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A non-enzymatic electrochemical sensor based on ZrO_2: Cu(I) nanosphere modified carbon paste electrode for electro-catalytic oxidative detection of glucose in raw Citrus aurantium *var.* sinensis

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ABSTRACT

In this work, a sensitive and stable ZrO_2-Cu(I) nanosphere mesoporous material modified non-enzymatic glucose sensor has been developed through simple, low cost chemistry.

ZrO_2-Cu(I) material was obtained by controlled co-precipitation method under ultra dilution conditions. Cyclic voltammetric tests were performed in order to evaluate the electrocatalytic activity ZrO_2-Cu(I) modified electrode. The modified electrode showed high sensitivity, wide linear range and very low detection limit of 0.25 mM, this indicates that the modified sensor is competent with that reported earlier. Spherical morphology of the active material, alkaline environment and presence of +1 copper have significantly enhanced the electro-catalytic oxidation of glucose on carbon paste platform. Also, the fabricated electrode showed excellent anti-interference nature. Electro-catalytic oxidation of glucose was demonstrated in real raw unpurified orange juice, this shows the selective electrocatalytic activity of the ZrO_2-Cu(I) nanosphere material towards glucose even in the presence of interferrants.

1. Introduction

Diabetes is characterized as a condition that hinders body's ability to monitor blood glucose levels. As per the WHO data in the year 2014, people suffering from diabetes are more than 422 million. Systematic monitoring and diagnosis of diabetes is of utmost importance. Undiagnosed diabetes may lead to high risk of vascular diseases (Sarwar et al., 2010). A systematic analysis of vision problems associated with diabetes status of an individual has been reported (Bourne et al., 2013). Also, Rajiv saran et al. reported the consequences of undiagnosed diabetes on kidney function (Saran et al., 2015).

There are many instrumental methods reported for monitoring glucose. A high performance liquid chromatographic technique, for the determination of glucose associated with red blood cells has been reported by Davis, McDonald, and Jarett (1978). E. King and R. Garner reported a colorimetric determination of glucose, the estimation of glucose was affected by various parameters (King & Garner, 2007). T. Daines and K. Morse devised a spectrophotometric method for the determination of glucose using o-toluidine as a complexing reagent (Daines & Morse, 1976). J. Baca et al. reported the determination of fasting glucose levels using liquid chromatography with electrospray ionization technique (Baca et al., 2007). Despite all these advances, these methods are not effective as they involve tedious pre-sampling process and experimental conditions. But, with due respect to all these research, it is the need of the situation to develop a fast and reliable electrochemical detection method. Electrochemical sensors are quite effective in addressing these problems. Hence, in our current research we developed a simple and highly reliable electrochemical sensor for the detection and quantification of glucose.

Electrochemical sensors are most reliable and effective tools for the electrocatalytic oxidation and detection of glucose. Various biosensors were developed for the detection of glucose using glucose oxidase (GOx) and also, they high selectivity and sensitivity (Kang, Park, & Ha, 2019). Nevertheless, these enzyme based sensors are sensitive to pH, temperature and humidity, glucose oxidase is sensitive and suffers de-naturation due to these factors and shows poor catalytic performance. Also, these enzymes are expensive and show poor stability due to their intrinsic nature. Due to these aspects, significant interest has been

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focused on the development of non-enzymatic sensors for the electrocatalytic oxidation of glucose.

In this path, noble metals such as silver (Rahmani, Hajian, Afkhami, & Bagheri, 2018), palladium (Huang, Wang, Lu, Du, & Ye, 2017), gold (Pajooheshpour et al., 2018), modified glossy carbon electrode (Wu, Guo, Huang, & Wang, 2018) and platinum (Weremfo, Fong, Khan, Hibbert, & Zhao, 2017) are extensively explored electrodes for enzymeless sensing. But, it is need of the current situation to design low cost, high sensitive and non-noble metal sensors. In this direction, metal sulphides (Sridhar & Park, 2018; Zhang et al., 2016), carbon nano tubes (Bagheri, Afkhami, Khoshsafar, Hajian, & Shahriyari, 2017), carbon dots (Shiri, Pajouheshpoor, Khoshsafar, Amidi, & Bagheri, 2017) and metal oxides (Karimiana et al., 2018) have been widely used for the development of sensors.

