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Non-enzymatic glucose sensing platform using self assembled cobalt oxide/graphene nanocomposites immobilized graphite modified electrode

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Abstract
A new strategy to prepare the densely packed cobalt oxide (Co_3O_4)/graphene nanocomposites by a self-assembly method were adopted in this work. A new non-enzymatic glucose determination has been fabricated by using Co_3O_4/graphene nanocomposites modified electrode as a sensing material. The nanocomposites were characterized using X-ray diffraction, X-ray photoelectron spectroscopy and field emission scanning electron microscopy, which confirms the successful formation of dense packed Co_3O_4/graphene nanocomposite. The results of Co_3O_4/graphene nanocomposites modified electrode exhibit good electrocatalytic activity toward the oxidation of glucose in 0.1 M NaOH by cyclic voltammetry. Under optimal conditions, the oxidation peak current was proportional to the glucose concentration in the range from 16.0 μM to 1.3 mM with a detection limit of 0.5 μM. The determination of glucose with the modified electrode shows the advantages of ease of preparation, high sensitivity and good stability. The analytical utility of the modified electrode as an amperometric sensor for the determination of glucose in the flow systems was evaluated by chronoamperometric studies. The practical application of the modified electrode for glucose determination has been evaluated in urine samples.

1 Introduction

In recent years, nanoscale devices have attracted significant attention because of their superior performances as they exhibit unique properties which differ from the bulk properties. A wide variety of nanomaterials with different sizes, shapes and compositions are now available [1]. The huge interest in nanomaterials is driven by their many desirable properties. The ability to tailor the size and structure and the properties of nanomaterials offer excellent prospects for designing novel sensing systems and enhancing the performance of the bioanalytical assay. Diabetes mellitus is a worldwide health care problem that seriously affects normal life of people [2]. Blood glucose level is a basic issue in the diagnosis and treatment of diabetes. Hence, there is a great demand for the development of glucose biosensor which can reliably and rapidly monitor the level of glucose in clinical diagnostics [3]. The conventional glucose oxidase (GOx) enzyme modified electrode is the most common class of amperometric biosensors for glucose detection because GOx enables catalytic oxidation of glucose with high sensitivity and selectivity [4, 5]. However, the GOx-based biosensors have several disadvantages, such as instability, high cost and complicated fabrication [6, 7]. Recently, it has been recognized that non-enzymatic glucose electrochemical sensors can offer a unique set of physical and practical properties that may be exploited in glucose detection as an alternative to the use of GOx-based biosensors.

Non-enzymatic glucose sensors were developed by various nanomaterials modified electrodes like precious metals and their alloys (Au, Pt, Pd, Pt–Au, Pt–Pd) [8, 9] transition metals and their oxides (Ni, Cu, CuO, NiO, CoO, Co_3O_4) [10–20] and transition metal complexes [21]. Amongst these materials, Co_3O_4 nanoparticles have demonstrated

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to be the promising material for non-enzymatic glucose sensor, supercapacitor, lithium ion battery, gas sensing and solar cells due to its low cost, good redox activity, environment friendly and relatively good conductivity. These nanomaterials can easily loss their shelf-life due to its aggregation and loss of their structural integrity by pulverization and the deterioration of the nanostructure. Hence, the modified electrode needs to keep maintain the size and structure of the nanomaterials without any passivation from electrode surface.

Graphene as a well known one atom thick two-dimensional graphitic carbon nanostructure with a single layer of carbon atoms densely packed in a honeycomb lattice. It has been utilized to be an efficient modified electrode material for electrochemical and biosensors in recent years, due to its superior electrical conductivity, mechanical properties, high surface-to-volume ratio, ultrathin thickness, structural flexibility, and chemical stability [22]. Meanwhile, graphene based modified electrodes showed good sensitivity, selectivity and stability towards for the electrochemical determination of biomolecules and glucose [23, 24]. These extraordinary features prompt the application of graphene and support to synthesize graphene based metal oxide nanocomposite hybrids for electrochemical determination of non enzymatic and enzymatic glucose sensors. To load a large number of metal oxides nanopaarticles, graphene was usually functionalized by some organic molecules based on physical absorption or covalent immobilization [25]. However, the poor immobilization usually resulted in leaching off metal oxides from the nanosheet during electrochemical analysis. Consequently, the prepared modified electrodes suffer from poor reproducibility, thermal, mechanical and chemical instability, regardless of high sensitivity and low detection limit. Therefore, more efforts are still needed to design novel metal oxide/graphene nanocomposites for developing reliable electrochemical glucose sensor.

