



An ascorbic acid amperometric sensor using over-oxidized polypyrrole and palladium nanoparticles composites

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ABSTRACT

We constructed a highly responsive ascorbic acid (AA) sensor utilizing over-oxidized polypyrrole (OPPy) and Palladium nanoparticles (PdNPs) composites (OPPy–PdNPs). In the presence of PdNPs, polypyrrole (PPy) was coated on a gold (Au) electrode through cyclic voltammetry (CV) and over-oxidized at a fixed potential in NaOH solution. The PdNPs were characterized using ultraviolet–visible (UV–vis) spectrum and transmission electron microscopy (TEM). The surface of OPpy–PdNPs on the Au electrode was investigated using field-emission scanning electron microscopy (FE–SEM). Results revealed that the OPpy–PdNPs-modified Au electrode (OPpy–PdNPs/Au) has the capacity to catalyze the oxidation of AA by lowering its oxidation potential to 0 V. The OPpy–PdNPs/Au electrode exhibited 2 different linear concentration ranges. In the low concentration range (1–520 μM), OPpy–PdNPs/Au exhibited a direct linear relation with current responses and had high sensitivity (570 μA mM⁻¹ cm⁻²) and a high correlation coefficient (0.995). In contrast, in the higher concentration range (120–1600 μM), the relationship between current responses and concentration of AA can be represented by a two-parameter sigmoidal equation. In addition, the sensor exhibited a short response time (less than 2 s) and a very low limit of detection of 1 μM. The electrochemical AA sensor constructed in this study was simple, inexpensive, reproducible, sensitive, and resistant to interference. Thus, the proposed sensor has great potential for detecting AA in complex biosystems and can be applied in various fields, particularly neuroscience.

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1. Introduction

Since the beginning of neuroscience, monoamines have been regarded as a neurotransmitter with very low extracellular concentrations, and have thus received great interest. Meanwhile, the extracellular concentration of ascorbic acid (AA) in the brain was much higher than that of monoamines. AA has been considered to be a simple antioxidant and has not received much interest previously. AA is an electroactive substrate with an oxidation potential that is very similar to that of monoamines, so that researchers have difficulty avoiding AA interference during experiments. Recently, AA was found to be a versatile molecule that is linked to the extracellular modulation of glutamate and, perhaps, monoamines as well (Rebec, 2006). We know that cigarette smoking can lead to depletion of AA, thus leading to a decrease in antioxidant levels (Lykkesfeldt et al., 1997, 2000). A study has suggested that AA may have a role in preventing lead-induced neurotoxicity in the

developing rat hippocampus (Zhang et al., 2007b). An increasing number of studies have focused on measuring the changes in AA in the setting of behavioral and mood changes. One of the most important issues for these studies is the development of a suitable method to detect AA.

Most of the methods for the determination of AA were developed based on its reducing properties. These methods lack specificity and are prone to interferences by other reducing agents in the sample (Strohecker and Henning, 1965). Electrochemical methods have gained the most success among the different methods. One disadvantage of current AA detection methods is the interference of monoamines, especially catecholamines (Liu et al., 2009; Malinauskas et al., 2004). Since selectivity is the most important characteristic of a sensor, it was proposed that the oxidation potential of AA should be lowered by modifying the electrode using catalysts. A single wall carbon nanotube (SWNT) was found to be capable of lowering the oxidation potential of AA to as low as 0 V compared with Ag|AgCl. Through microdialysis and an on-line electrochemical detection with a SWNT modified glassy carbon electrode fixed at a thin-layer radial flow cell, Mao et al. found that the extracellular AA during global cerebral ischemia of different brain regions such as

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the cortex, dorsal hippocampus, and ventral hippocampus were increased to varying degrees, while AA level in the striatum was depleted (Liu et al., 2009; Zhang et al., 2005). Using the same method, they also found that global two-vessel occlusion decreased the extracellular AA level in the striatum, whereas left middle cerebral artery occlusion could dramatically increase it (Liu et al., 2008). However, their method had two main problems: (1) the temporal resolution of microdialysis is in the range of one to several minutes even at faster sampling rates; and (2) only a drop- or dip-coating method can be used to modify the SWNT on electrode because the SWNT has no active site that allows for chemical modification.

