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Original Research

Novel synthesis and characterization of pristine Cu nanoparticles for the non-enzymatic glucose biosensor

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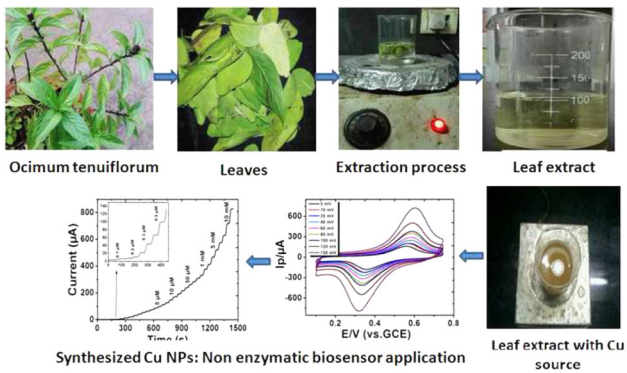
Abstract Non enzymatic electrochemical glucose sensing was developed based on pristine Cu Nanopartilces (NPs)/ Glassy Carbon Electrode (GCE) which can be accomplished by simple green method via *ocimum tenuiflorum* leaf extract. Then, the affect of leaf extract addition on improving Structural, Optical and electrochemical properties of pristine cu NPs was investigated. The synthesized Cu NPs were characterized with X-ray diffraction (X-ray), Uv–Visible spectroscopy (Uv–Vis), Fourier transformation infrared spectroscopy (FTIR), Particle size distribution (PSA), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS), Transmission electron microscopy (TEM) for structural optical and morphological studies respectively. The synthesized Cu NPs were coated over glassy carbon electrode (GCE) to study the electrochemical response of glucose by cyclic voltammetry and ampherometer. The results indicates that the modified biosensor shows a remarkable sensitivity (1065.21 μA mM^{-1} cm^{-2}), rapid response time (<3s), wide linear range (1 to 7.2 mM), low detection limit (0.038 μM at S/N = 3). Therefore, the prepared Cu NPs by the Novel Bio-mediated route were exploited to construct a non-enzymatic glucose biosensor for sustainable clinical field applications.

Graphical Abstract



1 Introduction

The accurate, fast and reliable determination of glucose is very important because the out of control glucose concentration leads to diabetes mellitus, which has become a global public health problem. The diagnosis and management of such health disorder requires a tight monitoring of blood glucose levels [1]. In the past few decades, the development of glucose sensors have four generations, first glucose sensor was developed in 1962. The first three generations involve the intermediate substance for oxidation of glucose which hindered by few limitations such as immobilization, poor stability, high cost, low reproducibility etc [2]. This causes for the development of the fourth generation sensors i.e., the Non enzymatic/Enzyme free glucose sensors, different kinds of nanomaterials can be used to sense the glucose which exhibits remarkable sensitivity and selectivity due to the advantages of high thermal and chemical stability [3–5].

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Synthesis of Cu NPs mainly includes hydrothermal [6], electrodeposition [7], chemical reduction [8], thermal decomposition techniques [9], unfortunately, most of these existing strategies are not ecofriendly. To the best of our knowledge, as nanotechnology advances, Most of the researcher's focused on the biological method to develop ecofriendly reducing and stabilizing agents such as plant extract, bacteria and fungi for easy enhancement of surface area and catalytic activity of the NPs through the eco-friendliness and also the biocompatibility nature of NPs [10–14]. Nevertheless, fabrication of pristine Cu NPs with cheap and renewable reducing agents with different morphology and nanostructure show different performances in non-enzymatic glucose detection, which are seriously significant to apply these biosensors for broad applications [15, 16].

Compared to noble metals, Cu, and their oxides is more significant to pay attention because low cost and scarcity seriously limit the application [17–20]. As is recognized to all, transition metals are outstanding electrocatalysts as a outcome of their capacity to accept various oxidation states and absorb other species on their surfaces to form intermediates and turn on them in the reaction process [21, 22]. For example, oxidizable non-noble metals such as Cu offer easy routes for the catalytic oxidation of carbohydrates at a constant applied potential [23]. As an electric material, Cu was largely considered for use as the substrate to fabricate metal-based modified electrodes to achieve non-enzymatic glucose detection [24, 25]. Furthermore, Cu based nanostructured materials can be easily synthesized by Ocimum tenuiflorum is a traditional medicinal plant of India and provide outstanding electrochemical activity.

This paper demonstrates simple green method for synthesis of pristine Cu NPs, which has a size range of 25–30 nm. As of now, a very few reports were mentioned, preparation of Cu NPs using *Ocimum tenuiflorum* leaves extract which acts as reducing and stabilizing agents. The proposed method represents simple, low cost, low energy, without the aid of inert atmosphere and low hazard aqueous synthesis. The synthesized NPs were characterized with XRD, UV–vis, FTIR, PSA, SEM-EDS and TEM. Finally, the pristine Cu NPs were used to study the glucose sensing phenomena with the aid of cyclic voltammetric (CV) and ampherometer measurements.

