

Supporting Information: Fractional surface termination of diamond by electrochemical oxidation

René Hoffmann^{*†}, Harald Obloh^{*}, Norio Tokuda^{†‡}, Nianjun Yang^{*}, Christoph E. Nebel^{*}

^{*}Fraunhofer-Institute for Applied Solid State Physics (IAF)

Tullastraße 72, Freiburg 79108, (Germany)

*rene.hoffmann@iaf.fraunhofer.de

[†]Graduate School of Natural Science and Technology, Kanazawa University,

Kanazawa, Ishikawa 920-1192 (Japan)

[‡]Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST)

Tsukuba, Ibaraki 305-8568 (Japan)

The molecular density of an attached nitrophenyl layer was calculated from the transferred charge needed for the conversion of nitrophenyl to aminophenyl: $R\text{-NO}_2 + 6 e^- + 6 H^+ \rightarrow R\text{-NH}_2 + 2 H_2O$. The charge was obtained from the peak area of cyclic voltammograms (Fig. S1).

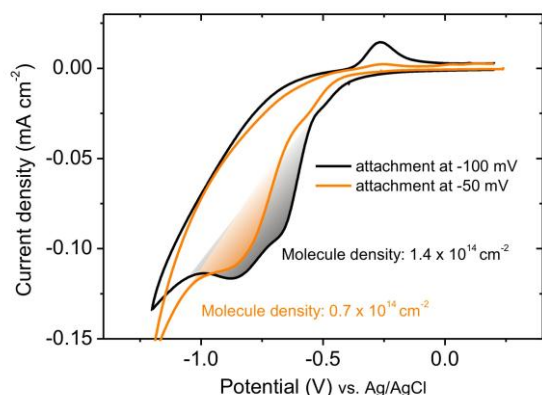


Figure S1. Cyclic voltammograms of the nitrophenyl to aminophenyl conversion of attached layers on H-terminated diamond in 0.1 M KCl containing 10% ethanol at 0.1 V s⁻¹. From the peak areas (highlighted) the transferred charge can be calculated, which leads to the density of attached molecules.

To test if nitrophenyl island formation is a result of slower attachment kinetics, the attachment was repeated with an attachment time 10 times longer, which resulted in similar fractional bonding (Fig S2). The evaluation of oxidation degree was found to be within the error range for both attachments, with $79 \pm 7 \%$ for 2 s attachment and $71 \pm 5 \%$ for 10 s attachment.

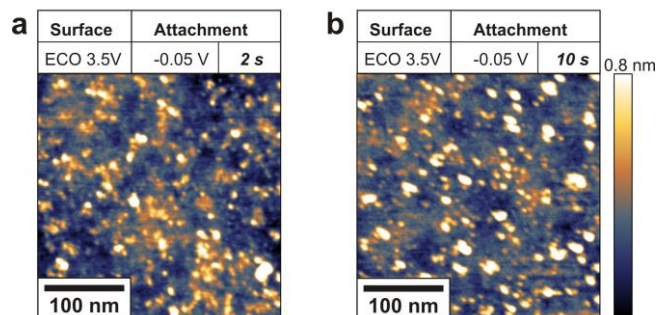


Figure S2. AFM images of attached linker molecules on electrochemically oxidized diamond at 3.5 V oxidation voltage with a) 2 s and b) 10 s attachment time.

Electrochemical impedance measurements with $\text{Fe}(\text{CN})_6^{3-/4-}$ were done at 546 Hz, where the for the used redox molecule the absolute value of the impedance was neither in the low-frequency diffusion limitation, nor in the high frequency saturation (purely capacitive). In Fig. S3, real and imaginary part of impedance measurements from 1 Hz to 135 kHz are plotted for different oxidation voltages. The used frequency is shown as black squares.

