



Sensitive Glucose Biosensor Based on ZnO/CuO Nanorods

Haneen Ali Jasim¹ · Osama Abdul Azeez Dakhil¹

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Abstract

ZnO/CuO nanorods (NRs) were synthesized in two stages to fabricate highly sensitive, stabilized, and ultrafast nonenzymatic glucose biosensors. The first stage was a simple low-cost two-step anodization method, and the second stage involved modification with ZnO NRs by a chemical bath deposition method. The obtained NRs were analyzed by x-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy-dispersive x-ray spectroscopy, photoluminescence spectroscopy (PL), and electrical studies. The XRD patterns of pure CuO NRs show that all peaks may be attributed to the monoclinic phase of CuO. However, the XRD patterns of the ZnO/CuO heterojunctions show a hexagonal phase structure for the ZnO NRs. The ZnO hexagonal NRs are densely interwoven with CuO NRs with lengths of 200–300 nm, according to FE-SEM micrographs. The PL emission spectra were found to be in the 406 nm range. This corresponded to an increase in the energy gap to 3.1 eV. The I–V characteristics of the biosensors were measured and evaluated at various glucose concentrations to determine their sensitivity and repeatability. The modified electrode achieved a wide linear range from 0.5 mM to 2 mM with a very low limit of detection (LOD) of 0.11 μM . The developed sensor had high sensitivity of 2225.5 $\text{mA mM}^{-1} \text{cm}^{-2}$. This result confirms that the sensor has considerable potential as a high-performance nonenzymatic glucose sensor using a simple, low-cost, and novel sensor design.

Keywords Copper oxide (CuO) · nanorods (NRs) · anodization method · ZnO/CuO heterojunction · chemical bath deposition method (CBD) · glucose biosensors · I–V characteristics · sensitivity

Introduction

The ability to accurately detect glucose levels in the blood is critical for clinical diagnostics in diabetes management.^{1–3} Traditionally, enzyme-based techniques with excellent selectivity were used to measure glucose levels.^{4–8} However, these methods had limitations such as time-consuming enzyme purification and immobilization procedures, denatured stability, high cost, and restricted sensitivity due to indirect electron transfer.^{9,10} Therefore, the rational design of an enzyme-free approach with excellent sensitivity and stability is critical. Because it detects without using a direct-electron-transfer shuttle, the electrochemical nonenzymatic

approach, direct electrocatalytic detection of glucose, has attracted substantial attention in such conditions.^{11–16}

The electrocatalyst must meet the following criteria to fabricate an electrochemical nonenzymatic glucose sensor: (1) high electrocatalytic activity; (2) large surface area; (3) efficient electron transfer from electrocatalysts to the conductive substrate; (4) good selectivity; (5) high stability; and (6) good reproducibility.^{17,18} There have been many nanomaterials employed to fabricate electrochemically nonenzymatic glucose sensors in the past, but only a few have succeeded in meeting all of the stringent requirements.^{19,20} The electrocatalysts were prepared as nanoparticles and then immobilized on conductive substrates with the help of certain polymers, such as Nafion, in a typical electrochemical nonenzymatic sensor fabrication process, which inevitably increased the series resistance, blocked the catalytic active sites, and impeded electrolyte diffusion, resulting in significantly reduced electrocatalytic activity, poor reproducibility, and low stability.^{21,22} As a result, designing electrocatalysts that are smoothly coupled to the conductive substrate seems to be a promising approach.

✉ Haneen Ali Jasim
haneenali@uomustansiriyah.edu.iq

✉ Osama Abdul Azeez Dakhil
dr.osama@uomustansiriyah.edu.iq

¹ Department of Physics, College of Science, Mustansiriyah University, Baghdad, Iraq

Electrochemical anodization stands out among the synthesis processes because of its versatility, low cost, and inherently faultless interaction between the conductive metal substrate and the anodized metal oxide nanostructures.^{23–26} Because of their superior electrocatalytic activity and the possibility of in situ direct etching from the conductive copper substrate, which allows for direct electron transfer at low potential, anodized cupric oxide nanorods (CuO NRs) have been demonstrated as one of the best candidates for fabricating electrochemical nonenzymatic glucose sensors.

