

A hierarchically structured composite of Mn_3O_4 /3D graphene foam for flexible nonenzymatic biosensor†

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We report a novel composite material of hierarchically structured Mn_3O_4 grown on three-dimensional graphene foam (3DGF). This hierarchical Mn_3O_4 /3DGF composite was fabricated as a flexible and freestanding biosensor for nonenzymatic determination of glucose and H_2O_2 , significant analytes in health care and food industry. The Mn_3O_4 /3DGF-based biosensor achieved high sensitivity, large linear range and low detection limit for the detection of both analytes, due to the synergistic effects of the two materials, which combines the high electrocatalytic activity of the nanostructured Mn_3O_4 network, and high conductivity and large surface area of 3DGF. This enzymeless biosensor also exhibited excellent performance for real-time detection of glucose and H_2O_2 in serum and food samples.

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Introduction

The determination of glucose level in blood is commonly used for medical diagnosis of diabetes mellitus, which is a worldwide health problem resulting from insulin dependency and hyperglycemia.¹ Hydrogen peroxide (H_2O_2) has been widely used as an oxidant in industrial processes, antibacterial reagent in food industry and cleaning agent in environmental protection.² Consequently, sensitive and reliable monitoring of these two analytes is of paramount importance in clinical, food and environmental analysis. Currently, most glucose and H_2O_2 sensors rely on enzyme-based electrodes which employ glucose oxidase, horseradish peroxidase or hemoglobin as a catalyst.^{3–6} Although the enzyme-based approaches provide an additional capability of selective measurement to the sensors, several drawbacks have hindered their widespread use. Due to the intrinsic nature of proteins, the enzymatic sensors have poor stability which prevents them from long-term and reproducible usage. In addition, the enzyme-based detection is susceptible to the environmental factors, such as pH, temperature, and humidity. Furthermore, the incorporation of enzymes also increases the manufacturing cost and complexity, and the insulating property of enzymes greatly compromises the sensitivity of biosensors. To address these issues, great effort has been dedicated in recent years to the development of enzymeless electrodes using metals,⁷ metallic nanoparticles,^{8,9} alloys^{10,11} and oxides^{12,13} as an electrocatalyst. However, many nonenzymatic electrodes display low sensitivity, poor selectivity

and severe surface fouling due to the adsorption of intermediates and chlorides.^{11,14} Hence, there is a great demand for the development of nonenzymatic biosensors with high sensitivity, good selectivity, and poison resistance at low cost for the efficient determination of both glucose and H_2O_2 .

Graphene has been integrated with other functional nanomaterials to fabricate composite materials. The attained synergistic effects of the graphene composite provide vast opportunities that lead to advances in energy harvesting/storage devices,^{15–19} transparent conductors^{20–22} and chemical/biosensors.^{23–25} Recently, highly conductive and seamless three-dimensional graphene foam (3DGF) with a microscopic network structure has been synthesized by template-directed chemical vapor deposition (CVD),²⁶ enabling the production of graphene with both high quality and relatively large quantity. The mechanical strength and flexibility of 3DGF allow it to be used as a freestanding electrode, where charge carriers could move along the continuous graphene skeleton with a small resistance. In addition, the three dimensional architecture of 3DGF provides a large surface area which allows for the construction of graphene-based nanocomposites without agglomeration. Recently, we reported a composite material of Co_3O_4 /3DGF for the nonenzymatic biosensing of glucose.²⁷ Despite extraordinarily high sensitivity it achieved, the Co_3O_4 /3DGF biosensor offers a relatively small linear response range (up to 80 μM) due to the thick coating layer of Co_3O_4 . Moreover, Co_3O_4 /3DGF could not be used for the detection of H_2O_2 . In the present work, we synthesized a novel composite material of hierarchically structured Mn_3O_4 /3DGF for the development of a highly sensitive and enzymeless sensor for detection of both glucose and H_2O_2 . Due to the excellent electrocatalytic activity of nanostructured Mn_3O_4 , good conductivity of graphene, great abundance of catalytic sites and high specific surface area of the composite material, the Mn_3O_4 /3DGF-based glucose sensor

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achieved a large linear detection range of 0.1–8 mM, which is 2 orders of magnitude larger than that of 3DGF/Co₃O₄. In addition, the material also showed the capability of highly sensitive and selective detection of H₂O₂. Moreover, thanks to the good stiffness of 3DGF, the composite material can be fabricated as a flexible and freestanding biosensor.