Combining the advantageous features of self assembled graphene stacks and Co_3O_4 nanoparticles, Co_3O_4/graphene nanocomposite modified electrode has been successfully constructed and used for the non-enzymatic glucose sensor. The structure and morphology Co_3O_4/graphene nanocomposite were confirmed using X-ray diffraction (XRD) and FESEM. The electrochemical property of the modified electrode was evaluated through cyclic voltammetry and electrochemical impedance spectroscopy. The Co_3O_4/graphene nanocomposite modified electrode exhibits a good electrocatalytic activity toward the oxidation of glucose with high sensitivity and remarkable stability in static and dynamic conditions. The practical utility of the modified electrode was also evaluated for the determination of glucose in urine samples.

2 Experimental

2.1 Instrumentation

Electrochemical measurements were performed in a conventional three-electrode electrochemical cell using CHI 760D electrochemical workstation (CH Instruments, USA) controlled by a personnel computer. A platinum wire and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The Co_3O_4/graphene nanocomposite modified electrode employed as the working electrode was prepared according to the procedure described below. A magnetic Teflon stirrer was provided for the convective transport during the amperometric measurements. All experiments were performed at ambient temperature. XRD analysis was performed using Bruker model D8 with Cu Kα radiation. Field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) data were obtained using a SU6600, HITACHI, Japan, equipped with an EDS analyzer at an accelerating voltage of 30 kV.

2.2 Synthesis of the Co_3O_4/graphene nanocomposite

The synthesis of the Co_3O_4/graphene nanocomposite was carried out using a slightly modified procedure with an earlier report [25]. For the synthesis of graphene amine, graphene oxide (300 mg) was dispersed in aqueous solution (200 mL) by ultrasonicator for 1 h. Hexamethylene diamine (0.01 mol) in 100 mL aqueous solution is slowly added into the graphene oxide solution and stirred continuously for 48 h. The resultant precipitate was collected, washed with anhydrous ethanol and dried in a vacuum oven (50 °C) for 24 h.

For the synthesis of Co_3O_4/graphene nanocomposite, graphene oxide (50 mg) was dispersed in water (100 mL) by pulse sonication. An aqueous solution of cobalt chloride (0.20 M, 14 mL) was added dropwise into the graphene oxide solution and was stirred for 15 min. Graphene amine (50 mg) was dispersed to the mixed solution containing ethanol (150 mL) and water (150 mL). Finally, graphene amine is slowly added to graphene oxide/cobalt chloride solution and stirred for 15 min, and with 1 equivalent of NaOH was slowly added to the above solution until the pH reaches 12. Finally H_2O_2 aqueous solution (8 mL, 1 wt%) were added dropwise to the above solution. Then the mixture was heated at 120 °C for 16 h. Then, the precipitate was washed with anhydrous ethanol and dried overnight at 60 °C in conventional oven. The Co_3O_4/graphene nanocomposite was ground and reduced at 400 °C in

a flow of Ar gas for 2 h. The schematic illustrations showing the preparation of Co_3O_4/graphene nanocomposites and electrocatalytic activity is shown in Scheme 1.

2.3 Fabrication of the Co_3O_4/graphene nanocomposite modified electrode

Before modification, the wax impregnated graphite electrode was prepared using an earlier reports [26, 27] by heating the spectroscopic grade graphite rods (0.3 cm circular diameter, 4.0 cm length) in molten wax with the application of suction for 30 min, until air bubbles ceased to evolve from the rods. Afterre-establishing the atmospheric pressure, the rods were removed before the paraffin solidified. The lower end of the electrode was polished using various grades of emery sheets with a fine mirror polish was obtained for surface modification of the electrode. The polished surface was then washed with methanol and distilled water. For surface modification, 1 mg of Co_3O_4/graphene nanocomposite was suspended in 1 mL of ethanol containing 1% Nafion solution and sonicated for 30 min. Then 10 µL of the suspension was cast on the polished paraffin impregnated graphite electrode surface and dried in air. The resulted Co_3O_4/graphene nanocomposite electrode was stored in air-tight container at room temperature.

