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Synthesis of CuO Nanrods Using Chemical Bath Deposition for a Nonenzymatic Glucose Biosensor

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ABSTRACT

In the present research, CuO NRs are produced on Indium Tin Oxide (ITO) using (CBD) growth process, and their electrochemical characteristics for glucose biosensors are studied. A field emission scanning electron microscope, x-ray diffractometer, energy dispersive x-ray, and UV-VIS spectroscopy were used to examine the morphology and crystallinity of a CuO film. The synthesized CuO film displays a monoclinic phase with average crystallite sizes of around (18–25) nm. CuO is composed of NRs aggregating together to construct flower and flower bud-like shape structures with a diameter between (20-80) nm and a thickness of the CuO film is about (158.5-285.7) nm. The energy gap of CuO NRs was 2.55 eV. The I-V characteristics of the biosensors were measured and evaluated at various glucose concentrations to determine their sensitivity. The electrocatalytic performance of the CuO for the detection of glucose was outstanding. With a very low limit of detection (LOD) of 0.45 µM and a sensitivity of 799 µA cm^{-2} Mm^{-1}, the electrode attained a wide linear range from 0.5 to 2 mM. This result highlights the sensor's tremendous potential as a high-performance non-enzymatic glucose sensor that makes use of an original, cost-effective, and straightforward sensor design.

KEYWORDS: Copper oxide; CBD method; I-V characteristics; glucose biosensor.

الخلاصة

في البحث الحالي، يتم إنتاج تحضير قضبان اوكسيد النحاس النانوية بأستخدام طريقة ترسيب الحمام الكيميائي والتي تكون مرسبة على ركائززجاجية مطلية بأوكسيد القصدير الإنديوم، ودراسة خصائصها الكهروكيميائية لأجهزة الاستشعار الحيوية للجلوكوز. تم استخدام المجهر إلكتروني الالكتروني الماسح، حيود الأشعة السينية، أشعة سينية مشتتة للطاقة، والتحليل الطيفي للأشعة فوق البنفسجية لفحص التشكل والبلورة لغشاء اوكسيد النحاس. يعرض غشاء اوكسيد النحاس المركب مرحلة أحادية الميل بمتوسط أحجام بلورية حوالي (18-25) نانومتر. يتكون اوكسبد النحاس من قضبان نانوية التي تتجمع معًا لإنشاء هياكل تشبه برعم الزهرة والزهرة بقطر يتراوح بين (20-80) نانومتروسمك غشاء حوالي (158.5-285.7) نانومتر. كانت فجوة الطاقة في قضبان اوكسيد النحاس النانوي حوالي 2.55 فولت. تم قياس وتقييم الخصائص الكهربائية (I-V) للمستشعرات الحيوية عند تركيزات الجلوكوز المختلفة لتحديد حساسيتها. كان أداء التحفيز الكهربائي لـأوكسيد النحاس للكشف عن الجلوكوز رائعًا. مع حد منخفض جدًا للكشف (LOD) يبلغ 0.45 ميكرومتر وحساسية 799 ميكرومتر سم -2 مم -1، حقق القطب نطاقًا خطيًا واسعًا من 0.5 إلى 2 مم. تسلط هذه النتيجة الضوء على الإمكانات النانوية الهائلة للمستشعر كجهاز استشعار جلوكوز غير إنزيمي عالي الأداء يستخدم تصميم مستشعر أصلي وفعال من حيث التكلفة ومباشر.

INTRODUCTION

Due to the requirement for precise and prompt glucose level monitoring for medical care and treating diabetes, the development of more sensitive and particular glucose sensors has received a lot of attention [1-5]. Due to their increased stability and lower cost, and low band gap values of (1.2–1.9) eV, CuO based sensors have been developed for the detection of glucose that does not include any enzyme [6-10]. Because CuO is non-hazardous, using it as a glucose sensor has many advantages. Additionally, CuO's constituents are widely distributed in nature [11]. CuO nanostructures can promote processes caused by electron transfer that occur at a lower voltage because they have a larger surface area. CuO, therefore, gives the development of the nonenzymatic glucose sensor more focus. The shape, size, and morphology of the material have an impact on its physicochemical characteristics. In order to enhance the performance of glucose sensors, major efforts have been made to synthesize

