

Electronic supplementary materials

Fabrication of an all-diamond microelectrode using chromium mask

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Experimental details.

BDD microelectrodes were prepared by growing BDD thin films on tungsten wires. Initially, the 100 μm diameter tungsten wires were electropolished in a solution of 2 M KOH to achieve a conical shape (ca. 20 μm in diameter at the tip). The BDD films were deposited on the tungsten wires using a 2.45 GHz microwave plasma-assisted chemical vapor deposition system (Model AX5250M, ASTeX, Inc., USA) with plasma power of 3.0 kW and deposition pressure of 60-75 Torr for 1-3 hours. The mixture of acetone and trimethoxyborane (B/C = 1%) was used as carbon source. Trimethoxyborane was not added to the carbon source for UDD deposition.

Cr electrodeposition was conducted in conventional Sargent bath: 250 g/L chromium trioxide and 2.5 g/L sulfuric acid. Constant current was applied to BDD microelectrode with platinum counter electrode. Bath temperature was controlled by circulating water through water jacket type glass (200 mL) using CW-05G (Lab Companion, Korea). Insertion of microelectrode to the bath was monitored by microscope connected to PC. Manipulators (NARISHIGE, Japan) were used for the positioning of microelectrode and microscope. Cr mask was removed by chronoamperometry in three electrode system of Ag/AgCl (sat. KCl) reference and platinum counter electrode.

Electrochemical procedures were conducted by ALS 852 C (CH Instruments, Inc., USA). Aqueous solutions were prepared using ultrapure water supplied from DIRECT-Q 3 UV (Merck Millipore Corporation) with a specific resistivity of 18.2 M Ω cm. Each step of electrode fabrication was evaluated by observing the electrode tip using scanning electron microscope (SEM, JCM-6000 Plus, JEOL, Japan) and Raman spectrometer (Acton SP2500, Princeton Instruments, U.S.A.). Raman spectra was obtained under excitation at 532 nm from a green laser diode.

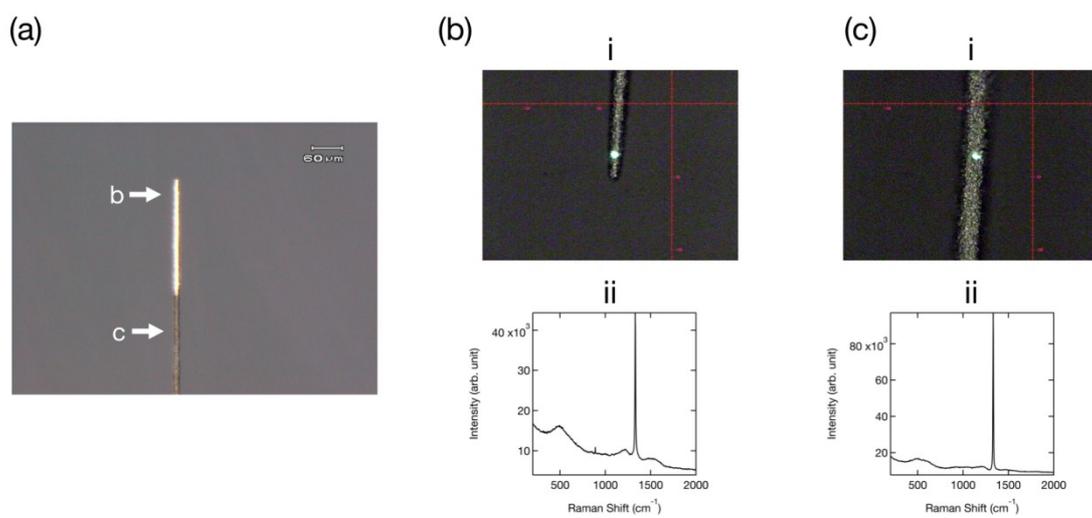


Figure S1. (a) Picture of BDD microelectrode masked by Ni on the tip. Tip (b) and body (c) were evaluated after UDD deposition by Raman spectroscopy. (i) show the observation spot and (ii) are the Raman spectra at each spot.

(a)



(b)



Fig. S2 Cr electrodeposition was conducted in convex-shaped Sargent bath in order to obtain still surface (a). Water droplets appeared on the electrode tip when the bath temperature was 50°C (b). Experiment in (b) was conducted using water.

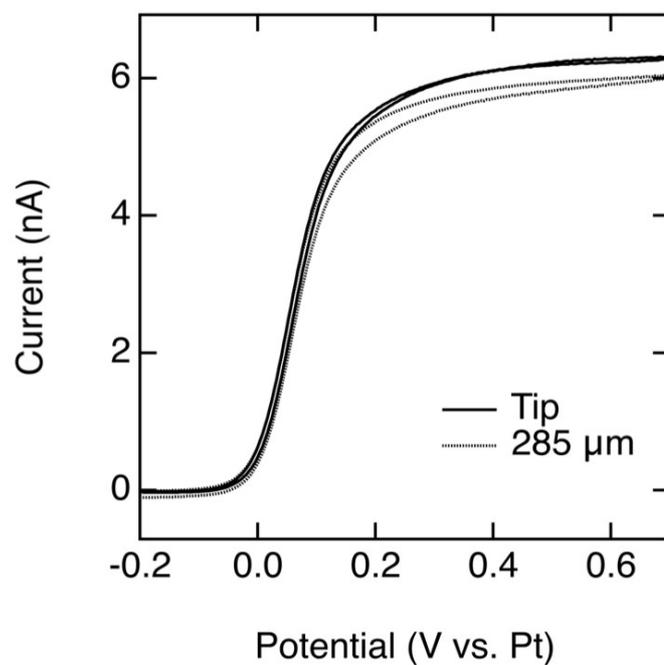


Fig. S3 Cyclic voltammograms of 1 mM $K_4[Fe^{II}(CN)_6]$ in 0.1 M KCl with different dip length of only tip (ca. 20 μm , solid line) and 285 μm (dotted line). Measurements were taken in the same set up as Fig. S2. In order to monitor the dip length, two electrode system with platinum as counter/reference electrode was used.