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Gold-nanoparticle-dispersed Boron-doped Diamond Electrodes for Electrochemical Oxidation of Oxalic Acid

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Electrochemical behavior of gold-nanoparticle-dispersed diamond electrodes have been studied for the oxidation of oxalic acid in phosphate buffer solution. Comparison is made with gold, as-deposited diamond and gold-implanted diamond. The electrodes combine the high catalytic activity of gold and the low background current of diamond electrodes. Moreover, the electrodes can overcome the problem of stability as it is found when using other electrodes.

Metal modification of highly boron-doped diamond (BDD) electrodes has attracted much attention since it had been reported that dispersion of metallic particles within an inert surface caused drastic increase of the catalytic activity and sensitivity of the electrode.[1] The preparation by using chemical precipitation, electrochemical deposition, and ion implantation has been reported.[1–4] Electrocatalytic activities of gold nanoparticles (Au-np) dispersed on Au, Pt, glassy carbon, and BDD electrodes toward O_2 reduction have been also recently investigated. Some reports have demonstrated notably high electrocatalytic activities towards oxygen reduction in acidic solution of electrochemically deposited Au-np on polycrystalline Au and BDD.[5–7] Yagi et al. has suggested that physical deposition could be more appropriate technique than electrochemical deposition to prepare small and homogeneously dispersed Au-np on a BDD surface.[5]

On the other hand, the urinary level of oxalic acid (OA) has long been recognized as an important indicator for the diagnosis of renal stone formation. OA oxidation has been studied at some electrode materials. Most of the investigations have been carried out at the Pt electrode. However, for the wealth of experimental evidence, as well as adsorption and fouling problems of Pt electrode, interest was also addressed to other metals like Pd and Au.[8,9] This present work is focused on electrochemical observation of gold-np-dispersed-BDD (Au-np-BDD) fabricated by physical deposition (laser ablation method) and gold-implanted BDD (Au-i-BDD) for the oxidation of oxalic acid.

BDD electrodes were deposited on Si(100) wafers in a microwave plasma-assisted chemical vapor deposition (MPCVD) system (ASTeX Corp.) Detail of the preparation has been described elsewhere.[10] A mixture of acetone and methanol in the ratio of 9:1 (v/v) was used as the carbon source. B_2O_3, as the boron source, was dissolved in the acetone–methanol solution at B/C atomic ratio of 1:100.

The apparatus for Au-np formation used in this work consists of laser-ablated Au-np source, as it has been described in detail elsewhere.[11] Generation of Au-np was performed by a Nd^{3+}:YAG laser (532 nm) focused onto a rotating Au disk. Then, Au-np was formed by cooling the plasma with helium atmosphere (2.5 kPa). The Au-np was transported into low pressure differential mobility analyzer (LPDMA),[12] which enables us to select the size of nanoparticles in diameter (1–10 nm). In this study, Au-np of ≈4.6 nm in diameter is homogeneously deposited on the BDD substrate in the spot size of $3\,\mathrm{mm}\phi$, deduced from TEM images of the same deposition method at amorphous carbon substrate (data is not shown). The spot consists of total 4×10^{-11} gold particles.

Au-i-BDD were fabricated by implantation method with 750 keV Au^+ with a dose of $5 \times 10^{14}\,\mathrm{cm}^{-2}$ (Tandetron 4117-HC, HVEE) by using Au rods as targets. Annealing process was performed at 850 °C for 30 min in an H_2 ambient (80 Torr).

The presence of Au on BDD surface for both Au-modified electrodes was further confirmed by XPS spectra (data is not shown), with clear peaks at binding energy of 84 and 87 eV corresponding to Au $4f_{7/2}$ and Au $4f_{5/2}$, respectively.

Electrochemical behavior of the electrodes was investigated for OA oxidation in phosphate buffer solution (PBS) pH 7. Figure 1 shows cyclic voltammetric (CV) responses of 100 μM OA at Au-np-BDD recorded along with the CVs at gold metal (Au), as-deposited BDD (AD BDD), and Au-i-BDD. A well-defined peak was observed at the potential of 1.3 V (vs Ag/AgCl) at Au-np-BDD. This potential is relatively similar to the oxidation potential at Au-i-BDD (1.3 V) and at as-deposited (AD) BDD (1.2 V) than at Au metal bulk (0.8 V).

