Gold nanoparticles decorated silicate sol-gel matrix embedded reduced graphene oxide and manganese ferrite nanocomposite-materials-modified electrode for glucose sensor application

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Abstract. Gold nanoparticles decorated on silicate sol-gel matrix embedded manganese ferrite (MnFe_2O_4)-reduced graphene oxide (rGO) nanocomposites were synthesized through a facile chemical method. The prepared samples were characterized by using powder X-ray diffraction (XRD), UV-vis absorption spectroscopy (UV-VIS), energy-dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analyses. The Au nanostructures on rGO- MnFe_2O_4 improved the electrocatalytic activity of the rGO- MnFe_2O_4 @Au composite-materials-modified electrodes towards glucose oxidation. Cyclic voltammetry and amperometric methods were used to evaluate the electrocatalytic activity of the rGO- MnFe_2O_4 @Au modified electrodes towards glucose oxidation in 0.1 M NaOH at a less-positive potential (0.2 V) in the absence of any enzyme or redox mediator. The nanocomposite-modified electrode (GCE/EDAS/rGO- MnFe_2O_4 @Au) was successfully used for the amperometric sensing of glucose and the experimental detection limit of 10 μM glucose was observed. The common interfering agents did not interfere with the detection of glucose. The present sensor showed good stability, reproducibility, and selectivity. The nanocomposite-modified electrode was successfully used for the determination of glucose in the urine sample.

Keywords. Manganese ferrite; reduced graphene oxide; gold nanostructures; modified electrode; glucose.

1. Introduction

Manganese ferrite (MnFe_2O_4), an eco-friendly material with favorable capacitive characteristics, is a suitable material for a wide range of applications such as Li-ion batteries, heterogeneous catalysts, gas sensors, etc.^{1–6} Though the ferrites are advantageous in the development of catalysis, certain limitations including defects, mechanical instability, poor electronic conductivity significantly impede them from wide applications in catalysis with high sensitivity, fast response and reliability.⁷ Considering the aforesaid issues, it is important to enhance the charge transport ability of ferrites by coupling them with highly conducting materials, such as single and multi-walled carbon nanotubes (CNTs),

noble metal nanoparticles and graphene.⁸ Based on the study, graphene has received considerable attention among other carbon supports as an attractive 2D supporting material owing to its high surface area, excellent thermal and electrical properties, high elastic behavior and extended charge carrier mobility. Graphite oxide and graphene oxide (GO) are the derivatives of graphene that can be used as carbon supports. The reduced GO (rGO) exhibits superior electrocatalytic properties efficiently over bare GO due to the restoration of a graphitic network of sp^2 bonds and makes it a promising material for catalysis. The rGO is usually obtained from graphene oxide by reduction.^{9,10} Recently, there were many studies about reduced graphene oxide-based metal oxides such as copper oxide,¹¹ nickel oxide¹² and cobalt

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oxide¹³ and they have been used in electrochemical sensors for glucose. To increase the catalytic activity of graphene-based metal oxide, it has been decorated with highly catalytic gold nanostructures (Au NSs) which increases the catalytic activity due to their unique chemical and physical properties, good biocompatibility and chemical stability. The amine functionalized silicate sol-gel matrix serves a multifunctional role such as reducing agent and stabilizing agent for the formation of Au NSs.^{14,15} The amine functionalized silicate matrix interacts with the rGO-metal oxides due to the presence of the amine groups.^{16,17}

The vital need for glucose detection has attracted widespread attention in the food industry, fermentation industry, biochemistry, clinical diagnosis and environmental protection. Therefore, it is important to develop a stable, sensitive, selective and reliable non-enzymatic electrochemical sensor due to the inherent problems associated with enzymes-based sensor.¹⁸ The non-enzymatic electrochemical sensing of glucose is generally based on the direct electrocatalytic oxidation of glucose on the surface of active electrode material.¹⁹ Consequently, advances in the direct electrochemical oxidation of glucose with high sensitivity and selectivity are greatly desired.