various CuO nanostructures, such as nanospheres, nanowires, and nanoflowers [12-14]. Nanostructures for sensing glucose have recently been developed on CuO foils, including nanosheets, nanowalls, and nanobelts [15-17]. Reports of CuO thin films being formed on substrates made of stainless steel, however, are uncommon. These nanostructures need to be created through a laborious and meticulous process as well. A more straightforward technique to create CuO nanostructures with greater catalytic activity for glucose sensing is still required. Different deposition processes are used to create CuO nanostructures such as seeds, tubes, rods, wires, belts, leaves, and needles [18]. Due to its simplicity, CBD has become more popular among these many approaches. The CBD method makes it simple to carry out chemical reactions at low temperatures (usually below 100 °C) in an open container. Comparing this procedure to the others makes it obvious that the CBD methodology gives the surface more stability and has a big impact on the surface's morphology and optical properties of CuO [19].

The goal of the research, development, and testing of a glucose biosensor based on a thin film of CuO nanostructured NRs was to create a stable CuO biosensor with high sensitivity and quick reaction time. The CBD method can be produced in a single step without the use of a strong reducing agent by carefully controlling the precipitation of the chemical from the solution onto suitable substrates.

The built-in sensor showed excellent long-term stability, high sensitivity, and a low detection limit for the detection of glucose.

MATERIALS AND METHODS

Materials

HMT, $C_6H_{12}N_4$, purity of 99.5 %, which was acquired from Hi-media India, and $Cu(NO_3)_2 \cdot 5H_2O$, purity of 99.9% were the materials utilized in the studies. ITO glass was provided using substrate from the Chinese company Yingke Optical Products, Co. Ltd. from Scharlau in Spain, 99.5% pure NaOH was acquired. Additionally, distilled water (DW) and absolute ethanol (C_2H_5OH) were applied. For the electrochemical tests, solutions containing glucose at concentrations of 0.5, 1, and 2 mM (Sigma Aldrich, 99.99 % purity) were prepared.

Preparation of the substrate

The ITO substrates (1.2×1.2 cm) were cleaned in an ultrasound cleaner with ethanol and DW for 20 min to eliminate impurities from the surface before being dried in an airflow.

Synthesis of CuO via CBD method

The chemical bath deposition technique used in the experiments is depicted in Figure 1. In 60 mL of DW, 0.02 M (0.22 g) of $Cu(NO_3)_2 \cdot 5H_2O$ with 0.02 M (0.168 g) of hexamethylenetetramine were dissolved and stirred for 15 minutes to ensure complete dissolution. The pH of the solution was kept at around 5. The ITO substrates were submerged vertically within the CBD system cell at a bath temperature of 80 °C for 2 hrs. After being washed in DW to remove the salts, the film was dried on a hotplate for 20 min at 50 °C, and it was then annealed for 2 hrs at 400 °C.