Results and discussion

Fig. 1a shows the SEM image of 3DGF grown by the ethanol-CVD method using nickel foam as a sacrificial template. The 3DGF reveals the macroporous network structure that replicates the nickel foam, hence exhibiting a continuous and smooth graphene skeleton without observable cracks or breaks, indicating that graphene sheets well maintain their original structure after removal of the Ni template without collapse. The width of the graphene skeleton is around 100 μm . In Fig. 1b, the observed wrinkles and ripples on the surface of the 3DGF skeleton result from difference in the thermal expansion coefficients of nickel and graphene.²⁸ Similar to the effect of wrinkles of chemically derived graphene,²⁹ these ripples on the 3DGF skeleton could contribute to the large surface area and the good mechanical strength of 3DGF. The surface morphology of Mn₃O₄/3DGF is shown in Fig. 1c and d, displaying good uniformity of Mn₃O₄ nanostructures on the graphene surface. The magnified SEM image (Fig. 1e) shows the highly porous and nanomesh-like structure of the Mn₃O₄, which is uniformly covered on the entire surface of 3DGF. The TEM image (Fig. 1f) shows that the

microstructure of Mn₃O₄ grown on graphene is composed of ultrathin nanoflakes with the dimension of 100–200 nm. With uniform distribution of the hierarchical structure at the nanometer scale, the Mn₃O₄ nanomesh offers abundant catalytic sites, which contributes to the high electrocatalytic activity of the composite material. The nanoporous Mn₃O₄ network together with the macroporous structure of 3DGF provides a high specific surface area, which was estimated by the Brunauer–Emmett–Teller (BET) method to be 1157.9 m² g^{−1}, much larger than that of ~ 850 m² g^{−1} of bare 3DGF.²⁶ The improved surface area allows for the rapid access of electrolyte ions, provides abundant active sites for the electrocatalytic reactions, and facilitates fast electron transport between the electrode materials and the analytes. Taking advantage of the flexibility and robustness of 3DGF, the composite material was fabricated as a flexible biosensor and used as a monolithic electrode for the measurement of analytes of interest (Fig. S1†).

The phase purity of the Mn₃O₄/3DGF composite was analyzed by XRD. As shown in Fig. 2a, the XRD spectrum of 3DGF shows two notable diffraction peaks at $2\theta = 26.5^\circ$ and 54.6° corresponding to the (002) and (004) reflections of graphitic carbon, respectively (JCPDS 75-1621). On the XRD spectrum of the Mn₃O₄/3DGF composite, besides the characteristic peaks of graphene, strong diffraction peaks are well indexed to the (101), (112), (103), (211), (224), and (004) phases of the tetragonal hausmannite Mn₃O₄ structure ($a = 5.762$ Å, $c = 9.469$ Å, JCPDS card no. 24-0734). The result shows that no impurity phase exists in the Mn₃O₄/3DGF composite. As a control experiment, we also investigated the XRD pattern of as-synthesized MnO_x/3DGF before calcination. The as-formed MnO_x on 3DGF did not show any diffraction peaks, possibly due to the poor crystallinity of MnO_x. The difference in the XRD patterns between the as-synthesized MnO_x/3DGF and the calcinated Mn₃O₄/3DGF suggests that significant change of the MnO_x crystal structure occurs during the calcination process. The phase purity of the Mn₃O₄/3DGF composite was also confirmed by energy-dispersive X-ray spectroscopy (EDX) (Fig. 3), showing strong peak signals of only C, Mn, and O, components of the Mn₃O₄/3DGF composite. In further analysis by Raman spectroscopy (Fig. 2b), 3DGF shows distinct peaks at 1581 cm^{−1} and 2725 cm^{−1}, which are attributed to the G and 2D bands of single- to a few layers of graphene.^{30,31} It is worth mentioning that the D band (~ 1350 cm^{−1}) cannot be discerned on the 3DGF spectrum, suggesting that the CVD-grown graphene foam possesses high quality since the D band is an