There have been attempts to make CuO nanorods or nanotubes on copper foil or sheets,^{27,28} but the two-dimensional surface of these substrates resulted in a limited catalytically active area, which hampered sensitivity. Because its biocompatibility and remarkable properties, such as low toxicity, high electron mobility, and ease of manufacture, have made it a popular choice, ZnO is a suitable electrode material for electrochemical glucose biosensors.^{29,30} At the physiological pH of 7.4, ZnO has isoelectric points (IEP) of 9.5, making it perfect for the adsorption of enzymes with low IEPs, such as GOx (IEP: 4.2–4.5). Diverse ZnO nanostructures with different morphologies, such as NRs,^{31–33} nanofilms,³⁴ nanosheets,³⁵ nano-combs,³⁶ and nanotubes,³⁷ are used in many studies on glucose sensors. Because it allows direct and quick electron transfer between the electrode substrate and enzyme,³⁸ the shape of the nanorods is perfect for enzyme immobilization. Nanorods grown directly on a substrate are also stable because the process is chemically and physically resistant.³⁹

Furthermore, the ZnO/CuO hetero-nanostructure is projected to improve performance and expand the range of applications for heterogeneous nanodevices. Some studies using CuO-ZnO nanocomposite to determine glucose using electrochemical methods were recently published. CuO nanoflowers/ZnO nanorods arrays were created by Soejima et al.⁴⁰ with a process of alkaline vapor oxidation. Thanks to the low-temperature one-step fabrication of the nanorod composite, the sensor performed well, with sensitivity of 1362.7A $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of less than 1 μA . Wu et al.⁴¹ developed a nonenzymatic glucose sensor using ZnO/CuO nanofibers. The linear range of the electrospinning nanofibers and sensor was up to 3.8 mM, with sensitivity of 467.5 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of 0.126 μA . Zhou et al.⁴² used the electrospinning procedure to fabricate ZnO/CuO hierarchical nanocomposites (HNCs). The sensitivity of the sensor on display was 3066.4 $\mu\text{A mM}^{-1} \text{cm}^{-2}$, with a linear range of 1.6 mM and a practical detection limit of 0.21 mM.

The objective of research, fabrication, and characterization of CuO nanorods (NRs) using anodization of copper

foil in an aqueous solution of potassium hydroxide (KOH) to generate certain NRs, this method was inspired by earlier research articles for the detection of an enzyme-free glucose sensor. Even though KOH is the most popular and cost-effective alkaline chemical, no reports on its use as a base for electrochemical copper anodization exist.

The chemical bath deposition (CBD) approach was used to generate a homogeneous growth of ZnO NRs on the CuO layer, resulting in a ZnO/CuO heterojunction. The nano-heterojunction has a unique feature: it may be made in one step without the need for a powerful reducing agent. In the detection of glucose, the constructed sensor demonstrated great long-term stability and high sensitivity with low detection limits.

Experimental

Materials

Cu foils (Sigma Aldrich, 99.99% purity) with a thickness of 250 μm (0.5 cm^2 of exposed geometric area) were cut into 1.2 \times 1.2 cm pieces. Potassium hydroxide (KOH, 99.5% purity) was obtained from Scharlau, Spain. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, purity 99.5%) was purchased from Scharlau, Spain, while hexamethylenetetramine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$, purity 99%) was obtained from HiMedia, India. Acetone, methanol, and ethanol (purity 99%, Scharlau, Spain) were also used. For electrochemical experiments, a glucose (Sigma Aldrich, 99.99%) solution with specific concentrations (0.5, 1, and 2 mM) was created.

Electrochemical Anodization of Cu Foil

Before anodization, the Cu foils were degreased for 10 min in acetone, methanol, and ethanol. After that, they were rinsed in distilled water (DW) and air-dried. The anodizing electrolyte was a 1 M KOH solution produced by dissolving 2.8 g of KOH in 50 mL of DW and stirring for 10 min. The electrochemical anodization was carried out in a handmade cylindrical Teflon cell. The cell features two electrodes: a Cu-foil working electrode and a graphite-sheet counter electrode. The electrode distance was established at 2 cm for all of the trials, and the two electrodes were immersed in the KOH solution. With an anodizing voltage of 6 V supplied to two electrodes, electrochemical anodization was carried out for a constant

time (30 min). After the reaction, a faint blue coating appeared on the Cu foil surface. The Cu foil was then removed from the solution and rinsed with DW before being dried and analyzed. CuO nanorods (NRs) were fabricated by heating a Cu(OH)₂ sample to 200 °C for 3 h. Finally, a dark brown CuO coating was produced on the surface of the Cu foil. Figure 1 shows the scheme of synthesis of the CuO NRs using the anodization method.

