

The effect of surface termination on glucose oxidation using Ni-modified diamond electrodes

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This study describes the decoration of hydrogen- and oxygen-terminated boron-doped diamond electrodes (BDD) with three different loadings of Ni. The Ni was deposited electrochemically for 600, 400 and 100 s on both hydrogen-terminated BDD (BDDH) and oxygen-terminated BDD (BDDO). SEM showed that all Ni particles were roughly spherical in shape, but distribution and size varied with electrode termination: a uniform coverage with a particle size dependent on deposition duration was achieved on BDDH, but on BDDO the particles deposited primarily along surface ridges and had similar sizes for all three deposition times.

The performance of the samples was then tested using glucose sensing as an exemplar application. It was found that glucose oxidation varies greatly between electrodes at concentrations similar to those found in human blood. The variability between the samples was attributed to surface differences between electrodes and the difference in particle location. Amperometry using BDDs decorated with the 100 s Ni deposition gave a stable current response with respect to glucose concentration in the range 0.1–13 mM with much higher glucose oxidation currents being observed for the Ni nanoparticles deposited on the hydrogenated diamond surface.

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1 Introduction Boron-doped diamond electrodes (BDD) have become practical electrodes for use in electrochemistry given the advances in chemical vapour deposition techniques that make BDD wafers with a boron concentration exceeding 10^{20} cm^{-2} readily available.[1–8] These BDD electrodes have numerous advantages over other common working electrodes: a wide potential window, low background current and excellent chemical stability.[1,9–12] Oxygen-terminated BDDs (BDDO) have additionally shown a resistance to oxygen interference,[13, 14] but more interestingly the BDD can be explicitly terminated to be either hydrophilic or hydrophobic.[10,15] The hydrophobic surface is achieved by hydrogen termination, which alters the electrochemical performance of the BDD,[11,16–19] whereas BDDO is hydrophilic.

The performance of BDDs as working electrodes can be further enhanced through modification of the surface

with metal or metal oxide particles.[8,20–24] Nickel, for example, is of increasing interest due to its potential utility in a range of applications including water splitting,[25, 26] the oxidation of methanol and other primary alcohols for use in green energy fuel cells,[27–30], and the oxidation of adenine, DNA, steroid hormones and glucose for sensing purposes.[31–33,25] Enzymatic glucose sensing is currently the most common method of glucose sensing, but suffers from the instability inherent to enzymes.[34] Another possibility is the enzyme-free oxidation of glucose, which has been the topic of much research.[6,24,27,25, 32,34–36] For example, glucose can be electrooxidised to glucolactone[37–39] by the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ catalytic redox couple[25,35,34], which can be obtained from oxidation of Ni metal in alkali solution.[33,35,40,41]

Given the importance of glucose sensing in fields ranging from medical applications to the food industry[42]

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and fuel cells,[6,43–45] there is a lot of work in the literature which documents the use of Ni particles for glucose oxidation, both on BDD and other substrates. However, most of the work currently reported in the literature that studies the use of Ni particles on BDD electrodes for glucose oxidation exclusively uses BDDO.[25,34,39,26] Given that BDDH has been shown to have increased conductivity and better electrical contact with deposited metal particles, one of the main aims of the work presented here was to compare the oxidation of glucose on Ni/BDDH to the identically decorated BDDO. Furthermore, Hutton *et al.* studied the effect of Ni loading on the oxidation of glucose, focussing only on the oxygen-terminated BDD electrode;[26] hence a secondary aim of this project was to fill this gap by studying three different amounts of deposited Ni and comparing the glucose oxidation results between the oxygenated and hydrogenated samples to determine not only the optimal surface termination of the BDD, but also the optimal Ni loading.

