Materials Science and Engineering C 46 (2015) 325–332

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Electrodeposition of quercetin on the electrospun zinc oxide nanofibers and its application as a sensing platform for uric acid

Majid Arvand *, Sepideh Tajyani, Navid Ghodsi

Electroanalytical Chemistry Laboratory, Faculty of Science, University of Guilan, Namjoo Street, P.O. Box: 1914, Rasht, Iran

ARTICLE INFO

Article history:
Received 11 April 2014
Received in revised form 12 August 2014
Accepted 21 October 2014
Available online 24 October 2014

Keywords:
Electrospinning
Electrodeposition
ZnO nanofiber
Uric acid
Quercetin

ABSTRACT

In a current study, a distinctive voltammetric method was developed for the determination of uric acid (UA) at a carbon paste electrode (CPE) modified with zinc oxide nanofibers (ZNFs) and quercetin (Q). ZNFs were fabricated via the electrospinning process. The electrode was prepared by electrodeposition of quercetin on a zinc oxide nanofiber carbon paste electrode (Q/ZNFs/CPE). The Q/ZNFs/CPE offered substantially lower overpotential for electro-oxidation of UA in acetate buffer solution (ABS) (pH 4.45) compared with Q/CPE, ZNFs/CPE and bare CPE. Furthermore, the effects of pH, scan rate, accumulation time and potential, interference effect and effect of quercetin electrodeposition on the surface of ZNFs/CPE were studied in detail. The studies suggested that the electrode reaction process was totally irreversible and adsorption controlled. Differential pulse voltammogram peak current of UA increased linearly with its concentration within two dynamic ranges and detection limit for UA was 0.05 μmol L^{-1} with RSD = 0.2%. The prepared electrode was applied for determination of UA levels in serum and plasma of a healthy person and the patient with leukemia. The results indicated that the proposed method was sensitive, selective, fast and simple for determination of UA.

1. Introduction

During the past decades, zinc oxide (ZnO) has had enormous commercial use, with thousands of tons produced each year. ZnO, an important semiconductor material with high binding energy (60 meV) and wide band gap (3.37 eV), recently has attracted considerable attentions in optoelectronic materials, nanosensors, ultraviolet lasers and field emission devices [1–3], which make ZnO a highly promising material in fabrication of sensors. In addition, it is inexpensive, nontoxic and chemically stable at room temperature [4]. One dimensional ZnO nanostructure with an effective morphology has an influence potentially in efficient construction and performance of nanoscale devices due to the quantum restriction of charge carriers in small extent [4]. Many researchers have focused on one-dimensional nanostructures such as nanowires [5], nanorods [6], nanoparticles [7,8], nanotubes [9] and nanofibers [10] which all have high surface to volume ratio. Among the one-dimensional nanostructures, nanofibers are particularly stimulating because of their long axial ratio, which has a profound impact on their physical and chemical characteristics. Different methods have been reported for synthesis of ZnO nanofibers such as chemical vapor deposition [5], template-based growth [6] and electrospinning [11]. Among these methods, electrospinning is a versatile, successful, simple and inexpensive method to make one dimensional nanofibers with high specific surface area and uniform diameters which make electrospinning highly competitive for fabrication of nanofibers [12].

Electrostatic fiber formation or electrospinning is a method that combines two techniques of electrospray and spinning. The conventional spinning processes including wet-, dry- and wet/dry-spinning techniques are capable of producing fibers with diameter in the micrometer range [13]. The electrospinning could be regarded for synthesis of micro- and nanosized fibrous materials with high length-to-diameter ratio and porosity, high specific surface area and controllable mean grain size [14].

Uric acid (UA, 2,6,8-tridroxypurine) is an important biomedical compound and plays essential roles in human metabolism as well as the central nervous and renal systems [15]. In humans, higher primates and in a particular species of dog (Dalmatians), UA is the final oxidation product of purine catabolism [16]. UA is presented in human blood serum, plasma, urine and saliva [17]. Serum UA is a risk factor for the oxidative stress, coronary heart disease and closely linked to vascular nitric oxide activity [18]. Elevated serum UA is associated with a risk of peripheral arterial disease, chronic kidney disease and silent brain infarction [19]. Increased consumption of serum UA can act as a scavenger of radicals and thus prevents from Parkinson's disease (PD). Reduced level of plasma UA leads to Schizophrenia and blood UA levels contributed with sleep-disordered breathing. However, low UA levels in plasma and urine associate with worse cognitive performance in PD [20,21]. UA is a pathogenic factor in pre-eclampsia for pregnant women. It plays a role in insulin resistance in older and pregnant women [22]. Other diseases, such as gout, leukemia and pneumonia are also

* Corresponding author.
E-mail address: arvand@guilan.ac.ir (M. Arvand).

http://dx.doi.org/10.1016/j.msec.2014.10.060
0928-4931/

associated with enhanced UA levels. An overproduction of uric acid can occur when there is an excessive cell breakdown and catabolism of nucleonic acids such as seen in gout and also excessive production and destruction of cells, as may occur in leukemia or during cancer therapy. Thus, monitoring of UA levels plays an important role in medicine and thus is routinely determined in the clinical laboratory. Several methods have been described for determination of UA in literatures including chemiluminescence [23], capillary electrophoresis [24], enzymatic–spectrophotometric [25], high-performance liquid chromatography [26] and electrochemical technique [27,28]. Most of these methods are complicated because they need derivatization or combination with various detection methods, but electrochemical approaches are simple, less tedious and inexpensive [29–35].

