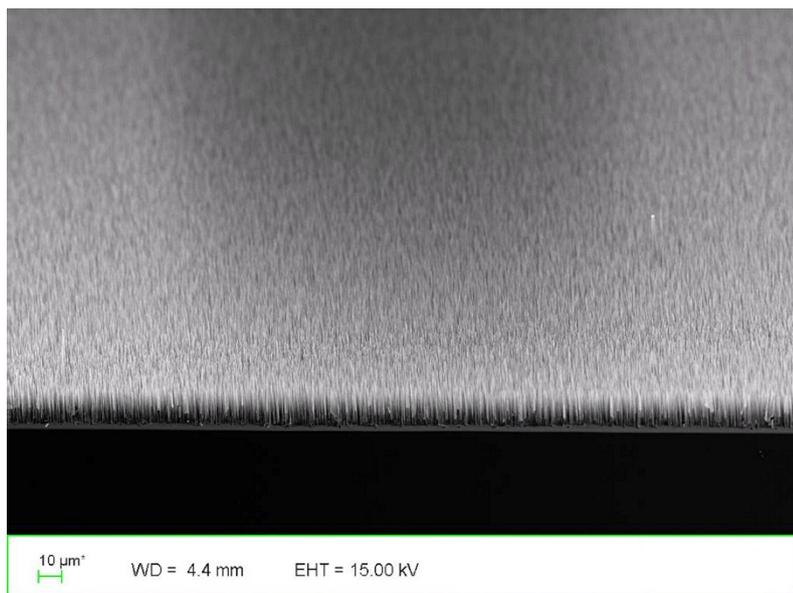


## Supporting information

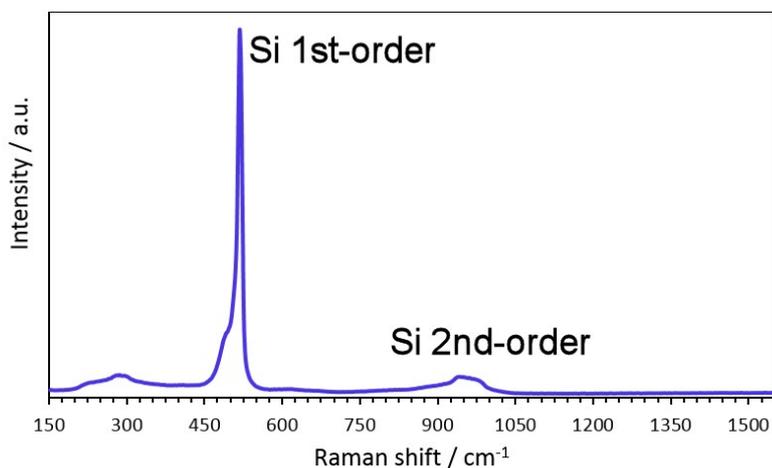
### Diamond-coated 'black Si' as a promising material for high-surface-area electrochemical electrodes and antibacterial surfaces

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A lower magnification view of the long-needle bSi can be seen in Figure S1a, showing the extent and uniformity of the coverage, and the corresponding Raman spectrum (514 nm) in Figure S1b showing the 1<sup>st</sup> and 2<sup>nd</sup>-order Raman peaks of Si. There were no other features present up to 3000 cm<sup>-1</sup>.