Here, a facile method for the synthesis of rGO-MnFe₂O₄ was developed by hydrothermal method. Further, the rGO-MnFe₂O₄ was decorated with the Au NSs *via* chemical synthesis method, carried out by treating amine functionalized silicate sol-gel matrix embedded rGO-MnFe₂O₄ with HAuCl₄ in aqueous solution at room temperature. The rGO sheets could be used as a template for the direct growth of MnFe₂O₄ to form an rGO-MnFe₂O₄. Both the electrical conductivity and surface area of the composite can be increased greatly, thus making the rGO-MnFe₂O₄ to be better support for Au NSs compared to the pure MnFe₂O₄ and rGO. An enzyme-less glucose sensor was constructed by using the EDAS/rGO-MnFe₂O₄@Au nanocomposite material. Assisting from their unique structural and functional properties of different components and synergistic effect, the resulting EDAS/rGO-MnFe₂O₄@Au nanocomposites-modified electrode showed enhanced electrocatalytic activity, high sensitivity and low limit of detection toward glucose sensing.

2. Experimental

2.1 Materials and methods

Graphite powder was purchased from Alfa Aesar. Manganese chloride tetrahydrate, ferric chloride hexahydrate, potassium permanganate (KMnO₄) and sulphuric acid (H₂SO₄)

were received from Alfa Aesar. Sodium hydroxide (NaOH) was obtained from Merck. N-[3-(Trimethoxysilyl)propyl]-ethylenediamine (EDAS), glucose and gold(III) chloride trihydrate were from Sigma-Aldrich. All the solutions were prepared by using doubly distilled water. All the reagents were used as received without further purification. Absorption spectra were recorded on an Agilent Technologies 8453 spectrophotometer by using 1 cm quartz cell. The powder X-ray diffraction patterns were recorded by using a Bruker AXS D8 diffractometer with Cu K α radiation (λ = 0.15418 nm) operating at 40 kV and 30 mA. The purity and the chemical composition of the prepared composites were analyzed by energy-dispersive X-ray spectroscopy (EDX). High-resolution transmission electron microscopy (HRTEM) images were obtained by using JEOL JEM 2100 instrument operating at 200 kV.

2.2 Synthesis of EDAS/rGO-MnFe₂O₄@Au nanocomposites

GO was synthesized from graphite powder by following the modified Hummers method as described elsewhere.²⁰ The rGO-MnFe₂O₄ nanocomposite was synthesized through one-pot hydrothermal method, in which the reduction of GO and the *in situ* formation of MnFe₂O₄ nanosheets occurred simultaneously (detailed experimental procedure is discussed in Supplementary Information). The rGO-MnFe₂O₄ was amine functionalized by using EDAS silane. The silicate sol-gel (SSG) matrix embedded rGO-MnFe₂O₄@Au (Au = 1, 2 and 3 mM) was prepared by using the following procedure. Briefly, 5 mg of rGO-MnFe₂O₄ was added to 5 μ L of 1 M EDAS silane in 5 mL of water and sonicated for 30 min followed by vigorous stirring. The EDAS/rGO-MnFe₂O₄ was obtained after 1 h. To this resulting solution, different concentrations of HAuCl₄ (1 or 2 or 3 mM final concentration) was added and stirred for 12 h. The formation of the brownish wine-red color solution indicated the formation of Au NSs at the composite. The aqueous mixture was centrifuged and washed three times with water and re-dispersed into 5 mL of water. The EDAS SSG was used as a capping as well as a reducing agent. For comparison studies, EDAS/MnFe₂O₄@Au, EDAS/rGO@Au, and EDAS/rGO-MnFe₂O₄ were prepared by using a similar procedure. The schematic representation of the preparation of EDAS/rGO-MnFe₂O₄@Au nanocomposite is given in Scheme 1A.

2.3 Electrochemical experiment

Electrochemical experiments were carried out by using a single compartment, a three-electrode cell with EDAS/rGO-MnFe₂O₄@Au nanocomposites-modified glassy carbon electrode (GCE) and dia 3 mm as working electrode, a platinum wire as an auxiliary electrode, and an Ag/AgCl/Cl⁻ (1 M KCl) as reference electrode under a nitrogen atmosphere. The measurements were performed at room temperature by using a CH Instruments Electrochemical Workstation (Model-760D).

Scheme 1. (A) Schematic representation of the preparation of EDAS/rGO-MnFe₂O₄@Au nanocomposite material. (B) Schematic representation of the electrocatalytic oxidation of glucose at the EDAS/rGO-MnFe₂O₄@Au nanocomposite modified GCE in 0.1 M NaOH at a scan rate of 50 mV/s.