Synthesis of ZnO/CuO Junctions by Chemical Bath Deposition (CBD)

In 60 mL of DW, 0.01 M (0.17 g) Zn(NO₃)₂·6H₂O and 0.02 M (0.084 g) HMT were dissolved and agitated for

15 min to ensure complete dissolution. The pH of the solution was maintained at around 5. The CuO film that had been prepared using the anodization method was immersed vertically inside the CBD system cell for 2 h at a bath temperature of 90°C. The salts were removed from the deposited layer of ZnO/CuO by washing it with DW and drying it for 15 min on a hotplate at 50°C. After that, the film was annealed at 80°C for 2 h. Figure 2 presents the scheme of synthesis of ZnO/CuO heterojunctions using CBD.

Characterization

A variety of tools were employed to characterize the films that were prepared. The structural properties were

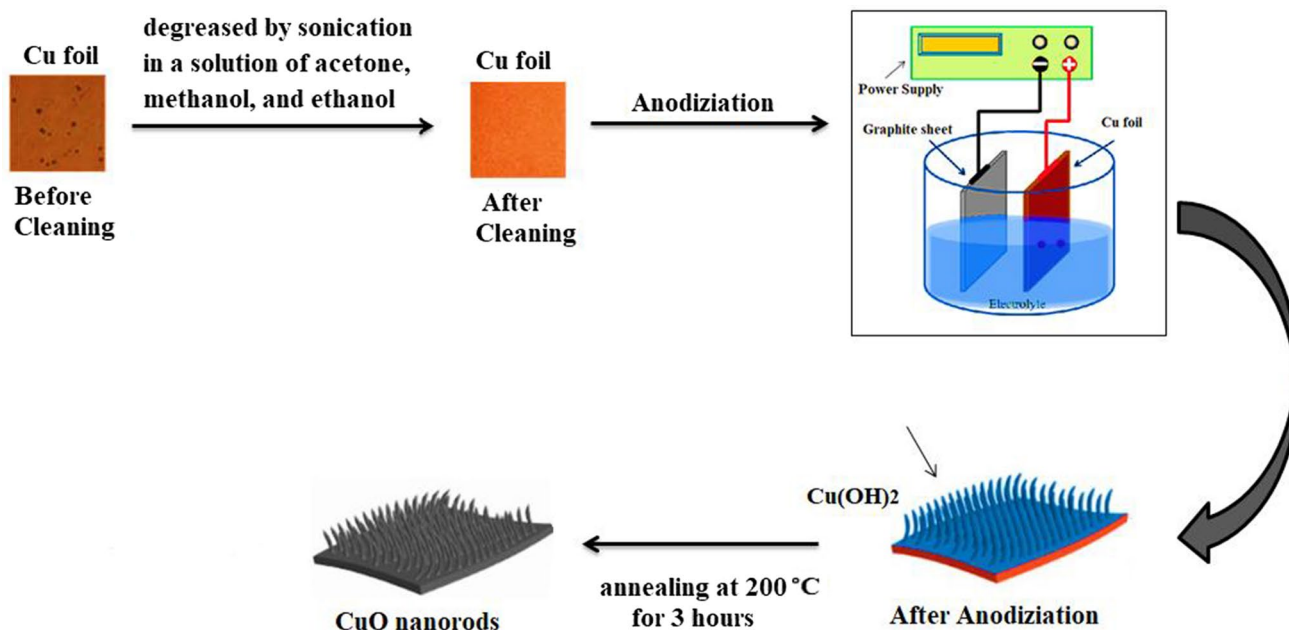


Fig. 1 Scheme of synthesis of CuO nanostructures via anodization method.

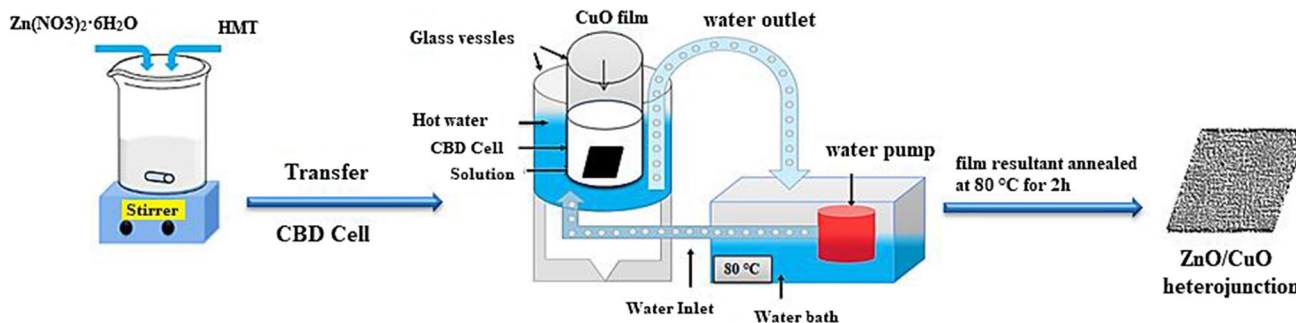


Fig. 2 Scheme of synthesis of ZnO/CuO heterojunction using chemical bath depositions setup.

