

Copper oxide-modified glassy carbon electrode prepared through copper hexacyanoferrate–G5-PAMAM dendrimer templates as electrocatalyst for carbohydrate and alcohol oxidation

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Abstract We describe the modification of a glassy carbon electrode by electro-deposition of copper hexacyanoferrate (CuHCF) in the presence of an amine-terminated dendrimer (PAMAM) as a template. The electrode containing the CuHCF template was cycled in alkaline solution to generate a layer of cupric oxide (CuO). The mechanism of the formation of CuO and its electrocatalytic activity were investigated by cyclic voltammetry. Scanning electron microscopy reveals that the CuO prepared by this method has a meso-porous grid-like appearance. The formation of CuO was identified by XPS analysis of the modified electrode. The ability of the CuHCF film towards the electrocatalytic oxidation of carbohydrates and alcohols was detected using cyclic voltammetry. The over-potential required for carbohydrate and alcohol oxidation is lowered by ~400 mV compared to other chemically modified electrodes reported in the literature. Simple methodology has been adopted in this work for the preparation of the catalytically active electrode, and this work also explains the structure directing effect of dendrimer and its influence on the electrocatalytic oxidation of analytes.

Keywords Copper hexacyanoferrate · Copper oxide · G5-PAMAM dendrimer · Glassy carbon electrode · Cyclic voltammetry · Electro-catalysis

Introduction

Electrochemical methods provide an effective and inexpensive way for the determination of carbohydrates, but direct oxidation at bare electrode is not suited for analytical application due to slow electrode kinetics and high over-potential required for the oxidation of carbohydrates. Non-enzymatic sensors for carbohydrate detection are more advantageous as enzymatic sensors suffer from stability problem for repeated trials and on the concurrency in estimation. Precious metals such as Pt, Au and Ag metal alloys and metal nanoparticles have been extensively investigated for the development of non-enzymatic sensors [1–10] wherein development of chemically modified electrode with good catalytic function has its practical significance [11]. Several methods such as sol–gel, electro-deposition and self-assembly techniques were adopted for preparing chemically modified electrode (CME) [12–14]. The advantage of using transition metals replacing noble metals is that they can oxidise carbohydrates and alcohols at constant and lower over-potential and therefore the instrumentation and operation are simplified. The basis of the response mechanism to glucose at these transition metals is the electron transfer mediation of the multi-valent metal redox couple of the anodised metal electrodes [15]. Copper oxide has been studied intensively because of its numerous applications in catalysis, semiconductors, batteries, biosensors, etc. [16–22].

Electrocatalysts based on nanometal oxides have attracted considerable interest in the bioanalytical area because of their large specific surface area, good biocompatibility, simple fabrication and good chemical and physical stability. Nanocopper oxide particles on nafion-coated Pt electrode and CuO nanorod-modified pyrolytic graphite electrode exhibit good response to oxidation of

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H₂O₂, glucose, fructose and sucrose [23, 24]. The process of surface modification provides an interesting platform to alter the basic structure of the underlying substrates and thereby physical and chemical properties could be modified to find applications in various fields such as sensors and catalysis. For example, Baldwin et al. chemically modified the copper compounds formed on the surface of glassy carbon electrode for carbohydrate detection [25]. Cu microparticles dispersed onto gold surface have been used as an amperometric sensor using glucose as a model compound [26]. Matsubara and co-workers reported a flow-through glucose detector based on a copper oxide film prepared by electroless plating and chemical oxidation [27]. Copper dispersed electrochemically in polymer films such as poly-1-naphthylamine and polyaniline were used for selective carbohydrate detection [28, 29]. Since the electrocatalytic property of CME was obviously affected by the physical and chemical state of modifiers on the electrode surface, developing various new film preparation methods is of great significance for improving the sensing capacity and catalysis of the electrode. Oxidation of carbohydrates in alkaline medium at Cu and Ni electrodes results in higher analytical currents when compared to Au and Pt electrodes. This has been attributed to a catalytic effect which involves multi-electron oxidation mediated by surface Cu and Ni oxide layers. It has been demonstrated that, among different analytes, glucose oxidation is most active in alkaline solution [30]. The oxidation of glucose in strong alkaline media is particularly interesting in sugar-fed fuel cells [31], but the most effective catalyst for methanol oxidation is platinum and its alloys in acidic condition. The high cost of these noble metals is often prohibitive towards their use and initiates the search for alternative catalytic materials [32–36]. Electrocatalytic oxidation of alcohols based on nickel hydroxide modified on glassy carbon surface in alkaline condition was reported by El-Shafei [34]. From the literature survey, it is clear that most of the reports on methanol oxidation were based on Pt-, Ru- or Pd-doped electrodes. Oxidation of alcohols in alkaline condition leads to better polarisation characteristics and opens up the possibility of using non-noble metals [37–41]. This shows that copper and nickel hydroxide-modified electrodes can serve as efficient catalyst for direct electron transfer in fuel cells operating under alkaline conditions. In our studies, we have used copper hydroxide films obtained by electrochemical conversion from copper hexacyanoferrate (CuHCF) films for carbohydrate and alcohol oxidation in alkaline condition in the presence of G5-PAMAM dendrimer.

