Deciphering Highly Sensitive Non-Enzymatic Glucose Sensor Based on Nanoscale CuO/PEDOT-MoS2 Electrodes in Chronoamperometry

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The present work demonstrates fabrication of a non-enzymatic glucose sensor based on CuO nanoparticles deposited over poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer infiltrated with nanoscale MoS2. Structural, morphological and elemental analyses of the fabricated sensor electrodes were performed via different characterization techniques like X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), elemental dispersive X-ray spectroscopy (EDX), and Fourier transform infra-red spectroscopy (FT-IR). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies of the hybrid nanoelectrode (CuO/PEDOT-MoS2) exhibited better redox activity and electron transfer in the CuO/PEDOT and CuO only systems. Accordingly, the electrochemical parameters of all the systems were determined and compared at large. The CuO/PEDOT-MoS2 hybrid electrode system offered a significant enhancement in the electroactive area (∼1.47 cm²) and rate constant (0.76 s⁻¹) upon oxidizing glucose into gluconic acid. In the CV responses, an augmented activity was monitored at +0.6 V which was considered as the dc bias potential in the chronoamperometric experiment for detecting glucose suitably. The sensor electrode yielded a low LOD of 0.046 μM and with a sensitivity magnitude as high as 829 μA mM⁻¹ cm⁻² over a wide linear range, between 30 μM to 1.06 mM of glucose concentration. Deployment of organic-inorganic nanomaterial based non-enzymatic sensor would find immense scope in non-clinical diagnostics and pharmaceutical applications for fast, convenient and smart sensing.

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Monitoring of glucose level in human body has become an essential and most common diagnosis in medical emergencies as well as in most of the routine check-ups. Undoubtedly, glucose sensors are believed to be one of the most demanding and widely used commercial sensors available at present time. Low cost, accurate measurement, higher sensitivity, and fast response time are some of the important parameters that describe a good sensor design.¹⁻³ In fact, the urge for a fast and accurate determination of glucose level in human body leads to the development of high precision glucose sensors. Although enzymatic glucose sensor offers very selective and accurate response, upon dealing with enzymatic sensors various parameters viz. temperature, pH, humidity must be suitably maintained along with extra measures for their storage, processing, and handling for a better performance of these biomolecule-immobilized sensors.⁴⁻⁶ Naturally, people look for alternative yet attractive strategy like deploying non-enzymatic glucose sensors due to their lower cost, easy processing and storage, faster response, and long lifespan. It was revealed that various metals in their oxide forms exhibit good electrocatalytic behaviour and could oxidize glucose directly e.g., cobalt,⁷ nickel,⁸ palladium,⁹ vanadium,¹⁰ copper,¹¹ molybdenum¹² etc. Their glucose oxidizing capability makes them potential candidates for selective and accurate detection of glucose present in the solution, or serum in very low concentration.¹³ Furthermore, close examination of these electroactive materials with conducting polymer (CP),¹⁴ graphene and its derivatives,¹⁵ MXenes,¹⁶ carbon nanotubes (CNTs),¹⁷ two dimensional (2D) transition metal dichalcogenides (TMDs),¹⁸ and other noble metal nanoparticles,²⁰⁻²¹ can not only enhance their electroactivity feature but also synergistically upgrade glucose sensing ability. Besides, inclusion of these CPs and 2D layered structures in definite proportions can not only increase the surface area of the electrodes for better incorporation of the electroactive materials but also enhances its conductivity and charge transfer kinetics.²²-

