



Copper oxide supported on three-dimensional ammonia-doped porous reduced graphene oxide prepared through electrophoretic deposition for non-enzymatic glucose sensing



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ABSTRACT

The paper reports on the preparation of N-doped porous reduced graphene oxide/copper oxide (ammonia-doped-prGO/CuO) nanocomposite on gold electrodes using electrophoretic deposition (EPD) from an ethanolic suspension of ammonia-doped-prGO and $\text{Cu}(\text{ClO}_4)_2$ by applying a DC voltage. The ammonia-doped-prGO/CuO nanocomposite film thickness is controlled by varying the deposition time. Morphological analysis using scanning electron microscopy (SEM) showed the formation of a 3-dimensional structure with CuO nanoparticles being homogeneously embedded in the graphene layer. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman analysis revealed that the deposited copper was in its oxidized form, mainly CuO. The Au/ammonia-doped-prGO/CuO electrode was successfully applied for non-enzymatic amperometric detection of glucose. Under optimized conditions, the electrode exhibited a sensitivity of $1210 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with a detection limit of $0.25 \mu\text{M}$ ($S/N=3$) over a wide concentration range ($0.25 \mu\text{M}$ to 6mM) at an applied potential of $+0.50 \text{V vs. Ag/AgCl}$. The electrode material displayed good stability, excellent selectivity, and accurate measurement in healthy and diabetic human serum samples.

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1. Introduction

Diabetes mellitus is characterized by an elevated glucose level in the blood, which can be caused by either inadequate production of insulin in the body (Type 1 diabetes) or by the inability of the body to use properly its produced insulin (Type 2 diabetes). Thus glucose monitoring is of critical importance for the diagnosis and treatment of diabetes. The conventional methods for measuring blood glucose levels rely on electrochemical or colorimetric readout schemes even though electrochemical sensors are the industry standard for glucose sensing.

Electrochemical glucose sensors can be classified into two categories: enzymatic and non-enzymatic sensors. It is well

acknowledged that these sensors, especially those based on glucose oxidase, have played an important role in blood glucose detection. While enzymatic sensors are accurate, specific and selective, their implementation requires enzyme immobilization on a solid support in a way that the enzyme retains its electrocatalytic activity [1]. Further, the long-term stability of the enzyme and its response dependence on pH and temperature are some of the hurdles to face when operating enzyme-based sensors.

The second class concerns the use of non-enzymatic electrodes as glucose sensors, relying on the direct oxidation of glucose in the sample [2,3]. While these sensors present the advantage to circumvent the limitations associated with the use of fragile enzymes, they mostly do operate only in alkaline media. Although this property might restrict their direct application for *in vivo* glucose sensing, *ex vivo* glucose electro-oxidation may be applied

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to other areas such as the food industry, and the development of fuel cells and batteries [2].

Glucose oxidation at copper oxide electrodes has been demonstrated earlier by Baldwin et al. [4,5], and implementation of non-enzymatic glucose sensors followed just a few years after [2,6]. With the advent of nanotechnology, a plethora of nanostructured materials have been investigated for non-enzymatic glucose sensing. Using nanostructured materials allows increasing the surface area and associated sensitivity. Furthermore, hybridization of metal (metal oxide) nanostructures with a carbon support was found to be an effective way for limiting nanostructures aggregation, which is inherent to their electrocatalytic performance. Furthermore, the presence of a carbon support improves the conduction path for electrons and thus facilitates electron transfer between the analyte and the electrode material.

Graphene, a 2D material, has been exploited in a plethora of scientific disciplines since it was reported to possess a range of unique and exclusive properties. The beneficial implementation of graphene as a sensor substrate has been demonstrated in several reports, encompassing the detection of a large variety of analytes including a diverse range of biomolecules, gases, metal ions, organic molecules . . . [7–10].

Electrophoretic deposition (EPD) technique revealed to be a very promising and appealing approach for thin film deposition and preparation of nanocomposites on electrode materials in a cost-effective way [11]. The method allows controlling the morphology, composition and thickness of the deposited films through adjusting the nature and concentration of the precursors and by tuning the applied potential and deposition time. For instance, the use of positively charged colloidal solutions offers the advantage of performing cathodic EPD, which in case of graphene oxide-metal salt solutions allows to achieve simultaneously graphene oxide reduction and deposition of metal/metal oxide nanoparticles. We have recently adopted cathodic EPD for the preparation of reduced graphene oxide rGO/Ni(OH)₂ [12,13], rGO/Cu [14], and carbon nanofibers/Co(OH)₂ [15] nanocomposite materials in one-step. The deposited composite films exhibited electrocatalytic activity for glucose oxidation and allowed its sensing in complex media with good sensitivity and selectivity.

