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Electrosynthesis of high-density polythiophene nanotube arrays and their application for sensing of riboflavin

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ABSTRACT

High-density arrays of polythiophene nanotubes were successfully prepared through electrochemical polymerization of the monomer in the pores of porous anodic alumina (PAA) template. The resultant polymeric tubular structures were identified by the field-emission scanning electron microscopy with a diameter of the order of ca 100 nm and a length of up to several micrometers. Different characterizations, including SEM, TEM and EDS, were employed to prove that conducting polythiophene nanotubes were synthesized successfully by this facile method. The synthesized polythiophene nanotubes were employed for proposing a new electrochemical sensor for Riboflavin (RF). Under optimal conditions, the suggested sensor could be used for determination of RF ranging from 0.01 to 65 μM with a low detection limit of 3 nM. The prepared sensor possessed accurate and rapid response to RF and good sensitivity, stability and repeatability. Furthermore it showed an average recovery of 97% in human plasma.

1. Introduction

π-conjugated conductive polymers, also known as "synthetic metals", have attracted considerable attention in both fundamental and applied studies, and through the last few decades a tremendous amount of research has been carried out in the field of conductive polymers [1,2]. So, the Nobel Prize in Chemistry has been awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa in 2000 for the discovery and development of conductive polymers [3].

Due to their special electrical, chemical and optical properties, light weight, redox activity and their processability, a variety of conductive polymers (e.g., polyacetylenes, polyanilines, polypyrroles, poly(p-phenylene-vinylene) and polythiophenes), especially their nanotublar structure, have garnered special attention due to the unique combination of electronic properties of conducting polymers and large surface area of nanotubes [3–8]

Among the conductive polymers, polythiophenes (PTs) have received great interest over the past few years due to their flexibility, ease of doping and good thermal and electrical stability that lead to some unique advantages of PTs for development of various applications. PTs have been studied for various applications, including organic field effect transistor, solar cells, supercapacitors, sensors, electrochromic devices and light emitting diodes [6,9,10].

"Template synthesis method" is one of the most effective methods for synthesis of nanoscale conjugating tubular polymers. Conductive polymer nanotubes have been synthesized chemically or electrochemically in the pores of a template. Electrochemical deposition in the pores of the template has attracted a good deal of research interest because with this method it is easy to control the length, diameter, shape and structural properties of nanotubes [11–13].

In this study we report the template electrosynthesis and characterization of polythiophene nanotubes, and sensing application of them toward riboflavin, since the performance of sensors and biosensors can be improved by using nanomaterials [14–19].

Vitamin B_2, also called riboflavin (RF), is one of the essential water soluble vitamins (the chemical structure is shown in Scheme 1). RF plays very important roles in living organisms, especially via its contribution towards the formation of two flavin coenzymes: flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD) [20,21]. In addition to energy production for the body by conversion of carbohydrates into glucose, RF also plays a key role in promoting growth, immunity, cell regeneration, antioxidation and cancer prevention [22,23].

The determination of trace amounts of RF is essential for the quality control of feed and pharmaceuticals. Several analytical methods have been developed for determination of RF due to its biological significance. These methods include liquid chromatography [24,25], chemiluminescence [26], spectrophotometry [27], fluorescence [28] and electrochemical methods [29]. Among these methods, electrochemical techniques have the advantages of high sensitivity and selectivity and also being inexpensive [30].

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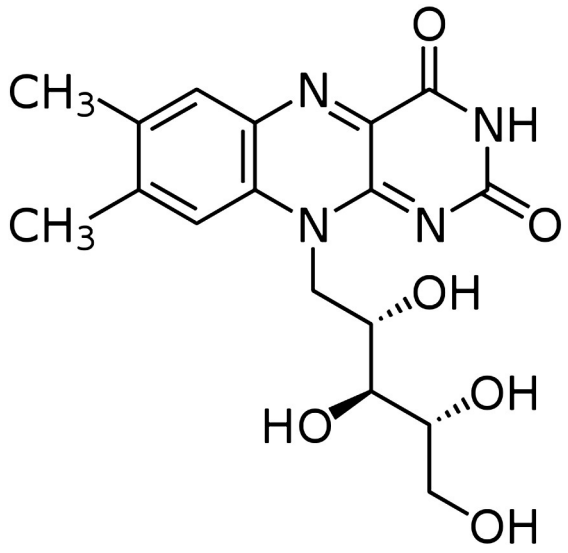

Scheme 1. The chemical structure of riboflavin.

However, there are only few reports on applying electroanalytical methods in the determination of RF [29,31,32], usually involving adsorptive stripping voltammetry at mercury electrodes under basic conditions [33,34].

To the best of our knowledge, nanostructured conducting polymers have never been used for modification of glassy carbon (GC) electrode for RF determination. Therefore, in this study we used conductive polymer nanotubes for GC electrode modification which exhibited very good activity towards RF detection and determination.