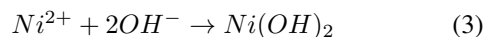
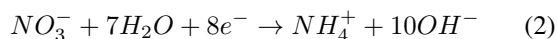
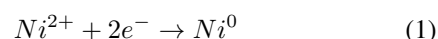
2 Experimental methods All six nominally identical polycrystalline BDDs ($[B] > 10^{20} \text{ cm}^{-2}$) used in this work were electrochemical grade and purchased from Element Six Co (UK). Throughout this work, water refers to Millipore water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$. 70% HNO_3 was purchased from Fischer Scientific and all other chemicals were of analytical grade, obtained from Sigma Aldrich and used without further purification. Deaeration was done by bubbling N_2 through the solution for at least 20 min. All electrochemistry was performed using a standard three-electrode cell comprising a Pt counter electrode, a 1 M Ag/AgCl reference electrode and the Ni decorated BDD as the working electrode with an area of 0.46 cm^2 connected to an Autolab potentiostat (Utrecht, Netherlands) operated using the GPES software.

2.1 Preparing the BDDs Three clean BDDs were oxygen terminated by refluxing in 70% HNO_3 for at least four hours. Hydrogen termination of another three BDDs was achieved by subjection to hydrogen plasma at 600°C , 45 torr and 1.5 kW power for 45 minutes.

Cleaning At the end of each experiment, the Ni was removed by submerging the BDD in a 3% FeCl_3 solution for ten minutes twice. Leaving the BDD in 3% FeCl_3 for longer periods or at higher concentrations of FeCl_3 resulted in trace amounts of Fe being deposited on the BDD. Nickel hydroxides were removed from the surface by first removing the hydroxide layers in 6 M HCl for at least 30 minutes, and then the Ni was removed using the 3% FeCl_3 as described. Cleanliness was confirmed by the absence of Ni redox peaks in the cyclic voltammogram taken in 0.1 M HNO_3 between 2.5 and -1.7 V at a scan rate of 0.1 Vs^{-1} , starting at 0 V. If necessary, the BDDs were submerged in aqua regia over night.

2.2 Ni deposition and enrichment Ni deposition was accomplished using amperometric deposition at -1.3 V for either 100, 400 or 600s in a 1 mM $\text{Ni}(\text{NO}_3)_2$ in 0.1 M

acetate buffer (pH=5). This procedure is known to deposit a mix of Ni metal and $\text{Ni}(\text{OH})_2$ as per the following reactions:[25]



The deposited Ni was then enriched with hydroxide by cycling between 0.15 and 0.55 V in a 1 M KOH solution as previously described by Toghill and Shpilevaya.[25,35] This enrichment process thickens the $\text{Ni}(\text{OH})_2$ layer by oxidising the Ni metal.[25] $\text{Ni}(\text{OH})_2$ will then undergo catalytic conversion to, and from, NiOOH during the oxidation of glucose.[25,33,34]

2.3 SEM Scanning electron microscopy (SEM) was used to ascertain the morphology and distribution of the as-deposited Ni particles on the conducting BDD substrates. The BDDH samples were imaged using a Hitachi S-4300 field emission scanning electron microscope as was the 100 s Ni deposition onto BDDO. Due to equipment unavailability, the 600 and 400 s Ni/BDDO were imaged using a different SEM. These two samples were imaged using a JEOL JSM-5610LV. An accelerating voltage of 20 kV was used for all samples.

2.4 Glucose measurements The sensitivity and behaviour of the Ni decorated BDDs were probed using glucose sensing. Ni/BDD systems have been previously used as glucose sensors, making glucose sensing an ideal test case for observing alterations in performance with both the Ni loading and the BDD termination.

Cyclic voltammetry Cyclic voltammetry (CV) was used to observe the general redox behaviour of glucose solutions with the Ni/BDD systems. Glucose concentrations ranging from 1 to 10 mM (similar to the glucose levels in human blood) in a 1 M KOH supporting electrolyte were tested with cyclic voltammetry between the potentials of 0.2 to 0.5 V at a scan rate of 0.05 Vs^{-1} . The solution was stirred at 700 rpm. This experiment also gave the oxidation potential of 0.47 V specific to the Ni/BDD system that was later used in the amperometric experiments.

