



Facile fabrication of biosensors based on Cu nanoparticles modified as-grown CVD graphene for non-enzymatic glucose sensing

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ABSTRACT

Copper nanoparticles modified as-grown monolayer and bilayer graphene on copper substrates have been used for non-enzymatic electrochemical glucose sensing. The high quality, continuous, full coverage graphene on copper substrate act as a good electrochemical electrode which obviating the tedious transfer processes. The present sensor shows excellent performance for glucose detection including a wide linear range of 0.02–2.3 mM, a low detection limit (1.39 μ M, S/N = 3), high sensitivity (379.31 μ A mM⁻¹ cm⁻²), fast response time (< 5 s), good selectivity to the general coexisted interferences, reliable stability, etc. We believe this kind of electrode has a great potential for practical glucose sensing applications and also promise for other biomolecules detection.

1. Introduction

Diabetes is a disease which causes a metabolic disorder in an individual, resulting in high blood sugar levels over a prolonged period. It has been reported that diabetes would be the seventh-leading cause of mortality [1]. The development of selective and sensitive anti-interferential methods of glucose detection is important in many areas such as clinical diagnostics, medicine, and the food industry [2,3]. Electrochemical sensors based on the immobilized the enzyme on an electrode has been widely used for making amperometric glucose detection sensors due to their high sensitivity and selectivity [4–6]. However, there are several drawbacks associated with enzyme-modified electrodes such as high cost, complicated enzyme fixation, hardly free from thermal or chemical deformations during storage, and difficult to control the reproduction of the process [7]. In contrast, non-enzymatic glucose sensors without the biological components have the advantage of stability, simplicity, reproducibility and low cost [8,9]. This kind of biosensor is based on the current response of glucose oxidation directly at the electrode surface with the participation of metal catalysts in an alkaline medium. Many electrocatalytic materials have been used to develop non-enzymatic electrodes such as Pt [10], Au [11–14], Ni [15] and Pd [16,17]. Among them, more economical non-precious transition metals, such as copper, have been investigated and shown good glucose oxidation catalyst performance [18]. It has been considered that

Cu(II)/Cu(III) is the reaction center of glucose oxidation [19]. With rapid advances in nanotechnology, various nanostructures bring remarkable electrocatalytic enhancements for non-enzymatic sensing [20–22].

Graphene is a single layer of carbon atoms arranged in two-dimensional (2D) honeycomb lattice. This strictly two-dimensional material exhibits exceptional structural, electrical, physical, optical, and biocompatible properties [23–25]. Graphene is favorable for electrochemical sensing because of its high surface area, mechanical strength, and electrical conductivity [26]. One of its promising applications is electrochemical sensing. Many researches in this field have been devoted to immobilizing different kinds of nanoparticles and aromatic biomolecules on the high specific surface area of graphene [27,28]. Since every atom in graphene is a surface atom, molecular interaction and electron transport through graphene can be highly sensitive to any absorbed molecules [29]. In the last few years, various forms of copper nanoparticles (CuNPs)-graphene based glucose sensors were developed with high sensitivity and good stability. Luo et al. fabricated a non-enzymatic glucose sensor based on Cu nanoparticles modified reduced graphene oxide (rGO) electrode which exhibited good sensitivity [30]. Further improvements were made when Ding et al. constructed a CuNPs decorated nitrogen-doped graphene (Cu–N–G) nanocomposite that showed enhanced electrocatalytic activity to glucose oxidation [31]. Maaoui et al. studied an N-doped porous reduced graphene oxide decorated with copper oxide nanoparticles

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(ammonia-doped-prGO/CuO) glucose sensor which also demonstrated high sensitivity [32]. Further, to realize graphene's full potential, a high quality, more easily reproducible graphene synthesis method that is defect free is required. One of the best graphene synthesis routes is the chemical vapor deposition (CVD) method on metallic surfaces, which yields the production of high quality single and multilayer graphene with larger surface areas [33,34]. Jiang et al. demonstrated a nonenzymatic glucose sensor combining Cu nanoparticles with the CVD grown graphene edge by a simple electrodeposition with a low detection limit [35]. Soganci et al. also prepared a nonenzymatic glucose sensor with copper nanoparticles deposited on CVD grown single-layer graphene which was transferred to an FTO glass slide. The sensor exhibited good performance [36].

For most electronic device applications, graphene must be transferred from the metal catalyst to a different substrate. This is necessary because the conductive substrate renders any conduction through graphene irrelevant [37]. This extra transfer step causes a number of significant problems. First, the mechanically delicate graphene can be easily damaged during transfer. Secondly, the transfer process itself introduces large amounts of defects in the graphene lattice, leading a sharp decrease in desired electric properties. Thirdly, these transfer procedures are often performed with contaminant trapped between graphene and the target substrate [38]. However, It has been proven that using graphene directly on a metallic substrate as a biosensing platform not only leads to an enhanced heterogeneous electron transfer rate and thus greater output signal intensity, but it also obviates the tedious substrate transfer process [39]. The electrochemical sensing approach is exemplified by a direct electron transfer between the sensing platform (graphene and its derivatives) and a target molecular [40]. This is promising to help realize non-enzymatic glucose sensing by combining electrocatalytic CuNP with CVD grown graphene without the need for the transfer process.