Recently, our group had reported that the OA oxidation at BDD electrodes strongly influenced by its surface termination.[13] At anodically oxidized (AO) BDD with O termination, repulsion phenomenon between oxygen surface and relatively negative charge of OA molecule blocked the oxidation reaction, resulting in higher potential and lower current than those at AD BDD (mainly has H-termination as it is deposited in H_2 plasma). It was reported that since the OA oxidation at AD BDD occurred at extremely high potential (≈1.2 V vs Ag/AgCl in pH 7) the

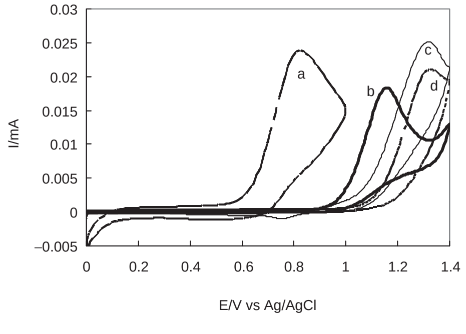
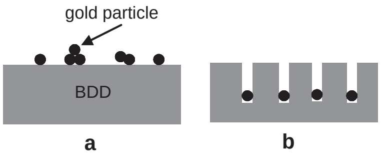


Figure 1. Cyclic voltammograms of 100 μM oxalic acid in 0.1 M phosphate buffer solution pH 7 at gold (a); as-deposited BDD (b); gold-nanoparticle-dispersed BDD (c) and gold-implanted BDD (d); data obtained in 100 mV s^{-1} scan rate.

surface termination was gradually oxidized to O termination after several cycles. As the consequence, oxidation potential shifted to more positive potential followed by the decreasing of oxidation current.[13] Similar effect was observed at Au-i-BDD, whereas at Au-np-BDD the OA oxidation responses remained in relatively stable potential and current, cycle to cycle. This is probably due to the position effect of gold particles, which are embedded deeply in near surface of Au-i-BDD ($\approx$200 nm depth; deduced with TRIM computer code) but deposited on the real surface of Au-np-BDD as shown in Scheme 1. It is considerable that repulsion and attraction effect of BDD surface is less at Au-np-BDD than at Au-i-BDD which has relatively wider surface area. However, the repulsion effect contributed by originally O-partial termination at BDD surface cannot totally be negligible as it is shown by the high potential of OA oxidation at all BDD and modified BDD electrodes. The stability of current responses at Au-np-BDD is shown by RSD of $\approx$5% for 10 cycles.



Scheme 1. Position image of gold particles at a gold-nanoparticle-dispersed BDD (a) and a gold-implanted BDD (b).

The pH dependence of the voltammetric peak current (Figure 2) shows the same behavior for Au-np-BDD and AD BDD, i.e., the peak potentials shifted linearly to more negative potentials with increasing pH, then remained at stable potential after pH 5, whereas at AO BDD the peak potentials continuously shifted to more negative potentials until pH 10.

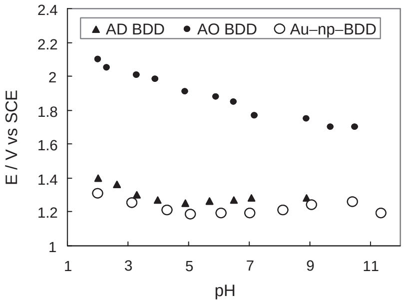


Figure 2. Plots of oxidation potentials of 100 μM oxalic acid in 0.1 μM PBS at as-deposited (AD) anodically oxidized (AO) and gold-nanoparticle-dispersed (Au-np-) BDD electrodes obtained at different pH.

Scan rate dependence at all electrodes shows that oxidation is controlled by adsorption mechanism. Johnson et al. proposed that OA oxidation mechanism at gold electrode was controlled by an anion adsorption with decarboxylation as the rate-determining step.[14] Referring to BDD electrodes, Comninellis et al. proposed a mechanism confined nearby the electrode surface, hydroxyl radicals could react with the organic substrate in solution.[15] Detailed mechanistic studies for OA at Au-np-BDD electrodes will be conducted in the future.

Furthermore, although the working potential window for the Au-np-BDD remained essentially the same as that for the Au metal, a very low background current is observed at Au-np-BDD electrode ($\approx$3.0 μA), which is much lower than that at Au electrode ($\approx$11 μA). The very low background current exhibited the improved signal-to-background current ratio (S/B) to be $\approx$3.5 times higher at Au-np-BDD than that at Au (Table 1). It seemed that with lower oxidation peak potential and considerably same S/B ratio, the use of AD-BDD would be more beneficial than Au-np-BDD. However, Au-np-BDD offers more advantage with its much higher stability[13] since at the modified electrodes Au particles give also contribution to the OA–electrode interaction.

Table 1. Comparison of potential, signal, background current and the S/B ratio of oxidation 100 μM oxalic acid in 0.1 M PBS at some electrodes

	E (V vs Ag/AgCl)	S (μA)	B (μA)	(S/B)
Au	0.8	23	11	2.1
As-deposited BDD	1.2	19	2.2	8
Au-np-BDD	1.3	25	3.0	7.3
Au-i-BDD	1.3	14	2.2	6

Finally, analytical performance was investigated by linear dynamic range, which is linear for concentration from 10 to 100 μM ($n = 5$). The lowest experimental detection limit was estimated to be 135 nM (by $S/N = 3$), which was $\approx$16 times lower than that of Au metal.

The aim of this letter is to present that metal clustered, especially gold-nanoparticle-dispersed diamond electrode deposited by laser vacuum, could be successfully used for electroanalytical purpose. The notable point is the importance of considering metal-modified position to overcome the stability problem of H-termination. As it is already known that H-termination surface strongly affects oxidation of negatively charge molecules, in this case oxalic acid, at diamond surface.

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