Abundant in nature, noble metal copper (Cu) is a d-block candidate being preferred due to its low toxicity, biocompatibility, viability, as well as good electrocatalytic activity. Whereas CuO, an oxidized form of Cu effectively oxidizes glucose to gluconic acid and can be a potential candidate for non-enzymatic electrochemical detection of glucose.²³ Rahim et al. employed ceramic material (SiO2/C-graphite) decorated CuO nanostructure for the detection of glucose, offering a detection limit of 0.06 μmol l⁻¹⁻¹, a sensitivity of 472 μA mmol⁻¹ l⁻¹ cm⁻² and having a linear range of 0.02–20.0 mmol l⁻¹⁻¹.²⁴ The sensor described offers not only good selectivity, but also better chemical stability and could detect glucose from human blood serum efficiently. Moreover, PEDOT is a widely used conducting polymer in the field of electrochemical sensors due to its good conductivity (100 S.cm⁻¹), water stability, electrochemical stability, ease in synthesis and surface functionalization capability.²⁵⁻²⁷ In case of non-enzymatic sensor, PEDOT acts as a conductive matrix for better incorporation/deposition of electroactive metal nanoparticles (NP) which result in a better redox activity, enhanced charge transfer kinetics and improved sensitivity of the composite system towards detection of analytes. Amizadeh et al. have developed a non-enzymatic sensor based on PEDOT:PSS/CuO/MWCNT matrix that predicts a very good sensitivity (663.2 μAmM⁻¹ cm⁻²), catalytic activity, as well as a wider linear range (up to 10 mM) but with a low detection limit of 0.23 mM. Again, incorporation of layered 2D nanostructures can improve the electrochemical activity of the system taking advantage of their synergistic effects.²⁸ Molybdenum disulphide (MoS2), being a TMD candidate has a layered structure, which consists of covalently bound S-Mo-S tri-layers separated by van der Waals bonding. Now-a-days, 2D MoS2 nanosystems have drawn significant attention as a support electrode material in the field of non-enzymatic sensing due to its graphene like structure but with tunable band gap, high catalytic activity, electrical conductivity and active surface area. It has been reported that, in most of the layered materials, the electron transfer rate is higher over the surfaces of the edges rather than the basal surfaces.²⁹ The larger interlayer spacing (~0.62 nm) of MoS2 can offer a better contact between the sites of the edges and the electrolyte that results in a higher electrochemical performance of the electrode.²⁹ In addition, composite of MoS2 with conducting polymer exhibits not only a synergistic increment in conductivity,
CuII is oxidized to cationic radical by way of depriving an electron as: dipole-dipole interactions between successive MoS2 sheets gets der Waal bond which basically exists in the form of intermolecular electrocatalytic process of copper (Cu) reduction (CuIII polymer is shown in Fig. 1. Also, the glucose oxidation by the forming PEDOT and consequently, PEDOT-MoS2 composite.

Figure 1. Schematic diagram of the glucose oxidation mechanism by as synthesized CuO/PEDOT-MoS2/ITO electrode.

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Physical characterization tools and techniques.—To exploit structural and crystallographic properties of the synthesized electrodes, XRD patterns were acquired on a BRUKER AXS (D8 FOCUS) diffractometer equipped with CuKα monochromatic radiation (λ = 1.5406 Å). On the other hand, Fourier transform infra-red (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 instrument. Scanning electron microscopy (SEM, JEOL-JSM-6390LV), field emission scanning electron microscopy (FE-SEM, JSM-7200F) and energy dispersive X-ray (EDX) spectroscopy techniques were employed to exploit the morphology and elemental constituents of the samples under study. All electrochemical measurements as regards our experiments such as, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronocoulometry were performed in GAMRY instrument (INTERFACE 1010E Potentiostat/Galvanostat/ZRA) via a three-electrode arrangement using Ag/AgCl as reference electrode, platinum wire as a counter (auxiliary) electrode and the as-synthesized specimen as working electrode. The XRD and FT-IR studies of the electrochemically derived composite electrodes are highlighted in the Supplementary (Fig. S1).

