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Carbon Nanotube Fiber-Based Flexible Microelectrode for Electrochemical Glucose Sensors

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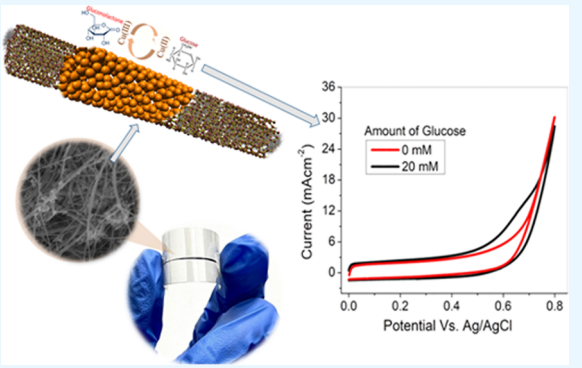
ABSTRACT: Electrochemical sensors are gaining significant demand for real-time monitoring of health-related parameters such as temperature, heart rate, and blood glucose level. A fiber-like microelectrode composed of copper oxide-modified carbon nanotubes (CuO@CNTFs) has been developed as a flexible and wearable glucose sensor with remarkable catalytic activity. The unidimensional structure of CNT fibers displayed efficient conductivity with enhanced mechanical strength, which makes these fibers far superior as compared to other fibrous-like materials. Copper oxide (CuO) nanoparticles were deposited over the surface of CNT fibers by a binder-free facile electrodeposition approach followed by thermal treatment that enhanced the performance of non-enzymatic glucose sensors. Scanning electron microscopy and energy-dispersive X-ray analysis confirmed the successful deposition of CuO nanoparticles over the fiber surface. Amperometric and voltammetric studies of fiber-based microelectrodes (CuO@CNTFs) toward glucose sensing showed an excellent sensitivity of ∼3000 μA/mM cm^2, a low detection limit of 1.4 μM, and a wide linear range of up to 13 mM. The superior performance of the microelectrode is attributed to the synergistic effect of the electrocatalytic activity of CuO nanoparticles and the excellent conductivity of CNT fibers. A lower charge transfer resistance value obtained via electrochemical impedance spectroscopy (EIS) also demonstrated the superior electrode performance. This work demonstrates a facile approach for developing CNT fiber-based microelectrodes as a promising solution for flexible and disposable non-enzymatic glucose sensors.



1. INTRODUCTION

A glucose sensor is an essential tool for monitoring the physiological level of blood sugar in diabetic patients.[1] Glucose concentration can be assessed in biological fluids through saliva,[2] ocular fluid,[3] sweat,[4] urine,[5] and interstitial fluid[6] for multiple purposes.[7] To determine the blood sugar level without adverse side effects, a variety of methods have been adopted including surface plasmon resonance,[8] chromatography,[9] calorimetry,[10] electrochemiluminescence,[11] and spectroscopy.[12] However, these methods have certain limitations such as shorter life span, high cost, less sensitivity, and chemical interferences.[13−15] Among different developed methods, the electrochemical approach has gained enormous attention because of low cost, ease of use, fast processing, long-term stability, and high selectivity and sensitivity.[16−18] The monitoring of glucose via electrochemical method has widely been explored with enzyme-based (glucose oxidase, GOx) glucose sensors to achieve high sensitivity.[19,20] However, enzymatic glucose sensors involve the complex immobilization procedure and have shorter life span with poor stability. Moreover, the catalytic activity of enzymes is also susceptible to pH change, temperature, and humidity which hindered the practical implementation of these glucose sensors. To overcome these limitations, enzyme-free glucose sensors have compelled the researchers to explore efficient and stable materials. Recently, the noble metals such as gold,[21] platinum,[22] and palladium[23] and their alloys[24,25] immobilized on different electrode surfaces are being employed to boost the electrocatalytic activity of sensors toward glucose detection. Copper-based materials are widely explored for the fabrication of non-enzymatic glucose sensors due to their high conductivity and low cost.[26−29] As copper has the ability to change its oxidation state, therefore, copper and its derivatives such as CuO,[30,31] Cu(OH)$_2$,[32,33] and CuS[34,35] with micro- to nanostructures and different dimensions have been employed as non-enzymatic glucose sensors.