Metal oxides which exist in the nature as minerals, the sensors based on them, possess better thermal stability, cyclic stability and shelf life compared to any enzyme and polymer based sensors (Afzal & Dickert, 2018; Liu, Liu, & Chen, 2013). In addition, these metal oxides show different polymorphs. Hence, there is wide scope for their investigation in the sensor field. Moreover, selectively designed nanostructures show unique chemical and physical properties. Hence, they might be good materials as electrocatalysts.

2. Experimental

2.1. Materials and methods

Zirconyl oxy chloride octa hydrate, copper chloride dihydrate, ammonia, KCl, NaOH, HCl, graphite, silicone oil and glucose were purchased from Merck chemicals, used without further purification. Orange fruit was obtained from the local market of Tumkur town; the raw juice was extracted for the analysis. The desired pH in the experimental runs was adjusted by adding HCl or NaOH as concerned. The X-ray patterns were recorded for all the samples with Panalytical x'pert X-ray diffractometer (PXRD), the FTIR spectra were recorded using Bruker-alpha Fourier transform infrared spectrometer. SEM micrographs were recorded with Zeiss field emission scanning electron microscope and TEM using JEOL JEM TEM instrument.

Cyclic voltammograms of the prepared sensor was studied in the potential range of −0.80 V to 0.80 V. Conventional three electrode setup of working electrode, platinum auxiliary and another platinum electrode as pseudo reference were used. Amperometric i-t response was recorded at a constant potential of 0.46 V under constant stirring conditions.

2.2. Choice of materials

Oxides of copper are good semiconductor materials (Fortunato, Barquinha, & Martins, 2012). Among them, Cu(I) is a p-type semiconductor, attracted much attention due to its excellent photovoltaic properties, transport properties and soforth (G. Han et al., 2018; J. Han et al., 2018; Rosas-Laverde et al., 2018). However, pure Cu(I) suffers thermal and structural instability (Kwon, Soon, Han, & Lee, 2014), which significantly limits its application in the development of sensors (Sun et al., 2018).

Zirconia has been identified as an ideal host for copper due to its high thermal stability, chemical resistance. Also, zirconia is an excellent material used in the field of catalysis (Korsunska, Polishchuk, Kladko, Portier, & Khomenkova, 2017), optical devices (Marcaud et al., 2018), fuel cells (Shim, Chao, Huango, & Prinz, 2007) and electrochemical sensors (Wang et al., 2015). Zirconia is used for many applications due to wide band gap (Emeline et al., 1998), optical transparency (Peuchert, Okano, Menke, Reichel, & Ikesue, 2009), high mechanical strength (Dehestani & Adolfsson, 2013) and high refractive index (Lee et al., 2008). Zirconia nanomaterials not only provide the stability but also improve conduction due to the presence of oxygen vacancy defects. These defects significantly influence the formation and stabilization of +1 oxidation of copper (Parashuram, Sreenivasa, Akshatha, Kumar, & Kumar, 2017).

In this work, the prepared ZrO_2-Cu(I) nanosphere material exhibited excellent electrocatalytic activity, good reproducibility and selectivity even in presence of other common interferrants with good linear range and detection limit.

2.3. Preparation of ZrO_2-Cu(I) nanomaterial and fabrication of sensor

ZrO_2:Cu(I) material was prepared by simple co-precipitation method. In brief, 60 mmol of $ZrOCl_2{\cdot}8H_2O$ and 3 mmol $CuCl_2{\cdot}2H_2O$ were kept under magnetic stirring. Then, liquor ammonia (25% Merck) was added at a stirring rate of 1000 rpm till the pH of the solution becomes 7.5. Thus obtained bluish white precipitate was isolated by centrifugation, washed several times with water, dried and further calcinated at 500 °C for 4 h.