In this work, high quality, full coverage monolayer and bilayer graphene on a Cu substrate was synthesized using the CVD method. It is then utilized directly as an electrode material, thereby obviating the tedious transfer processes, with the added benefit of avoiding manufacturing defects, as well. Subsequently, the CuNPs-graphene composite-based electrode can be used for the amperometric sensing of glucose with high sensitivity and excellent selectivity (Scheme 1). Furthermore, the sensor was used for the detection of glucose in human blood serum samples, which exhibits the potential for the practical clinical glucose sensing application.

2. Experimental

2.1. Chemicals

Glucose, uric acid (UA), ascorbic acid (AA), dopamine hydrochloride (DA), D-fructose, potassium ferricyanide ($K_3[Fe(CN)_6]$) were purchased from Aladdin Chemical Reagent Company (Shanghai, China). Copper sulfate ($CuSO_4$) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Other chemicals were analytical grade and used without further purification. Deionized water ($>18\text{ M}\Omega\text{ cm}^{-1}$) was used for all experiments. Blood serum samples were obtained from School of Life Science, Tianjin University.

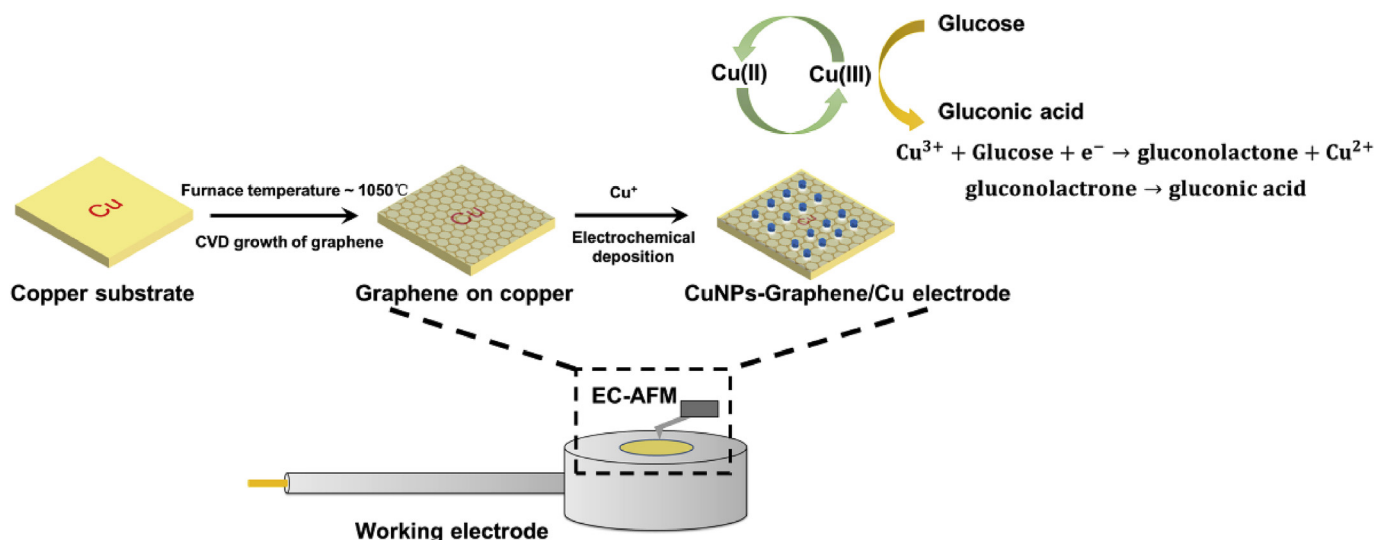
2.2. Instruments

Scanning electron microscopy (SEM) analysis was performed using a Hitachi SU3500 (at an acceleration voltage of 15.0 kV, Japan). In situ electrochemical atomic force microscopy (EC-AFM) images were performed via Park NX10 (with a liquid probehead, Korea). AFM detected mode was acquired by non-contact (NCM) mode. Spectroscopic characterization of the CuNPs-graphene was carried out using Raman spectroscopy (Renishaw, England). X-ray photoelectron spectroscopy (XPS) experiments were performed in a PHI 1600 VersaProbe - Scanning ESCA Microprobe (ULVAC-PHI, Japan/USA) instrument.

Electrochemical measurements were performed using a CHI 760E electrochemical workstation (Shanghai CH Instrument Co., China). A conventional three-electrode system was employed. The CuNPs-graphene on the Cu foil substrate was used as the working electrode and was sealed against the bottom of a homemade electrochemical cell by means of a Teflon O-ring. The exposed working surface was 0.49 cm^2 and electrical contact was made to a copper plate. Saturated calomel electrode (SCE) was used as reference electrode and a platinum wire as counter electrode. Electrochemical impedance spectroscopy (EIS) was performed with the same three-electrode system in an electrolyte solution of 0.1 M KCl containing 10 mM $[Fe(CN)_6]^{4-/3-}$. A 5 mV amplitude of sine voltage signal was applied with a frequency range from 0.1 Hz to 100 kHz.