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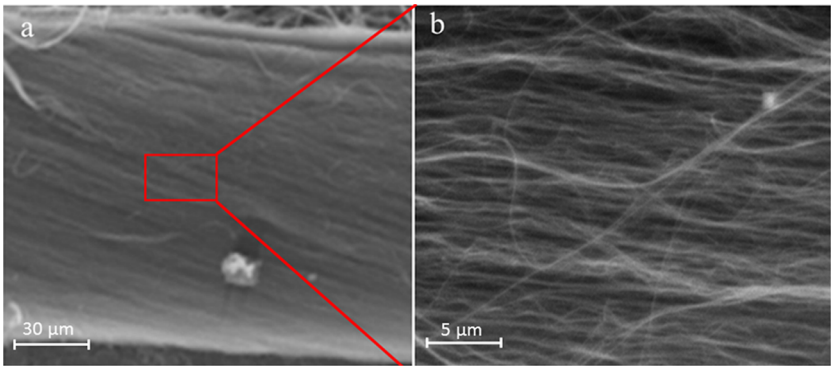

Figure 1. SEM images of bare CNT fibers at (a) lower and (b) higher resolution.

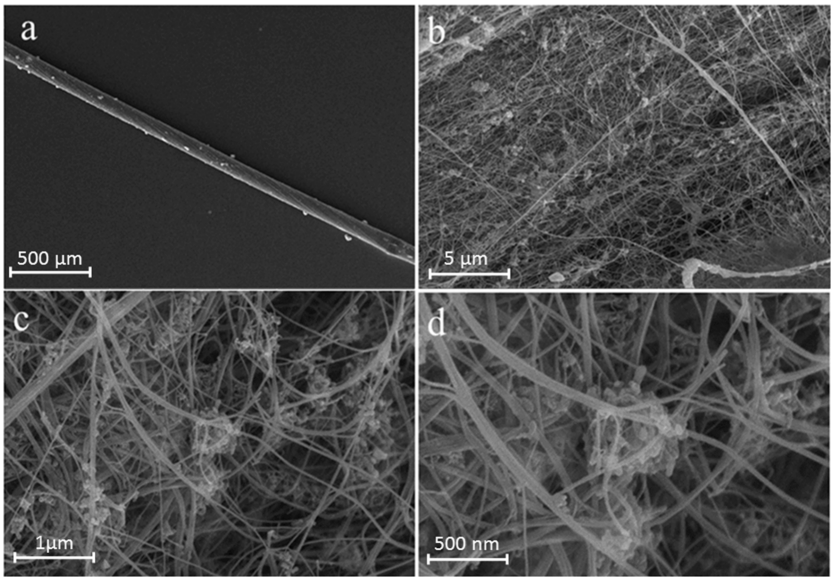

Figure 2. SEM images of CuO nanoparticle-modified CNT fibers with (a) 500 μm-, (b) 5 μm-, (c) 1 μm-, and (d) 500 nm-scale resolution.

Carbon-based materials including graphene,[36] carbon fibers,[37,38] carbon nanotubes,[39] and carbon cloth[40] have been widely used as a new class of electroactive supports toward biosensors. Dilmac et al. worked to improve the sensitivity using functionalized graphene oxide which showed a sensitivity of ~20 μA/mM cm^2 and a low detection limit of 6 μM with a linear range from 0.02 to 4.48 mM.[41] Another effort with the CNT−graphene hybrid material (CNTs/G) has been made by Badhulika et al. for electrochemical glucose detection, and it exhibited a sensitivity of 11.06 μA/mM cm^2 with a linear range of 1−7 mM.[42] Kangkamano and co-workers replaced graphene with chitosan cryogel using CNTs to improve sensitivity, and their composites yielded a sensitivity of 27.7 μA/mM cm^2 with the linear range from 0.001 to 1 mM.[43] The f-SWCNTs/Si/SiO_2 wafers were further investigated by Gonzalez et al., and very low sensitivity (5 nA/mM) with a detection limit of 5 mM was reported.[44] CNT-based materials, no doubt, are promising for electrochemical biosensors; however, their profound electrode fabrication with the binder approach (Nafion) limits their adaptability.