Graphite, silicone oil and ZrO_2-Cu(I) were taken in 7:3:1 wt proportion and mixed to get a homogeneous blend. The paste obtained was packed into the 0.5 ml plastic syringe. A copper wire was then pierced into the paste for external electrical contact and this electrode was kept in dark for 24 h before performing the electrochemical experiments. The tip of the syringe was carefully polished to mirror finish sequentially with 1.0, 0.3, and 0.05 μm Al_2O_3 slurry on a polishing cloth, then the electrode was washed with water to remove adsorbed carbon. The modified electrode was labeled as Gr/Zr-Cu. A similar procedure was used to prepare the unmodified bare graphite electrode.

3. Results and discussion

3.1. Characterization of ZrO_2-Cu(I) nanomaterial

ZrO_2-Cu(I) nanomaterial was characterized by XRD Fig. S1. ZrO_2-Cu (I) showed intense diffraction peaks positioned at 2θ values 30.32, 35.25, 50.63, 60.30 and 63.15 with cubic phase indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) facets and it belongs to Fm-3 m space group, the XRD data of ZrO_2-Cu(I) was in good agreement with the standard having PDF number 27-997. In the XRD spectrum there are no significant peaks of copper, which indicates the high order dispersion of copper in the zirconia lattice (Duwez & Odell, 1947).

FTIR spectrum of ZrO_2-Cu(I) was shown in Fig. S2. The intense and strong band at around 500 cm^{-1} is ascribed to deformation bending modes of Zr-O-Zr (Phillippi & Mazdiyasni, 1971), weak band at 1628 cm^{-1} is attributed to OH bending mode and the wide band centered 3420 cm^{-1} is ascribed to the stretching of O—H group (Platero & Mentruit, 1994). Bands at 1012 cm^{-1} and 505 cm^{-1} are attributed to the different modes of vibration of Cu—O bonds.

Morphology of the ZrO_2-Cu(I) nanomaterial was observed by TEM Fig. 1b–d. It is clearly seen that, copper is embedded in the zirconia nanostructures indicating core-shell model. This particular construction would result in stable, reproducible and high performance electrochemical sensor. The SEM data also revealed the same features with particles of porous and spherical morphology Fig. 1a.

3.2. Cyclic voltammetric analysis of glucose at Gr/Zr-Cu electrode

Electrocatalytic behavior of Gr/Zr-Cu electrode was investigated by cyclic voltammetry at pH = 10. No obvious peak was observed for bare graphite electrode, when they are exposed to buffer solution of pH = 10 without analyte, in the scan range of −0.8 V to 0.8 V as shown in (Fig. S3). As observed from the CVs of modified electrode at pH = 10, the peak at −0.105 V indicates the formation of Cu(II), owing to the transformation of Cu(I) to Cu(II). The peak at −0.62 V is attributed to the transition of Cu(II) to Cu(I) (Fig. S3) (Yan et al., 2018).