investigated using x-ray diffraction (XRD) or field-emission scanning electron microscopy (FE-SEM). $\theta/2\theta$ scans with a Bragg range of 20° – 80° were performed with a PIXcel diffractometer equipped with a monochromatic $\text{CuK}\alpha$ x-ray source. A Zeiss SIGMA VP-FESEM was used to image the morphology of the formations. Measurements of photoluminescence (PL) can be used to describe semiconductor materials and features, and portray the specimen's energy structure. The 340 nm wavelength was used to excite the specimens and investigate transition energy at ambient temperature (Shimadzu RF-5301PC spectrofluorometer).

Electrochemical (Glucose Biosensor) Measurements

A Keithley 2430-C SourceMeter (SMU) instrument with a contact check/GPIB interface (1 kW pulse mode) was used to conduct the electrochemical experiments. All electrochemical tests were carried out utilizing a three-electrode apparatus [a working electrode (WE), a counter electrode (CE), and a reference electrode (RE) as indicated in Fig. 3]. The WE was the ZnO/CuO heterojunction, the CE was graphite, and the RE was Ag/AgCl. Cyclic voltammetry (CV) was used at a scan rate of 200 mVs^{-1} to characterize the electrodes in 0.1 M (NaOH) (supporting electrolyte) with various concentrations of glucose (0.5, 1, and 2) mM. ZnO/CuO chronoamperometric responses were measured at +0.1 V. The electrodes were kept at room temperature in the air.

Results and Discussion

The results of ZnO /CuO heterojunction can be described in this section.

X-ray Diffraction (XRD) Analyses

XRD patterns were used to identify the phase properties of the ZnO/CuO NRs as shown in Fig. 4. Except for the Cu (111) substrate, the diffraction peaks of the mixed ZnO/CuO heterojunction are exactly indexed to a mixture of monoclinic CuO (JCPDS 45-093948) and hexagonal ZnO (JCPDS 36-1451). Furthermore, in a ZnO/CuO heterojunction, the relative strength of the prominent diffraction peak of CuO is larger than that of ZnO. We discovered that ZnO NRs had three crystallinity maxima at 31.7° , 34.4° , and 47.4° , corresponding to crystallographic ZnO planes indexed by hkl Miller indices of (100), (002), and (102), respectively⁴³; and ZnO is associated with CuO

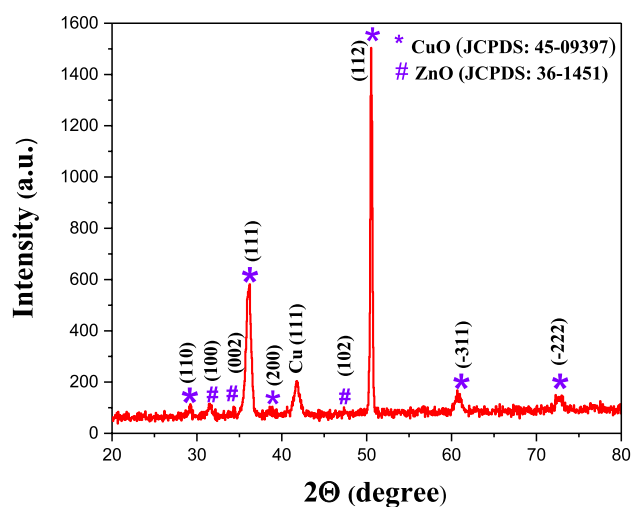


Fig. 4 XRD of ZnO/CuO heterojunction, peaks of CuO (JCPDS no.45-09397) are marked with “*” and ZnO (JCPDS no.36-1451) are marked with “#”.