A 0.1 M NaOH solution was used as supporting electrolyte and the sensing studies were carried out with the successive addition of glucose solution. A 5 μL of EDAS/rGO-MnFe₂O₄@Au was dropped on a cleaned GCE (polished with 1.0, 0.3 and 0.05 μm alumina). Then the solvent of the slurry was slowly evaporated at room temperature. The schematic illustration of electrochemical oxidation of glucose using the nanocomposite material modified electrode is shown in Scheme 1B.

3. Results and Discussion

3.1 Spectral study of EDAS/rGO-MnFe₂O₄@Au nanocomposites

The formation of EDAS/rGO-MnFe₂O₄@Au nanocomposite materials was primarily confirmed by the absorption spectroscopy. The absorption spectra of the EDAS/MnFe₂O₄@Au-2, EDAS/rGO@Au-2, and

Figure 1. Absorption spectra of EDAS/MnFe₂O₄@Au-2 (a), EDAS/rGO@Au-2 (b), EDAS/rGO-MnFe₂O₄@Au-1 (c), EDAS/rGO-MnFe₂O₄@Au-2 (d) and EDAS/rGO-MnFe₂O₄@Au-3 (e).

EDAS/rGO-MnFe₂O₄@Au (Au = 1, 2 and 3 mM) nanocomposites were recorded and shown in Figure 1. The EDAS/MnFe₂O₄@Au-2 showed a broad absorption band at 440 nm (Figure 1a) originating from the intrinsic band-edge absorption of MnFe₂O₄²¹ and the surface plasmon resonance (SPR) band due to the Au NS around 550 nm was also observed.²² The band observed in EDAS/rGO@Au-2 was red-shifted to 268 nm (Figure 1b) due to the disappearance of C=O groups in GO, ensuring the reduction of GO to rGO during the hydrothermal treatment. In addition, the SPR band of Au NSs was observed at around 530 nm for EDAS/rGO@Au-2 the nanocomposite.²³ The EDAS/rGO-MnFe₂O₄@Au-1 nanocomposite (Figure 1c) showed a typical SPR absorption band for Au NSs at 525 nm with a characteristic band for rGO and MnFe₂O₄ around 260 and 400 nm, respectively. The absorption band at 525 nm was observed due to the formation of spherical Au nanoparticles (NPs). The SPR band can be tuned by varying the particle size, shape as well as the surrounding dielectric medium of the Au NSs. When the concentration of Au increased to 2 and 3 mM (Figure 1(d and e)) the SPR band was red-shifted to around 540 and 552 nm, respectively, which is indicative of the formation of Au network structure or larger size particles.²⁴

3.2 HRTEM characterization of EDAS/rGO-MnFe₂O₄@Au nanocomposites

To evaluate the morphology of EDAS/rGO-MnFe₂O₄@Au nanocomposites the HRTEM images were recorded. Representative HRTEM images shown in Figure 2 reveal the morphologies of EDAS/rGO-MnFe₂O₄@Au nanocomposites prepared with the different concentrations of Au. The HRTEM image of GO

and MnFe₂O₄ shown in Figure 2a, b. The HRTEM image (Figure 2c) of the rGO/MnFe₂O₄ reveals that the nanosheet-like MnFe₂O₄ structures are highly dispersed on the rGO sheets. Thus, the nanocomposite material prevented itself the aggregation and restacking of the MnFe₂O₄ and the rGO sheets, respectively. The EDAS/rGO-MnFe₂O₄@Au-1 shows the formation of spherical Au NPs which are accommodated on the EDAS/rGO-MnFe₂O₄ composite (Figure 2d). When the concentration of Au was increased to 2 mM (Figure 2e), the morphology of the Au spherical NPs changed to Au network structure and in addition, some nanoparticles were found to be smaller in size on the surface. The presence of these Au network structures resulting in a shift in the absorption at 540 nm in the absorption spectrum was observed (Figure 1d). When the concentration was increased to 3 mM, it was found that the Au nanostructures got aggregated to give larger particles owing to the increased population of Au (Figure 2f). The d-spacing value of 0.235 nm observed for the EDAS/rGO-MnFe₂O₄@Au-2 nanocomposite showed the (1 1 1) crystal plane of Au (Figure 2g). To further confirm the structure of the obtained nanocomposite, typical SAED pattern of the EDAS/rGO-MnFe₂O₄@Au-2 nanocomposite is shown (inset of Figure 2f). The SAED pattern of Au showed the face-centred cubic crystal structure of Au and the calculated distances 0.25, 0.22, 0.14 and 0.12 nm agree well with the values reported in literature²⁵ for (111), (200), (220) and (311) planes of Au, respectively (JCPDS File No. 04–0783). The EDX analyses of (Figure 2h) rGO/MnFe₂O₄@Au-2 reveal that the presence of the individual elemental composition of carbon, oxygen, Au, Mn and Fe on EDAS/rGO-MnFe₂O₄@Au-2.