Amperometry Amperometric measurements were used to determine whether the current would increase linearly with glucose concentrations when the glucose concentration was decreased. Briefly, the Ni/BDD electrode was put in a 1 M KOH solution for 50 s after which aliquots of concentrated glucose were injected at intervals of 50 s, in a stirred solution. The potential was held at the glucose oxidation potential at 0.47 V, as found by cyclic voltammetry, for the duration of the experiment.

3 Results and discussion

3.1 Deposition of Ni Ni was deposited onto both the oxygenated and hydrogenated BDD (BDDO and BDDH) from a deaerated 1 mM $\text{Ni}(\text{NO}_3)_2$ solution for 600, 400

and 100 s respectively. The charge equivalents of Ni deposited on each electrode, as found by integrating the deposition curve, is given in Table 1. The distribution and

Table 1 Ni deposition (in mC) on BDDH and BDDO

	600 s	400 s	100 s
BDDH	430	240	70
BDDO	310	220	65

morphology of the as-deposited Ni was then inspected using SEM, shown in Fig. 1.

The most striking difference between the Ni on BDDO and on BDDH is the difference in particle distribution on the electrode surface; on BDDH the Ni particles have a uniform distribution showing no preference for flat or pitted areas. Conversely, on BDDO the Ni preferentially sits in pitted areas or along ridges (Fig. 1D-F). As shown in Fig. 1, BDDH (Fig. 1A-C) has a Ni nanoparticle coverage which increases with the deposition time – these particles diminish in both size and number for the 100 s deposition. The particle size of the 600 s Ni is approximately twice as large on BDDO compared to BDDH; the difference in amount deposited resulting in the different coverages as previously described. For the 100 s deposition, however, the particles are more than one order of magnitude larger on BDDO than BDDH. All samples have a Ni morphology that is approximately spherical. The uniform coverage of Ni on the hydrogenated surface in comparison to the oxidised surface is likely to correlate to the additional conductivity from the so-called surface conductivity of the hydrogenated surface.

3.2 CV response to glucose oxidation Following deposition, the Ni was enriched to Ni hydroxide in 1 M KOH for 500 cycles between 0.15 and 0.55 V so as to improve the electrochemical activity of the sample. The enriched Ni on BDD was then used to probe the redox behaviour of differing glucose solutions (1-10 mM) in 1 M KOH. The voltammograms, together with the current density versus glucose concentrations plots, are shown in Fig. 2 for BDDH and Fig. 3 for BDDO. In the forward scan, the oxidation peak is that to NiOOH which is then reduced by the irreversible oxidation of glucose such that on the back scan Ni(OH)₂ is again oxidised to NiOOH. The small reduction peak is the reduction of residual NiOOH to Ni(OH)₂. [25]

The two fits for the current response to glucose concentration shown in Fig. 2 and 3 are for all ten glucose concentrations (red dashed line) and for the concentration range 4-10 mM (blue solid line). The response of Ni/BDDH to glucose is most linearly dependent on the glucose concentration for the 400 s Ni deposition (Fig. 2B and F) and the data is most scattered (lowest R² value) for the 600 s Ni deposition (Fig. 2A and D). There seems to be rather little correlation between the current response observed to glucose and the Ni coverage however. The data is also very scattered particularly at low glucose concentration; the dif-

ference in R² value shows that the current response is more linear with respect to glucose concentration if the lowest concentrations are not included in the analysis. Two conclusions seem to be indicated. Firstly the oxidation of glucose at these Ni modified diamond electrodes is likely to be controlled by diffusion of glucose to the densely covered Ni nanoparticle array rather than being limited by a surface reaction at the surface of the Ni nanoparticles. [26] Hence changes in Ni nanoparticle coverage have virtually no effect on the magnitude of the oxidation current observed. Secondly, some other factor which is especially prominent at low glucose concentration seems to have a salient effect in controlling the current response observed as witnessed by the scatter in the current response observed. Given the sensitivity of the electrode to the conditioning to produce the Ni hydroxide layer, this is most probably associated with the level of oxidation of the surface of the Ni nanoparticles which is difficult to maintain at a constant level as the electrode is used.

