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Fabrication and Characterization of Probes for Combined Scanning Electrochemical/Optical Microscopy Experiments

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A technique that combines scanning electrochemical microscopy (SECM) and optical microscopy (OM) was implemented with a new probe tip. The tip for scanning electrochemical/optical microscopy (SECM/OM) was constructed by insulating a typical gold-coated near-field scanning optical microscopy tip using electrophoretic anodic paint. Once fabricated, the tip was characterized by steady-state cyclic voltammetry, as well as optical and electrochemical approach experiments. This tip generated a stable steady-state current and well-defined SECM approach curves for both conductive and insulating substrates. Durable tips whose geometry was a ring with <1 μm as outer ring radius could be consistently fabricated. Simultaneous electrochemical and optical images of an interdigitated array electrode were obtained with a resolution on the micrometer scale, demonstrating good performance of the tip as both an optical and an electrochemical probe for imaging microstructures. The SECM feedback current measurements were successfully employed to determine tip−substrate distances for imaging.

A variety of different scanning probe microscopy (SPM) techniques have been used to provide diverse information about substrate surfaces and interfacial processes as well as to fabricate structures on surfaces at submicrometer resolution. In recent years, many contributions have been devoted to the combination of two or more SPM techniques to study micro- or even nanostructures with higher sensitivity and selectivity and to its application for various systems, e.g., scanning electrochemical microscopy (SECM)/photoelectrochemical microscopy (PEM),[1−3] SECM/atomic force microscopy (AFM),[4−10] and AFM/near-field scanning optical microscopy (NSOM).[11−13]

We have been interested in combining SECM and optical microscopy (OM). In SECM, the tip current, which depends on the probe−substrate distance and the conductivity of a substrate, is monitored while the microelectrode tip is moved above a substrate. The SECM technique has been applied for imaging conductivity and electrochemical activities of substrates, the examination of electron-transfer rates, and high-resolution fabrication.[14,15] By combining SECM with OM, optical properties can also be simultaneously studied with the acquisition of electrochemical information of interesting microsystems and allow one to carry out photoelectrochemical investigations of interfaces with high spatial resolution and fabrication with in situ characterization of submicrometer patterns on substrates. We describe here the fabrication of SECM/OM probe tips that allow simultaneous micrometer-level optical and electrochemical imaging.

To accomplish SECM/OM, the most important feature is the design and construction of a special probe tip, which can serve not only as a light source but also as a microelectrode. The concept of the fabrication of SECM/OM probes is similar to that of SECM/PEM probes[1−3] or electrodes for photoelectrochemical experiments.[16,17] The procedure includes (1) heating and pulling optical fibers, (2) metal coating, (3) electrical insulation, and (4) exposing an electrode at the end of the tips. A schematic diagram of the prepared tip is shown in Figure 1a. The first step is to prepare a typical NSOM tip. The preparation method is described elsewhere.[18−22] Briefly, a single-mode optical fiber was heated and pulled or etched down to a tiny point (diameter, 50−100 nm) and

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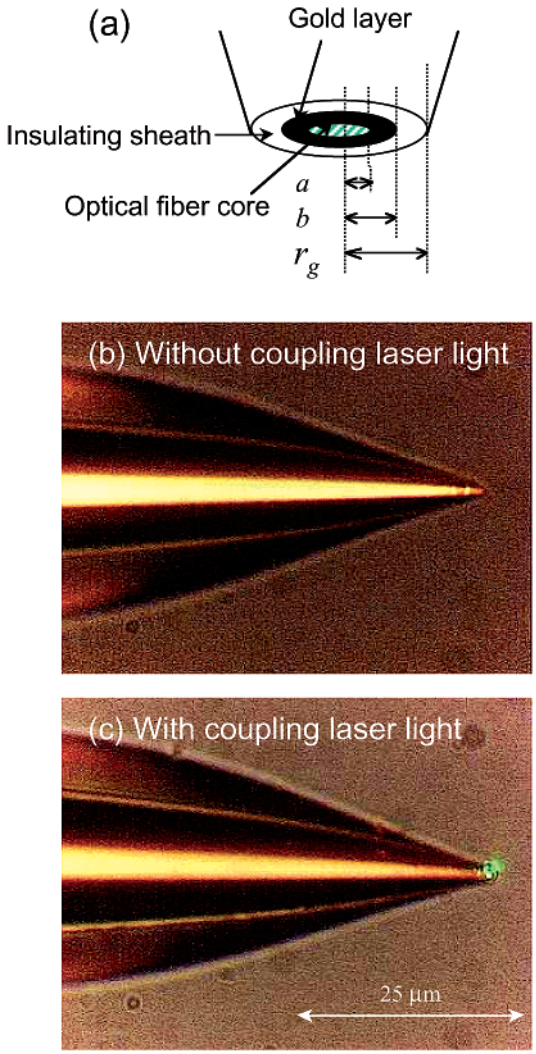

Figure 1. (a) Schematic diagram of an ideal tip: the inner (*a*), outer (*b*), and outermost radii including insulating sheath (r_g). Optical microscopy images of the anodic paint insulated tips (b) without and (c) with coupling of Ar ion laser light at 514 nm.

then these tapered optical fibers are coated with a reflective metal, such as aluminum, to prevent loss of light from the sides of the tapered optical fibers. A deposited metal layer can also be used as an electrode material in SECM/OM. In this experiment, therefore, gold was used for a metal coating instead of the more conventionally used aluminum, because gold is a stable electrode material as well as a reflective metal that can be vacuum-evaporated easily.