2 Materials and methods

2.1 Chemical reagents

Copper sulphate ($CuSO_4$ $5H_2O$), Sodium Hydroxide (NaOH), Glucose, Ascorbic acid (AA), Uric acid (UA), Fructose, Galactose, Lactose and N, N-dimethyl formamide were analytical grade chemical reagents, purchased from Sigma-Aldrich and used without any further purification. Ultrapure water was used throughout all the experiments. *Ocimum tenuiflorum* leaves collected from green house which we specially grown up for the green synthesis of Nanomaterials (CNST, IST, JNTUH, INDIA).

2.2 Characterization techniques

All the electrochemical experiments were performed on the Metrohm Autolab B. V (JNTUH, India) in a standard three-electrode system. The modified (Cu/GCE) was used as working electrode, while the Ag/AgCl electrode and platinum wire were used as reference and counter electrode, where as NaOH acts as supporting electrolyte which are purged with deoxygenated N_2 gas. All the electrochemical measurements were carried out at room temperature. The crystallinity and phases were characterized by using X-ray diffraction (XRD) with Bruker D8 Advance diffractometer (CuKα radiations, $\lambda = 1.5418$ Å) in the range 20°–80° (2θ). An optical property of the nano particles were analyzed using Systronics Double Beam UV–Vis spectrophotometer 2202. The particle size distributions were done by Nano particle analyser S Z-100. The chemical composition was performed by using Fourier transform infrared spectroscopy (perkinelmer-FTIR spectrum-100) at wavelength range of 450–4000 cm^{-1}. The scanning electron microscopy (SEM JEOL-JSM-7600F) with energy dispersive spectroscopy (EDAX) and transmission electron microscopy (TEM) were recorded using (JEM-Model 100CX II) to estimate morphological and crystalline properties of samples.

2.3 Preparation of leaf extract and synthesis of the Cu NPs

Healthy Fresh leaves of Ocimum tenuiflorum leaves were collected and washed with distilled water. Then, fine cut into pieces to easy release of plant extract from leaves and were boiled at 80 °C in the presence of 100 ml deionized water for 1 h. The resultant extract were filtered and stored at 4 °C for further experiment. From the above solution, 5 ml were added to 1 mM aqueous $CuSO_4$ $5H_2O$ solution, and boiled with constant stirring to enhance the interaction of plant extract with Cu source at 80 °C for 3 h. Then the color of extract turn from pale brown to sea green, colour change indicates reduction of Cu NPs. The obtained solution was purified by continual centrifugation at 5000 rpm for 20 min followed by re-dispersion of pellets in deionized water. Then the Cu nanoparticles were dried in oven at 80 °C. The possible mechanism involved in the formation of Cu NPs can be explained via the following steps: (1) Flavonoids (FlOH) are a large group of polyphenolic compounds acts as reducing and stabilizing agents, which actively adsorbed on the surface, and form complex structure with Cu metal

salts. (2) Simultaneous reduction of Cu metal involves the transformation of flavonoids from ketones to carboxylic acids, indeed that chelate the ions, which plays a key role in the reduction of Cu^{2+}. (3) Cu^{2+} was capped with polyphenols and alkaloids, which will prevent oxidiation for formation of Cu NPs. This means that they are involved in the stages of initiation (nucleation), growth and NPs formation stages [26, 27] are shown in Eq. (1)–(4).

$$nFlOH + Cu^{+1e} \rightarrow nFlOX \cdot + nCu^{0}(\text{Nucleation}) \quad (1)$$

$$nCu^{0} + Cu^{+1e} \rightarrow Cu_{n}^{+1e}(\text{Growth}) \quad (2)$$

$$Cu_{n}^{+1e} + Cu_{n}^{+1e} \rightarrow Cu_{2n}^{+2e} \quad (3)$$

$$\left(Cu_{n}^{+2e}\right)n + (FlOH)n \rightarrow \text{metalic Cu NPs} \quad (4)$$

2.4 Fabrication of Cu/GCE modified electrode

The GCE with a diameter (3 mm) was polished with 0.3 and 0.05 µM of aluminum slurry. Then, the electrode successively cleaned by ultrasonification in ethanol and water. Finally, washed with water and dried to obtain cleaned surface of GCE. Thereafter, 10 mg of pristine Cu NPs was dispersed in 40 µL of N, N-dimethyl formamide by ultrasonification for 2 h then, 5 µL of the dispersed solution was dropped on the cleaned surface of GCE, dried in air at room temperature for several hours.

3 Results

The XRD profiles of as synthesized pristine Cu NPs using *Ocimum tenuiflorum* leaf extract as shown in Fig. 1a. The XRD peaks reflects high crystallinity with diffraction angles at 43.6°, 50.9° and 74.8°, which matched with JCPDS no. 71-4610 corresponds to the (111), (200) and (220) crystallographic planes consisting of face centered cubic structure (FCC) [28]. The crystallite size of the obtained NPs were estimated to be 22 nm using Debye-Scherrer Equation ($D = k\lambda/\beta\cos\theta$), where D is the crystallite size, λ is the wavelength of X-rays, β is the full width half maximum and θ is the Braggs angle. The pattern was very clean, with no formation of impurities such as copper oxide and plant extract.

