



3-mercaptopropylphosphonic acid modified gold electrode for electrochemical detection of dopamine

Yu Chen^a, Li-Rong Guo^a, Wei Chen^b, Xiao-Jing Yang^a, Bo Jin^b, Li-Min Zheng^{a,*}, Xing-Hua Xia^{b,*}

^a State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

^b Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

ARTICLE INFO

Article history:

Received 10 August 2008

Received in revised form 25 December 2008

Accepted 31 December 2008

Available online 8 January 2009

Keywords:

Phosphonic acid groups

Self-assembly

Selectivity

Dopamine

Electrocatalysis

ABSTRACT

It is reported for the first time that the phosphonic acid terminated self-assembled layers assembled on a gold surface could be used as a functional interface to sensitively and selectively detect dopamine (DA) in the presence of highly concentrated ascorbic acid (AA). X-ray photoelectron spectroscopic (XPS) and reductive desorption measurements proved that the 3-mercaptopropylphosphonic acid [HS-(CH₂)₃-PO₃H₂, MPPA] was successfully immobilized on the gold surface via S–Au bond. Making use of the electrostatic interactions between the negatively charged phosphonic acid groups on the electrode surface and DA and AA, the MPPA modified electrode was successfully used to electrochemically discriminate between DA and AA. Cyclic voltammetry measurements shown that the MPPA modified electrodes almost completely inhibited the electrochemical reaction of AA. Therefore, DA can be selectively and sensitively determined by using the differential pulse voltammetry technique although high concentration of AA is present.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Dopamine (DA) is a ubiquitous neurotransmitter in mammalian brain tissues. It plays an important role in the functioning of the central nervous, renal, hormonal and cardiovascular systems [1]. Dysfunction of the dopaminergic system in the central nervous system is related to neurological disorders such as schizophrenia, Parkinson's disease and to HIV infection [2]. Therefore, real time monitoring of the DA level in real system shows an important issue in diseases diagnosis. Since most of the neurotransmitters, e.g. DA, are electrochemical active, hence, electrochemical techniques have been proved to be potential approaches for this issue due to the advantages of high sensitivity and easy miniaturization [3]. However, many other electrochemical species such as ascorbic acid (AA) coexist with DA. Their electrochemical responses will certainly interfere in the detection of DA. In addition, the bare electrodes usually suffer from a fouling effect due to the accumulation of oxidized products on the electrode surface, which results in rather poor selectivity and sensitivity [4].

Up to now, various approaches have been suggested to overcome all these problems in the selective and sensitive measurement of DA. Among these, surface modification of the electrodes with charged materials shows an important approach for decreasing the contribution of other electrochemical species via the electrostatic repulsion and increasing the sensitivity due to the surface enrichment of DA. The amine group of DA is positively charged ($pK_a=8.87$), whereas the

hydroxyl next to the carbonyl group of AA is negatively charged at physiological pH ($pK_a=4.10$) [5]. Thus, the electrode with charged materials would repel/attract the negatively charged AA, while it correspondingly attract/repel the positively charged DA at physiological pH values, which would protect the electrode surface from the AA interference. Modification of the electrode can be usually achieved by polymer films [6,7] and monolayers films [8–11]. The electrodes coated with polymer films such as Nafion [12,13] usually suffer from a slow response because of the low diffusion coefficient of the analytes in the films, and from the memory effects due to the strong binding affinity between cations and Nafion. These problems could be avoided if monolayers are assembled on the electrode surfaces (gold and carbon). In the last few decades, therefore, substantial efforts have been devoted to the development of electrochemical biosensor based on electrodes modified with monolayers. The electrocatalytic oxidation of DA and AA has been studied on carboxylic [8,10] and sulfonic acid [9] terminated monolayers modified electrodes. Novel electrochemical and physical properties of the modified electrodes have been observed. Comparing with the carboxylic terminated monolayers, sulfonic acid terminated monolayers is anticipated to achieve a better electrochemical differentiation between DA and AA than that of carboxylic terminated monolayers because sulfonic acid groups are fully dissociated at neutral pH, and the higher negative charge density for sulfonic acid will result in higher repulsion for the AA and higher attraction for DA. However, Dalmia et al. [9] have observed that the peak potential for DA oxidation on the sulfonic acid terminated monolayers modified electrode obviously shifted to higher potential as compared to the corresponding carboxylic acid terminated monolayers modified electrode. This anomalous result could be