3 Results and discussion

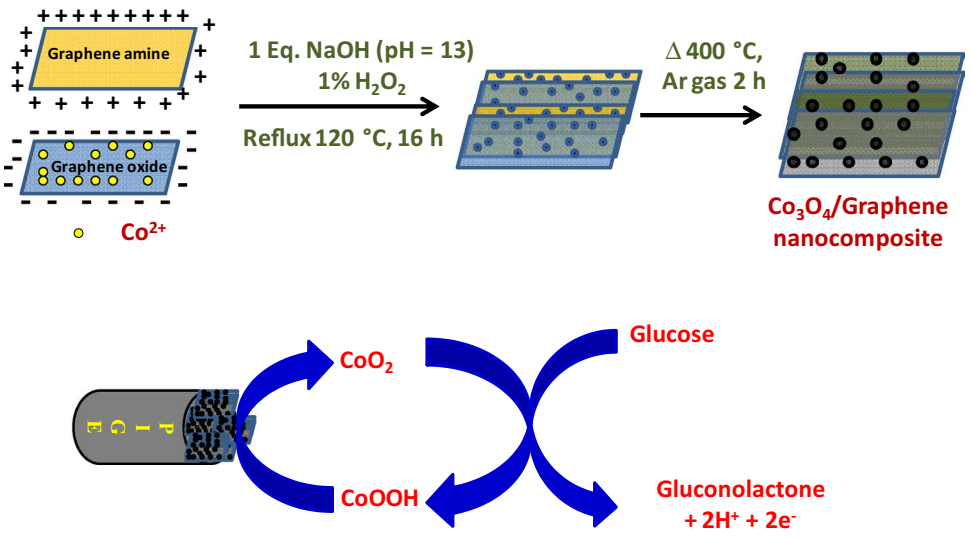
3.1 XRD and XPS of Co_3O_4/graphene nanocomposite

The crystal structure formation of Co_3O_4/graphene nanocomposites was confirmed by XRD. Figure 1a shows the XRD patterns of Co_3O_4/graphene nanocomposites and commercial Co_3O_4 (for comparison). For Co_3O_4 nanoparticles, the 2θ values of 19.0°, 31.2°, 36.8°, 38.5°, 44.8°, 49.0°, 55.6°, 59.3° and 65.2° were clearly distinguishable, indicates the nanocomposite was phase pure. The peak positions are in good agreement of Co_3O_4 (space group *Fd-3m* JCPDS No. 01-073-1701). It demonstrates the as prepared nanocomposite is cubic crystal of Co_3O_4. For reference, the XRD pattern of commercial Co_3O_4 also displayed in Fig. 1a. The XRD pattern of commercial Co_3O_4 and Co_3O_4/graphene nanocomposites showed same characteristics, confirming the formation of Co_3O_4. The average crystalline size was determined from the half width of the diffraction peaks using the Debye–Scherrer formula and was found to be approximately 15 nm. Further, broad diffraction broad peaks of 2θ between 19° and 27° correspond to the graphitic domains of the graphene stacks.

To further confirm the presence of Co_3O_4 in graphene nanocomposites, X-ray photoelectron spectroscopy (XPS) measurements were carried out. High resolution XPS peaks on Co (2p), the binding energies are located at 780.18 and 795.28 eV with correspond to Co $2p_{3/2}$ and Co $2p_{1/2}$ of Co_3O_4, respectively, as shown in Fig. 1b. These observations are consistent with earlier reports [28].

3.2 FESEM images of Co_3O_4/graphene nanocomposite

The structure and morphology of the Co_3O_4/graphene nanocomposite were characterized using FESEM as shown in Fig. 2a. It can be seen that, the edges of the graphene sheets were corrugated and densely aligned with few millimeters thick and the graphene sheets interconnected with Co_3O_4 nanoparticles inside. No significant aggregation of Co_3O_4 and graphene was observed in the morphology, indicating that the graphene were



Scheme 1 Schematic illustration of the fabrication of Co_3O_4/graphene nanocomposite and electrocatalytic oxidation mechanism of glucose at the modified electrode

