

# Surface Modification of Boron-Doped Diamond with Microcrystalline Copper Phthalocyanine: Oxygen Reduction Catalysis

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Surface modification of boron-doped diamond (BDD) with copper phthalocyanine was achieved using a simple and convenient dropcast deposition, giving rise to a microcrystalline structure. Both unmodified and modified BDD electrodes of different surface terminations (namely hydrogen and oxygen) were compared via the electrochemical reduction of oxygen in aqueous solution. A significant lowering of the cathodic overpotential by about 500 mV was observed after modification of hydrogen-terminated (hydrophobic) diamond, while no vol-

tammetric peak was seen on modified oxidised (hydrophilic) diamond, signifying greater interaction between copper phthalocyanine and the hydrogen-terminated BDD. Oxygen reduction was found to undergo a two-electron process on the modified hydrogen-terminated diamond, which was shown to be also active for the reduction of hydrogen peroxide. The lack of a further conversion of the peroxide was attributed to its rapid diffusion away from the triple phase boundary at which the reaction is expected to exclusively occur.

## Introduction

Boron-doped diamond (BDD)<sup>[1]</sup> electrodes, which are produced by chemical vapour deposition, represent an interesting alternative carbon-based electrode material for use in electrochemistry. The electrode shows advantageous electrochemical properties including low pseudocapacitive background currents, a wide operating potential window and excellent electrochemical stability in comparison to traditional carbon materials.

As-grown thin film diamond is largely hydrogen terminated and the "alkane-like" surface is thus hydrophobic.<sup>[2]</sup> Upon treatments such as anodic polarisation,<sup>[2a,3]</sup> potential cycling,<sup>[4]</sup> and oxygen plasma,<sup>[2b]</sup> oxygen-containing groups can be introduced onto the diamond surface, consequently rendering it hydrophilic. The surface-chemical composition can therefore be altered to influence properties such as hydrophobicity and the electron-transfer kinetics.<sup>[2b,5]</sup>

To impart additional functionality to the diamond, the surface of the substrate can be modified with electrocatalytic materials. The common approaches towards the attachment of such materials onto diamond electrodes include electrochemical deposition,<sup>[6]</sup> photochemical reaction,<sup>[7]</sup> electropolymerisa-

tion,<sup>[8]</sup> and ion implantation.<sup>[9]</sup> These typically involve at least some level of instrumentation or covalent linkage.

The relatively simple technique of dropcasting a coating onto diamond is rather limited however, but some examples from the literature are listed in Table 1.<sup>[10]</sup> These modifiers are

**Table 1.** Some examples of modification of boron-doped diamond (BDD) via dropcasting.

| Modification method                | Modifier                                      | Diamond surface      | Ref.  |
|------------------------------------|---|----------------------|-------|
| Dropcast                           | Pt/Sn nanoparticles                           | O-BDD <sup>[a]</sup> | [10a] |
| Dropcast                           | Pt nanoparticles                              | O-BDD                | [10b] |
| Dropcast, calcination              | IrO <sub>2</sub> nanoparticles                | O-BDD                | [10b] |
| Dropcast                           | Nafion  | –                    | [10c] |
| Dropcast                           | Carbon black                                  | O-BDD                | [10d] |
| Dropcast                           | Au/TiO <sub>2</sub> nanorod composites        | H-BDD <sup>[b]</sup> | [10e] |
| Dropcast (with EDC) <sup>[c]</sup> | Heme undecapeptide;<br>Horseradish peroxidase | O-BDD,<br>H-BDD      | [10f] |
| Dropcast (with Nafion)             | Pt–RuO <sub>2</sub> /C composite              | H-BDD                | [10g] |

[a] O-BDD: O-terminated BDD. [b] H-BDD: H-terminated BDD. [c] EDC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide.

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predominantly particulate in nature. The limited use of such physical immobilisation is likely due to the general notion of diamond having greater chemical inertness relative to common carbon electrodes. Nevertheless, a few recent reports on diamond have described the observation of adsorptive behaviour of molecular compounds such as quinzarin,<sup>[11]</sup> methyl viologen,<sup>[12]</sup> and anthraquinonedisulfonate<sup>[12b]</sup> from solution. Therefore, in this paper we explore the attachment of molecular modifiers, in the form of microcrystals on diamond, using copper phthalocyanine as an exemplar.