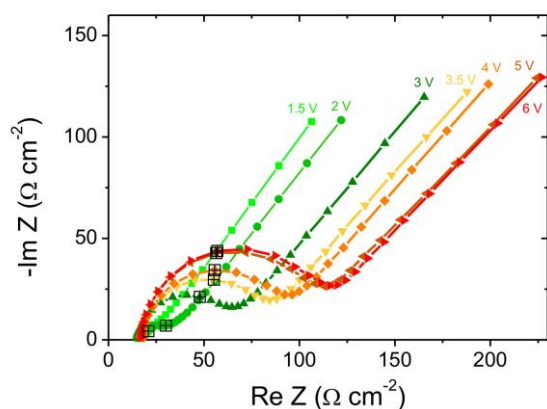


Figure S3. Impedance measurements of 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ on electrochemically oxidized diamond electrodes between 1 Hz and 135 kHz. The black squares indicate the measurements at 546 Hz, which were used for determination of the surface oxidation degree.

The proposed model of electrochemical oxidation includes a linear oxidation-voltage oxidation-time dependency. This could be confirmed for impedance measurements and oxidation at 1.5 V, where a close to linear dependency is expected for short oxidation times, before hyperbolic saturation occurs (Fig. S4).

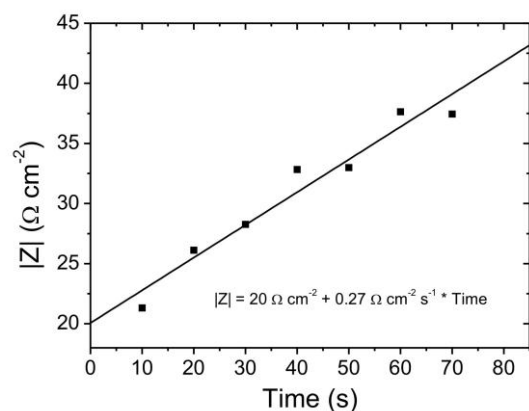


Figure S4. Absolute values of the impedance of 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ on electrochemically oxidized diamond electrodes (oxidation voltage 1.5 V).

A possible model for electrochemical attachment implicates a linear current-voltage characteristic of electrochemical surface treatments. Indeed, for high overpotentials, such a behavior was observed (Fig S5).

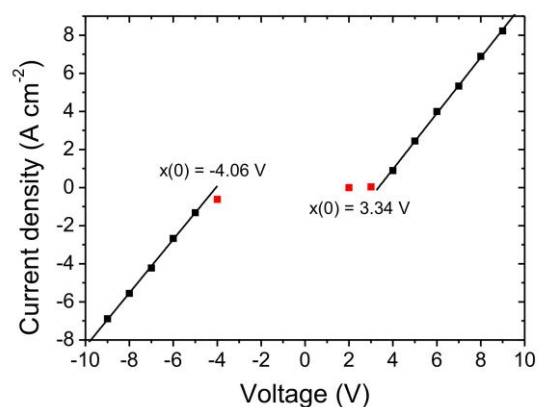


Figure S5. Current-voltage characteristic of the used electrochemical surface treatments. At sufficient overpotential for hydrogen / oxygen evolution, the treatments show linear ohmic behavior with a corresponding resistance of 15Ω .

We also recorded an AFM image of a surface oxidized at 1.5 V (Fig S6). Though the evaluation is less reliable in this case due to mutual steric inhibition of nitrophenyl molecules and the need of a different height threshold (since the spacing between islands is too small for the AFM tip to reach the diamond surface), the obtained 19 % oxidation degree agree well with the discussed model.

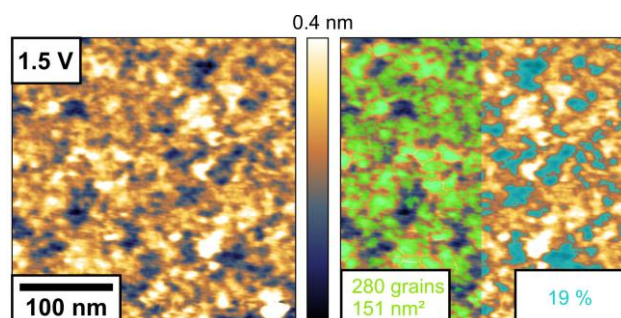
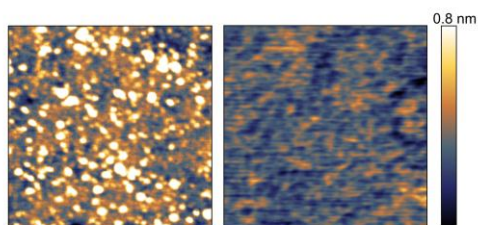


Figure S6. AFM image of nitrophenyl molecules attached to diamond electrochemically oxidized 3.5 V vs. a platinum counter electrode for 10 seconds. Compare to figure 2 in the manuscript.