Results and Discussion

Morphological features and elemental analyses.—In Figs. 2a –2e, each set essentially characterize two FE-SEM micrographs captured at lower and higher magnifications along with the EDX spectrum shown in the right. The inner shell electronic absorption spectra of the EDX response confirm the elemental constituents present in our samples. The FE-SEM micrograph shows a fairly uniform distribution of electrodeposited CuO NPs with partial agglomeration over the ITO substrate in the form of clusters (Fig. 2a). The EDX response shows the K-shell absorption spectra of Cu and O that confirms the formation of CuO in the film. The presence of a lower atomic % of O with respect to Cu would indicate that the outer layer of the NPs experience effective oxidation while the inner atoms remain intact/unoxidized. Also, it is possible that creation of oxygen vacancies/point defects in the synthesized NPs may lead to higher atomic % of Cu. The homogeneous distribution of electropolymerised PEDOT over the electrode is shown in Fig. 2b and from the magnified image one can clearly see the PEDOT grains later, CuO is electrodeposited over the PEDOT-MoS2 yielding CuO/PEDOT-MoS2 film casted over the ITO substrate. Moreover, the details of synthesis of electrodeposited CuO/ITO and CuO/ PEDOT/ITO electrodes can be found in the Supplementary section (available online at stacks.iop.org/ECSA/1/046504/mmedia).
covering the whole substrate, thereby resulting in the increase in surface texture. These conductive PEDOT grains not only increase the surface roughness of the solid film but also provide a larger surface area for the electrodeposition of CuO NPs. The surface coverage of the PEDOT film by metal oxide NPs where the formation of polymer grain clusters can be seen over the surface, is shown in Fig. 2c. In case of CuO/PEDOT, these electrodeposited metal NPs act as a binder to wrap the polymer grains together to form larger clusters. The deposition of the metal NPs over the conductive surface of large grain cluster of the polymer is also shown. Here, rather than agglomeration of CuO NPs as observed in the case of ITO substrate, they seem uniformly deposited over the PEDOT. The presence of all the elemental constituents of PEDOT and CuO/PEDOT can be traced in the EDX spectra, as shown in Figs. 2b and 2c. The FE-SEM image of MoS$_2$ incorporated PEDOT film can be found in Fig. 2d. Here, we expect electropolymerization of EDOT in presence of exfoliated MoS$_2$ sheets, leading to the formation of the polymer film by entrapping the MoS$_2$ sheets of

Figure 2. FESEM micrograph of (a) CuO, (b) PEDOT, (c) CuO/PEDOT, (d) PEDOT-MoS$_2$, and (e) CuO/PEDOT-MoS$_2$ along with the EDX spectra shown on the right-hand side.
different areal dimension in and over the PEDOT matrix. The incorporation of MoS$_2$ in the PEDOT matrix is also evident from the L-shell absorption spectra of Mo found in the EDX pattern of Fig. 2d. The rough surfaces of the PEDOT-MoS$_2$ films substantiates the effective deposition of metal NPs over the polymer-TMDc composite system. Herein, we can clearly view the MoS$_2$ sheets dispersed in the polymer along with CuO NPs over the surface of the composite film. The appearance of C, O, Cu, S and Mo inner shell absorption spectra in the EDX of Fig. 2e substantiates the presence of relevant elements in the CuO/PEDOT-MoS$_2$ composite system.

**Electrochemical studies.**—Cyclic voltammetry (CV) of the fabricated Electrodes was performed at a scan rate of 20 mV s$^{-1}$ across the potential window of −0.2 to +0.7 V. As can be noticed, with the use of PEDOT polymer the current response of the CV-cycle increases substantially as compared to the mere electrodeposited CuO NPs (Fig. 3a). As mentioned earlier, the conducting polymer matrix not only provides a high surface area for the electrodeposition of CuO but also enhances the electron transfer mechanism by hopping of carriers in addition to doping/de-doping of electrolytic ions in the polymer matrix at varying potential. To be mentioned, incorporation of MoS$_2$ nanosheets in the PEDOT host matrix has further augmented the current response of CV as can be seen in the figure. MoS$_2$ being a conductive 2D structure is believed to enhance the electron transfer synergistically by way of shortening the diffusion path length for the ion transport in the composite CuO/PEDOT-MoS$_2$.

Impedance spectra for all the three systems under study were acquired in the frequency range of 0.1 Hz−1 MHz at an applied dc bias voltage of 0 V w.r.t. the reference as shown in Fig. 3b. The long tail that is observed at a lower frequency region for CuO electrode indicates high Warburg impedance ($W_z$) due to carrier diffusion followed by weak capacitive feature. The magnified portion of the EIS plot at a higher frequency region and the fitted spectra with corresponding equivalent circuit is inserted in Fig. 3b. The fitted EIS spectra for all the three systems are provided separately in Supplementary section, Fig. S2. In fact, all the three systems follow the similar Randle equivalent circuit as shown in the figure. To be mentioned, in the equivalent circuit, $R_1$ is series resistance that appears due to resistance imposed by obstruction to ion flow in the electrolytic solution. $R_2$ is essentially charge transfer resistance ($R_{ct}$) between the electrode-electrolyte interface obtained directly from the diameter of the suppressed semicircle in the fitted curve. The $R_{ct}$ value drops from 38.93 Ω to as low as 7.31 Ω after incorporation of MoS$_2$ in the PEDOT matrix as compared to CuO only electrode thereby indicating significant interfacial charge transfer in the whole CuO/PEDOT-MoS$_2$ system. The parameter $C_2$ stands for the electric double layer capacitance ($C_{dl}$) which gets lowered with the inclusion of MoS$_2$ in the PEDOT host, indicating efficient faradic charge transfer at the electrode-electrolyte interface. Additionally, $C_3$ is the augmented capacitance that may arise due to the development of interfaces/interlayers in between CuO-PEDOT and MoS$_2$-PEDOT polymer composites. Moreover, the Warburg impedance is due to diffusion of the redox species towards the working electrode in the electrolytic solution. As can be found from Table I, the parameter $W_z$ experiences a declining trend as for the CuO/PEDOT-MoS$_2$ composite electrode and would therefore indicate a better mobility of the redox species.