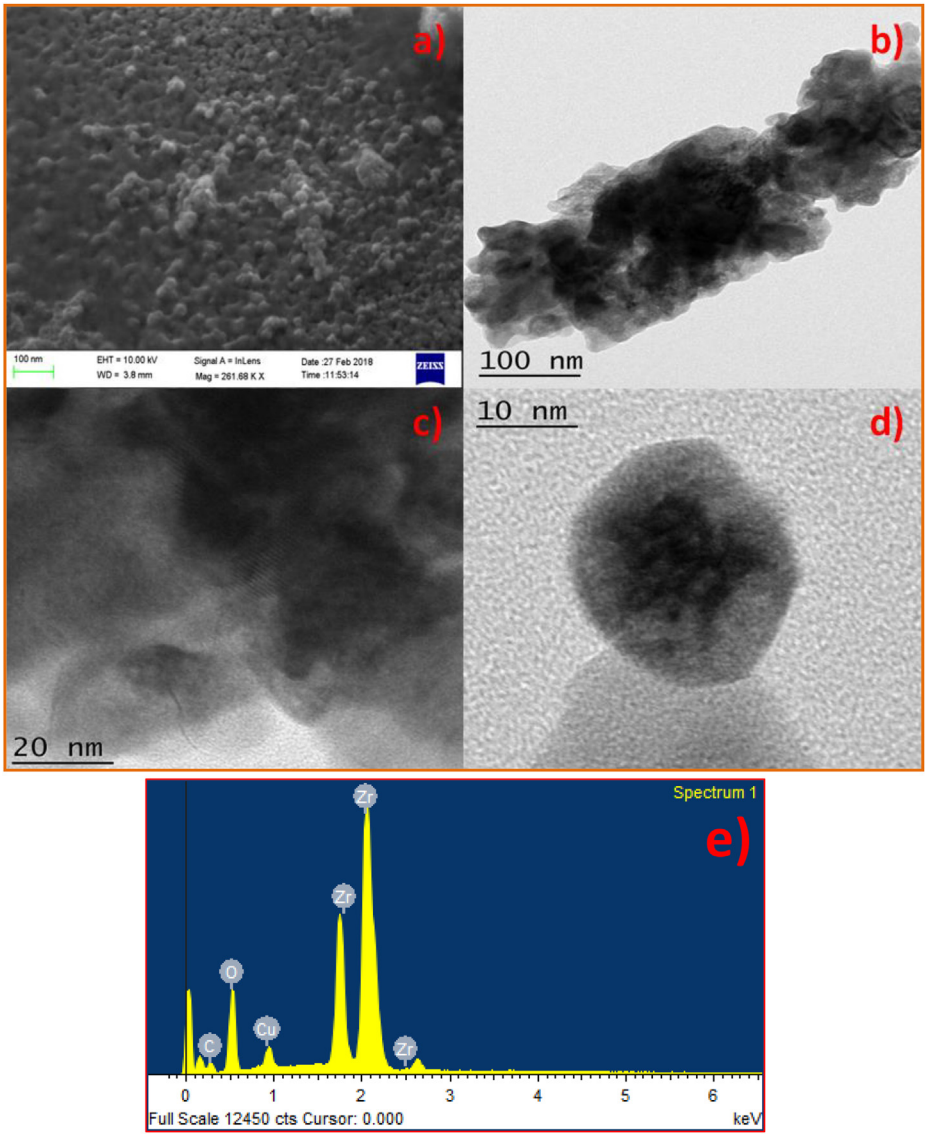

Fig. 1. a) FESEM image of ZrO_2:Cu(I), b) and c) TEM image with agglomerated particles. d) TEM image clearly showing the spherical morphology e) EDX spectrum of ZrO_2:Cu(I).

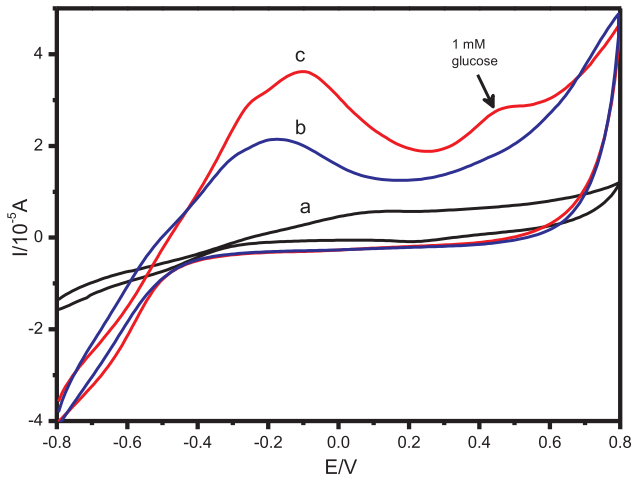

Fig. 2. a) CV of bare graphite with 1 mM glucose in 0.1 N NaOH b) CV of Gr/Zr-Cu electrode in 0.1 N NaOH c) CV of Gr/Zr-Cu electrode with 1 mM glucose in 0.1 N NaOH.

3.3. Effect of pH

The pH of electrolytic solution under study, will influence the electrocatalytic oxidation of glucose at Gr/Zr-Cu electrode. Variation of both peak current and peak potential with respect to pH was examined by recording the cyclic voltammograms Fig. S4a. From the figure it is clearly evident that, there is no significant improvement in the peak current between the pH 2 to 6, further increase in pH improved the oxidation of glucose and a maximum current was recorded at a pH of 12 with peak current value of 1.87 μA.