As per the previous reports, depending on the particle size, copper NPs display various absorption intensities at the related wavelengths, ultra small Cu NPs (below 5 nm) appear at 230 to 270 nm wave length [29, 30]. While larger copper NPs coupled with ultra small (above 50 nm) display a surface Plasmon peak at 560–570 nm [31, 32]. Whereas, observed here in Fig. 1b that the pristine Cu NPs exhibits very small peaks or shoulders at 342.2 nm wavelength and there a rapidly increase in absorbance at wavelength below

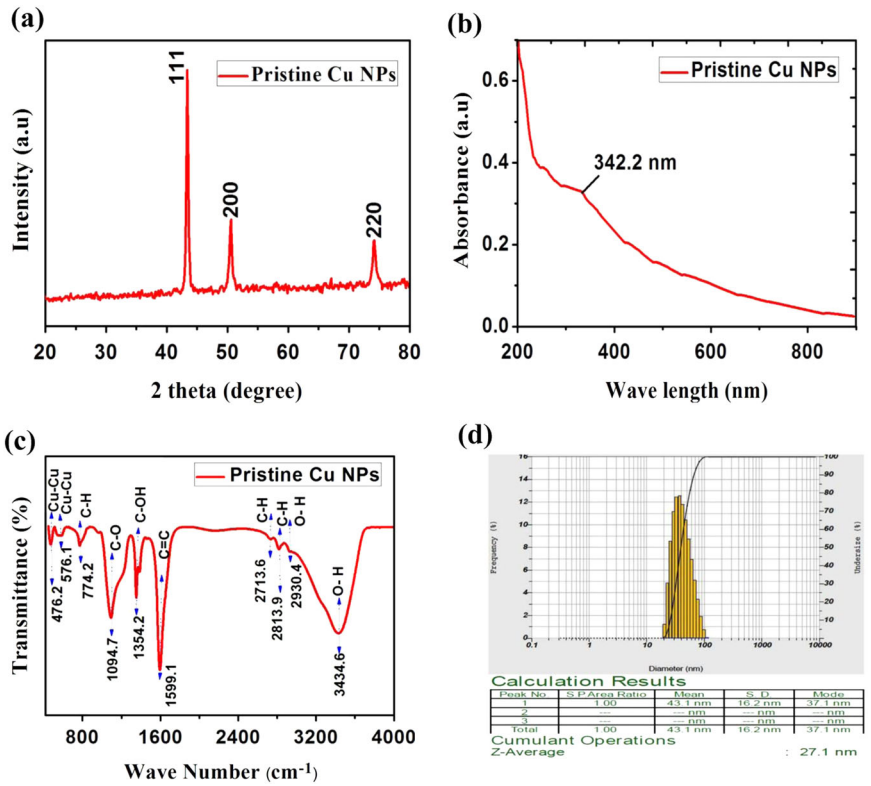

Fig. 1 Shows pristine Cu NPs synthesized with 5 ml of Ocimum tenuiflorum leaf extract **a** XRD pattern **b** Uv–Vis spectra **c** FTIR spectra **d** PSA with calculation results

350 nm, reflects that the particle size as 20–30 nm, which were exactly correlated with XRD and TEM results.

The FTIR spectrum as shown in Fig. 1c, pristine Cu nanoparticles exhibits bands at 3128.6 and 2930, 2813 and 2713, 1599, 1354, 1094 and 775 which represent free OH molecules and OH group forming hydrogen bonds, stretching C–H modes, stretching alkenes C=C bonds, carbonyl group stretching C–OH band, stretching C–O alcohols and ethers, and C–H deformation band out of plane vibrations, respectively. These peaks appeared due to the presence flavonoids and other phenolic bio compounds, plays a considerable role in the reduction of metal ions and formation of the corresponding metal nanoparticles. Cu metal network were assigned 576 and 476 cm^{-1} to the Cu–Cu metal complex [33, 34].

The obtained particle size analyzer result shown in Fig. 1d, the average (mean) particle size, standard deviation and most commonly found peaks in the distribution (mode) as 43.1, 16.2 and 37.1 nm. The average particle sizes of the samples are in nearly multiples of the crystal size. The bio-synthesized method is suitable to obtain the uniform distribution of the particles.

Typical SEM images at 1 µm magnification confirmed that the pristine Cu have grown with well defined morphology and shows with relatively non homogenous, smooth spherical shape, high density, attributed to bio-mediated process using leaf extract and thus stabilized to get pristine Cu NPs which is as shown in Fig. 2a. Further, the Cu NPs estimated by EDS in Fig. 2b which confirms the signal characteristic of Cu only without any unknown signals, proves the purity of sample. This reflects the successfully synthesized Cu NPs.

Figure 2c and d shows 100 and 50 nm magnification HRTEM images. indicates the formation of agglomerated spherical shape Cu NPs. The 100 nm magnification image indicates pristine Cu NPs is spherical and more agglomerated surface than the 50 nm magnification image. The result reveals the high crystalline NPs with average particle diameter found to be approximately 25–30 nm as observed in the XRD [35, 36].

