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Facile Growth of Cu_2O Nanowires on Reduced Graphene Sheets with High Nonenzymatic Electrocatalytic Activity Toward Glucose

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In this work, we demonstrate the fabrication of a unique hybrid structure by directly growing ultrathin Cu_2O nanowires (about 5 nm in diameter) onto reduced graphene oxide (rGO) sheets via a facile solvothermal method. This is a facile process carried out at 120°C for 6 h, in which only cupric acetate and rGO sheets are used as initiating materials, ethylene glycol as the solvent and reducing agent, and soldium acetate as precipitator, without employing any additional surfactant. Furthermore, the as-obtained nanocomposites-modified glassy carbon electrode (GCE) shows significantly improved electrochemical performance in nonenzymatic amperometric glucose detection, exhibiting the good linear behavior with glucose concentrations ranging from 10 μM to 0.1 mM with a high gradient of 80.17 μA/mM. More importantly, interference from the oxidation of common interfering species under physiological conditions, such as uric acid, dopamine, and ascorbic acid, is effectively avoided. Therefore, these nanocomposites may be a promising electrode material for the determination of glucose.

I. Introduction

Cuprous oxide (Cu_2O), as an important p-type semiconductor material, has garnered considerable attention due to its potential applications in solar energy conversion, biosensors, photocatalysis, and coherent propagation of excitons.[1–4] Especially, there are a great amount of interests in enzyme-free glucose sensors due to their high electrocatalytic activity resulting from multielectron oxidation mediated by surface metal oxide layers.[5–9] Although numerous nanostructured Cu_2O materials with various morphologies, such as nanocubes, nanowires (NWs), nanospheres, and hollow nanostructures, have been reported, it is still challenging to synthesize high active Cu_2O with controllable size, morphology, and high crystallinity.[10–13] These unique structures and electrical properties endow them with new and important catalytic activities. However, the synthesized Cu_2O NWs are prone to agglomerating, which greatly limits their applications in enzyme-free glucose sensors. This obstacle may be overcome by employing Cu_2O NWs loaded on the graphene sheets. Graphene, a monolayer of carbon atoms with a close-packed two-dimensional (2D) lattice in honeycomb-like arrangements, has attracted much attention due to its high surface area, high chemical stability, and unique electrical, mechanical, thermal, and optical properties.[14,15] It can serve as an ideal building block for the fabrication of a variety of functional materials.[16–19]

Herein, we demonstrate a facile solvothermal method for a direct growth of ultrathin Cu_2O NWs (about 5 nm in diameter) onto reduced graphene oxide (rGO) sheets to form rGO–Cu_2O NWs composites. This is a facile process, in which only cupric acetate monohydrate [$Cu(Ac)_2 \cdot H_2O$) and rGO sheets are used as initiating materials, ethylene glycol (EG) as the solvent and reducing agent, and soldium acetate (NaAC) acts as precipitator, without employing any additional surfactant. It is reported that when rGO sheets is mixed in a copper salt solution, Cu^{2+} is selectively bonded with carboxyl through a mutual electrostatic attraction.[20] However, to our knowledge, this is the first time for us to assemble Cu_2O NWs onto rGO sheets via a facile and direct route. By directly growing such monodisperse Cu_2O NWs on the rGO support, which is able to take advantage of both components. As expected, the as-prepared rGO–Cu_2O NWs composite-modified glassy carbon electrode (GCE) shows high sensitivity and fast amperometric response to glucose detection. In addition, interference from the oxidation of common interfering species present in body fluids, such as uric acid (UA), dopamine (DA), and ascorbic acid (AA), is effectively avoided.

II. Experimental Procedure

All reagents were of analytical grade, purchased from the Shanghai Chemical Reagent Factory (Shanghai, China), and were used as received without further purification.

(1) Growth of Cu_2O NWs onto rGO Sheets

In a typical procedure, GO was first prepared from pure graphite using a modified Hummer's method,[13,21] and rGO sheets were synthesized in a similar manner to what we reported previously.[22,23] 0.1 g of cupric acetate monohydrate [$Cu(Ac)_2 \cdot H_2O$], 0.082 g of NaAc, and 40 mg of rGO were dissolved in 35 mL of EG with the assistance of ultrasonication for 30 min. The mixture was subsequently transferred to a 50 mL Teflon-lined stainless steel autoclave, and heated at 120°C for 6 h. Finally, the as-synthesized product was collected and washed with water and absolute ethanol for several times, and then dried under vacuum at 60°C for 4 h. For comparison, pure Cu_2O NWs were also prepared under the same condition except rGO was not added.

