

# Boron-doped diamond nanograss array for electrochemical sensors

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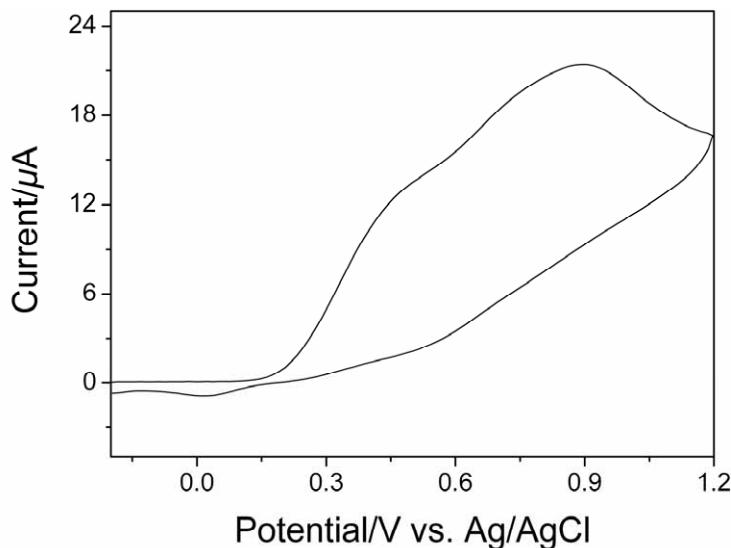
## Experimental

**Chemicals and apparatus:** All chemicals were analytical grade and used as received. Milli-Q water (>18 MΩ cm) was used throughout. The supporting electrolyte was 0.07 M phosphate buffer solution (PBS), prepared with Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. Electrochemical measurements were performed on a CHI660c electrochemical workstation with a three-electrode electrochemical cell. The geometric area of the working electrode was 0.07 cm<sup>2</sup>. A Ag/AgCl (saturated KCl) reference electrode and a Pt wire counter electrode were used.

**Preparation of the BDD film and the BDD nanograss array:** Polycrystalline boron-doped diamond (BDD) thin films were grown on Si(111) substrates using microwave plasma chemical vapor deposition (MPCVD) in an 8-kW MPCVD reactor (Seki Technotron Corp., Model AX6500). A mixture of acetone and methanol in the ratio of 9/1 (v/v) was used as the carbon source. B<sub>2</sub>O<sub>3</sub> as the boron source was dissolved in the acetone-methanol solution at the preferred concentrations. The bubbling of the acetone-methanol-B<sub>2</sub>O<sub>3</sub> solution was carried out by high-purity hydrogen gas. The amount of boron atoms in the diamond films was evaluated using a CAMECA IMS-6f instrument. When a boron to carbon (B/C)

weight ratio in the solution was 10,000 ppm, the boron doping level in the diamond film estimated by IMS measurement was  $2.1 \times 10^{21} \text{ cm}^{-3}$ . The nanograss arrays were obtained by etching experiments performed in a parallel-plate reactive ion etching plasma system with radio frequency (RF) powering at 13.56 MHz (SAMCO, RIE-10NR). For all experiments the RF power was 300 W, the pressure of the O<sub>2</sub> plasma was 20 Pa, and the total O<sub>2</sub> flow rate was 10 sccm. As a primary ion, O<sub>2</sub><sup>+</sup> accelerated at 5.5 kV was used. The samples were characterized by field-emission scanning electron microscopy (LE01530VP, Zeiss, Germany). The as-grown BDD film was obtained with hydrogen-termination. The BDD nanograss array was obtained with oxygen-termination by oxygen plasma etching. To compare the difference between BDD film and BDD nanograss array and confirm the effect of nanostructure, the BDD film with oxygen-termination was obtained by the following process: the as-grown BDD film was immersed in 0.1 M KOH, and a potential of +2.6 V vs SCE was applied for 75 min.

**Keywords:** boron-doped diamond; nanograss array; electrochemical sensor; dopamine; uric acid



**Figure S1.** CVs for a mixture containing  $5 \times 10^{-4}$  M DA and  $5 \times 10^{-4}$  M UA in 0.07 M PBS (pH 7.0) obtained on the as-grown BDD film. The scan rate was 50 mV s<sup>-1</sup>.