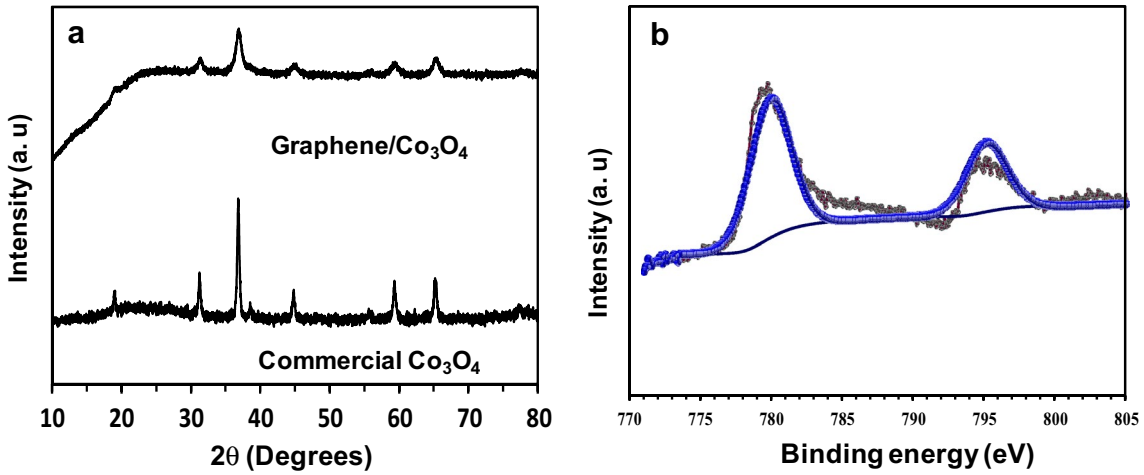


Fig. 1 **a** XRD pattern of commercial Co_3O_4 and Co_3O_4/graphene nanocomposite. **b** High resolution XPS spectrum for Co 2p core regions of Co_3O_4/graphene nanocomposite

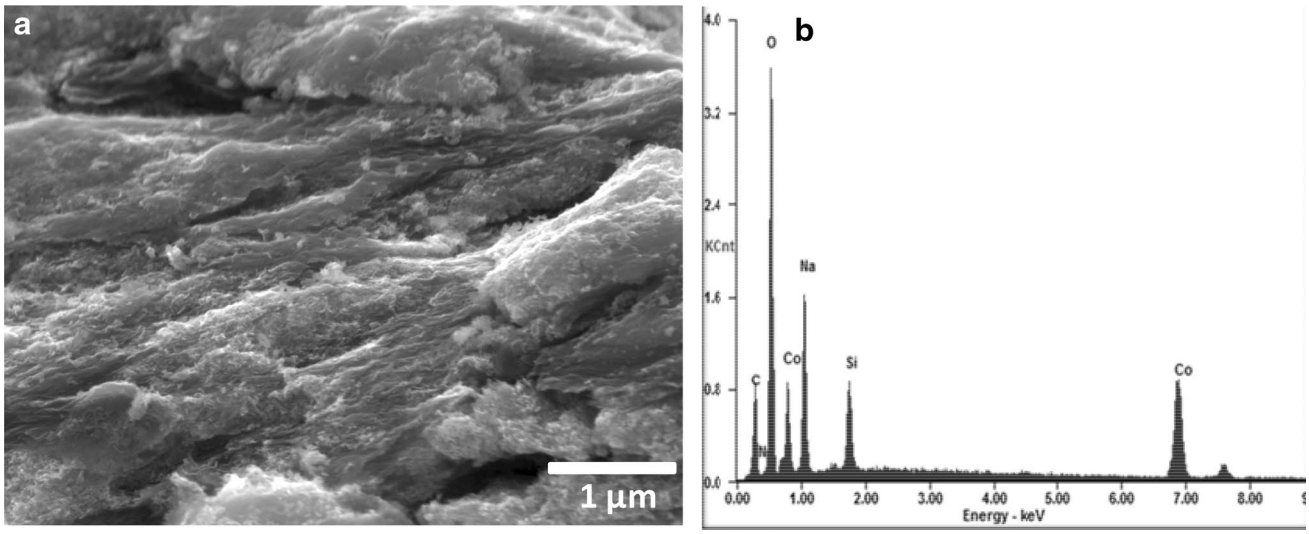


Fig. 2 **a** FESEM image and **b** EDS spectrum of Co_3O_4/graphene nanocomposite

alternatively packed inside of Co_3O_4 nanoparticles. The average diameter of these Co_3O_4 particles was about ~ 15–20 nm. These morphology results the Co_3O_4 is strongly packed in graphene layers, it cannot be easily come out from the graphene stacks. Hence the Co_3O_4/graphene nanocomposite modified electrode has excellent stability towards glucose oxidation. In order to confirm that Co_3O_4 has successfully sandwiched inside the graphene layers, EDS analysis was also evaluated. Figure 2b shows the EDS spectra for Co_3O_4/graphene nanocomposite of the elements of Co, O, and C are obviously observed.