Glucose oxidation with the synthesized electrodes could be visualized from the CV responses in presence and absence of glucose in the solution. The CV was run under the potential window of −0.2 to +0.7 volt at a scan rate of 20 mV s$^{-1}$ in 0.1 M NaOH solution in Figs. 4a–4c. In absence of glucose, there is no peak or hump appeared in the CV responses. But a proportional increases in the oxidation current can be monitored upon varying the glucose concentration from 0.1 mM to 0.5 mM in the solution. In the figures we can see that after addition of glucose, the oxidation current starts increasing beyond +0.3 V potential followed by appearance of an oxidation hump around +0.4 V and this current hike remains constant up to +0.6 V. Upon comparing the CV responses of the three systems, a synergistically enhancement in current could be obtained in favour of CuO/PEDOT-MoS$_2$. Without doubt, it offers a potentially more efficient electrode candidate for non-enzymatic sensing of glucose. In addition, the CV responses of Figs. 4a–4c exhibited an enhanced, stabilized current over +0.6 V for our electrodes in 0.1 M NaOH solution as the glucose concentration was varied unevenly. This is the reason why this voltage was considered w.r.t. reference as a fixed dc bias potential in the amperometric (I−t) feature, depicted in Fig. 4d. Different concentration of glucose was added to observe the activity of CuO/PEDOT-MoS$_2$ sensor in 0.1 M NaOH solution at a dc bias potential of +0.6 V and a significant enhancement in amperometric current could be obtained in the I−t response after every addition of glucose in the solution.

**Estimation of electrochemical parameters.**—To understand the electroactivity of the electrode materials, we need to estimate several important electrochemical parameters, like diffusion coefficient of the redox species towards the electrode, electroactive area of the

![](https://i.imgur.com/7J5z5J.png)

Figure 3. (a) Cyclic voltammetry (CV) response, and (b) electrochemical impedance spectroscopy (EIS) plots of CuO only, CuO/PEDOT and CuO/PEDOT-MoS$_2$ electrodes. A magnified view of the segment in -Z’ vs Z’ plot as well as equivalent RC circuit are also shown as inset in (b).
In this section, first we calculate the electroactive area of our specimen electrodes for oxidation of glucose in 0.1 M NaOH solution by using Randle-Sevcik equation. To do this, we require the value of diffusion coefficient \( D \) of glucose towards the surface of the synthesized electrode systems. The determination of \( D \) can be ascertained through the Cottrell equation which gives a relation between the amperometric current \( I_t \) vs time \( t \) as given below:

\[
I_t = nFD^{1/2}C\pi^{-1/2}A_o t^{-1/2},
\]

where, \( n (=1) \) is number of electron transfer takes place, \( F \) (=96485 coulomb/mol) is Faraday’s constant, \( C (=0.2 \text{ mM}) \) is concentration of glucose, \( A_o (=0.5 \text{ cm}^2) \) is geometrical area of the electrode, and \( D \) is diffusion coefficient. The slope, \( \zeta \) of the obtained \( I_t \) vs \( t^{-1/2} \) plot can be expressed as,

\[
\zeta = nFD^{1/2}C\pi^{-1/2}A_o
\]

or,

\[
D = \frac{\pi \zeta^2}{n^2F^2A_o^2C^2}.
\]