Fig. S4b shows the variation of potential with pH, oxidation potential significantly moved towards lower value with increase in the pH, a minimum oxidation potential was observed at a pH of 10, further at pH 12 the oxidation potential increased. Hence, pH 10 was selected to be optimum for the electrochemical experiments at Gr/Zr-Cu electrode.

Under lower pH values, absence of ^{-}OH ions resulted in poor oxidation current response. Moreover, in acidic conditions formation of $Cu(OH)_2$ and CuOOH were feeble. Better oxidation current response was observed at neutral and above neutral pH values, which is evident from the dramatic increase of peak current and decrease of peak potential with pH.

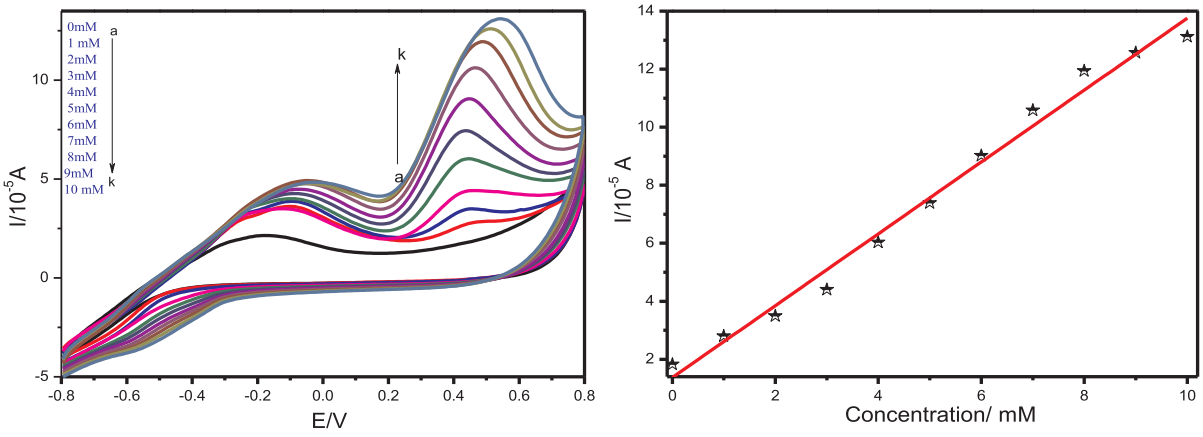

Fig. 3. a) Cyclic voltammograms of 1–10 mM glucose with scan rate of 100 mVs^{-1} at Gr/Zr-Cu electrode, (b) calibration graph of current v/s concentration of glucose.

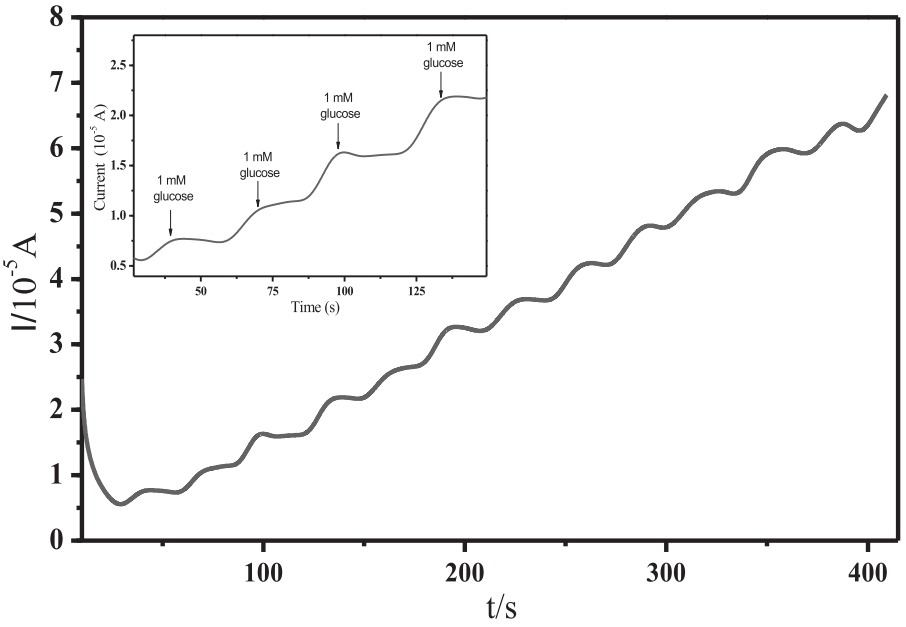

Fig. 4. Amperometric i-t response of Gr/Zr-Cu electrode with 1 mM glucose incremental injection.