There have been only several reports of the modification of diamond film electrodes with metallophthalocyanines. These were performed by vacuum deposition<sup>[13]</sup> or after photochemical modification with 4-vinylpyridine.<sup>[14]</sup> We demonstrate that a simple dropcast method can be effective for the immobilisation of metallophthalocyanine onto diamond as well. In particular, we compare the influence of two different commonly used surface terminations, namely hydrogen and oxygen, on the interaction of metallophthalocyanine with diamond. Moreover, we show that the dropcasting leads to an array of microcrystals of copper phthalocyanine on the BDD surface.

Metallophthalocyanines are well known as catalysts for homogeneous and heterogeneous chemical reactions,<sup>[15]</sup> amongst which is the capability to lower the overpotential for the oxygen reduction reaction,<sup>[16]</sup> hence, this process is chosen to examine the metallophthalocyanine–diamond system in this work. Moreover the reduction of oxygen is of considerable technological importance, for instance in the development of fuel cells.<sup>[17]</sup> In respect of oxygen reduction, diamond is especially useful for studying cathodic reactions without interference from water electrolysis owing to its large overpotential for hydrogen evolution<sup>[1b,e]</sup> and its outstanding stability under reductive conditions.

## Results and Discussion

In this section, oxygen reduction is first investigated at unmodified BDD electrodes to provide a starting point for studying the reaction. Next, the cathodic process is examined at copper-phthalocyanine-modified diamond to compare the effects of differing surface terminations. Included is also a study of the behaviour of the modified hydrogen-terminated diamond towards the reduction of hydrogen peroxide.

### Oxygen reduction at unmodified diamond electrode

The electrochemical reduction of oxygen in aqueous solutions can proceed by the following two general pathways: either a direct four-electron route or a two-electron hydrogen peroxide mechanism.<sup>[18]</sup> Both pathways are described below for neutral conditions at pH 7.

#### Direct 4-electron pathway



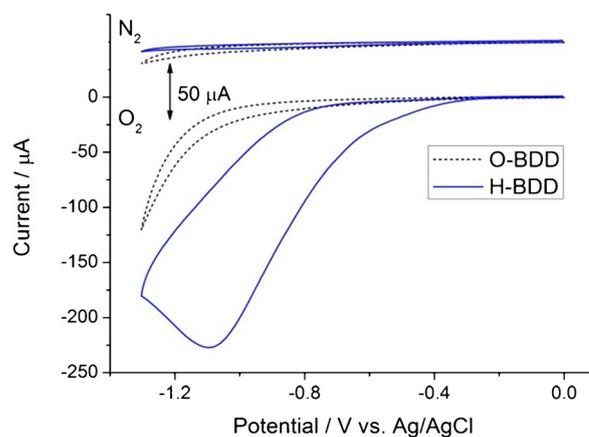
#### Peroxide pathway



The direct four-electron process is expected to exhibit a single voltammetric wave. For the peroxide route, there are two possibilities: a) the potentials for the sequential electron transfers could be well separated, resulting in two distinct voltammetric waves, or b) the reduction of peroxide could occur

at or near the oxygen reduction potential, leading to a single voltammetric wave.

Cyclic voltammetry was first carried out on the unmodified boron-doped diamond with surface terminations of hydrogen and oxygen, in both O<sub>2</sub>- and N<sub>2</sub>-saturated phosphate buffer solution (PBS) at pH 7, to provide a basis for understanding the oxygen reduction at these electrodes. The cyclic voltammograms obtained are shown in Figure 1. In the N<sub>2</sub>-saturated so-



**Figure 1.** Cyclic voltammograms for H-terminated (H-BDD, solid line) and O-terminated (O-BDD, dashed line) BDD electrodes in N<sub>2</sub>-saturated (above) and O<sub>2</sub>-saturated (below) 0.1 M PBS pH 7. Scan rate: 100 mV s<sup>-1</sup>. The potential was swept in a negative direction from 0 V.