Herein, we have introduced the structured CNTs in the form of highly dense fibers modified with CuO nanoparticles for efficient electrochemical glucose sensors. Well-aligned helical arrangements and the fibrous carbon conjugated system of CNT fibers with a large surface area improve the electrical conductivity.[45−47] Compared to carbon fibers and polymer composite fibers, CNT fibers show a high bending stiffness of 1.96 × 10^{-7} Pa[48] and improved relaxation behavior.[49] Furthermore, a facile binder-free fabrication method has been adopted to design a fiber-shaped microelectrode (CuO@CNTFs). Electrochemically deposited CuO@CNTFs demonstrated a remarkably higher electrocatalytic activity with a high sensitivity of ~3000 μA/mM cm^2, a detection limit of 1.4 μM, and a wider linear range of up to 13 mM. The highest mechanical strength, superior electrocatalytic properties, cost effectiveness, and flexible nature could make these materials as promising electrodes for wearable biosensors in future.

2. EXPERIMENTAL SECTION

2.1. Electrodeposition of CuO at CNT Fibers. CNT fibers were prepared via the wet chemical process by the Prof. Huisheng Peng (Fudan University China) group and used as received. The electrodeposition of CuO over CNT fibers was carried out in a glass cell with a three-electrode system using an electrochemical chronoamperometric (CA) method. In the first step, 100 mM KCl and 10 mM $CuCl_2$ were used as a precursor solution in 20 mL of deionized water. A constant potential of −0.40 V was applied for 20 s, with CNT fibers (attached on a glass substrate) as the working electrode. The platinum wire and Ag/AgCl electrode served as the counter

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and reference electrode, respectively. After electrodeposition, the CNT fiber was removed from the glass substrate and rinsed with distilled water thoroughly, to remove the additional ions. The modified fiber was then calcined at a temperature of 200 °C for 3 h.

2.2. Electrochemical Measurements. Cyclic voltammetry (CV) and CA methods were performed using the Gamry Reference 3000 potentiostat/galvanostat/ZRA. All electrochemical experiments were carried out in a three-electrode glass cell containing 0.1 M KOH aqueous as an electrolyte. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively. For electro-oxidation behavior of glucose, CV measurements were performed with an anodic potential window of 0 to 0.8 V versus Ag/AgCl reference electrode. For CA measurements, constant stirring was carried out, and the potential within the faradic region of 0.6 V was applied to the electrolyte solution with glucose, while the change in current with respect to glucose concentration was monitored after the intervals of 30 s. Electrochemical impedance spectroscopy (EIS) was carried out with the AC frequencies from 0.1 Hz to 1 MHz and a DC potential of 0.6 V.

3. RESULTS AND DISCUSSION

3.1. Material Characterization. Scanning electron microscopy (SEM) was used to examine the morphology of bare and CuO@CNTFs. Figure 1 shows densely populated CNT fibers with each entity providing a higher mechanical strength and having a large number of charge carrier pathways. As compared to the powder form of CNTs, their aligned structure (shown in Figure 1) has a beneficial impact of providing a smooth flow of charges. The powder form of CNTs has many interfaces which hinder the electrochemical charge transfer process, whereas one-dimensional CNTs with a constraint path provide a better flow of charges to increase the overall performance of electrodes.

SEM images of CuO-modified CNT fibers at different magnifications are shown in Figure 2a–d. Figure 2a illustrates the successful deposition of CuO nanoparticles over the surface of CNT fibers, and the nature of the metals plays the most crucial role in the electrodeposition, leading to differential nucleation, growth kinetics, size, and number of nanoparticles per unit area. pH of the electrolyte solution also determines the uniformity of the nanoparticles deposited over the electrode surface, and the KCl solution can also affect the morphology of Cu nanoparticles. Specifically, the presence of the higher number of Cl^- ions reduced the probability of collision between the Cu^{+2} ions, leading to the control nucleation of Cu nanoparticles during electrodeposition. Figure 2b–d represents their in-depth analysis at different magnifications. The size of CuO nanoparticles was found to be in the range of 70–100 nm. These deposited nanoparticles will provide the electrocatalytic sites for glucose oxidation, while the CNT fiber (single entity) yields a path for the internal flow of charges.

Successful deposition of the CuO over the CNT fiber was further confirmed by EDX analysis. Elemental mapping distribution of the modified CNT fiber has been shown in Figure 3. A portion of the modified electrode (CuO@CNTFs) of the SEM image in Figure 3a was considered for the elemental mapping which represents the uniform distribution of the copper and oxygen in Figure 3b,c, respectively.

