

Diamond Microelectrodes for Catecholamine Neurotransmitter Detection

Heidi B. Martin*, Brett D. Blankenship*, Jill C. Venton**, John C. Angus*, and R. Mark Wightman**

*Chemical Engineering Department
Case Western Reserve University, Cleveland, OH 44106

** Chemistry Department
University of North Carolina, Chapel Hill, NC 27599

We present the development of boron-doped diamond film microelectrodes for electrochemical detection of catecholamine neurotransmitters. Carbon fiber based microelectrodes have predominantly been used to monitor dynamics of neurochemical events in the extracellular space within the brain, *e.g.*, refs.1,2. These electrodes have made great advances possible: low detection limits and an improved level of understanding of biological and pharmacological processes in healthy and dysfunctional systems. Yet, these electrodes are plagued by long term stability problems, due to surface passivation by oxidation. Fast voltammetric scanning rates (100-1000 V/s) are necessary for dynamic measurements, and a correspondingly high baseline current exists, making detection of basal neurotransmitter levels difficult; stimulation of neurotransmitter release from neuron synapses is required.

Conductive diamond is a chemically and mechanically robust electrode that enables new chemistries and lower analyte concentrations to be investigated because of its low baseline current and wide potential water window of water stability.³⁻⁶ Diamond electrodes demonstrate, by far, the most stable response of any carbon-based electrode, also without requiring extensive pretreatment to regenerate the electroactive surface.^{5,7} Preliminary testing of diamond electrodes as detectors of various bioanalytes, *e.g.*, dopamine,^{7,8} serotonin,⁹ and sulfa drugs,¹⁰ have shown the potential of diamond biosensors. Diamond surfaces are not completely inert; their surface termination^{4,8,11} influences the electrochemical properties. Yet, diamond's surface chemistry is simpler than present electrodes, and thus, provides a versatile, yet more predictable electrode surface to engineer.

Highly conductive, boron doped diamond was deposited onto tungsten substrates by hot-filament assisted chemical vapor deposition. Two types of fabrication strategies were successfully used: (1) depositing the diamond film on the tungsten substrate, and then selectively insulating it to achieve the appropriate electrode area, and (2) selectively depositing diamond onto a pre-constructed tungsten microelectrode. For fabrication via the first method, etched tungsten wires were coated with polycrystalline diamond, insulated with amorphous Teflon and then the desired electrode area re-exposed. Low (**Fig. 1a**, 150x) and high (**Fig. 1b**, 5kx) magnification images of a diamond-coated tungsten wire are pictured; the geometric diameter of the tip, prior to insulating it, was <10 microns. The surface chemistry of the diamond film was controlled to promote Teflon adhesion. Hydrogen termination of the diamond surface promoted adhesion of Teflon, whereas oxygen termination did not. Electrochemical deposition of trifluoromethylphenyl groups via a diazonium precursor promoted Teflon adhesion further. The Teflon was removed from the desired electrode area with an electron beam.

For fabrication via the second method, diamond was selectively deposited onto tungsten microelectrodes, consisting of an etched tungsten wire within a quartz capillary.

The diamond microelectrode response to dopamine and other catecholamine neurotransmitters were characterized using flow injection analysis and these characteristics compared with those of surface-modified carbon fiber electrodes. Initial tissue measurements to monitor dopamine concentrations in an anaesthetized rat and brain slices were conducted.

Acknowledgments

This research has been supported by NIH and the Case School of Engineering (HBM).

References

1. R.M. Wightman, L.J. May, and A.C. Michael *Anal. Chem.* **60**, 769A-779A (1988).
2. P.A. Garris and R.M. Wightman *Synapse* **20**, 269-279 (1995).
3. H.B. Martin, A. Argoitia, A.B. Anderson, U. Landau and J.C. Angus, *J. Electrochem. Soc.* **143**, L133-L136 (1996).
4. H.B. Martin, A. Argoitia, J.C. Angus, and U. Landau, *J. Electrochem. Soc.* **146** (1999) 2959-2964.
5. G.M. Swain, A.B. Anderson, and J.C. Angus, *MRS Bulletin* **23** (1998) 56-60.
6. R. Tenne and C. Levy-Clement, *Israel J. Chem.* **38** (1998) 57-73.
7. H.B. Martin, J.C. Angus, and R.M. Wightman, "Diamond Microelectrodes for Catecholamine Neurotransmitter Detection," in preparation.
8. E. Popa, H. Notsu, T. Miwa, D.A. Tryk, and A. Fujishima, *Electrochem. Solid St. Lett.* **2** (1998) 49-51.
9. B.V. Sarada, T.N. Rao, D.A. Tryk, and A. Fujishima, *Anal. Chem.* **72** (2000) 1632-1638.
10. T.N. Rao, B.V. Sarada, D.A. Tryk, and A. Fujishima, *J. Electroanal. Chem.* **491** (2000) 175-181.
11. M.C. Granger, M. Witek, J.S. Xu, J. Wang, M. Hupert, A. Hanks, M.D. Koppang, J.E. Butler, G. Lucazeau, M. Mermoux, J.W. Strojek, and G.M. Swain, *Anal. Chem.* **72**, (2000) 3793-3804.

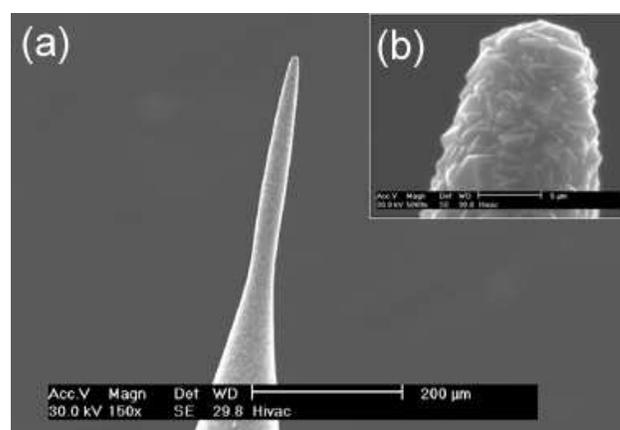


Fig. 1: Low (a, 150x) and high (b, 5kx) magnification scanning electron images of a diamond-coated tungsten wire; these tips were insulated to create diamond microelectrodes. The geometric diameter of the tip, prior to insulating it, was < 10 microns.