The single step chronoamperometric response of the synthesized electrodes were taken for 30 s in presence and absence of glucose in the solution, as shown in Fig. 5a. After addition of 0.2 mM glucose, the amperometric current response increases (represented by scattered red lines) as shown in Fig. 5a. The \( I_t \) vs \( t^{-1/2} \) could be plotted from the dynamic amperometric response obtained after the addition of 0.2 mM glucose where the slope of the linear-fit is proportional to the diffusion coefficient \( D \) as mentioned in Eq. 2 (Fig. 5b). In the present case, the calculated values of diffusion coefficients are \( 1.7 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}, 9.1 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}, 4.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \) for the CuO only, CuO/PEDOT and CuO/PEDOT-MoS\(_2\); respectively.

The CV response of these electrode systems were acquired by varying the scan rates, from 10 mV s\(^{-1}\) to 130 mV s\(^{-1}\) and considering 0.1 M NaOH as the electrolyte and 0.2 mM glucose as

| Electrode       | \( R_1 \) (\( \Omega \)) | \( R_2 \) (\( \Omega \)) | \( C_2 \times 10^{-6} \) (F) | \( C_3 \times 10^{-6} \) (F) | \( W \times 10^{-6} \) (S.s\(^{1/2}\)) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| CuO            | 24.16         | 38.93          | 20.23          | 61.44          | 54.95          |
| CuO/PEDOT      | 34.31         | 14.66          | 25.08          | 1078           | 369.80         |
| CuO/PEDOT-MoS\(_2\) | 41.14 | 7.31           | 18.98          | 1379           | 437.16         |