Quercetin (3,3′,4′,5,7-pentahydroxyflavone) is a kind of flavonoid, naturally presented in the plant kingdom and usual human diet. Quercetin is widely distributed in fruits and vegetables [36]. It is reported that quercetin has antiviral, anti-cancer, anti-inflammatory, anti-allergic and anti-tumor properties and can protect human colonocyte DNA from oxidative attack in vitro [37]. Quercetin like other flavonoids has high propensity for electron transfers and is a free radical scavenger [36]. Cyclic voltammetry studies usually show well-defined reversible redox peaks for quercetin (vs. Ag/AgCl/KCl sat). There are some reports on the electrochemical behavior of quercetin whereas just a few reports are available on electrodes modified with quercetin in literatures [37–40].

In this paper, we described surface modification of ZNFs/CPE by electrochemical deposition of quercetin, and the prepared electrode was utilized for electrochemical determination of UA. The selectivity and sensitivity of the modified electrode were investigated. Furthermore the effects of pH, scan rate, accumulation time and potential, interference effect and effect of quercetin electrodeposition on the surface of ZNFs/CPE were studied in detail [41–43]. After optimization of experimental condition, this modified electrode was used for quantification of UA levels in serum and plasma of a healthy person and a patient suffering from leukemia [44–46]. Up to now, no other works in the literatures have been reported on the preparation of a modified electrode by electrochemical deposition of quercetin on ZNFs/CPE.

2. Experimental

2.1. Chemicals and reagents

Polyvinyl alcohol (PVA, MW = 72,000–75,000 g mol^{-1}) and UA were purchased from Fluka Chemical Company (Buchs, Switzerland). Triton-X 100, zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), ethanol, quercetin ($C_{15}H_{10}O_7$) and graphite powder were purchased from Merck (Darmstadt, Germany). All the solvents and reagents were of analytical grade and used without further purification. Acetate buffer solution (ABS, pH 4.45) was prepared by mixing a solution of 0.1 mol L^{-1} sodium acetate and 0.1 mol L^{-1} acetic acid. Aqueous solutions of UA were freshly prepared as required. The stock solution of quercetin was freshly prepared with ethanol and distilled water. All other solutions were prepared with distilled water.

2.2. Apparatus

Electrochemical measurements were carried out using a PalmSens electrochemical analyzer connected to a personal computer. A regular three-electrode system including a modified electrode as working electrode, a saturated Ag/AgCl electrode as reference electrode and platinum rod as counter electrode was used to obtain the electrochemical data. All the pH solutions were measured via the Metrohm pH meter (Model 827, Swiss made). The ZnO nanofibers were prepared with a homemade electrospinning device. A model CM10 transmission electron microscope (TEM; Philips) and a scanning electron microscope (SEM; Electroanalyzer Sama 500) were used to characterize the morphology of the carbon paste and the ZnO nanofibers.

2.3. Preparation of ZnO nanofibers

ZnO nanofibers were fabricated via the electrospinning process, followed by thermal treatment. In a typical method [47] 0.02 g Triton-X 100 and 20 g PVA solution (PVA 15 wt.%) were mixed, then 0.9 g zinc acetate was added to the solution. The mixture was stirred for 10 h at 25 °C and sonicated for 20 min till a homogeneous gel was obtained. The gel was then loaded into a plastic syringe and conjoined to a high voltage power supply. The optimum distance between the needle and the collector plate was 11 cm and it was kept fixed throughout the electrospinning process. A 15 kV electrical potential is exerted between the syringe and the collector. Then the calcination process occurred at 510 °C in air for 3 h to remove all the organic parts of PVA that converted the precursor into nanofiber. Pure nanofibers were also fabricated by the same exact process.

2.4. Preparation of modified electrode

The carbon paste modified with ZnO nanofibers was prepared by mixing the different amounts of graphite powder and ZnO nanofibers with appropriate amount of paraffin oil. Then the paste was packed into a plastic Ertalon and a copper rod was embedded into the paste to provide electrical connection. This electrode was named as ZNFs/CPE. The carbon pate electrode was prepared in a similar way and was named as CPE.

2.5. Electrodeposition of quercetin

The prepared electrode was placed in a 1.1×10^{-4} mol L^{-1} solution of quercetin in 0.1 mol L^{-1} phosphate buffer solution (PBS, pH 7), and it was electrodeposited by ten voltammetric cycles of potential range between −0.2 and 1.0 V at 100 mV s^{-1}. In this procedure, a deposited layer of quercetin was deposited onto the surface of modified electrode (Q/ZNFs/CPE). Afterward, the modified electrode was washed with distilled water to remove weak physically adsorbed molecules.

2.6. Human blood plasma sample preparation

Plasma sample was taken from a 17 year old patient suffering from leukemia and a healthy person with the same age and the same gender. The blood was separated out by centrifugation at 10,000 rpm for 6 min at room temperature. The yellowish part of the blood was separated and 100 μL of obtained plasma was diluted with 100 mL of ABS (pH 4.45).

3. Results and discussion

3.1. Structural characterization of ZnO nanofibers

The morphology of electrospun nanofibers was well controlled under the optimized electrospinning conditions and the uniform ZnO nanofibers were successfully prepared with large surface areas. The morphology of ZNFs was determined by SEM and TEM. The crystal structure and phase composition of the prepared ZNFs were also confirmed by XRD. The elemental composition of ZnO nanofibers was confirmed by EDS measurement. Fig. 1(A) shows high-magnification SEM micrograph of PVA/$Zn(CH_3COO)_2$ fibers (before calcination). It shows that the electrospun nanofibers are randomly and evenly distributed. The nanofibers are free of beads. To find out the surface morphology and modifying effect of ZNFs on the CPE, SEM images before and after adding optimum amount of ZNFs to CPE were recorded. Fig. 1(B) shows the surface of carbon paste with optimum amount of ZNFs and Fig. 1(C) shows the unmodified carbon paste surface. The results illustrate that by the presence of ZNFs, the surface area and