Although the diamond surface had a non-negligible roughness, figure S7 shows, that it was possible to distinguish between nitrophenyl molecules and the inherent roughness. Furthermore it is shown, that the applied electrochemical cleaning was able to remove the nitrophenyl molecules from the surface.

a



b

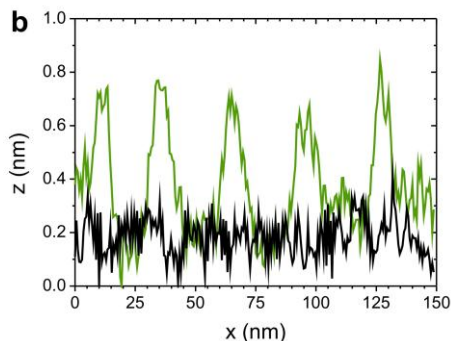


Figure S7. a) AFM measurements of a sample with nitrophenyl molecules (electrochemically oxidized at 2V) on the left and a sample which was electrochemically cleaned by oxidation at 3 V on the right. b) Height profiles of a sample with nitrophenyl molecules and a sample after electrochemical cleaning.

The comparison of the AFM analysis of nitrophenyl attachment to the XPS data confirms that the former can be used for a measure of the oxidation degree of the diamond surface. AFM furthermore allows characterization of local surface termination differences. The formation of linker molecule islands for electrochemical oxidation is in contrast to wet chemical oxidation by boiling in acid, as is shown in Figure S8a. The latter leads to a more evenly distributed attachment of linker molecules, even if some islands can be seen. This indicates that the island formation is at best only partially governed by a cooperative nitrophenyl attachment mechanism. A further confirmation of that result is the nitrophenyl attachment on a H-terminated surface, which was limited by a short reaction time (Figure S8b). Here, although 40 % of the surface remained free of nitrophenyl molecules, the nitrophenyl distribution was homogeneous with a much higher number of islands (800 islands). A similar observation was made for electrochemical oxidation at higher voltages and shorter times. While oxidation at +2 V for 10 s and +10 V for ~1 s (3 times until an oxygen gas bubble stopped the oxidation, ~0.3 s) both led to a similar fraction of oxidized area (74 % and 68 %, respectively) the number of islands differs significantly from 289 to 682, respectively (Figure S8c). This comparison shows that the island formation is due to local surface properties rather than solely different kinetics of the attachment reaction.

In our previous investigations, a surface treatment at 3.5 V for 10 s (compare figure 2b) has been found to mediate high activity of immobilized cytochrome c, which was ascribed to hydrophilic as well as hydrophobic interaction between the protein and diamond. The average hydrophobic island size of 86 nm² is larger than the size of a single protein (~20 nm²). The reported density of active proteins was ~80 molecules on an area of 50 x 50 nm. The size comparison in figure 4d between an AFM measurement of proteins¹ and the measurement from figure 2b shows that this number of proteins, possibly situated at the hydrophobic/hydrophilic boundaries, is at least reasonable, even though the activity might as well be related to other effects of the surface treatments like the electric field in the Helmholtz layer or surface roughness.

