



Solvothermal Synthesis of Nickel Oxide Nanoparticles Decorated Graphene Sheets for Electrochemical Detection of Glucose

JIANPING XU, FUCHENG YE and CHUNYAN WANG*

Fundamental Science on Radioactive Geology and Exploration Technology Laboratory, Department of Materials Science and Engineering, East China Institute of Technology, Nanchang 330013, Jiangxi Province, P.R. China

*Corresponding author: Tel/Fax: +86 794 8258320; E-mail: chunyanwang@ecit.cn

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In this study, we proposed a facial solvothermal approach to the *in situ* decoration of nickel oxide nanoparticles on the surface of solvothermal reduced graphene (NiO@SRG). The high dispersion of NiO nanoparticles with the uniform size distribution could be easily obtained *via* using simple solvothermal process. Moreover, the as-prepared NiO@SRG modified glassy carbon electrode (GCE) exhibited better non-enzymatic electrocatalytic responses towards glucose detection and the limit of detection is 1.15 μM ($S/N = 3$) in alkaline media. In addition, this electrode material possessed some important advantages such as low cost, easy preparation, good stability and high reproducibility. The influence of some interfering species was investigated and the result indicated that these foreign substances did not interfere significantly on the detection of glucose. This new findings demonstrate that NiO@SRG is a promising candidate of advanced electrode material in electrochemical sensing and other electrocatalytic applications.

Keywords: Synthesis, NiO nanoparticles, Solvothermal reduced graphene, Enzyme-free glucose detection.

INTRODUCTION

Graphene, a mono- or few layers of sp^2 -hybridized carbon atoms, has attracted considerable attention as the new member of carbon allotrope family owing to its ultra-large surface area, excellent conductivity, high mechanical stiffness, chemical inertness¹⁻³, good biocompatibility⁴ and low manufacturing cost⁵. These fascinating properties of graphene have been exploited in various fields such as supercapacitors⁶, resonators⁷, sensors⁸, polymer nanocomposites⁹, field-effect transistors¹⁰, lithium-ion batteries¹¹ and organic photovoltaic cells¹² *etc.* Moreover, graphene-based composites with other functional nanomaterials lead to vast unprecedented possibilities because of their synergistic effects^{13,14}.

The development of biosensor has become an active research field in chemical and biological analyses, clinical detection and environmental monitoring¹⁵. Owing to high sensitivity and good selectivity of enzymatic biosensor, the applications of enzyme such as enzyme biosensor for glucose dehydrogenase and glucose oxidase are attractive^{16,17}. However, the biggest defect of enzymatic glucose sensors is that their stability is not good enough originating from their intrinsic dependence on enzyme activity^{18,19}. In order to solve this problem, great efforts have been devoted to developing nonenzymatic biosensors to avoid the disadvantages of enzymatic sensors^{20,21}.

To date, several approaches have been explored to prepare graphene hybrids such as PtNi-graphene²², Cu_2O @graphene²³ and Co_3O_4 /graphene²⁴ for constructing high performance enzyme-free glucose sensors.

Nickel oxide (NiO) is a transition metal oxide with intriguing electronic, optical, electrochemical and electrocatalytic properties. NiO-based nanocomposites have demonstrated great potentials in the applications of electrochemical sensors²⁵, heterogeneous catalysts²⁶, capacitors²⁷ and Li-ion rechargeable batteries²⁸.

In this present work, we develop a simple and efficient solvothermal method for the large-scale synthesis of the NiO@SRG composite directly from graphene oxide (GO) in dimethyl acetamide. This approach uniformly anchors nickel oxide on the 2D graphene sheets. It demonstrates remarkable performance in enzyme-free electrochemical detection of glucose.

EXPERIMENTAL

Raw materials: Graphite powder was obtained from Alfa Aesar (Shanghai Carbon Co., Ltd., China), with a particle size of 100 μm . Ascorbic acid, dopamine and uric acid were purchased from Alfa Aesar. Nickel nitrate, KOH, glucose and other chemicals were bought from Shanghai Chemical Factory (Shanghai, China) and used without further purification. All

chemicals were of analytical grade and solutions were prepared with deionized water from a pure system (>18 M Ω , Purelab Classic Corp., USA).

