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Sensitive electrochemical detection of NADH and ethanol at low potential based on pyrocatechol violet electrodeposited on single walled carbon nanotubes-modified pencil graphite electrode



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ARTICLE INFO

Article history:

Received 2 February 2014

Received in revised form

21 June 2014

Accepted 25 June 2014

Available online 3 July 2014

Keywords:

Pyrocatechol violet

Single-walled carbon nanotubes

Pencil graphite electrode

Dihyronicotinamide adenine dinucleotide

Ethanol

ABSTRACT

In this work, the electrodeposition of pyrocatechol violet (PCV) was initially investigated by the electrochemical surface plasmon resonance (ESPR) technique. Subsequently, PCV was used as redox-mediator and was electrodeposited on the surface of pencil graphite electrode (PGE) modified with single-wall carbon nanotubes (SWCNTs). Owing to the remarkable synergistic effect of SWCNTs and PCV, PGE/SWCNTs/PCV exhibited excellent electrocatalytic activity towards dihyronicotinamide adenine dinucleotide (NADH) oxidation at low potential (0.2 V vs. SCE) with fast amperometric response (< 10 s), broad linear range (1.3–280 μM), good sensitivity (146.2 $\mu\text{A mM}^{-1} \text{cm}^{-2}$) and low detection limit (1.3 μM) at signal-to-noise ratio of 3. Thus, this PGE/SWCNTs/PCV could be further used to fabricate a sensitive and economic ethanol biosensor using alcohol dehydrogenase (ADH) via a glutaraldehyde/BSA cross-linking procedure.

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1. Introduction

Dihyronicotinamide adenine dinucleotide (NADH) and its oxidized form nicotinamide adenine dinucleotide (NAD^+) are significant coenzymes which participates in a variety of enzymatic reactions via more than 300 dehydrogenases [1]. Therefore many studies have focused on the electrochemical oxidation of NADH to develop NAD^+ -dependent enzymatic biosensors using for environmental, food control, clinical analysis [2,3]. However, the direct oxidation of NADH at conventional electrodes requires a high overpotential positive of 0.6–0.8 V vs. SCE [4] and suffers from low sensitivity and the fouling of the electrode surface by its oxidation products, which cause loss of selectivity, reproducibility and stability [5,6].

Considerable effort has been devoted to identify new electrode materials or efficient electron-transfer mediators as the catalysts to allow the electrochemical determination of NADH at low potential, e.g. azine dyes [7,8], quinones [9], metal nanoparticles [10,11] and carbon nanomaterials [12,13]. Carbon nanotubes (CNTs) have received considerable attention for this purpose. Many studies have demonstrated that CNTs can be used to

fabricate the nanostructured macroscopic electrodes, biosensors, and nanobioelectronic devices due to their nanometer size, lack of toxicity, good electrocatalytic properties, and efficient accumulation of biomolecules as well as minimization of surface fouling [14]. Furthermore, endowment SWCNTs with redox properties could efficiently accelerate the oxidation speed of NADH [15].

The purpose of this work is to develop the electrocatalysis of NADH and to fabricate an enhanced performance ethanol biosensor. Pyrocatechol violet (PCV) is used as mediator and electrodeposited on the SWCNTs-modified pencil graphite electrodes (PGEs). PCV is a sulfone phthalein dye prepared from condensing two moles of pyrocatechol with one mole of *o*-sulphobenzoic acid anhydride. It has been demonstrated that materials from catechol and gallate families, containing OH groups bonded to the adjacent carbon atoms of the aromatic ring, strongly adsorbed on various inorganic materials. It is important to note that such bonds improved charge transfer between inorganic and organic materials [16]. Moreover, SWCNTs exhibit a special sidewall curvature and possess a π -conjugative structure, which allows them to interact with PCV through π - π electronic interactions.

PGE was applied due to the following advantages: (a) high electrochemical reactivity with a wide polarized potential domain in aqueous solutions; (b) a variety of easy methods of surface modification by electrochemical, chemical and mechanical treatment; (c) high stability at slightly degraded surface activity;

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(d) low cost and usable as disposable electrochemical tool; and (e) a renewal surface which is simpler and faster than polishing procedures, common with solid electrodes, and results in good reproducibility for the individual surfaces [17,18]. Thus, recently many scientists have focused on the use of these electrodes in various electroanalytical applications due to the useful properties of PGEs [19–21].

In addition, PCV electrochemical deposition was investigated initially by electrochemical surface plasmon resonance (ESPR).

2. Experimental

2.1. Reagents

Alcohol dehydrogenase (ADH) (EC 1.1.1.1, from *Saccharomyces cerevisiae*, ≥ 300 units mg^{-1}), β -nicotinamide adenine dinucleotide reduced disodium salt hydrate (NADH), β -nicotinamide adenine dinucleotide sodium salt from *S. cerevisiae* (NAD^+) and bovine serum albumin (BSA) were purchased from Sigma. Proca-techol violet (PCV) was obtained from Sangon Chemicals (China). Single-wall carbon nanotubes (SWCNTs), produced by HiPco[®] process (Purified, CNI grade, lot no. Po313), were purchased from Carbon Nanotechnologies, Inc. and were further functionalized as described earlier [22]. The chemically modified SWCNTs were dispersed in distilled water leading to a concentration of 0.1 mg ml^{-1} . All other chemicals were of analytical grade and used without further purification. Phosphate buffer solution (PBS) was $0.1 \text{ M K}_2\text{HPO}_4$ and KH_2PO_4 and its pH was adjusted with H_3PO_4 or KOH solutions. Twice-distilled water was used throughout the experiment. Beers and liquors were purchased in local supermarkets.