3.3 XRD analyses of EDAS/rGO-MnFe₂O₄@Au nanocomposite

The formation and crystalline nature of the Au nanoparticles present in the EDAS/rGO-MnFe₂O₄ nanocomposites prepared using different concentrations of Au were studied by XRD analysis (Figure 3). The XRD spectrum of EDAS/MnFe₂O₄@Au-2 (Figure 3(a)) shows the well-defined diffraction peaks at the 2θ values of 35.07, 56.5, 65.9° and 78.4° which are indexed to (3 1 1), (5 1 1), (4 4 0) and (4 4 4) crystal plane reflections of spinel-type MnFe₂O₄, respectively (JCPDS 73-1964).²⁶ The three diffraction peaks that appeared at 38.8°, 44.9° and 61.9° are indexed to the (111), (2 0 0) and (2 2 0) diffraction planes of Au, respectively (JCPDS 04–0783).²⁷ In addition to the characteristic peaks for MnFe₂O₄ and Au, a slight hump around 2θ value of 26.5° (Figure 3(b–d)) was observed due to the presence of rGO in the nanocomposites.²⁸ Thus the XRD results

Figure 2. HRTEM images of GO (a), MnFe_2O_4 (b), $\text{rGO-MnFe}_2\text{O}_4$ (c), EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-1 (d), EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2 (e), EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-3 (f), lattice fringes of EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2 (g) and EDX of EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2. Inset (Figure 2g): SAED pattern of EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2.

Figure 3. XRD patterns obtained for EDAS/ MnFe_2O_4 @Au-2 (a), EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-1 (b), EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2 (c) and EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-3 (d).

confirm the formation of crystalline Au nanostructures on the EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ composite and the integration of individual component in the nanocomposite.

These d-spacing values and the obtained crystal planes from XRD data were found to be in good agreement with the SAED data.

3.4 Electrocatalytic oxidation of glucose

3.4a Voltammetric studies of glucose oxidation at GCE/EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2: To examine the electrocatalytic performance of the prepared EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au nanocomposite materials, the cyclic voltammetric (CV) experiment was performed to study the oxidation of glucose. Figure 4A exhibits the CV curves recorded at the bare GCE (a), GCE/EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ (b), GCE/EDAS/ rGO (c), GCE/EDAS/ MnFe_2O_4 (d), GCE/EDAS/ rGO @Au-2 (e), GCE/EDAS/ MnFe_2O_4 @Au-2 (f) and GCE/EDAS/ $\text{rGO-MnFe}_2\text{O}_4$ @Au-2 (g) for 5 mM glucose in 0.1 M NaOH at a scan rate of 50 mV/s, which is a suitable medium for gold based non-enzymatic glucose sensors.²⁹ Bare GCE, GCE/EDAS/ rGO and GCE/EDAS/ MnFe_2O_4 did not show any characteristic voltammetric signal for the

Figure 4. (A) CVs recorded for 5 mM glucose in 0.1 M NaOH with a scan rate of 50 mV s⁻¹ at (A): bare GCE (a), GCE/EDAS/rGO-MnFe₂O₄ (b), GCE/EDAS/rGO (c), GCE/EDAS/MnFe₂O₄ (d), GCE/EDAS/rGO (e), GCE/EDAS/MnFe₂O₄@Au-2 (f) and GCE/EDAS/rGO-MnFe₂O₄@Au-2 (g). (B): GCE/EDAS/rGO-MnFe₂O₄@Au-1 (a), GCE/EDAS/rGO-MnFe₂O₄@Au-2 (b) and GCE/EDAS/rGO-MnFe₂O₄@Au-3.

