



Electrochemical reactions of catechol, methylcatechol and dopamine at tetrahedral amorphous carbon (ta-C) thin film electrodes



Tommi Palomäki^a, Sara Chumillas^b, Sami Sainio^a, Vera Protopopova^c, Minna Kauppila^d, Jari Koskinen^c, Víctor Climent^b, Juan M. Feliu^b, Tomi Laurila^{a,*}

^a Department of Electrical Engineering and Automation, School of Electrical Engineering, Aalto University, P.O. Box 13500, 00076 Aalto, Finland

^b Instituto Universitario de Electroquímica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

^c Department of Materials Science and Engineering, School of Chemical Technology, Aalto University, P.O. Box 16200, 00076 Aalto, Finland

^d Department of Applied Physics, School of Science, Aalto University, P.O. Box 11000, 00076 Aalto, Finland

ARTICLE INFO

Article history:

Received 7 July 2015

Received in revised form 3 September 2015

Accepted 4 September 2015

Available online 10 September 2015

Keywords:

Tetrahedral amorphous carbon

Glassy carbon

Dopamine

Catechol

Polydopamine

Cyclic voltammetry

ABSTRACT

The electrochemical reactions of dopamine, catechol and methylcatechol were investigated at tetrahedral amorphous carbon (ta-C) thin film electrodes. In order to better understand the reaction mechanisms of these molecules, cyclic voltammetry with varying scan rates was carried out at different pH values in H₂SO₄ and PBS solutions. The results were compared to the same redox reactions taking place at glassy carbon (GC) electrodes. All three catechols exhibited quasi-reversible behavior with sluggish electron transfer kinetics at the ta-C electrode. At neutral and alkaline pH, rapid coupled homogeneous reactions followed the oxidation of the catechols to the corresponding o-quinones and led to significant deterioration of the electrode response. At acidic pH, the extent of deterioration was considerably lower. All the redox reactions showed significantly faster electron transfer kinetics at the GC electrode and it was less susceptible toward surface passivation. An EC mechanism was observed for the oxidation of dopamine at both ta-C and GC electrodes and the formation of polydopamine was suspected to cause the passivation of the electrodes.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Quinones are naturally occurring molecules in the human body. They can be found as free quinones, protein cofactors and in the mitochondrial electron transfer chain. Interestingly, quinones can also form toxins through electrochemical reactions, causing several cytotoxic effects in the body [1]. In addition, the electrochemistry of the catechol/quinone pair has importance in the electrochemical detection of several neurotransmitters such as dopamine and adrenaline that have a readily oxidizing hydroquinone moiety [2,3].

Dopamine (DA) is one of the most important neurotransmitters in the brain, affecting cognitive, behavioral and motor functions. Abnormal dopamine transmission has been associated with several neurological disorders such as Parkinson's disease, schizophrenia, ADHD and Huntington's disease [4]. In order to understand the underlying role of dopamine in neurological functions and diseases, it is important to accurately measure its concentration in vivo. Electrochemical sensors based on carbon materials have been used extensively in the detection of dopamine and neurotransmitters in general [5].

In vivo measurements pose several challenges: firstly, dopamine is present at very low concentrations while several other neurotransmitters,

occurring at higher concentrations, interfere with its electrochemical detection; secondly, the release and uptake of dopamine at the neuron terminals occur in rapid transients on a sub-second timescale [3]. Thus, the sensor must not only be sensitive and selective, it must also have a fast response time. Lastly, the sensor needs to be biocompatible and resistant to biofouling to remain stable and reliable during long-term implantation in living systems. The electrode material is a key factor in determining the performance of the sensor under these conditions.

Diamond-like carbon (DLC) has received increasing attention, because it has many attractive properties for electrochemical sensor applications: chemical inertness, wide potential window, low background current and excellent mechanical properties [6–8]. DLC films can be deposited at room temperature allowing the use of a wide array of substrate materials and making it compatible with modern micro- and nanofabrication processes [8]. For in vivo use, DLC has also good biocompatibility [9] and resistance to bacterial adhesion [10]. Despite its potential, only few studies have investigated the application of DLC in the detection of neurotransmitters [11–13].

