Surface Enhanced Raman Spectroscopy (SERS) of Electrochemically Generated Gradients of Organothiols on Gold

A Summary Report to The Electrochemical Society for the 2001 Edward G. Weston Summer Research Fellowship

by Karin Balss

A major focus of our group is the spatial and temporal control of electrochemical reactions on thin gold electrode surfaces.[1,2] One area of active interest is spatially patterning organothiols. Mixed components of self-assembled monolayers (SAMs) such as ω-substituted alkanethiols are a useful way to manipulate the chemical and physical properties at a solid-liquid interface. The ability to control the distribution of SAMs has exciting possibilities to tailor surfaces for specific applications such as active transport of biological and chemical species. Achieving directed motion is dependent upon the detailed spatial distribution of chemical species in the transition region between components; therefore a variety of spectroscopic and microscopic techniques have been utilized to examine the transition region. We are interested in chemically mapping the distribution with surface-enhanced Raman spectroscopy (SERS) and imaging (SERI).

The gradients in molecular surface coverage are formed by spatially mapping the electrosorption reaction onto the electrode. In-plane potential gradients are created by injecting current into thin (20 ≤ d ≤ 50 nm) gold films. This potential gradient depends on the amount of current injected, the voltage offset and the resistivity of the film. The electrosorption properties of thiols[3,4] are translated onto the surface by adjusting the magnitude and position of this potential drop so that one end of the film is poised positive of the stripping potential, favorable for adsorption, and the other end poised negative, unfavorable for adsorption. When electrical contact is broken, the film can be immersed in a second solution to cover the bare regions of gold. The system that is created contains three regions; two regions that are predominately one component and a transition region that contains both component thiols.

The fellowship work presented here is focused on searching for a suitable substrate-analyte combination that meets the requirement for surface enhancement and for the electrochemical gradient formation. The 2-component gradients consist of para-substitut-

FIG. 1. SERS spectra of BMT (top) and ClBMT (bottom) on 55 Å mass thickness gold island films. The peaks designated with arrows will be used to construct images of 2-component gradients consisting of BMT and ClBMT. Raman spectra were obtained with a Spex 500M monochromator equipped with a 600 grove/mm holographic grating and a Photometrics CCD camera. An Ar+ pumped Ti:Sapphire laser was used to excite at 752.5 nm. A holographic super notch plus filter (Kaiser) was used to reject the Rayleigh line.
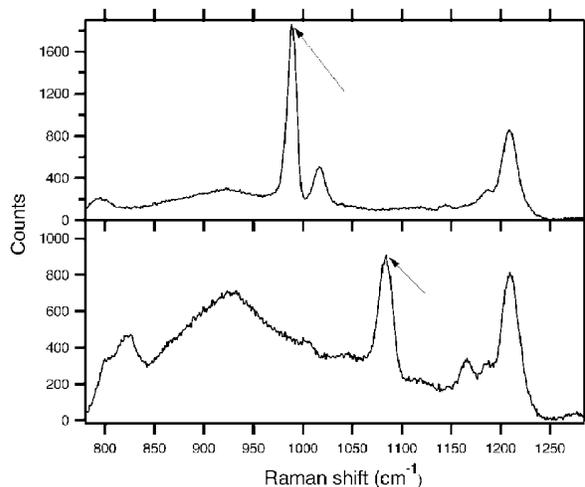
FIG. 2. 1 x 1 μm topography images from contact mode atomic force microscopy (AFM) of electrochemically roughened gold substrates. The original as-deposited 1000 Å film is shown in panel a. The height scale is 30 nm in a and 50 nm in b-e. Panel f is a plot of the rms roughness of the films as a function of number of ORCs in 0.1 M KCl. Typical anodic charge passed per sweep was 6 mC/cm².
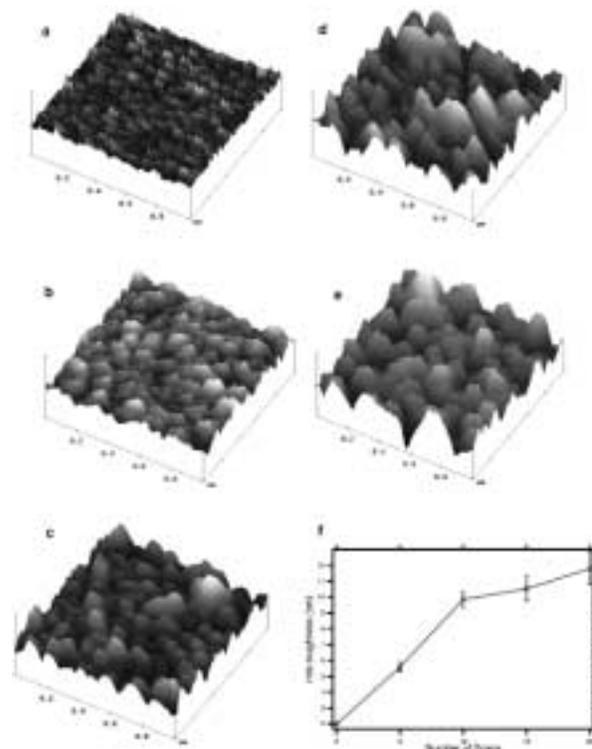
ed aromatic thiols, since they provide a larger Raman cross section compared to straight chain alkylthiols. In addition, the aromatic thiols chosen must have at least one distinctive mode, because SER imaging is being performed on these samples. Several aromatic candidates were characterized for their ability to form well-ordered monolayers (utilizing surface plasmon resonance (SPR) spectroscopy and 4-point probe resistivity