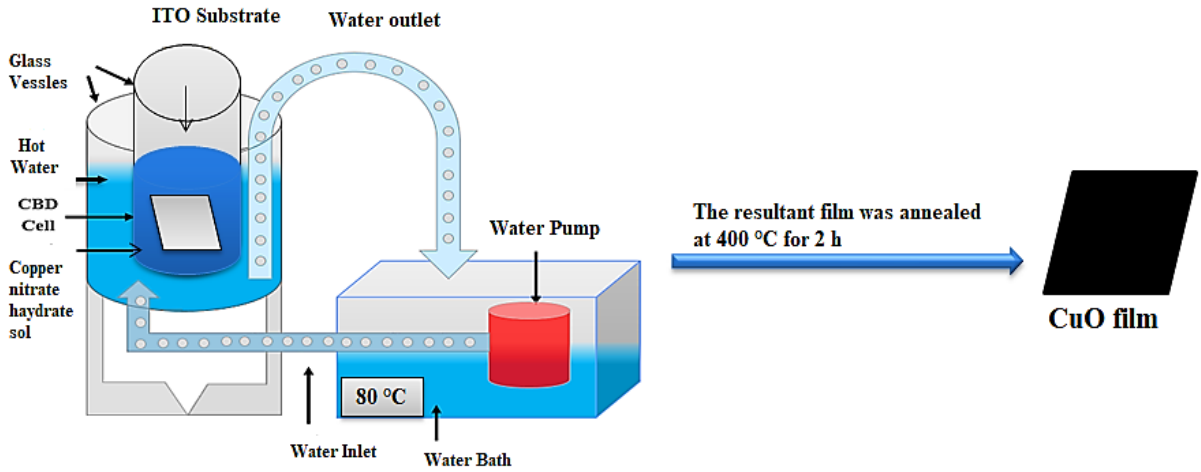

Figure 1. Scheme for the chemical bath deposition technique used to synthesize CuO.

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Characterization

Using θ/2θ scans on a PIXcel diffractometer, the structures of the CuO films were examined using X-ray diffraction (XRD) in the 20°-80° range. Using a Zeiss SIGMA VP-Field-emission scanning electron microscope, their morphologies were examined (FE-SEM). The absorption was measured using a double beam Li-2800 spectrophotometer over the wavelength range of 200 to 900 nm.

The electrochemical glucose bio-Sensor characterization

A Keithley 2430-C source meter unit (SMU) instrument with a contact check/GPIB interface and a 1 kW pulse mode was used to conduct the electrochemical investigations (A Tektronix Company). The three-electrode setup seen in Figure 2 which comprises a working electrode, counter electrode, and reference electrode was employed in all of the electrochemical tests (RE). CuO nanostructures, graphite, and Ag/AgCl were used to approximate the WE, CE, and RE, respectively. Using a source meter unit (SMU) device with a sweep delay of 200 ms, the electrodes were evaluated in 0.1 M NaOH (supporting electrolyte) with different concentrations of glucose (0.5, 1, and 2). CuO chrono-amperometric responses were measured at 1 V. At 1 V, CuO chrono-amperometric responses were recorded. At room temperature (20 °C), the electrodes were kept in the air. To ensure that the tests could be reproduced, they were all performed at room temperature and at least three times.

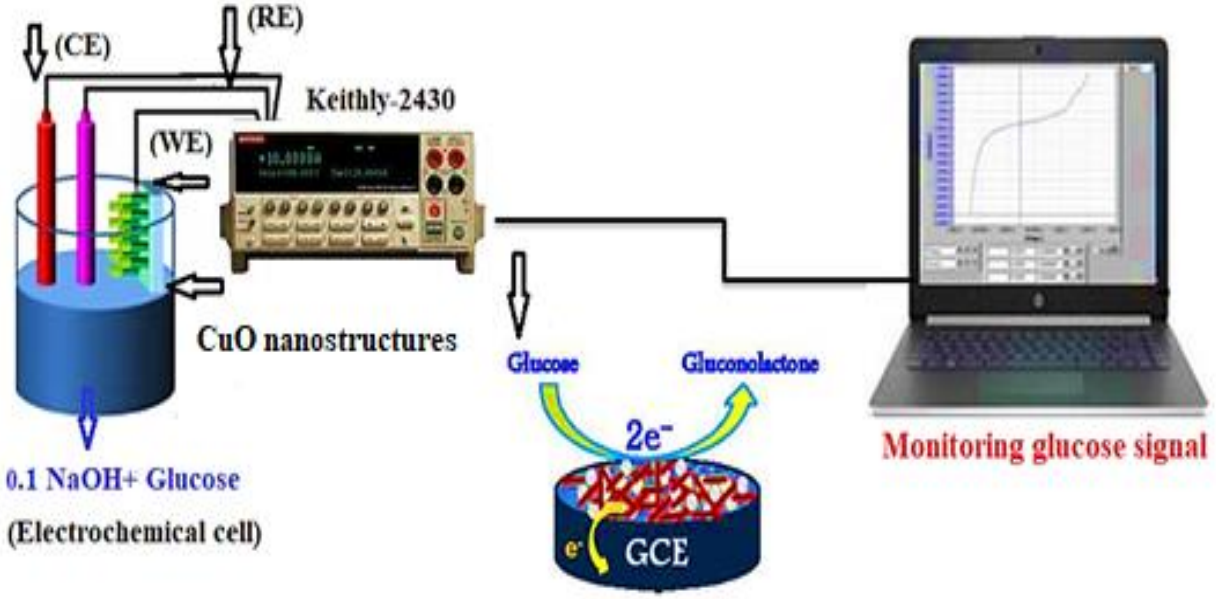

Figure 2. Enzyme-free glucose sensor based on CuO nanostructures.