oxidation of glucose. The GCE/EDAS/rGO-MnFe₂O₄ showed poor electrocatalytic response towards glucose oxidation. On the other hand, the Au deposited nanocomposite-modified electrode displayed good electrocatalytic response towards glucose. Figure 4A (e and f) show GCE/EDAS/rGO@Au-2 and GCE/EDAS/MnFe₂O₄@Au-2 to be effective for glucose oxidation. However, the surface area and conductivity of MnFe₂O₄ is relatively low, which limited its application as support. Significantly, the GCE/EDAS/rGO-MnFe₂O₄@Au (Figure 4A(g)) shows the highest peak current density among the other modified electrodes. The phenomenon indicates that the enhanced catalytic activity of Au NSs on the combination of rGO-MnFe₂O₄ create a synergistic effect, which achieves an excellent electrocatalytic activity of glucose oxidation.

The mechanism of the glucose direct oxidation is connected to the formation of gold hydroxide sites (Au[OH]_{ads}) which are formed by chemisorption of hydroxide anion at the Au NSs.³⁰ A small current response was observed in Figure 4A(g) at -0.47 V during the positive scan corresponding to the electrosorption of glucose, by releasing one-proton per glucose molecule.^{31–33} The GCE/EDAS/MnFe₂O₄@Au-2 showed the same signal at the potential of -0.38. Accompanied by electrosorption of glucose, the accumulation of concomitant intermediates at the electrode surface inhibited the direct oxidation of glucose on the active sites of Au and hence gave rise to a small anodic current peak at -0.04 V. At a more positive potential,

the oxidation of adsorbed glucose showed an anodic peak at 0.2 V due to the partial discharge of OH⁻ from GCE/EDAS/rGO-MnFe₂O₄@Au. However, the formation of gold oxide at a scanning potential above 0.4 V leads to a decrease in the Au[OH]_{ads} active sites that limited the electrocatalytic activity towards glucose oxidation. In the reverse scan the observed strong oxidation peak near 0.09 V was associated with the recovery of active Au[OH]_{ads} sites by the reduction of gold oxides and thus glucose can be re-adsorbed and oxidized.^{34,35}

The electrocatalytic oxidation of glucose was also performed using the GCE/EDAS/rGO-MnFe₂O₄@Au containing different amounts of Au (1, 2 and 3 mM) concentration. Figure S1 (Supplementary Information) shows the electrochemical performances of GCE/EDAS/MnFe₂O₄@Au-1, GCE/EDAS/rGO-MnFe₂O₄@Au-2, and GCE/EDAS/rGO-MnFe₂O₄@Au-3 in 0.1 M NaOH at a scan rate of 50 mV/s. The voltammograms obtained at all the three modified electrodes showed two peaks at 0.43 V and 0.10 V, due to the presence of Au catalysts. In the absence of glucose, the anodic and cathodic peaks located at about 0.43 V and 0.10 V corresponding to the oxidation of gold and subsequent reduction of the gold oxides, respectively.^{36,37} Figure 4B shows that the peak current density was further increased when the concentration of Au increased from 1 mM to 2 mM in the composites, due to the higher catalytic activity of the nanocomposite through the optimum loading of Au network on EDAS/rGO-MnFe₂O₄. When the Au concentration

Figure 5. (A) Amperometry response obtained for GCE/EDAS/rGO-MnFe₂O₄@Au-2 upon successive addition of glucose in the concentration range from 10 μ M to 8.3 mM in 0.1 M NaOH solution at an applied potential of 0.2 V. Inset: Enlarged view of the i-t response of single addition of 100 μ M glucose. (B-D): Calibration curves obtained at different concentration addition of glucose: (B) 10 μ M, (C) 50 and 100 μ M, (D) 500 and 1000 μ M. (E): 0.1 mM of each fructose, mannose, maltose, sucrose, lactose, 0.04 mM uric acid (UA), 0.1mM acetamidophenol (AP), 0.1mM ascorbic acid (AA) as well as 1 mM glucose at the potential of 0.2V. (F): Spike test response obtained at GCE/EDAS/rGO-MnFe₂O₄@Au-2 for urine samples.

Table 1. Determination of glucose concentration in urine sample (n = 3).