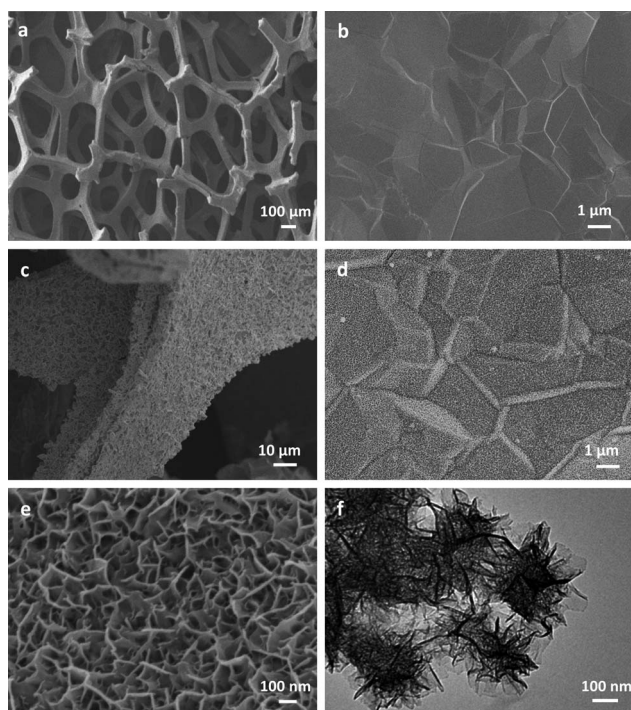


Fig. 1 (a and b) Low- and high-magnification SEM images of the CVD-grown 3DGF. (c and d) Low- and high-magnification SEM images of the Mn₃O₄/3DGF composite. (e and f) SEM and TEM images of the hierarchically structured Mn₃O₄ nanomesh grown on the surface of the 3DGF skeleton.

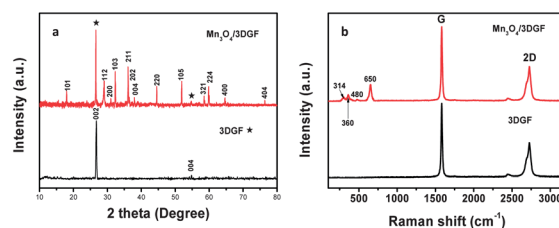


Fig. 2 XRD (a) and Raman (b) spectra of 3DGF (black) and the Mn₃O₄/3DGF composite (red).

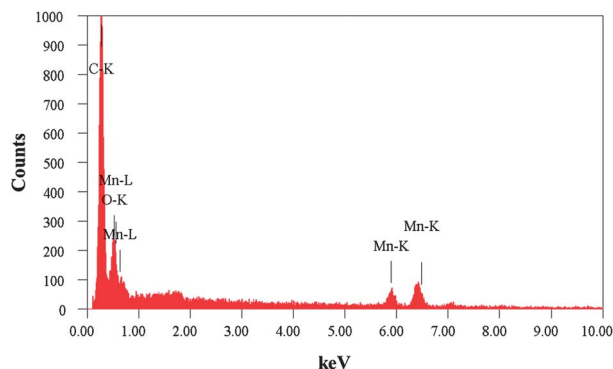


Fig. 3 Energy-dispersive X-ray (EDX) spectrum of the $\text{Mn}_3\text{O}_4/3\text{DGF}$ composite material.

indication of defects and distorted carbon.^{32,33} On the Raman spectrum of $\text{Mn}_3\text{O}_4/3\text{DGF}$, the peaks observed at 314, 360, 480 and 650 cm^{-1} are ascribed to the characteristic A_{1g} , $F_{2g}(1)$, $F_{2g}(2)$ and E_g modes of crystalline Mn_3O_4 , respectively.^{34,35} Both XRD and Raman spectroscopy results corroborate successful integration of the Mn_3O_4 with the 3DGF. The content of Mn_3O_4 in the composite was measured by thermogravimetric analysis (TGA) (Fig. 4). The large weight loss appeared at $\sim 600^\circ\text{C}$ for both 3DGF and $\text{Mn}_3\text{O}_4/3\text{DGF}$ results from the decomposition of 3DGF carbon, which combust completely at 800°C . The total weight loss of $\text{Mn}_3\text{O}_4/3\text{DGF}$ is 55.84 wt%, we can thus estimate the amount of Mn_3O_4 present in the composite to be 44.16 wt%.