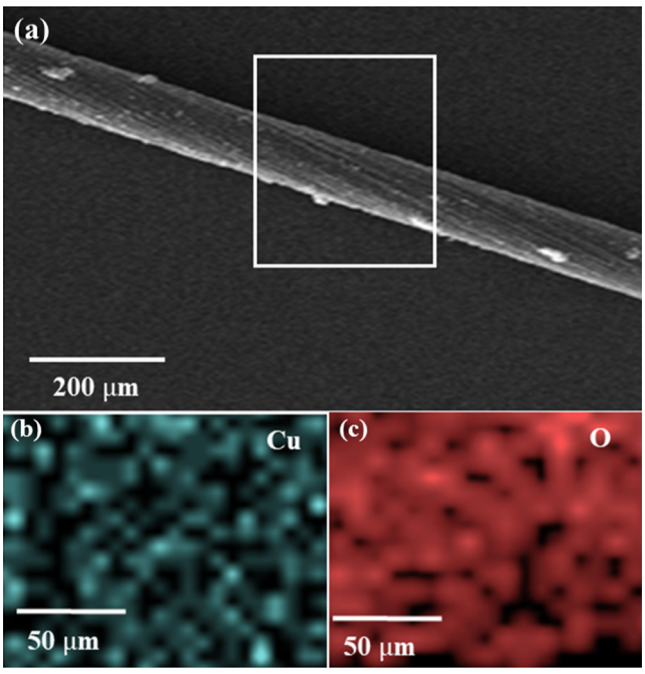

Figure 3. (a) SEM image of CuO@CNTFs and its corresponding (b,c) energy-dispersive spectra for the elemental X-ray mapping.

3.2. Electrocatalytic Oxidation of Glucose. CV was used to check the electrochemical behavior of fabricated electrodes for glucose sensing application. In this respect, Figure 4 illustrates the comparison of the electrocatalytic activity of modified CuO@CNTFs-based electrodes in the absence and presence of glucose in basic medium, whereas the unmodified CNT fiber-based electrode did not exhibit appreciable activity. The CuO@CNTFs did not produce any oxidation peak in 0.1 M KOH solution in the absence of glucose. However, the addition of glucose (20 mM) to the solution initiated the faradaic current at 0.51 V followed by an oxidation peak at 0.6 V, which can be attributed to the oxidation of glucose at the modified CNT fiber. The absence of a cathodic peak in the voltammogram demonstrates an entire irreversibility of the glucose oxidation reaction occurring on the electrode surface.

According to the reported mechanism of glucose oxidation at CuO, Cu(III) acts as an electron transfer medium to oxidize glucose into gluconolactone.[50] The basic media also plays an important role here in which hydroxyl ions convert CuO into an active form, that is, CuO(OH), which electrochemically oxidizes glucose to gluconolactone. Figure 4b demonstrates the electrocatalytic performance evaluation of bare and CuO@CNTFs electrodes, in the presence of glucose (20 mM) with 0.l M KOH as the electrolyte at a scan rate of 50 mV/s. The CuO@CNTFs electrode displayed a significantly higher current for the glucose oxidation as compared to the bare electrode. This higher value of oxidation current is attributed to the cumulative effect of electrocatalytic activity of CuO nanoparticles and larger surface area of CNT fibers.

The results of linear sweep voltammetry (LSV) and CV obtained at different concentrations of glucose at a fixed scan rate of 50 mV/s in 0.1 M KOH solution are shown in Figure 5a–d. In Figure 5a, the addition of increasing concentrations of glucose in the electrolyte solution (0.1 M KOH) made the anodic peak current increase, which illustrates the fast electro-

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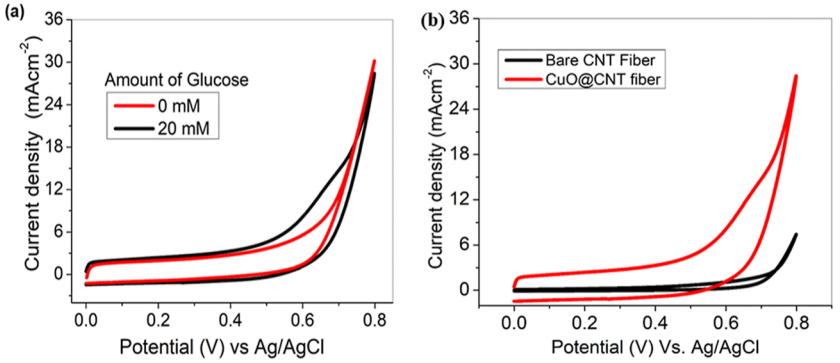

Figure 4. Cyclic voltammograms of the (a) modified fiber electrode with and without glucose and (b) bare and modified fiber electrode in the presence of 20 mM glucose, in 0.1 M KOH at 50 mV/s.