(2) Characterization

Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer (Eindhoven, the Netherlands) using the Cu$K\alpha$ radiation at a scanning rate of $0.06° \, s^{-1}$. Scanning electron

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microscopy (SEM) was performed with a Hitachi S-4800 scanning electron microanalyzer (Tokyo, Japan) with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution TEM were conducted at 200 kV with a JEM-2100F (Tokyo, Japan) field-emission TEM, after dispersing the as-prepared nanocomposites in ethanol and depositing several drops of the suspension on the carbon-coated copper grids and dried under ambient conditions. Thermogravimetric analysis (TGA) of the products was performed on a Netzsch STA 449C (Selb, Germany) thermal analyzer.

(3) Electrochemical Measurements

All electrochemical measurements were conducted on a CHI840C electrochemical workstation with a conventional three-electrode setup at room temperature.[22] The as-obtained nanocomposites-modified GCEs were employed as the working electrode, a saturated Hg/Hg_2Cl_2 electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was $0.1M$ NaOH containing $0.1M$ KCl, and deionized water was used throughout the experiments. For calibration experiments, amperometric measurements were carried out at 0.55 V, while a certain amount of 0.01 or 0.1 mM glucose was added into 40 mL of electrolyte under a magnetically stirred condition to obtain a stepwise increase to reach a final concentration 0.1 or 1 mM.

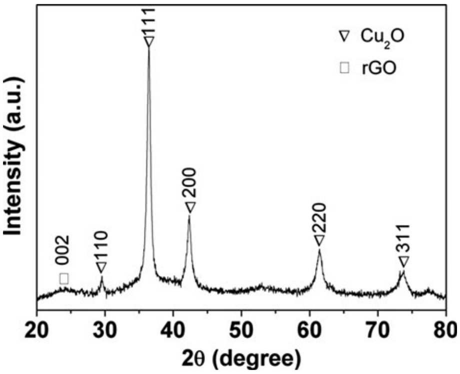

Fig. 1. X-ray diffraction pattern of the as-prepared rGO–Cu_2O nanowires composites.

III. Results and Discussion

The XRD pattern of the as-prepared rGO–Cu_2O NWs is shown in Fig. 1. The pattern obviously consists of two sets of diffraction peaks (rGO and Cu_2O), the diffraction peaks marked by squares indexed to the (002) diffraction of rGO sheets.[23] The clear diffraction peaks centered at 2θ of 29.6°, 36.4°, 42.3°, 61.3°, and 73.5° are corresponding to the (110), (111), (200), (220), and (311) crystal planes of the cubic Cu_2O (JCPDS standard card no. 78-2076, $a = b = c = 0.4267$ nm), respectively. No other diffraction peaks are detectable, indicating the pure phase Cu_2O NWs obtained under the presented experimental condition.

The morphologies of the as-obtained rGO sheets and rGO–Cu_2O NWs composites are examined by SEM image. Figure 2(a) shows the as-obtained rGO consists of corrugated and crumpled sheets, which are of the intrinsic nature of 2D membrane structures, thermodynamically stabilized by bending.[24] From Fig. 2(b), it is clearly seen that Cu_2O NWs are uniformly distributed on the surface of rGO sheets. The morphology and structure of the rGO–Cu_2O NWs composites are further elucidated by TEM measurements, as shown in Fig. 2(c) and (d). Uniform Cu_2O NWs with about 5 nm in diameter are anchored on rGO sheets, in good agreement with the SEM observation. A representative high-resolution TEM image with fast-Fourier transform [inset in Fig. 2(d)] reveals a lattice spacing of 0.25 nm which matches well with that of cubic Cu_2O. Highly dispersed Cu_2O NWs on rGO supports provide larger surface areas and possess the advantages in catalytic activity and sensor sensitivity.[25] For quantifying the amount of Cu_2O in the Cu_2O–rGO NWs composite, TGA was carried out in air from room temperature to 800°C at a rate of 10°C/min. As can be seen in Fig. 3, the first drop in weight loss (up to ~60°C, 4.55%) is due to the desorption of absorbed water molecules on the product. The second weight loss of 38.82% (60°C~360°C) corresponds to the loss of part of rGO. A weight loss (the

