Metal-Modified Diamond Electrode as an Electrochemical Detector for Glucose

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Nickel- and copper-modified diamond electrodes were fabricated in view of their application for carbohydrate detection. Both electrodes produced well-defined and reproducible voltammograms for 1 mM glucose in alkaline media. These electrodes exhibited excellent electrochemical stability with low background current for at least one week in a flow injection analysis system, indicating good adherence of the metal clusters to diamond. These results indicate the promising use of nickel- and copper-modified diamond electrodes for the detection of carbohydrates and amino acids.

Electrochemical detection of carbohydrates is very attractive due to the possibility of high sensitivity and wide dynamic range. Metal electrodes such as nickel and copper are known to oxidize carbohydrates in alkaline solution.[1] The advantage of Ni and Cu electrodes is that they produce quite stable responses. These electrodes have been widely used in liquid chromatography and capillary electrophoresis.[1] However, dispersion of metallic particles within an organic polymer or simply on an inert surface results in a drastic increase in the catalytic activity and sensitivity of the electrode.[2–4] A stable, inert electrode with low background current would be the best choice for the deposition of metal electrocatalysts. Glassy carbon (GC) electrodes lack some of these requirements, with additional problems such as weak adherence of the metal particles to the substrate.[2] Conductive diamond films appear to be well suited to overcome these problems.

Highly boron-doped diamond (BDD) electrodes are known to be superior to conventional GC electrodes in electroanalysis due to the wide electrochemical potential window, low background current and negligible adsorption of chemical species on the electrode surface.[5,6] Like other carbon electrodes, diamond is very inactive for the oxidation of glucose and other carbohydrates. These properties make diamond a good substrate for modification with metal catalysts. In this study, we introduce nickel- and copper-modified boron-doped diamond electrodes (Ni-BDD, Cu-BDD) and examine them for electrochemical detection of glucose by cyclic voltammetry and flow injection analysis with electrochemical detection (FIA-ED).

The boron-doped diamond thin films were deposited on conductive silicon wafers by use of microwave plasma chemical vapor deposition (MPCVD). The details of the deposition procedure were reported earlier.[6] The deposited films were highly crystalline, as determined by Raman. Ni-BDD was prepared by depositing 100 µL of 10 mM $Ni(NO_3)_2$ solution on the surface of the BDD, drying at 30 °C for more than 8 h and washing with purified water. The electrode was electrochemically conditioned in 0.2 M NaOH by cycling the potential between 0.0 and +0.8 V (vs SCE) until no further increase in the anodic peak current at +0.48 V vs SCE was observed. The significance of this peak is discussed below. Cu-BDD was prepared by single step potentiostatic deposition of Cu on the diamond surface in 50 mM H_2SO_4 solution containing 1 mM $CuSO_4$. The deposition was carried out at –0.12 V vs SCE for 22 min. Prior to copper modification, the diamond surface was pretreated electrochemically at +2.0 V (vs SCE) for 1 h in 0.1 M NaOH solution. Such an oxidative pretreatment was necessary to achieve strong adherence of Cu particles. Oxidative treatment is known to improve the adherence of the diamond surface by making it to hydrophilic.[7] In the case of Ni-BDD, this treatment showed no effect. The amount of metal deposited on the diamond surface was estimated to be 25 µg/cm^2 for Ni and 30 µg/cm^2 for Cu.

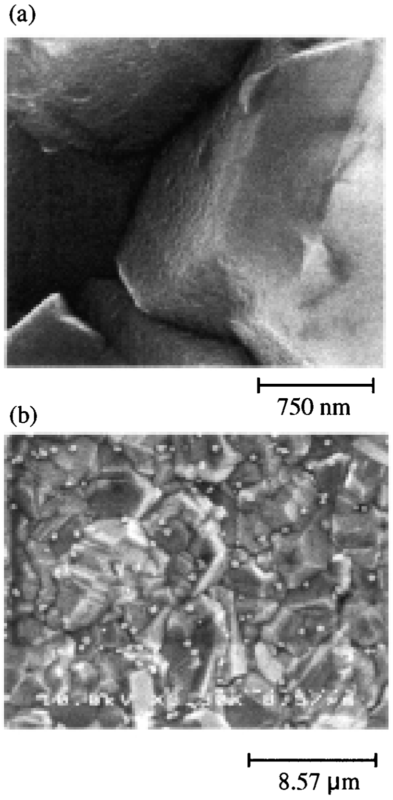

Figure 1. SEM images of (a) Ni-BDD, and (b) Cu-BDD.

Figure 1 shows scanning electron microscopic images of (a) Ni-BDD and (b) Cu-BDD. This figure clearly shows the partial coverage of Ni and Cu on the diamond surface. In the case of Ni-BDD, the metal appears to have completely covered some facets of the diamond grains in the film, indicating that certain faces are more active than others for nickel deposition. These Ni films appear to be continuous and relatively rough in comparison to the unmodified surface. The presence of Ni on diamond was further confirmed by XPS spectra which showed a sharp peak at a binding energy 855 eV corresponding Ni $2p_{3/2}$. However, in the case of Cu-BDD, the copper electrodeposited randomly as small spherical particles with an average diameter of 250 nm. These particles are dispersed both at the grain boundaries and on the facets. This shows that the active sites for Cu nucleation are inhomogeneously distributed on the diamond surface. Irrespective of the differences in the deposition patterns, both metals cover the diamond surface discontinuously, which is an advantage, which can lead to minimization of the background current and noise and thus improvement of the sensitivity.

