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Research paper

Amorphous carbon thin film electrodes with intrinsic Pt-gradient for hydrogen peroxide detection

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ABSTRACT

Nanoscale amorphous carbon thin films with intrinsic Pt gradient show great promise as new electrode materials for electrochemical detection of hydrogen peroxide. Embedding the Pt particles in the carbon matrix during the fabrication process allows tighter integration than, for example, adding them after the fabrication on top of the substrate. Especially, this approach can offer excellent electrochemical properties combined with CMOS compatibility, which is crucial for further device development. Here we provide extensive in depth electrochemical and physicochemical characterization of these novel materials by cyclic voltammetry (CV), chronoamperometry (CA), rotating disk electrode (RDE) experiments, transmission electron microscopy (TEM), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Equipped with these detailed results on these materials we proceed to present some suggestions how the physicochemical properties correlate with the results from electrochemical measurements. (i) It is shown that coarsening of the initially very finely dispersed structure occurs both under electron bombardment during TEM imaging as well as during cyclic voltammetry in H_2SO_4. (ii) Further, it is shown that OH is adsorbed on small Pt islands much more strongly compared to the bulk Pt, which may heavily influence hydrogen peroxide redox reactions on these Pt-containing amorphous carbon films. (iii) Finally, we proceed to demonstrate that despite these complications, these materials show linear response for hydrogen peroxide reduction in neutral phosphate buffered saline combined with very fast response times.

1. Introduction

Hydrogen peroxide (H_2O_2) is a simple molecule with a high standard electrochemical potential [1] making it a powerful oxidizing agent on appropriate substrates. H_2O_2 has been proposed to be formed as a reaction intermediate in the oxygen reduction reaction [2–4] which makes it an interesting species for fuel cell research and development. In living organisms, cells produce H_2O_2 in the mitochondria to control growth and apoptosis and it might also have a key role in aging [5]. Some tumor cell lines have been suggested to be able to produce large amounts of H_2O_2 in vivo which could, for example, enhance their invasion and metastasis formation [6]. Moreover, endogenous H_2O_2 can inhibit dopamine release and have a role in the etiology of neurodegenerative disorders, such as Parkinson's disease [7]. Several oxidative enzymes such as glucose oxidase [8], glutamate oxidase [9], and cholesterol oxidase [10] produce H_2O_2 allowing the indirect electrochemical detection of their otherwise electroinactive substrate molecules. Thus, sensors for H_2O_2 detection are in demand in not only industrial but also various healthcare related applications.

Electrochemical sensors are utilized in the detection of various analytes owing to their scalable size and good temporal resolution. Noble metals, such as platinum, gold and silver, as well as their alloys, show good catalytic activity towards H_2O_2 oxidation and reduction [11–17]. Especially the mechanism for electrochemical oxidation of H_2O_2 on Pt has been studied widely by Hall, Khudaish and Hart [18–22]. Also, both H_2O_2 reduction and oxidation on polycrystalline Pt have been studied by Katsounaros et al. [23]

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Diamond-like carbon (DLC) is a carbon allotrope with high sp^3 content. The DLC family consist of amorphous carbons (a-C) and their hydrogenated alloys [24]. Tetrahedral amorphous carbon (ta-C) is the form of DLC with the highest sp^3 fraction[25]. In addition to low surface roughness [26], ta-C has good electrochemical properties, such as large water window and low background signal [27], making it suitable for sensor applications. We have previously shown that Pt can be alloyed with ta-C film to form an amorphous carbon (a-C) thin film with an intrinsic Pt islands distribution and that these thin film electrodes can detect H_2O_2 [28]. Furthermore, we showed that GluOx can be immobilized on these carbon thin film surfaces enabling the detection of glutamate [29]. Embedding Pt into the carbon matrix instead of depositing the particles on top of the substrate provides more tight integration, which can enhance the electrochemical properties. Moreover, this approach provides CMOS compatibility, which is especially important for device fabrication. Despite these initial successful steps with sensor applications, basic structural, chemical and electrochemical properties of these new materials are not unambiguously known at the moment. Especially the evolution of various structural nanosized features during electrochemical measurements and their implications to the electrochemical behavior of the materials have not been previously addressed. Hence, here we investigate in detail the electrochemical properties of a-C/Pt electrodes by utilizing cyclic voltammetry (CV), chronoamperometry (CA) and rotating disk electrode (RDE) experiments. We also present in depth characterization of these films by TEM, Raman spectroscopy, XPS and AFM as well as provide some insight about the correlations of these properties with the observed electrochemical behavior.

2. Experimental

2.1. Sample Preparation

Samples consisted of 20 nm thick underlying titanium layer and approximately 7 nm thick a-C layer gradient-alloyed with Pt. Samples with only an 8 nm thick Pt layer were fabricated as controls. Substrates were highly conductive p-type boron-doped (100) Si wafers with 0.001–0.002 Ωcm resistivity (Ultrasil, USA) or NaCl crystals (Ted Paella, Inc., USA) without Ti layer for TEM sample fabrication. Si wafers were cleaned by standard RCA-cleaning procedure before deposition.