RESULTS AND DISCUSSION

XRD analyses

In order to understand the structural properties of CuO films prepared by the chemical bath deposition process on ITO substrate are represented in Figure 3. The Figure observed the XRD patterns of CuO contain characteristic peaks at 2θ values= 35.7°, 38.8°, and 48.9° which could be indexed as (022), (111), and (-202) respectively. All of the diffraction peaks for CuO's monoclinic phase are in good agreement with the standard diffraction data, according to the XRD patterns (JCPDS 45-0937). The average crystallite size of CuO nanostructures with strong peaks (the preferred orientation) was calculated using the Debye-Scherrer formula [20]:

$$D = 0.9\lambda/\beta\ cos\theta \quad (1)$$

Where λ, β, and θ are the wavelength, the full width at half the maximum intensity (FWHM) in radians, and the diffraction Bragg angle, respectively.

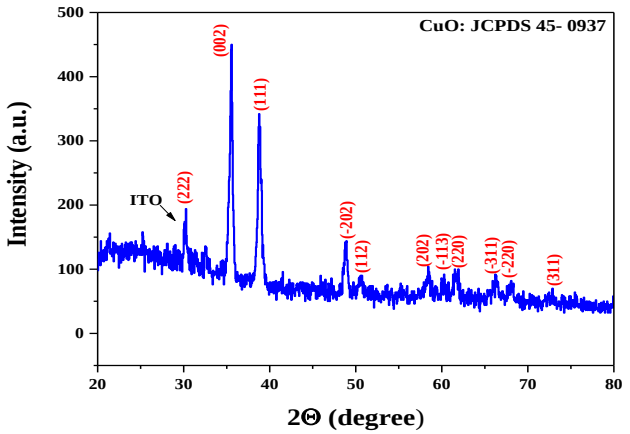

Figure 3. The XRD pattern of the CBD-prepared copper oxides (CuO).

The average crystallite size was estimated to be about (18-25) nm.

FE-SEM Morphological study

The FE-SEM images and cross-section of CuO NRs produced by the CBD technique are shown in Figure 4A. The CuO is composed of NRs with different directions aggregating together to construct flower and flower bud-like shape structures that have a smooth surface and very sharp tips with a diameter between (20-80) nm. As in the cross-sectional image in Figure 4B, the thickness of the CuO film is about (158.5-285.7) nm.