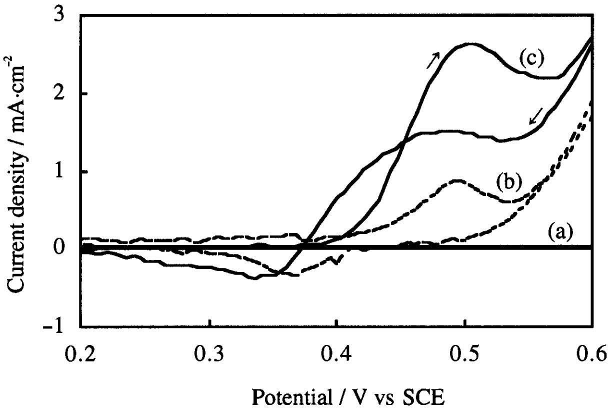

Figure 2. (a) Cyclic voltammogram for 3 mM glucose at bare BDD in 0.2 M NaOH; (b) background voltammogram at Ni-BDD in 0.2 M NaOH; (c) cyclic voltammogram for 3 mM glucose at Ni-BDD in 0.2 M NaOH. The potential sweeprate was 100 mV/s.

Figure 2a shows a cyclic voltammogram obtained for a bare diamond electrode in 0.2 M NaOH solution containing 1 mM glucose. No Faradaic response was observed within the potential window. Furthermore, the background current was very low, as mentioned previously. However, Ni-BDD produced a peak-shaped voltammogram even in the absence of glucose, as shown in Figure 2b. As previously reported,[1,2] the anodic and cathodic peaks at +0.48 and +0.36 V vs SCE, respectively, can be attributed to the Ni (II)/Ni(III) couple. A significant increase in the anodic peak current at +0.48 V is observed in the presence of 3 mM glucose (Figure 2c). The voltammograms obtained in the presence of glucose were very reproducible. The voltammetric response of Cu-BDD is very similar to that of Ni-BDD, except that the oxidation occurs at 0.58 V vs SCE.

The presence of a metal oxide/hydroxide film with two different oxidation states at the metal surface appears to be a prerequisite for the electrooxidation of glucose.[8] In the case of Ni-BDD, Ni(III) acts as a strong oxidant, reacting with the organic compound in a rate-limiting step by abstraction of a hydrogen atom to yield a radical. Further reaction of the radical with additional surface sites results in product formation. A similar mechanism applies to the Cu-BDD electrode.

Figure 3 shows the amperometric response of Ni-BDD for 20-µL injections of 1 mM glucose in 30 mM NaOH solution, with 30 mM NaOH as the mobile phase. A highly reproducible response, with a peak variability less than 3% (n = 11) was observed. The operational potential of +0.45 V vs Ag/AgCl was selected from the hydrodynamic voltammogram for these measurements. In the case of Cu-BDD the operational potential was +0.625 V. The background current for Ni-BDD in Figure 3 is as low as 100 nM, which enables the detection of glucose to be carried out with high sensitivity. This value is at least one order of magnitude lower than that for the bulk Ni electrode, with the response for glucose also being higher for the modified diamond electrode. Both Ni-BDD and Cu-BDD showed excellent stability for one week with regular use. Experiments to examine long-term stability are in progress. Under similar conditions, metal-modified GC electrodes were stable only for one day due to adherence problems. Thus, diamond appears to provide a highly suitable substrate for metal modification. However, it should be noted that highly alkaline conditions (pH ≥ 12) are necessary to achieve high sensitivity.

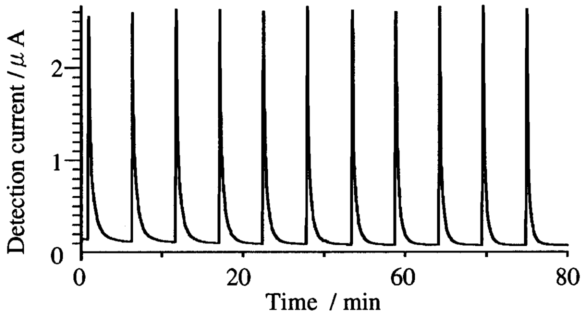

Figure 3. Amperometric response of a Ni-BDD for repetitive injections of 1 mM glucose in a flow injection analysis system. The mobile phase was 30 mM NaOH, and the applied potential was +0.45 V vs Ag / AgCl.

The aim of this letter is to present the advantages of diamond as an inert substrate for metal modification and use in the detection of glucose and other carbohydrates. The notable points about these electrodes are the strong adherence of the metal to the substrate, high sensitivity and excellent stability. Furthermore, diamond, being resistive to corrosion, can be reused by cleaning the electrode by ultrasonication and redeposition of the metal. Such experiments with several cycles of metal deposition on the same diamond electrode were successful in our laboratory.

References

1 W. Buchberger, *Fresenius' J. Anal. Chem.*, **354**, 797 (1996).
2 I. G. Casella, E. Desimoni, and T. R. I. Cataldi, *Anal. Chim. Acta*, **248**, 117 (1991).
3 J. M. Zadeii, J. Marioli, and T. Kuwana, *Anal. Chem.*, **63**, 649 (1991).
4 P. F. Luo and T. Kuwana, *Anal. Chem.*, **66**, 2775 (1994).
5 T. N. Rao and A. Fujishima, *Diamond Relat. Mater.*, **9**, 384 (2000).
6 T. N. Rao, I. Yagi, T. Miwa, D. A. Tryk, and A. Fujishima, *Anal. Chem.*, **71**, 2506 (1999).
7 I. Duo, P-A. Michaud, W. Haenni, A. Perret, and Ch. Comninellis, *Electrochem. Solid-State Lett.*, **3**, 325 (2000).
8 M. Fleischmann, K. Korinek, and D. Pletcher, *J. Electroanal. Chem.*, **31**, 39 (1971).