measurements),[5] the ability to observe the stripping potential in alkaline solution and to observe SERS peaks on gold island films. Figure 1 contains spectra of the two aromatic thiols chosen, benzenemethanethiol (BMT) and *p*-chlorobenzenemethanethiol (ClBMT).

Next, a suitable substrate for both SERS and for generating gradients was determined. We have chosen to examine electrochemically roughened gold

Feeling Old?

this magazine recently received an e-mail that asked the question, "Are you feeling old yet?" The e-mail continued, "The people who are starting college this fall across the nation were born in 1982." It then proceeded to list many other facts to help you determine just how old you felt, such as "Most have never seen a TV set with only 13 channels, nor have they seen a black-and-white TV. They have always had cable."

ECS has an antidote for feeling old. In 2002, The Electrochemical Society will celebrate 100 years of existence, old enough to make the rest of us feel like pre-college students again. Readers of *Interface* can look forward to regular items given over to "ancient history." So look for the distinctive ECS Centennial logo and enjoy the "Centennial Moments" coming your way.

The ECS Centennial Meeting, **May 12-17, 2002,** will be celebrated in the Society's birthplace of Philadelphia, Pennsylvania. It's always more fun to celebrate when somebody else turns 100, and there are plenty of surprises planned. Don't forget to mark your calendar now and look for more Centennial year announcements.

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(continued from the previous page)

films for this purpose. Figure 2 displays a series of topography images from contact mode atomic force microscopy. After initially cycling in 1 M H_2SO_4 to remove impurities,[6] the 1000 Å thick gold films were subjected to a series of oxidation-reduction cycles (ORCs) in 0.1 M KCl electrolyte.[7,8] As the number of ORCs is increased, the rms roughness of the film increases. Efforts are underway to characterize the surface enhancement as a function of roughness.