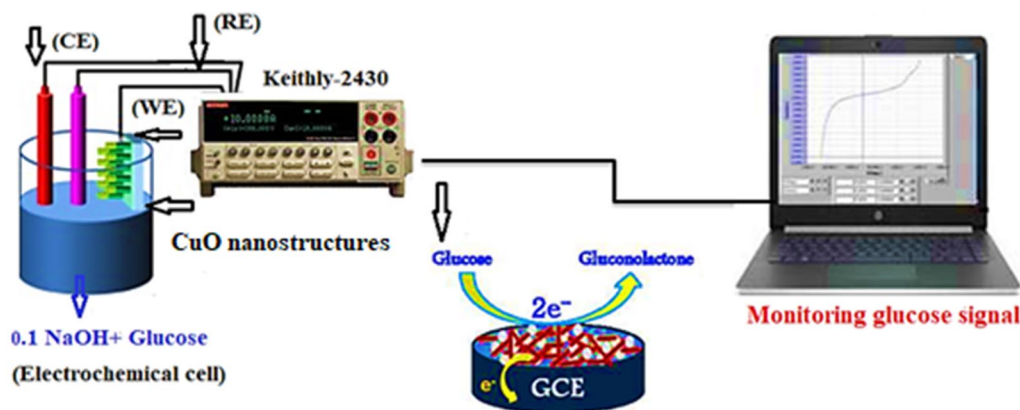


Fig. 3 Nonenzymatic glucose sensor based on ZnO/ CuO heterojunction.

(110), (111), (112), (200), (−311), and (−222) crystallographic planes.⁴⁴

The Debye–Scherrer formula⁴⁵ was used to calculate the average crystallite size (*D*) of the ZnO/CuO heterojunctions:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

As a result of the heat treatment process, the thick film suffers from microstrain and dislocations. The dislocation density (δ) is calculated using the equation⁴⁶:

$$\delta = \frac{1}{D^2} \tag{2}$$

The microstrain ϵ of the film was determined using the following formula:

Table I Structural parameters of ZnO/CuO heterojunction

Mat	2θ(°) Exp	2θ(°) JCPDS	(h k l)	d (Å)	FWHM (deg)	D (nm)	δ(10 ¹⁰) cm ⁻²	ε10 ⁻³
CuO	35.5	35.4	002	2.5	0.40	20	2.32	1.6
	51.1	51.1	112	1.7	0.15	28	2.92	0.5
	61.5	61.4	220	1.5	0.62	15	2.53	2.3
	72.5	72.4	311	1.3	0.32	30	1.06	1.1
	74.9	75.0	004	1.2	0.25	39	2.67	0.8
ZnO	31.7	31.7	100	2.7	0.17	17	4.28	0.6
	34.5	34.4	002	2.5	0.16	20	3.73	0.7
	47.6	47.6	102	1.9	0.42	25	4.29	1.6



Fig. 5 FE-SEM surface images of ZnO/CuO heterojunction (a, b), cross-section image (c).

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

Table I shows the crystallite size (D), dislocation density (δ), and microstrain (ε) of ZnO/CuO hetero-nano-structures calculated from the XRD patterns. The crystallite sizes were estimated to be about 15–25 nm.

Field-Emission Scanning Electron Microscopy (FE-SEM) Morphological Study

Figure 5a and b show FE-SEM images of the ZnO/CuO NRs at various magnifications. As can be observed, the Cu substrate has been evenly covered with a dense layer of ZnO/CuO NRs. Rough morphology was observed for the ZnO/CuO heterojunctions because of surface decoration with ZnO (Fig. 5b). It can be seen that the ZnO hexagonal NRs are highly interconnected with CuO NRs, and represent a more active surface area for catalysis. ZnO was found to be uniform and to have grown perpendicularly over the CuO layer. The ZnO/CuO NRs displayed an average diameter of around 200–300 nm. The thickness of the ZnO/CuO films is between 120 and 496 nm, according to the cross-sectional image in Fig. 5c.

The energy-dispersive X-ray (EDX) spectrum (Fig. 6) showed three elements, namely O, Cu, and Zn, indicating that the weight percentages of Cu and Zn, which are 62.8% and 28.2%, respectively, varied significantly. This shows that the stems of the NRs are composed of a mix of CuO and ZnO, with CuO being the most abundant.

Photoluminescence (PL) Measurements

The PL spectra of the ZnO/CuO NR heterojunctions were measured at room temperature using an excitation wavelength of 320 nm and revealed a clear peak at 406 nm as shown in Fig. 7, indicating a more effective absorbing material for sensor applications.⁴⁷ By application of Planck's equation

$$(E_g = hc/\lambda) \quad (4)$$

E_g of ZnO/CuO nano-heterojunctions which are equal to 3.1 eV.