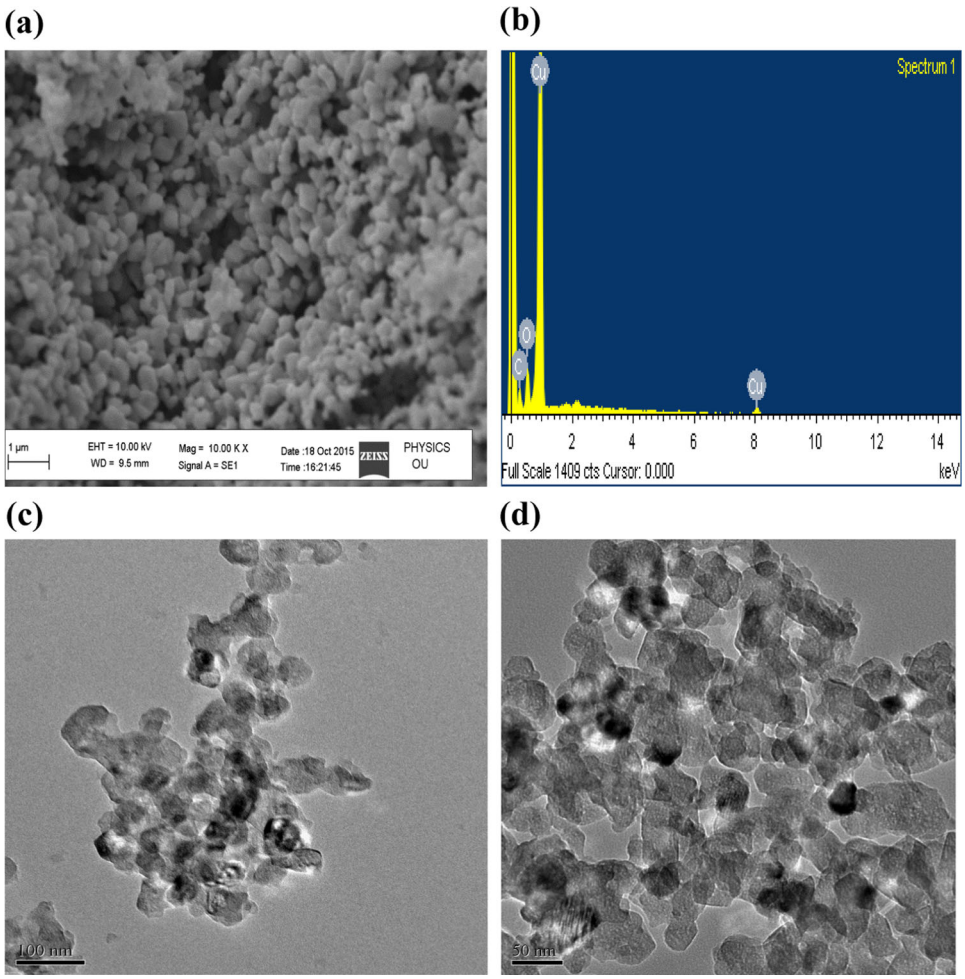

Fig. 2 Shows synthesized Cu NPs **a** SEM image **b** EDS pattern **c** TEM image at 100 nm **d** TEM image at 50 nm Magnification

4 Discussion

The non enzymatic glucose sensing properties were estimated by using Pristine Cu NPs/GCE modified electrode towards glucose oxidation in the absence and presence of glucose as shown in Fig. 3a, which represents the observable oxidation (Ep = 0.55 V, Ip = 157 μA) and reduction (Ep = 0.37 V, Ip = 197.2 μA) peak currents in the presence of 1 mM glucose due to the oxidation of Cu NPs at the scan rate of 5 mV. However, in the absence of glucose, a negligible amount of peaks currents observed for Bare GCE and Cu/GCE. The electrochemical oxidation of Cu based electrode against glucose oxidation mechanism involves multiple steps. In NaOH solution, at the farward scan Cu(0) is first oxidized to $Cu(OH)_2$ at a potential of 5 mV. As the potential is scanned into more positive the $Cu(OH)_2$ is further oxidized to Cu(III) forming CuOOH. The Cu(III)/Cu (II) redox couple plays an important role in oxidation of glucose to gluconolactone, which in turn caused the increase of anodic current. The process could be simply summarized as follows: [37–40].

$$Cu + 2OH \rightarrow Cu(OH)_2 + 2e^- \quad (5)$$

$$Cu(OH)_2 + OH- \rightarrow CuOOH + e^- \quad (6)$$

$$CuOOH + glucose + e^- \rightarrow Cu(OH)_2 + glucolactone \quad (7)$$

Figure 3b investigates the different scan rates (5 to 150 mV) of Cu/GCE modified electrode on the oxidation of glucose in the 0.1 M NaOH. The anodic peak current (at 150 mV scan rate Ep = 0.63 V, Ip = 710.7 μA) potential shift to a more positive region with the increase in the scan rate, and are mainly due to the increased oxidation of glucose. In the same way, the cathodic peak current (at 150 mV scan rate Ep = 0.32 V, Ip = 770.2 μA) also shifted to the low potential regions, which illustrates that the electrochemical kinetics is surface adsorption controlled process for glucose molecules. Figure 3c shows the peak current were directly proportional to the square root of the scan rates between 5 to 150 mV s^{-1}, reflects a diffusion controlled electrochemical process.

Moreover, the electron transfer ability between electrolyte and electrode surface with the 1 to 10 mM glucose concentration were investigated using CVs in 0.1 M NaOH at 60 mV s^{-1}. As shown in Fig. 3d, the electrochemical oxidation of anodic peak current is clearly increased with the decrease in cathodic peak, which depends on the increase in the glucose concentration. This result suggests, the Cu/GCE modified electrode suitable for the detection of glucose level.

