

Electrochemical Treatment of Metal Compounds at Conductive Diamond Electrode

~ Fabrication for Metal Nano-Cluster ~

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Introduction

The as-deposited diamond surface is terminated by hydrogen atom, however the termination atoms can be changed by the surface treatment i.e. the anodic oxidation and the chlorination with the UV radiation under chlorine atmosphere. It is well known that on diamond surface, by introducing the oxygen contained functional groups, the negative electric field can be generated and it gives the repulsive force to the compounds with negative charge in process of electrochemical reaction^{1,2}. The purpose of this study is to isolate metal nano-particles reductively generated on the electrode, by controlling of this electrostatic repulsive force. Moreover the nano-cluster fabrication will be applied to the electrochemical treatment of the organometallic complex. The ligand of the organometallic complex was decomposed at anode and the center metal was recovered at cathode as nano-particles.

Experimental

(1) The pretreatment of the oxygen-termination was performed by keeping the constant voltage at 4 V vs. Ag/AgCl for 30 min. in 0.1 M H₂SO₄. The reduction precipitation treatment was carried out with cyclic voltammetry in 1 mM copper sulfate. The dependence of the composition of metal particle on the supporting electrolyte was examined. (2) The same reduction treatment and deposition were performed for Cu-EDTA solution.

Results

Although the stripping peak for copper was obtained near 0 V vs. Ag/AgCl on the hydrogen-terminated diamond electrode, the peak was not obtained on the electrode after anodic oxidation treatment surface. This result is considered that the reduced Cu⁰ is peeled off from the oxygen-terminated electrode surface. In case of used 0.1 M Na₂SO₄ as the supporting electrolyte, many copper particles were generated on the surface of the electrode after continuous potential cycling for 10 hours. The electric contact with the particles generated in 0.1 M Na₂SO₄ is so weak that the nano-particles can be easily peeled off by to wash in ultrasound bath. On the other hand, the particles were not obtained on the electrode surface in used 0.1 M KCl as supporting electrolyte, however the nano-particles were confirmed in solution side. The diameters of particle in Na₂SO₄ and KCl were 2 μm and 200 nm, respectively (Fig. 1 and Fig. 2). A cause of the decrease in the particle size might be attributable to the minus ions of the supporting electrolyte.

The same phenomena could be obtained for the electrochemical treatment of the organometallic complex, even in the co-existence of the ligands. The size of the copper particles was drastically decreased to approximately 10 nm in diameter, and the particles could be peeled off from the electrode surface both in Na₂SO₄

and KCl. Moreover the anodic peak for the oxidation of EDTA (> 1 V vs. Ag/AgCl) was observed, suggesting that the ligand could be oxidized (Fig. 3). These results indicate that there is possibility to electrochemically treat the persistent Cu-EDTA by the recovery of the center metal at cathode as nano-cluster and the oxidation of the ligand of the organometallic complex at anode.

References

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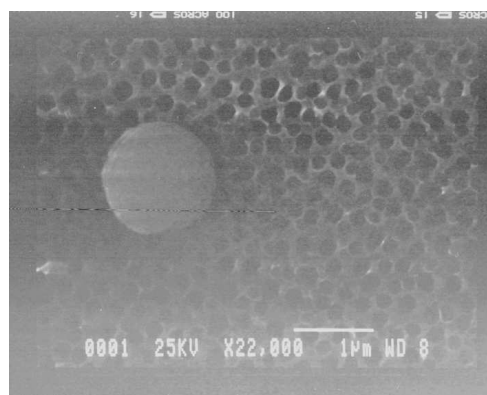


Fig. 1. The SEM image of the copper particle after 10 hrs. potential cycling in aqueous CuSO₄ (1 mM, 0.1 M Na₂SO₄).

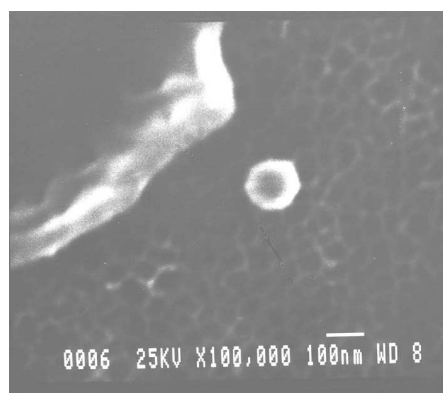


Fig. 2. The SEM image of the copper particle after 10 hrs. potential cycling in aqueous CuSO₄ (1 mM, 0.1 M KCl).

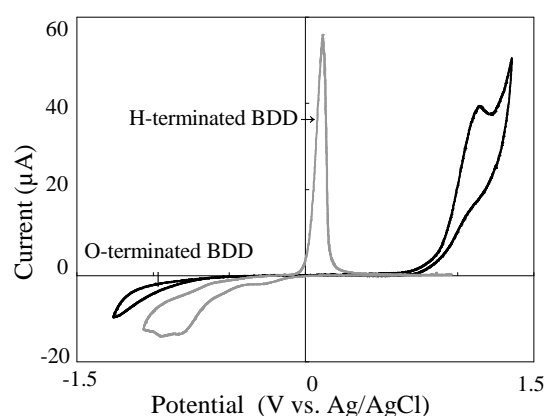


Fig. 3. Cyclic voltammograms in 1 mM Cu-EDTA (0.1 M KCl) at a potential sweep rate 20 mVs⁻¹ on the BDD electrode.