2.3. Preparation of CuNPs-graphene/Cu electrodes

Scheme 1 is a schematic representation of the design of a CuNPs-graphene/Cu sensing electrode and the corresponding sensing mechanism schematic is also shown in the scheme.



Scheme 1. CuNPs-graphene/Cu bioelectrode fabrication steps and the possible glucose sensing mechanism.

Graphene was grown on Cu foils by CVD method. 1.5 cm $\times$ 1.5 cm Cu foils (purity: 99.99%, thickness: 25 μ m) were used as metallic catalyzer after extensively cleaning with acetone, ethanol and DI water. Graphene was grown on etched Cu foils by ambient pressure CVD at 1050 $^{\circ}$ C with CH₄, H₂ and Ar gases. The etched Cu foil was set in a quartz tube and heated to 1050 $^{\circ}$ C in 80 min under 200 sccm Ar gas and 50 sccm H₂ gas, followed by an annealing step at 1050 $^{\circ}$ C for 40 min. For the following growth step, 1 sccm CH₄ was introduced into the quartz tube for 15 min under 10 sccm H₂ and 200 sccm Ar gas. Eventually, the graphene CVD growth system was cooled down to room temperature with Ar and H₂ protection.

The CuNPs were electrodeposited on the graphene/Cu electrode using 0.1 mM CuSO₄ in 0.01 M H₂SO₄ solution. A constant potential of -0.4 V (vs.SCE) was applied to the graphene/Cu electrode. The deposition time was determined to be 2000 s.

3. Results and discussion

3.1. Characterization of morphology and composition

The morphology of as-grown graphene on Cu foil was investigated by SEM. As shown in Fig. 1a, the graphene film is present with bilayer (darker regions) and large area of uniform monolayer (brighter area). The continuous uniform graphene was evenly grown on copper substrate. More evidence was carried out by using optical microscopy which has been used to great effect for identifying graphene flakes on dielectrics such as silicon oxide. The optical micrographs Fig. S1 shows graphene transferred to silicon oxide wafer and also exhibited that the alternately dark and bright continuous monolayer and bilayer graphene reaching full surface coverage of the substrate.

The SEM image of the CuNPs decorated graphene composite (Fig. 1b and c) reveals that the Cu-NPs with sizes of 100–350 nm were uniformly deposited on the graphene surface (inset, Fig. 1b). The electrodeposition process was observed using in situ electrochemical atomic force microscopy, which could measure the topographical and surface properties simultaneously in operando conditions without damaging the sample at nanoscale resolution [41,42]. We investigated the nanoparticle structure morphology over a series of deposition intervals. Fig. 1d–h shows the structural changes of CuNPs on graphene surface per 500 s in 0.1 mM CuSO₄ aqueous solution with applied -0.4 V. The Cu particle nucleated

on graphene surface and agglomerated with the deposition time. After 2000s, the size of the CuNPs has increased to 237 nm. The morphology of graphene unchanged during the electrodeposition process observed from AFM images.

Further spectroscopic characterization was performed by Raman scattering spectroscopy, which is a useful analytical technique to investigate the information of the defects, ordered, the quality and the number of layers of graphene [43]. Fig. 2a shows the Raman spectrum comparison of as-grown graphene on copper substrate and the CuNPs-graphene/Cu composite prepared by electrodeposition. Both the as-grown CVD graphene and CuNPs-graphene display two specific graphene bands at 1580 cm^{-1} (G peak) and 2690 cm^{-1} (2D peak), corresponding to the E_{2g} phonon of C sp² atoms and a breathing mode of six-atom rings respectively [44]. The intensity ratio (I_{2D}/I_G) and the full width at half maximum (FWHM) of the 2D band of brighter area and darker regions were 2.6, 31 cm^{-1} and 1.2, 50 cm^{-1} , respectively. These data confirm the presence of monolayer and bilayer graphene [45,46]. The peak seen at ~ 1350 cm^{-1} appears due to the defect in the graphene film, and is known as the D band, which is caused by electron interaction between the graphene and the metal nanoparticles [47]. For defect comparison, the spectrum of graphene transferred to silicon oxide substrate under the same conditions was shown in Fig. S2. The absent of the D peak of the graphene on the Cu substrate indicates the as-grown graphene is quite homogenous [44].