Synthesis of solvothermal reduced graphene (SRG) and NiO@SRG: Graphene oxide was fabricated by a modified Hummers method according to the literature²⁹. The process has been described in previous work³⁰. Graphene oxide is used as a supporting matrix to synthesize graphene-based composites because it contains large numbers of hydrophilic groups and can be obtained as low cost in a large scale. The typical synthesis process of NiO@SRG hybrids is as follows: 50 mg graphene oxide and 25 mg Ni(NO₃)₂ were dispersed into 50 mL *N,N*-dimethyl acetamide (DMAc) by ultrasonication for 2 h and the pH value of the solution was adjusted to around 10. Subsequently, the mixture was put into an autoclave and heated at 180 °C for 10 h. The as-synthesized precursor suspension was filtered and washed several times with deionized water and ethanol respectively, then dried at 70 °C *in vacuo* for 24 h. Finally, the precursor powder was annealed at 500 °C for 3 h in argon atmosphere. For comparison, pure solvothermal reduced graphene was prepared by the same method without Ni(NO₃)₂.

Preparation of solvothermal reduced graphene and NiO@SRG modified glass carbon electrode: 1 mg solvothermal reduced graphene or NiO@SRG powder was dispersed in 1 mL dimethylformamide (DMF). 10 μ L of sonicated pure SRG or NiO@SRG DMF suspension was dropped on the pretreated bare glassy carbon electrode using a micropipette tip and dried in air. After the film was dried, nafion solution (1.5 % in ethanol) was pipetted on the sample surface for protection. Electrochemical measurements were performed at a standard three-electrode electrochemical cell on a CHI 842 electrochemical Station (CH Instrument, USA) with a modified glassy carbon electrode as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference.

The structure of the samples was examined by X-ray powder diffractometer (XRD, Shimadzu, X-6000, CuK α radiation); X-ray photoelectron spectroscopy (XPS, K α) analyses were carried out on a Thermo Fisher X-ray photoelectron spectrometer system equipped with Al radiation as a probe, with a chamber pressure of 5 \times 10⁻⁹ Torr. The source power was set at 72 W and pass energies of 200 eV for survey scans and 50 eV for high-resolution scans were used. The analysis spot size was 400 μ m in diameter. The morphology was investigated using a JEOL, JSM 5800-LV scanning electron microscope (SEM) operated at 5 kV. Thermogravimetric analysis (TGA) was analyzed under an air atmosphere at a heating rate of 10 °C/min (Q50, TA Instrument).

RESULTS AND DISCUSSION

Fig. 1 represents the schematic procedure of the preparation of SRG and NiO@SRG composites. Hydrophilic graphite oxide was first synthesized from graphite according to a modified Hummers method. Then, individual graphene oxide (GO) nanosheets were fabricated by exfoliating graphite oxide under ultrasonication in water. Thereafter, Ni(NO₃)₂ solution was added to the graphene oxide nanosheets colloid suspension under stirring. Finally, the composites of graphene

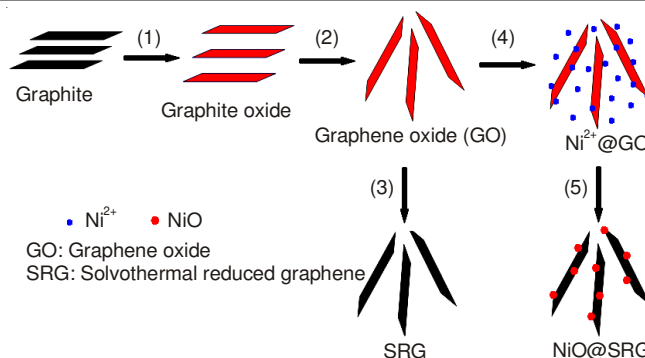


Fig. 1. A proposed scheme of the formation route of SRG and NiO@SRG composites. (1) Oxidation of graphite (gray planes) to graphite oxide (yellow planes) with greater interlayer distance. (2) Exfoliation of graphite oxide by sonication in water solution. (3) Solvothermal synthesis of reduced graphene. (4) Absorption of Ni(NO₃)₂ solution on the graphene oxide nanosheets. (5) Formation of graphene-supported NiO nanoparticles by the reduction of graphene oxide sheets and Ni ions

decorated by NiO nanoparticles were obtained *via* solvothermal reduction. Besides pure SRG was prepared by the same method without Ni(NO₃)₂.

