

Dopamine Sensor Based on a Composite of Silver Nanoparticles Implemented in the Electroactive Matrix of Calixarenes

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Received: April 5, 2011

Accepted: July 2, 2011

Abstract

A sensitive electrochemical sensor based on a composite containing silver nanoparticles and a redox active thiacalixarene with catechol fragments in the substituents at the lower rim has been developed and used for dopamine detection. The electrochemical investigation of thiacalixarene in homogeneous solution and on the electrode interface showed the reversible character of the redox conversion of catechol fragments and its involvement in the chemical reduction of silver which resulted in formation of uniform nanoparticles of 4–6 nm in diameter. The use of such a material for electrode modification made it possible to record a high amplitude cathodic signal at -700 mV that was proportional to the dopamine concentration within 1 nM–1 μ M. (limit of detection 0.5 nM).

Keywords: Dopamine detection, Silver nanoparticles, Thiacalixarene, Amperometric sensor

DOI: 10.1002/elan.201100197

1 Introduction

Dopamine (DA) belongs to the family of neurotransmitters that play a key role in the functioning of cardiovascular, renal, hormonal and central nervous systems of mammals [1,2]. Deficiency in DA is associated with Parkinson's disease [3], schizophrenia and some other neuropsychiatric disorders [3,4]. For this reason, monitoring of DA levels in vivo is considered as an important marker for diagnostics purposes.

Various methods have been proposed for DA detection. The traditional analytical methods based on spectroscopy [5] and HPLC [6] are sensitive but do not provide continuous monitoring of DA in living tissues. As an alternative, electrochemical methods based on DA oxidation have been intensively investigated. They possess many advantages over traditional techniques, e.g. miniaturization potentialities, fast and reversible response toward micromolar concentration of DA, long lifetime, easy operation and data processing. However, the oxidation signal of DA on unmodified electrodes overlaps with those of some oxidizable components of biological liquids, e.g. ascorbic and uric acids [7,8]. The concentrations of interferences in biological fluids are usually much higher than those of an analyte and prevent DA detection in vivo. To overcome this limitation, two strategies are elaborated based on the use of 1. anionic species and 2. specific mediators of electron transfer. The coating of the

electrodes with anionic materials provides electrostatic repulsion of ascorbic and uric acids, which are present in the anion form within the physiological pH range ($pK_a = 4.1$ and 5.27 , respectively, against $pK_{a1} = 8.6$ – 8.8 for DA [9]). Nafion [10], melamin [11], and polystyrene sulfonate composite [12] show excellent discriminating features to determine DA in nanomolar concentrations. However the use of polymers increases the diffusional barrier of DA transfer and hence can increase the response time and suppress the reversibility of the sensor in a series of measurements. For this reason, discriminating species are often coupled with mediators that improve the sensitivity of DA oxidation. Nanosized mediators like metal nanoparticles [13–17], metal oxides [13,18,19], and carbon nanotubes [12,20–25] are of major interest because they provide an extended access to the redox centers and increase their surface concentration. The characteristics of some DA sensors based on nanosized mediators are summarized in Table 1.

Silver nanoparticles have obtained increasing attention in the past decade due to their efficiency in catalysis and biomedical applications [26,27]. They are usually obtained by chemical or electrochemical reduction of appropriate salt performed in the presence of stabilizing components, e.g. poly(vinylpyrrolidone) [28,29], poly(*N*-isopropylacrylamide) [30], mercaptopropyltrimethoxysilane sol-gel network [31], polyethylene imine [32], and polyaniline [33]. The nanosilver dispersions have found applica-