These results are obtained by the synergistic effect arising due to electrocatalytic activity of Gr/Zr-Cu electrocatalyst and ^{-}OH ions during the electrocatalytic oxidation of glucose.

Hence, from the pH experiments a clear mechanism for the oxidation of glucose can be established (Mechanism 1). Presence of ^{-}OH ions during the electrochemical oxidation of glucose was vital. That is, oxidation of cuprous from of copper is facilitated due to the presence of ^{-}OH ions only.

According to the mechanism, in alkaline condition cuprous oxide has been oxidized to cupric hydroxide, which on further oxidation gave copper oxyhydroxide. Thus form oxyhydroxide oxidizes glucose to gluconic acid in presence of ^{-}OH ions. Finally, reduction of cupric hydroxide gave back cuprous oxide.

$Cu_2O + 2OH^- + H_2O \rightarrow 2Cu(OH)_2 + 2e^-$

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

$CuOOH + Gulcose + OH^- \rightarrow Gluconic\ acid$

$2Cu(OH)_2 + 2e^- \rightarrow Cu_2O + H_2O + 2OH^-$

Mechanism 1: Oxidation of glucose at Gr/Zr-Cu electrode in presence of ^{-}OH ions.

3.4. Electrocatalytic activity of Gr/Zr-Cu electrode towards glucose

To explore the electrocatalytic activity of Gr/Zr-Cu electrode, cyclic voltammetric technique was used. Fig. 2 shows cyclic voltammogams (CVs) of bare carbon paste and Gr/Zr-Cu electrodes, in absence and presence of 1 mM glucose. No sign for oxidation of glucose was observed at bare carbon paste electrode. However, there is a dramatic increase in the anodic peak current at Gr/Zr-Cu electrode at a potential of 0.46 V, due to the addition of 1 mM glucose, this indicates high electrocatalytic oxidation of glucose at Gr/Zr-Cu electrode. The electrocatalytic activity was further examined at different concentrations (1–10 mM) of glucose Fig. 3a, the graph shows that, the oxidation peak current increases linearly with increase in concentration. This indicates quantitative and reliable detection of glucose at Gr/Zr-Cu electrode. The linearity is given by the regression equation $I_{pa} = 0.126\ (\mu A(mM)^{-1}) + 1.152C\ (mM)$ Fig. 3b.

Table 1
Comparison of electrochemical performance of Gr/Zr-Cu electrode with literature.

Electrode material	Linear range	Electrode modification method	LOD (μM)	Real sample analyzed and method	Reference
CuO nanowires/Cu	0.4 μM–2 mM	Solid adsorption of CuO onto Cu electrode.	0.049	Blood serum glucose/cyclic voltammetry	(Zhuang, Su, Yuan, Sun, & Choi, 2008)
CuO nanofibers	6 μM–2.5 mM	Casting CuO-NF on GCE	0.8	Standard glucose samples/Amperometry	(Wang, Zhang, Tong, Li, & Song, 2009)
CuO NPs-MWCNTs	10 μM–0.3 mM	MWCNT/PSS/Cu casting on GCE	0.5	Blood serum glucose/cyclic voltammetry	(Wu et al., 2010)
CuO nanoellipsoids	0.1 mM–3 mM	Casting Nafion-impregnated CuO powder onto GCE	0.072	Blood serum glucose/Amperometry	(Zhang et al., 2014)
Cu_2O/graphene	0.3 mM–3.3 mM	Cu_2O/ GNs modified glassy carbon (GC)	3.3	–	(Liu et al., 2013)
CuS nanoflakes	0.001 mM–2 mM	Drop casting on glossy carbon electrode	0.19	Urine sample/cyclic voltammetry	(Yan et al., 2018)
MoO_3 nanorods	0.175 mM–0.165 mM	Drop casting on nickel foam	104.17	–	(Sharma, Gangan, Chakraborty, & Rout, 2017)
Pt-Ru catalyst	1.0 mM–3.0 mM	Drop casting on glossy carbon electrode	300	–	(Kwon, Kwen, & Choi, 2012)
ZrO_2-Cu(I)	1 mM–10 mM	ZrO_2-Cu(I) modified carbon paste	250	Orange Juice (Citrus aurantium *var.* sinensis)/cyclic voltammetry	This work