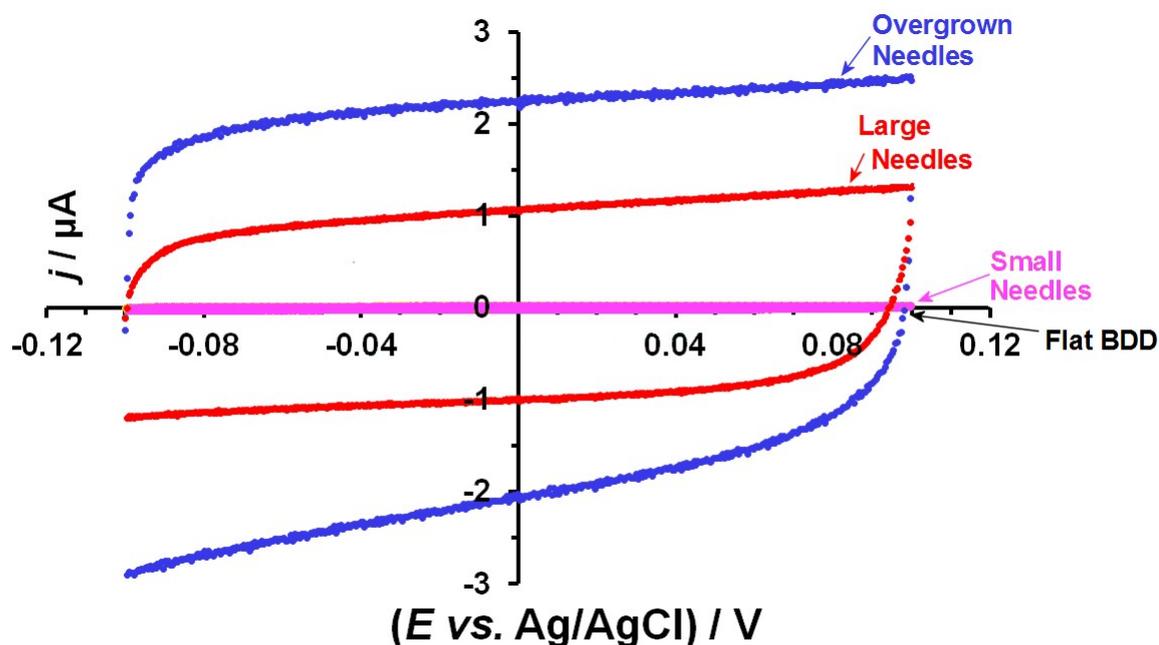


**Figure S1a.** A lower magnification SEM image of the bSi long needles (Courtesy of Colin Welch).

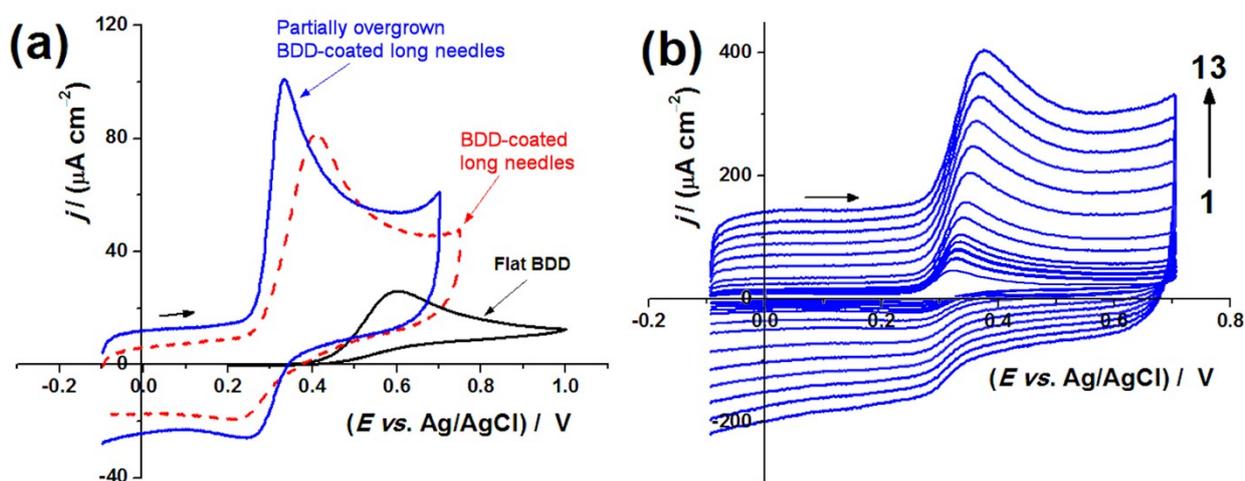


**Figure S1b.** Raman spectrum (514 nm) of the bSi long needles showing the 1<sup>st</sup> and 2<sup>nd</sup>-order Raman peaks of Si.

Cyclic voltammograms were first recorded for the various diamond electrodes only in the presence of background electrolyte solution ( $\text{KNO}_3$ ), recording the capacitive current at a range of scan rates. The CVs recorded for the different electrode types all appeared quasi-rectangular in shape, as shown in Figure S2.



**Figure S2.** Cyclic voltammograms recorded only in the presence of background electrolyte solution ( $\text{KNO}_3$ ) for the 4 types of diamond electrode.