Rather similar behaviour is observed superficially on the Ni on BDDO electrodes. Again scatter in the data is observed at low glucose concentrations and the current response seems to show no particular correlation to the Ni particle concentration indicative of diffusion controlled rather than surface limited behaviour. However it is noteworthy that the current density observed in the CV data is approximately an order of magnitude smaller on the oxidised electrode compared to the hydrogenated electrode. The most obvious explanation for this – a current seemingly independent of nanoparticle density but much lower than the diffusion limit seen on the hydrogenated surface is that macroscopic regions (of dimension of the order or greater than the glucose diffusion layer thickness of the order of 100 μ m in these experiments) are electrochemically inactive so significantly reducing the current response. This partially correlates with the very heterogeneous deposition of Ni seen in the SEM analysis which also suggests significant areas of the electrode are likely to remain unmodified by the presence of Ni.

3.3 Amperometric glucose response Amperometry was then used to gauge the sensitivity of the best of the Ni/BDD samples, and the responses are shown in Fig. 4. As was also found by cyclic voltammetry, the signal from BDDH is significantly higher than for BDDO. However, this does not correspond to an increase in sensitivity in the oxidation of glucose in the concentration range of interest here; as can be seen in sample data high concentrations (1-13 mM) of glucose, or lower concentrations (0.1-1.3 mM) BDDO can easily be detected at these Ni treated BDDH and BDDO electrodes. However, whilst some modified electrodes worked well considerable variability in performance was sometimes seen as in Fig. 4A. The variability of the glucose peaks observed by CV is reduced in these potentiostatic measurements, except perhaps for BDDO in the 1-10 mM glucose range, which may suggest that some part of the variability may have arisen from the Ni reduc-