Transition metal hexacyanoferrates are widely used in the construction of amperometric biosensors for their excellent catalytic properties and selective detection. Metal hexacyanoferrates decrease the kinetic barrier leading to

lower operation potentials. The conversion of metal hexacyanoferrate to their corresponding oxides has been previously reported [42]. In this communication, we report the catalysis of CuO obtained through surface derivatisation of copper hexacyanoferrate on a GC electrode electrochemically deposited in the presence of G5-PAMAM dendrimer solution. Literature survey shows that there are no reports based on CuHCF film electro-deposition in the presence of G5-PAMAM dendrimer templates on glassy carbon surface. Further, the structure directing properties of dendrimer during the formation of CuHCF films and hence its effect on the CuO formation has been investigated in this work. The literature so far reported on the electrocatalysis of carbohydrates and alcohols is based on CuO prepared by chemical methods. No attempt has been made so far to prepare electrocatalytically active films of CuO by electrochemical methods. Further, the preparation of the film in presence of the dendrimers aids in the formation of mesoporous grid-shaped CuO. Dendrimers have unique core-shell structures possessing core, interior shells consisting of repeating branching units and terminal groups. PAMAM dendrimers facilitate the synthesis of metal nanoparticles since metal ions like Cu²⁺, Co²⁺, Pt²⁺ and Pd²⁺ are known to partition into the dendrimer [43–46]. The terminal functional groups like –NH₂, –COOH and –OH serve as handles for attaching the dendrimers to electrode surface. Moreover, a single dendrimer molecule can incorporate a large number of metal atoms, which increases the loading of metal atoms on the electrode surface. The present work describes the results of electrocatalytic oxidation of β-glucose, D-glucose and methanol at CuO/GC surface.

Experimental methods

Reagents

Analytical-grade CuCl₂·4H₂O, KCl, KOH, K₄[Fe(CN)₆], HCl, CuSO₄·5H₂O (All Merck) were used as received. All stock solutions were prepared using triply distilled water. G5-PAMAM dendrimer was purchased from Aldrich.

Instrumentation

Cyclic voltammograms were recorded using PARSTAT2263. A conventional three-electrode setup was used with glassy carbon electrode as the working electrode, Pt electrode as counter-electrode and calomel electrode (1 N KCl) as the reference electrode. X-ray photoelectron spectroscopic studies were carried out using Multi-lab 2000 model, Thermo Scientific, UK, having Al K_α source with a binding energy of 1,486.4 eV that was used for the study. Initially, a full scan from –10 to 1,100 eV

was performed and later on individual scans of 50–100 eV with a step energy of 0.5 eV were carried out in order to analyse the presence of specific elements. The recorded XPS spectra were analysed using the XPS peak fitting software programme. The energy scale has been adjusted on the carbon peak (C 1 s) spectra at 284.5 eV. SEM images of the electrode surface were taken using Hitachi S3000-H, Japan, and the images were recorded at 25 kV using a secondary electron detector.

Copper oxide electrode fabrication and electrocatalytic oxidation of carbohydrates and alcohols

Surface modification of GC surface was carried out after polishing with alumina slurry on emery paper and cleaning ultrasonically for 10 min in distilled water and ethanol, respectively. CuHCF modification on GC surface was carried out by electro-deposition in a clear solution consisting of potassium ferricyanide (0.5 mM), HCl (0.1 M), KCl (0.5 M) and Cu complexed-G5-dendrimer solution (10 mM of CuSO₄ solution was mixed with 9.08 μM G5-PAMAM dendrimer and kept aside for 1 week before electro-deposition so that effective complexation between metal and dendrimer takes place) by cycling the potential between -0.6 to +1 V vs Hg/Hg₂Cl₂ (1 N KCl) at 50 mV s⁻¹ for 15 min. The formation of CuHCF on GC surface and its morphological characteristics were analysed using SEM and XPS. A control experiment was carried out by modifying another glassy carbon electrode with CuHCF in the absence of dendrimer for comparing the electrocatalytic effect of CuHCF films in the presence and in the absence of dendrimer. CuHCF-modified electrodes were rinsed with KCl solution and air-dried. Conversion of CuHCF to CuO was performed by potential cycling in 0.5 M KOH for 10 cycles in the potential range from -1.2 to 0.5 V at a scan rate of 50 mV s⁻¹ (Scheme 1).

Experiments were performed at room temperature. The electrocatalytic activity of chemically modified electrode towards alcohol and carbohydrate oxidation in alkaline medium was studied using cyclic voltammetry. Lower homologous alcohol like methanol and simple carbohydrate like glucose were used for the electrocatalytic studies.