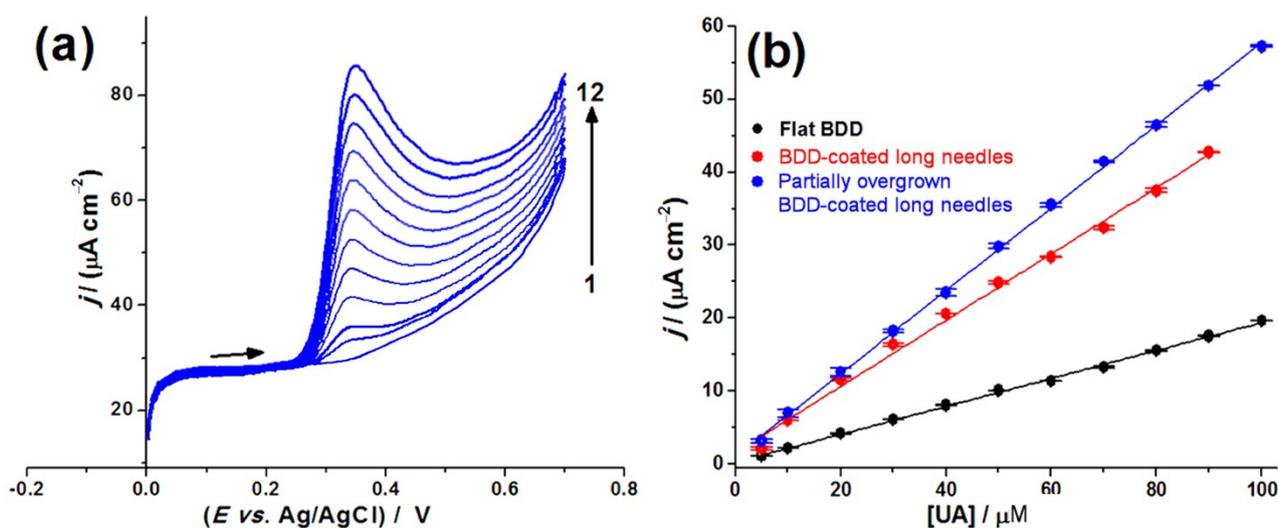


**Figure S3.** (a) CVs recorded in 0.2 M phosphate buffer solution ( $\text{pH} = 7.0$ ) containing  $2.0 \times 10^{-4}$  M UA using flat BDD, BDD-coated bSi long needles and partially overgrown BDD-coated bSi long needles. Potential scan rate =  $50 \text{ mV s}^{-1}$ . (b) An example of a set of CVs recorded at 13 different scan rates (1:  $10 \text{ mV s}^{-1}$  to 13:  $400 \text{ mV s}^{-1}$ ) in the same buffer solution as before containing  $2.0 \times 10^{-4}$  M UA. This data set was recorded using the BDD-coated bSi long-needle electrode.

The electrochemical response experiments for detection of DA were repeated with UA as the analyte and the diamond-coated bSi long-needle electrode. Figure S3(a) shows CVs for UA in buffer solution for the two BDD-coated bSi electrodes compared to the flat BDD control. Here, the

structured surface sharpens the oxidation peak and increases its signal fivefold, again making it easier to detect and locate. The peak shifts position from +0.6 to +0.35 V. The reduction peak is also enhanced and shifted to +0.28 V. Figure S3(b) shows an example of a set of CVs recorded at 13 different potential scan rates with fixed UA concentration. A plot (not shown) of peak current density,  $j$ , versus the square root of the scan rate was confirmed to be linear, indicating that UA voltammetric response also was controlled only by diffusional mass transport.

The improvement of UA response on the microstructured BDD electrodes was evaluated in terms of analytical sensitivity by the construction of analytical curves by linear scan voltammetry (LSV). Figure S4(a) shows an example of LSVs recorded for different UA concentrations, using the BDD-coated bSi long-needle electrode. The linear response to concentration can be seen in Figure S4(b) for the three electrodes in question, along with their relative sensitivities. The following values of analytical sensitivity were recorded for UA:  $0.19 \text{ A cm}^{-2} \text{ M}^{-1}$  (flat BDD);  $0.45 \text{ A cm}^{-2} \text{ M}^{-1}$  (BDD-coated bSi long needles) and  $0.57 \text{ A cm}^{-2} \text{ M}^{-1}$  (partially overgrown BDD-coated bSi long needles). Interestingly, again the analytical sensitivity increased by using either of the microstructured BDD electrodes and the same analytical sensitivity as before was measured for the partially overgrown BDD-coated bSi long needle electrode, which was again higher than for the other electrodes. Based on the best voltammetric response of DA and UA on the BDD-coated bSi long needles, the next task was to test the response with both analytes present simultaneously.



**Figure S4.** (a) LSVs recorded in 0.2 M phosphate buffer solution (pH = 7.0) containing 12 different UA concentration levels (1: 0.0 (blank solution) to 12:  $1.0 \times 10^{-4}$  M) using the BDD-coated bSi long needles at a fixed potential scan rate of  $100 \text{ mV s}^{-1}$ . (b) Linear response of current density  $j$  ( $\mu\text{A cm}^{-2}$ ) against UA concentration for the two BDD-coated electrodes and the BDD control. The corresponding linear best-fit equations and correlation coefficients,  $r$ , are: Flat BDD  $j = 0.26 + 0.19[\text{UA}]$ ,  $r = 0.999$ ; BDD-coated long needles  $j = 1.6 + 0.45[\text{UA}]$ ,  $r = 0.996$ ; Partially overgrown BDD-coated long needles  $j = 1.1 + 0.57[\text{UA}]$ ,  $r = 0.999$ .