4.1 Ampherometric measurements

Figure 4a showed the well-defined ampherometric current-time response in the 0.1 M NaOH at the working potential

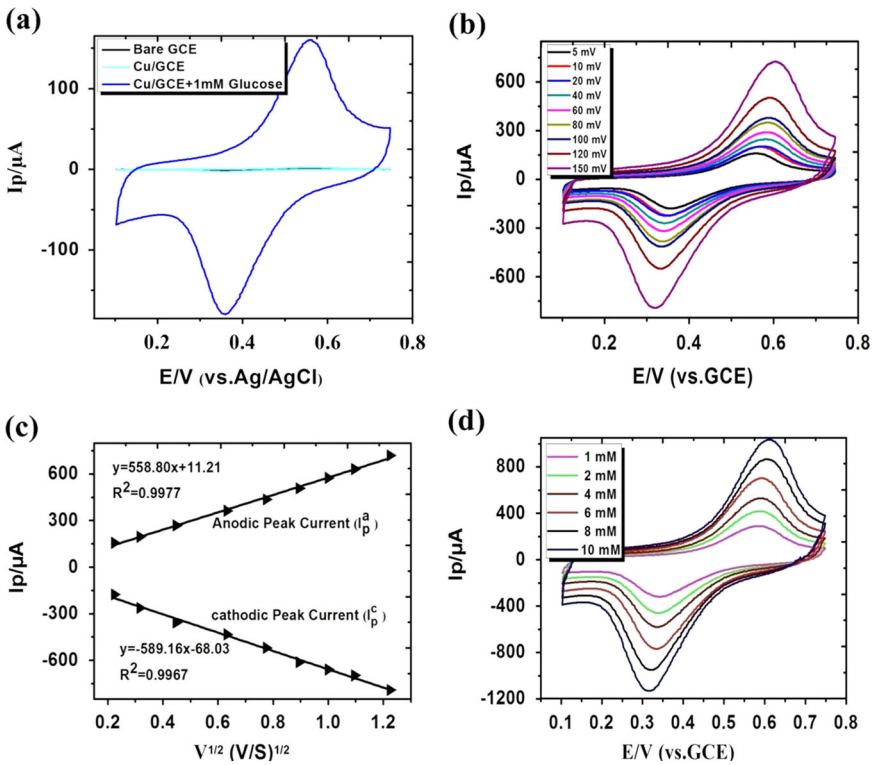

Fig. 3 **a** Shows CVs in the presence and absence of glucose **b** CVs of Cu/GCE modified electrode at scan rate from 5 to 150 mV s^{-1} **c** square route of different scan rates **d** CVs of Cu/GCE in the presence of 1 to 10 mM glucose concentration

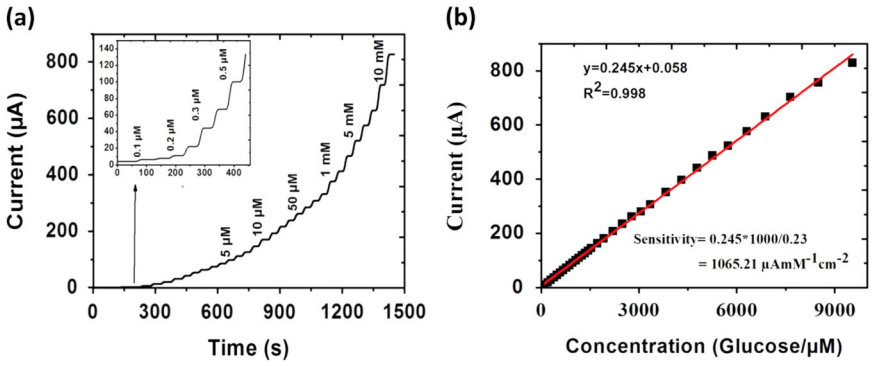

Fig. 4 **a** Steady state amperometric i-t curve (*Inset*: 0.1–0.5 μM of glucose) **b** Calibration plot of steady-state current vs. concentration of glucose

Table 1 Comparison of non-enzymatic glucose sensor parameters for Cu/GCE modified electrode with previous report modified electrodes

Modified electrode	Sensitivity ($\mu A\ mM^{-1}\ cm^{-2}$)	Response time (s)	Linear range (μM)	LOD (μM)	Ref.
Cu flowers	65.56 μA $mmol^{-1}$ L	–	2–75 μM	1	[42]
Cu octahedral cages/GCE	–	3	8–93 μM	4	[43]
Cu nano wires/GTE	1100	<2	1.6–5 μM	1.6	[38]
Cu nano wires	927	–	0.002–0.075 mM	1	[44]
Cu nanostructures	420	–	Up to 3	0.035	[45]
Cu film	220 ± 6	3	0.01 to 0.5 mM	0.5	[46]
Cu nanoporous	220	–	0.01–0.5 mM	40	[47]
Cu implanted BDD	6.4*10–3	–	0.001–0.05	1.50	[48]
Cu nanoparticles	256 ± 3	–	0.02–0.03 A.	250 nM	[20]
Cu nano rods	1490	5	100 nM to 0.80 mM	0.008	[49]
Green synthesis of Cu Spherical NPs	1065.21	<3	1 to 7.2 mM	0.046	This work

of 0.55 V was optimized to achieved a good sensitivity, linearity and a high analyte dependent current with the successive 10 μm addition of glucose performed a higher current sensitivity than cyclic voltammetry.

