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Attachment of Gold Nanoparticles to Glassy Carbon Electrodes via a Mercaptobenzene Film

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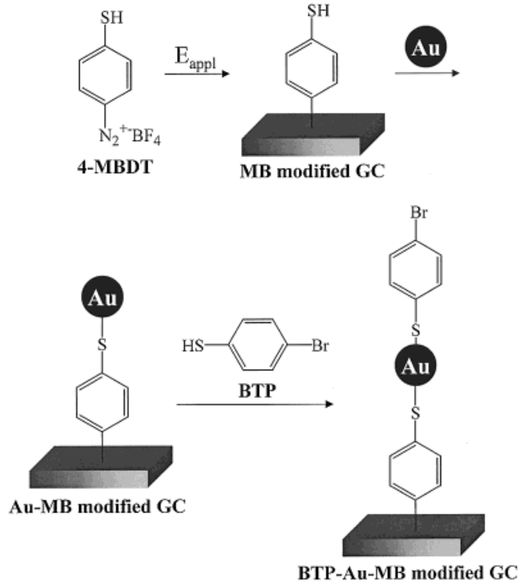
Metal nanoparticles have a wide range of properties of potential importance to electronics, magnetism, catalysis, and analysis.[1−13] In many instances, the assembly of such particles into nanostructured systems has exploited the simplicity and versatility of monolayers prepared from bifunctional molecules (e.g., dithiols[4,7] and diisocyanides[14,15]) which act as coupling agents for linking to substrates such as gold or platinum. This communication extends the range of usable substrates to carbon-based materials by describing the ability to bind gold nanoparticles to glassy carbon electrodes (GCEs) through a sulfhydryl-terminated monolayer that is formed by the electrodeposition of 4-mercaptobenzenediazonium tetrafluoroborate (4-MBDT).

Scheme 1 summarizes each step in the overall preparative process.[16] The first step depicts the electrochemical formation of the 4-mercaptobenzene (MB) monolayer.[19] The second step illustrates linkage of the nanoparticles to the GCE via the sulfhydryl moiety of the monolayer. The MB monolayer is formed on freshly polished GCEs by cycling the applied potential between +600 and −600 mV in a 10 mM solution of 4-MBDT until the electrode was passivated and the observed current decayed to background levels (3−4 cycles). This process reflects the irreversible one-electron reduction of the diazonium group[19−21] (half-wave potential: −480 mV versus Ag/AgCl/saturated NaCl). After sonication in neat acetonitrile for 10 min and drying under a stream of high-purity nitrogen, an aqueous solution (20 μL) of uncoated, 30-nm gold particles was pipetted onto the MB-modified GCE and allowed to stand for 24 h in an environment saturated with water vapor. Finally, the electrodes were again rinsed and dried in the same way as the freshly polished GCEs.

Scheme 1. Construction of Au-Modified Glassy Carbon Electrode with 4-MB Linking Layer



Two sets of characterizations were used to examine the effectiveness of coupling the particles to the MB-coated GCE. The results from the first set of characterizations are shown by the atomic force microscopy[22] (AFM) images (2.0 × 2.0 μm) in Figure 1. Figure 1 presents the topographic images of MB-modified GCE before (a) and after (b) exposure to the gold particle solution. The AFM image of MB-modified GCE is similar to those reported in the literature for both uncoated and monolayer-coated GCEs.[27,28] It is characterized by features less than 30 nm in height and a large number of striations originating from the polishing process. After exposure to the 30-nm gold particles, the image shows the sample has developed a "pebbled" appearance, indicative of the presence of a fairly dense layer of the nanoparticles. The particles have the expected height of ∼30 nm, as revealed

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(16) Gold nanoparticles (30 nm) were from BBInterational. GCEs (Tokai, GC-20) were polished sequentially with 1.0, 0.3, and 0.05 μm Alumina powder (Buehler), sonicated for 10 min each in water and acetonitrile, and then dried under a directed stream of high-purity nitrogen prior to use.[21] 4-MBDT was synthesized according to a previously reported procedure.[22]

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(22) AFM images were obtained with a Nanoscope IIIa AFM (Digital Instruments), which was equipped with a 150-μm scanner and oxide-sharpened Si_3N_4 cantilevers (Nanoprobes, Digital Instruments).[23] Images obtained at much higher magnification also showed slightly elongated particle shapes, as expected from the effect of tip convolution.[24−26] XPS data were obtained using a Physical Electronics Industries 5500 surface analysis system equipped with a hemispherical analyzer, Torroidal monochromator, and multichannel detector. Monochromatic aluminum Kα radiation (1486.6 eV) at 300 W was used for excitation. Binding energies were referenced to the C(1s) emission band at 284 eV. See ref 23 for further details.