The electrocatalytic behavior of Mn_3O_4 toward the oxidation of glucose was studied by cyclic voltammetry (CV) in 0.1 M NaOH solution. Fig. 5a shows the CVs of $\text{Mn}_3\text{O}_4/3\text{DGF}$ measured at different scan rates. At the scan rate of 5 mV s^{-1} , two pairs of redox peaks are observed at the potentials of 0.16 V/0.03 V (I/II) and 0.26 V/0.18 V (III/IV), which may attribute to the reversible transition between $\text{Mn}_3\text{O}_4/\text{MnOOH}$ and $\text{MnOOH}/\text{MnO}_2$, respectively. With an increase of the scan rate, both the anodic- and cathodic peak currents increase. The intensities of redox currents exhibit good linearity against the scan rate (Fig. 5b), indicating a surface-confined electrochemical process. Upon the introduction of glucose, notable current increase at the anodic peak (III) is observed on the CV curve at a scan rate of 20 mV s^{-1} , while the cathodic peak currents remain constant (Fig. 5c). The result suggests that the

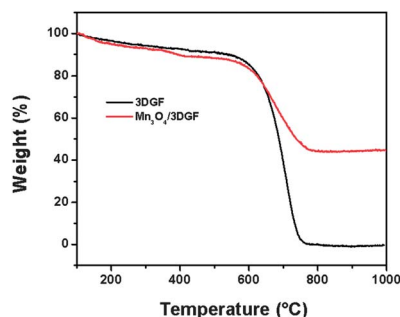


Fig. 4 TGA curves of 3DGF and the $\text{Mn}_3\text{O}_4/3\text{DGF}$ composite.

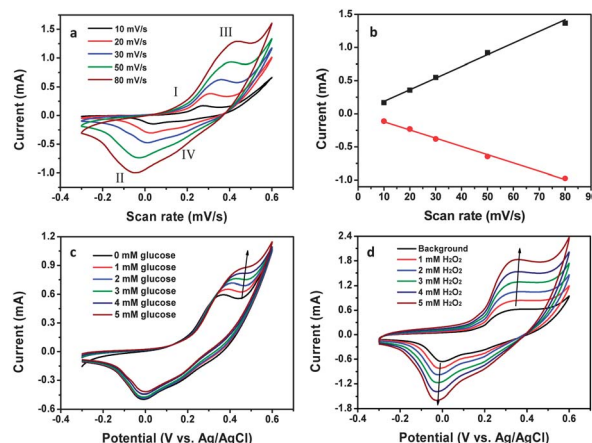
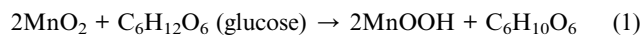
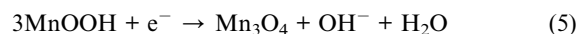
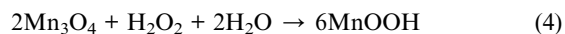
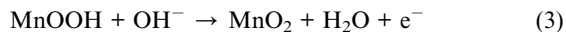


Fig. 5 (a) CV curves of the $\text{Mn}_3\text{O}_4/3\text{DGF}$ composite electrode recorded at different scan rates (from inside to outside: 10, 20, 30, 50 and 80 mV s^{-1}) in 0.1 M NaOH solution. (b) Plots of the scan rate versus peak currents at (II) and (III). (c) CVs of the composite electrode recorded at 20 mV s^{-1} in the presence of different concentrations of glucose (from inside to outside: 0, 1, 2, 3, 4, and 5 mM). (d) CVs of the composite electrode recorded at 20 mV s^{-1} in the presence of different concentrations of H_2O_2 (from inside to outside: 0, 1, 2, 3, 4, and 5 mM).

electrooxidation of glucose could be catalyzed by MnO_2 presumably due to the following reaction:



In contrast, when H_2O_2 was added, increase of both anodic and cathodic peak currents was observed with the increase of H_2O_2 concentration (Fig. 5d). This could contribute to the bi-electrocatalytic property of nanostructured Mn_3O_4 toward H_2O_2 . We propose the possible mechanism as follows. On one hand, upon the addition of H_2O_2 , MnO_2 is reduced to MnOOH , which is then electro-oxidized back to MnO_2 (eqn (2) and (3)). This reaction results in the increase of anodic current at peak (III). On the other hand, Mn_3O_4 could be oxidized by H_2O_2 to MnOOH , which is further electrochemically reduced back to Mn_3O_4 (eqn (4) and (5)), resulting in the increment of cathodic current at peak (II).



