Journal of Electroanalytical Chemistry 738 (2015) 113–122

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Fabrication of modified glassy carbon electrode using graphene quantum dot, gold nanoparticles and 4-(((4-mercaptophenyl)imino)methyl) benzene-1,2-diol by self-assembly method and investigation of their electrocatalytic activities

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ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 1 November 2014
Accepted 11 November 2014
Available online 22 November 2014

Keywords:
Graphene quantum dots
Gold nanoparticles
Modified electrode
Glutathione
Uric acid
Tryptophan

ABSTRACT

Results of this paper related to fabrication of a simple, reproducible, stable and sensitive glassy carbon electrode (GCE) modified by assembly of graphene quantum dot (GQDs), gold nanoparticles (AuNPs) and 4-(((4-mercaptophenyl)imino)methyl)benzene-1,2-diol (MIB). The GQDs were electrostatically assembled on GCE and electrochemically reduced in 0.1 M phosphate buffer solution (pH = 7.0) with the cyclic voltammetry method at the scan rate of 50 mV s^{-1} for 15 cycles in order to reduce the oxygen functional groups. These results lead to the formation of electrochemically reduced graphene quantum dots film on GCE (ERGQD/GCE). In the next step, electrodeposition of gold nanoparticles was successfully performed at constant potential of −0.2 V (vs. SCE) for 40 s on ERGQDs/GCE. The constructed Au/ERGQDs/GCE was characterized with scanning electron microscopy (SEM) and electrochemical techniques. Furthermore, to improve electrocatalytic activity and charge injection, a self-assembled monolayer of functionalized molecules was grafted on the electrode surface by immersion of Au/ERGQD/GCE in aqueous solution (1.0 mM) of MIB. Finally, the electrocatalytic activity of MIB/Au/ERGQD/GCE was investigated by the simultaneous determination of glutathione (GSH), uric acid (UA) and tryptophan (Trp) using differential pulse voltammetry (DPV). This modified electrode enhanced the oxidation currents of GSH, UA, and Trp compared to bare GCE. Under the optimum conditions, the calibration curve of GSH was linear in the range of 0.03–40.0 μM and 40.0–1300.0 μM and the detection limit of 9 nM was obtained. According to the results obtained in this study, the electrocatalytic activity of the present modified electrode was highly reproducible and stable.

1. Introduction

The self-assembly is one of the most accepted methods for the fabrication of nanomaterials on conducting substrates. Molecular self-assembly on solid surfaces is provided by the precise interaction between molecule–molecule and molecule–substrate interplays that can be tuned by varying molecular building blocks, surface chemistry and structure as well as substrate temperature [1]. An example of self-assembly phenomena is formation of monolayers of organic molecules on surfaces. This monolayers, self-assembled on the surface of a metal or a semiconductor electrode can improve the electrochemical potential of the injected carriers [2,3].

Graphene, a novel class of carbon-based nanomaterial, consist of a single layer of carbon atoms attached together by sp^2 covalent bonds [4,5]. It is demonstrated as an individual of graphite which is produced of many graphite layers held together by vander Waals force of attraction [4,6]. However, electronic and opto-electronic application of graphene is limited because the graphene is a zero-bandgap semiconductor. Graphene sheets, which are smaller than 100 nm, are called graphene quantum dots (GQDs). The quantum confinement and edge effects of GQDs lead to various electronic, optoelectronic properties, large surface area and high conducting nature. According to these properties, GQDs selected as excellent candidate for manufacturing of electrochemical sensors [7–9]. It also can be applied as an appropriate material for the construction of electrode surface to improve the electrocatalysis. There are some reports on electrochemical sensors constructed with GQDs [10,11], nevertheless only few reports were available in the literature for the fabrication of graphene quantum dots on substrates using the self-assembly method [12].

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http://dx.doi.org/10.1016/j.jelechem.2014.11.021
1572-6657/

Electrochemical reduction of graphene oxide (GO) has attracted great attention in recent years, since it is considered as a green approach. Furthermore, a thin film of reduced graphene can be formed easily on the surface of conducting substrates by this method [13–15].

Electroanalytical chemists attracted to the gold nanoparticles (AuNPs) because of their good biological compatibility, excellent conducting capability, high surface-to-volume ratio, unique structural, magnetic, optical and catalytic properties. Recently many research articles using AuNPs for various electrochemical applications such as bioassays, biosensor, chemical sensor and electrocatalysis have been published [16–18].

Glutathione (GSH) and glutathione disulfide has physiological importance due to their implications in a series of medical conditions including diabetes, Parkinson's disease and cancer. It is known that glutathione plays antioxidant role in the human body [19]. Moreover its ability to scavenge physiological free radicals is particular importance considering the nitric oxide release associated with inflammatory disorders [20,21]. Consequently, tolerance of physiological glutathione concentrations have been correlated with patients suffering from Alzheimer's disease [22], Parkinson's disease [23,24], diabetes mellitus [25], atherosclerosis [26], arthritis [27], epilepsy [28], aging [29], as well as numerous types of cancer [30]. Therefore, it is necessary for simple, rapid and cheap assays to aid clinical diagnostics. Various techniques have been used for quantitative GSH determination including high-performance liquid chromatography [31], spectrofluorimetry [32], spectrophotometry [33], chemiluminescence [34] and capillary electrophoresis combined with electrochemical detection [34]. All of these techniques require time-consuming sample preparation, costly equipment and trained person to operate. But electrochemical techniques exhibit advantages such as simplicity, rapidity, high sensitivity and low cost for the analysis of biological compounds including GSH [35,36].

