

Mercaptobenzene Films-A Versatile Modification Strategy for Carbon Substrates

J. H. Granger and M. D. Porter

Center for Combinatorial Sciences, The Biodesign Institute at Arizona State University, 1001 S. McAllister Avenue, Tempe, AZ 85287-6401

The use of nanoparticles (metallic or semiconductor) has received much recent interest due to their potential applicability to electronics, magnetism, and catalysis [1-3]. Most platforms for nanoparticle deposition typically involve metal substrates with a bifunctional linking molecule (i.e., a dithiol or diisocyanide) for attachment. Although successful, this approach limits the substrate identity to precious metals (e.g. gold, silver and platinum), which may be cost-prohibitive to mass production of nanoscale devices.

Carbonaceous materials have not been widely used in the creation of nanoparticle surface domains due to the dearth of possible linking chemistries and difficulty in fabricating nanoscale features. The electroreduction of substituted arenediazonium salts [4-6] presents an interesting approach to link nanoparticles to a carbon surface. As illustrated in Figure 1, a thiol-terminated carbon surface can be created by the electroreduction of 4-mercaptobenzenediazonium tetrafluoroborate (4-MBDT) to form a covalently bound film. This mercaptobenzene (MB) film subsequently provides a means to attach nanoparticles to the carbon surface. Furthermore, the recent use of pyrolyzed photoresist films (PPF), which can be photopatterned to create MEMS devices, expands the options for using carbon as a machinable substrate.

We have already reported the use of this method to attach 30 nm gold nanoparticles to a glassy carbon electrode [7]. Herein, we describe the extension of this strategy to incorporate other nanoparticles (Ag and CdS) and substrates (PPF), and the creation of photopatterned nanoparticle arrays by "thiolate" photolithography.

Additionally the surface properties of the Au/MB-modified electrode were explored by formation of a 4-aminothiophenol (ATP) monolayer on the gold nanoparticles, and the subsequent electrochemical reductive desorption (ERD) of the thiol without disruption of the underlying gold-MB bond.

[1] Martin, C. R.; Mitchell, D. T. *Anal. Chem.* 1998, 70, 322A-327A.

[2] Rolison, D. R. *Chemical Properties of Nanomaterials*; Institute of Physics Publishing: Bristol, 1996.

[3] Wang, Z. L. *Nanomaterials for Nanoscience and Nanotechnology*; Wiley-VCH Verlag GmbH: Weinheim, 2000.

[4] Bourdillon, C.; Delamar, M.; Demaille, C.; Hitmi, R.; Moiroux, J.; Pinson, J. J. *Electroanal. Chem.* 1992, 336, 113-123.

[5] Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* 1992, 114, 5883-5884.

[6] Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* 1995, 119, 11254.

[7] Harnisch, J. A.; Pris, A. D.; Porter, M. D. *J. Am. Chem. Soc.* 2001, 123, 5829-5830.

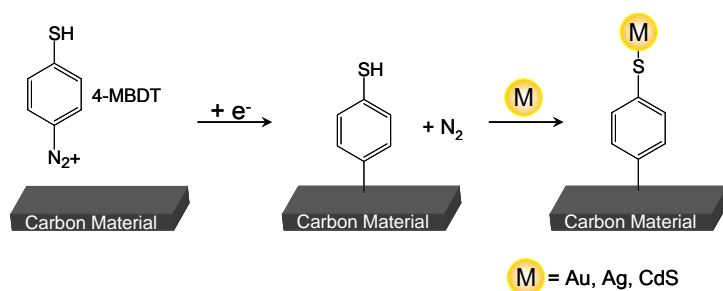


Fig. 1: Electrochemical formation of mercaptobenzene (MB) film, and subsequent attachment of nanoparticles to a carbonaceous surface.

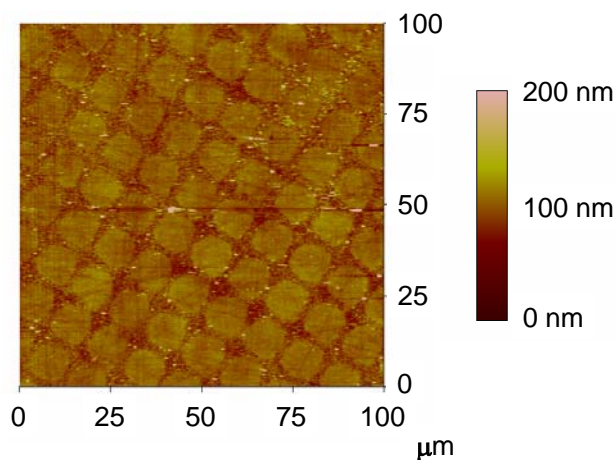


Fig. 2: AFM contact mode height image of a photopatterned mercaptobenzene-modified glassy carbon electrode after Au nanoparticle deposition.