Real samples	Added (μ M)	Found (μ M)	RSD (%)	Recovery (%)
Human urine	50	48.05	4	96
	100	97.54	2.5	98
	500	502.94	2	101

further increased to 3 mM the size of Au nanostructures increased, as is evident from the TEM analyses, which decreased the catalytic activity of Au. At the Au

nanocomposite modified electrodes, the current response for glucose oxidation increased with increasing the Au concentration from 1 to 2 mM, and a further

increase of Au concentration decreased the peak current density. Hence, the 2 mM Au in the nanocomposite (GCE/EDAS/rGO-MnFe₂O₄@Au-2) exhibited higher catalytic current density than the other nanocomposites. The CV recorded at the EDAS/rGO-MnFe₂O₄@Au-2 nanocomposite-modified electrode at different scan rates (25–350 mV s⁻¹) for the oxidation of 5 mM glucose in 0.1 M NaOH is shown in Figure S2, Supplementary Information. The catalytic peak current density (Figure S2 (a, b)) corresponding to glucose oxidation increased with increasing scan rates and the plot of peak current density versus square root of scan rate displayed a linear relation (Figure S3). This observation shows that the electrocatalytic oxidation of glucose at the GCE/EDAS/rGO-MnFe₂O₄@Au-2 nanocomposite-modified electrode followed a diffusion-controlled process at the modified electrode. Furthermore, the anodic peak potential (E_{pa}) of the reaction is proportional to log (scan rate) and from this plot, it is possible to estimate the Tafel slope to obtain information on the rate-determining step. The slope of the line was calculated as 62 mV and the Tafel slope 'b' was estimated according to the equation ($E_p = (\log v)/2 + \text{const}$, so $b = 124 \text{ mV}$) for the totally irreversible diffusion-controlled process (Figure S2 (inset)). The value of Tafel slope indicates that one-electron transfer process is the rate-limiting step assuming a transfer coefficient of 0.5 for α .³⁸ Assuming that the glucose oxidation mechanism is similar to the one described by Fleischmann *et al.*,³⁹ the abstraction of a hydrogen atom from the α -carbon with electron transfer to the electrode is most preferred rate-determining step for glucose oxidation. The electrochemical stability of the GCE/EDAS/rGO-MnFe₂O₄@Au-2 dipped in 0.1 M NaOH was tested by 25 continuous potential cycling between -0.6 and +0.6 V in 10 mM glucose at a scan rate of 50 mV s⁻¹ (Figure S4, Supplementary Information). After 25 cycles, the loss in the integrated current density in the CV for GCE/EDAS/rGO-MnFe₂O₄@Au-2 was only 5%.

3.4b Non-enzymatic electrochemical sensing of glucose: To obtain an optimal amperometric response for glucose, the effect of different applied potentials at the GCE/EDAS/rGO-MnFe₂O₄@Au-2 was investigated. The amperometric response of the electrode at different applied potentials of 0.0 V and 0.2 V in the concentration range of 0.5 mM to 6 mM glucose with each addition in 0.1 M NaOH were studied in Figure S5, Supplementary Information. The oxidation current density of glucose increased sharply and higher current density response was observed at 0.2 V. So the potential of 0.2 V was chosen as the working potential for

Table 2. Summary of some reported Au/graphene and metal oxide/graphene-based electrochemical sensors for the detection of glucose.

Sensor material	Response time (s)	Detection potential (V)	Linear range (mM)	Interferents studied	Ref.
CuO/rGO	—	0.4	0.4 μM –33–12	AA, UA and DA	11
NiOHSS-RGO	3	0.45	0.6246–258.4 μM 0.2584 μM –10.50	AP, AA, UA, cysteine	12
AuNPs/GONR	5	0.2	0.05–4.92	AA, AP, UA	43
AuNWs	2	–0.4	1–10	AA	44
Au NPs/CNTs-graphene	—	0.55	0.01–6.1	AA, UA, DA, lactose, Suc, Fru	45
3D porous Au-graphene	3	0.0	0.1–16	AA, AP, UA	46
Co ₃ O ₄ -rGO	2	0.55	0.0005–1.277	AA, UA, DA, Gal, Fru	47
AuNP/BSA/RGO	5	0	0.02–1.6 1.6–16.6	AA and UA	48
NA/NiONF-GO	5	0.6	0.002–0.60	AA, UA, DA, AP	49
EDAS/rGO-MnFe ₂ O ₄ @Au-2	3	0.2	0.01–0.05 0.1–0.8 1.3–8.3	AA, UA, AP, Lactose, Gal, Man, Fru and Maltose	This Work