Figure 4b shows the calibration plot for sensor current response is directly proportional to glucose concentration in the range of 1 to 10 mM with a sensitivity of 1065 μA $mM^{-1}\ cm^{-2}$ with a correlation coefficient of 0.998. The detection limit was estimates as 0.038 μM which depends on signal to noise ratio (S/N = 3).

The response time and linear range was <3s and 1 to 7.2 mM. In sequence to further, estimate the superiority of sensor, a comparison were done with other non enzymatic glucose sensor. This comparison showed that the green synthesized pristine Cu NPs are more comparable or improved advantages than other reported works as shown in Table 1.

4.2 Repeatability, reproducibility and stability studies of Cu/GCE modified electrode

The repeatability, reproducibility and stability of Cu/GCE modified electrode against glucose were evaluated by ampherometric measurements in 0.1 M NaOH solution containing 1.0 mM glucose. The repeatability of sensor was estimated similarly for the prepared three electrodes to detect 1.0 mM glucose, the relative standard deviation (RSD) of about 2.95%, and the results indicates excellent repeatability. The reproducibility of glucose sensor tested by conducting six amperometric measurements with one single electrode at 1.0 mM glucose, the obtained relative RSD as 2.28%, and the results indicated outstanding sensor reproducibility. The long term Cu/GCE electrode stability also examined by storing of electrodes at room temperature then the current response remained 93.2% of its original one after 10 days by measuring 1.0 mM glucose, reflecting the good stability of Cu/GCE towards the oxidation of glucose.

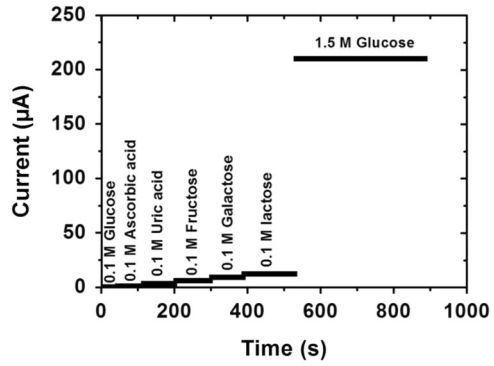

Fig. 5 Amperometric i-t response curve for Cu/GCE to the glucose and interfering substances

Thus, the modified glucose sensor might be suitable for fabrication of sensor device.

4.3 Interference study

The Interference studies were performed by observing the interfering substances in the blood glucose serum, generally which are easily oxidizable substance such as uric acid, ascorbic acid, lactose, galactose and fructose and contains 30–50 times lower than glucose level [41]. These interfering substances act as distracters for hindering the performance of glucose sensor, so it is important to execute for selectivity studies. Figure 5 shows amperometric*i*-t response for Cu/GCE at 1.5 mM glucose with the addition of interference substances such as each one of 0.1 mM of glucose, ascorbic acid, uric acid, fructose, galactose and lactose, then the current response increased by 5.2%. This result represents the selectivity of glucose detection was satisfied.

5 Conclusions

The pristine Cu NPs were prepared successfully via Bio mediate process using Ocimum tenuiflorum leaf extract. The crystalline size of the NPs calculated with XRD pattern. The elemental composition confirmed by EDS and chemical composition of the NPs by FTIR. SEM and TEM confirmed the spherical shape Cu NPs with a particle size of about 25–30 nm which were correlated with XRD and PSA. The fabricated Cu/GCE modified electrode performed excellent analytical sensor features such as sensitivity of 1065.21 μA mM^{-1} cm^{-2}, detection limit of 0.038 μM (S/N = 3), linear range of 1 to 7.2 mM with a response time less than 3 s, excellent repeatability, reproducibility and stability achieved higher activity towards the oxidation of glucose. Green synthesized NPs performing excellent catalytic activity toward glucose oxidation due to less toxic, smooth surface and decrease of particle size than the chemical and physically synthesized nanostructures. Hence, Pristine Cu NPs act as a sustainable application for Non-enzymatic glucose sensors.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