2.2. Apparatus and instrumentations

A CHI 660D electrochemical workstation (CH Instrument) was used for cyclic voltammetry and amperometric measurements. All electrochemical studies were performed with a conventional three electrode system. A saturated calomel electrode (SCE) and a Pt wire electrode were used as reference and counter electrodes, respectively. All the potentials mentioned below are relative to SCE. The working electrode was a home-made pencil graphite electrode (PGE). The pencil leads were obtained from Dena Co. Ltd., China. All leads had a total length of 85 mm and a diameter of 2 mm. The pencil leads were used as received. The morphology of the modified electrodes was investigated with a XL-30E scanning electron microscope (SEM). Static water contact angle measurements were performed by the sessile drop technique using an Optical Tensionmeter (Theta Lite, Finland), under ambient laboratory conditions. A drop of distilled water was applied to the surface of bare and modified PGE, and the contact angle measurements were carried out within 30 s of the contact. An ESPRIT instrument (Echo Chemie B.V., Utrecht, Netherlands) was used to perform the optical measurements of the Surface Plasmon Resonance (SPR) angle and cyclic voltammetry was carried out with a potentiostat (AUTOLAB) from Echo Chemie (Utrecht, Netherlands). The ESPRIT instrument is based on the Kretschmann configuration [23] with a scanning-angle setup. In this system, the intensity of reflected light is minimum in the resonance angle. This angle can be measured over a range of 4° in this equipment by using a photodiode detector. The incidence angle was varied by using a vibrating mirror (rotating over an angle of 5° at 77 Hz in 13 ms), which directs p-polarized laser light onto a $1 \text{ mm} \times 2 \text{ mm}$ spot of the sensor disk via the hemicylindrical prism of BK7 glass. In each cycle, the reflective curves were scanned on both forward and backward movements of the mirror. In this vibrating mirror

set-up, the resolution was 1 m° . The light source (LASER) of the system is composed of the laser diode with emission wavelength of 670 nm. In the experiments, a gold sensor disk containing a hemicylinder was mounted into a pre-cleaned SPR cuvette. In order to obtain high inertness, it was made of Teflon[®]. The solutions were injected into the cuvette using a syringe with a stainless steel needle (Fig. 1). In order to avoid contamination on gold surface between the polymerization experiments was adopted the procedure previously reported [24]. The SPR angle shifts ($\Delta\theta$) were converted into mass uptake using a sensitivity factor of 120 mdeg (milli-degrees) corresponding to 100 ng cm^{-2} of molecular loading, and the MW of each immobilized molecule [25].

The determination of ethanol contents in wine samples was performed on an Agilent 6890N GC equipped with a FID (Palo Alto, CA, USA). An Agilent HP-INNOWAX capillary column ($30 \text{ m} \times 0.32 \text{ mm i.d.}$, film thickness $0.1 \mu\text{m}$) was employed for separation. Ultra-high purity (99.999%) nitrogen was used as the carrier gas at flow rate of 1.0 mL/min . The injection volume was $1.0 \mu\text{L}$ and all the injections were performed in a split ratio of 1:10. The column temperature was set isothermally at 90°C . The injector and detector temperatures were at 250 and 280°C , respectively.

2.3. Preparation of SWCNTs, PCV and SWCNTs/PCV modified electrodes

A pencil graphite electrode (PGE) was polished carefully with $0.05 \mu\text{m}$ alumina particles on silk followed by sonication in deionized water and ethanol, and dried in air prior to use. The modification of PGE with SWCNTs was performed by casting $4 \mu\text{L}$ of SWCNTs aqueous solution (0.1 mg ml^{-1}) on the electrode surface and dried in air. The electrochemical deposition of PCV as performed over the surface of bare PGE and PGE/SWCNTs, respectively, in a 0.1 M PBS (pH 7) containing 1 mM PCV and 0.1 M KCl , through cyclic voltammetry between -0.2 and 0.5 V for 20 cycles at a scan rate of 20 mV s^{-1} . The modified electrodes obtained above were denoted as PGE/PCV and PGE/SWCNTs/PCV, respectively.

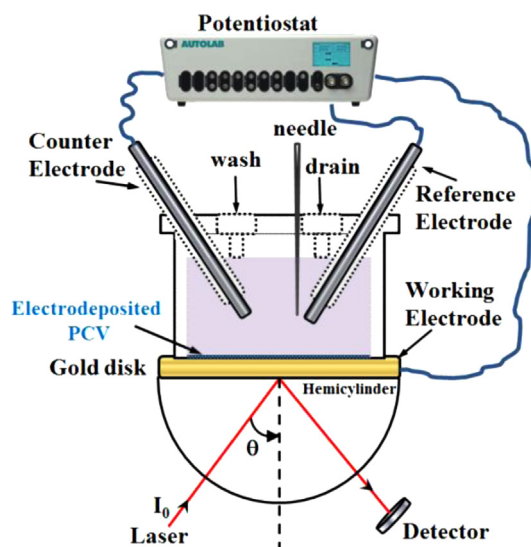


Fig. 1. Schematic diagram of SPR spectroscopy using the Kretschmann configuration. The light source (laser) of the SPR system is composed of a laser diode with an emission wavelength of 670 nm. A scanning mirror with a frequency of 76 Hz was used to obtain an angle scan of 4000 m° in approximately 13 ms. θ represents the angle of incident light.

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