* Corresponding authors. Tel.: +86 25 8331 4502; fax: +86 25 8359 7436.

E-mail addresses: lmzheng@nju.edu.cn (L.-M. Zheng), xhxia@nju.edu.cn (X.-H. Xia).

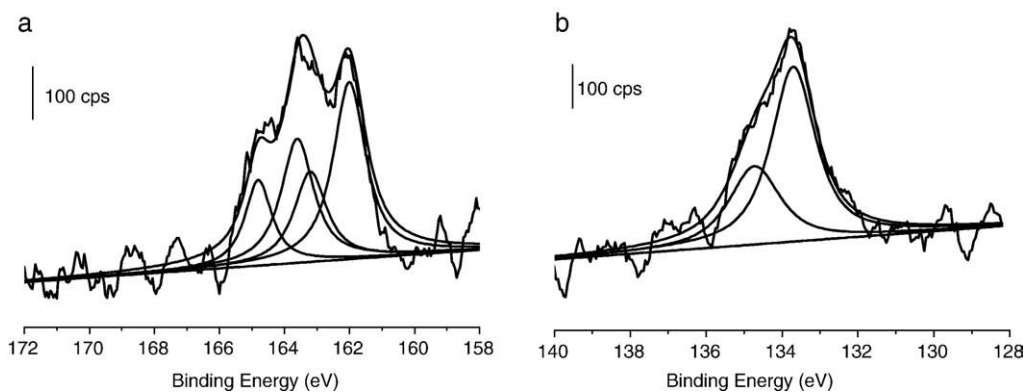


Fig. 1. XPS spectra of the MPPA/Au in the (a) S(2p) and (b) P(2p) regions.

explained by the fact that the sulfonic acid end groups are a hard Lewis base and have higher affinity for a hard Lewis acid, i.e. sodium ions than a soft Lewis acid, i.e., DA [9].

Although the oxidation of both AA and DA has been widely studied at these carboxylic terminated and amidocyanogen terminated monolayers modified electrodes, the determination of DA in phosphonate or organophosphate terminated monolayers modified electrodes has not been reported. Phosphonates and organophosphates are structurally similar. The organophosphate has 4 oxygens with an alkyl group connected via a phosphoester bond, while the phosphonates have 3 oxygens with a carbon attached directly to phosphorus. The lack of a hydrolyzable C–O–P linkage makes the phosphonate compounds more stable in aqueous solution than the organophosphate compounds. Generally, the phosphonic acid groups are more acidic than the carboxylic acid groups with the same carbon chains length. Consequently, the phosphonic acid modified layer carrying negative charges strongly repels the negatively charged AA, while attracts the positively charged DA in the environment of physiological pH. Moreover, the phosphonic acid groups are amphoteric groups in physiological pH in term of Bronsted–Lowry concept, thus, the competition adsorption between sodium ion and dopamine should be eliminated. Therefore, in the present work, we firstly studied the electrochemical behavior of a 3-mercaptopropylphosphonic acid [HS-(CH₂)₃-PO₃H₂, MPPA] modified gold electrode and its electrocatalysis toward the oxidation of DA and AA. As expected, the MPPA modified gold electrode shown prominent electrocatalytic activity toward the oxidation of DA at physiological pH, while negligible electrochemical response for AA was observed. In addition, the charging current of the MPPA modified gold electrode was much lower than that of the corresponding 3-mercaptopropionic acid modified electrode, which should further enhance the electroanalysis sensitivity of the analysts. Therefore, selective and sensitive electrochemical determination of DA on MPPA modified gold electrode can be achieved in the presence of highly concentrated AA. This functional interface is promising for the construction of DA biosensors with high selectivity and sensitivity for monitoring of the DA level in real physiological system.