Future work will focus on generating 2-component gradients consisting of BMT and ClBMT on electrochemically roughened gold substrates. SERS will be utilized to chemically map the distribution on the electrode surface. In addition, *in situ* imaging studies under potential control will also be performed. These *in situ* chemical composition maps will be invaluable in answering fundamental questions about the gradient formation process. ■

Acknowledgments

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Bright Light from Thin Layer Electrochemical Cells

A Summary Report to The Electrochemical Society for the 2001 Colin Garfield Fink Summer Research Fellowship

by Russell G. Maus

A thin layer cell for dc electrogenerated chemiluminescence is relatively simple to construct, in which two reflective electrode surfaces are maintained parallel to each other.[1] A solution containing a high concentration of an electrochemically active molecule capable of electrogenerated chemiluminescence is placed in the cell and a potential is applied to the electrodes. Radical cations are formed at the cathode while radical anions are formed at the anode. These species quickly diffuse away from the surface at which they were created. Although the direction of diffusion is random, the size constraints of the cell cause a large majority of the radicals to encounter a complementary radical formed at the opposite electrode. An electron transfer reaction then occurs and produces an excited state species that relaxes to ground state via a radiative process.

In this research effort we used high concentrations (~ 50 mM, near saturation) of 9, 10 diphenylanthracene (DPA) dissolved in benzonitrile containing no electrolyte. A diagram of the electrochemical cell is shown in Fig. 1. To maximize the transmitted light, indium tin oxide on substrate glass was used as one electrode while a platinum disk was used as the other electrode. By holding two electrode surfaces parallel with a surrounding glass tube we were able to simulate a thin layer cell design. Current and light output for the device are shown in Fig. 2. Significantly more light output is seen for the negative potential sweep. Reduction of tin at the ITO counter electrode at large negative potentials is thought to cause irreversible damage to the electrode surface and therefore lower light levels.[2] A spectrum of the emitted light is shown (Fig. 3). The light output of the cell, observed using a low power microscope objective was noted to be spatially and temporally random possibly due to electrohydrodynamic convection.[3] The collected light intensity was found to be 0.082 mW (370-700 nm). The spectrum agrees well with fluorescence spectra previously acquired for DPA. Had the cavity been more reflective on both sides an interference pattern might have been established in the cell and manifest in the output spectrum.

A second generation cell is being constructed that uses electrodes of similar size so that the current density is constant within the cell. The electrodes
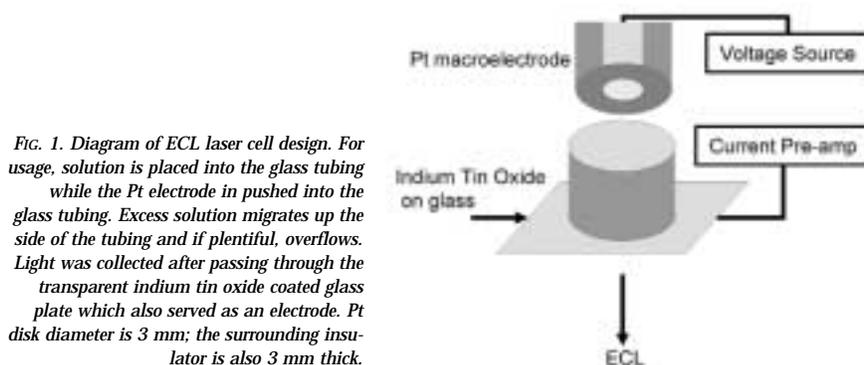
FIG. 1. Diagram of ECL laser cell design. For usage, solution is placed into the glass tubing while the Pt electrode in pushed into the glass tubing. Excess solution migrates up the side of the tubing and if plentiful, overflows. Light was collected after passing through the transparent indium tin oxide coated glass plate which also served as an electrode. Pt disk diameter is 3 mm; the surrounding insulator is also 3 mm thick.
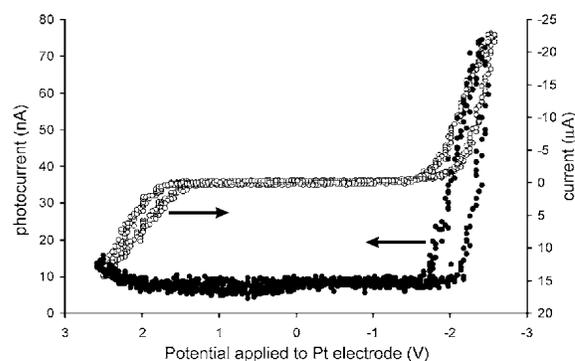
FIG. 2. Measurement of light and current at cell during voltage scan (192 mV/s). (○ current data, ● photocurrent at PMT).
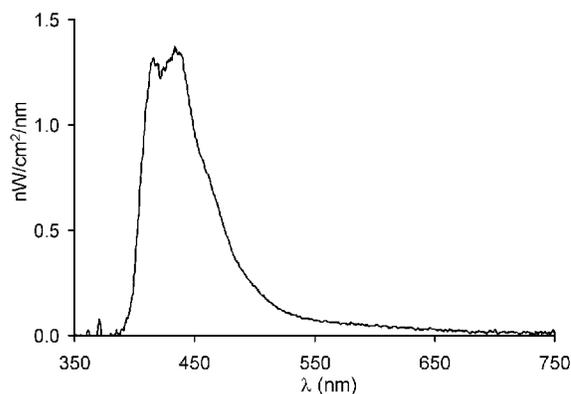
FIG. 3. Emission spectrum of ECL during dc (+2.3 V) excitation.