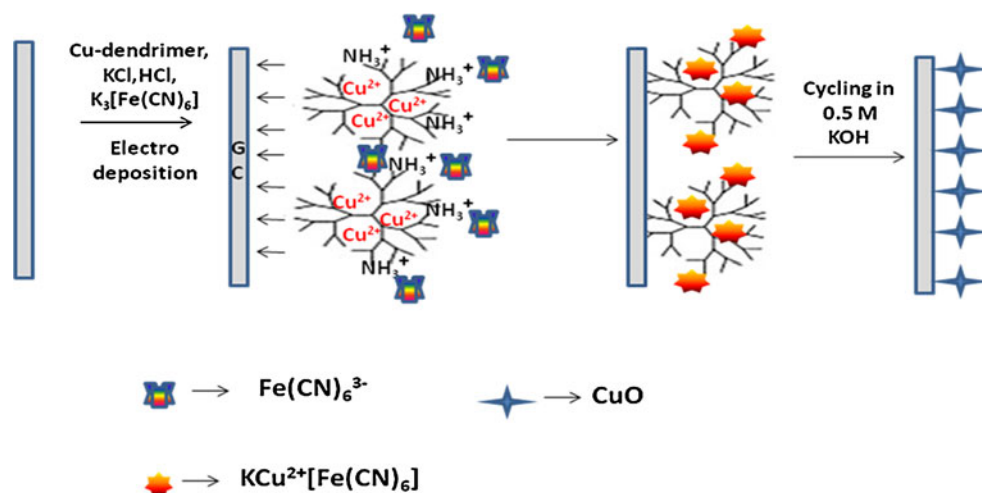
Results and discussion

Characterisation of copper (II) hexacyanoferrate-modified GC surface

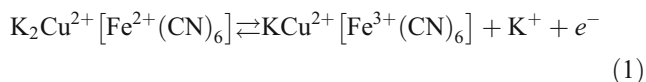
In this work, chemical modification of GC by CuHCF was carried out by electrochemical cycling by direct mixing of copper complexed dendrimer solution and Fe(CN)₆³⁻ solution in the presence of KCl + HCl. Literature reports suggest a two-step procedure for CuHCF modification, in which a thin layer of copper was deposited on the working electrode via a reduction process and then the second step involves polarisation of working electrode anodically at 1 V in K₃Fe(CN)₆ solution for a given period [47–52]. This preparation route results in the coprecipitation of Cu²⁺ and Fe(CN)₆⁴⁻. Only S.M. Chen et al. have reported the preparation of CuHCF film by direct mixing of Cu²⁺ and Fe(CN)₆³⁻ by electrochemical cycling [53]. In this work, CuHCF modification is carried out by direct mixing in the presence of G5-PAMAM dendrimer as template.

The electrochemical response of CuHCF film-modified GC electrode in the presence of dendrimer at various scan rates in 0.5 M KCl is shown in Fig. 1. The inset shows the plot of current vs scan rate which depicts a linear response. The observed redox couple at 0.6 V vs NCE is assigned to FeII/III redox couple in CuHCF and the electron transfer reaction governing this process is also represented [54–56]. Copper hexacyanoferrate can also exhibit the redox activity

Scheme 1 Schematic representation showing the methodology used for CuHCF deposition on GC and conversion to CuO via potential cycling in 0.5 M KOH. The first step shows Cu²⁺-complexed dendrimer approaching the GC surface along with Fe(CN)₆³⁻; the second step shows CuHCF formation; the third step indicates CuO formation via potential cycling



of interstitial copper ions: $\text{Cu}^+/\text{Cu}^{2+}$. This peak appears very close to 0.4 V vs NCE; this is due to unreacted copper electro-deposited on GC surface [57, 58]. Bharathi et al. reported a similar electrochemical response for CuHCF modified on gold substrate using mercapto propanoic acid SAM [59]. The mechanism of CuHCF film formation on GC surface is shown in Scheme 1.



Variation in peak-to-peak separation values (ΔE_p) observed for films prepared in the presence of dendrimer is listed in Table 1. Cathodic and anodic peak separation is found to be 3 mV at a scan rate of 10 mV/s. This shows that electron transfer is more facile for electrode modified using PAMAM dendrimer. Peak current is proportional to scan rate, confirming surface-confined electron transfer reaction. Faradaic charge associated with the process is determined by integrating the area under redox peak and found to be $27 \mu\text{C}/\text{cm}^2$ for a dendrimer-modified electrode. The surface coverage, Γ is given by

$$\Gamma = \frac{q}{nFA} \quad (2)$$

where Γ is the molecular surface coverage on the electrode, q is the charge associated with the redox process, n is the number of electrons, F is the Faraday's constant and A is the geometric area of the electrode used for analysis. The estimated surface coverage is $1.25 \times 10^{-8} \text{ mol cm}^{-2}$ for this electrode. These parameters suggest the formation of multi-

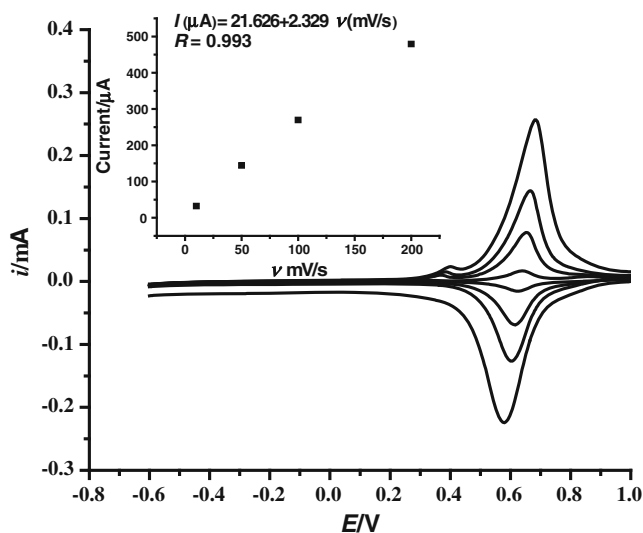


Fig. 1 Cyclic voltammograms of CuHCF films prepared in the presence of dendrimer in 0.5 M KCl at different scan rates. Inner to outer—10, 50, 100 and 200 mV s^{-1} . Inset shows the plot of peak current vs scan rate