XPS analysis was used to characterize the chemical nature and bonding of different elements in the CuNPs-graphene composite. The XPS scan spectrum displays distinct peaks 284.5 eV (C 1s, 60.2 at. %), 530.4 eV (O 1s, 18.9 at. %), and a contribution at 932.5 eV due to Cu 2p (20.9 at. %) (Fig. S3). The high resolution XPS spectrum of the C 1s shows two peaks at 284.5 and 285.3 eV corresponding to the sp²-hybridized carbon and sp³-hybridized carbon [48] (Fig. 2b). The peak in 284.5 eV is much larger than the peak in 285.3 eV, indicating the presence, but small amount of defects in graphene after electrodeposition [49]. The result is consistent with Raman Spectra analysis. The O 1s XPS spectrum shown in Fig. 2c could be fitted to two constituents: C=O (531.5eV) and C–OH oxygen (532.5 eV) [50]. Moreover, the high-resolution spectrum of Cu 2p obviously showed binding energy peaks at 932.4 and 952.3eV corresponding to Cu 2p_{3/2} and Cu 2p_{1/2} (Fig. 2d). The presence of Cu²⁺ is further confirmed by the shake-up satellite peaks at 943.8 and 946.7 eV, characteristic of materials having a d⁹ configuration in their ground state

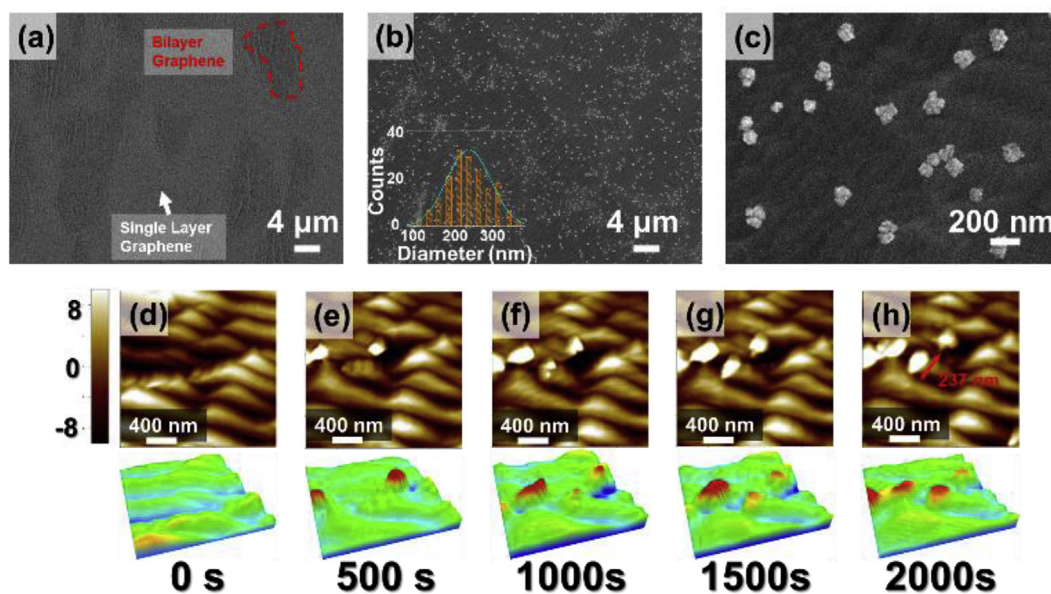


Fig. 1. SEM images of uniform film of graphene (a); Graphene-CuNPs composite (b and c); In situ AFM images of CuNPs electrodeposited on graphene film acquired from 0 s to 2000 s, (d) 0 s (e) 500 s (f) 1000 s (g) 1500 s (h) 2000 s.

