Analytical Biochemistry 488 (2015) 22–27

Contents lists available at ScienceDirect

Analytical Biochemistry

journal homepage: www.elsevier.com/locate/yabio

Highly sensitive and selective uric acid biosensor based on a three-dimensional graphene foam/indium tin oxide glass electrode

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ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form
9 July 2015
Accepted 10 July 2015
Available online 6 August 2015

Keywords:
Chemical vapor deposition
Nickel foam
Graphene foam
Uric acid
Ascorbic acid
Biosensor

ABSTRACT

A three-dimensional (3D) continuous and interconnected network graphene foam (GF) was synthesized by chemical vapor deposition using nickel foam as a template. The morphologies of the GF were observed by scanning electron microscopy. X-ray diffraction and Raman spectroscopy were used to investigate the structure of GF. The graphene with few layers and defect free was closely coated on the backbone of the 3D nickel foam. After etching nickel, the GF was transferred onto indium tin oxide (ITO) glass, which acted as an electrode to detect uric acid using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The GF/ITO electrode showed a high sensitivity for the detection of uric acid: approximately 9.44 mA mM^{-1} in the range of 25 nM–0.1 μM and 1.85 mA mM^{-1} in the range of 0.1–60 μM. The limit of detection of GF/ITO electrode for uric acid is 3 nM. The GF/ITO electrode also showed a high selectivity for the detection of uric acid in the presence of ascorbic acid. This electrode will have a wide range of potential application prospects in electrochemical detection.

Uric acid (UA) is a very important biological molecule in higher primates and humans (blood: 0.1–0.5 mM; urine: 2 mM). It is a weak organic acid that exists mainly as a monosodium salt under physiological conditions. Usually, UA can be irreversibly oxidized in aqueous solution and allantoin is the major product [1,2]. Extreme abnormalities of UA levels are symptoms of many diseases, including pneumonia, gout, and fatal hyperuricemic nephropathy [3]. Ascorbic acid (AA) is an antioxidant that exists in many vegetables, fruits, and biological fluids (blood: 0.1 mM; urine: 0.6 mM). AA in the body fluids is related to several diseases such as cancer, diabetes mellitus, and hepatic disorders.

Electrochemical methods have been proved to be a very promising way in which to detect UA and AA by virtue of the electroactive nature of biomolecules. In general, UA and AA coexist in biological fluids such as blood and urine. However, UA and AA are oxidized at potentials that are very close to each other and result in overlapped voltammetric responses at conventional solid electrodes [4]. A futuristic requirement for prognosis and diagnosis of disease is just to have a drop of blood instead of a cylinder of blood that is required in the current routine health test and further to provide an immediate report and diagnosis to patients. Therefore, it is important to develop a simple, reliable, and effective electrode to selectively and sensitively detect UA in the presence of AA in routine analysis [5–7].

Graphene is a one-atom-thick planar sheet of sp^2-boned carbon atoms that are densely packed in a honeycomb crystal lattice [8]. It shows remarkable electrocatalytic and sensing properties due to its high intrinsic carrier mobility and large surface area [9]. Since it was discovered in 2004 [10,11], it has been extensively investigated in biosensors.

Graphene can be achieved by several techniques such as micromechanical exfoliation of graphite [12], chemical oxidation of graphite followed by exfoliation and oxygen elimination [13], and chemical vapor deposition (CVD) onto transition metal substrates (typically Ni and Cu) [14,15]. Among all of the methods, chemically derived graphene has been widely adopted because of low-cost and large-scale production of grapheme. However, this integrated graphene shows poor electrical conductivity and high contact

Abbreviations used: UA, uric acid; AA, ascorbic acid; CVD, chemical vapor deposition; GF, graphene foam; 3D, three-dimensional; ITO, indium tin oxide; PBS, phosphate-buffered saline; XRD, X-ray diffraction; CV, cyclic voltammetry; DPV, differential pulse voltammetry; SEM, scanning electron microscopy; RSD, relative standard deviation.

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http://dx.doi.org/10.1016/j.ab.2015.07.007
0003-2697/

resistance owing to serious structural defects in graphene sheets introduced during the exfoliation and reduction process. CVD is a promising and readily accessible approach to prepare high-quality and defect-free graphene with outstanding electrical conductivity. A few-layer continuous graphene film grown onto a nickel film deposited on an oxidized silicon wafer via CVD was used to detect various biological molecules [16]. However, it is limited for the improvement of biomolecule detection by the effective surface area due to the planar electrode.

In this work, a graphene foam (GF) with a three-dimensional (3D) continuous and interconnected network was prepared on nickel foam by CVD. When the nickel was etched, the 3D GF was transferred onto indium tin oxide (ITO) glass, acting as the working electrode to detect UA and AA. The 3D GF/ITO electrode demonstrates a high sensitivity for the detection of UA and selective determination of UA in the presence of AA.

