

**Supporting Information for
Photochemical functionalization of hydrogen-terminated diamond surfaces: a
structural and mechanistic study**

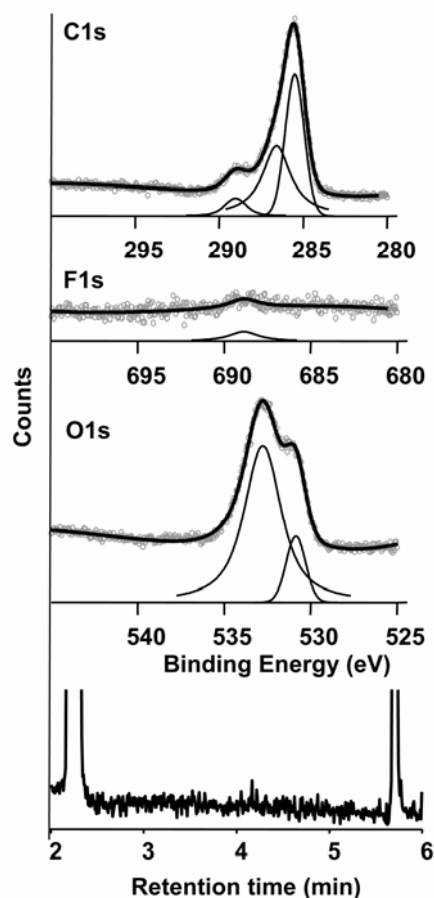
Beth M. Nichols[†], James E. Butler[‡], John N. Russell, Jr.[‡], and Robert J. Hamers[†]

[†]Dept. of Chemistry, University of Wisconsin-Madison, 1101 University Avenue,
Madison, WI 53706

[‡]U.S. Naval Research Laboratory, 4555 Overlook Avenue, S.E., Washington, DC

Corresponding Author: rjhamers@wisc.edu

Reactivity of oxidized diamond surfaces:



The reactivity of oxidized diamond surfaces was investigated using a H-terminated NCD sample that was oxidized in 5:3 sulfuric acid:hydrogen peroxide, rinsed in DI water, and then dried under nitrogen. TFAAD was then placed on the sample, covered with a quartz disk, and illuminated with 254 nm light for 260 minutes under dry nitrogen. At the end of the experiment, the remaining liquid phase was collected by rinsing the diamond with methanol. The diamond surface was cleaned with methanol and chloroform, dried under N₂ and then characterized via XPS.

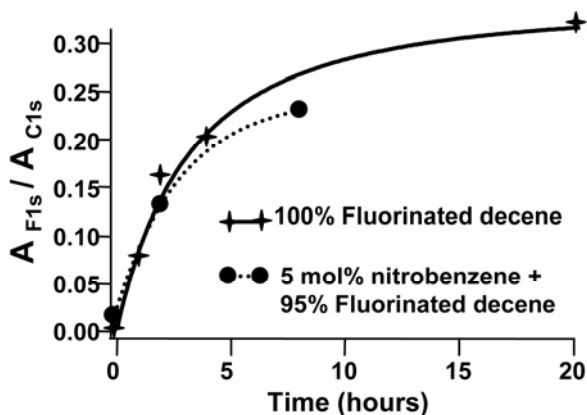
The figure below shows the resulting C(1s), F(1s) and O(1s) XPS spectra for the diamond and the GC for the collected liquid phase. Integration of the XPS peak areas and correcting for the sensitivity factors yields $A_{F(1s)}/A_{C(1s)}=0.011$. This value is much smaller than that observed on the H-terminated sample, demonstrating that the functionalization of oxidized diamond is extremely inefficient. The GC has two peaks: the methanol marker (2.2 min) and the TFAAD peak (5.8 min). The lack of any additional peaks indicates that no new species (byproducts of the photochemistry) have been produced.

Solution phase electron trapping:

In order to help identify whether the surface functionalization involves the anions formed in solution, we conducted experiments in which small quantities of molecules that act as electron scavengers and form stable anions were added to the functionalized alkene. We hypothesized that if anions produced by photoejected electrons were directly responsible for the reaction, then the addition of electron scavengers to the solution-phase would decrease the rate of photochemical modification with the TFAAD. In these experiments we used nitrobenzene which acts as an efficient electron scavenger in organic matrixes. [1] Since nitrobenzene has both N and O as part of its structure, we used perfluorodecene (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene) in place of the TFAAD; this ensures that any O(1s) or N(1s) signal on the terminated surface comes solely from nitrobenzene, while the F(1s) signal comes from the perfluorodecene.

The figure below quantifies the reaction efficiency via a comparison of the $A_{F(1s)}/A_{C(1s)}$ ratio as a function of illumination time for the reaction of H-terminated nanocrystalline diamond with pure perfluorodecene and with a mixture of 5% nitrobenzene /95% perfluorodecene. For reaction with pure perfluorodecene, the reaction self-terminates and reaches a limiting area ratio of $A_{F(1s)}/A_{C(1s)} = 0.30$ after illuminating for approximately 15 hours with 254 nm. When the H-NCD is exposed to the mixture of 5 mol% nitrobenzene/95% perfluorodecene, the data suggest a very similar initial reaction rate during the first 5 hours. In this regime, the corrected O(1s) and N(1s) signals were either below the noise baseline or were less than 2% of the corrected C(1s) signal. As exposure times were increased beyond 5 hours, the $A_{F(1s)}/A_{C(1s)}$ ratio for the solution containing nitrobenzene continued to increase, but at a lower rate than was observed in the neat perfluorodecene experiments. At these longer exposure times, we also observe an increase in N(1s) and O(1s) signal intensity. These data suggest that at long times (i.e. >5 hours) nitrobenzene also reacts with the surface, thereby decreasing the amount of surface area available for reaction with the perfluorodecene.

More importantly, at illumination times of <5 hours there is no significant difference in reaction rate between the pure perfluorodecene and the 5% nitrobenzene /95% perfluorodecene mixture. This indicates that nitrobenzene has no significant effect on the rate of reaction of perfluorodecene with H-terminated NCD.



1. Afanasslev A M, Okazaki K, and Freeman G R 1979 *J. Phys. Chem.* **83** 1244.