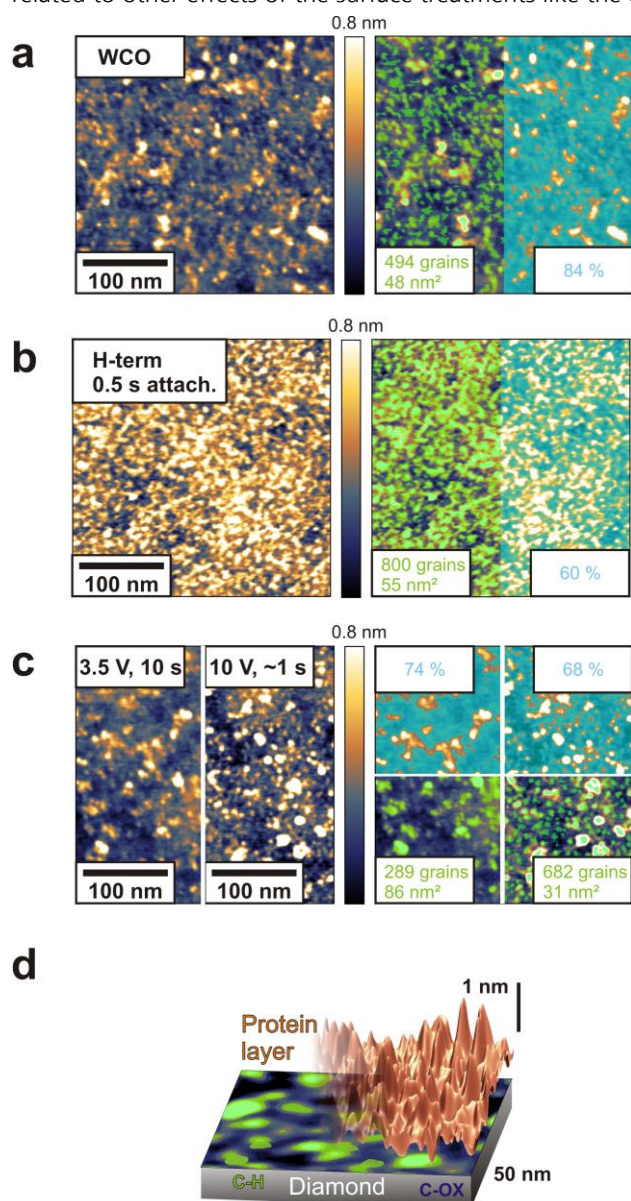


Figure S8. AFM images of nitrophenyl molecules attached for 2 seconds on a) wet chemically oxidized (WCO) diamond and b) attached for 0.5 seconds on electrochemically H-terminated diamond. Grain analysis gives grain number and average size (green) of nitrophenyl covered area and the relative surface fraction (cyan) of non-covered diamond. c) Comparison of nitrophenyl attachment after electrochemical oxidation at 3.5 V for 10 s and at 10 V for ~1 s. d) Size comparison of the fractionally hydrogen- (green) and oxygen (blue) terminated diamond surface and immobilized cytochrome c.

Boron incorporation can be inhomogeneous in diamond. Resulting local differences in conductivity might be the source of the pattern formation during electrochemical surface treatments. We modeled a simple surface profile as a sum of sine waves, to represent local conductivity differences (dashed line in Figure S8). The solid lines in Figure S8 show that oxidation at higher voltages can lead to a more homogeneously oxidized surface, using equation 1 of the manuscript. Electrochemical oxidation at 2 V or more leads to significant evolution of oxygen gas. This may accumulate to bubbles at remaining H-terminated, hydrophobic patches and locally block further oxidation.

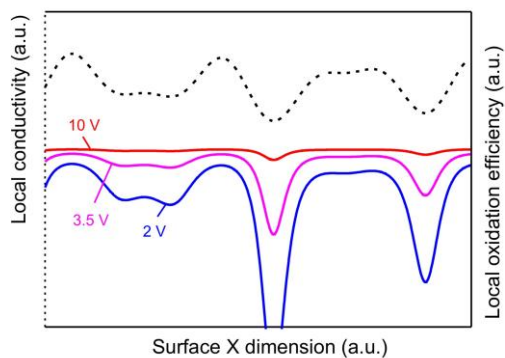


Figure S9. On a simple, modeled conductivity profile, using equation 1 in the manuscript, local conductivity differences (dashed line) lead to local variation in the oxidation efficiency of electrochemical surface termination. High overpotentials even out local variations.