Table I. EIS derived physical parameters obtained after proper fitting.
Figure 5. (a) Amperometric (I-t) response in presence and absence of 0.2 mM glucose, (b) Cottrell plot (I vs t^{-1/2}), (c) current vs voltage response with scan rate variation in cyclic voltammetry (CV), (d) Randle-Sevcik (i_p vs ν^{1/2}) plot, (e) i_p vs scan rate (ν) plot, (f) E_p vs log | (scan rate) | plot; for (I) CuO only, (II) CuO/PEDOT, and (III) CuO/PEDOT-MoS_2 electrode systems.
redox entity (Fig. 5c). Here, the current in the anodic region increases on increasing the scan rate due to the oxidation of glucose at that potential range.\textsuperscript{35,36} But appearance of the cathodic peak is due to the reduction of Cu (III) to Cu (II) itself, as glucose oxidation is an irreversible process. In accordance with the Randle-Sevcik proposition the anodic peak current is plotted with respect to square root of the scan rate, as can be found in Fig. 5d. The fitted line exhibits a good linearity and would indicate adequate diffusion-controlled charge transfer process.\textsuperscript{17} From Randle-Sevcik equation, we have the relation between the peak current ($i_p$) vs the scan rate ($ν$) as, \[ i_p = \frac{n^2 F^2 C_i A y}{4 R T} \] And at room temperature ($T = 300 \text{ K}$), we would obtain, \[ i_p = \frac{2.69 \times 10^5 \times n^{3/2} A^{1/2} C y^{1/2}}{R T}; \] where \( n \) is no. of electron transfer, \( A \) takes place in the redox process, \( R \) stands for universal gas constant in SI units while other symbols have their usual meaning. Also, we can write electroactive area, \( A = \frac{2.69 \times 10^5 \times n^{3/2} C y^{1/2}}{i_p} \). From the slope ($η_2$) of the curve $i_p$ vs square root of scan rate ($ν^{1/2}$) shown in Fig. 5d, the electroactive area for the CuO, CuO/PEDOT and CuO/PEDOT-MoS\textsubscript{2} are estimated as, 0.81 cm\textsuperscript{2}, 1.10 cm\textsuperscript{2} and 1.47 cm\textsuperscript{2}; respectively. The area was believed to be covered by all the oxidative active sites throughout the surface of the synthesized electrode. On the other hand, for calculation of the concentration of surface ionic species/glucose over the electrode systems, we employed Brown-Anson model that offers a relation between peak current ($i_p$) and the scan rate ($ν$) as given below:\textsuperscript{39} \[ i_p = n^2 F^2 C_i A y \nu^{1/2}, \] \[ \eta = \frac{n^2 F^2 C_i A y}{4 R T} \] Apparently, $i_p$ vs $ν$ gives a good linear relationship, as depicted in Fig. 5e. To be mentioned, the slope, $η_2$ of this linear fit is directly proportional to the surface concentration of ionic species, $C_i$. Thus, \[ C_i = \frac{4 R T}{n^2 F^2 \eta} \] and we obtain, \( C_1 = 1.64 \times 10^{-9} \text{ mol cm}^{-2}, 3.67 \times 10^{-9} \text{ mol cm}^{-2} \) and \( 2.47 \times 10^{-9} \text{ mol cm}^{-2} \) for the CuO, CuO/PEDOT and CuO/PEDOT-MoS\textsubscript{2}; respectively. Lastly, Laviron’s equations for the irreversible process are employed to study the electron transfer kinetics of the electrode for oxidation of glucose as follows:\textsuperscript{39} \[ E_p = E'_0 - \frac{2.3 R T}{\alpha n F} \log \frac{RTk}{\alpha n F} + \frac{2.3 R T}{\alpha n F} \log \nu \] In the above equation, $E_p$ is the peak redox potential, $E'_0$ is formal standard potential, $α$ is transfer coefficient and $k$ is heterogeneous reaction rate constant. By solving the Eq. 4, we can easily determine the values of $α$ and $k$. For this purpose, we have plotted peak potential ($E_p$) vs log ($ν$) and the $E_p = f (\log ν)$ plot yielded a straight line with slope equivalent to $\frac{2.3 R T}{\alpha n F}$, as depicted in Fig. 5f.\textsuperscript{39} The values of $α$ of the system electrodes are estimated for the oxidation of glucose. The values of formal standard potential ($E'_0$) are estimated from the $y$-intercept of the linearly fitted line of the peak potential ($E_p$) vs scan rate ($ν$) plot\textsuperscript{40} (supplied in Fig. S3). Now, putting the value of $α$ and solving Eq. 4, the value of rate constant $k$, for CuO, CuO/PEDOT and CuO/PEDOT-MoS\textsubscript{2} electrodes can be determined. The respective values are, 0.30 s\textsuperscript{-1}, 0.46 s\textsuperscript{-1} and 0.76 s\textsuperscript{-1}. \[ \begin{align*} \text{Amperometric detection of glucose and selectivity test.} & - \text{Sensing of glucose by CuO, CuO/PEDOT and CuO/PEDOT-MoS}_2 \text{ electrodes are performed by chronoamperometric technique at a fixed dc potential of +0.6 V w.r.t. the Ag/AgCl in 0.1 M NaOH solution. Typical } \text{I–t} \text{ plots of the three electrodes with successive addition of glucose at different concentrations are shown in Fig. 6a.} \\
\end{align*} \] The increase in current value monitored in the amperometric response after each addition of glucose in the solution indicating that glucose oxidation has taken place over the sensor electrode at a dc bias potential of +0.6 V. It was seen that the $I–t$ response of CuO NP only electrode requires more time to stabilize after the injection of glucose and the current response tending to saturate at 0.75 mM. While in case of CuO/PEDOT system, the response time for glucose detection declines and one gets a relatively lower current response with the corresponding addition of glucose. In contrast, CuO/PEDOT-MoS\textsubscript{2} electrode exhibits a notable current change at relatively lower concentration of glucose. Moreover, here, we observe a higher magnitude of current as compared to the other two electrodes upon successive additions of glucose. Thus, CuO deposited PEDOT-MoS\textsubscript{2} electrode seems to be a better electrode material for glucose sensing. The selectivity of the prepared sensor towards glucose has been confirmed by testing its interaction with other coexisted interfering molecules like ascorbic acid (AA), uric acid (UA) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) during the acquisition of amperometric $I–t$ characteristics, as shown in Figs. 6b and S4 (Supplementary section). Although the glucose level in blood is ten times higher than these coexisted species, interactions of these interferents with our prepared sensor electrode needs to be inspected for a reliable glucose monitoring. Accordingly, we have added H\textsubscript{2}O\textsubscript{2}, ascorbic acid and uric acid (each having concentration of 0.1 mM) in the solution to observe their interaction with CuO/PEDOT-MoS\textsubscript{2} during the I–t response taken at a bias potential of +0.6 V. To be mentioned, the plot shows an augmented current response on addition of varying concentration of glucose in first three subsequent steps. However, addition of H\textsubscript{2}O\textsubscript{2}, AA, and UA of 0.1 mM each in the solution did not show any remarkable change in I–t response towards these aforesaid analytes. It is worth mentioning here that, an additional 150 μM of glucose in the solution could result in an enhancement in the amperometric current. Therefore, MoS\textsubscript{2} infiltrated PEDOT based sensor displays substantially high redox activity and consequently, high selectivity for glucose. The I–t non-linear trace of CuO/PEDOT-MoS\textsubscript{2} plot along with the magnified portion of the curve featuring response at a lower concentration of glucose addition can be found from Fig. 6c. Prior to addition of 30 μM glucose, the chronoamperometric response was allowed to attain a stable baseline feature. The concentration of glucose in the solution would increase upon subsequent additions, featuring a proportional rise in the measured amperometric current. Change in current ($ΔI$) vs corresponding concentration of added glucose ($ΔC$) can be found in Fig. 6d. Here, the error bars were assigned w.r.t. the standard deviation of current change ($ΔI$), corresponding to all glucose additions having similar concentration. A standard deviation of 2.56 μA is obtained for the first six additions of glucose having 30 μM concentrations each. The plot essentially shows a good linearity in the concentration range of 30 μM to 1.06 mM and with a regression equation, $y = -0.414x - 5.71$; where, $y$ is current shift in the amperometric response and $x$ is corresponding concentration of glucose. The limit of detection (LOD) of our glucose sensor was calculated from the relation: \[ \text{LOD} = \frac{3 \times σ}{S}; \] where $S$ is the slope of the $ΔI$ vs $[C]$ plot and $σ$ is standard error in $y$-intercept.\textsuperscript{41} From the linear plot of Fig. 6d, the LOD of CuO/PEDOT-MoS\textsubscript{2} based sensor was estimated to be 0.0467 μM and with a sensitivity value of 829 μA·mM\textsuperscript{-1}·cm\textsuperscript{-2}. Moreover, the stability, repeatability and reproducibility aspects of CuO/PEDOT-MoS\textsubscript{2} composite sensor electrode are inspected, and depicted in Figs. S5, S6, and S7; respectively (Supplementary section). The sensor electrode retains its stability up to more than 20 cycles of CV run in 0.1 M NaOH solution. For repeatability test, we have repeated the amperometric sensing experiment and compared the obtained responses with the previously monitored data. It was found that the LOD and sensitivity values obtained from all the sensing experiments were quite indistinguishable from each other thereby signifying much desired repeatability of the test sensor. The reproducibility feature was checked by taking the CV responses on the same CuO/PEDOT-MoS\textsubscript{2} electrode over different days in presence of glucose. In this case, the sensor exhibits a quite good % recovery on the sensing performance up to 5 days of use. In addition, the validity of the prepared glucose sensor was examined by determining the glucose concentration in a commercially
available, clinically recommended oral rehydration solution (ORS) (Fig. S8, Supplementary section), which contains 75% glucose along with other minerals like Na, K, Cl etc. The concentration of glucose in the prepared ORS samples was determined by using the as proposed calibration equation: 