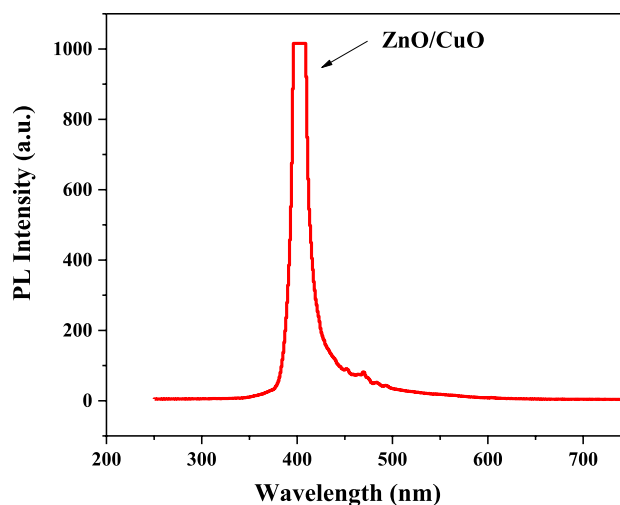


Fig. 7 PL spectra of ZnO/CuO NRs heterojunction.

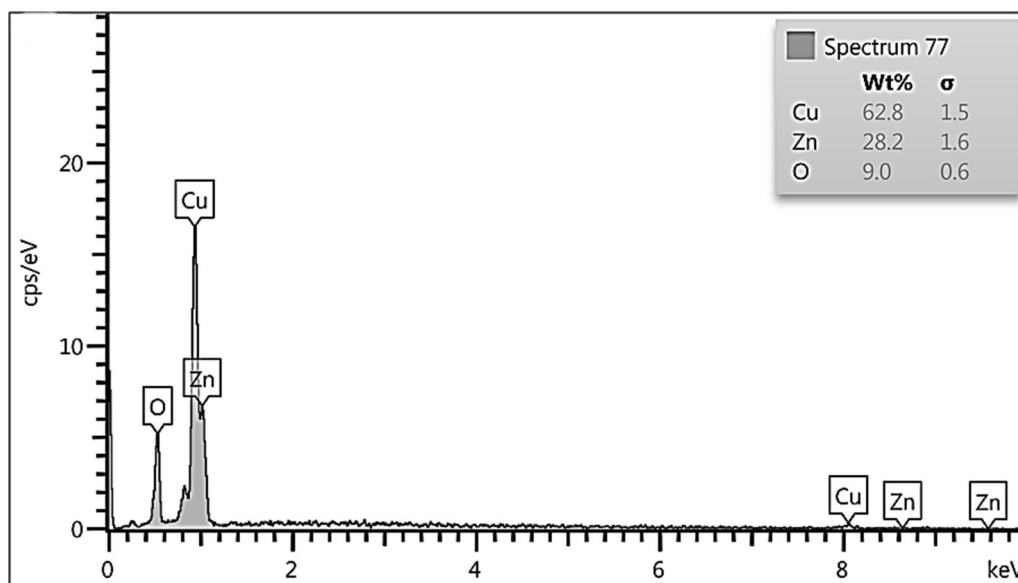


Fig. 6 EDX analysis of ZnO/CuO heterojunction.

Electrochemical Characterization of the Glucose Biosensor

The most important parameters of the proposed biosensor were measured and characterized to assess its functionality and efficacy in performing high-precision measurements. By studying and interpreting the electrical response of the glucose biosensor, the electrical responsiveness of electrode sensors can be improved by examining their I–V characteristics, and an estimate of their sensitivity can thereby be obtained. I–V characteristic curves are generally used to electrically parameterize and mathematically characterize the behavior of various components of a biosensor within an electronic circuit.

In the absence of glucose or in the presence of varying glucose concentrations in the range of 0.5–2 mM dissolved in 0.1 M sodium hydroxide (NaOH) solution, the