are made of fiber optics that have been coated with aluminum followed by an insulating material. In this way, any light generated in the cell can be quickly and easily collected and transmitted to a spectrometer. The end is then highly polished and sputtered with platinum to form an electrode surface. It was determined that in order to maximize the efficiency of the device, it is imperative that current density be maintained between the electrode surfaces. Efficiency of the device is highest when the electrode surfaces are of equal size and aligned with each other.

Interest in a bright electrochemically driven source has been present in electrochemical circles for nearly 25 years. Indeed, the feasibility of electrochemically driven laser was addressed in detail by Heller and Jernigan in 1977.[4] The advantages of an electrochemically driven laser lie mostly in simplicity of design and size. Replacing a conventional dye laser that requires either a flashlamp or external laser to pump it with a design that requires neither and can pump itself might be advantageous to many current dye laser users. ∎

Maus

Acknowledgments

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Redox-Active Dendrimers: Toward the Construction of Switchable Guest Encapsulation Systems

A Summary Report to The Electrochemical Society for the 2001 Joseph W. Richards Summer Research Fellowship

By Charles O. Noble IV

Spherical polymers known as dendrimers have recently drawn attention as hosts for the encapsulation of guest molecules.[1,2] The ultimate goal of the work described here is a dendrimer that is capable of physically trapping guests by a mechanical action that is reversible (upon the introduction of an external stimulus) to facilitate the triggered release of the guest.

To achieve the goal of having a dendritic host molecule whose encapsulation/release mechanism is chemically triggered, oligo(pyrroles) were placed at the periphery or the "tips" of a poly(propylene imine) dendrimer (Fig. 1). Oligo(heteroarene)s have significantly different structures (orientation of heterocycle rings) when in their oxidized (doped) or reduced (undoped) states.[3,4] Thus, the molecular-scale mechanical properties of the two oligo(pyrrole) oxidation states should allow for control over the nature of the dendrimer exterior, and the incarceration properties of the dendrimer.

The concept of oligomerizing a dendrimer's pyrrole termini was illustrated by previous work from this group using electrochemical methods.[5,6] The earlier synthetic method was limited to dendrimers having only 16 pyrroles; however, larger dendrimers are desired for the encapsulation of guests. Recently, the formation of high-generation, pyrrole-terminated poly(propylene imine) dendrimers (referred to as DAB dendrimers) was achieved by peptide coupling of ω-(N-pyrrolylalkane)carboxylic acids to the 1° amines of amine-terminated DAB dendrimers, DAB-Am$_X$ (X = 32, 64), resulting in pyrrole-terminated DAB dendrimers (DAB-(COC$_Y$Py)$_X$, Y = 3, 5 and X = 32, 64).