3.3 Electrochemical behavior of Co_3O_4/graphene nanocomposite modified electrode

The electrochemical behavior of Co_3O_4/graphene nanocomposite modified electrode was studied by cyclic voltammetry. Cyclic voltammetric investigations of the Co_3O_4/graphene nanocomposite modified electrode reveals (Fig. 3) two pairs of well-defined redox peaks corresponding to the immobilized Co_3O_4/graphene nanocomposite when the potential was swept in the range from − 0.2 to 0.6 V at a scan rate of 20 mV/s in 0.1 M NaOH (curve b). The bare electrode under similar condition does not

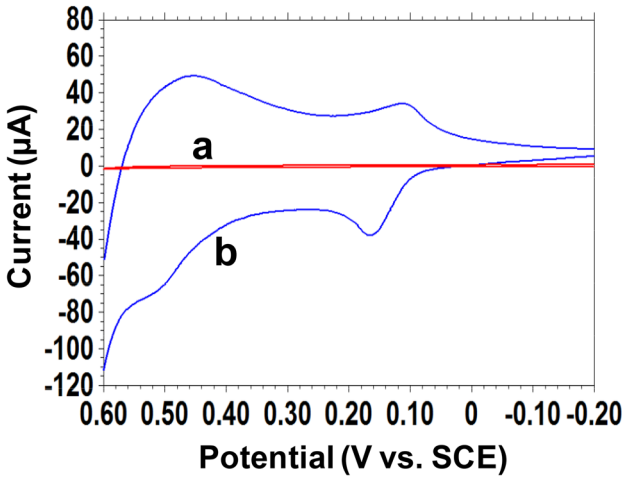


Fig. 3 Cyclic voltammograms of the (*a*) bare electrode and (*b*) Co_3O_4/graphene nanocomposite modified electrode in 0.1 M NaOH at the scan rate of 20 mV/s

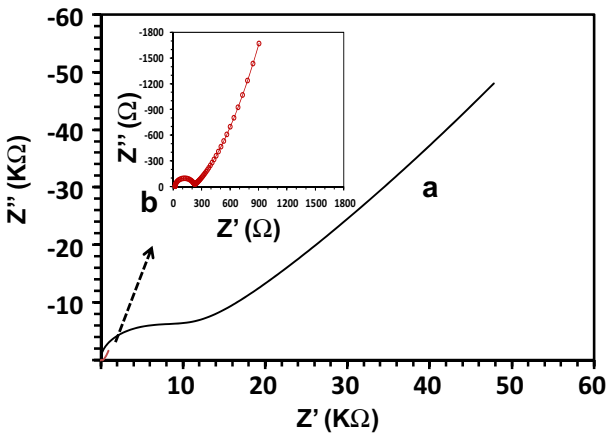


Fig. 4 EIS of bare and Co_3O_4/graphene nanocomposite modified electrode in 5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution, with the frequency swept from 1 Hz to 0.1 MHz. Inset: enlarged view of Co_3O_4/graphene nanocomposite modified electrode

show any characteristic wave (curve a). Co_3O_4/graphene nanocomposite modified electrode exhibited a first anodic peak at + 0.20 V and a cathodic peak at + 0.11 V attributed to conversion of Co_3O_4 and CoOOH and second anodic peak at + 0.52 V and a cathodic peak at + 0.47 V can be assigned to the transition between CoOOH and CoO_2. These redox reactions suggesting that hydroxyl ion participates in the electrochemical redox reaction of Co_3O_4. According to this result, it seems that the electrochemical behavior of the Co_3O_4/graphene nanocomposite modified electrode in alkaline solution is similar to that of Co_3O_4/MWNT [13] and nanoporous Co_3O_4 [14] alloy electrode in the alkaline solution. This possible mechanism with two redox reactions can be represented in the following reactions [28].