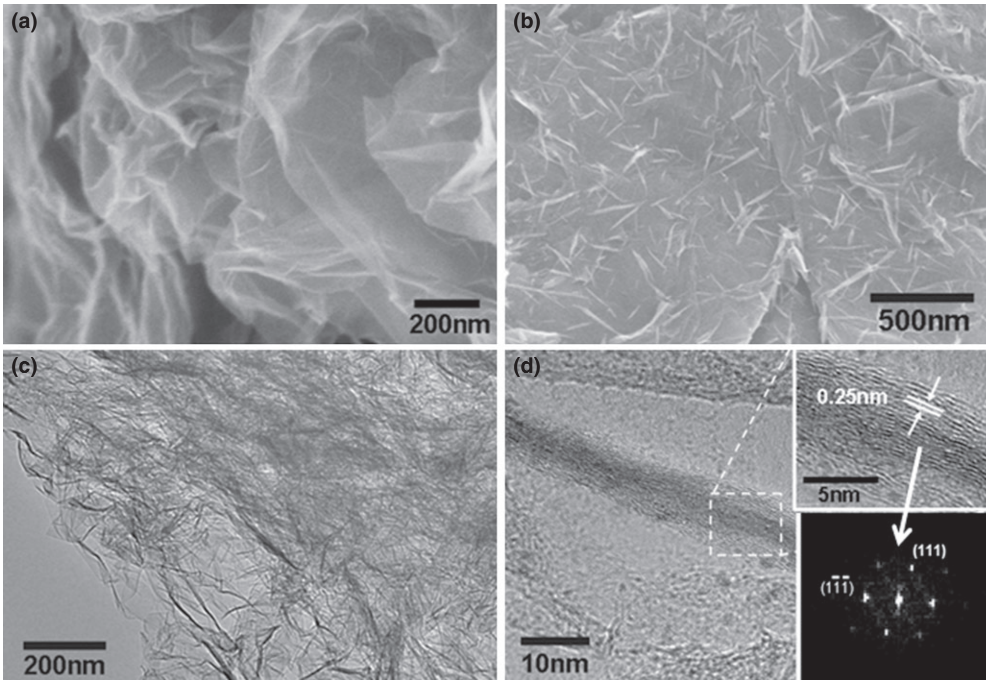

Fig. 2. Scanning electron microscopy images of: (a) rGO sheets and (b) rGO–Cu_2O nanowires (NWs) composites; and (c) transmission electron microscopy and (d) high-resolution TEM images with fast-Fourier transform of the as-obtained rGO–Cu_2O NWs composites.

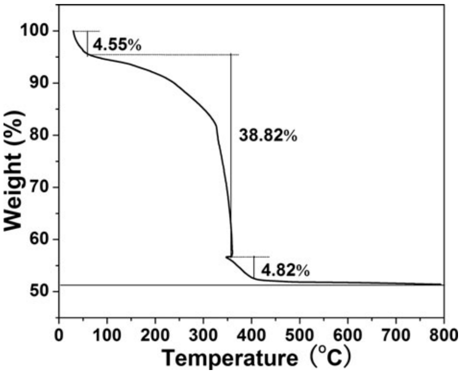

Fig. 3. Thermogravimetric analysis of the as-prepared rGO–Cu_2O nanowires composites.

conversation of rGO to CO_2) and a weight increase (the conversation of Cu_2O to CuO) happen simultaneously during 360°C~405°C, but the weight loss is larger than the weight increase. According to the reaction: $Cu_2O + 1/2O_2 = 2CuO$, it should be a theoretical weight increase of 5.16%. Thus, the net weight loss would be 9.98% in this period, and the content of Cu_2O in the composite is about 46.13%. However, the pure Cu_2O obtained without addition of rGO support in reactive system shows conglomerated NWs, as shown in Fig. 4(a) and (b), indicating the rGO sheets are in favor of the dispersion of Cu_2O NWs.