Next, real-time and enzymeless detection of glucose was studied by addition of various concentrations of glucose to a homogeneously stirred 0.1 M NaOH solution at a fixed potential of 0.4 V, where the most significant increase of voltammetric current was observed. Fig. 6a shows the amperometric responses of the $\text{Mn}_3\text{O}_4/3\text{DGF}$ monolithic electrode to successive addition of 1 mM and 100 μM glucose. A remarkable increase and fast response of amperometric current is observed

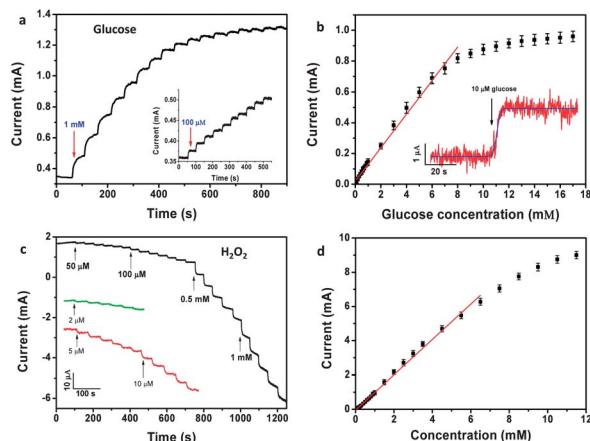


Fig. 6 (a) Amperometric response of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ composite electrode at 0.4 V upon the successive addition of 1 mM and 100 μM glucose (inset). (b) Calibration curve of the composite material-based glucose sensor. The inset shows the current response of the composite electrode toward the addition of 10 μM glucose. (c) Amperometric response of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ composite electrode toward successive addition of H_2O_2 at 0 V. (d) The calibration curve of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ electrode for H_2O_2 .

by the $\text{Mn}_3\text{O}_4/\text{3DGF}$, which reaches 95% of the steady state current within 5 s upon the addition of glucose. The calibration curve of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ is plotted in Fig. 6b, showing a high sensitivity of $360 \mu\text{A mM}^{-1} \text{cm}^{-2}$ and a large linear range of 0.1–8 mM. The sensitivity of $\text{Mn}_3\text{O}_4/\text{3DGF}$ is much superior to those enzymatic or enzymeless glucose sensors based on chemically derived graphene,^{10,36–44} most of which are in the range of 1–50 $\mu\text{A mM}^{-1} \text{cm}^{-2}$. Furthermore, in contrast to the small linear range of Co_3O_4 -based enzymeless glucose sensors,^{12,27} the $\text{Mn}_3\text{O}_4/\text{3DGF}$ could be used to study the sugar level in human blood, which is usually in the range of 4.4–6.6 mM.¹ As shown in the inset of Fig. 6b, $\text{Mn}_3\text{O}_4/\text{3DGF}$ also exhibits a limit of detection as low as 10 μM ($S/N = 3$). The performance of our glucose sensor is compared with other nonenzymatic glucose sensors in Table 1. The $\text{Mn}_3\text{O}_4/\text{3DGF}$ shows both high

Table 1 Comparison of the analytical performance of various nonenzymatic glucose biosensors^a

Sensing material	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Detection limit (μM)	Linear range	Ref.
Co_3O_4 nanofiber	36.25	0.97	Up to 2.04 mM	48
$\text{Co}_3\text{O}_4/\text{3DGF}$	3390	0.025	Up to 80 μM	27
NiO/MWCNT	436	160	Up to 12 mM	49
MWCNT	4.36	1	2 μM –11 mM	50
Porous Au	11.8	5	2–10 mM	51
Mesoporous Pt	9.6	—	0–10 mM	52
Pd/SWCNT	160	0.2 ± 0.05	0.5–17 mM	53
Pt-Pb alloy/ MWCNT	17.8	1.8	Up to 11 mM	54
Pt-Ni alloy/ graphene	20.42	10	Up to 35 mM	55
$\text{Mn}_3\text{O}_4/\text{3DGF}$	360	10	0.1–8 mM	This work

^a MWCNT: multi-walled carbon nanotubes.