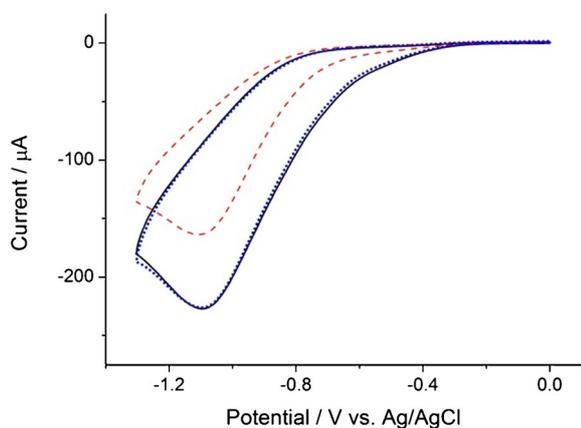
lution, both the hydrogen- and oxygen-terminated diamond gave very little response. However, in the O<sub>2</sub>-saturated solution, the two types of surfaces gave rise to a different response. At the O-terminated surface there was no apparent peak, whereas at the H-terminated surface, a large and irreversible voltammetric peak was observed with a peak potential at -1.09 V (vs. Ag/AgCl), which can be attributed to the irreversible reduction of oxygen to hydrogen peroxide,<sup>[19]</sup> as given by Equation 2. The two-electron reduction of oxygen on the H-terminated diamond is typical of the peroxide pathway commonly seen on carbon electrodes.<sup>[18b,20]</sup>

The standard potential for the two-electron reduction of oxygen is +0.281 V (SHE) at pH 7 and the large overpotential on the H-terminated surface is consistent with the work of Yano et al.<sup>[19]</sup> which found the oxygen reduction to be highly inhibited on as-grown diamond. This was attributed to a lack of adsorption sites for oxygen and/or reduced intermediates, a low density of states, or a potential drop within a thin (~2 nm) surface layer.

As the reduction of oxygen involves the addition of hydrogen, and the cathodic reaction is only observed on the H-terminated surface but not the O-terminated surface, there exists the possibility of the surface hydrogen providing the stoichiometric source. The surface density of carbon bonds on diamond and, hence, the maximum coverage of H, is ~10<sup>15</sup> cm<sup>-2</sup>. Assuming an electron transfer for each H reacted, the charge required to exhaust the surface H in this case is ~7 × 10<sup>-5</sup> C. The charge passed on the cathodic sweep for the H-terminat-

ed surface in  $O_2$ -saturated solution is  $1.1 \times 10^{-4} C$ , therefore, a single scan should exhaust the surface H if it is reacting.

Consecutive cyclic voltammetric scans were thus carried out, and the voltammograms are shown in Figure 2. The second

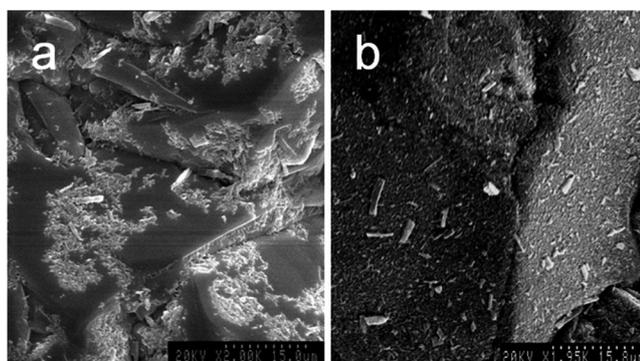


**Figure 2.** Cyclic voltammograms for H-terminated BDD electrode in  $O_2$ -saturated 0.1 M PBS pH 7 showing initial scan (solid line), second scan (dashed line), and subsequent scan after stirring (dotted line). Scan rate:  $100 \text{ mVs}^{-1}$ .

scan showed a decrease in the peak current, which can be attributed to the slow removal of reaction products from the reaction sites. After the solution was stirred by bubbling with oxygen, the subsequent voltammogram showed a restoration of the peak current to that of the initial value. This confirms that the H-terminated diamond is indeed electrocatalytic compared to the O-terminated surface.