2. Materials and methods

2.1. Reagents

All the chemical reagents used in this work were of analytical grade (AR). Dopamine, ascorbic acid, epinephrine and 3-mercaptopropionic acid were purchased from Sigma-Aldrich (St. Louis, U.S.A.) and used without further purification. Phosphate buffer solution (PBS) was prepared by using Na₂HPO₄ and NaH₂PO₄. 3-mercaptopropylphosphonic acid [HS-(CH₂)₃-PO₃H₂, MPPA] was synthesized according to a developed literature procedure [14] (see supporting information S1). Freshly prepared solutions of DA and AA were used in all experiments.

All the aqueous solutions were prepared with Millipore water having a resistivity of 18.2 MΩ (Purelab Classic Corp., USA).

2.2. Pretreatment of Au substrates

Gold sheet (1.0 cm in diameter, 99.99%) was used for XPS experiments. It was pretreated by immersing in a 1:3 mixture of H₂O₂ (30%)/H₂SO₄ (98%) for 4 h at room temperature (*Warning: this solution reacts strongly with organic compounds and should not be stored in closed containers. It must be handled with extreme caution.*), followed by rinsing with Millipore water and absolute ethanol subsequently.

Gold disk electrode (CHI, 2 mm in diameter) sealed with a polymer shell was used for electrochemical measurements. Before deposition of the MPPA self-assembled monolayers (SAMs), the gold disk electrode was pretreated as described previously [15]. It was polished with Al₂O₃ powder (0.3 and 0.05 μm) and sonicated in absolute ethanol and Millipore water (each for ~3–5 min). After rinsed with Millipore water, it was immersed into concentrated HNO₃ for 10 min and then thoroughly rinsed with Millipore water. Finally, the Au electrode was subjected to electrochemical pretreatment by consecutive potential cycling in a 0.5 M H₂SO₄ solution within a potential window between –0.30 and +1.60 V (vs. SCE) at 50 mV/s. The cycling was continued until a reproducible voltammogram showing the presence of gold oxide formation and reduction was obtained. The real surface area of the bare polished gold electrodes was determined from the cyclic voltammogram by integration of the cathodic peak for the reduction of the surface gold oxide in 0.5 M H₂SO₄ [16–18]. Typically, the real surface area of the gold disk electrode after pretreatment was 0.0736 cm². A roughness factor (ratio of the real to geometric surface area) of 2.3 ± 0.2 was obtained.

2.3. Preparation of MPPA modified gold electrode

The pretreated Au electrode was immersed in a 4 mM MPPA solution in the dark for 24 h. After the electrode was rinsed carefully with ethanol for 1 min and Millipore water for another 1 min consecutively, the MPPA modified gold electrode (MPPA/Au) was obtained. For comparison, 3-mercaptopropionic acid modified gold electrode was also prepared using the same procedure as that for the MPPA/Au electrode.

2.4. Apparatus

The electrochemical measurements were performed in a conventional three-electrode electrochemical cell using a CHI 660 C electrochemical analyzer (CHI, Shanghai Chenchua Co.). A Pt sheet auxiliary electrode and the saturated calomel reference electrode (SCE) were used. All potentials refer to the SCE. The bare Au electrode and the modified Au electrodes were used as the working electrodes. The electrolyte was purged with high purity nitrogen for at least

Download English Version:

<https://daneshyari.com/en/article/1268891>

Download Persian Version:

<https://daneshyari.com/article/1268891>

[Daneshyari.com](https://daneshyari.com)