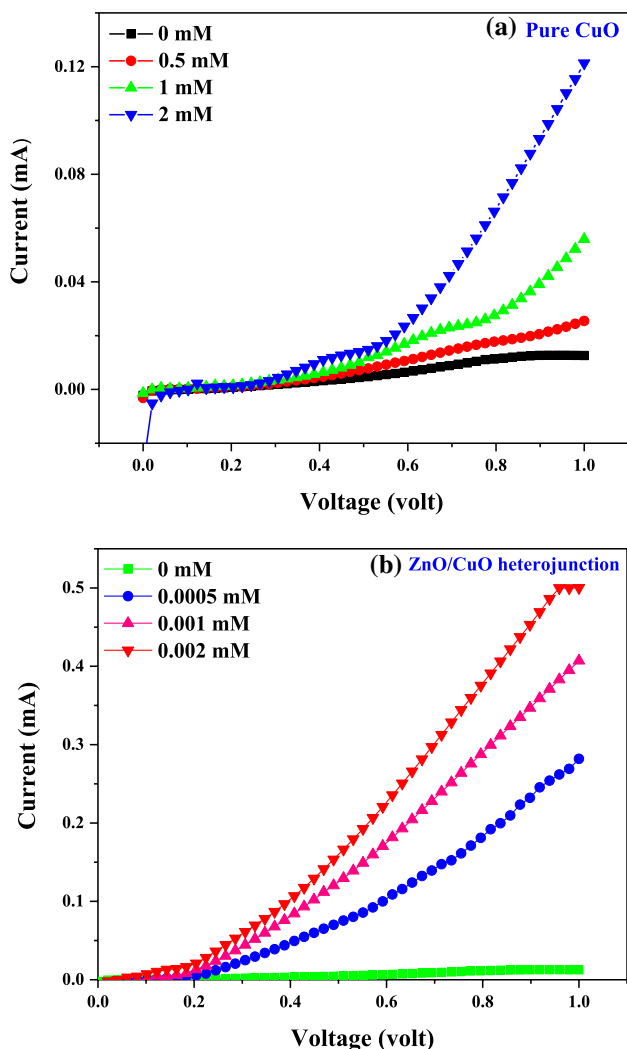


Fig. 8 I–V characteristics of (a) CuO and (b) ZnO/CuO heterojunctions with different glucose concentrations.

current response of biosensors can be investigated as a function of the applied voltage (0–1 V), as seen in Fig. 8a and b. The modified ZnO-on-CuO layer clearly shows the effective conductivity of the electrode, demonstrating that NaOH (aq) is the best solution for safeguarding and improving the conductivity of the system. In an alkaline environment, the reaction of ZnO/CuO is as follows:

- (1) $CuO + OH^- \rightarrow CuOOH + e^-$ or $CuO + H_2O + 2OH^- \rightarrow Cu(OH)_4^- + e^-$
- (2) $Cu(III) + Glucose + e^- \rightarrow Gluconolactone + Cu(II)$
- (3) $Gluconolactone \rightarrow Gluconic\ acid\ (hydrolysis)$

The results indicate that the modification of the CuO with ZnO NRs effectively improves the oxidizing ability of the CuO, owing to the numerous ZnO NRs growing on the large surface area of the CuO electrode; this indicates surface control of the electrochemical process.

The maximum current (and hence the maximum glucose biosensor response) was obtained when the direct test was performed for the 2 mM glucose concentration, indicated by the maximum current of 0.5 V attained in a ZnO/CuO heterojunction compared to pure CuO. In addition, as shown in Fig. 9, the response is linear, and the conductivity may be estimated using the slope of the linear relationship. The regular behavior of the sensor could be explained by the establishment of a short circuit between the granular nanostructure following temporal relaxation, which leads to a rapid increase in the overall current throughout the sensor. The reaction increases as the duration of the test increases for most of the glucose concentrations examined.

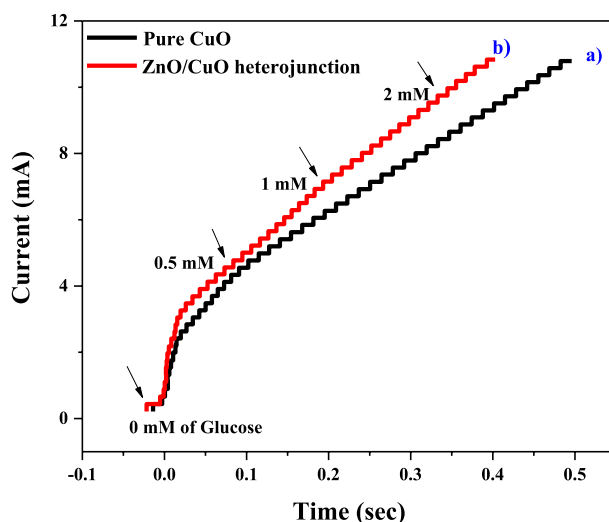


Fig. 9 I–t curves of (a) pure CuO and (b) ZnO/CuO heterojunctions with increasing glucose concentration.