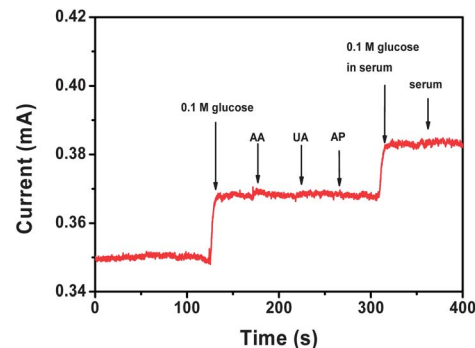


Fig. 7 Amperometric response of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ composite electrode toward the addition of glucose and various interferential compounds.

sensitivity and large linear range toward glucose detection. Good selectivity of our glucose biosensor was demonstrated by negligible current response to the addition of 0.1 mM uric acid (UA), ascorbic acid (AA) and acetaminophen (AP), common electroactive species coexisting in blood (Fig. 7). Additionally, the practicability of the glucose sensor was examined by adding glucose-free and glucose-containing serum to the electrolyte (Fig. 7). The $\text{Mn}_3\text{O}_4/\text{3DGF}$ showed insensitivity to the glucose-free serum sample, which contains a large quantity of various proteins and interferential molecules. Upon the addition of serum supplemented with 0.1 mM glucose, the $\text{Mn}_3\text{O}_4/\text{3DGF}$ showed comparable response to 0.1 mM glucose in PBS. The above results demonstrate that the $\text{Mn}_3\text{O}_4/\text{3DGF}$ -based glucose sensor has excellent selectivity and great potential for *in situ* determination of the blood glucose level. The analytical performance study of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ was extended to the detection of H_2O_2 , a significant chemical in environmental and food industry. Well-defined steady state cathodic current was obtained within 3 s upon the addition of H_2O_2 at the optimal reduction potential of 0 V (Fig. 6c). The calibration curve depicted in Fig. 6d reveals that the $\text{Mn}_3\text{O}_4/\text{3DGF}$ -based H_2O_2 sensor achieved a dynamic linear range of 2 μM to 6.5 mM, with a high sensitivity of $1.03 \text{ mA mM}^{-1} \text{cm}^{-2}$, and a detection limit of 1 μM ($S/N = 3$). The sensitivity of our $\text{Mn}_3\text{O}_4/\text{3DGF}$ -based sensor is apparently superior to previously reported H_2O_2 biosensors that used manganese oxide as an electrode material.^{2,45–47} The interferential study showed that at the potential of 0 V, the $\text{Mn}_3\text{O}_4/\text{3DGF}$ is relatively inert to glucose, fructose, glutamine, ascorbic acid, uric acid and nitrite, which commonly exist in food (Table S1†). The practical usage of the H_2O_2 biosensor was performed by determination of H_2O_2 concentration in the ultra-high-temperature (UHT) processed milk sample. The recovery results illustrate that the $\text{Mn}_3\text{O}_4/\text{3DGF}$ -based H_2O_2 sensor could give exact recovery ($\geq 95\%$) with small R.S.D values (Table S2†). The stability of the biosensor for glucose and H_2O_2 detection was evaluated every five days over a month period (Fig. S2†). Results show that the biosensor maintains 90% of its original response to both analytes after a month of storage. The excellent performance of the $\text{Mn}_3\text{O}_4/\text{3DGF}$ composite toward nonenzymatic biosensing could be contributed to the synergistic effect of Mn_3O_4 and 3DGF. While

the superior electrochemical activity of hierarchically structured Mn_3O_4 enables the efficient electrocatalytic reaction of glucose and H_2O_2 , the large surface area and high conductivity of the 3DGF facilitate the rapid access of electrolyte ions and fast electron transport. The coordination between these two materials greatly enhanced detection performance of the sensor.