Sample fabrication procedure consisted of direct current magnetron sputtering (DC-MS) for Ti layer and dual filtered cathodic vacuum arc (FCVA) deposition for carbon and platinum layers. Both deposition systems were installed in one chamber. The DC-MS system was equipped with a circular, water-cooled magnetron sputtering source with 2 inch Ti target. Ti layers were deposited to enhance adhesion under the following deposition conditions: discharge power was fixed at 100 W, total pressure was 0.67 Pa, Ar gas flow rate was 29 sccm, deposition temperature was close to room temperature, and deposition time was 350 s. Cathodic arc deposition system (Lawrence Berkeley National Laboratory, USA) was equipped with a 45° bent magnetic filter for reduction of macroparticle contamination and two cathodes in a dual cathode configuration. The cathodes were 6.35 mm 99.95% purity graphite (Goodfellow) and 99.99% purity Pt rods (Goodfellow). A pulse forming network (PFN) was used to strike the triggerless arc. The PFN was controlled with custom made National Instruments hardware and LabView software. To obtain Pt-doped a-C the following functions were used to control the number of pulses for carbon and Pt:

$$C\ : 50 - 0.5x^2 \quad Pt\ : 1 + 0.5x^2 \quad 0 \le x \le 9, x \in Z$$

resulting in a total of 360 pulses of carbon and 155 pulses of Pt. The functions were chosen so that on each cycle the number of carbon pulses decreases and Pt increases, giving a surface with high Pt content.

The arc current pulses had an amplitude of 0.7 kA and 0.6 ms pulse width. During the deposition, the 2.6 mF capacitor bank was charged to 400 V and pulse frequency was 1 Hz. Total pressure during the deposition process was no more than 1.3×10^{-4} Pa. The distance between the substrate holder and the filter was about 20 cm. During the depositions, the samples were at floating potential and rotation was used to ensure homogeneous film deposition (rotational velocity 20 rpm).

After deposition, the wafers were cut into rectangular chips with an automated dicing saw. Samples were stored dry at room temperature. Before electrochemical characterization and H_2O_2 experiments, circular area was defined from the sample with PTFE tape (Irpola Oy, Finland).

2.2. Physical Characterization

The sample morphology was studied with high-resolution transmission electron microscopy (HRTEM) and scanning probe microscopy (Ntegra Aura, NT-MDT Company, Russia). HRTEM was performed with Technai F20 operated at 200 kV. The samples deposited on the NaCl crystals were dissolved in water and subsequently deposited on TEM grids. Scanning probe microscopy, operated in ambient atmosphere, was used for atomic force microscopy (AFM). The measurements were carried out in 'scanning by sample' mode in contact mode with a Si tip (NSG01, NT-MDT Company, Russia) which had typical curvature and typical force constant of 6 nm and 5.1 N/m, respectively. Obtained topography maps were processed with Matlab.

Visible Raman spectroscopy for the ta-C and Pt-doped samples was performed with LabRAM HR (Jobin Yvon Horiba). An argon laser with λ=488 nm (power 10 mW) and BX41 (Olympus) microscope and 100 x objective lens with a spot size of less than 1 μm was used. The I(D)/I(G) ratio was found by fitting a double Gaussian fitting function. The I(D)/I(G) ratio is known to correlate with the sp^2/sp^3 fraction and the density of the film [24,30].

XPS was carried out with Kratos ULTRA electron spectrometer (Kratos Analytical, Manchester, UK) using monochromated Al Kα X-ray irradiation at 100 W. Samples were measured after overnight pre-evacuation using ash-free cellulose filter paper as *in-situ* reference material [31]. Fitting of the high resolution data was done assuming Gaussian lineshapes. The binding energies (BE) were calibrated by using C 1 s at 285.0 eV as the reference [32]. Pt was fitted into two doublets by using predefined BE split and predefined Pt 4f 7/2:5/2 split ratios.

2.3. Electrochemical Measurements

Electrochemical experiments were performed with a Gamry Reference 600 potentiostat (Gamry Instruments), CHI 630E potentiostat (CH Instruments, Inc.) or a digital recorder (eDAQ ED401) and a potenciostat (Edaq EA161) coupled to a signal generator (PAR 175). In rotating disk electrode experiments with a Radiometer Analytical rotating motor (Model EDI101) was utilized. Reference electrode was a Ag/AgCl/KCl sat'd electrode (+0.199 vs. SHE, Radiometer Analytical) and counter electrode a carbon rod or a Pt wire.

In order to clean the samples, they were first subject to potential cycling in nitrogen purged and blanketed 0.15 M H_2SO_4 (diluted in deionized water with resistivity of 18.2 MOhm cm from Merck Millipore Emsure 95-97% H_2SO_4) for at least 100 cycles between −0.2 V and 1.2 V vs. Ag/AgCl with 1 V s^{-1}. Electrochemical