DAB-(COC$_Y$Py)$_X$ dissolved in organic solvents are capable of being intramolecularly oligomerized by chemical oxidation of the pyrrole termini with FeCl$_3$. The oligomerization reactions were performed at dendrimer concentrations of 10 μM to avoid dendrimer aggregation (as supported by dynamic light scattering studies); thus preventing inter-dendrimer connections.

IR spectra of the DAB-(COC$_Y$Py)$_X$ treated with FeCl$_3$ in chloroform solu-

DAB-(COC$_5$Py)$_{32}$ *oligo*-DAB-(COC$_5$Py)$_{32}$
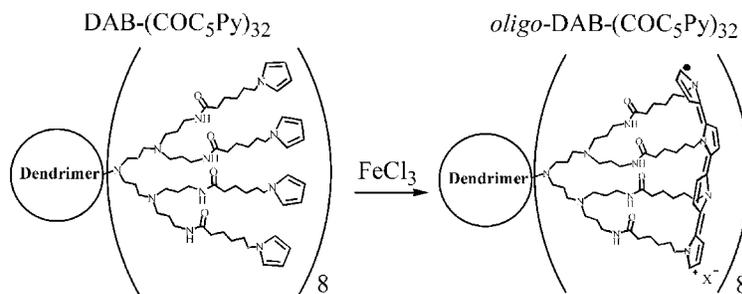
Fig. 1. Schematic illustrating the oligomerization of the pyrrole groups of DAB-(COC$_5$Py)$_{32}$ by chemical oxidation with FeCl$_3$.
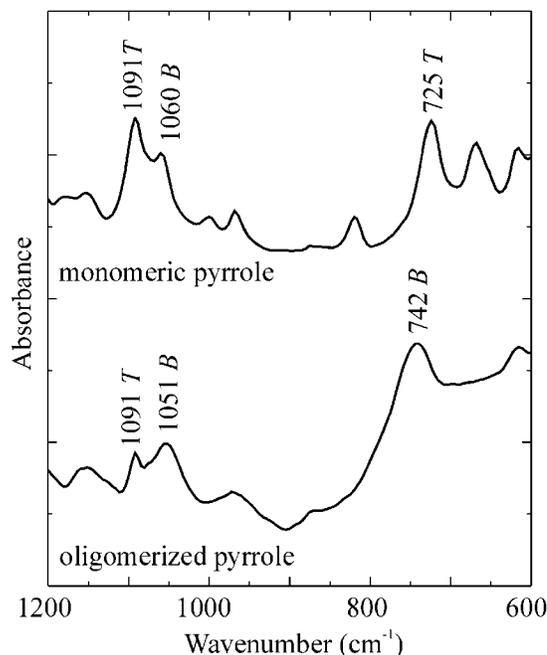
Fig. 2. IR spectra of DAB-(COC$_5$Py)$_{32}$ before and after oxidative oligomerization with FeCl$_3$ in CHCl$_3$.

tion indicate that oxidation of the DAB-(COC$_{3,5}$Py)$_{32}$ results in oligomerization of the pyrrole monomers about the periphery (Fig. 2). An end-group analysis method was used to confirm connectivity between the pyrrole monomers.[7] The spectrum of DAB-(COC$_5$Py)$_{32}$ before oxidation is characteristic of the dendrimer being terminated by monomeric pyrrole groups. In particular, the 725 cm^{-1} tail band (T), along with the lack of bands at 795 cm^{-1} and 765–780 cm^{-1} and the presence of the more intense T-band at 1091 cm^{-1} (versus the backbone (B) band at 1060 cm^{-1}) supports the presence of only monomeric pyrrole groups in the dendrimer. The IR spectrum of DAB-(COC$_5$Py)$_{32}$ after oxidation (referred to as oligo-DAB-