Table 1 Peak separation (ΔE_p) values of CuHCF prepared in the presence of dendrimer at various scan rates

Scan rate (ν) (mV s^{-1})	E_{pa} (V)	I_{pa} (A)	E_{pc} (V)	I_{pc} (A)	ΔE_p (mV)
10	0.635	1.6×10^{-5}	0.632	-1.5×10^{-5}	3
50	0.648	7.7×10^{-5}	0.612	-6.8×10^{-5}	36
100	0.667	1.4×10^{-4}	0.609	-1.2×10^{-4}	58
200	0.680	2.6×10^{-4}	0.580	-2.2×10^{-4}	100

layers of CuHCF on GC surface [60]. The CV response of CuHCF film-modified GC electrode prepared in the absence of dendrimer at various scan rates and the peak potential data are given in the supporting information (S1 in “Electronic supplementary material”; Table 1).

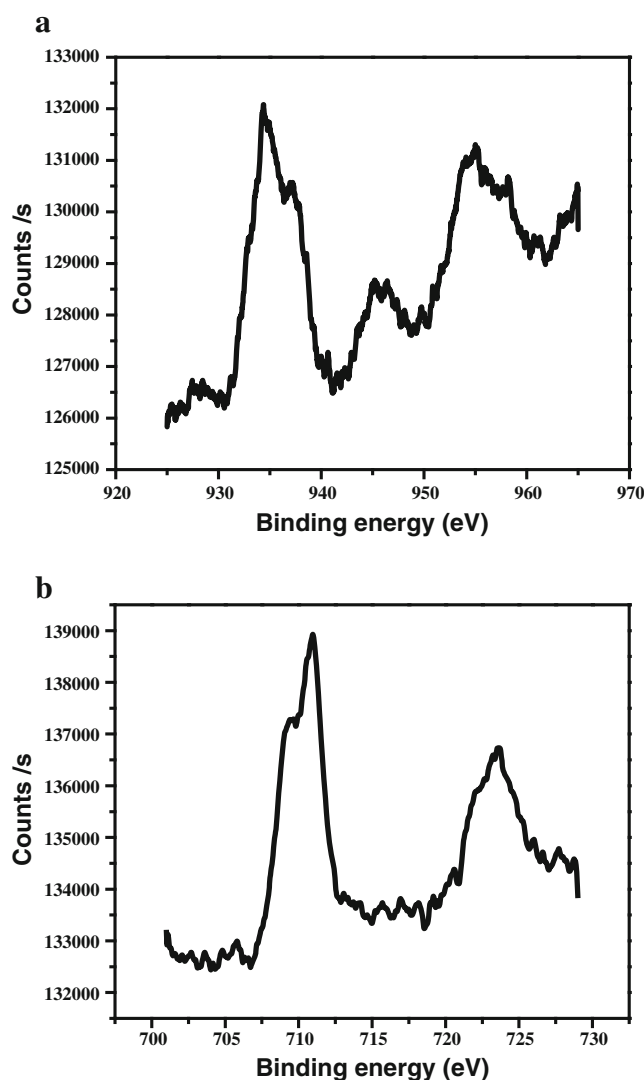


Fig. 2 XPS spectra of CuHCF prepared in the presence of dendrimer solution: **a** Cu 2p, **b** Fe 2p

Fig. 3 SEM image of CuHCF film prepared in the **a** absence of dendrimer and **b** presence of dendrimer