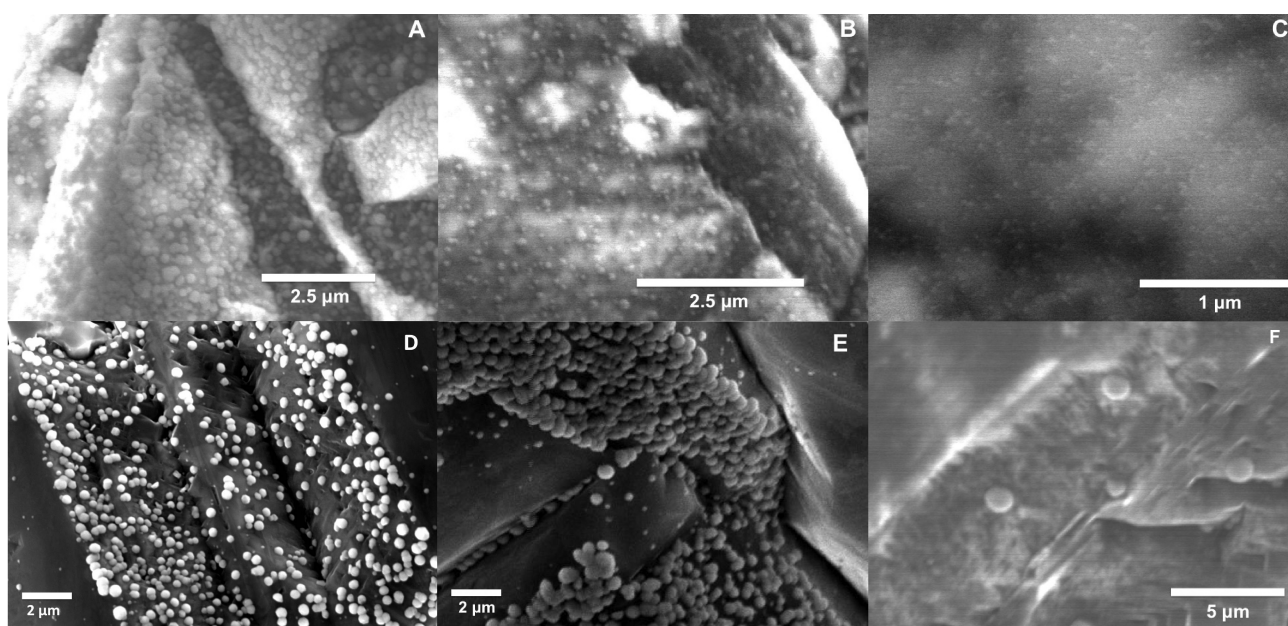


Figure 1 SEM images of 1 mM $\text{Ni}(\text{NO}_3)_2$ in 0.1 M acetate buffer deposited at -1.3 V for 600 (A), 400 (B) and 100 s (C) on BDDH and on BDDO for 600 (D), 400 (E) and 100 s (F). All images were recorded using a 20 kV accelerating voltage.

tion peak which was traversed in CV but not in the potentiostatic method discussed in this section.

4 Conclusion This work investigated the effect of BDD termination on the oxidation of glucose aided by hydroxide-enriched Ni particles. The Ni particles were deposited on the clean, explicitly terminated BDD by a potentiostatic method for 600, 400 and 100 s to achieve different Ni loadings. The as-deposited Ni was then enriched to $\text{Ni}(\text{OH})_2$ prior to being used for glucose sensing. BDDH was found to have slightly higher Ni loadings than BDDO and a more uniform Ni particle coverage, showing that Ni deposits and nucleates differently on BDDO compared to BDDH. This might arise from the surface conductivity of the hydrogenated surface which tends to equalise out the conductivity variations seen in the oxidised surface due to the uneven distribution of the boron dopant. Furthermore, cyclic voltammetric oxidation of glucose showed that there was quite considerable variation in electrode sensitivity, which was attributed to variations in the activity of the Ni nanoparticles which depends critically on their level of oxidation. On the whole, less variations were seen for Ni nanoparticles on the oxidised surface compared to the hydrogenated surface. Significantly larger glucose oxidation currents were observed on the hydrogenated surface compared to the oxidised surface. This was attributed in part to large parts of the Ni modified diamond electrode being inactive due to the absence of deposited Ni in those areas. For the best Ni modified electrodes, reliable glucose detection was demonstrated in the range 0.1–13 mM.

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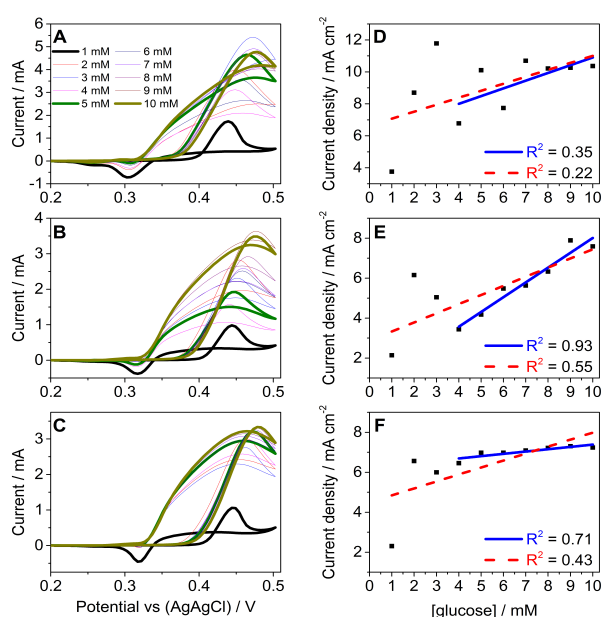


Figure 2 CV response of 1-10 mM glucose in 1 M KOH on A) 600 s B) 400 s and C) 100 s deposition of 1 mM Ni on BDDH. The thick curves on each graph is for 1, 5 and 10 mM of glucose. D-F shows the current response with respect to glucose concentration for 600, 400 and 100 s respectively. The blue, solid line marks the linear correlation between the current density and the glucose concentration using only the latter data points ($n=7$), while the red, dashed line is the linear correlation using all ten concentrations ($n=10$).