Recently, tetrahedral amorphous carbon (ta-C), a form of highly sp³-bonded, undoped DLC, was shown to be able to detect dopamine and possess favorable properties to be used as a substrate for in vivo electrodes [14,15]. More importantly, it was shown that it is possible to build on top of ta-C hybrid carbon structures that exhibit very good selectivity and excellent sensitivity toward dopamine [16,17]. As ta-C

* Corresponding author.

E-mail address: tomi.laurila@aalto.fi (T. Laurila).

forms a large part of these novel hybrid electrodes it is of utmost importance to understand the physicochemical properties of ta-C thin films in contact with electrolytes and neurotransmitters. However, the electrochemical behavior of neurotransmitters at ta-C electrodes has not been investigated in-depth and the role of ta-C in the electrochemical properties of the hybrid carbon electrodes is not known precisely. Thus, this work completes our in-depth characterization of ta-C materials carried out during the last two years [14,16–21] and provides the necessary electrochemical information needed to proceed to work with the more complex hybrid carbon materials.

In this work, the electrochemical behavior of dopamine, catechol (CA) and methylcatechol (MC) was investigated at ta-C thin film electrodes. The reaction mechanisms of these molecules were studied by cyclic voltammetry (CV) with varying scan rates at different pH values in sulfuric acid and phosphate-buffered saline (PBS) solutions. Since most carbon electrodes are prone to surface fouling [22], the rate and extent of passivation of ta-C were examined by scanning several consecutive cycles with CV and analyzing the surface by X-ray photoelectron spectroscopy (XPS). The results were compared to the oxidation of these compounds at glassy carbon (GC) electrodes.

2. Material and methods

2.1. Ta-C thin film preparation

Tetrahedral amorphous carbon electrodes were fabricated on p-type Si (100) wafers (Ultrasil) with 0.001–0.002 $\Omega \cdot \text{cm}$ resistivity. A titanium interlayer was deposited before the ta-C layer to enhance adhesion. All wafers were cleaned by standard RCA cleaning procedure before the deposition. Direct current magnetron sputtering (DC-MS) and dual-filtered cathodic vacuum arc (FCVA) deposition systems were used for titanium and carbon deposition, respectively. It is to be noted that both systems are installed in one deposition chamber. Samples were placed in a rotating holder (rotational velocity used was 20 rpm). The vacuum in the chamber was pumped down by dry scroll vacuum pump (Edwards XDS10) and by a cryo-pump (Cryo-Torr, Helix Technology Corporation). In order to achieve a low vacuum, a high vacuum throttle valve was used. The DC-MS system was equipped with a circular, water-cooled magnetron sputtering source with a 2 in. Ti target (Kurt J. Lesker Company) and a DC generator (DCO2 BP). The shutter was utilized for controlling the sputtering time. Pre-sputtering of 2 min was carried out for cleaning the surface of the Ti target. Titanium interlayers were deposited under the following deposition conditions: discharge power was fixed at 100 W, total pressure was 0.67 Pa, Ar gas flow rate was 28 sccm, deposition temperature was close to room temperature and deposition time was 350 s. The FCVA system (Lawrence Berkeley National Laboratory) was equipped with a 60° bent magnetic filter for the reduction of the macroparticle contamination. Two 99.997% graphite rods (Goodfellow) with a diameter of 6.35 mm were used as the carbon cathodes and they were surrounded by a cylindrical anode. The arc current pulses had an amplitude of 0.7 kA and pulse width of 0.6 ms. Each pulse was triggered at 1 Hz frequency. The 2.6 mF capacitor bank was charged to 400 V. The number of pulses was 360. The distance

between the substrate holder and the filter was about 20 cm. Total pressure during the deposition process was no less than 1.3×10^{-4} Pa.

2.2. Cyclic voltammetry

Cyclic voltammetry (CV) was carried out with a μ Autolab type III potentiostat (Metrohm Autolab). The reference electrode was an Ag/AgCl reference electrode (+0.197 V vs SHE) (Crison Instruments) and a platinum wire was used as the counter electrode. Only new ta-C electrodes and freshly polished GC electrodes were used for each measurement. GC electrodes with a diameter of 3 mm were polished with a 0.05 μm alumina polishing suspension (Buehler) for 3 min, sonicated in distilled water for 5 min and thoroughly rinsed in distilled water before each experiment.