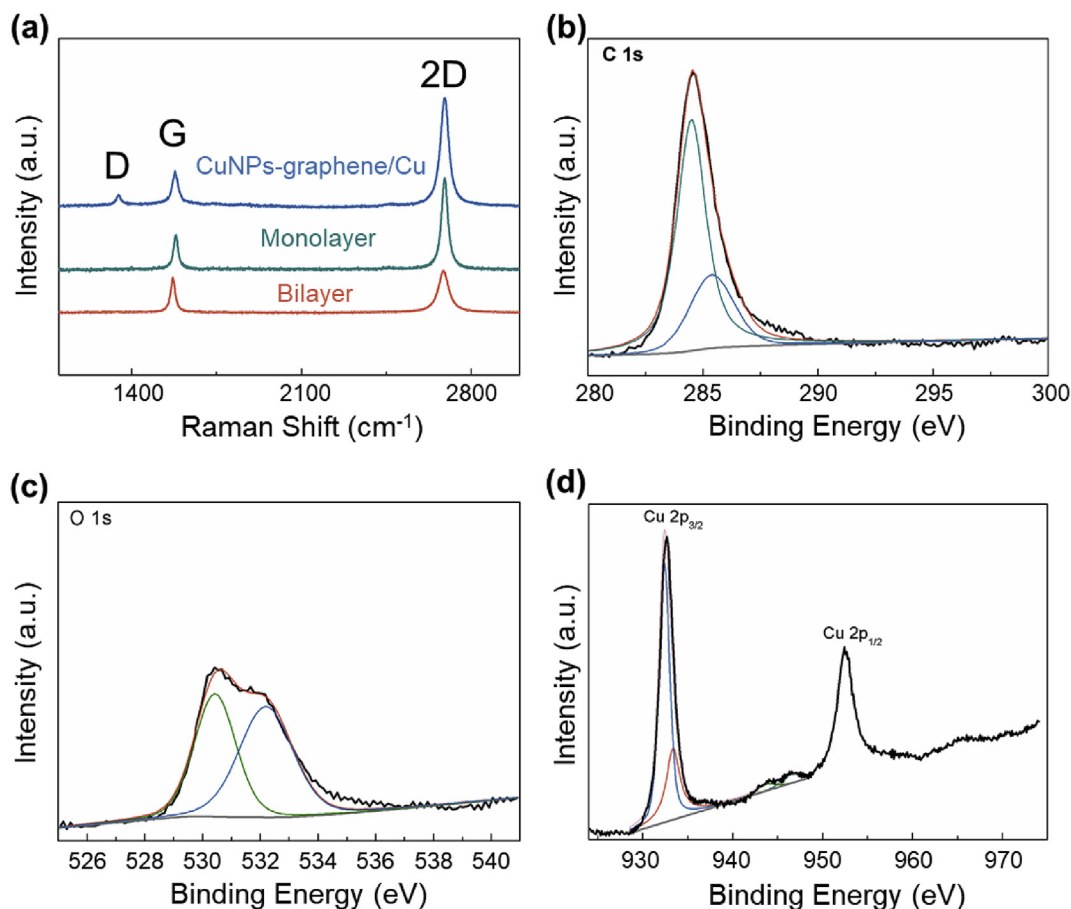


Fig. 2. Raman Spectra of monolayer, bilayer graphene and CuNPs-graphene composite on Cu substrate (a); The high-resolution XPS C 1s spectra (b), O 1s spectra (c) and Cu 2p spectra (d) of CuNPs-graphene/Cu.

