Electrochemical Deposition of metal nanoclusters on Diamond Electrode for Electroanalytical Applications

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Electrochemical detectors have been widely used in flow injection analysis (FIA) and HPLC systems. Electrochemical detectors for these systems are usually equipped with glassy carbon electrode. However, there are several analytes, which are not electroactive at this electrode. Metal electrodes or metal-modified carbon electrodes have been adopted for the analysis of a large number of chemical species. Copper has emerged as a unique electrocatalyst for the analysis of several kinds of species. Nucleotides, amino acids, carbohydrates and oxalic acid were successfully analysed combining IC, CE and HPLC with amperometric detection at copper electrode. Similarly, Iridium metal has been known to be excellent electrocatalyst for H_2O_2 reduction especially in reduction mode. Dispersion of metallic particles into organic polymer or simply on an inert surface results in a drastic increase in the catalytic activity and sensitivity of the electrode. A stable inert electrode with low background current is the best choice for the deposition of metal electrocatalysts. The widely used glassy carbon electrodes lack some of these requirements with additional problems such as weak adherence of the metal particles to the substrate. Conductive diamond films appear to be best suited to overcome these problems to a greater extent. Diamond is excellent substrate especially for electrodeposition of nanoparticles because the nucleation cites are randomly distributed on the diamond surface

Highly boron-doped diamond thin films were deposited by use of a microwave plasma chemical vapor deposition system on silicon (100) wafers. A film thickness of approximately 40 μm was achieved after 10 hours deposition. Cu-modified diamond was prepared by single step potentiostatic deposition of Cu on diamond surface in 50 mM H_2SO_4 solution containing $CuSO_4$. The deposition was carried out at -0.12 V vs SCE for 22 min at -0.25 V for 1 min. Prior to copper modification, the diamond surface was pretreated electrochemically at +2.0 V (vs SCE) for 1 hour in 0.1 M NaOH solution. Ir was electrochemically deposited on anodically treated diamond surface at -0.9 V vs SCE in 0.1 M acetate buffer (pH, 5) containing Ir solution.

Figure 1 shows the SEM image of Cu-modified diamond. Cu metal nanoparticles were randomly grown on diamond surface at specific sites. When concentration of $CuSO_4$ was increased, while the deposition time was reduced to a few seconds, the growth of the copper started from these nucleation sites and grown like flowers. In case of Ir, the metal nanoparticles were deposited mainly at the grain boundaries. Figure 2 shows the hydrodynamic voltammograms at copper-modified diamond electrodes for several carbohydrates. All the carbohydrates exhibited good current response. The sensitivity of these electrodes was found to be much higher in comparison to bulk copper electrode. Similarly, Ir-modified diamond electrodes exhibited excellent sensitivity for H_2O_2 reduction at -0.14 V vs SCE and no interference of ascorbic acid or uric acid were observed at this potential. These results indicate the promising use of metal-modified diamond electrode in electroanalysis.

Figure 1. SEM image of Cu-modified diamond electrodes

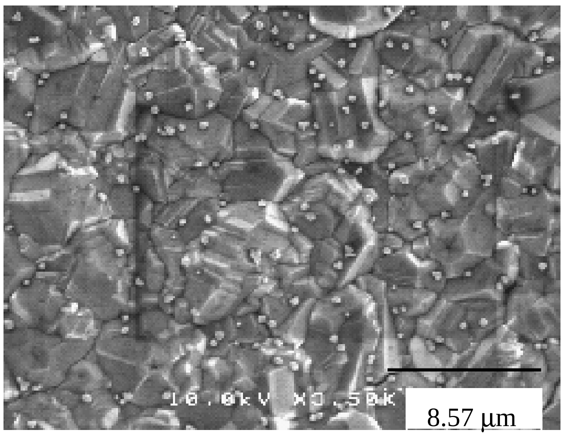

Figure 2. Hydrodynamic voltammograms obtained by flow injection analysis with electrochemical detection for various carbohydrates at Cu-modified diamond electrode. The mobile phase was aqueous 0.1 M NaOH.