\[ y = a + bx \]

A low value of standard error (\(\sim\) ±1%–2%) suggests high reliability of our fabricated sensor towards determining glucose level in real samples.

Interpretation and Comparison

We obtained electrochemical parameters for different investigated electrode specimens, as can be found in Table II. Along with other parameters, the electroactive area, \(A\) and rate constant, \(k_s\) of the redox processes were seen to be increased significantly after introduction of PEDOT-MoS\(_2\) conductive matrix. Consequently, a better electroactivity of CuO/PEDOT-MoS\(_2\) system towards glucose sensing has been witnessed. An extremely low value of LOD of 0.046 \(\mu\)M and a sensitivity as high as 829 \(\mu\)A. mM\(^{-1}\) cm\(^{-2}\) would indicate a better redox activity in the conversion of glucose into gluconic acid. Furthermore, addition of other interfering molecules like, AA and UA yielded no signs of improvement in the amperometric current. A strong natural oxidant, \(\text{H}_2\text{O}_2\) was also added in the solution to observe adequate changes occurred in the redox processes. Undoubtedly, our sensor module did not respond to other analytes as no change in amperometric current could be observed in the \(I-I_t\) response which stipulates better selectivity towards glucose only (at an applied bias voltage of +0.6 V). The association of nanoscale metal oxide (CuO) with conducting polymer can execute higher current density as compared to its pristine form. In the past, Lakhdari et al. developed NiFe-PANi based hybrid electrode for the non-enzymatic detection of glucose. They obtained a fairly good LOD of 0.5 \(\mu\)M in the concentration range of 10 \(\mu\)M to 10 mM while offering a typical sensitivity of 1050 \(\mu\)A. mM\(^{-1}\) cm\(^{-2}\). Similarly, Kim et al. designed a potentiometric glucose sensor by immobilizing Au-NPs over benzoic acid-functionalized poly-terthiophene (p-TBA) and could achieve a detection limit of 0.19 \(\mu\)M in the linear