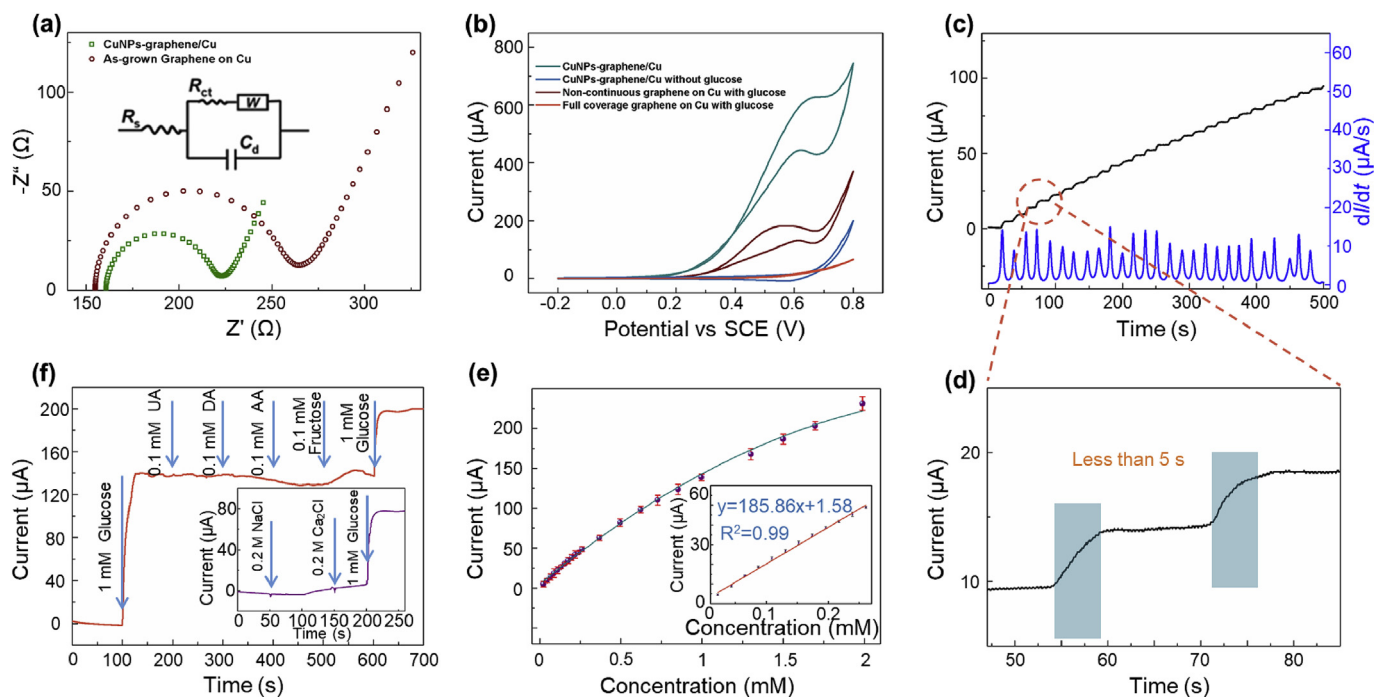


Fig. 3. (a) Electrochemical impedance spectroscopy (EIS) of CuNPs-graphene/Cu composite and graphene/Cu in [Fe(CN)₆]^{4-/-3-} containing 0.1 M KCl solution; (b) Cyclic voltammograms of CuNPs-graphene/Cu and graphene/Cu electrode in the absence and presence of 5.0 mM glucose in 0.1 M NaOH; (c) Amperometric responses of CuNPs-graphene/Cu electrode in 0.1 M NaOH with a dropwise addition of 20 μM glucose at 15 s interval (detection potential: 0.5V). (d) Response time of the sensor; (e) Calibration curve for glucose detection. Inset: amplification of the calibration curve with the linear fitting result; (f) Amperometric response of CuNPs-graphene/Cu electrode with the additions of 1.0 mM glucose and in the presence of 0.1 mM UA, AA, DA and fructose. Inset is in the presence of 0.2 M NaCl and CaCl₂, respectively.

[32]. The information indicated that high specific surface area copper nanoparticles has been slightly oxidized in atmosphere [51].

3.2. Electrochemical characterization

Electrochemical impedance spectroscopy (EIS) is a typical technique used to gather information on electron transfers between the electrolytes and the electrode surface. The resulting impedance diagram can be explained in terms of electrical equivalent circuits or in terms of Faradaic impedance which depends on the electrode reactions [52]. Fig. 3a shows the Nyquist plots obtained for graphene/Cu and CuNPs deposited on graphene/Cu in 10 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ containing 0.1 M KCl solution from 0.01 to 1.0×10^5 Hz. An equivalent circuit model (inset, Fig. 3a) was employed to fit the impedance data, where R_s is the solution resistance, W is the Warburg impedance and C_d is the capacitance. A semi-circular area at high frequency corresponds to the electron transfer-limited process and linear portion at lower frequencies corresponds to the diffusion process. The diameter of the semicircle obtained from the Nyquist plot is equivalent to the electron transfer resistance (R_{ct}) which normally reflects the conductivity and the electron transfer process [53]. The graphene/Cu electrode shows a large semicircle of about 97Ω . When CuNPs were deposited on the graphene film, the R_{ct} value was decreased to 55Ω and with a steeper straight line in the low frequency region. The results indicate that graphene films act as a strong platform for the dispersion of nanoparticles and the uniform dispersed CuNPs exhibit higher conductivity and improved heterogeneous electron transfer processes [30].

3.3. Electrocatalytic oxidation of glucose

The catalytic activity of nanoparticle depends heavily on the size of nanoparticle [54,55]. Catalytically active surface leading to improved current response and catalysis at the nanoscale. The electrochemical catalytic activity effect of varying electrodeposition times on the graphene/Cu were investigated in 0.1 M NaOH containing 5 mM glucose. Fig. S4 shows the oxidation peak current of the CuNPs-graphene/Cu electrode prepared under different electrodeposition times. It can be easily observed that the peak current response increased with the increment of Cu electrodeposition time and achieved a maximum value at 2000 s. Therefore, an optimized Cu electrodeposition time (2000 s) was used in subsequent experiments.

The electrocatalytic activity of unmodified graphene/Cu electrode and CuNPs-graphene/Cu electrodes was recorded in 0.1 M NaOH solution with the absence and presence of 5 mM glucose at a scan rate of 100 mV s^{-1} . As shown in Fig. 3b, no peak current was obtained in 0.1 M NaOH solution. Upon the addition of 5 mM glucose, it can be seen that an irreversible glucose oxidation peak at 0.65 V (vs SCE) was obtained at the CuNPs-graphene/Cu electrode. The enhancement of electrocatalytic performance of CuNPs-graphene/Cu electrode compared with graphene/Cu is considered to be the result of large surface area and high electrocatalytic activity provided by CuNPs, confirming the CuNPs plays an important role in the electrocatalytic performance towards glucose oxidation [31]. For metallic nanoparticles catalysis, one of their properties is their high number of surface atoms that increases with decreasing particle size. CuNPs serve as active sites that enhance electrocatalysis of glucose on the electrode surface [56]. Furthermore, the effect of different scan rates on the glucose oxidation at