Uric acid (UA) is a product of the metabolic breakdown of purine nucleotides. Physiological concentration of UA for a normal healthy person is within a certain range, and abnormal changes in its concentration level are symptoms of some diseases like gout, hyperuricemia, Lesch–Nyhan syndrome, leukemia, and pneumonia [37]. Among different methods used for the determination of UA, electrochemical methods are more facile, less expensive and less time-consuming than the other methods [38].

Tryptophan (Trp) an essential amino acid in humans and herbivores is a precursor to the neurotransmitter serotonin. The availability of serotonin in the brain depends on blood Trp levels, which can regulate the psychoneural control of spontaneous changes through presynaptic inhibition of hippocampal cholinergic terminals. Thus, being simple, sensitive and inexpensive detection of Trp has great importance. Accordingly various methods have been devised and applied for the determination of Trp [39–41], which the electrochemical detection has been of considerable interest in the case of electroactive compounds [42–44].

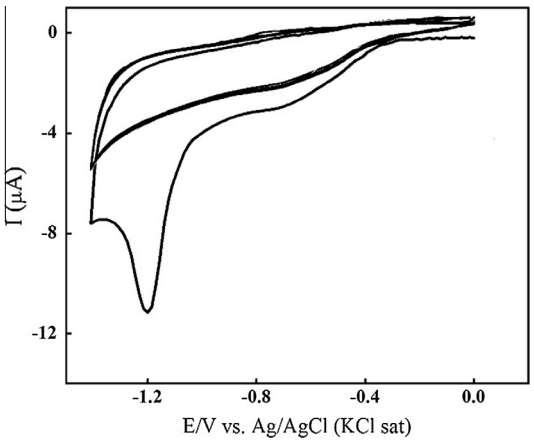

Fig. 1. Electrochemical reduction of assembled GQDs on GC electrode (15 cycles) in 0.1 M PBS (pH = 7.0) at a scan rate of 50 mV s^{-1}.

To the best of our knowledge, there have been no report on the fabrication of self-assembled monolayer (SAMs) by GQDs, AuNPs and 4-(((4-mercaptophenyl)imino)methyl) benzene-1,2-diol (MIB) for simultaneous detection of GSH, UA and Trp. In the present study, we described a simple and facile method for the fabrication of the GCE modified with GQDs, AuNPs and MIB as a novel electrode. Initially, a simple method for the first time is presented for making of electrochemically reduced graphene quantum dot (ERGQDs) films by the reduction of the assembled GQDs on GCE. Then AuNPs was successfully electrodeposited and finally a monolayer of MIB self-assembled on the electrode. The GQDs/GCE, ERGQDs/GCE, Au/ERGQDs/GCE and MIB/Au/ERGQDs/GCE modified electrodes were characterized by scanning electron microscopy (SEM) and electrochemical techniques. The electrocatalytic activity of the MIB/Au/ERGQDs/GCE electrode was examined by electrocatalysis and determination of GSH. Afterwards, we evaluated the analytical performance of the MIB/Au/ERGQDs/GCE electrode with simultaneous determination of GSH, UA and Trp in synthetic solutions and diluted blood serum samples.

2. Experimental details

2.1. Materials

Graphite powder, potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), $HAuCl_4{\cdot}3H_2O$ (pro analysis grade), glutathione (GSH), uric acid (UA), tryptophan (Trp) and other reagents were purchased from Merck Company (Darmstadt, Germany). Phosphate buffer solution (PBS) 0.1 M was prepared in the pH range of 2.0–11.0. Double distilled water was used for preparing all solutions.

2.2. Instrumentation

The electrochemical measurements and AC electrical impedance spectra were carried out with potentiostat/galvanostat Eviumstat. A three-electrode cell were used with GCE as a working electrode, platinum wire as a counter electrode, and KCl-saturated Ag/AgCl as a reference electrode. TEM measurement was performed on Philips EM 208S at operating voltage of 100 kV. Scanning electron microscope (SEM) measurements were carried out with VEGA 3 SEM. Fourier transform infrared (FT-IR) spectra were measured by a BRUKER EQUINOX 55 single beam spectrometer. UV–visible absorption spectra were recorded at room temperature on a double beam UV/vis spectrophotometer (OPTIZEN 3220UV).

2.3. Synthesis of graphene quantum dots

The hydrothermal method was applied for synthesis of GQDs [45]. Graphene oxide (GO) was synthesized using the Hummer's method with a slight modification [46]. Micrometer-sized graphene sheets (GSs) were gained by thermal deoxidization of graphene oxide sheets in a tube furnace at 300 °C for 2 h with a heating rate of 5 °C min^{-1} in nitrogen atmosphere. Then 0.05 g of these obtained graphene sheets were oxidized in a mixed solution of concentrated H_2SO_4 (10 mL) and HNO_3 (30 mL) for 20 h under mild ultrasonication (300 W, 37 kHz). The oxidized graphene sheets were diluted and refined with microporous membrane. Then,