1. Guo M, Fang H, Wang R, Yang Z, Xu X. Electrodeposition of chitosan-glucose oxidase biocomposite onto Pt–Pb nanoparticles modified stainless steel needle electrode for amperometric glucose biosensor. J Mater Sci: Mater Med. 2011;22:1985–92.
2. Hsu C-L, Lin J-H, Hsu D-X, Wang S-H, Lin S-Y, Hsueh T-J. Enhanced non-enzymatic glucose biosensor of ZnO nanowires via decorated Pt nanoparticles and illuminated with UV/green light emitting diodes. Sensor Actuat B. 2017;238:150–9.
3. Hsu C-W, Su F-C, Peng P-Y, Young H-T, Liao S, Wang G-J. Highly sensitive non-enzymatic electrochemical glucose biosensor using a photolithography fabricated micro/nano hybrid structured electrode. Sensor Actuat B. 2016;230:559–65.
4. Wang C, Sun Y, Yu X, Ma D, Zheng J, Dou P, Cao Z, Xu X. Ag–Pt hollow nanoparticles anchored reduced graphene oxide composites for non-enzymatic glucose biosensor. J Mat Sci: Mat in Elect. 2016;27:9370–8.
5. Tian K, Prestgard M, Tiwari A. A review of recent advances in nonenzymatic glucose sensors. Mater Sci Eng C. 2014;41:100–18.
6. Rahmatolahzadeh R, Aliabadi M, Motevalli K. Cu and CuO nanostructures: facile hydrothermal synthesis, characterization and photocatalytic activity using new starting reagents. J Mat Sci: Mat in Elect. 2017;28:148–56.
7. Zhao S, Wang T, Wang L, Xu S. A non-enzymatic glucose amperometric biosensor based on a simple one-step electrodeposition of Cu microdendrites onto single-walled carbon nanohorn-modified electrode. J Solid State Electrochem. 2015;19:831–9.
8. Khan A, Rashid A, Younas R, Chong R. A chemical reduction approach to the synthesis of copper nanoparticles. Internat Nano Lett. 2016;6:21–6.
9. Effenberger FB, Sulca MA, Teresa Machini M, Couto RA, Kiyohara PK, Machado G, Rossi LM. Copper nanoparticles synthesized by thermal decomposition in liquid phase: the influence of capping ligands on the synthesis and bactericidal activity. J Nanoparticle Res. 2014;16:2588
10. Sastry ABS, Aamanchi RBK, Sree Rama Linga Prasad Ch, Murty BS. Large-scale green synthesis of Cu nanoparticles. Environ Chem Lett. 2013;11:183–7.
11. Woźniak-Budych MJ, Przysiecka Ł, Langer K, Peplińska B, Jarek M, Wiesner M, Nowaczyk G, Jurga S. Green synthesis of