### Effect of surface termination on the interaction of copper phthalocyanine with diamond towards oxygen reduction

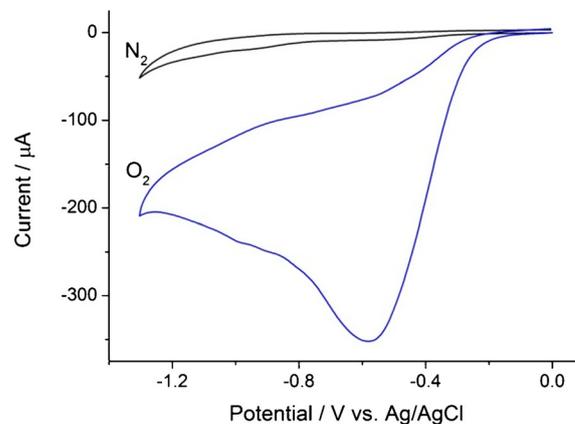
A simple dropcast technique was used to immobilise copper phthalocyanine onto the diamond electrode as described in the experimental section, and the surface morphology of the modified H- and O-terminated electrodes were characterised by scanning electron microscopy (SEM). As revealed by the SEM micrographs in Figure 3, the structure of the modified



**Figure 3.** SEM micrographs of copper-phthalocyanine-modified a) H-terminated, b) O-terminated BDD. The scale bars represented by dotted lines are  $15.0 \mu\text{m}$  (a) and  $15.8 \mu\text{m}$  (b). Frame dimensions ( $h \times w$ ) are  $\sim 69 \times 58 \mu\text{m}$  (a) and  $\sim 73 \times 61 \mu\text{m}$  (b).

electrodes both consisted of microcrystalline deposits of varying sizes up to about  $7 \mu\text{m}$  in length across the diamond surface.

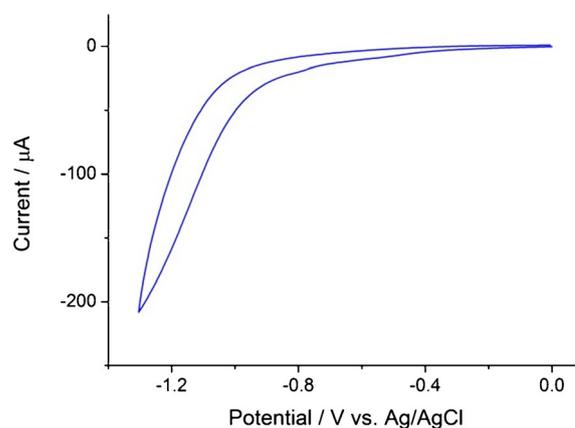
The cyclic voltammograms on the modified H-terminated surface in both  $O_2$ - and  $N_2$ -saturated PBS are shown in Figure 4. While the curve obtained in the  $N_2$ -saturated solution



**Figure 4.** Cyclic voltammograms for copper-phthalocyanine-modified H-terminated BDD in  $N_2$ -saturated (above) and  $O_2$ -saturated (below) 0.1 M PBS pH 7. Scan rate:  $100 \text{ mVs}^{-1}$ .

is relatively featureless, a large and irreversible cathodic peak was observed at  $-0.58 \text{ V}$  (vs. Ag/AgCl) in the  $O_2$ -saturated solution attributed to the reduction of oxygen. This represents a significant decrease in overpotential of over  $500 \text{ mV}$  compared to the unmodified H-terminated electrode and demonstrates the substantial electrocatalytic effect as a result of copper-phthalocyanine modification. The behaviour for the modified O-terminated diamond is very different, however, as shown in Figure 5. No apparent peak was observed for the voltammetric response in  $O_2$ -saturated solution.