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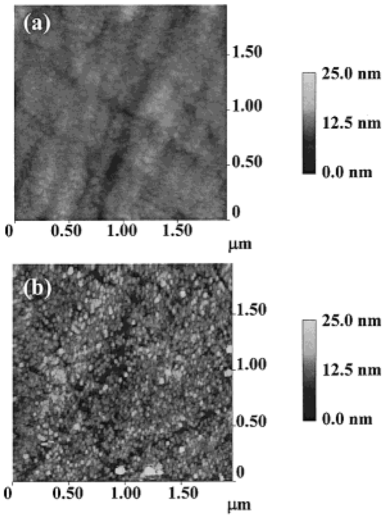

Figure 1. (a) AFM tapping mode image of MB-modified glassy carbon. (b) AFM liquid contact mode image of MB-modified glassy carbon electrode after deposition of gold nanoparticles.

by cross-sectional contour plots of the surface topography (not shown). Imaging also showed that the particles remained attached to the GCE surface even after sonication in water or acetonitrile for 15 min, whereas particles deposited onto unmodified GCE were easily removed by sonication. Adherence after sonication supports the robust coupling of the particles to GCE with the sulfhydryl moiety of the MB monolayer.

The second set of characterizations used X-ray photoelectron spectroscopy (XPS).[22] These results are shown in Figure 2, and include survey spectra for freshly polished and MB-modified GCEs, and for MB-modified GCEs after exposure to the nanoparticles. As illustrated in Figure 2a, freshly polished GCE shows the expected bands in the C(1s) and O(1s) regions at 287 and 532 eV, respectively. After the electrolysis of 4-MBDT (Figure 2b), bands for the S(2s) singlet (located at 228 eV), and S(2p) couplet (centered at 164 eV) appear. The two sulfur bands are diagnostic of an unreacted sulfhydryl species, and the presence of these features is consistent with the expected composition of the MB-monolayer.

In addition to the characteristic bands for the MB film, the XPS spectrum for the particle-modified sample (Figure 2c) contains Au(4f) bands at 88 and 85 eV, which further support the successful deposition of the gold nanoparticles. The spectrum also shows that the centroid of the S(2p) band is shifted ~1 eV lower in binding energy after particle deposition to 163 eV. We attribute this shift to the immobilization of the gold particles through the formation of gold thiolate linkages.[29]

We also tested the ability to modify the nanostructured assembly as a possible avenue for manipulating the surface properties of the immobilized particles as well as for generating three-dimensional motifs. After attachment of gold particles to GCE, some samples were immersed in a dilute (1 mM) ethanolic solution of 4-bromothiophenol (BTP) for 24 h. Analysis of these samples by XPS (Figure 2d) shows the presence of the BTP adsorbate based on the bands centered at 70 eV for the emission of Br(3d) electrons. In other preliminary experiments, we have successfully modified the immobilized nanoparticles with a ferrocene terminated thiol (i.e., HS-$(CH_2)_{11}O_2CFc$), demonstrating the potential flexibility of our synthetic strategy.

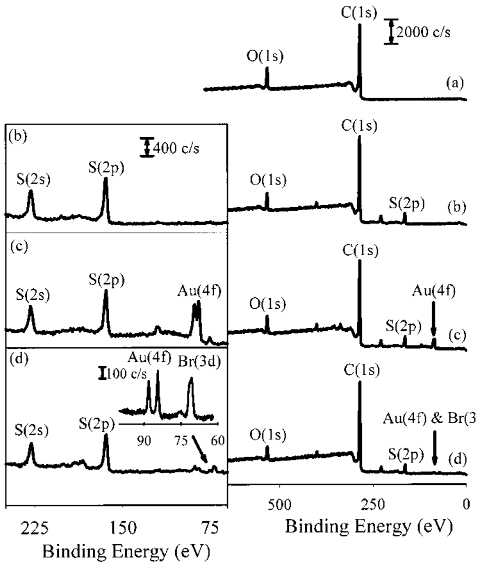

Figure 2. XPS spectra for (a) unmodified glassy carbon, (b) MB-modified glassy carbon, (c) Au−MB-modified glassy carbon, and (d) BTP−Au−MB-modified glassy carbon. The insets are the expanded region from 60 to 250 eV for MB-, Au−MB-, and BTP−Au−MB-modified glassy carbon.

In conclusion, we have developed an approach to robustly anchor gold nanoparticles to carbon surfaces via an electrodeposited mercaptobenzene monolayer, extending the range of the platforms that can be used to prepare nanostructured assemblies. Studies are underway to examine the scope of this approach. We are, for example, beginning to explore the utility of this process to create three-dimensional motifs by the subsequent modification of the gold colloid layer, the coupling properties of which may be manipulated by the nature of the functional groups on an adsorbing thiol (e.g., labile protecting groups).[30] We are also pursuing the construction of patterned arrays of nanoparticles via "thiolate" photolithography.[31]

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