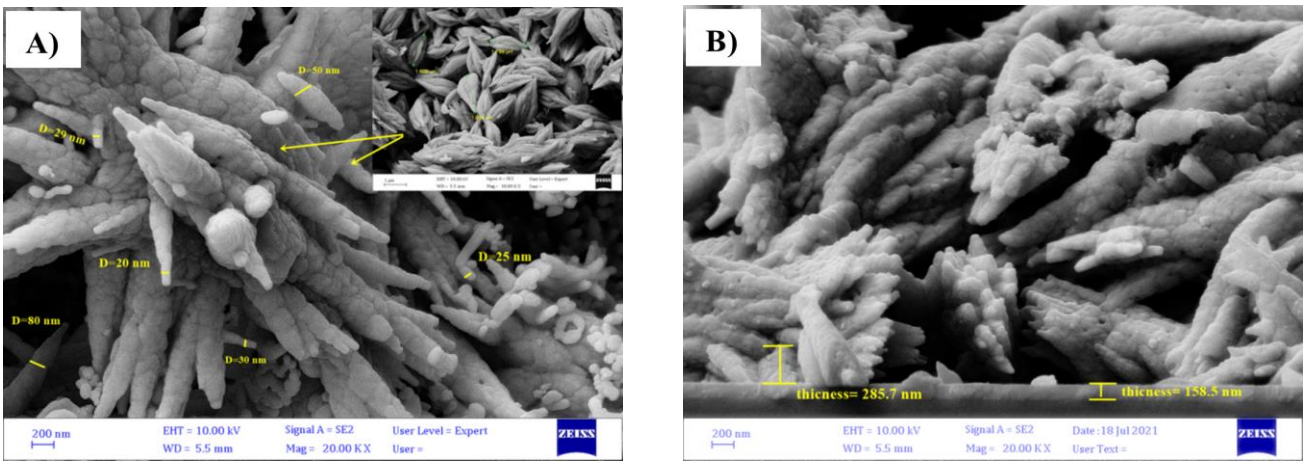

Figure 4. FE-SEM surface images of (A) CuO as prepared by CBD method and (B) cross-section image.

The energy dispersive X-ray analysis (EDX) has been utilized to investigate the chemical composition of the pure CuO as prepared using the CBD method as shown in Figure 5. As determined through EDX analysis, four significant peaks have been recorded related to copper and oxygen. The weight percentages consisted of 83.7 % of the Cu element and 16.3 % of the O element which is in agreement with the XRD result.

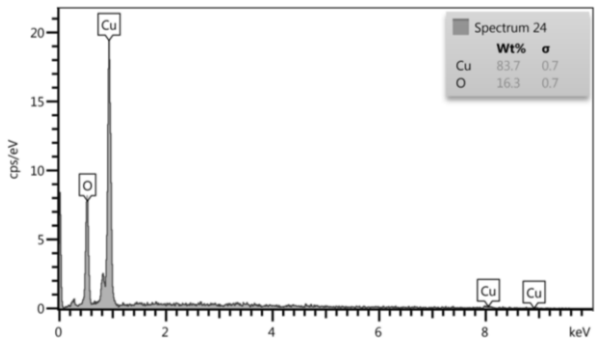

Figure 5. The EDX studies of CuO were made using the chemical bath deposition technique.

UV–vis spectral analyses

Figure 6A shows the absorption spectrum as a function of the wavelength of CuO using the CBD method. The incident light has wavelengths between 200 to 900 nm. The results show the absorption spectra centered at the wavelength of 351 nm. The energy band gap (E_g(dir)) of the CuO sample was calculated from $(\alpha h\upsilon)^2$ versus the photon energy ($h\upsilon$) plot shown in Figure 6B. The E_g(dir) values of the pure CuO film were found to be 2.55 eV. However, the small shift in the energy gap may be caused by the variation of the crystalline size throughout the sample or strain induced in CuO causing quantum confinement in the structures.

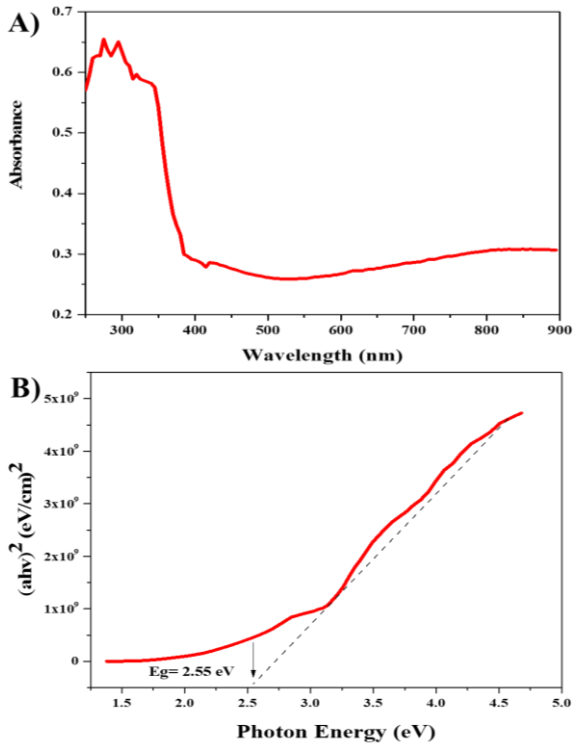

Figure 6. UV-vis absorption of A) CuO and B) Tauc plots of direct transitions of CuO created using the CBD approach.