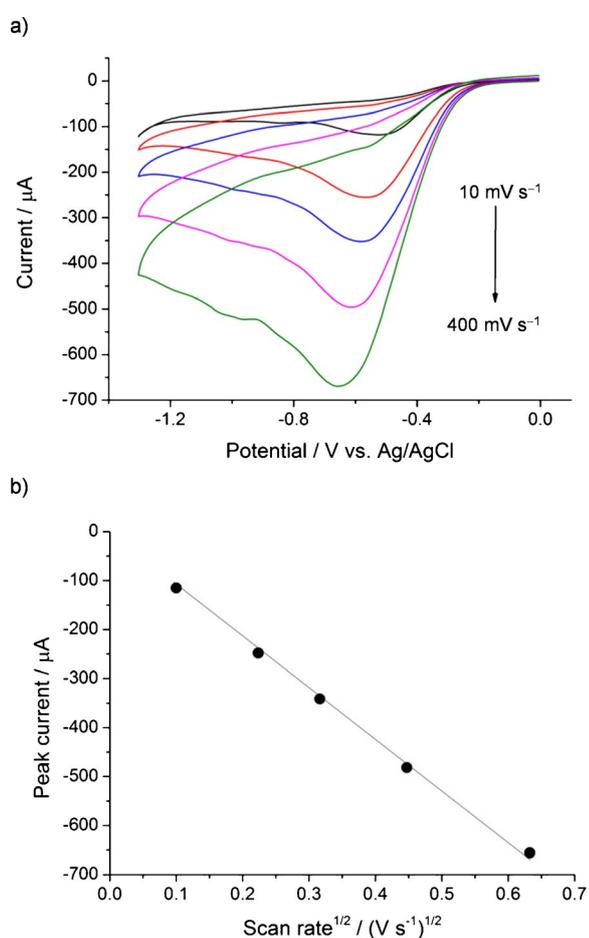
Based on the results above, it is clear that the surface chemical termination has an effect on the interaction between copper phthalocyanine and diamond. Only on the H-terminat-



**Figure 5.** Cyclic voltammogram for copper-phthalocyanine-modified O-terminated BDD in  $O_2$ -saturated 0.1 M PBS pH 7. Scan rate:  $100 \text{ mVs}^{-1}$ .

ed surface is there significant interaction with the metallophthalocyanine based on the observation of its positive impact on the electrocatalysis of oxygen reduction. This is likely due to the hydrophobic interaction between copper phthalocyanine and the (hydrophobic) H-terminated surface.<sup>[12a]</sup> As for the oxidised diamond electrode, the hydrophilic surface is expected to have much weaker interaction with the nonpolar compound. From the absence of a voltammetric peak in an O<sub>2</sub>-saturated solution, it can be inferred that the electrical connection of copper phthalocyanine microcrystallites to the O-terminated diamond is therefore inferior to the case of the H-termination.

Figure 6a displays the voltammetric data obtained at scan rates from 10 to 400 mV s<sup>-1</sup>, and the linear dependence of the peak current on the square root of the scan rate is shown in



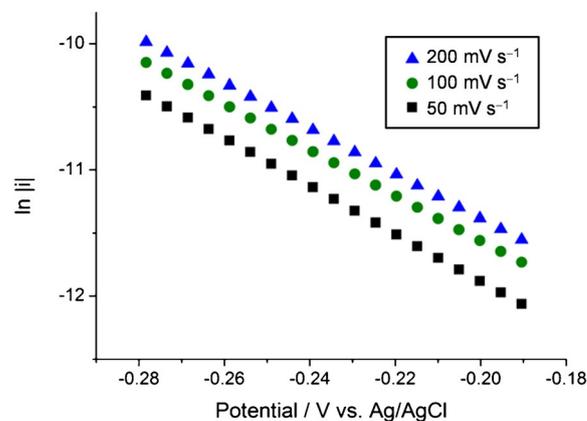
**Figure 6.** a) Cyclic voltammograms for copper-phthalocyanine-modified H-terminated BDD in O<sub>2</sub>-saturated 0.1 M PBS pH 7 at scan rates from 10–400 mV s<sup>-1</sup>. b) Plot of peak current against square root of scan rate.

Figure 6b, indicating the reduction of oxygen on the modified surface is a diffusion-controlled process at the modified H-terminated surface. The peak current for the transport-limited irreversible *n*-electron-transfer reaction is described in Equation 4:

$$i_{peak} = -0.496 \sqrt{(n' + \alpha_{n'})} nFA [O_2] \sqrt{\frac{FvD}{RT}} \quad (4)$$

where  $i_{peak}$  is the peak current,  $n'$  is the number of electron transferred before the rate limiting step,  $\alpha_{n'}$  is the transfer coefficient of the rate determining step,  $F$  is the Faraday constant,  $A$  is the electrode area,  $[O_2]$  is the oxygen concentration,  $v$  is the scan rate,  $D$  is the diffusion coefficient,  $R$  is the gas constant, and  $T$  is the absolute temperature.