GONR: Graphene oxide nanoribbon, Gal: Galactose, Man: Mannose, Maltose, Suc: Sucrose, Fru: Fructose, NPG: nanoporous gold, NWs: nanowires, BSA: NA: nafion, NF: nanofiber.

further experiments. The glucose sensing performance was evaluated by the current-time curves for the successive addition of glucose in the concentration range from 10 μM to 8 mM which were recorded at an applied potential of 0.2 V. An enhanced current density response was observed as shown in Figure 5A due to the presence of Au NSs deposited on rGO-MnFe₂O₄.⁴⁰ The electrocatalytic activity of rGO-MnFe₂O₄@Au nanocomposite is considered as a result of the combination of three factors: First, it is the catalytic activity of Au NSs. Second, the rGO provides good electrical conductivity and acts as a support for the MnFe₂O₄ and Au material. Because of the abundant oxygen-containing functional groups, large numbers of homogeneous MnFe₂O₄ and Au NSs can be formed on the surface of rGO sheets.⁴¹ Finally, after the modification of MnFe₂O₄ on GO, they provide an extra surface area to attach more Au NSs.⁴² Therefore, rGO-MnFe₂O₄@Au would induce more electroactive sites for the catalytic oxidation reaction of glucose. The proposed sensor showed multilinear detection ranges from different sensitivities up to 50, 700 and 8300 μM , respectively (Figure 5(B–D)). The limit of detection (LOD) was estimated at 2.0 μM using the formula $\text{LOD} = 3\sigma/\text{slope}$ and the sensitivity of the modified electrode was found to be 83 $\mu\text{A cm}^{-2} \text{mM}^{-1}$ for glucose detection. It should be noted that a response time of 3 s to attain steady-state current density was observed.

To ensure the selectivity of the developed sensor for glucose, the GCE/EDAS/rGO-MnFe₂O₄@Au-2 was evaluated in the presence of common interferents at an applied potential of 0.2V. The common interference species such as fructose, mannose, maltose, lactose, uric acid, acetamidophenol and ascorbic acid were studied. The addition of acetamidophenol, ascorbic acid to 1mM glucose solution resulted in a sharp increase in the current density response and did not interfere with the glucose detection (Figure 5E). In order to detect the practical applicability, the designed GCE/EDAS/rGO-MnFe₂O₄@Au-2 was tested to determine glucose in human urine samples. The urine samples were diluted 10 times using 0.1 M NaOH and used. Figure 5F shows the current density-time curves for the successive additions of glucose standard solution mixed with the urine sample. Table 1 shows a high recovery of glucose with the relative standard deviation (RSD%) value in the range from 2 to 4. The linear range of glucose detection and the applied potential were compared with the recent reports and summarized in Table 2. Compared to the previous reports, the present sensor offered better electrocatalytic performance with a wide detection range and low applied potential.

4. Conclusions

In the present work, EDAS/rGO-MnFe₂O₄@Au nanocomposite has been synthesized and characterized. The GCE/EDAS/rGO-MnFe₂O₄@Au-2 nanocomposite exhibited the best electrocatalytic response towards glucose oxidation in 0.1 M NaOH solution when compared to other catalyst studied. The enhanced electrochemical behavior is mainly attributed to the optimized loading of Au NSs on rGO-MnFe₂O₄ nanocomposite and its catalytic properties. The EDAS/rGO-MnFe₂O₄@Au-2 modified electrode displays good selectivity, good sensitivity (83 $\mu\text{A cm}^{-2} \text{mM}^{-1}$) and low detection limit (2 μM). The GCE/EDAS/rGO-MnFe₂O₄@Au-2 was successfully applied to detect glucose in urine sample indicating that the GCE/EDAS/rGO-MnFe₂O₄@Au-2 based non-enzymatic glucose sensor has a great potential in real sample analysis.

Supplementary Information

The details of the Synthesis of rGO/MnFe₂O₄ nanocomposite and Figures S1–S5 are available at www.ias.ac.in/chemsci.

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