In the simple solvothermal process, EG serves as both solvent and reducing agent, and it evidently plays a critical role in the nucleation and growth of the Cu_2O NWs. Figure 5(a) shows the XRD pattern of a sample prepared in water. All the peaks can be indexed to a monoclinic phase of CuO with lattice constants of $a = 4.692$, $b = 3.428$, and $c = 5.137$ Å (JCPDS standard card no. 80-1916). No diffraction peaks from impurities such as $Cu(OH)_2$ and Cu_2O are detected. This result indicates that the as-obtained samples are composed of a pure phase CuO. And for the synthesis carried out in an aqueous solution, only agglomerated CuO particles are formed [SEM, Fig. 5(b)]. As has already been reported, acetaldehyde (CH_3CHO) is produced from the dehydration of EG at high temperature, and it donates hydrogen atoms which can act as a reducing agent.[26,27] Cu_2O particles can therefore nucleate through the reduction in $Cu(Ac)_2$ with the produced hydrogen atoms. Moreover, EG can serve as a ligand to form chain-like coordination complexes with Cu(II), and the chain-like glycolate precursors connect to produce a wire-like morphology during heating.[28] It should be emphasized here that the use of NaAc as a mild precipitator is critical for the formation of dispersed uniform Cu_2O NWs at a lower temperature. Without the addition of NaAc, a higher temperature (160°C) is needed to obtain Cu_2O NWs in the solvothermal process.

To investigate the electrocatalytic activity of pure Cu_2O NWs and rGO–Cu_2O NWs composites-modified GCE toward the oxidation of glucose, the corresponding cyclic voltammograms (CVs) were obtained in the absence and presence of glucose in $0.1M$ of NaOH solution at a SCE sweep rate of 50 mV/s. Figure 6(a) shows that the rGO–Cu_2O NWs composites-modified GCE exhibits significantly enhanced catalytic activity toward glucose. When 1 mM glucose was added at SCE of 0.55 V, response current increased from 5.22 to 14.65 μA for pure Cu_2O, but from 37.45 to 75.77 μA for rGO–Cu_2O NWs composites. The enhanced activity may be assigned to the Cu(II)/Cu(I) redox couple and the addition of rGO. Firstly, rGO has a large surface area and improves the dispersion of Cu_2O NWs in rGO–Cu_2O composite. Secondly, the electron transfer in rGO–Cu_2O composites can be improved due to the superior electron conduction of rGO. In addition, the stability for the rGO–Cu_2O composite-modified GCE after activation is also examined by recording 10 consecutive CV curves in the absence of glucose (1) and in the presence of 1 mM glucose

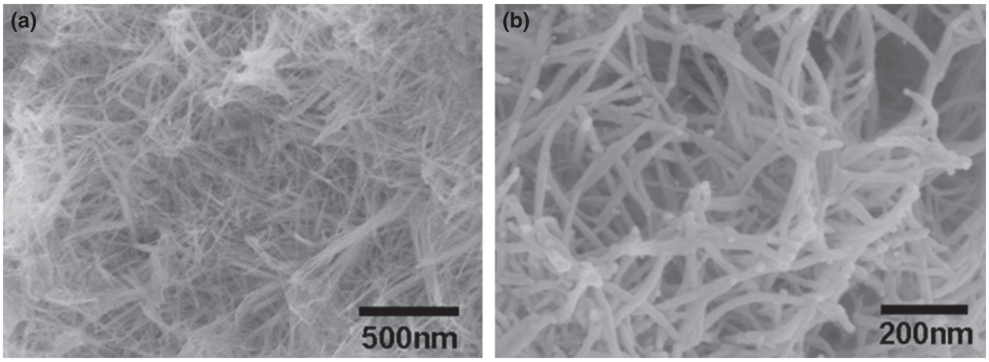

Fig. 4. Scanning electron microscopy images of pure Cu_2O nanowires obtained without addition of rGO support: (a) at low-magnification and (b) at high-magnification.