(COC$_5$Py)$_{32}$) is characteristic of a DAB dendrimer having an oligo(pyrrole) exterior. The T-band at 725 cm^{-1} has been replaced by a B-band at 742 cm^{-1}, and the B-band at 1051 cm^{-1} is less intense than the T-band at 1091 cm^{-1} for the DAB-(COC$_5$Py)$_{32}$ that has been exposed to FeCl$_3$ oxidant. The IR spectra of DAB-(COC$_3$Py)$_{32}$ before and after oxidation are nearly identical to those for DAB-(COC$_5$Py)$_{32}$, indicating that the 2-carbon difference in the chain length to the pyrroles has little effect on the oligomerization efficiency.

The ability to form an oligo(pyrrole) shell about the periphery of DAB dendrimers provides an avenue for the development of novel host encapsulation systems. Such systems, having a

redox-active mechanical action, will allow for the development of dendrimers capable of the stimulated encapsulation and release of guest molecules. It is envisioned that these redox-triggered dendrimer systems will be applicable to a variety of areas, including preconcentration and delivery of analytes in miniaturized analytical systems, and in drug delivery schemes. ∎

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Efforts Toward the Electrochemical Cyclization of Unsaturated Anilides

A Summary Report to The Electrochemical Society for the 2001 F. M. Becket Summer Research Fellowship

By Jon D. Parrish

Recently, work has been published describing the chemical oxidation of unsaturated anilides (Fig. 1) using IBX (o-iodoxybenzoic acid).[1-3] The conditions reported require the use of 2-5 equivalents of this potentially explosive reagent[4] and the use of a sealed tube. The authors have proposed a single electron transfer mechanism that creates an amidyl radical (Fig. 2) as an intermediate. The radical readily cyclizes onto the appropriately distanced olefin to afford oxazolidinones (Fig. 3, R_2 = O) and lactams (Fig. 3, R_2 = CH_2). This reaction seemed well suited to the application of anodic oxidation to avoid the use of IBX and greatly simplify the reaction conditions described.

Substrates were prepared by two methods. Carbamates (R_2 = O, substrates 1a-1c of Table I) were prepared by stirring an alcohol with the appropriate aromatic isocyanate in benzene. Concentration and recrystallization afforded the desired carbamate. Amides (R_2 = CH_2, 1d-1e) were prepared by stirring aniline derivatives with the acid chloride in ethyl ether. Evaporation of the solvent and recrystallization or chromatography afforded the desired amide.

Cyclic voltammetry was performed in freshly distilled acetonitrile using a glassy carbon working electrode, platinum wire counter electrode and a reference electrode comprised of a silver wire immersed in 0.01 M solution of silver nitrate in acetonitrile. All potentials are referenced to this electrode (approximately 0.3 V compared to the saturated calomel reference electrode).

As seen in Table I, all of the substrates examined readily undergo an irreversible oxidation. The methoxy-substituted substrates (1b and 1e) show two separate one-electron oxidation peaks, whereas the other substrates show a single oxidation peak. This voltammetric data supported our hope that preparative scale oxidation should afford the desired cyclized material (Fig. 3). Unfortunately, we have so far been unable to successfully cyclize these substrates. We have examined a variety of conditions and

have adjusted various parameters such as solvent, electrolyte and electrode material. In all cases, only recovered starting material was isolated. We will continue to examine this interesting reaction, and feel confident that our continued research will yield a preparatively useful method. ■

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FIG. 1. *IBX mediated cyclization of unsaturated anilides.*

Table I. Oxidation potentials of variously substituted amides and carbamates.

Substrate	R_1	R_2	$E_{pa}1$	$E_{pa}2$
1a	H	O	1.62	-
1b	OMe	O	1.19	1.55
1c	Cl	O	1.62	-
1d	H	CH_2	1.59	-
1e	OMe	CH_2	1.13	1.52

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