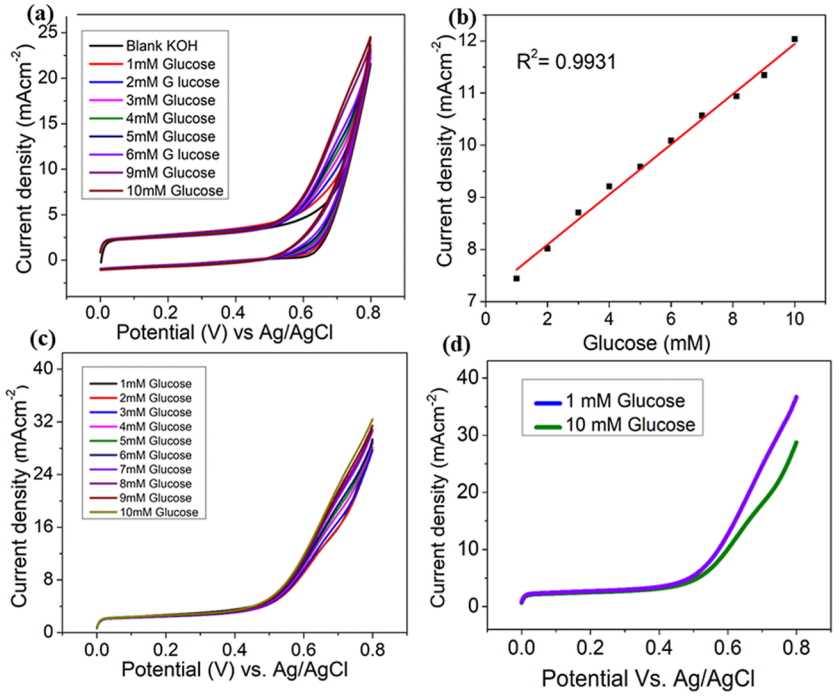

Figure 5. (a) CV for different concentrations of glucose (0−10 mM), (b) its calibration curve, (c) LSV for different concentrations of glucose, and (d) LSV with the lowest and the highest concentration, in 0.1 M KOH for CuO@CNTFs as the working electrode at a scan rate of 50 mV/s.

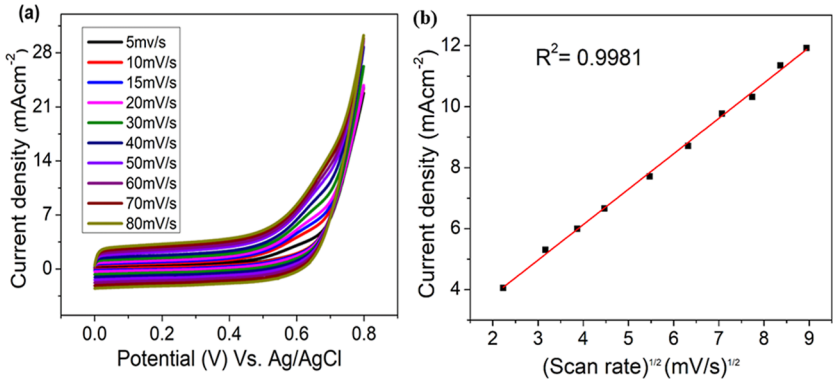

Figure 6. (a) CV of CuO@CNTFs in 0.1 M KOH at different scan rates and (b) its calibration curve for anodic peak current as a function of square root of scan rate.

oxidation of glucose attributed to enhanced catalytic properties of the CuO nanoparticles. The anodic peak current (Figure 5c) in LSV was also enhanced with the gradual increase in glucose concentration, which further supported the findings of CV. As shown in Figure 5a, the peak potential shifts to a more positive zone, which illustrates the slight change in electrolyte solution