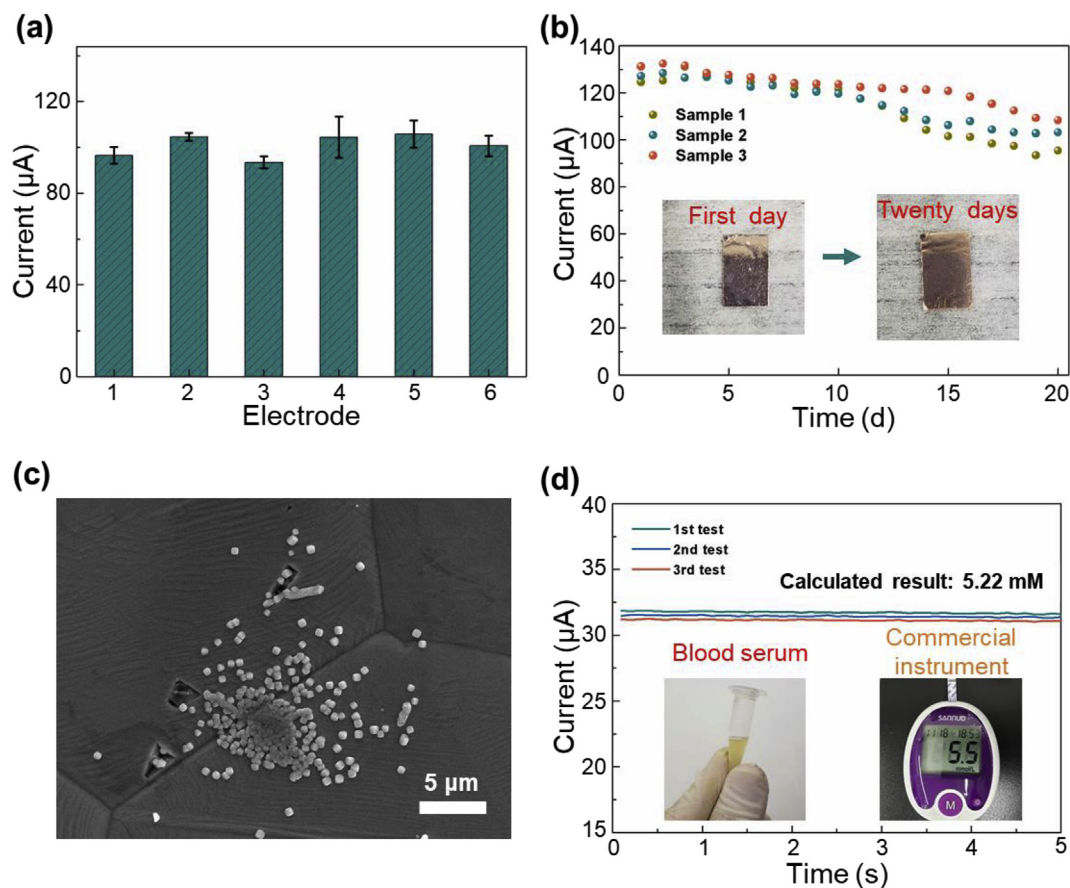


Fig. 4. (a) Amperometric responses of six different CuNPs-graphene/Cu sensors to 1 mM glucose in 0.1 M NaOH; (b) Stability of three non-enzymatic sensor in 20 days; (c) SEM images of CuNPs-graphene/Cu sensors after stability measurement (d) 5 s amperometric responses of blood serum of three CuNPs-graphene/Cu sensors and right insert shows the commercial instrument measure result.

CuNPs-graphene/Cu electrode in 0.1 M NaOH was investigated. As shown in Fig. S5, the anodic peak current of glucose oxidation is proportional to the increasing scan rate indicating a surface adsorption electrochemical kinetics [30] which is consistent with the most accepted glucose electrocatalysis mechanism [1,19,36,57,58]. Under an anodic bias in alkaline environment, Cu has been oxidized to Cu(II) species and then turned to higher oxidation species such as CuO^+ or $\text{CuO}(\text{OH})$ while the surface bound hydroxide species radicals are capable oxidizing carbohydrates near the surface. The electron transfer from glucose to Cu(III) generates radical intermediates and further converted to hydrolyzate gluconic acid. Cu(III) species act as an important electron transfer mediator in the catalytic oxidation process of glucose [59,60]. Thus, the copper nanoparticles deposited on high quality graphene have showed a higher electrocatalytic activity toward the oxidation of glucose, while graphene improved the conductivity and electron transfer rate.

It is necessary to discuss the case of a non-continuous graphene film covered the copper which the underlying copper surface exposed to the solution. This heterogeneous electrode surface has two kinds of electrochemical activity toward to glucose in alkaline solution [61]. The no coverage copper substrate has favorable electrochemical property towards glucose. It will exhibit microelectrode type response which large coverage of graphene made only nano- or micro-bands of the underlying metal are exposed [61,62]. In Fig. 3b the wine color line shows a voltammetry response of graphene/Cu for which the growth has been stopped before reaching full Cu surface coverage compared with full coverage graphene/Cu (orange color). The microelectrode type not full coverage graphene/Cu exhibits electrocatalytic activity toward the oxidation of glucose in the potential range of 0.30–0.6 V [63]. After nanoparticle deposition, this kind of micro-electrode decorated with nanoparticles give an enhanced electrocatalytic activity towards the analyte.