Conclusions

In conclusion, we synthesized a novel composite material of hierarchical Mn_3O_4 /3DGF and evaluated it for enzyme-free detection of glucose and H_2O_2 . The composite showed good flexibility and mechanical strength which enabled it to be used as a flexible and freestanding biosensor. In addition, the macro- and nanoporous structure of the composite was highly accessible to the medium that greatly facilitated the diffusion of electrolyte ions, resulting in extremely high sensitivity, large linear range, and low detection limit for the detection of both glucose and H_2O_2 . Such high sensing performance of the biosensor could be attributed to the synergistic effect of the two nanomaterials, *i.e.*, the electrocatalytic property of nano-structured Mn_3O_4 and the large surface area of 3DGF. We believe that, due to its unique structure, well-defined crystallinity and high electrochemical activity, the hierarchical Mn_3O_4 /3DGF composite could also be beneficial to other applications, such as lithium-ion batteries and supercapacitors.

Experimental section

Growth of the 3DGF network

The 3DGF was synthesized using a template-based ethanol-CVD method previously reported by us.^{27,56} Briefly, the nickel foam (thickness ~ 0.5 mm, purchased from Alantum Advanced Technology Materials, China) was placed in the center of a quartz tube furnace and heated up to 1000°C at a rate of $50^\circ\text{C min}^{-1}$. The temperature was maintained at 1000°C for 10 min under ambient pressure with a gas flow of Ar (50 sccm) and H_2 (25 sccm) in order to remove the oxide layer from the surface of nickel foam. Ethanol was then bubbled into the furnace as a carbon source by an Ar flow. The concentration of ethanol was controlled by the flow rate of Ar. After 20 minutes of growth, the sample was taken out from the furnace and rapidly cooled down to room temperature at a cooling rate of $100^\circ\text{C min}^{-1}$ under the protection of Ar/ H_2 flow (Ar : H_2 = 50 : 25). In order to remove the nickel foam template, the as-prepared 3DGF was first dipped into the solution of 4.5% poly(methyl methacrylate) (PMMA with a molecular weight of 996 000) for several seconds, followed by drying at 90°C for 1 h. After that, the PMMA coated 3DGF networks were immersed into 3 M HCl at 80°C to etch away the nickel substrate. Finally, the PMMA layer was removed by hot acetone vapor followed by annealing at 450°C under Ar/ H_2 flow.

Synthesis of the Mn_3O_4 /3DGF composite and electrode fabrication

A hierarchically structured Mn_3O_4 network was grown on the surface of 3DGF by an electrochemical deposition method.

The electrodeposition was performed using an electrochemical workstation (CHI 760D, CH instrument Inc, USA) with a conventional three-electrode system, with 3DGF as a working electrode, Pt foil as a counter electrode and Ag/AgCl as a reference electrode. Under room temperature, a constant potential of 0.5 V was applied in an aqueous solution of 0.01 mol L^{-1} manganese acetate for 600 s to achieve the uniform coating of MnO_x on the skeleton of 3DGF. The product was then washed with double-distilled water several times and dried by ultrapure nitrogen flow. Finally, the sample was calcinated at 400°C in air for 5 h to obtain the highly crystalline Mn_3O_4 on 3DGF. The composite was then affixed to a flexible PET substrate by silicon rubber to use as a freestanding electrode and a flexible biosensor.

Apparatus

The surface morphology and microstructure of the sample were investigated using a field-emission scanning electron microscope (FESEM, JSM6700F, JEOL) operated at 5 kV and a transmission electron microscope (TEM, JSM2100F, JEOL) operated at 200 kV. The TEM sample was prepared by sonicating the composite material in ethanol for 3 min followed by casting one drop of the obtained dispersion on the TEM copper grid. The crystallographic information was collected by X-ray diffraction (XRD; Bruker, D8 Advance X-ray diffractometer, Cu $K\alpha$ radiation, $\lambda = 1.5406\text{ \AA}$). The Raman spectra were obtained with a WITeK CRM200 confocal microscopy Raman system (488 nm laser wavelength, 2.54 eV, WITeK, Germany). Thermogravimetric analysis (TGA) was conducted on a TA Instrument 2960 from 100°C to 1000°C under an air flow at a heating rate of $10^\circ\text{C min}^{-1}$.

All the electrochemical tests including cyclic voltammetry (CV) and amperometry were performed in a three-electrode electrochemical cell, with the Mn_3O_4 /3DGF composite, Pt wire and Ag/AgCl serving as working, counter and reference electrodes, respectively. 0.1 M NaOH aqueous solution was used as an electrolyte throughout the experiment.

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