$$Co_3O_4 + OH^- + H_2O \rightarrow 3CoOOH + e^- \quad (1)$$

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^- \quad (2)$$

The impedance changes occurring at the electrode–electrolyte interfaces can be known by EIS. Figure 4 shows the Nyquist plots of bare and Co_3O_4/graphene nanocomposite modified electrode. The Nyquist plot shows a semicircle in high frequency corresponds to the interfacial charge transfer resistance (R_{ct}), which is the most directive and sensitive factor showing the changes at the electrode–electrolyte interfaces. It can be seen that, the bare electrode (curve a) exhibits the largest R_{ct} (9557 Ω), and it might be attributed to the wax impregnated graphite electrode surface acting as a barrier for the electrochemical process and hindering the access of the redox probe, $[Fe(CN)_6]^{3-/4-}$, to the electrode surface [29]. Compared with bare electrode, R_{ct} is greatly decreased (190 Ω) at the Co_3O_4/graphene nanocomposite modified electrode (curve b) due to the excellent electrical conductivity of Co_3O_4/graphene nanocomposite.

3.4 Electrocatalytic oxidation of glucose

Figure 5a shows the cyclic voltammograms of the Co_3O_4/graphene nanocomposite modified electrode in the presence of various concentrations of glucose. The catalytic current for glucose oxidation showed corresponding linearity in the concentration range of 16.0 μM to 1.3 mM. The linear regression equation is expressed as I_{pcat} (μA) = 0.2708 x + 6.3151, [glucose]/(μM) with correlation coefficient R^2 = 0.9909 (Fig. 5b). The detection limit for glucose determination was found to be 0.51 μM. The mechanism of electrocatalytic oxidation of glucose at the modified electrode is shown in Eq. (3):

$$2CoO_2 + C_6H_{12}O_6(\text{glucose}) \rightarrow 2CoOOH + C_6H_{10}O_6(\text{gluconolactone}) + 2H^+ + 2e^- \quad (3)$$

The cyclic voltammogram for the bare electrode and with addition of 1.3 mM of glucose to 0.1 M NaOH is shown in the inset of Fig. 5a. The response obtained for glucose oxidation at a bare electrode is very poor when compared to the modified electrode. When the Co_3O_4/graphene nanocomposite modified electrode was used for oxidation compared to the bare electrode and the current response is also increased almost ten-fold, which makes the modified electrode as an effective sensor for glucose oxidation. The working potential, detection limit and linear concentration range of other related modified electrodes for glucose detection are reported in Table 1.

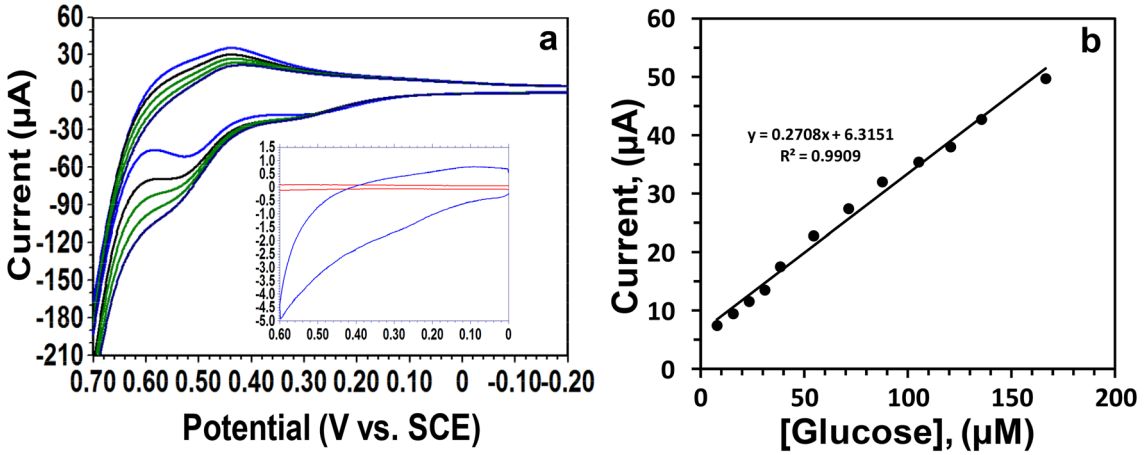


Fig. 5 **a** Cyclic voltammograms of Co_3O_4/graphene nanocomposite modified electrode in the absence and presence of 1 mM of glucose (inset) bare electrode in the absence and presence of 1 mM glucose in 0.1 M NaOH (scan rate 20 mV/s). **b** Calibration plot for the determination of glucose

Table 1 Comparison of various nano metal oxide-based sensors for glucose detection with previous reports