Glucose biosensor measurements

I-V characteristics

We begin by evaluating and interpreting the glucose biosensor's electrical response. By examining the I-V measurements, we can improve the electrical responsivity and determine the sensitivity of electrode sensors. The current response of the biosensors as a function of the applied voltage (0-1) was evaluated in Figure 7. The Figures describe the various I-V characteristics of CuO as synthesized by the CBD approach in the absence and presence (0.5-2) mM of glucose dissolved in 0.1 M NaOH as the electrolyte.

The NaOH solution did not show any peak (in the absence of glucose). The greatest current oxidation peak was observed at 0.99 V following the addition of (0.5, 1, and 2) mM of glucose. Thus, the approximately 0.99 V oxidation peak may be the result of glucose oxidizing on the CuO working electrode surface. CuO NRs enhanced the performance of the CuO/ITO electrode and amplified its electrocatalytic activity toward glucose oxidation due to their significant surface area, high surface energy, and higher electron transfer capacity [21]. The nearly linear current-increasing behavior seen in CuO served as evidence for this.

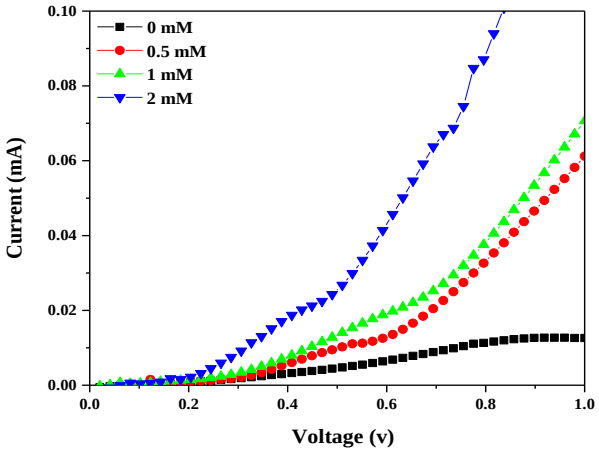

Figure 7. The I-V properties of CuO as produced using the CBD technique with various glucose concentrations.

Using different glucose concentrations, Figure 8 displays the current-time curve for the CuO NRs electrode at (0-1) V (vs. Ag/AgCl) in 0.1 M NaOH solution. It is clear that clear and quick amperometric reactions are detected, with the exception of NaOH, which similarly does not respond to glucose.

The calibration curve for CuO NRs electrodes is shown in Figure 9. The corresponding sensitivity, linear range, correlation coefficient, and detection limit are summarized in the figure below. The highest glucose bio-sensing performance in this study is shown by the CuO NRs electrode, which has a sensitivity of 799 µA mM^{-1} cm^{-2}, a correlation value of R2= 0.99, a longer linear range from 0.5 mM to 2 mM, and a lower practical detection limit of 0.45 µM.

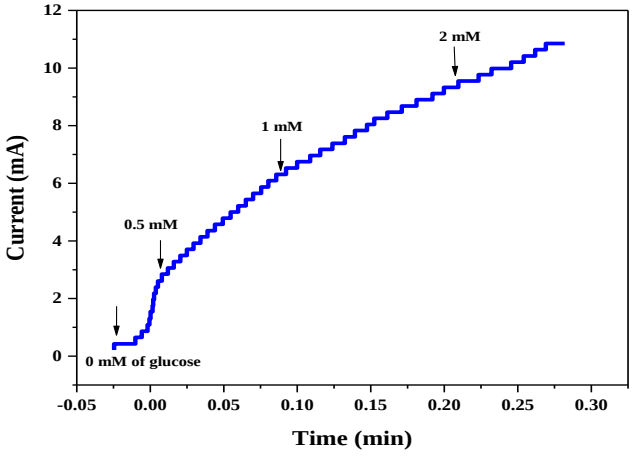

Figure 8. The current-time curves of CuO NRs with an increase in glucose concentration.