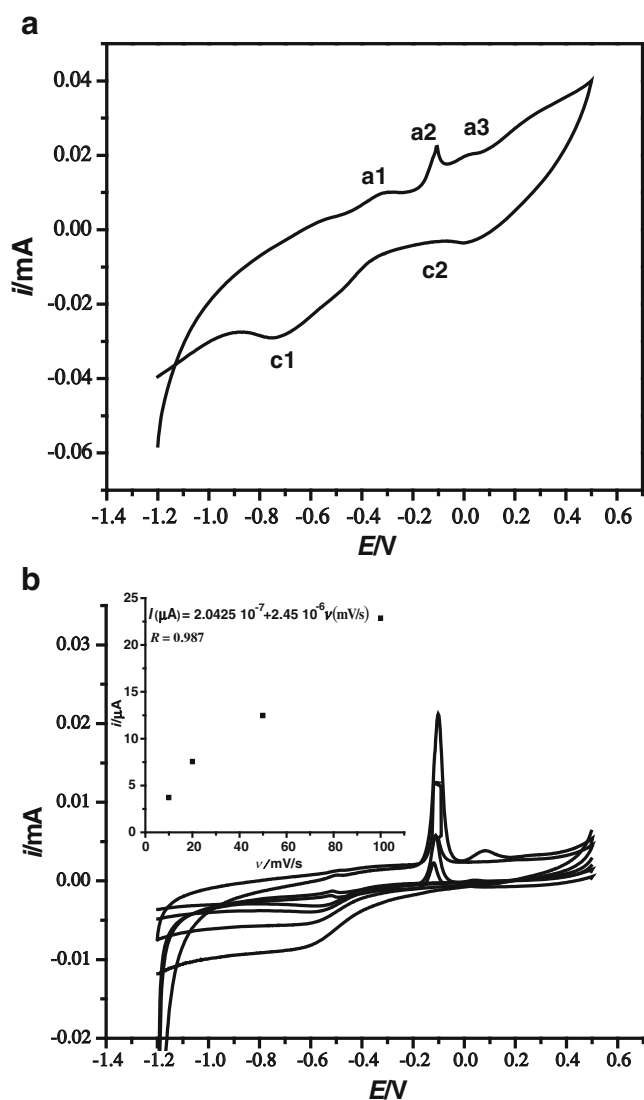
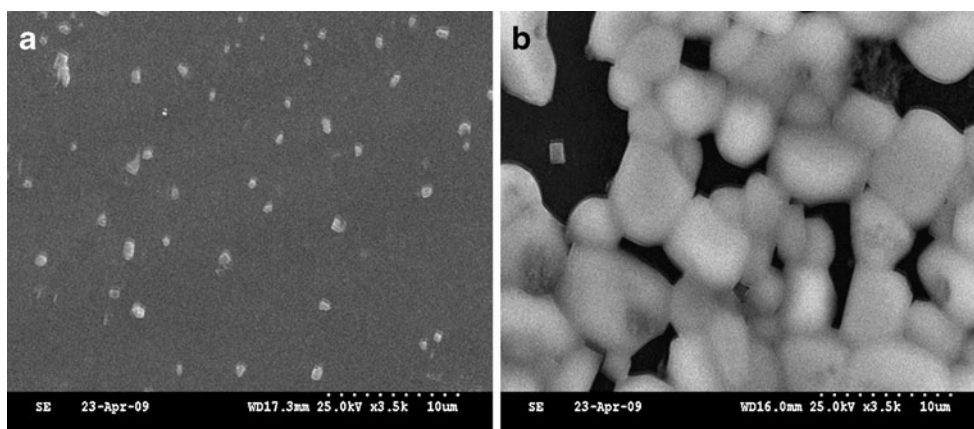


Fig. 4 **a.** Cyclic voltammogram of CuO/GC in 0.5 M KOH solution at 50 mV s^{-1} . **b.** Cyclic voltammograms of CuO/GC in 0.5 M KOH under different scan rates (inner to outer 10, 20, 50 and 100 mV s^{-1}). Inset shows the plot of current vs scan rate

XPS was used to analyse the oxidation state of the CuHCF films on GC surface. The XPS response of Cu 2p and Fe 2p of CuHCF is shown in Fig. 2a, b. From the figure, it is clear that the peak corresponding to Cu (2p3/2) and Cu (2p1/2) appears at 935 and 955 eV followed by a satellite peak at 943 eV. Peaks corresponding to Fe (2p3/2) and Fe (2p1/2) appearing at 712 and 723 eV, respectively, indicate the presence of Fe 2p electrons on this modified electrode. Comparison with standard data indicates that Cu and Fe are in a bivalent state [61, 62]. The SEM images of these two electrodes are shown in Fig. 3a, b. Continuous growth of film is observed for electrode prepared in the presence of dendrimer and a non-uniform appearance is observed for electrode modified in the absence of dendrimer. In the former case, the deposition solution consists of Cu^{2+} ions complexed with dendrimer molecules. A dendrimer molecule can incorporate a large number of metal ions and a complexed dendrimer molecule acts as nuclei for the deposit and this aids in uniform deposition over the