2. Experimental

Conducting polythiphene nanotubes were synthesized through electrochemical polymerization method using nonporous PAA template, which was purchased from Whatman Co.

2.1. Materials

PAA membranes (Anodisc 13 with 100 nm pore diameter) were purchased from Whatman (UK). Acetonitrile was purchased from Merck and was used after drying with molecular sieves under argon atmosphere. All other chemicals not mentioned here were of analytical reagent grade and were used as received. All the voltammetric studies were carried out at room temperature (25 ± 0.1 °C) in 0.04 M Britton Robinson (BR) buffer, prepared from acetic acid, phosphoric acid and boric acid. The solutions were prepared in deionized water and deoxygenated by bubbling high purity (99.99%) nitrogen gas through them for 15 min prior to the experiments. A stock solution of 0.01 mM riboflavin was prepared before use and protected from light with aluminum foil.

2.2. Apparatus

Electrochemical measurements were performed with a μ-Autolab electrochemical system (Eco Chemie, Ultec, The Netherlands), equipped with NOVA software (upgrade 1.7). A conventional three-electrode cell was employed for all electrochemical experiments incorporating a KCl-saturated Ag/AgCl reference electrode and a platinum counter electrode.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis were performed using a FEI Quanta 250 FEG. A transmission electron microscope (TEM) image was taken with a Zeiss LEO 912 Omega operating at 80 kV.

2.3. Preparation of polythiophene nanotubes (PTN)

Before electropolymerization of thiophene, a thin layer of 70 nm gold was sputtered on one side of the PAA membranes to make the surface electrically conductive and serve as working electrode during electrodeposition.

Conductive polythiophene nanotubes (PTN) were prepared by electrochemical polymerization of thiophene in a three electrode system. They were fabricated by potentiostatic electropolymerization of monomer at 1.4 V versus Ag/AgCl in an acetonitrile solution of 25 mM thiophene and 100 mM tetrabutylammonium perchlorate. After electropolymerization, the membrane had a dark brown color indicative of the formation of PTNs.

2.4. Modified electrode preparation

The fabrication of modified GC electrode is summarized as follows: after electropolymerization, PAA templates was rinsed with deionized water and dissolved in 1 M NaOH etching solution, then washed several times by deionized water and ethanol and then dispersed in 10 ml ethanol and ultrasonicated for 5 min to get a dark brown homogeneous solution (0.5 mg/ml). The resulting PTNs were examined for modification of GC electrode. The bare GC electrodes (2 mm diameter) were carefully polished with alumina slurry (0.05 μm) on a polishing cloth and sonicated successively in deionized water and ethanol.

A 0.2-wt.% chitosan solution was prepared by dissolving 20 mg of chitosan flakes into 10 ml of 1.0% acetic acid and stirred for 3 h at room temperature until complete dissolution.

The GC electrodes were treated by dropping a suspension (10 μl) of the homogeneously dispersed PTN–ethanol solution and 5 μl of the chitosan solution on the surface of the cleaned electrode (the effect of PTN amount on the sensing performance was also investigated. For this purpose different amounts of homogeneous PTN solution (2 to 20 μl) were dropped on the electrode surface. With regard to the sensor performance, 10 μl has been chosen as the optimized value). Then, modified electrodes were dried in air to form a PTN film on the electrode surface. The prepared electrodes are denoted as PTN/GC electrode and were employed for electrochemical sensing of RF.

2.5. SEM and TEM sample preparation

The structure of PTNs grown in PAA template was investigated by SEM and TEM. To obtain SEM images of PTNs, a piece of the PAA template embedded with PTNs was fixed to a specimen mount. 1 ml of NaOH 1.0 M was dropped on the surface of the sample to partially dissolve the template, and then they were rinsed with water and ethanol for several times. Another SEM sample was prepared by completely dissolving the template in the solution containing 1.0 M NaOH. Nanotubes are then washed several times by deionized water and ethanol. The specimen for TEM was also prepared by completely dissolving the PAA template in 1.0 M NaOH. The residual nanotubes were carefully rinsed with deionized water and ethanol and then dispersed into ethanol solution via ultrasonication. A copper grid was dipped into the solution and then dried before TEM measurement.

3. Results and discussion

3.1. Morphology and structure of PTNs

The SEM images of as-prepared structures which are displayed in Fig. 1 confirm the formation of nanotubes and show uniform cylindrical nanotubes with a high aspect ratio. A top view SEM micrograph of the synthesized PTN after partial etching of the PAA template in 1.0 M NaOH is displayed in Fig. 1a. From this image one can see the well packed nanotube arrays with the diameter of about 100 nm standing perpendicular to PAA template. PTNs in the pores of PAA template

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