It is well-established that the enhanced electrochemical activity of reduced graphene oxide is directly connected to the high density of edge defects [16]. Furthermore, it has been recently demonstrated that graphene doping with heteroatoms such as ammonia, boron, sulfur, phosphorus . . . endows the material with improved electrochemical properties [17]. With the aim to enhance the electrocatalytic activity of CuO-rGO nanocomposites towards glucose oxidation, we propose in the present study to combine high surface area, ammonia-doping and EPD for the construction of a glucose sensor. This has been achieved in a stepwise process through the synthesis of porous reduced graphene oxide (prGO) from rGO and its subsequent ammonia doping to give N-prGO. CuO/N-prGO modified Au electrode was prepared in one-step through cathodic EPD technique. The electrocatalytic activity of the resulting electrode was evaluated for glucose oxidation in alkaline media. The electrode exhibited good sensitivity and selectivity with a detection limit of 0.25 μM. The sensor was successfully applied for accurate glucose detection in healthy human serum samples and diabetic patients.

2. Experimental

2.1. Materials

Copper perchlorate (Cu(ClO₄)₂), potassium permanganate (KMnO₄), hydrazine monohydrate (N₂H₄·H₂O), liquid ammonia, hydrogen peroxide (H₂O₂), sulphuric acid (H₂SO₄), phosphoric acid

(H₃PO₄), sodium hydroxide (NaOH), glucose, uric acid (UA), ascorbic acid (AA), dopamine hydrochloride (DA), cysteine (Cys), fructose, lactose, galactose, phenol, and ethanol were purchased from Sigma-Aldrich.

Graphene oxide (GO) powder was purchased from Graphenea, Spain.

Human serum samples were kindly provided by the Centre Hospitalier Universitaire (CHU) Lille.

2.2. Preparation of ammonia-doped porous reduced graphene oxide (N-prGO)

Reduced graphene oxide (rGO) was prepared from GO precursor using hydrazine reduction. Briefly, to 5 mL GO aqueous suspension (0.5 mg/mL) was added hydrazine hydrate (0.50 mL, 32.1 mM) and heated in an oil bath at 100 °C for 24 h over which the reduced GO gradually precipitated out the solution. The product was isolated by filtration over a PVDF membrane with a 0.45 μm pore size, washed copiously with water (5 × 20 mL) and methanol (5 × 20 mL) and dried in an oven at 100 °C overnight.

The synthesis of prGO was achieved using a previous method reported by us [18]. rGO powder (100 mg) was dispersed in 30% H₂O₂ (100 mL), ultrasonicated for 30 min and the mixture was refluxed for 12 h at 60 °C. The obtained solution was filtered and the recovered prGO powder was dialyzed to remove H₂O₂ and to separate from small sized graphene quantum dots.

The synthesis of ammonia-doped-prGO was carried out by mixing prGO powder and liquid ammonia (1:30 w/v) by ultrasonication before being transferred into a 50 mL Teflon[®] coated stainless steel autoclave and heated for 24 h at 200 °C. The acquired solution was separated by filtration followed by washing with ethanol/water (1:1) mixture solution to completely remove the ammonia. The product was kept for drying in an oven at 60 °C overnight [18].

2.3. Coating of gold electrodes with ammonia-doped-prGO by electrophoretic deposition (EPD)

The gold electrode was prepared by vacuum deposition of 5 nm of titanium and 50 nm of gold onto cleaned glass slides. The anodic electrophoretic deposition (EPD) was carried out by using a two-electrode cell containing an aqueous suspension of ammonia-doped-prGO (0.5 mg/mL) by applying a DC voltage of 30 V for 30 s. The cathode was a platinum foil (1 × 2 cm²), while the gold electrode was used as anode. The two electrodes are separated by 1 cm and are placed parallel to each other. After deposition, the interface was washed with deionized water (three times), followed by blow drying with nitrogen.

2.4. Preparation of Cu oxide nanoparticles loaded ammonia-doped-prGO modified gold electrodes by EPD

A suspension of ammonia-doped-prGO (0.5 mg/mL) and Cu (ClO₄)₂ (1 mg/mL) in ethanol was ultrasonicated for 30 min and used for cathodic EPD by applying a DC voltage of 30 V for 30 s. After deposition, the interfaces were rinsed with deionized water (three times) followed by blow drying with nitrogen gas. The ammonia-doped-prGO/CuO NPs modified gold electrode was activated by cycling 15 times between 0.2 to 1.0 V in NaOH (0.1 M) at a scan rate of 50 mV s⁻¹.

2.5. Determination of glucose content in human serum using a colorimetric method

A standard calibration curve for glucose was obtained by mixing a freshly prepared phenolic solution (1 mL; 5 wt%) with 1 mL

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