3.5. Effect of amount of catalyst ZrO_2-Cu(I) on the electrocatalytic performance

The influence of varying the amount active material ZrO_2-Cu(I) on the electrocatalytic activity of Gr/Zr-Cu electrode was studied. Fig. S5 shows the CVs of 10 wt%, 30 wt% and 50 wt% ZrO_2-Cu(I) modified graphite electrodes. Obviously, high current response was obtained for 30 wt% active material loaded electrode. When the amount of active material increased from 10 to 30 wt%, the electrocatalytic activity significantly improved, which may be due to increase in number of catalytic active sites. Further, when 50 wt% of active material is used, the catalytic activity decreased, this tendency may be attributed to the decrease in the conduction because of insulating nature of zirconia. Thus, 30 wt% of active material was optimum and used in further work.

3.6. Effect of scan rate

Influence of scan rate on the current response at Gr/Zr-Cu electrode was studied to understand the electrochemical process occurring at the modified electrode. Fig. S6a shows the CVs of 10 mM glucose with different scan rates (50–250 mVs^{-1}). Oxidation peak current increased linearly with increase of scan rate and followed the linear regression equation $I_{pa} = 0.07438\ \nu\ (\mu AV^{-1}s) + (-8.7825\ A)$ with R^2 0.9978 Fig. S6b, which indicate the oxidation of glucose at Gr/Zr-Cu electrode is typically surface controlled electrochemical process.

3.7. Anti interferrant studies and amperometric analysis of Gr/Zr-Cu electrode

Designing interference free non-enzymatic electrochemical sensor is still a great challenge in glucose sensing. Because, the species like DA, AA & UA are also oxidized in presence of the electrocatalyst producing unwanted interfering electrochemical signals. Hence, selection of suitable conditions makes it essential to avoid the interference.

The amperometric response of Gr/Zr-Cu electrode upon successive introduction of glucose to 0.1 mM NaOH under dynamic condition was investigated, which is shown in Fig. 4. The amperometric current response increased with successive injection of glucose, with a rapid response time of < 5 s, which indicate high electrocatalytic efficiency of Gr/Zr-Cu electrode for the oxidation of glucose. The amperometric response was linear with concentration (1–10 mM) and the detection limit was found to be 0.25 mM (n = 8) and the limit of quantification was 0.85 mM (n = 8), as per the 3sd/m, where sd = standard deviation in the intercept of calibration plot and m is the slope.

The electrocatalytic performance of present sensor with other relevant sensors was presented in Table 1. The sensor showed lower detection limit and a good linear range. The lower detection limit may be attributed to the easy inter conversion of Cu(I) & Cu(II) states and excellent electrocatalytic activity of Gr/Zr-Cu electrode. In brief, ZrO_2-Cu (I) is a good electrocatalytic material for glucose sensing, even though some noble metal and composites showed good electrocatalytic performance.

The selective determination of glucose in presence of other common interferrants is another significant parameter. Hence, electrocatalytic current response of Gr/Zr-Cu electrode towards glucose was evaluated in presence of 0.1 mM of interferrants like uric acid (UA), ascorbic acid (AA) and dopamine (DA). No interferrants signals were observed, this is due to high selectivity of Gr/Zr-Cu electrode towards oxidation of glucose, these results indicates that, Gr/Zr-Cu electrode is a interferrant free electrocatalytic sensor Fig. S7.

