Sensors and Actuators B 212 (2015) 457–463

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Modification of carbon aerogel electrode with molecularly imprinted polypyrrole for electrochemical determination of dopamine

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ARTICLE INFO

Article history:
Received 30 September 2014
Received in revised form 3 February 2015
Accepted 4 February 2015
Available online 19 February 2015

Keywords:
Dopamine
Molecularly imprinted polypyrrole
Carbon aerogel
Electrochemical sensing
Highly selective detection

ABSTRACT

Carbon aerogel (CA) was prepared by sol–gel process at ambient pressure drying. A novel electrochemical sensing platform with electrocatalytical activity and molecular recognition capabilities was developed for the detection of dopamine (DA), based on the modification of molecularly imprinted polypyrrole (MIPPy) onto a CA surface by electropolymerization and molecular imprinting techniques. The optimum sensing conditions could be provided with pyrrole-DA molar ratio of 1.5:1. The performance of the fabricated sensor was evaluated and the results indicated that the sensor exhibited high sensitivity in DA detection, with a linear range from 0.007 to 35 μM and a limit of detection of 0.0004 μM. Moreover, the sensor showed high selectivity towards DA in comparison to other interferents. The practical application of the sensor was also realized in the selective detection of DA in real samples.

1. Introduction

DA, an important catecholamine neurotransmitter in biological organisms, is correlated with the severity and progression of certain neurological disorders known as Alzheimer, drug addiction, schizophrenia and Parkinson [1,2]. Therefore, detection and quantification of DA is vitally important for the diagnoses, monitoring, prevention and treatments of the mentioned and other similar diseases. Some analytical methods have been developed for DA detection, including high performance liquid chromatography-mass spectrometry (HPLC-MS) [3], HPLC-fluorescence [4], gas chromatography-mass spectrometry (GC-MS) [5], Surface Plasmon Resonance [6], fluorescence [7] and electrochemical sensors [8–11]. Among them, electrochemical analytical technique is the most attractive and promising method due to its high sensitivity, technical simplicity, fast response, good controllability, low cost and real-time analysis [12,13]. The performance of the electrochemical sensors mainly depends on the electrode material, especially the selection and fabrication of sensing materials. Despite many advances in electrochemical DA sensors, many of these sensors still do not meet the growing demand for more sensitive and selective detection of DA. Thus, the further development of simple, facile and cost-efficient methods with high sensitivity and selectivity for DA detection is highly desirable.

Molecular imprinting is a promising technique for the preparation of polymers which possess specific recognition sites. By means of a synthetic organic polymer matrix, the imprints of the template molecule are created in the polymer. After the template is removed from the polymer network, recognition sites complementary to the template molecule in shape and size can be obtained. Owing to evident advantages such as physical and chemical stability, easy preparation and low cost, molecularly imprinted polymers (MIPs) prepared by electropolymerization have been widely used as recognition elements for the development of electrochemical sensors [14–16]. Compared with other preparation procedures of MIPs-based sensors (e.g., coating, composite-making), electropolymerization can directly produce a rigid, uniform and compact MIPs film on an electrode surface with any shape and size [17]. More importantly, MIPs film based on electropolymerization possesses high stability, reproducibility, adherence, electrocatalytical activity and conductivity, and the thickness, morphology and density of the film can be easily controlled by the polymerization conditions [18]. With regard to the selection of the polymer materials, polypyrrole (PPy) is very suitable for in vivo recording of DA due to high conductivity, good biocompatibility and ease of electro-deposition onto a variety of conductive surfaces [19,20]. Moreover, the amine groups in PPy may be favorable for improving the biomolecular sensing [21].

CA is a kind of mesoporous carbon materials with an interconnected three dimensional network structure and possesses

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http://dx.doi.org/10.1016/j.snb.2015.02.057
0925-4005/

high specific surface area, low density, suitable pore size distribution, excellent stability and distinguished electrical conductivity [22]. Its high surface area can provide much more multidimensional spaces for electrochemical modification of conducting polymer, and the excellent conductivity of CA may promote the electrochemical oxidation of molecules on the electrode surface, and facilitate the charge transfer in the oxidation reaction [23]. In the present work, a novel kind of MIP-based electrochemical sensor was fabricated by electropolymerizing pyrrole in the presence of DA onto a CA surface. The constructed sensor was characterized by Fourier transform infrared (FTIR) spectrometer and differential pulse voltammetry (DPV). Under the optimized conditions, the sensor exhibited excellent performance for DA detection.

2. Experimental

2.1. Materials and apparatus

Resorcinol, formaldehyde, sodium carbonate and pyrrole were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). DA, norepinephrine (NE), epinephrine (EP), uric acid (UA) and ascorbic acid (AA) were obtained from Aladdin Chemical Reagent Co. (China). Other chemicals were of analytical grade, and purchased from Shanghai Chemical Reagent Co. (China). Phosphate buffer solution (PBS, 0.1 M, pH 7.0) was prepared by mixing the stock solution of NaH_2PO_4 and Na_2HPO_4. All solvents and chemicals in this work were used without further purification unless otherwise stated. Deionized (DI) water (resistivity of 18 MΩ cm) was obtained from a Millipore Milli-Q Water System (Millipore Inc.), and was used throughout the experiments.