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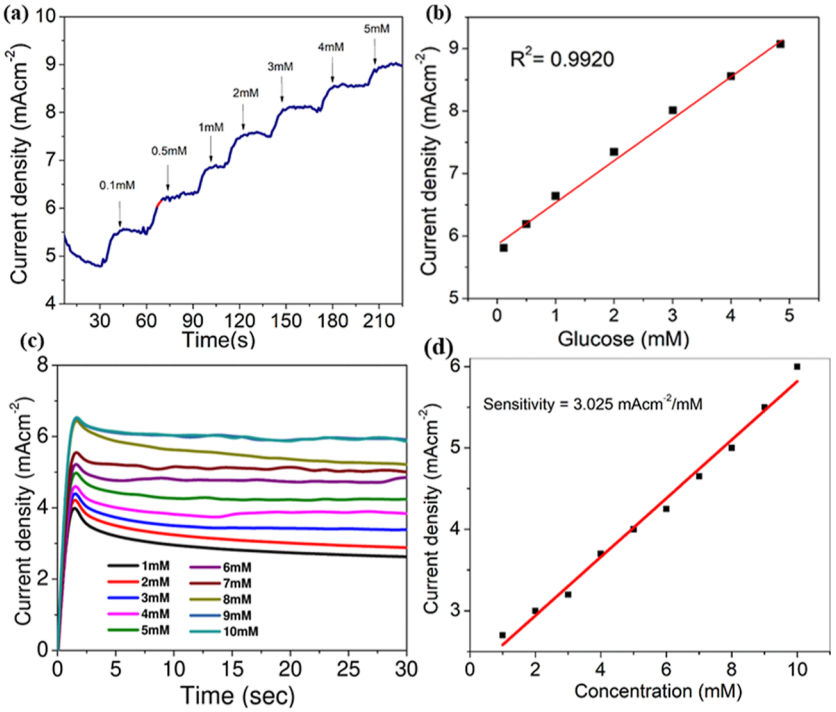

Figure 7. (a) Stair behavior of the amperometric curve of the modified (CuO@CNTFs) fiber electrode with the addition of glucose at 0.6 V vs Ag/AgCl and (b) its respective calibration curve. (c) Straight amperometric behavior for the different concentrations of glucose and (d) corresponding calibration curve.

pH. Moreover, a gradual increase in anodic peak current with increasing concentration of glucose is witnessed along with positive shift in anodic potential, indicating the absence of fouling consequence at the CuO@CNTFs. The linearity of the calibration curve shown in Figure 5b, derived from the CV curves, depicts an excellent sensitivity of the electrode toward a glucose concentration of up to 10 mM. Figure 5d represents the LSV with lowest concentration and the highest concentration, which displays a consistent increase in current with increasing glucose concentration.

In order to explore the mass transfer phenomenon at the CuO@CNTFs electrode, voltammograms were recorded at different scan rates ranging from 5 to 80 mV/s, under the same conditions of the analyte and electrolyte (20 mM glucose and 0.1 M KOH). A gradual increase in the scan rate resulted in the higher oxidation current accordingly, as shown in Figure 6a. It also elaborated that electrochemical oxidation of glucose took place at 0.6 V, and the process is further accelerated by the redox couple, that is, Cu-II ⇌ Cu-III. The respective calibration plot in Figure 6b shows that anodic peak current is directly proportional to the square root of scan rate. Moreover, Figure 6a also illustrates that by increasing the scan rate, the anodic peak potential (E_p) shifts toward a more positive value that reflects the process on the electrode surface as a diffusion-limiting process. Mechanistically, CuO in the presence of hydroxyl ions (alkaline medium) shows the following redox chemical process during the transition between Cu(II) ⇌ Cu(III) species.[51]

$$CuO + OH^- \rightarrow Cu(OH)_2 + H_2O$$

$$Cu(OH)_2 + OH^- \rightarrow CuO(OH) + H_2O$$

$$CuO(OH) + \text{glucose} \rightarrow CuO(OH)_2 + \text{gluconolactone}$$

Electrochemical double-layer capacitance (C_{dl}) also played a key role, and it has been calculated for the bare and modified electrodes (CuO@CNTFs) within the non-faradaic region (voltage), as shown in Figure S1 in the Supporting Information. Double-layer capacitance for the modified carbon nanotube fiber has been found to be 35.02 mA cm^{-2} which is far superior as compared to the bare electrode (18.64 μA cm^{-2}). Higher double layer capacitance attributes with larger electrochemical surface area which boosted the activity of modified electrode.

