**Boron Doped Diamond Ultramicroelectrodes: A Generic Platform for Sensing Single Nanoparticle Electrocatalytic Collisions**

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I – Fabrication of the BDD UMEs

Boron doped diamond (BDD) ultramicroelectrodes (UME) were fabricated by laser cutting (Nd:YAG laser Oxford Lasers Ltd, UK, 3 µm diameter beam, laser power and frequency set as 5W and 20 kHz, respectively) a 600 µm thick free-standing polycrystalline boron doped diamond (BDD) wafer (Element Six Ltd, Ascot). The high quality BDD wafer (DIAFILM EA grade) was grown by Element Six such that all facets contained boron at concentrations above the metal-like limit, with negligible levels of sp² carbon.¹ The top surface was lapped to produce a ~nm surface finish.² The final “top hat” structure (Figure S1) consisted of a circular base, of typical diameter 1 mm, with a protruding cylinder of typical height 100 µm and diameter in the range 50-100 µm. The BDD was then acid cleaned using documented procedures¹ to remove any sp² carbon resulting from the laser cutting procedure.

In order to establish electrical contact to the BDD structure, the backside of the “top hat” structure was graphitized using the laser. This generates sp² carbon which provides an electrical connection between the BDD and silver conductive paste (silver DAG, Agar Scientific). The BDD was then set in epoxy resin to seal the electrode, provide a suitable handling size, and enhance mechanical stability of the electrical contact. The BDD was placed with the graphitised side face down on masking tape and inserted into a Teflon mould. The mould was filled with insulating epoxy (Delta Resins Ltd) and left to set for 24 hours. The masking tape was then removed to reveal the graphitised side, which was then electrically attached to tinned copper wire using Ag-loaded conducting epoxy (Circuitworks, ITW Chemtronics). After the wire was attached, additional epoxy was added to seal the wire and Ag-contact and left for another 24 hours. This process is summarised diagrammatically in Figure S1. The top side of the epoxy was then carefully polished using a successive set of polishing pads (Buehler, Germany), until the BDD was exposed. It is essential during this stage that the epoxy is polished away in such a manner that only the very top of the BDD emerges, in order to reveal a co-planar disc electrode.
**II – Electrodeposition of Pt NPs and Au NPs on BDD UME**

The surface of the BDD UME was electrodeposited with Pt NPs in accordance with the procedure described in reference 2. In brief, a potential of -1 V vs. SCE was applied to the BDD UME, for 2 s, immersed in a solution of 0.5 mM K$_2$PtCl$_6$ and 0.1 M HClO$_4$. Electrochemical modification of BDD UME with Au NPs was carried out following reference 3; here a potential of -0.9 V vs. SCE was applied for 2 s, in a solution containing 0.1 mM KAuCl$_4$ and 0.2 M NaClO$_4$.

**III – Synthesis and Characterisation of NPs**

Colloidal solutions of Pt and Au NPs were prepared by chemical reduction of the metallic salt in an aqueous solution employing sodium citrate as a capping agent. NPs were characterised with TEM (JEOL 2000fx) and tapping mode (TM)-AFM (Bruker Enviroscope, Nanoscope IV, Bruker-Veeco California). For TEM analysis, a drop of the colloidal solution was placed on a holey carbon TEM grid and dried in air. For AFM analysis, 50 µL of NP solution was drop-casted on an atomically flat mica substrate and dried with nitrogen.

The synthesis procedure employed for Pt NPs (2-6 nm diameter) was reported by Too and co-workers. A solution of H$_2$PtCl$_6$ (0.0326 g, 7.95 × 10$^{-5}$ mol and sodium citrate (0.0314 g, 1.07 × 10$^{-4}$ mol) was added to a round-bottomed flask and vigorously stirred. Ice-cooled NaBH$_4$ was then injected into the solution, which was left stirring for 30 minutes. The solution turned from orange-yellow to jet
black, signifying the presence of Pt NPs. Figure S2, shows TEM and AFM (Figure S2) characterisation of the Pt NP diameter and distribution size.

Figure S2: (a) TEM and (b) AFM characterisation of chemically synthesised Pt NPs.

Au NPs were made using two different synthetic procedures. The first, as detailed by Yang and co-workers,\textsuperscript{4} involved adding sodium citrate (0.100 g, 0.340 mmol) to 31.5 ml of water in a round-bottomed flask and heating to 90 °C. Cooled HAuCl\textsubscript{4} (9.50 mg, 0.0280 mmol) in 3.50 ml of water was quickly added to the solution under vigorous stirring. The solution was left to react for 30 minutes. During the reaction the solution changed colour from bright yellow to ruby red signifying the presence of colloidal Au-NPs. TEM and AFM analysis, Figure S3, revealed NPs of sizes in the range 9 - 16 nm.

Figure S2: (a) TEM and (b) AFM characterisation of chemically synthesised Pt NPs.
Figure S3: (a) TEM and (b) AFM characterisation of chemically synthesised Au NPs.

Smaller Au NPs (2-6 nm) were made using a synthesis reported by Murphy and co-workers. Sodium citrate (2.94 mg, 5 μmol) and HAuCl₄ (3.38 mg, 5 μmol) were dissolved in 20 ml of water and put on ice. 0.6 ml of NaBH₄ (2.2 mg, 60 μmol) was then added rapidly under vigorous stirring, upon which the solution changed colour from bright yellow to orange, indicating the presence of smaller Au NPs. TEM and AFM images of the NPs is shown in Figure S4.
IV – Sensing Nanoparticle Collisions

In a typical experiment, the BDD UME was immersed in phosphate buffer solution (pH=7.2) and held at the defined potential in a two electrode electrochemical cell. N$_2$ was bubbled through a vial containing 10 ml of 10 mM hydrazine in 50 mM phosphate buffer solution for 30 seconds. After ensuring a low and constant background current, the electrodes were withdrawn and a small quantity (on the µl scale) of NP solution was injected into the solution followed by gentle N$_2$ bubbling to stir the solution and to disperse the NPs. About 15 seconds later, the N$_2$ bubbling was stopped to allow the solution to settle for 15 more seconds. The BDD UME and either a non-leak Ag/AgCl reference electrode (DRI REF, World Precision Instruments) or SCE reference electrode were then placed into the solution and an $i$-$t$ curve recorded. For convenience, all potentials are converted with respect to SCE. All $i$-$t$ curves were recorded at time intervals of $1 \times 10^{-4} \text{ s}^{-1}$.
V – Au NP Collisions

The $i-t$ response for hydrazine oxidation at a 50 µm diameter disc BDD UME in a solution containing Au NPs of diameters ranging from 2-6 nm, (Figure S4) is shown in Figure S5. The collision response shows current jumps between 18 – 55 pA, in agreement with the predicted current according to the NP size range.

Figure S5: An $i-t$ trace recorded at a 50 µm BDD UME in 10 mM hydrazine and 50 mM phosphate buffer solution with Au NPs. The electrode was held at +0.4 V vs. SCE reference.

References