The first problem can be addressed by utilizing a series of microelectrodes that allows in vivo electrochemical detection of AA, such as carbon fiber microelectrode (CFE) and Pt microelectrode. Mao et al. utilized SWNTs to modify CFE for in vivo detection of AA in rat brain (Zhang, et al., 2007b). In relation to the second problem, there are a number of reports on electro-oxidation of AA using conducting polymer-modified electrodes for analytical purposes (Malinauskas et al., 2004). Electro-deposited polymers have the capacity to catalyze AA oxidation, allow the generation of stable coatings on electrodes surface, and can successfully modify the fixed direction of even versatile electrodes. Poly(vinyl alcohol) (Li and Lin, 2006), poly(Evans Blue) (Lin et al., 2008), poly(phenosafranin) (Selvaraju and Ramaraj, 2003), Poly(*p*-aminobenzene sulfonic acid) (Jin et al., 2005), multi-walled carbon nanotubes with poly(methylene blue) composite film (Yogeswaran and Chen, 2008), poly(3,4-ethylenedioxy)thiophene (Vasanth and Chen, 2006), poly(malachite green) (Yang and Wang, 2007), and polyaniline nano-networks (Zhan et al., 2008) modified electrodes have the ability to determine AA, UA, and DA levels through differential pulse voltammetry (DPV), cyclic voltammetry (CV), or linear sweep voltammetry. Among the electro-polymers, polyaniline has been extensively studied for AA sensor construction. Zhang et al. developed an AA sensor by synthesizing a polyaniline–camphorsulfonic acid composite film on a platinum electrode surface, which shifted the anodic peak potential of AA from 0.63 V at the bare platinum electrode to 0.34 V with greatly enhanced current response (Zhang and Dong, 2004). Zhang electro-deposited a polyaniline- β -naphthalenesulfonic acid composite film to decrease the oxidation potential of AA (Zhang, 2007). A polyaniline-modified Pt electrode has been used for sensing AA in beverages (Kilmartin et al., 2008). A copper nanoparticle/polyaniline-modified GCE was capable of sensing AA at an applied potential of 0.2 V compared with Ag|AgCl (Xi et al., 2010). Bartlett et al. electrodeposited a polyaniline films on a platinum needle type microelectrodes that could be applied to AA oxidation in human plasma at a potential of 0.1 V and pH 7 compared with saturated calomel electrode (Bonastra and Bartlett, 2010). Although most electro-polymers exhibited the capability to catalyze AA, the oxidation potential of AA remained at a value that could cause concomitant monoamine oxidation. Furthermore, most of the detection methods utilized CV, DPV (Ren et al., 2006; Zhang et al., 2008; Xiao et al., 2011), or linear scanning voltammetry. These techniques lack temporal resolution, which is very important in neuroscience.

Polypyrrole (PPy) is one of the most extensively used conducting polymers in bioanalytical sensors (Adeloju and Wallace, 1996). The versatility of this polymer is determined by a number of factors: redox activity, ion exchange and ion discrimination capacities, electrochromic effect based on electrochemical polymerization conditions and charge/discharge processes, strong absorptive properties (Atta et al., 2010) toward gases (Chehimi et al., 1999), proteins (Azioune et al., 2005), DNA (Saoudi et al., 2000), catalytic activity (Khomeenko et al., 2005), and corrosion protection properties (Hien et al., 2005). Most of these properties

are dependent on the synthesis procedure (Ramanaviciene and Ramanavicius, 2004). PPy is seldom used in AA sensors.

In order to address these issues, this study aimed to design an electrochemical sensor for AA detection through the electro-deposition of OPPy and PdNPs composites film. We utilized the electrochemical method of current–time response in order to determine the shortest temporal resolution. The performance of the obtained electrodes in terms of linear range, reproducibility, response time, and stability were investigated.

2. Experimental

2.1. Materials

Polyvinyl pyrrolidone (PVP) and Py were purchased from Sigma-Aldrich Co., Ltd. HCl, PdCl₂, NaH₂PO₄, Na₂HPO₄, and KCl were obtained from Beijing Chemical Reagents Company (Beijing, China). All reagents were used as received without further purification. Other chemicals were of analytic grade and were used as received unless stated otherwise. Water was purified through a Michem ultrapure water apparatus (Michem, Chendu, China, resistivity > 18 M Ω). Au disk electrodes were purchased from Gaos Union Electrochemistry Company (Wuhan, China).

Artificial cerebrospinal fluid (aCSF) was prepared with 124 mM NaCl, 4 mM KCl, 2 mM MgSO₄ · 7H₂O, 2 mM CaCl₂, 26 mM NaHCO₃, 1.25 mM NaH₂PO₄ · 2H₂O, and 10 mM glucose (pH 7.2). It was freshly prepared prior to use. The phosphate buffer saline (PBS, 0.1 M Na₂HPO₄-NaH₂PO₄-KCl, pH 7.4) was prepared from a PBS tablet (Sigma).

2.2. Apparatus

Transmission electron microscopy (TEM) was performed with a JEOL-100CX electron microscope under 80 kV accelerating voltage. Field-emission scanning electron microscopy (FE-SEM) was performed with a Hitachi S-4800 under 5 kV accelerating voltage (Hitachi, Japan). Absorption spectra were obtained using a U-1700 spectrophotometer (Hitachi, Japan). The X-ray photoelectron spectroscopy (XPS) analysis was done with a K-Alpha XPS spectrometer (Thermo Fisher). All electrochemical measurements were performed on a CH Instruments 660 A electrochemical Workstation (CHI-660 A, CH Instruments, Texas, USA).

2.3. Preparation of PdNPs

In a typical experiment, an ethanol aqueous solution of PdCl₂ (2.0 mM, 50 mL), HCl (1.67 M, 100 μ L), and PVP (0.2775 g) was refluxed to generate a dark brown colloid (as evidenced by UV–vis spectroscopy and the identification of the surface plasmon resonance). In order to obtain more evenly distributed PdNPs, reflux and stirring were continued for another 3 h. The prepared PdNPs were directly used without purification.

2.4. Electrode modification

An Au disk electrode ($\varphi=2$ mm) was polished with 0.05 μ m alumina slurry on a synthetic cloth to obtain a mirror-like surface. It was sonicated in ultrapure water and ethanol for 5 min each. Finally, the electrode was rinsed with ultrapure water and dried with a stream of air.

In a typical experiment, the modification of the PPy–PdNPs membrane on Au was performed using CV in a mixture of 0.1 M PPy+PdNPs colloid solution and 0.1 M KCl (the mixture was

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