rifampicin-loaded copper nanoparticles with enhanced antimicrobial activity. J Mat Sci: Mat in Med. 2017;28:42
12. Sinha T, Ahmaruzzaman M. Green synthesis of copper nanoparticles for the efficient removal (degradation) of dye from aqueous phase. Environ Sci and Pollution Res. 2015;22:20092–100.
13. Peralta-Videa JR, Huang Y, Parsons JG, Zhao L, Lopez-Moreno L, Hernandez-Viezcas JA, Gardea-Torresdey JL. Plant-based green synthesis of metallic nanoparticles: scientific curiosity or a realistic alternative to chemical synthesis? Nanotechnol Environ Eng. 2016;1:4
14. Umer A, Naveed S, Ramzan N, Rafique MS. Selection of a suitable method for the synthesis of copper nanoparticles. World Publication Company. 2012;7:1230005–18.
15. Liu L, Chen Y, Lv H, Wang G, Hu X, Wang C. Construction of a non-enzymatic glucose sensor based on copper nanoparticles/poly (*o*-phenylenediamine) nanocomposites. J Solid State Electrochem. 2015;19:731–8.
16. Wang G, He X, Wang L, Gu A, Huang Y, Fang B, Geng B, Zhang X. Non-enzymatic electrochemical sensing of glucose. Microchimica Acta. 2013;180:161–86.
17. Si P, Huang Y, Wang T, Ma J. Nanomaterials for electrochemical non-enzymatic glucose biosensor. RSC Adv. 2011;3:2487–3502.
18. Jing W. Electrochemical biosensing based on noble metal nanoparticles. Microchimica Acta. 2012;177:245–70.
19. Chen X, Wu G, Cai Z, Oyama M, Chen X. Advances in enzyme-free electrochemical sensors for hydrogen peroxide, glucose, and uric acid. Microchimica Acta. 2014;181:689–5.
20. Liu X, Yang W, Chen L, Jia J. Synthesis of copper nanorods for non-enzymatic amperometric sensing of glucose. Microchimica Acta. 2016;183:2369–75.
21. Satheesh Babu TG, Ramachandran T, Nair Bipin. Single step modification of copper electrode for the highly sensitive and selective non-enzymatic determination of glucose. Microchimica Acta. 2010;169:49–55.
22. Jafarian M, Forouzandeh F, Danaee I, Gobal F, Mahjani MG. Electrocatalytic oxidation of glucose on Ni and Ni-Cu alloy modified glassy carbon electrode. J Solid State Electrochem. 2009;13:1171–9.
23. Wang GF, He XP, Wang LL, Gu AX, Huang Y, Fang B, Geng BY, Zhang XJ. Non-enzymatic electrochemical sensing of glucose. Microchim Acta. 2013;180:161–86.
24. Chen KF, Xue DF. Cu-based materials as high-performance electrodes toward electrochemical energy storage. Funct Mater Lett. 2014;7:1430001.
25. Wu HX, Cao WM, Li Y, Liu G, Wen Y, Yang HF, Yang SP. In situ growth of copper nanoparticles on multiwalled carbon nanotubes and their application as non-enzymatic glucose sensor materials. Electrochim Acta. 2010;55:3734–40.
26. Shende S, Ingle AP, Grade A, Rai M. Green synthesis of copper nanoparticles by Citrus medica Linn. (Idilimbu) juice and its antimicrobial activity. World J Microbiol Biotechnol. 2015;31 (6):865–73.
27. Nasrollahzadeh M, Sajadi SM, Khalaj M. Green synthesis of copper nanoparticles using aqueous extract of the leaves of Euphorbia esula L and their catalytic activity for ligand-free Ullmann-coupling reaction and reduction of 4-nitrophenol. RSC Adv. 2014;4:47313.
28. Cheng G, Walker ARH. Green synthesis of copper nanoparticles and conducting nanobiocomposites using plant and animal sources. Anal Bioanal Chem. 2014;4:19507–11.
29. Ghosh SK, Rahman DS, Ali AL, Kalita A. Surface plasmontunability and emission sensitivity of ultrasmall fluorescent copper nanoclusters. Plasmonics. 2013;8:1457–68.
30. Biswas S, Miller JT, Li Y, Nanda kumar K, Kumar CS. Developing a millifluidic platform for the synthesis of ultra small nanoclusters: ultra small copper nanoclusters as a case study. Small. 2012;8:688–98.
31. Singh M, Sinha I, Premkumar M, Singh AK, Mandal RK. Structural and surface plasmon behavior of Cu nanoparticles using different stabilizers. Colloid Surf A. 2010;359:88–94.
32. Pileni MP, Lisiecki I. Nanometer metallic copper particle synthesis in reverse micelles. Colloids Surf A. 1993;80:63–8.
33. Rice KP, Walker EJ Jr., Stoykovich MP, Saunders AE. Solvent-dependent surface plasmon response and oxidation of copper nanocrystals. J Phys Chem C. 2011;115:1793–9.
34. Zhang Y, Zhu P, Li G, Zhao T, Fu X, Sun R, Zhou F, Wong C. Facile preparation of monodisperse, impurity-free, and anti-oxidation copper nanoparticles on a large scale for application in conductive ink. ACS Appl Mater Interfaces. 2014;6:560–7.
35. Yu W, Xie H, Chen L, Li Y, Zhang C. Synthesis and characterization of monodispersed copper colloids in polar solvents. Nanoscale Res Lett. 2009;4:465–70.
36. You H, Yang S, Ding B, Yang H. Synthesis of colloidal metal and metal alloy nanoparticles for electrochemical energy applications. Chem Soc Rev. 2013;42:2880–904.
37. Zhang H, Jin M, Xia Y. Noble-metal nanocrystals with concave surfaces: synthesis and applications. Angew Chem Int Ed. 2012;51:7656–73.
38. Fan Z, Liu B, Liu X, Li Z, Wang H, Yang S, Wang J. A flexible and disposable hybrid electrode based on Cu nanowires modified graphene transparent electrode for non-enzymatic glucose sensor. Electrochim Acta. 2013;109:602–8.
39. Luo L, Zhu L, Wang Z. Non enzymatic amperometric determination of glucose by CuO nanocubes-graphene nanocomposite modified electrode. Bioelectrochemistry. 2012;88:156–63.
40. Marioli JM, Kuwana T. Spherulitic copper–copper oxide nanostructure-based highly sensitive nonenzymatic glucose sensor. Electrochim Acta. 2015;10:165–78.
41. Kumar SA, Cheng HW, Chen SM, Wang SF. Preparation and characterization of copper nanoparticles/zinc oxide composite modified electrode and its application to glucose sensing. Mater Sci Eng C. 2010;30:86–91.
42. Zhao Y, Zhao J, Ma D, Li Y, Hao X, Li L, Yu C, Zhang L, Wang Z. Synthesis, growth mechanism of different Cu nanostructures and their application for non-enzymatic glucose sensing. Colloids Surf A Physico chem Eng Asp. 2012;409:105–11.
43. Ensafi AA, Abarghoui MM, Rezaei B. A new non-enzymatic glucose sensor based on copper/porous silicon nanocomposite. Electrochim Acta. 2014;123:219–26.
44. Zhang YC, Su L, Manuzzi D, de los Monteros HVE, Jia WZ, Huo DQ, Hou CJ, Lei Y. Biosens Bioelectron. 2012;31:426–32.
45. Zhao Y, Zhao JZ, Ma DC, Li YL, Hao XL, Li LZ, Yu CZ, Zhang L, Lu Y, Wang ZC. Colloids Surf A. 2012;409:105–11.
46. Sun F, Li L, Liu P, Lian YF. Nonenzymatic electrochemical glucose sensor based on novel copper film. Electroanalysis. 2011;23:395–401.
47. Ivandini T, ASato R, Makide Y, Fujishima A, Einaga Y. Ptim-planted boron-doped diamond electrodes and the application for electrochemical detection of hydrogen peroxide. Diamond Relat Mater. 2004;13:2003.
48. Sattayasamitsathit S, Thavarungkul P, Thammakhet C, Limbut W, Numnuam A, Buranachai C, Kanatharana P. Fabrication of nanoporous copper film for electrochemical detection of glucose. Electroanalysis. 2009;21:2371.
49. Male KB, Hrapovic S, Liu Y, Wang D, Luong JHT. Electrochemical detection of carbohydrates using copper nanoparticles and carbon nanotubes. Anal Chim Acta. 2004;516:35.