| Electrochemical parameters of the three prepared electrode systems. |
|-------------------------|-----------------|-----------------|-----------------|-----------------|
| \(D\) \((\text{cm}^2 \text{s}^{-1}) \times 10^{-4}\) | \(A\) \((\text{cm}^2)\) | \(C_i\) \((\text{mol cm}^{-2}) \times 10^{-9}\) | \(\alpha\) | \(k_s\) \((\text{s}^{-1})\) |
| CuO | 1.7 | 0.811 | 1.64 | 0.355 | 0.30 |
| CuO/PEDOT | 9.1 | 1.10 | 3.67 | 0.434 | 0.46 |
| CuO/PEDOT-MoS\(_2\) | 4.3 | 1.47 | 2.47 | 0.787 | 0.76 |

Figure 6. (a) Merged amperometric \((I-t)\) response of CuO, CuO/PEDOT and CuO/PEDOT-MoS\(_2\) electrode, (b) selectivity test of CuO/PEDOT-MoS\(_2\), (c) amperometric response of the CuO/PEDOT-MoS\(_2\) with inset magnified portion, (d) Change in current \((\Delta I)\) vs change in concentration \((\Delta [C])\) plot.
Among these electrodes, the latter gave a better redox activity and length of electron transfer. A comparative view of sensing para-glucose was performed by chronoamperometric technique for all the NaOH solution were estimated and compared. Direct sensing of glucose concentrations. The present work describes progressive electrochemical route for fabrication of sensing electrode that allows a direct binder free growth of the polymer and metal NPs over the conductive ITO substrate. It is pertinent to note that, use of binder for the adhesion of the materials can lower the conductivity by introducing unavoidable contact resistance in the film. Conversely, PEDOT as a conducting polymer can facilitate efficient charge transfer in the electrode-electrolyte interface by shortening the path length of electron transfer. A comparative view of sensing parameters, selectivity, LOD etc. of other non-enzymatic sensors and this work can be found in Table III.

Conclusions

Structural, morphological and elemental studies were carried out for electrochemically deposited CuO, CuO/PEDOT and CuO/PEDOT-MoS₂ films and then employed for sensing glucose. Among these electrodes, the latter gave a better redox activity and charge transfer efficiency. Different electrochemical parameters viz. diffusion coefficient (D), electroactive area (A), surface concentration of electroactive species (Cᵣ) and heterogeneous rate constant (kₒ) for the synthesized electrodes towards oxidation of glucose in 0.1 M NaOH solution were estimated and compared. Direct sensing of glucose was performed by chronoamperometric technique for all the electrode-types and a much better response could be obtained for the PEDOT-MoS₂ electrode. The proposed sensor exhibits an exceptionally good selectivity towards glucose in a wide linear range of 30 μM–1.06 mM. The LOD and sensitivity of our sensor were estimated to be 0.046 μM and 829 μA mM⁻¹ cm⁻², respectively. As compared to many other electrode materials, the CPs are relatively less toxic and subject to degradation after use. Also, incorporation of CPs with the electroactive metal oxide nanoparticles certainly calls for a new test-bed of an organic-inorganic hybrid system for better non-enzymatic detection of the target redox analyte. Our designed electrode sensor is expected to detect precisely small glucose level with excellent selectively in biological solutions and commercial food products. In this direction, more investigation is required to tackle interfacial properties so that sensing and detection mechanism could reach next level of relevance.

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