text{M}$ UA, $300\mu\text{M}$ AA and $300\mu\text{M}$ DA.

modified electrode gave a linear relationship between the current and concentration of glucose, in the concentration range below $500\mu\text{M}$ with a correlation coefficient of 0.9929 as depicted in figure 6b. A high sensitivity of $121.7\mu\text{AmM}^{-1}$ with a detection limit of $38\mu\text{M}$ at S/N ratio 3 was obtained. The fabricated electrode responded quickly to the change of glucose concentration and it quickly reached about 95% of the steady state current within 5 s, which was faster than those reported for the other CuO based literature using CuO nanorods (10s),⁴² PtPb/MWCNTs (12s),⁴³ Cu/SWCNT/Nafion (10s),⁴⁴ and mesoporous platinum modified nanoplatinum rod electrode (100s).⁴⁵ The characteristics of the modified electrode are shown in table 1.

The performance of the proposed sensor was compared with other reported cuprous oxide non-enzymatic sensors as shown in table S1. As summarized, it can be observed that the modified electrode exhibits higher sensitivity, better linear range, fast and sensitive catalytic performance than other, which might be due to the fast electron transfer ability and excellent catalytic activity of Cu_2O nanocubes.^{46–48}

Reproducibility of the electrode was tested with $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode four times and evaluated their amperometric current response at 0.6 V. Results showed deviation of less than 2%, hence the performance of the electrode is highly reproducible. The modified electrode is kept in a closed container

at ambient atmospheric conditions when not in use. Amperometric current response of the modified electrode was checked every two days which lasted up to four weeks. All the fourteen experiments showed stable characteristics; sensitivity of the electrode showed a deviation less than 2%. This shows that the electrode prepared by this method is highly reproducible and stable. One of the important analytical factors for an amperometric biosensor is the selectivity of the sensor to target analyte. It is well-known that uric acid (UA) and ascorbic acid (AA) are common interfering species during catalytic oxidation of glucose. Generally, the physiological level of glucose is about 3–8 mM, which is higher than that of other interfering species viz. ascorbic acid (AA), uric acid (UA) and dopamine (DA). Moreover, the concentration of glucose in human blood is more than 30 times that of interference species.^{49–52}

Thus, the interference test was run by measuring current changes caused by the addition of UA, AA and DA during glucose sensing. Amperometric response was obtained by successive injection of $100\mu\text{M}$ glucose and interfering species ($300\mu\text{M}$ AA, UA and DA). As shown in the figure 7, the response of the Cu_2O -modified electrode to $300\mu\text{M}$ glucose is not affected by the addition of these interferences. Thus, the present electrode can successfully avoid interferences from UA, AA and DA. To evaluate the applicability, the biosensor was used for the determination of glucose concentration in human urine by standard addition method. Prior to analysis, the urine sample was diluted 10 times using 0.1 M NaOH electrolyte without further pretreatments. For this, urine samples were obtained from healthy people to detect glucose. Here, $80\mu\text{L}$ of urine sample is injected into 20 mL of 0.1 M NaOH solution and the corresponding current response was recorded at +0.6 V. Figure S4 demonstrates the real sample amperometric analysis of modified electrode by the standard addition of glucose in 0.1 M NaOH solution using chronoamperometric method. By the standard addition of pure glucose into the solution with urine sample, the recovery of glucose was determined and the corresponding results are shown in table 2. As seen, there is a satisfactory agreement between the results obtained from the fabricated $\text{Cu}_2\text{O}/\text{Nafion}/\text{GC}$ electrode sensor and those measured by the biochemical analyser in a local hospital.

Table 2. Determination of glucose in human urine samples.

Sample	Spiked (mM)	Found (mM)	Biochemical analyser (mM)	Recovery (%)
1	0.08	0.0799	0.0795	100.4
2	0.1	0.1001	0.1008	99.4

4. Conclusion

In summary, Cu₂O nanocubes were synthesized and used as an electrode material for glucose sensor applications. The Cu₂O nanocubes were synthesized by one-step chemical route with L-ascorbic acid as reductant. The fabricated sensor was used to detect glucose in alkaline medium and results indicated that the sensor exhibited good linear response ranging from 0 to 500 μM, a high sensitivity (121.7 μA mM⁻¹), low detection limit (38 μM), good stability and satisfactory anti-interference ability. The direct electron transfer between Cu₂O and electrode is due to the reaction sites of numerous Cu₂O nanocubes interconnected on the electrode surface. Thus, the proposed Cu₂O based sensor offers potential applications in biosensors and catalysis.

Supplementary information

Supplementary information includes Diffusive reflectance UV, XPS, Real sample analysis of modified electrode in 0.1 M NaOH solution (figures S1–S4) and table S1. For details, see www.ias.ac.in/chemsci.

Acknowledgements

This work was carried out with the help of VIT management through research scholarship. This work was also conducted under the framework of Research and Development Program of the Korea Institute of Energy Research (KIER) (B3-2467-07).

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