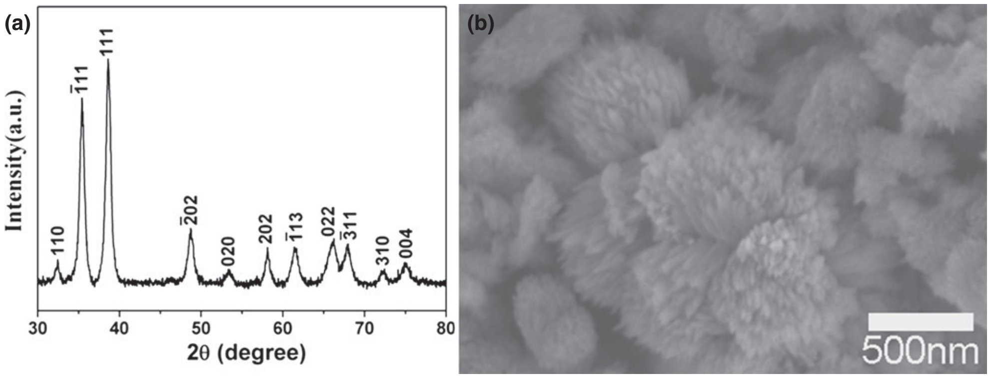

Fig. 5. (a) X-ray diffraction pattern and (b) scanning electron microscopy image of the as-prepared CuO particles in water at 120°C for 6 h.

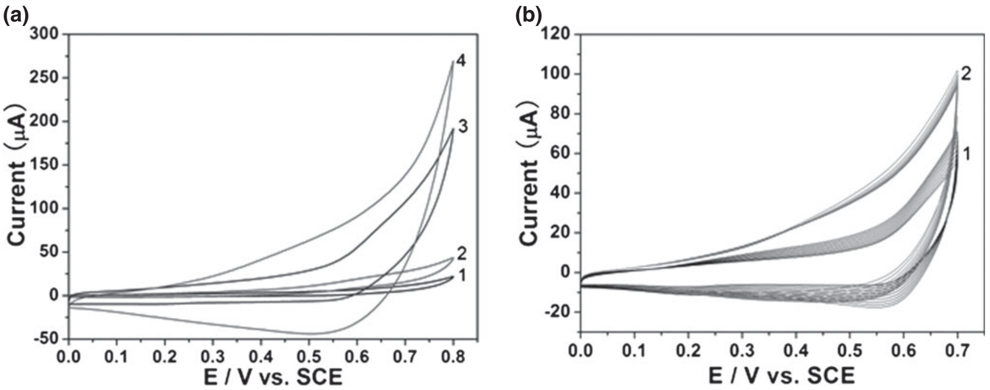

Fig. 6. (a) Cyclic voltammograms obtained at pure Cu_2O nanowires (NWs) (1 and 2) and rGO–Cu_2O NWs composites-(3 and 4) modified glassy carbon electrode in the absence of glucose (1 and 3) and in the presence of 1 m*M* glucose (2 and 4) in 0.1*M* NaOH solution containing 0.1*M* KCl, scan rate: 50 mV/s. (b) 10 consecutive cyclic voltammograms curves of the rGO–Cu_2O NWs composites-modified electrode in the absence of glucose (1) and in the presence of 1 m*M* glucose (2) in 0.1*M* NaOH solution containing 0.1*M* KCl.