3.3. Amperometric Response of CuO@CNTFs. In order to explore the sensitivity of the fabricated electrode (CuO@CNTFs) as a flexible and wearable glucose sensor, its amperometric response was evaluated at a constant potential of 0.6 V with successive addition of 0.1 mM glucose in the presence of 0.1 M KOH after an interval of 30 s. All amperometric measurements were performed under constant solution stirring to ensure proper mixing of glucose with the electrolyte. A staircase incremental behavior for the current was observed by the successive addition of glucose, with a response time of almost 6 s, as shown in Figure 7a. A calibration straight line derived from the staircase behavior shown in Figure 7b represents that the modified fiber electrode has a good linear range. The current−time response increased immediately after the addition of glucose and reached ≈95% of the steady-state value within a time of 5 s (Figure 7c). The CuO@CNTFs fiber-based microelectrode has a broad linear response of up to 10 mM concentration having a correlation coefficient of 0.9940 and provides an optimum sensitivity of 3.025 mA/cm^2 mM, as shown in Figure 7c,d. The limit of detection (LoD) for the sensor was also calculated using the same calibration straight line of Figure 7d with the help of standard deviation (σ) and slope (m), and it was found to be 1.4 μM. High sensitivity, lower LoD, and better linear range of

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Table 1. Comparison of Electrochemical Performance of CuO@CNTFs with Some of the Reported Sensors in the Literature

electrode material	sensitivity (μA/mM cm^2)	LoD (μM)	linear range	ref.
βMnO_2/CFF	1650.6	1.9	up to 4.5 mM	52
AuNP@CuONW/Cu_2O/CF	1.619	0.9	2.8−2000 μM	53
CFP/GWs/Cu_2O		0.21	0.5−5166 μM	54
CF-BDD	388 nA/mM		3.75−50 mM	55
Au-Pt coated/Nf	165.83	268	15−30 mM	56
CuSn/CNFs	291.4	0.08	0.1−9000 μM	57
CuO/PANI-NF/FTO	1359	0.24	0.25 μM−4.6 mM	58
Cu/Cu_2O/SCF	28,071	2.46	up to 7.8 mM	59
Ni-MOF/RGO/CF	852	0.6	6 μM−2.09 mM	60
NiAu/CP	4035.4	0.2	1 μM−3000 μM	61
nylon fiber/PPy MIP		0.12 ± 0.01 mM	0.1−1.0 mM	62
CuO/NF/GCE	483.0	200 nM	0.10−10.85 mM	63
Co_3O_4@CuO/CC	5405	0.38		64
3D Ni−Fe/CFP	7.90	0.031	0.05 μM−0.2 mM	65
Ni−MoO_4/CNF	301.77	50 nM	0.0003−4.5 mM	66
PANI/CNTF	52.91	2	1.56−50 mM	67
poly(*o*-toluidine) NF/metal composite	37	0.027	up to 30 mM	68
CNT fiber	0.308	0.38	0.0015−0.098 mM	69
CuO@CNTFs	**~3000**	**1.4**	**up to13 mM**	**this work**

the fabricated electrodes (unique structure-modified CNT fibers) make them a promising alternative for the commercially available glucose sensors. Comparative data of our work with different electrode materials presently used in glucose sensing applications have been given in Table 1. The results revealed that synergistic effects of CuO and CNT fibers led to superior electrocatalytic activity and excellent conductivity.

3.4. Stability Test. The stability of the fabricated electrode has been evaluated via a comparison of the 1st and 15th CV cycle, as shown in Figure 8. CVs for the CuO@CNTFs

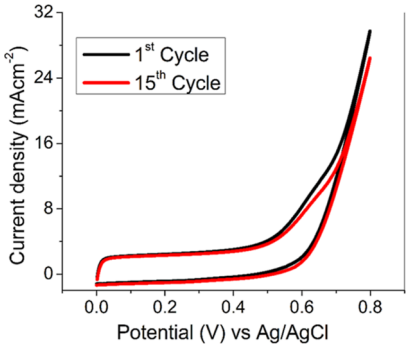

Figure 8. Comparison of the 1st and 15th CV cycle of the CuO@CNTFs microelectrode in 20 mM glucose at a scan rate of 50 mV/s.

electrode were recorded in 0.1 M KOH solution, with 20 mM concentration of glucose, for 15 cycles. The anodic peak current of the 15th cycle is found to be nearly the same as that of the first cycle, which indicates that no observable change has occurred on the electrode surface by glucose electro-oxidation, thus exhibiting good stability.