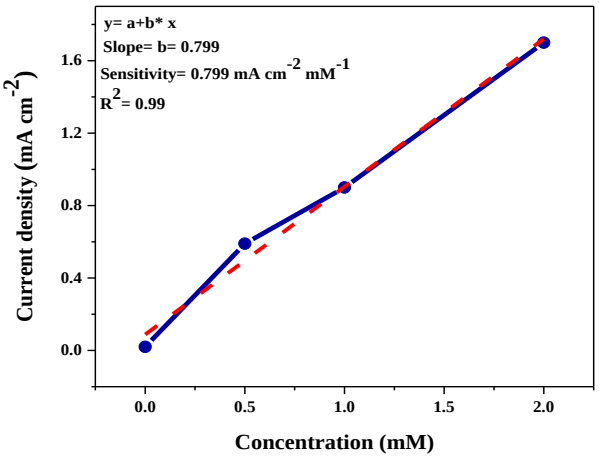

Figure 9. Electrode response and a calibration curve of CuO with the addition (o.5, 1, and 2) mM of glucose.

CONCLUSIONS

In this study, a CuO NRs electrode that is a good glucose sensor has been created employing an easy deposition process on indium tin oxide (ITO). According to the results of the current investigation, the produced CuO thin film displays a monoclinic phase with flower and flower bud-like form structures, which improves the electrochemical characteristics. The energy gap of CuO NRs was 2.55 eV. The CuO electrode had a good sensitivity of 799 µA mM-1 cm^{-2}, a linear range of up to 2 mM, and a projected limit of detection of 0.45 µM. Furthermore, the suggested as-synthesized method used in this work could be applied to the manufacture of large and effective wide-range electrodes in biosensors.

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Disclosure and conflict of interest: The authors declare that they have no conflicts of interest.

REFERENCES

[1] J. D. Newman and A. P. Turner, "Home blood glucose biosensors: a commercial perspective," Biosensors and bioelectronics, vol. 20, no. 12, pp. 2435-2453, 2005. https://doi.org/10.1016/j.bios.2004.11.012

[2] K. J. Cash and H. A. Clark, "Nanosensors and nanomaterials for monitoring glucose in diabetes," Trends in Molecular Medicine, vol. 16, no. 12, pp. 584-593, 2010. https://doi.org/10.1016/j.molmed.2010.08.002

[3] C. Deng, Y. Peng, L. Su, Y.-N. Liu, and F. Zhou, "On-line removal of redox-active interferents by a porous electrode before amperometric blood glucose determination," Analytica Chimica Acta, vol. 719, pp. 52-56, 2012. https://doi.org/10.1016/j.aca.2012.01.008

[4] M. Wei et al., "Electrochemical non-enzymatic glucose sensors: recent progress and perspectives," Chemical Communications, vol. 56, no. 93, pp. 14553-14569, 2020. https://doi.org/10.1039/D0CC05650B

[5] Y. Qiao et al., "High-performance non-enzymatic glucose detection: using a conductive Ni-MOF as an electrocatalyst," Journal of Materials Chemistry B, vol. 8, no. 25, pp. 5411-5415, 2020. https://doi.org/10.1039/D0TB00131G

[6] Z. Zhuang, X. Su, H. Yuan, Q. Sun, D. Xiao, and M. M. Choi, "An improved sensitivity non-enzymatic glucose sensor based on a CuO nanowire modified Cu electrode," Analyst, vol. 133, no. 1, pp. 126-132, 2008. https://doi.org/10.1039/B712970J

[7] Y. Ding, Y. Wang, L. Su, M. Bellagamba, H. Zhang, and Y. Lei, "Electrospun Co3O4 nanofibers for sensitive and selective glucose detection," Biosensors and Bioelectronics, vol. 26, no. 2, pp. 542-548, 2010. https://doi.org/10.1016/j.bios.2010.07.050

[8] L. Zhang, H. Li, Y. Ni, J. Li, K. Liao, and G. Zhao, "Porous cuprous oxide microcubes for non-enzymatic amperometric hydrogen peroxide and glucose sensing," Electrochemistry Communications, vol. 11, no. 4, pp. 812-815, 2009. https://doi.org/10.1016/j.elecom.2009.01.041