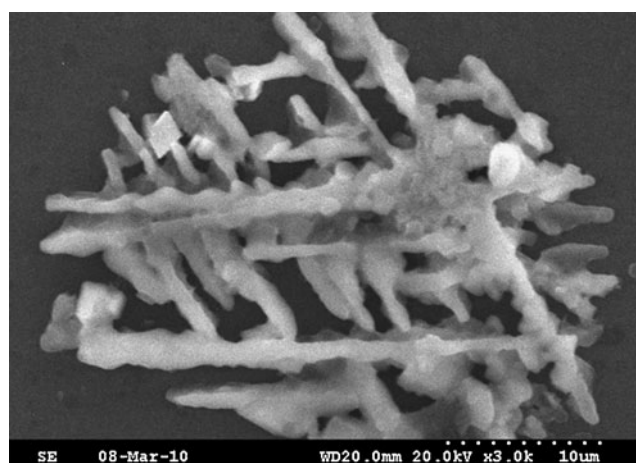


Fig. 5 SEM image of CuO prepared after cycling CuHCF in 0.5 M KOH

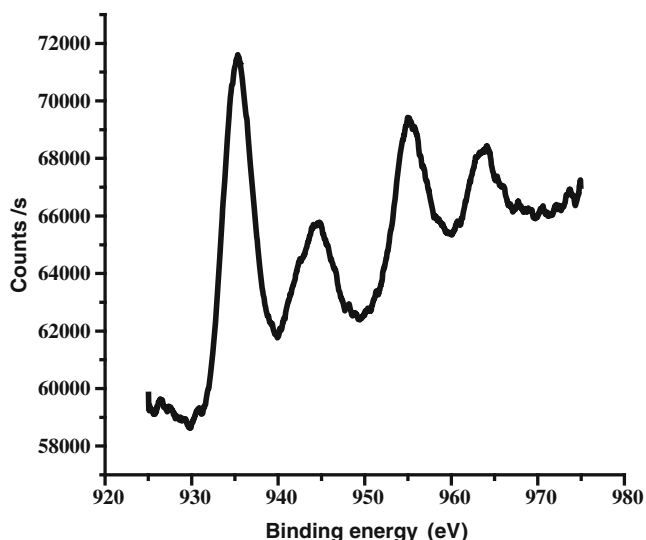


Fig. 6 XPS of CuO/GC-modified electrode

entire region of the substrate. This type of directing influence is lacking for an electrode modified in the absence of dendrimer. A similar influence of dendrimers has been observed during the deposition of Cu [63].

Formation of copper oxide on glassy carbon and its electrochemical behaviour

Metal hexacyanoferrate-modified electrode is converted to their oxides by a process of electrochemical potential cycling. CuHCF-modified GC was converted to CuO by potential cycling between -1.2 to 0.5 V for 10 cycles at a scan rate of 50 mV s^{-1} in 0.5 M KOH. Cyclic voltammograms of CuO/GC in 0.5 M KOH are shown in Fig. 4a. Three anodic peaks, a1, a2 and a3, and two cathodic peaks, c1 and c2, are clearly seen in the voltammograms. The anodic peaks correspond to the oxidation of Cu to Cu_2O – (a1), Cu_2O to CuO – (a2) and $[Cu(OH)_2]$ – (a3). According to Jayalakshmi et al. [64], cathodic peak c2 is due to the reduction of a3. So, cathodic peak c2 corresponds to the reduction of $Cu(OH)_2$

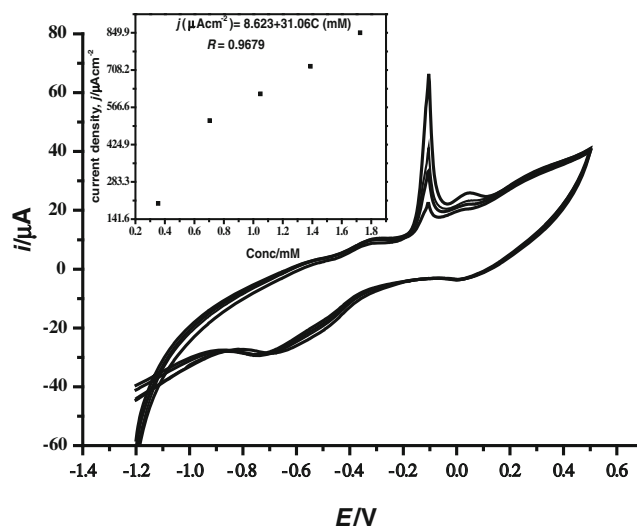
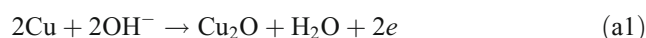


Fig. 7 Cyclic voltammogram of CuO/GC in 0.5 M KOH for different concentrations of D-glucose at a scan rate of 50 mV s^{-1} . Inner to outer— 0.3546 , 0.704 , 1.048 , 1.388 and 1.724 mM D-glucose. Inset shows the plot of current density vs concentration

to Cu_2O and cathodic peak c1 corresponds to the reduction of Cu_2O to Cu [11, 65].



The cyclic voltammograms of CuO/GC in 0.5 M KOH shows an increase in current with scan rate as it proceeds from 10 to 100 mV s^{-1} . Figure 4b shows the plot of current vs scan rate and it is found to be linear, which indicates that the process is surface-confined. A SEM image of CuO prepared by cycling in 0.5 M KOH is given in Fig. 5. It is clear from the figure that the CuO film has a meso-porous grid like structure. From this the structure directing influence of G5-PAMAM dendrimer can be seen clearly.

Table 2 Comparison of oxidation potentials of glucose using various electrodes

Electrode type	Potential for glucose oxidation	Reference
CuO nanospheres	+ 0.6 V vs Ag/AgCl	Reitz et al. [67]
CuO nanowire-modified copper electrode	+ 0.33 V vs Hg/HgCl ₂	Wang et al. [68]
CuO nanowires	+ 0.49 V vs Hg/HgCl ₂	Zhang et al. [69]
CuO nanorod bundles	+ 0.6 V vs Hg/HgCl ₂	Batchelor et al. [70]
Porous CuO microcubes	+ 0.61 V vs Ag/AgCl	Zhang et al. [71]
Cu nanoparticles	+ 0.65 V vs Hg/HgCl ₂	Xu et al. [72]
CuO/MWCNTs	+ 0.4 V vs Ag/AgCl	Jiang et al. [73]
CuO/GC modified in the presence of dendrimer	-0.125 V	Our work

In order to confirm the oxidation state of the modified film, XPS analysis was performed, which is shown in Fig. 6. From the analysis, it is clear that copper exists in a divalent state having mainly d^9 character. The XPS detected Cu (2p3/2) and Cu (2p1/2) at 935.44 and 955.11 eV, respectively. The main peaks at 935.44 and 955.11 eV are accompanied by satellite peaks at 944.6 and 963.7 eV, which corresponds to Cu^{2+} state [66]. The absence of Fe^{2+} peak 712 eV confirms the complete conversion of CuHCF to CuO.