Tafel analyses on the above data are shown in Figure 7, and an average value for  $(n' + \alpha_{n'})$  of 0.46 was derived from the gradients of the plots. The concentration of oxygen in a saturated solution is 1.3 mM,<sup>[21]</sup> and the diffusion coefficient for oxygen is  $2.1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.<sup>[22]</sup> Using these values and the gradient of the linear plot in Figure 6b, the number of electrons transferred is calculated using Equation 4 to be 2, indicating the reduction of oxygen to hydrogen peroxide.

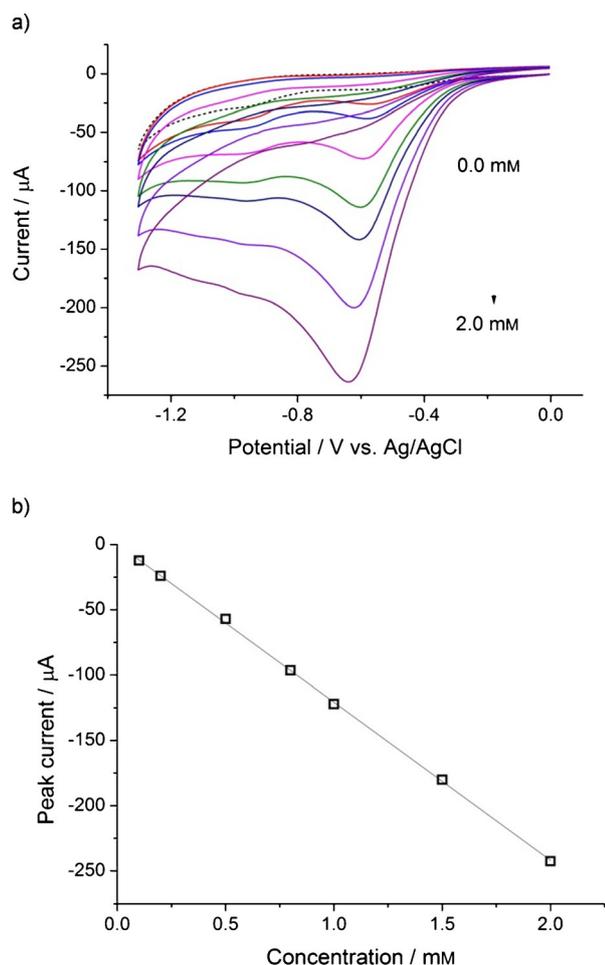


**Figure 7.** Tafel plots of cathodic current for O<sub>2</sub>-saturated 0.1 M PBS pH 7 at scan rates from 50–200 mV s<sup>-1</sup>.

### Reduction of hydrogen peroxide at the modified H-terminated diamond

From the results above, the copper-phthalocyanine-modified H-terminated diamond exhibits a two-electron reduction in O<sub>2</sub>-saturated solution. It has been reported that oxygen can undergo a four-electron reduction at certain metallophthalocyanines.<sup>[16c-e]</sup> Therefore, the possibility of the electrochemical reduction of the hydrogen peroxide on the modified diamond surface was further investigated.

The unmodified H-terminated diamond surface was examined by cyclic voltammetry in an N<sub>2</sub>-saturated solution, and the measurement was featureless for the reduction of hydrogen peroxide. Standard addition of hydrogen peroxide was then conducted on the copper-phthalocyanine-modified H-terminated diamond in an N<sub>2</sub>-saturated PBS to study the reaction without contribution from dioxygen. Figure 8a shows the cyclic voltammograms of hydrogen peroxide for concentrations of 0.0 to 2.0 mM, with a peak potential of  $-0.57$  V (vs. Ag/AgCl) at 0.1 mM. The magnitude of the peak current increases linearly with the hydrogen peroxide concentration, as shown in