[9] J. Chen, W.-D. Zhang, and J.-S. Ye, "Nonenzymatic electrochemical glucose sensor based on MnO2/MWNTs nanocomposite," Electrochemistry Communications, vol. 10, no. 9, pp. 1268-1271, 2008. https://doi.org/10.1016/j.elecom.2008.06.022

[10] X. Zhang, A. Gu, G. Wang, Y. Huang, H. Ji, and B. Fang, "Porous Cu-NiO modified glass carbon electrode enhanced nonenzymatic glucose electrochemical sensors," Analyst, vol. 136, no. 24, pp. 5175-5180, 2011. https://doi.org/10.1039/c1an15784a

[11] A. Oral, E. Menşur, M. Aslan, and E. Başaran, "The preparation of copper (II) oxide thin films and the study of their microstructures and optical properties," Materials Chemistry and Physics, vol. 83, no. 1, pp. 140-144, 2004. https://doi.org/10.1016/j.matchemphys.2003.09.015

[12] E. Reitz, W. Jia, M. Gentile, Y. Wang, and Y. Lei, "CuO nanospheres based nonenzymatic glucose sensor," Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis, vol. 20, no. 22, pp. 2482-2486, 2008. https://doi.org/10.1002/elan.200804327

[13] P. Zhang, L. Zhang, G. Zhao, and F. Feng, "A highly sensitive nonenzymatic glucose sensor based on CuO nanowires," Microchimica Acta, vol. 176, no. 3, pp. 411-417, 2012/02/01 2012. https://doi.org/10.1007/s00604-011-0733-x

[14] X. Wang, C. Hu, H. Liu, G. Du, X. He, and Y. Xi, "Synthesis of CuO nanostructures and their application for nonenzymatic glucose sensing," Sensors and

Actuators B: Chemical, vol. 144, no. 1, pp. 220-225, 2010. https://doi.org/10.1016/j.snb.2009.09.067

[15] L. Tian and B. Liu, "Fabrication of CuO nanosheets modified Cu electrode and its excellent electrocatalytic performance towards glucose," Applied Surface Science, vol. 283, pp. 947-953, 2013. https://doi.org/10.1016/j.apsusc.2013.07.048

[16] X. Zhang et al., "Fabrication of CuO nanowalls on Cu substrate for a high performance enzyme-free glucose sensor," CrystEngComm, vol. 12, no. 4, pp. 1120-1126, 2010. https://doi.org/10.1039/B919749D

[17] T.-K. Huang et al., "Glucose sensing by electrochemically grown copper nanobelt electrode," Journal of Electroanalytical Chemistry, vol. 636, no. 1-2, pp. 123-127, 2009. https://doi.org/10.1016/j.jelechem.2009.08.011

[18] H. Siddiqui, M. Qureshi, and F. Z. Haque, "Surfactant assisted wet chemical synthesis of copper oxide (CuO) nanostructures and their spectroscopic analysis," Optik, vol. 127, no. 5, pp. 2740-2747, 2016. https://doi.org/10.1016/j.ijleo.2015.11.220

[19] S. K. Shaikh, S. I. Inamdar, V. V. Ganbavle, and K. Y. Rajpure, "Chemical bath deposited ZnO thin film based UV photoconductive detector," Journal of Alloys and Compounds, vol. 664, pp. 242-249, 2016. https://doi.org/10.1016/j.jallcom.2015.12.226

[20] R. Saadon and O. A. Azeez, "Chemical route to synthesis hierarchical ZnO thick films for sensor application," Energy Procedia, vol. 50, pp. 445-453, 2014. https://doi.org/10.1016/j.egypro.2014.06.054

[21] A. A. Aljubouri, A. D. Faisal, and W. K. Khalef, "Fabrication of temperature sensor based on copper oxide nanowires grown on titanium coated glass substrate," Materials Science-Poland, vol. 36, no. 3, pp. 460-468, 2018. https://doi.org/10.2478/msp-2018-0051

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