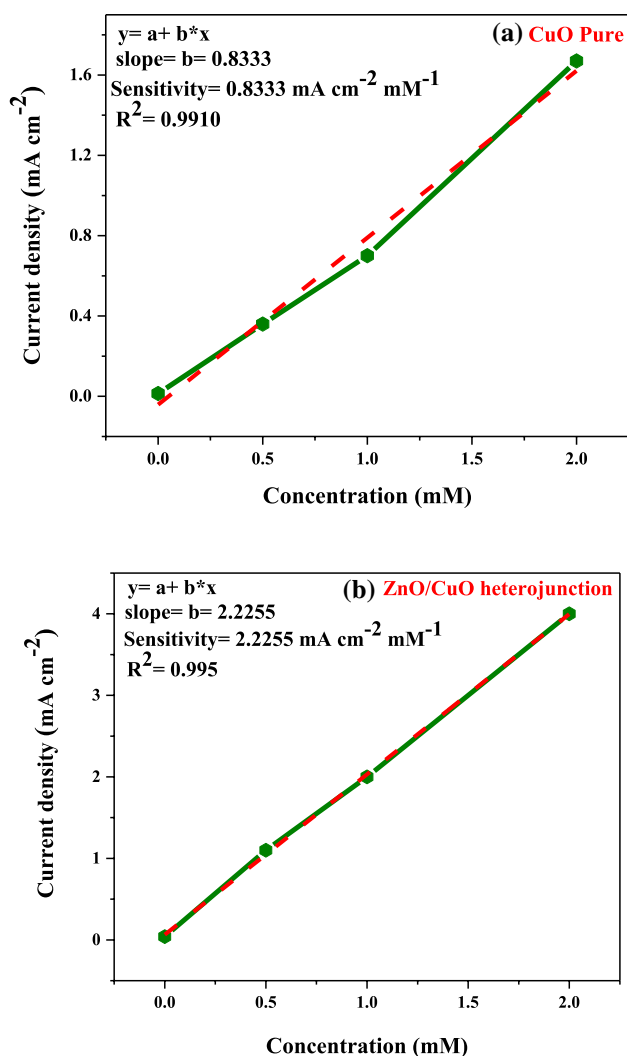


Fig. 10 Electrode response and a calibration curve of (a) CuO and (b) ZnO/CuO heterojunction with the addition of glucose (0.5, 1, and 2) mM.

The growth of ZnO perpendicularly onto the CuO layer is expected to improve the glucose detection sensitivity. Because ZnO is biocompatible, this might be due to an improved chemical interaction with the biomolecules that are being studied. Figure 9 shows the sensitivity of CuO and ZnO/CuO heterojunctions for glucose detection without the use of enzymes. The current density of the CuO biosensor shows a linear dependence on glucose content, with a correlation coefficient $R^2 = 0.9910$. The current density of the ZnO/CuO biosensor likewise follows a quadratic pattern as a function of glucose level with a significant correlation coefficient ($R^2 = 0.995$) as seen in Fig. 10a and b. The analytical performance of other enzyme-free glucose sensors utilizing various CuO and corresponding support metal/oxide nanostructures were compared with the present work in terms of sensitivity, limit of detection, and linear working range; the comparisons are summarized in Table II.

Conclusions

Highly sensitive ZnO/CuO NR sensors were successfully synthesized using the CBD/anodization method. The films were characterized using a variety of techniques. After modification, the CuO material exhibited good electrocatalytic performance when used as an electrode to detect glucose. During measurements of glucose using a three-electrode cell, the ZnO/CuO heterojunction sensor achieved excellent glucose sensitivity of $2225.5 \mu\text{A cm}^{-2} \text{ Mm}^{-1}$, with a detection limit of $0.1 \mu\text{M}$ and a linear range of up to 2 mM, which is greater than that of pure CuO. The results show that the morphology of CuO NRs prepared using the anodization method plays an important role in improving the effectiveness of the electrode for glucose sensing without the use of mediators. The novel glucose biosensor proposed here has several advantages such as being enzyme-free, simple to fabricate, low-cost, and easy to preserve on a long-term basis. Thus, it can feasibly be used for future clinical applications.

Table II Comparison of various free-enzymatic electrochemical sensors based on CuO electrodes

Electrode	Methods	Sensitivity $\mu\text{A cm}^{-2} \text{ Mm}^{-1}$	Linear Range (mM)	Lower limit of Detection (LOD) μM	Ref.
CuO/ZnO/FTO	Solution Process	1142	Up to 7	0.0139	48
Ag NPs/CuO NFs-ITO	Electrospinning	1347	0.0005–0.55	0.0073	49
Mesoporous CuO	Nanocasting method	26.6	0.1–3	0.23	50
CuO NRs	Anodization	833.3	0.5–2	0.2	This work
ZnO/CuO	Chemical bath deposition	2225.5	0.5–2	0.1	This work

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Author's Contribution The experimental work of this study and the used illustrations was carried out by H.A.J. Manuscript drafting, interpretation of results, and final review was done by O.A.A.D. Initial drafting of the manuscript was done by both authors.

Data Availability The article contains all of the data that back up the study's findings (and any supplementary files).

Conflict of interest The authors declare that they have no conflict of interest.

Human and Animal Rights The authors declare that the paper does not involve any human study subjects, and as such, no consent is required. The authors also testify that this is an original article that has not been submitted elsewhere in any way or language.

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