Catechol (Sigma-Aldrich), 4-methylcatechol (Sigma-Aldrich) and dopamine hydrochloride (Alfa Aesar, Johnson Matthey Company) were dissolved in either 0.5 M H_2SO_4 (Merck Suprapur) or 0.1 M PBS. The concentration of the catechols was always 1 mM. Neutral PBS (pH 7.2) was prepared from 0.05 M NaH_2PO_4 and 0.05 M Na_2HPO_4 (Sigma-Aldrich) and basic PBS (pH 10.8) from 0.05 M Na_2HPO_4 and 0.1 M NaOH. The pH of the H_2SO_4 solution was 0.65. pH values were measured with a Crison Basic 20 + pH-meter.

All the solutions were deoxygenated with argon for at least 10 min prior to measurements and the atmosphere in the electrochemical cell was purged during the experiments. All the measurements were conducted at room temperature. The cyclic voltammograms were recorded at scan rates of 10, 50, 200, 500 and 1000 mV/s. The peak current ratios were calculated from the baseline-corrected value of the reduction peak.

2.3. X-ray photoelectron spectroscopy (XPS)

The surface composition of the ta-C samples was analyzed with an SSX-100 ESCA in ultra-high vacuum using Al- K_{α} irradiation (1486.6 eV). The fitting of the C 1s peaks was done using three components with a mixture of 80% Gaussian and 20% Lorentzian. The first component at 284.4 eV corresponded to sp^2 carbon atoms, the second at 285.3 eV to sp^3 and the third component at 287.1 eV to other carbon bonds [23,24].

3. Results and discussion

3.1. Physical and chemical characterization of ta-C

The tetrahedral amorphous carbon (ta-C) thin films used in this study have been characterized in detail previously [14]. Here, we briefly summarize the main findings. The surface of ta-C was smooth with an average surface roughness of 1.6 ± 0.25 nm defined by atomic force microscopy (AFM). Transmission electron microscope (TEM) micrographs showed that the ta-C layer was completely amorphous and it was confirmed by X-ray reflectivity (XRR) and electron energy loss spectroscopy (EELS) measurements that the ta-C contained a high amount of sp^3 -bonded carbon.

The XPS results for ta-C are summarized in Table 1. For the ta-C samples that had not undergone cyclic voltammetry (samples 1 and

Table 1

XPS results showing the elemental composition of ta-C samples. Samples 1 and 2 are reference samples that did not undergo cyclic voltammetry. Samples 3 and 4 were scanned 10 cycles in 1 mM DA in PBS (pH 7.2) at a scan rate of 10 and 50 mV/s respectively. Samples 5 and 6 were scanned 10 cycles in 1 mM DA in PBS (pH 10.9) at a scan rate of 10 and 50 mV/s respectively.

| Sample | Element (at.%) | | | | | | | |
|--------|----------------|----------------------|----------------------|--------|--------|---------|---------|---------|
| | C (1s) | C (1s) sp^2 | C (1s) sp^3 | O (1s) | N (1s) | Ti (2p) | Si (2s) | Na (1s) |
| ta-C-1 | 7.2 | 46.7 | 32.0 | 12.0 | 1.1 | 0.29 | 0.67 | – |
| ta-C-2 | 8.0 | 48.2 | 32.1 | 9.5 | 0.95 | 0.49 | 0.71 | – |
| ta-C-3 | 9.3 | 36.0 | 24.6 | 22.7 | 6.5 | 0.07 | 0.4 | 0.3 |
| ta-C-4 | 11.1 | 34.7 | 28.1 | 19.1 | 6.1 | – | 0.4 | 0.6 |
| ta-C-5 | 10.0 | 43.5 | 21.1 | 18.2 | 4.9 | – | 0.4 | – |
| ta-C-6 | 11.1 | 28.6 | 34.6 | 18.7 | 5.8 | – | 0.2 | 0.8 |

Download English Version:

<https://daneshyari.com/en/article/701961>

Download Persian Version:

<https://daneshyari.com/article/701961>

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