Materials and methods

Chemicals and reagents

Nickel foam was supplied by Alantum Advanced Technology Materials (China). ITO glass (specific resistance of <10 Ω, Zhuhai Kaivo Electronic, China) was used for the fabrication of electrodes. UA, AA, phosphate-buffered saline (PBS), and poly(methyl methacrylate) were purchased from Sigma–Aldrich. Ethyl lactate was purchased from Tokyo Chemical Industry. Deionized water was obtained by purification through a Water Purifier (Sichuan Wortel Water Treatment Equipment, China). HCl (37%) and acetone were obtained from Beijing Chemical (China).

Synthesis of 3D GF and electrode

Nickel foam was used as the 3D template for the growth of GF. The growth of a few layers of graphene on the nickel foam by CVD has been reported elsewhere [17,18]. In brief, the nickel foam was reduced with H_2 flow (200 sccm) at 1010 °C for half an hour before the CVD growth (gas ratio of $CH_4/H_2 = 20{:}200$). After etching nickel, the obtained GF (1×1 cm) was transferred onto ITO glass, acting as the electrode, to detect UA and AA.

Characterizations of 3D GF

The morphologies of 3D GF were observed on a field-emission scanning electron microscope (JSM7000F, Jeol) with an accelerating voltage of 20 kV. The structure of GF was investigated by X-ray diffraction (XRD) (Rigaku Rotaflex D/Max system) with Cu Kα radiation ($\lambda = 0.15406$ nm). Raman spectrum was recorded using a micro-Raman system (Renishaw In-Via RM-1000) with an excitation wavelength of 514 nm at room temperature.

Electrochemical measurements

Electrochemical measurements were performed in a 0.1-M PBS solution (pH 7.4) in a three-electrode cell using a VMP3 electrochemical workstation (Bio-Logic Science Instruments, France). An Ag/AgCl electrode and a platinum wire acted as the reference electrode and counter electrode, respectively, whereas the 3D GF/ITO electrode served as the working electrode. The area of the GF/ITO electrode is 0.7 cm^2. Cyclic voltammetry (CV) experiments were carried out at a scan rate of 50 mV s^{-1}. Differential pulse voltammetry (DPV) responses were recorded over a potential range of −0.2–0.6 V with the parameters as reported previously [18].

Results and discussion

Preparation and characterizations of 3D GF

Fig. 1 shows a schematic of the 3D GF/ITO electrode preparation procedures and redox reactions of UA and AA at GF/ITO electrode. The 3D macroporous and interconnected nickel foam is used as the template to prepare GF by CVD. After removal of nickel, GF retains the morphology of nickel foam. The prepared GF is transferred onto the surface of ITO glass, acting as the electrode, to detect UA and AA.

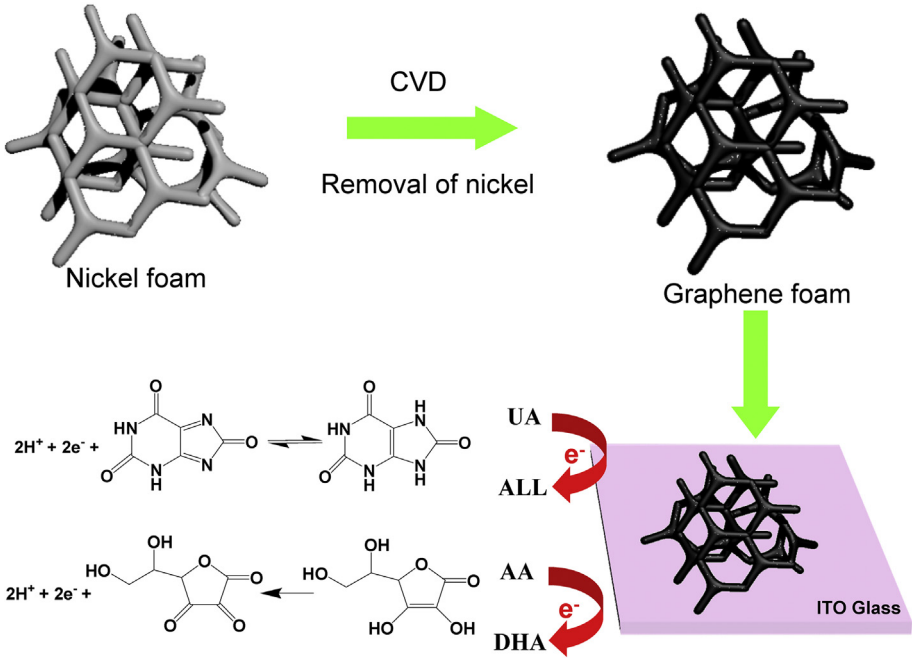

Fig.1. Schematic of preparation procedures of 3D GF/ITO electrode and redox reactions of UA and AA at GF/ITO electrode. ALL, allantoin; DHA, Docosahexaenoic acid.