Powder X-ray diffraction (XRD) measurements were employed to investigate the crystal phase and the structure of the products. Fig. 2a shows XRD patterns of the as-prepared SRG and NiO@SRG composite. The broad peak (002) of SRG (black pattern) centered at around 23.2° is observed corresponding to an interlayer spacing of about 0.38 nm calculated according to Bragg's equation. In contrast, the interlayer distance of the (002) peak for graphite powder³¹ is 0.337 nm ($2\theta = 26.3^\circ$). The increased interlayer spacing of graphene can be ascribed to the presence of a small amount of residual oxygen-containing functional groups or other structural defects³². The diffraction peak at around 43° is associated with the (100) plane of the hexagonal structure of carbon³³. The diffraction peaks of the NiO@SRG composite are consistent with (JCPDS, No. 65-6920) and the broad diffraction peak around 23° could be attributed to the graphene nanosheets. Three characteristic diffraction peaks appearing at 36.2, 43.6 and 62.8° could be readily indexed as (111), (200) and (220), respectively. Moreover, there is no peak of impurities detected, indicating that almost all of the nickel is converted into the NiO nanostructures after solvothermal reduction and thermal treatment at 500 °C. This suggests that NiO nanoparticles have been successfully loaded onto the graphene sheets.

To further confirm that it is NiO nanoparticles loaded on the graphene sheets, we undertook the X-ray photoelectron spectroscopy (XPS) spectrum measurement on the hybrids on glass slide. Fig. 2b indicates that the nickel exists as nickel(II) in the nanoparticles and further supports that NiO have been effectively assembled on the surface of SRG.

The highly dispersed nanoparticles on supports with larger surface areas have unique properties with advantages for catalytic activity and sensor sensitivity³⁴. As shown in Fig. 3, the anchored NiO nanoparticles distributed evenly on the graphene nanosheets without obvious aggregations. These SRG nanosheets with monolayer or double-layered nanostructure possess huge surface areas and particles can deposit on both sides and surfaces of these sheets³⁵. Thus, such

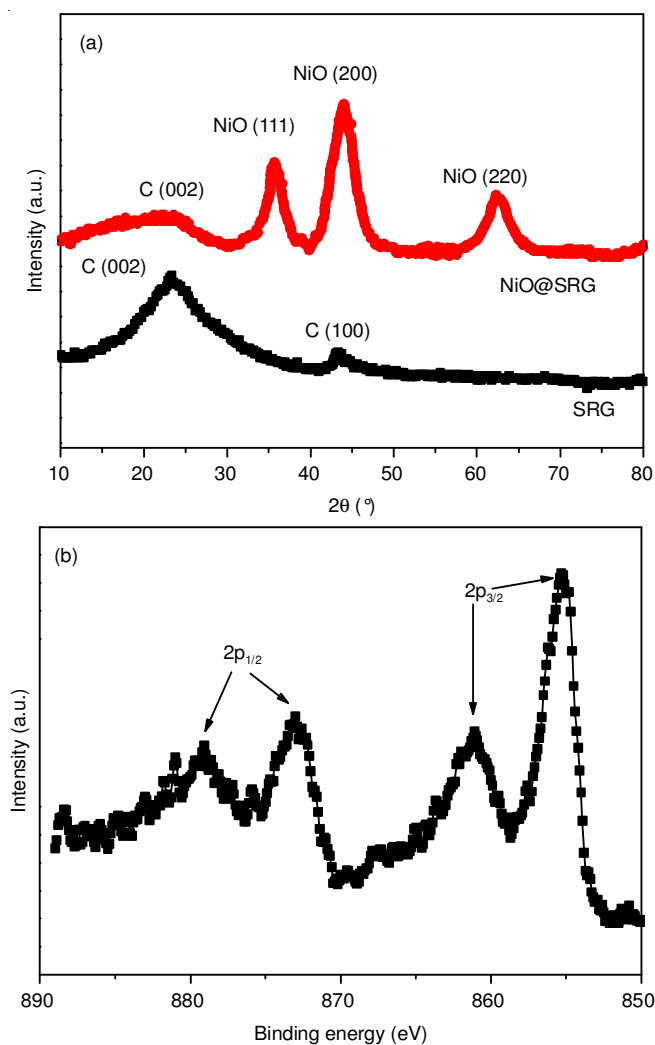


Fig. 2. (a) XRD patterns of as-prepared SRG and NiO@SRG; (b) XPS spectrum of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ of the as-prepared NiO@SRG composites deposited on a glass slide

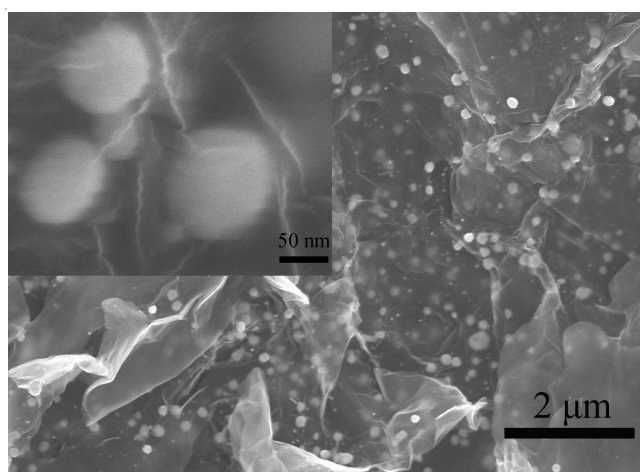


Fig. 3. Typical SEM image of the as-prepared NiO@SRG composites

integration of two-dimensional supports with large surface areas and the highly dispersed nanoparticles can be an exciting material for use in future nanotechnology.