3.4. Amperometric measurement of glucose

Fig. 3c displays the typical current–time plot for the CuNPs-graphene/Cu electrode upon successive step increases with the addition of 20 μM glucose every 15 s in 0.1 M NaOH solution at +0.5 V. The CuNPs-graphene/Cu electrode showed a well-defined, stable amperometric response with the addition of glucose. $\text{d}i/\text{d}t$ response represent the sensor has a very sharp current changing in a short reaction time. It took less than 5 s (Fig. 3d) to reach the steady-state current, indicating the fast response time towards oxidation. The calibration curve of the currents of the assembly to the concentrations of glucose is shown in Fig. 3e. The proposed electrode gave a linear response to glucose in the range from 20 μM to 2.3 mM. A linear relationship of non-enzymatic electrode was observed between 0.01 and 0.25 mM glucose concentration satisfying the equation $y = 185.86x + 1.58$ and $R^2 = 0.99$. The electrode has a sensitivity of $379.31 \mu\text{A mM}^{-1} \text{cm}^{-2}$ and a low detection limit 1.39 μM ($S/N = 3$) for glucose sensing. This linear concentration range is suitable for the determination of glucose level in blood and urine samples. The comparison of performance of non-enzymatic sensors toward to the oxidation of glucose has shown in Table S1.

3.5. Anti-interference property, reproducibility, and long-term stability

To evaluate the selectivity of the non-enzymatic sensor, we have tested the effect of interferents that normally co-exist with glucose in human blood serum. Considering the concentration of glucose is about 30 times higher than interfering species in human blood, the interference experiment was carried out by successive addition of 1.0 mM glucose and 0.1 mM interfering species in 0.1 M NaOH solution at a potential of +0.5 V. As shown in Fig. 3f, the additions of UA, AA, DA and fructose caused very small increases in the current, whereas the addition of glucose causes a large increase in the current. Metals based non-enzymatic sensor has been reported will lose the activity due to the poisoning effect of chloride ions [57]. More ion interference test was utilized adding a high

concentration of chloride ions from 0.2 M NaCl and CaCl_2 (Fig. 3f inset). The two kinds of interference exhibiting a negligible current response compare with the addition of 1.0 mM glucose. CuNPs-graphene/Cu electrode did not show any significant change in the presence of interfering species, which indicates that it has high selectivity for glucose detection.

Reliable reproducibility and long-term stability of sensors were of critical importance for practical applications. In the last few years, various forms of copper nanoparticles (CuNPs) - rGO based material were developed in glucose sensing. rGO is highly disordered with many vacancy defects and even reduce the graphene oxide, there was still some oxygen functional groups in or on the rGO's surface [64]. It was hard to control graphene property precisely. CVD synthesis process provide a fine control in graphene thinness, continuous and growth size. The as-grown graphene by CVD method has a reliable reproducibility lead to production of high quality, continuous, full substrate coverage graphene. We used four independently fabricated CuNPs-graphene/Cu electrode under identical conditions to investigated the reproducibility. The current responses upon 1 mM glucose in 0.1 M NaOH solution of six sensors was shown in Fig. 4a. A relative standard deviation (RSD) of 4.9% was obtained, indicating the reliability of the sensor. The stability of glucose sensors was evaluated by measuring its amperometric current response to glucose during a period of 20 days at a time interval of 24 h, as shown in Fig. 4b. The sensor retained about 80% of its initial current response to 1 mM glucose in 0.1 M NaOH aqueous solution at +0.5 V vs. SCE, suggesting a good stability of the electrode. For investigating the current attenuation reason, SEM of the electrode surface was carried out for stability measurement (Fig. 4c). CuNPs migrate on graphene surface and aggregate to bigger copper island. With the surface agglomeration of the nanoparticles, the mass-transport of the detect molecule from the particle maybe changed. More discussion will spread on surface energy and diffusion mechanisms of graphene supported nanoparticles in the future work.

3.6. Human serum samples measurement

In order to examine the real applicability of the CuNPs-graphene/Cu non-enzymatic sensor, it was applied to determine glucose in human blood serum samples. Optimized experiment condition was adding 1 mL of blood serum sample into 30 mL 0.1 M NaOH solution with stirring diluted. The current response at 0.5 V of CuNPs-graphene/Cu electrode was recorded and the concentration was calibrated by the equation in Fig. 3e inset. A glucose result of the blood serum sample was measured for three times. The current response was shown in Fig. 4d and the calculated glucose concentration was 5.22 mM as determined for the healthy patient. The other results are shown in Table S2 and well in agreement with commercial instrument test results, indicating that the CuNPs-graphene/Cu non-enzymatic sensor has a great potential to be used for real clinical samples glucose sensing.

4. Conclusions

In the present study, we have fabricated a CuNPs-graphene/Cu composite without the graphene-transfer process and utilizing for sensitive and specific detection of glucose. High quality, continuous graphene has been synthesized on Cu film using CVD technique and CuNPs has been immobilized over it using potentiostatic electrodeposition. The designed non-enzymatic sensor demonstrates good performance, fast response time, and high sensitivity with the further advantages of facile fabrication, low cost, good reproducibility, and perfect specificity to blood glucose in the presence of common interferents. As-grown graphene on Cu substrate has been demonstrated with great potential for practical glucose sensing applications and shows promise for the detection of other biomolecules too.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2019.113527>.

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