Electrochemical Detection of Hydrogen Peroxide with Ferrocene-Immobilized Diamond Electrodes

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Conductive boron-doped diamond (BDD) thin film has been expected as an alternative electrode material for elecrtoanalysis, due to its attractive properties; wide potential window, low background current, as well as physical stability and chemical inertness. Thus, high-sensitive analytical results have been reported for many types of electro-active species, from metals to bio-related organic compounds. In order to expand the applicability for electroanalysis of BDD electrodes, immobilizing functional materials, such as catalytic metals, metal oxides and enzymes, on the surface have been investigated. As is generally known, as-prepared CVD diamond surfaces are hydrogen-terminated, and the surfaces can be oxidized with various oxidation treatments to form oxygen-containing surface functionalities. The functionalities on diamond surfaces are considered to exhibit some reactivity comparable to those of organic compounds, thus they can be used for generating covalent bonds to immobilize functional molecules. In this study, ferrocene, which has been known as a good electron mediator, was covalently immobilized on BDD electrode surfaces, and the properties for a hydrogen peroxide sensor were investigated.

BDD thin films were prepared on n-type highly-conductive silicon wafer substrates by means of microwave plasma-assited (MP) CVD method. The carbon source was a mixed solution of acetone and methanol (9:1, v/v), with dissolved B_2O_3 (10,000 ppm B/C atomic ratio). Oxidation of BDD surfaces were carried out by employing a laboratory-made UV-ozone cleaner, which consists of a chamber to fill oxygen gas with a low-pressure Hg lamp. Immobilization of ferrocene derivatives were achieved with esterification between ferrocenecarboxylic acid and hydroxyl group on UV-ozone treated (50 min.) BDD surfaces with dicyclohexylcarbodiimide (DCC) method. For electrochemical measurement, a conventional elecrtrochemical glass cell with a Pt wire and an Ag/AgCl electrode as a counter and reference electrodes, respectively, was used. Voltammetry was carried out using a digital potentiostat.

In order to immobilize ferrocene to BDD surfaces, as-prepared, hydrogen-terminated, surfaces were oxidized to generate hydroxyl group by UV-ozone treatment. Figure 1 shows a treatment time dependence of O/(O+C) atomic ratio estimated by XPS analysis. Oxygen atomic concentration on the as-prepared surface was found to be ca. 5 %. After UV-ozone treatment for 10 min., the concentration remarkably increased to ca. 18 %, and the value was found to be almost constant up to 60 min. (15-20%). These values and the behavior are very similar to those seen in the reports involving other oxidation methods. Constant O/(O+C) ratio might show full coverage of oxidation species on the diamond surface. Therefore, in the present case, more than 10 min. of UV-ozone treatment should be sufficient to form oxygen-containing functionalities.

Immobilization of ferrocene on BDD surface was confirmed with XPS, and the electrochemical properties were investigated. Figure 2 shows LSV for 0.1 M Na_2SO_4 at ferrocene-immobilized BDD in the presence of 10 mM H_2O_2. Cathodic current in the potential region more negative than –0.2 V vs. Ag/AgCl was found to increase with addition of H_2O_2 to the electrolyte, and a shoulder peak was observed at ca. -0.6 V vs. Ag/AgCl. These features indicate that the cathodic current was based on the reduction of H_2O_2. Ratio of the cathodic current at -0.6 V vs. Ag/AgCl to the background was found to be 5.3, while the values were 1.2 and 1.6 at the as-prepared and the UV-ozone treated (oxidized) BDD electrodes, respectively. That implies the catalytic property of ferrocene for reduction of H_2O_2, and applicability of the ferrocene-immobilized BDD electrode to an electrochemical H_2O_2 sensor.

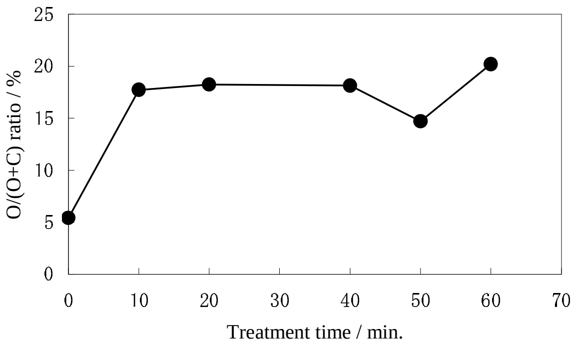

Fig. 1 O/(O+C) atomic concentration ratio of UV-ozone treated BDD surfaces for various treatment time. The atomic concentration was estimated from C1s and O1s XPS peak area.

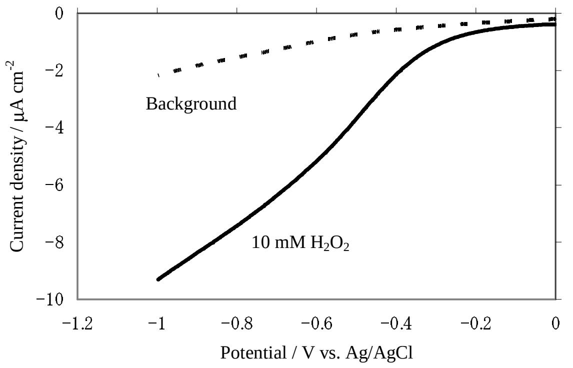

Fig. 2 LSV for 10 mM H_2O_2 in 0.1 M Na_2SO_4 at a ferrocene-immobilized BDD electrode. Broken line represents the background (0.1 M Na_2SO_4).