Electrocatalytic activity of carbohydrates and alcohols on CuO/GC

Surface-immobilised layer often imparts fast electron transfer characteristics to the underlying substrate. Hence, the possibility of $Cu(OH)_2$ -modified layer towards alcohols and carbohydrates oxidation was investigated. We found that analytes D-glucose, β -glucose and methanol did not exhibit any characteristic redox peak on bare glassy carbon electrode. The electrochemical response for the modified electrode in presence of D-glucose, β -glucose and methanol was recorded. The cyclic voltammetric response for CuO/GC for various concentrations of KOH was analysed. The different concentrations of KOH used are 0.2, 0.5, 2 and 5 M. Glucose addition in 0.5 M KOH medium shows good catalytic current response. An increase in the anodic current response due to oxidation of respective analytes and the absence of the cathodic peak reveal electro-catalysis. The oxidation process occurs at a potential of -0.108 V for β -glucose, -0.125 V for D-glucose and -0.122 V for methanol. Literature survey reveals that the exact mechanism of oxidation of glucose in alkaline medium at Cu-based modified electrode is still not

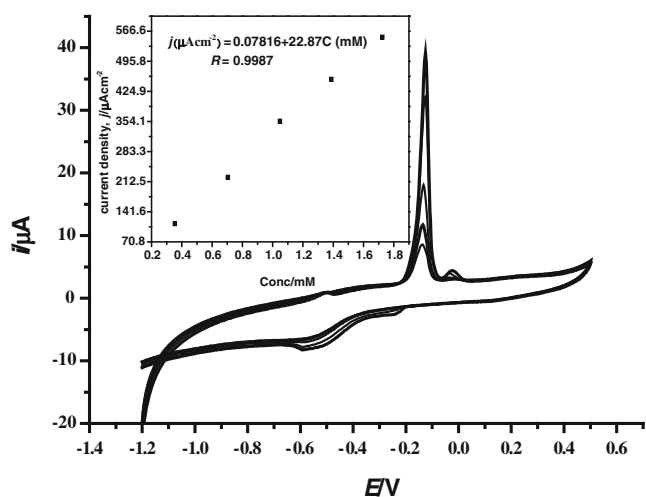


Fig. 8 Cyclic voltammograms of CuO/GC in 0.5 M KOH for different additions of β -glucose at a scan rate of 50 mV s^{-1} . Inner to outer—0.3546, 0.704, 1.048, 1.388 and 1.724 mM β -glucose. Inset shows the plot of current density vs concentration

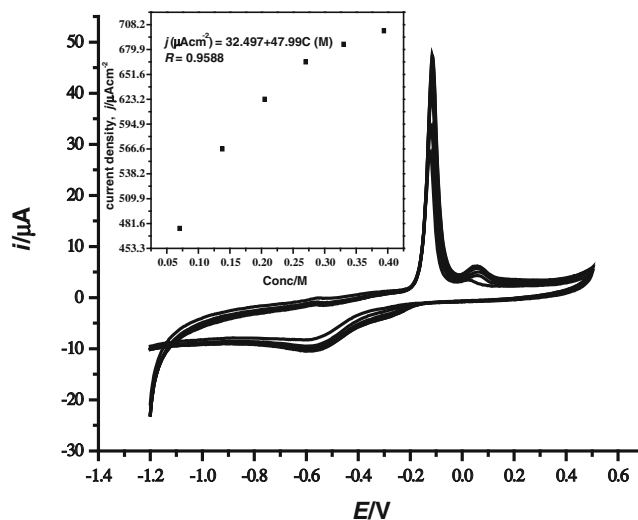


Fig. 9 Cyclic voltammograms of CuO/GC in 0.5 M KOH solution for different concentrations of methanol at a scan rate of 50 mV s^{-1} . Inner to outer 0.0173, 0.0342, 0.0505, 0.664, 0.082 and 0.097 M. Inset shows the plot of current density vs concentration

well studied [7, 25], but the most accepted mechanism suggests that oxidation of glucose takes place by removal of hydrogen, leading to the formation of enediol intermediate, which is further oxidised to gluconolactone and gluconic acid [29]. From the analysis, it is clear that CuO/GC prepared in the presence of G5-dendrimer has better ability for carbohydrate and alcohol oxidation. Oxidation of the analytes occurs at the peak potential corresponding to $Cu(II)/Cu(I)$ transition, and the addition of analytes causes an increase in anodic current density. Also, the increase in the ratio of anodic peak current density to cathodic peak current density in the