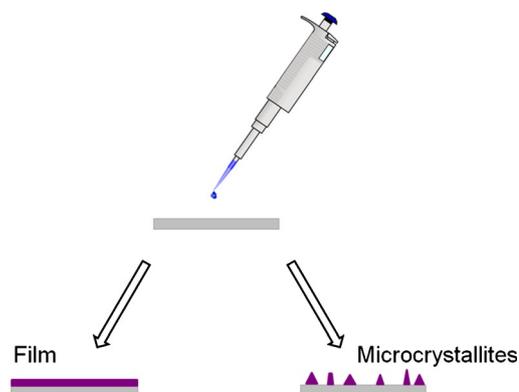
**Figure 8.** a) Cyclic voltammograms for copper-phthalocyanine-modified H-terminated BDD in N<sub>2</sub>-saturated 0.1 M PBS pH 7 containing 0.0–2.0 mM H<sub>2</sub>O<sub>2</sub> (dashed line: 0.0 mM). Scan rate: 100 mV s<sup>-1</sup>. b) Plot of peak current against concentration of H<sub>2</sub>O<sub>2</sub>.

Figure 8b, and the gradient of the calibration plot is  $-121.4 \mu\text{A mM}^{-1}$ .

Tafel analyses on the descending portion of the voltammetric curve yielded an average value of  $\alpha$  to be 0.30. Together with the gradient of the calibration plot and the diffusion coefficient of hydrogen peroxide ( $8.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ),<sup>[23]</sup> the number of electrons per molecule transferred can be calculated using Equation 4, giving a value close to 2. This indicates that the reaction as described by Equation 3 is taking place at the copper-phthalocyanine-modified H-terminated diamond.

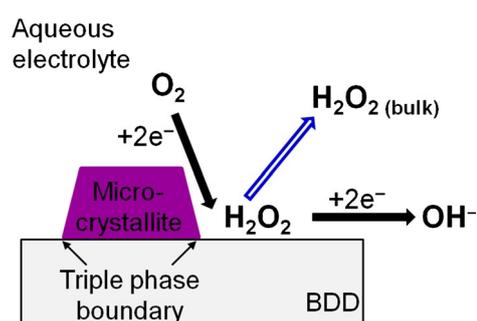
The cathodic peak potential for the reduction of hydrogen peroxide is very similar to that for the reduction of oxygen, and the reactions of both compounds have been demonstrated on the modified H-terminated diamond as above. Therefore, this suggests that the reduction of oxygen should in principle be able to undergo an overall four-electron reaction via the stepwise mechanism with hydrogen peroxide as the intermediate, as described earlier. However, it is clear that oxygen reduction progresses according to Equation 2 with no further electrochemical reduction of hydrogen peroxide.

The key to this apparent conundrum likely lies in the structure of the surface deposition. As illustrated in Figure 9, the dropcast modification of molecular compounds could result in the formation of a continuous film or an array of microcrystallites on the electrode surface. In the former case, hydrogen



**Figure 9.** Schematic diagram of the possible surface formation via dropcast modification.

peroxide is expected to further react via Equation 3. However, the results above are suggestive of the case for the microcrystalline array, in which the charge transfer is thought to occur at the triple phase boundary formed between the copper phthalocyanine microcrystallite, the diamond, and the aqueous solution.<sup>[24]</sup> At the junction of contact of the three phases, the catalyst, electrons, and reactants are all present in adequate proximity for the reaction to occur. The fact that the reduction of oxygen is an overall two-electron process probably has to do with the microcrystallites behaving in effect as a random array of “microelectrodes” (Figure 10), allowing the hydrogen peroxide formed in this instance to diffuse radially into the



**Figure 10.** Schematic diagram showing possible outcomes of H<sub>2</sub>O<sub>2</sub> during O<sub>2</sub> reduction at the triple phase boundary.

bulk phase at a rapid rate before it can undergo further conversion according to Equation 3. Indeed the presence of microcrystallites on the modified diamond surface has been evidenced earlier by SEM in Figure 3, and this supports our inference of a triple-boundary process.

## Conclusion

The dropcast coating of boron-doped diamond electrodes has been studied as a facile method for the surface modification of diamond with molecular materials. The electrochemical behaviour of unmodified and copper-phthalocyanine-modified diamond electrodes was examined via the reduction of oxygen, a reaction known to be catalysed by metallophthalocyanines. Such physical immobilisation was found to be sensitive to the diamond surface termination. Hydrogenated diamond modified in such a manner was able to significantly decrease the overpotential for the cathodic reaction by about 500 mV when compared to the unmodified electrode. Oxidised diamond, however, displayed no such electrocatalysis even after modification by the copper macrocycle. These effects may be attributable to the greater interaction between the nonpolar molecular modifier and the "alkane-like" hydrogen-terminated surface, through forces such as hydrophobic interaction.