Owing to the unique properties of metallic oxide nanoparticles (MONPs), decoration of metallic oxide nanoparticles

on graphene sheets can be an alternative strategy for the construction of two-dimensional graphene-based hybrids for use as sensor. Their rough surfaces probably endow them with a higher electrochemical active area. Herein, glucose is selected as the model analyte of interests which is motivated by the practical medical needs for diagnosis of human diseases such as diabetes and hyperglycemia. Besides, cyclic voltammograms is used to study the electrocatalytic behaviour of the SRG and NiO@SRG composite. The performances of bare glassy carbon electrode and the two modified electrodes to 1 mM glucose were measured by cyclic voltammograms in 50mM NaOH. As shown in Fig. 4, there is no obvious oxidation peak for glucose for both bare glassy carbon electrode (1) and SRG/GCE (2) in the scanned range. However, the background current was higher at the SRG/GCE than that at the bare glassy carbon electrode, indicating the active surface area of the SRG/GCE increased. The NiO@SRG/GCE exhibits high oxidation peak (curve 3) under the same conditions, suggesting good catalytic activity of the composite to glucose oxidation in alkaline solution. Such excellent electrocatalytic activity of the NiO@SRG nanohybrids may be attributed to high catalytic active sites which provided by the NiO nanoparticles and SRG. The latter plays an important role in the increasing of the efficient electroactive surface area and provides the conductive bridges for accelerating the electron-transfer. Moreover, the typical anodic peak is due to the oxidation of glucose by NiOOH in alkaline medium³⁶.

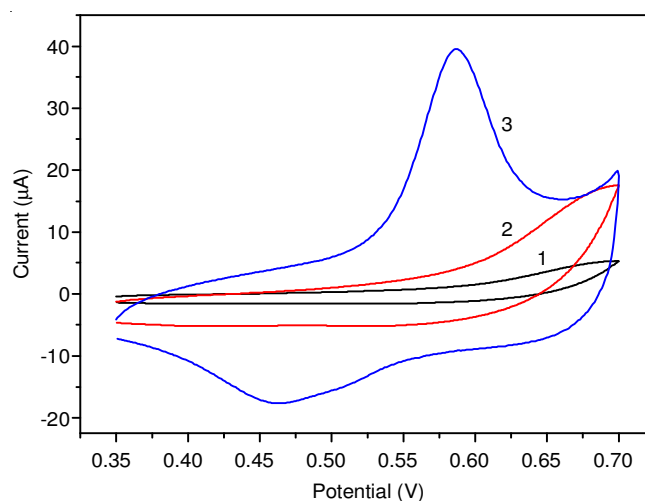


Fig. 4. Cyclic voltammograms of bare glassy carbon electrode (black line), SRG (red line) and NiO @ SRG (blue line) modified glassy carbon electrode in 50 mM NaOH solution containing 1 mM glucose at a scan rate of 50 mV/s

Fig. 5a shows the current response at NiO@SRG modified glassy carbon electrode for a successive addition of glucose at about 100 s in 50 mM NaOH at optimal potential of 0.60 V. It is observed that notable enhancement of amperometric response was obtained and the steady-state current was achieved less than 3s after each addition of glucose solution, which expresses an extraordinarily fast rapid and sensitive response to glucose. Moreover, there is a much larger current response of the NiO@SRG electrode than that of SRG electrode. The results indicate that the as-obtained NiO@SRG nanohybrids exhibit

very sensitive and rapid response property, which is ascribed to the highly electroconductivity and large active surface area of the nanohybrids. The inset in Fig. 5a shows that the correlation between the amperometric responses and glucose concentration range from 0.1 mM to 2 mM at NiO@SRG modified glassy carbon electrode. The current response of NiO@SRG exhibits a good linear ($R^2 = 0.998$) dependence on glucose concentration with a detection limit of 1.15 μM estimated at a signal-to-noise ratio of 3. The sensitivity of the glucose-free sensor is 516 $\mu\text{A}/\text{mM cm}^2$.