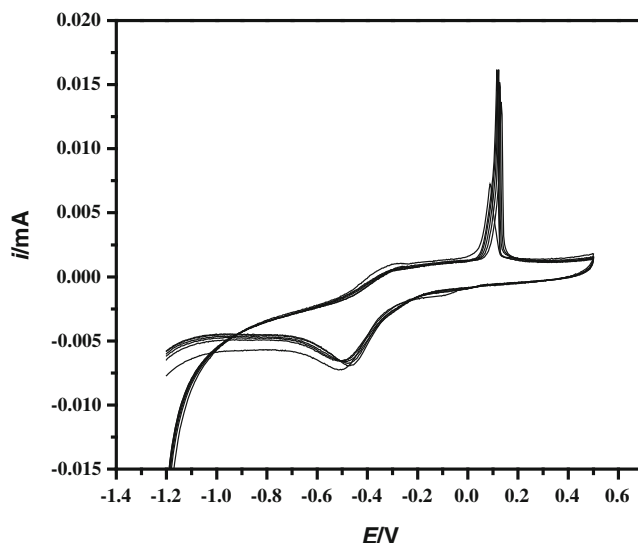


Fig. 10 Cyclic voltammograms of CuO/GC in neutral pH for different concentrations of D-glucose at 50 mV s^{-1} . Inner to outer—0.3546, 0.704, 1.048, 1.388 and 1.724 M

presence of methanol and carbohydrates indicates that Cu(OH)₂-modified electrode can be used as an efficient catalyst for methanol and carbohydrate oxidation.

Moreover, it was found that over-potential required for the oxidation of analytes is less. A comparison of glucose oxidation potentials of various electrodes is given in Table 2. The potential observed for glucose oxidation and methanol oxidation is found to be very low compared to other electrodes reported in the literature (approximately 400 mV less). The appearance of peak at negative direction and the large anodic current response show that CuO/GC-modified electrode, in the presence of dendrimer, shows better ability to accelerate electron transfer between analytes added and GC electrode surface. Figure 7 shows cyclic voltammograms for D-glucose addition. CV response shows that the current goes on increasing after each addition of D-glucose. Oxidation occurs at a potential of -0.125 V vs NCE for D-glucose; the cyclic voltammogram of the modified electrode in glucose solution exhibits no increase in characteristic cathodic peak current, showing that the reaction is electrocatalytic in nature. Inset picture shows the plot of current density vs concentration of D-glucose. From the graph, it is clear that current density increases linearly with concentration. The regression equation was found to be $j(\mu\text{A cm}^{-2}) = 8.623 + 31,068.2 C(\text{M})$. The modified electrode shows a current density of $849 \mu\text{A cm}^{-2}$, with a correlation coefficient of 0.967, while adding β -glucose oxidation takes place at -0.108 V vs NCE, which is shown in Fig. 8. There is a slight shift in oxidation potential towards the positive side compared to D-glucose. Current density vs concentration plot for β -glucose addition is shown in inset. The graph shows that peak current values exhibited a linear dependence on concentration with $R = 0.9987$ and regression equation was found to be $j(\mu\text{A cm}^{-2}) = 0.07816 + 22,875.7 C(\text{M})$. Cyclic voltammograms for CuO/GC in the presence of methanol are shown in Fig. 9. It shows that oxidation occurs at a potential of -0.122 V. In this case also, we observed an increase in current response with analyte addition. There is a slight shift in potential towards the positive side for each addition. Inset shows the current density vs concentration plot for methanol addition. The regression equation was found to be $j(\mu\text{A cm}^{-2}) = 32.497 + 47.99 C(\text{M})$ with a current density value of $680 \mu\text{A cm}^{-2}$.

Anodic peak current goes on increasing for several additions of analytes in the case of electrode modified in the presence of dendrimer. Electrode prepared in the absence of dendrimer shows poor catalytic current response as revealed by a small increase in the catalytic current for the addition of analytes and the catalytic response was obtained only for a few additions of the analyte (“Electronic supplementary material”). Cyclic voltammograms of CuO/GC (absence of dendrimer) in the presence of β -glucose, D-glucose and methanol are given in the supporting informa-

tion (Figs. S2, S3 and S4 in “Electronic supplementary material”). From the above analysis, it is clear that the catalytic activity of the electrode can be improved by modifying electrode in the presence of dendrimer.

Applicability in neutral pH

The applicability of the modified electrode for sensing applications at neutral pH was verified by studying the electro-catalysis of glucose in phosphate buffer ($pH=7.2$). Figure 10 shows the cyclic voltammetric response for glucose addition in neutral medium. There is an increase in anodic current, but a shift in potential towards the more positive side is observed. The over-potential required for the oxidation of D-glucose was found to be $+0.15$ V. Further, each addition shows a shift in potential towards the negative direction. This result shows that the analysis can be extended to neutral pH, indicating the suitability of the electrode for glucose analysis in biological systems with a shift in the potential of detection from -0.125 to $+0.15$ V. Selectivity can be obtained by combining electrochemical detection with HPLC.

Conclusions

In this investigation, we have discussed the preparation of CuO electrode through a CuHCF template for its application as an electrocatalyst for carbohydrate and methanol oxidation. The structure directing the influence of PAMAM dendrimer has resulted in the formation of an electrochemically reversible CuHCF template film and leads to the formation of uniform, continuous meso-porous grid-like structures on the glassy carbon electrode as revealed by SEM. The use of PAMAM dendrimers has resulted in the formation of highly active catalyst material. The electro-catalysis of carbohydrates and alcohols as shown by the cyclic voltammograms reveals that the CuO electrode exhibits very low over-potentials for the oxidation of glucose and methanol when compared to literature reports. The applicability of the CuO electrode for sensing applications in neutral media has also been demonstrated in phosphate buffer ($pH=7.2$).

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