Modified electrode	Fixed potential (V)	Electrolyte	Linear range (μM)	Detection limit (μM)	Ref.
Co_3O_4 nanoparticles/GCE	+0.59	0.1 M NaOH	5–800	0.1	[15]
NiO/Ni foam	+0.55	0.5 M NaOH	5–5500	0.4	[16]
CuO nanospheres	+0.60	0.1 M NaOH	Upto 2600	1.0	[17]
Functionalized NiNP	+0.55	0.1 KOH	1.6–1400	0.5	[11]
Functionalized CuNP	+0.35	0.1 M NaOH	6.6–1300	2.2	[12]
Co_3O_4 needle/graphene	+0.60	0.1 M NaOH	50–300	< 10	[18]
Co_3O_4/graphene	+0.58	0.1 M NaOH	Upto 80	0.025	[19]
Co_3O_4/GO hydrogel	+0.62	0.1 M NaOH	250–10,000	250	[20]
Co_3O_4/graphene nanocomposite	+0.58	0.1 M NaOH	16–1300	0.5	This work

3.5 Amperometry

Linear sweep voltammetric (LSV) studies were carried out in order to evaluate the influence of flow conditions on the catalytic oxidation of glucose as a function of the applied potential. LSVs of bare electrode and the modified electrode obtained in presence of 440 μM of glucose in a stirring solution of 0.1 M NaOH at the scan rate of 20 mV/s (Fig. not shown). The electrocatalytic activity of the modified electrode permitted the convenient detection of glucose at lower potentials with high sensitivity when compared to the bare electrode. In the presence of glucose, the current response increases from +0.40 V, reaching a maximum value at +0.55 V with a sigmoidal shape. This behavior illustrates that the oxidation of glucose is greatly enhanced at the modified electrode due to the electrocatalysis. Hence, a potential of +0.58 V was selected as the working potential for amperometric determination of glucose using modified electrode under hydrodynamic conditions.

The amperometric response of the Co_3O_4/graphene nanocomposite modified electrode for the electrocatalytic oxidation of glucose was carried out. The current–time response obtained for the modified electrode in a stirred solution (300 rpm) for successive increments of 0.5 mL of 1 mM glucose is shown in Fig. 6a (curve B). The same amount of concentration of glucose toward bare electrode also tested (curve A), which shows a very poor amperometric response was observed. The step-wise current response increases for increasing concentrations of glucose. The plot of catalytic current vs. glucose concentration is shown in Fig. 6b. A good linear response was obtained over the low range from 8.2 μM to 76 μM glucose with a slope of 0.175 μA/μM (sensitivity) and a correlation coefficient of 0.9913 for the part of the shown amperogram. High sensitivity can be attributed to the synergistic augmentation of densely packed graphene and Co_3O_4 nanocomposite towards glucose oxidation. Such a good response of the

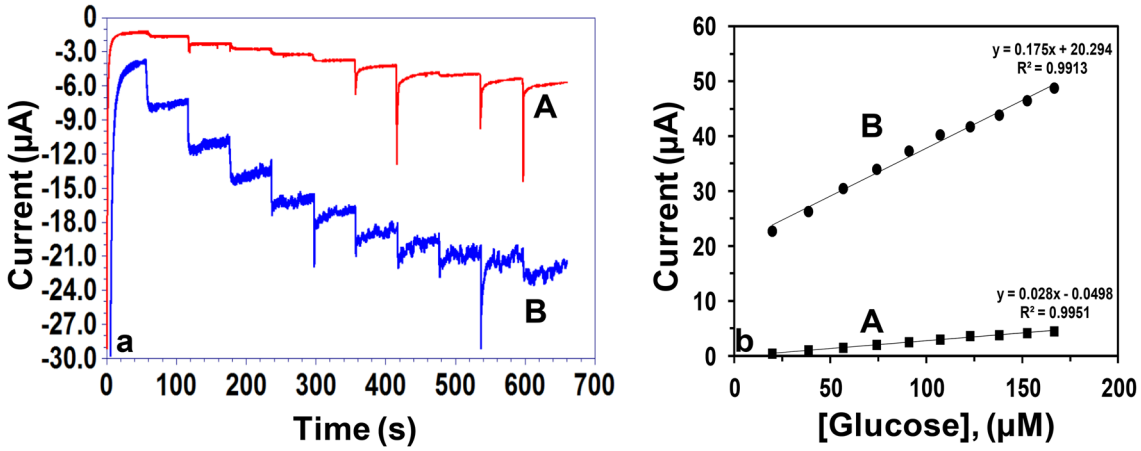


Fig. 6 **a** Typical amperometric current response of the (*A*) bare and (*B*) Co_3O_4/graphene nanocomposite modified electrode and upon the successive injection of 0.5 mL of 1 mM glucose in to 0.1 M NaOH. **b** Calibration plot for the determination of glucose