To estimate the selectivity of as-prepared composites towards glucose detection, some possible interfering electroactive compounds (such as NaCl, NaH_2PO_4 and sodium citrate) biomolecules (such as ascorbic acid, dopamine and uric acid) which normally coexist with glucose for physiological processes in human metabolism were examined. Considering that the concentration of glucose in the human blood is about 30 times of ascorbic acid, dopamine or uric acid³⁷, the

amperometric responses towards the addition of 0.1 mM glucose and 0.01 mM other interferences were investigated in 50 mM NaOH solution at +0.60 V as shown in Fig. 5b. The results indicate that the current responses towards the interfering species are much weaker than that toward glucose, so they can be neglected. NiO@SRG composites exhibit high selectivity for glucose detection, which makes them as a promising candidate for glucose analysis.

Stability and reproducibility of the NiO@SRG composite-based sensor were investigated respectively. Ten successive measurements of 0.1 mM glucose on the same modified glassy carbon electrode and the relative standard deviation (RSD) was 2.8 %, indicating that the sensor has a good stability. Besides, detection of 0.1 mM glucose using eight electrodes fabricated independently with the same procedure results in a RSD of 3.5 %. The excellent stability and reproducibility suggest that NiO@SRG is a promising electrode material in electrochemical sensing.

Conclusion

We have developed a simple and effective solvothermal approach to the *in situ* decoration of nickel oxide nanoparticles on the surface of graphene nanosheets. Moreover, the as-prepared NiO@SRG modified glassy carbon electrode exhibits excellent electrocatalytic oxidation of glucose in alkaline media. The non-enzymatic glucose sensor exhibits high sensitivity and selectivity, long term stability and reproducibility for glucose detection. It is believed that such a facile and low-cost assembly approach will provide a new avenue for the large-scale production of various functional hybrid materials for electrochemical sensing and other electrocatalytic applications.

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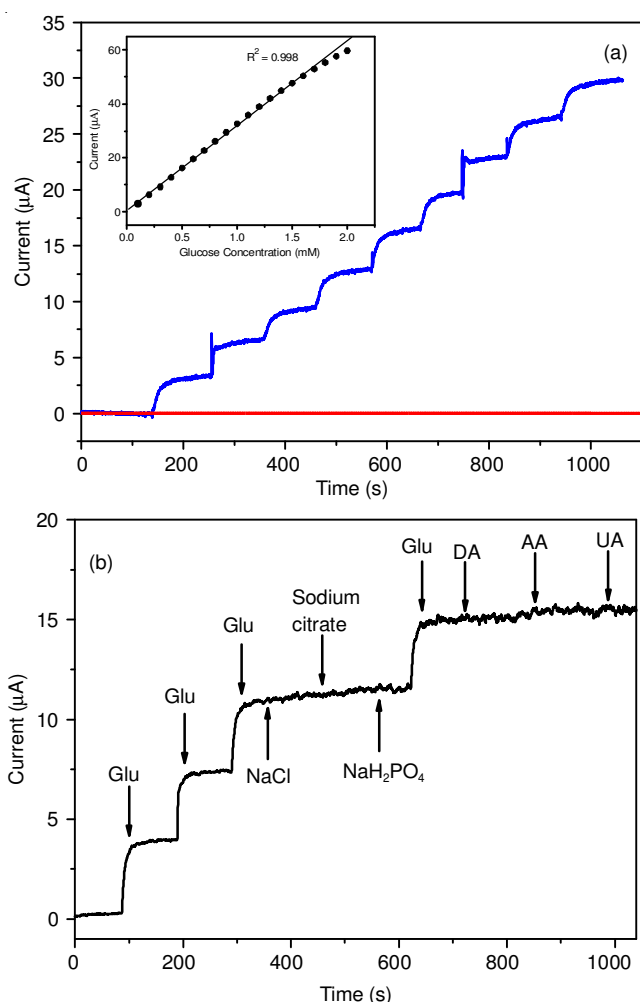


Fig. 5. (a) Current-time responses at 0.60 V with an successive increasing glucose concentration of 0.1 mM per 100 s for the NiO@SRG modified glassy carbon electrode (blue line) and SRG modified glassy carbon electrode (red line). Inset: the dependence of the current response vs. glucose concentration at NiO@SRG modified glassy carbon electrode; (b) interference measurement of the NiO@SRG modified glassy carbon electrode in 50 mM NaOH at +0.60 V, (a) successive additions of 0.1 mM glucose and 0.01 mM other interferences [NaCl , NaH_2PO_4 , sodium citrate, ascorbic acid (AA), dopamine (DA) and uric acid (UA)]

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