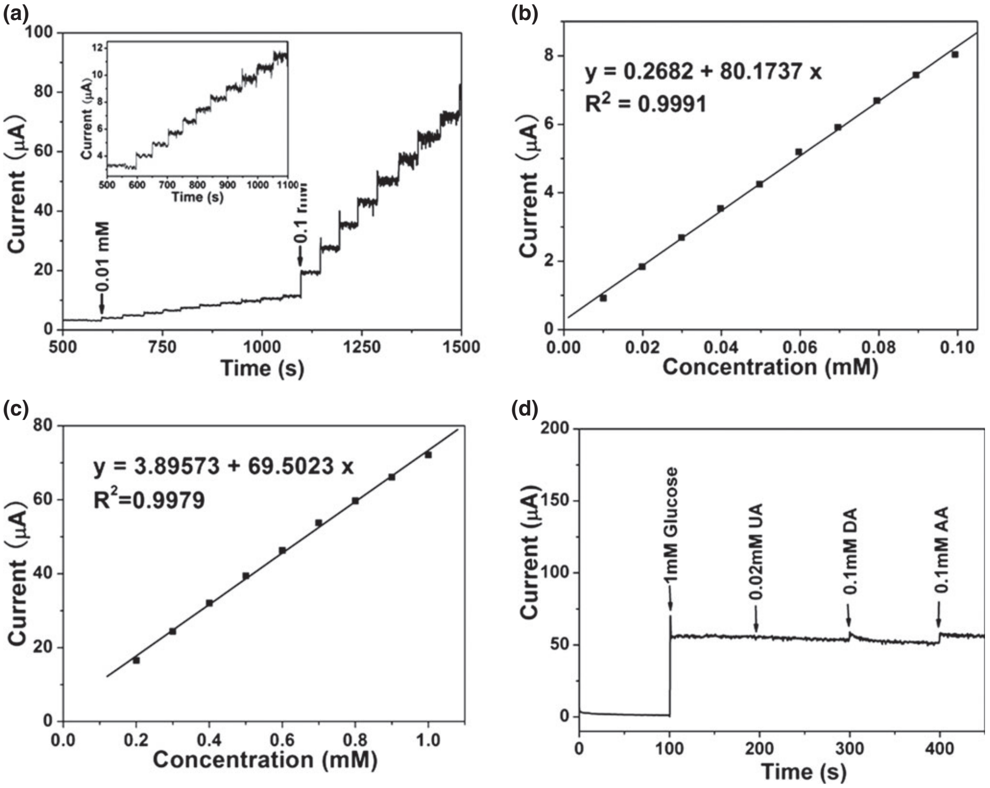

Fig. 7. (a) The amperometric response of the rGO–Cu_2O NWs composites-modified electrode upon addition of glucose, with working SCE was 0.55 V; The linear fitting at lower concentration range (b) and higher concentration range (c); (d) Amperometric response of the nanocomposites electrodes to additions of 1 mM glucose, 0.02 mM UA, 0.1 mM DA, and 0.1 mM AA in 0.1*M* NaOH containing 0.1*M* KCl, with working SCE was 0.55 V.

(2) in 0.1*M* NaOH solution containing 0.1*M* KCl at a scan rate of 50 mV/s [Fig. 6(b)]. No obvious peak current change is observed, which demonstrates the rGO–Cu_2O composite-modified GCE is very stable.

Figure 7(a) shows the well-defined steady-state amperometric response of the as-prepared rGO–Cu_2O composite-modified GCE to nonenzymatic glucose sensing with successive addition of glucose to 0.1*M* NaOH at an applied SCE of 0.55 V. The response time toward the oxidation of glucose is less than 2 s, revealing a rapid and sensitive response to glucose, which may be ascribed to the excellent electrocatalytic property and rapid charge-transfer behavior of the rGO–Cu_2O nanocomposite electrodes. The calibration plot [Fig. 7(b)] shows a linear range between 0.01 and 0.1 m*M* with a high gradient of 80.17 μA/mM and a great correlation coefficient of 0.9991. More detailed examination of Fig. 7(c) reveals a linear relationship with a similar correlation coefficient of 0.9979 over the concentration range of 0.2~1 m*M*. In this case, there is a gradient of 69.50 μA/mM. It is well-known that the oxidizable compounds such as UA, DA, and L-AA are normally coexisted with glucose in real samples. Although at low concentrations relative to glucose, they often interfere with the determination of glucose because of their high electron-transfer rates. To evaluate the selectivity of the new sensors, the interference effect of 0.02 m*M* of UA, 0.1 m*M* of DA, and 0.1 m*M* of AA at the physiological level on the amperometric response of 1 m*M* glucose was studied. At this level, the current response to these electroactive interfering species is almost negligible, compared with that of glucose at an applied SCE of 0.55 V in 0.1*M* NaOH solution containing 0.1*M* KCl [Fig. 7(d)].

IV. Conclusions

In summary, we have developed a simple one-pot solvothermal method to synthesize rGO–Cu_2O NWs composites with a uniform morphology in EG at 120°C for 6 h. Through this method, ultrathin Cu_2O NWs with about 5 nm in diameter are well dispersed on the surface of rGO sheets. The as-obtained nanocomposites preserve the good dispersity and uniformity of the initial rGO sheets and exhibit a better catalytic activity than pure Cu_2O NWs toward direct oxidation of glucose. The linear current response range of rGO–Cu_2O NWs composites-modified GCE to glucose is from 0.01 m*M* to 1 m*M*, with a gradient of no less than 69.50 μA/m*M*. The composites-modified GCE also exhibits excellent selectivity and sensitivity for glucose in the presence of UA, DA, and AA. As a result, the as-prepared nanocomposites are proved to be a promising electrode material for the determination of glucose.

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