3.5. Electrochemical Impedance Spectroscopy. The charge transfer resistance (R_{ct}) behavior of the modified electrode (CuO@CNTFs) as compared to the bare CNT fiber was evaluated by EIS. The Nyquist plots showing a small arc in the high-frequency region are related to a charge transfer-controlled process, whereas the straight line in a low-frequency region corresponds to the diffusion-controlled process. Moreover, in the high-frequency region, the intercept at the *x*-axis gives the value of equivalent series resistance (R_e) of the electrode. The Nyquist plot is shown in Figure 9 with curve

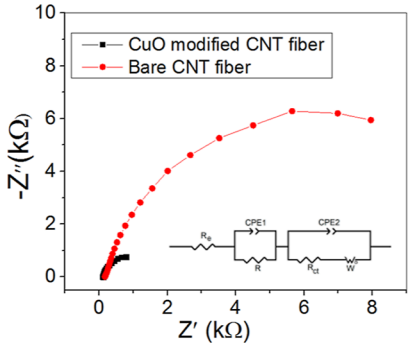

Figure 9. Nyquist plot of modified (CuO@CNTFs) and bare CNT fiber microelectrodes in 0.1 M KOH in the presence of 20 mM glucose in the frequency range of 0.1 Hz−1 MHz with an applied DC voltage of 0.6 V.

fitting display as the inset. The curve fitting includes the circuit element solution resistance (R_e), charge transfer resistance (R_{ct}), constant phase elements CPE1 and CPE2, and Warburg impedance.[70] Warburg impedance is due to diffusion of ions from the bulk electrolyte to the electrode, and it appears in a straight line at low frequency. The semicircle at high frequency represents the electron transfer-limited process, and its diameter is equivalent to R_{ct}, which is related to the charge transfer processes undergone at the electrode/electrolyte interface. Both modified and bare CNT fiber microelectrodes exhibited almost the same values of solution resistance (~100 Ω). R_{ct} for CuO@CNTFs calculated form the smaller semicircle was found to be ~1 kΩ which is too large for the unmodified CNT fiber electrode (~8 kΩ). Lower charge transfer resistance for modified CNTFs verified and confirmed the outcomes presumed from the voltammetry and amperometric studies.

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4. CONCLUSIONS

In summary, a flexible microelectrode composed of highly dense CNT fibers with a diameter of ∼100 μm and a few centimeters in length, decorated with CuO nanoparticles, has been introduced as an efficient electrochemical glucose sensor. A simple electrodeposition process has been adopted to incorporate the CuO nanoparticles over the surface of the CNT-based microelectrode. The composite (CuO@CNTFs) microelectrode showed excellent performance toward electrochemical glucose sensing in basic media with high sensitivity (∼3000 μA/mM cm^2), low detection limit (1.4 μM), and wide linear range (up to 13 mM). The excellent performance of flexible microelectrode might be attributed to the synergistic effect of the electrocatalytic activity of CuO nanoparticles and the increased conductivity of highly dense aligned carbon nanotube fibers. In a nutshell, the CNT fiber-based microelectrodes can provide a way of developing wearable biosensors to analyze the glucose from human biofluids.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c06594.

Cyclic voltammetry and double-layer capacitance (PDF)

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Author Contributions

S.M. and A.A. generated the idea for the utilization of CNT fibers as glucose sensors and carried out all experiments for electrode fabrication. M.J., S.N., M.A.A., and A.H. provided their assistance for electrochemical analysis (CV, LSV, EIS, and Chrono). A.R.A., A.N., M.I., and N.A. helped with material characterization (SEM analysis). Validation, visualization, and funding acquisition, while M.A. and A.A. provided their input to refine and write up the manuscript.

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Notes

The authors declare no competing financial interest.

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