3.8. Application of the present sensor for the determination of glucose in real raw orange juice

To ascertain the practical application of Gr/Zr-Cu electrode, the current responses towards glucose in freshly obtained orange juice were

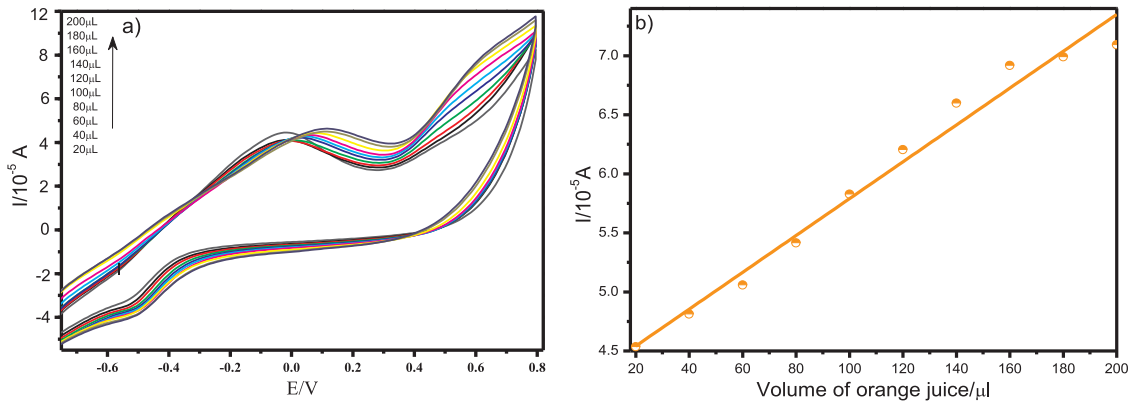

Fig. 5. a) Cyclic voltammograms with orange juice 20 μL–200 μL at Gr/Zr-Cu electrode. b) Linearity curve with orange juice 20 μL–200 μL at Gr/Zr-Cu electrode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

studied, CV response with increasing volume of orange juice was presented in Fig. 5 and a linear current response was observed for the successive introduction of orange juice. From the diagram it is clearly evident that, introducing 20 μL of unpurified raw orange juice triggered the oxidation peak current of glucose at a potential of 0.55 V, this slight shift in the potential compared to that with pure glucose may be due to the complex composition of the orange juice. It was also observed that, the Gr/Zr-Cu electrode effectively detected glucose in the wide volume range of orange juice 20 μL–200 μL, with linear regression coefficient $R^2 = 0.9897$. These results also clearly eradicated the influence of other interferrants. Since, the Gr/Zr-Cu electrode selectively sensed glucose in presence of other sugars such as fructose, sucrose and glucose including other flavonoids in the raw orange juice. This demonstrates that, the Gr/Zr-Cu is a robust electrode for the electrocatalytic detection of glucose.

Glucose recovering ability of the sensor was tested and compared with the data obtained from commercial strip glucometer. Analytical recoverability for the addition of 2, 4 and 6 mM of pure glucose to orange juice are showed in Table S1, good recoverability of 99.03–100.39% (± 1%) towards glucose was obtained at Gr/Zr-Cu electrode.

3.9. Stability tests

To test the stability, Gr/Zr-Cu electrode was kept in dark condition for a period of 180 days. The electrode showed high retention of sensitivity towards the detection of glucose after a period of 180 days also as shown in Fig. S8a. It is also observed that, 180 days preserved Gr/Zr-Cu electrode showed a linear response with increasing concentration of glucose from 1 mM to 10 mM Fig. S8b. It is observed that, the electrode retained 42.32% (± 1%, n = 5) reproducibility with respect to oxidation peak current response even after 180 days.

4. Conclusions

In the present work, we developed a ZrO_2-Cu(I) modified carbon paste non-enzymatic glucose sensor. The sensor may not used for the low concentration of glucose levels. However, the prepared sensor was effective in accelerating the electrocatalytic oxidation of glucose due to high catalytic active sites and easy interconvertible oxidation state of copper. Under optimized conditions the Gr/Zr-Cu sensor showed a good linear range, lower detection limit and good shelf life. The sensor also showed excellent anti interferrant detection of glucose, indicating high selectivity of present sensor towards glucose detection, its practical applicability of this sensor to detect glucose in real orange juice. All these features shows Gr/Zr-Cu electrode is attractive and promising for the enzymeless electrochemical determination of glucose.

Declaration of Competing Interest

All the authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2019.125178.

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