On the modified H-terminated diamond, the electrochemical reduction of oxygen occurred through a diffusion-control two-electron cathodic process via the peroxide pathway. In addition, the modified electrode showed activity for the electrochemical reduction of hydrogen peroxide at similar potentials as well. The role of microcrystallites is proposed to lead to the curtailment of the oxygen reduction at the peroxide stage due to the rapid diffusion of the reaction product away from the triple phase boundary at where the reaction is thought to occur. SEM characterisation of the surface morphology confirmed the presence of microcrystallites on the modified H-terminated diamond.

## Experimental Section

**Materials:** Copper(II) phthalocyanine (dye content > 99%, Aldrich), CH<sub>3</sub>CN (> 99.7%, Rathburn), H<sub>2</sub>O<sub>2</sub> (35 wt%, Alfa Aesar), KH<sub>2</sub>PO<sub>4</sub> (≥ 99.0%, Sigma Aldrich), and K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (≥ 99.0%, Sigma Aldrich) were used as received. All aqueous solutions were prepared using ultrapure H<sub>2</sub>O (~18.2 MΩ cm at 25 °C). O<sub>2</sub> and N<sub>2</sub> were obtained from BOC gases. Gases were bubbled through for at least 15 min to saturate the solution, and an O<sub>2</sub> or N<sub>2</sub> atmosphere was kept over the solution during the experiment.

**Apparatus:** Electrochemical experiments were conducted at 22 ± 1 °C using a μ-AUTOLAB III potentiostat (Eco-Chemie, Utrecht, Netherlands), with a standard three-electrode configuration comprising a platinum coil counter electrode, and an Ag/AgCl (1 M KCl) reference electrode, against which working electrode potentials are referred, along with the working electrode. Hydrogen plasma treatment of the electrode surface was carried out with a microwave plasma system. Surface morphology was characterised by a Hitachi 520 SEM (Tokyo, Japan) operating at an accelerating voltage of 20 kV.

**Electrode preparation:** Boron-doped polycrystalline diamond (Element Six Co.) with a B doping concentration of ~5 × 10<sup>20</sup> cm<sup>-3</sup> was used as the working electrode, which was mounted in a home-built polytetrafluoroethylene (PTFE) holder with an area of 0.44 cm<sup>2</sup> being exposed to the electrolyte. An oxidised (O-terminated) diamond electrode was prepared by potential cycling in 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub> between potentials of -1.5 V and +2.5 V until

a stable scan was observed. To produce a hydrophobic H-terminated surface, the electrode was exposed to a hydrogen plasma at 60 mbar pressure, 1.5 kW microwave power at a temperature of 600 °C for 30 min. After this treatment, the substrate heater was switched off, and the sample was left exposed to the hydrogen plasma which was gradually reduced in power until the plasma extinguished and the sample cooled to RT under flowing hydrogen. This procedure yielded an electrode surface which X-ray photoelectron spectroscopy (XPS) confirmed was largely free of adsorbed hydrocarbons or sp<sup>2</sup> material which can adsorb if the "cool-down" period is not carefully controlled.

To modify the diamond electrode, 50 μL of copper phthalocyanine (1 mg in 1 mL acetonitrile) was pipetted onto the electrode surface in aliquots of 2–3 μL and allowed to dry in air between aliquots. This volume was found to give maximal voltammetric response, indicating the optimal coverage of the electrode. Three "blank" voltammograms were run in O<sub>2</sub>-saturated PBS pH 7 (0.1 M) to equilibrate each freshly prepared electrode before further experiments were conducted. The electrode-to-electrode response was generally reproducible and stable at least over the length of the experiments. Modified electrodes were sonicated in acetone to remove the attached phthalocyanine.

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**Keywords:** boron-doped diamond · catalysis · copper phthalocyanine · oxygen reduction · surface modification

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