Infrared (IR) spectra were recorded on Nicolet 200SXV FTIR spectrometer using a KBr wafer. Raman spectra were recorded on a Raman spectrometer (InVia, Renishaw Co., UK). All electrochemical measurements were performed with a CHI660C electrochemical workstation (CH Instrument, Shanghai Chenhua Co. Ltd., China). Cyclic voltammetry (CV) and DPV were carried out using a conventional three-electrode system with MIPPy/CA or PPy/CA as the working electrode, Ag/AgCl as the reference electrode, and a Pt wire as the counter electrode.

2.2. Fabrication of the MIPPy/CA electrode

The preparation of CA was performed according to the previous reports with some modification [23]. Briefly, the solution of resorcinol, formaldehyde, DI water and sodium carbonate with molar ratio of 1:2:14.5:0.001 was mixed and stirred for 1 h at room temperature. The obtained homogeneous solution was then placed in a cuboid glass with the interlayer distance of 0.3 cm at 25 °C for one day, at 50 °C for another day, and at 90 °C for 3 more days. The resulting organic wet gel (RF) was washed with ethanol for 3 days and dried under ambient condition for 5 days to produce massive dry gel with integrated structure. Subsequently, the RF aerogel was converted to CA in nitrogen atmosphere at 1000 °C for 5 h and then cooled down to room temperature.

The resultant CA electrode with an effective working area of 1.5 cm × 2.0 cm was immersed into 0.1 M PBS (pH 7.0) containing 0.015 M pyrrole and 0.01 M DA. Subsequently, CV was performed for electrochemical polymerization of pyrrole on the CA in the potential range from −0.2 to 0.80 V at a scan rate of $100\,mV\,s^{-1}$ for 7 cycles. After that, the embedded DA was removed by scanning between −0.2 V and 0.6 V in a 0.1 M PBS for several cycles until no obvious oxidation peak for DA could be observed. Thus, the MIPPy modified electrode for DA monitoring was obtained and denoted as MIPPy/CA electrode. For comparison, the nonimprinted PPy-modified electrode was prepared using the same procedure mentioned above but without the addition of DA, and denoted as PPy/CA electrode. The film thickness modified on CA can be controlled by the electropolymerization time or cycle, and can be estimated according to the total charges passed in the cell. The film thickness with ca. 33 nm was employed in our study, unless otherwise stated.

2.3. Electrochemical measurements

Prior to measurement, the electrode was incubated in 0.1 M PBS (pH 7.0) containing DA or interferent for 10 min under stirring. Thereafter, the DPV measurement was performed in the scan range from −0.2 to 0.6 V at a scan rate of $100\,mV\,s^{-1}$. The pulse amplitude, pulse width, pulse period and quiet time were 50 mV, 0.05 s, 0.1 s and 2 s, respectively. After the measurements, the

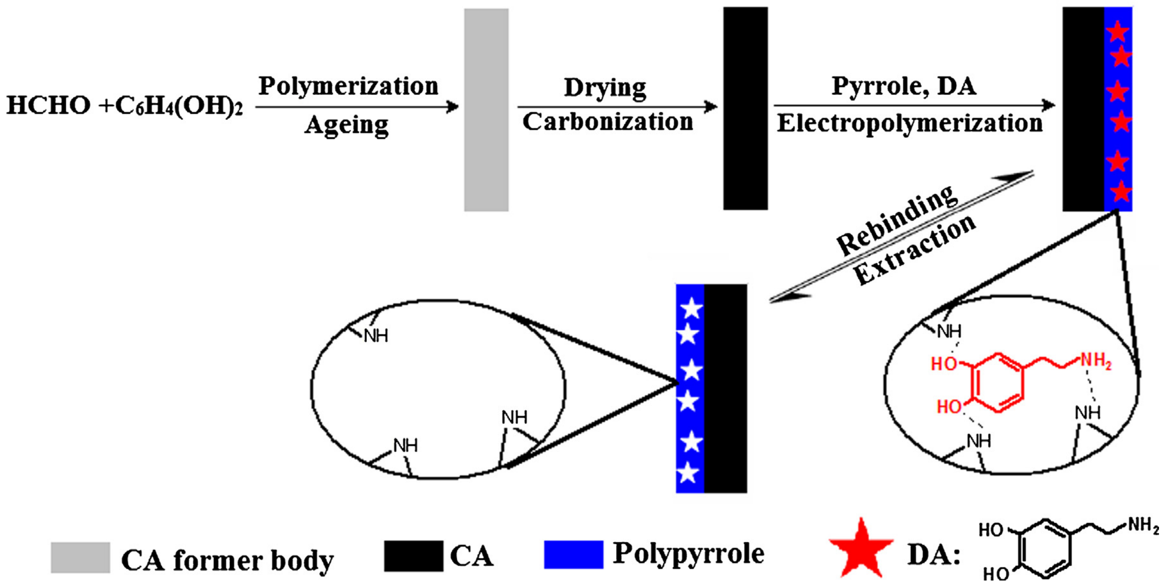

Fig. 1. Schematic representation for the preparation of the MIPPy/CA electrode.