DIAZONIUM DERIVED ARYL FILMS
ON GOLD ELECTRODES

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The modification of electrode surfaces by the chemical or
physical attachment of organic films is a versatile
methodology for controlling electrochemical reactivity.
Although numerous approaches are known, modification
schemes are typically restricted to a specific electrode
material. The electrochemical reduction of diazonium
salts has been shown to be an effective means of
covalently binding aryl films to graphite carbon
electrodes.1 Recently, researchers have investigated this
method for modifying metal surfaces.2,3 In addition,
different laboratories have reported that aryl films can
form on surfaces immersed in diazonium salt solutions by
self-assembly.4,5 We are assessing the versatility of
electrochemical deposition and self-assembly of
diazonium salts for the chemical tailoring gold surfaces
and are investigating the stability of these layers.

In the work to be presented, diazonium salts are
electrochemically reduced at gold electrodes. The
resulting films are characterized by a number of
techniques. Figure 1 shows a typical cyclic
voltammogram of 2.5 mM nitrobenzene (NB) diazonium
salt (0.1 M Bu4N BF4 in ACN) at a gold electrode. On
the first sweep, a single cathodic peak is observed
corresponding to the reduction the diazonium moiety to
form an aryl radical. Very little current is observed in the
second sweep, presumably because a blocking layer is
generated on the electrode after generation of the aryl
radicals. This behavior is identical to that observed on
carbon electrodes.1 Figure 2 provides infrared (IR)
spectroscopic characterization of the layer resulting from
the electrochemical deposition of diazonium derived
nitrobenzene (dNB). The top spectrum is a transmission
IR spectrum of NB diazonium salt powder. Of note is the
intense band at 2300 cm-1 corresponding to the N-N
stretch of the diazonium group. The lower spectrum is
the IR reflection absorbance spectrum (IRRAS) of a dNB
film on gold. We observe several characteristic bands
that point to the deposition of a NB film on gold. Importantly, the inset spectrum shows the region around
2300 cm-1 where no evidence of the diazonium group is
present. This indicates that the film is generated by the
electrochemically produced NB radicals and not by
physiosorption of the dNB starting material.

Also to be presented is a comparison of dNB layers on
gold with monolayers formed from the spontaneous
adsorption of thiol derived nitrobenzene (tNB). To test
the relative stability of these films we have exposed them
to rigorous sonication, solvent extraction and have
explored their displacement with octadecanethiol (ODT).
The blocking of electron transport to solution redox
probes and IRRAS were used to probe the intergrity of the
films before and after treatment. Our results show that a
significant portion of diazonium derived NB films survive
the treatments implying that they are strongly bound to
the gold surface. Notably, dNB films resist displacement
by ODT to a greater extent than tNB.

Both dNB and tNB films have also been characterized by
ellipsometry and x-ray photoelectron spectroscopy. The
results of these studies indicate that the electrochemical
reduction of diazonium results produce multilayer films
on gold surfaces analogous to that observed on carbon
electrodes.1

Finally, we will present preliminary results characterizing
aryl films on gold produced by self-assembly from
diazonium salt solutions. We believe this method
effectively produces monolayers on both planar surfaces
and on gold nanoparticles.

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