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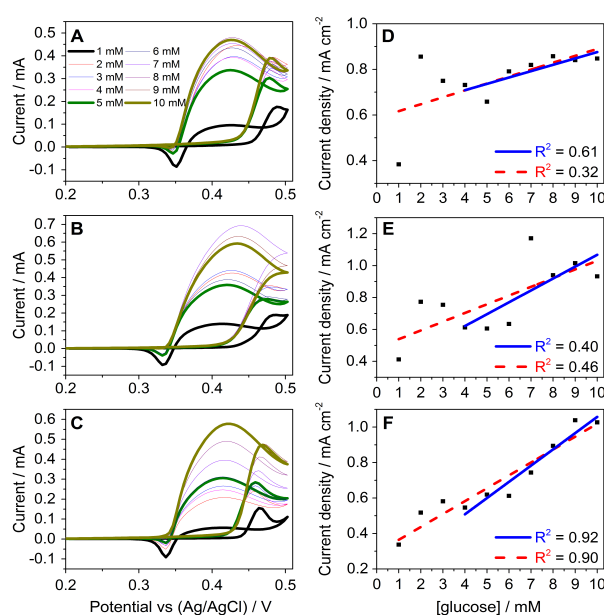


Figure 3 CV response of 1-10 mM glucose in 1 M KOH on A) 600 s B) 400 s and C) 100 s deposition of 1 mM Ni on BDDO. The thick curves on each graph is for 1, 5 and 10 mM of glucose. D-F shows the current response with respect to glucose concentration for 600, 400 and 100 s respectively.

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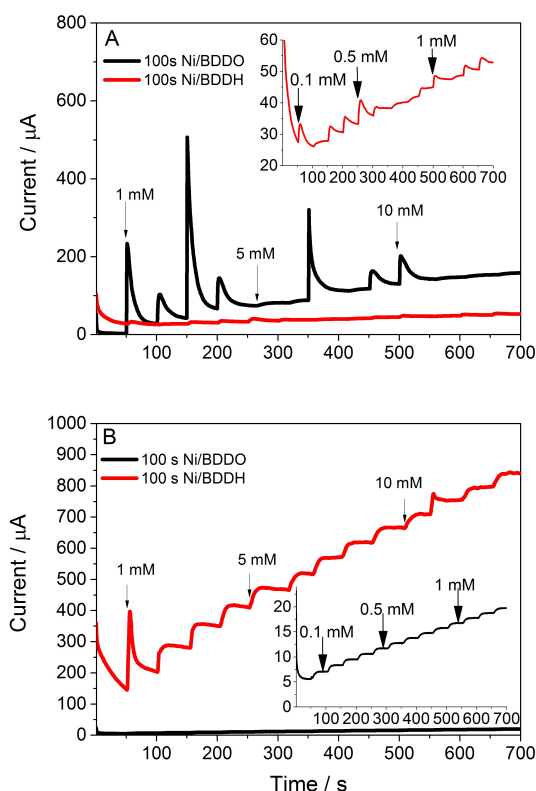


Figure 4 Amperometric measurements off 100 s deposition of 1 mM Ni on BDDO (black) and BDDH (red) taken at 0.47 V in a stirred supporting electrolyte of 1 M KOH with 1 mM and 0.1 mM glucose injected every 50 s. A) shows the variable behaviour of the glucose oxidising system and B) stable electrodes with reproducible behaviour.

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