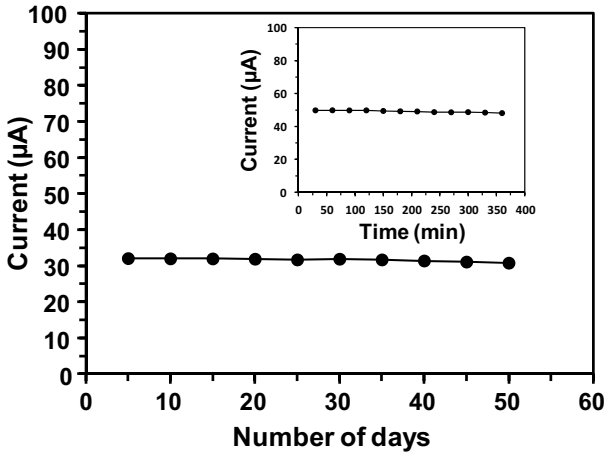


Fig. 7 Long term stability response of the Co_3O_4/graphene nanocomposite modified electrode towards the oxidation of 82 μM glucose. Inset: current response of Co_3O_4/graphene nanocomposite modified electrode towards the sensing of 162 μM glucose under dynamic conditions for 6 h

modified electrode for oxidation of glucose under dynamic conditions justifies its feasible application in flow systems.

3.6 Stability

The shelf-time of the Co_3O_4/graphene nanocomposite modified electrode for the oxidation of glucose was monitored by recording the anodic current response at an interval of 5 days for 82 μM glucose over a period of 60 days. The modified electrode suffered a current loss of 5.6% at the end of the 60 days showing that the modified electrode was appreciably stable for glucose determination as shown in Fig. 7. The long-term response of the modified electrode was checked by recording the anodic current for the oxidation of 163 μM glucose for every 30 min over an extended period of 6 h and almost a constant response was obtained as shown in inset of Fig. 7. It can be noticed from the Fig. 7, the modified electrode exhibits almost constant response suggesting the stable electrocatalytic oxidation toward glucose determination due to the Co_3O_4 nanoparticles which has strongly interconnected densely within the graphene layers.

Table 2 Determination of glucose in urine samples (n = 3)

Urine samples	Spiked (μM)	Found[a] (μM)	Recovery (%)
Sample 1	25	26.1 ± 0.4	104.4
	50	52.4 ± 0.4	104.8
Sample 2	25	25.6 ± 0.4	102.4
	50	51.8 ± 0.4	103.6

[a]Average of three measurements

3.7 Real sample analysis

In order to study the analytical performance of Co_3O_4/graphene nanocomposite modified electrode towards glucose determination, the modified electrode was applied to the direct analysis of urine samples. As shown in Table 2, two human urine samples were analyzed for glucose determination. In order to fit into the linear range, all the samples used for detection were diluted to 100 times with 0.1 M NaOH without any treatment. The dilution can actually help in reducing the matrix effect of real samples. To ascertain the correctness of the results, the samples were spiked with certain amounts of glucose was detected. The recovery rates of the spiked samples were found between 102.4 and 104.8%.

4 Conclusions

In summary, a new strategy to prepare the densely packed cobalt oxide (Co_3O_4)/graphene nanocomposites by a self-assembly method and its application in non-enzymatic glucose sensor was fabricated. The Co_3O_4/graphene nanocomposite modified electrode displayed substantially higher electrocatalytic activity and faster response to glucose oxidation with a higher current response than conventional bare electrode. This Co_3O_4/graphene nanocomposite modified electrode based electrochemical sensor has a low detection limit of 0.5 μM and a very high sensitivity of 0.2708 μA/μM, and its response is linear from 16.0 μM to 1.3 mM glucose concentration. On comparison with the self assembled densely packed Co_3O_4/graphene nanocomposite, the modified electrode has superior electrochemical performance characteristics combined with long-term stability and good reproducibility.

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