Various techniques have been attempted in the fabrication of tiny microelectrodes for electrical insulation and exposure of only the tip apex. Typical ultramicroelectrodes used in SECM are fabricated by insulating the electrode material, which is a platinum microwire, except for the apex of that wire, which serves as the electrode area. To insulate the sides of the tip, many different techniques have been implemented: rf sputtering of insulating materials,[23] simply dipping metal wires into a varnish,[24] pushing the tip through a molten glass bead[25] or molten wax,[26,27] electrodeposition of an insulating polymer,[28−30] and CVD techniques of insulating materials.[10,31]

Removal of the insulating material at the end of the tip to open up a metal electrode area is usually attained by polishing or cutting,[1−3,16,17,23,28−31] although milling with a focused electron[32] or ion beam[10] or touching the tip to a surface using scanning tunneling microscopy[27] has also been reported. Recently, the fabrication of an electrooptical probe that has a ring shape similar to our SECM/OM probe has been described. For this probe, polishing was also used to expose an electrode area.[33] Cutting and polishing, however, are not easily performed on an optical fiber probe because of the fragility of the optical fiber and the different hardness of the insulator and optical fiber materials. In addition, polishing or cutting the pulled end of the optical fiber diminishes the high resolution by increasing the aperture size of the tip. Thus, other techniques of insulation, which can protect the end of a tip from being covered completely, are necessary to keep the advantage of high resolution obtained with a small aperture size. Simple insulation of a tip by electrodeposition of electrophoretic paint has also been used for the preparation of a carbon-fiber microelectrode,[34] a nanometer-sized Pt electrode,[35,36] and a combined SECM/AFM probe[6,7] after this insulation technique was first introduced to insulate Pt/Ir scanning tunneling microscopy tips.[37]

The prepared probe tip was characterized by optical and electrochemical methods as well as by SECM at both conductive and insulating substrates. We successfully acquired simultaneous electrochemical and optical images at the micrometer level of an interdigitated array (IDA) electrode using the prepared tip. In addition to a tiny tip, another critical problem in SPM is that the probe tip must be positioned in close vicinity above a substrate. For this purpose, optical detection of the shear force[38] and, more recently, a tuning fork technique have been employed in NSOM.[39,40] In terms of controlling the tip−substrate distance, the SECM feedback current is an alternative promising candidate for the

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feedback signal. Although the electrochemical activity of samples should be constant to employ SECM current as a feedback signal, it has the advantage compared to shear force of a decreased tip−sample interaction, (important with soft samples) and is readily applied in liquid media. This is another motivation to investigate a combined SECM/OM in addition to its capacity as a novel tool for electrochemical and optical studies of various systems.

EXPERIMENTAL SECTION

Materials. $Ru(NH_3)_6Cl_3 \cdot 10H_2O$ was obtained from Strem Chemicals. KCl (EM Industries, Inc.) was used as a supporting electrolyte. Solutions were prepared with 18 MΩ cm^{-1} deionized water (Milli-Q, Millipore Corp. Bedford, MA) with reagent grade compound without further purification. A 20 mM $Ru(NH_3)_6^{3+}$/0.1 M KCl aqueous solution was used for all experiments. A substrate for the SECM/OM imaging experiment was an IDA electrode, which has 30-μm gold bands spaced by 25-μm glass.

Tip Preparation. (a) Pulling Fibers. Optical fiber tips were prepared by stripping ∼2 cm of the polymer coating from the center of 1-m-long optical fiber (Newport Corp., F-SA, core diameter, 3.7 μm; cladding, 125 ± 2 μm). The exposed portion of a fiber was rinsed with absolute ethanol, dried, and then pulled with a CO_2 laser (20 W maximum) puller (P-2000, Sutter Instruments). The shape of the tips depended on the pulling parameters,[41] typically, as follows: heat, 260; velocity, 26; delay, 126; and pull, 100.

(b) Gold Evaporation. Gold was deposited by vacuum evaporation onto the tapered end of the fiber to a length of ∼2 cm while the fiber was rotated at an angle of ∼45° relative to the horizontal (where gold source was located) at a speed of ∼30 revolutions/min during evaporation. To confirm that light was emitted from only the end of the tip, that is, the absence of pinholes in the gold coating layer, the prepared gold-coated tip was examined under an optical microscope while Ar ion laser light was coupled to the other end of the tip. A good gold coating of the tip showed a small aperture at the end but no light from the sides of the tip.

For electrical contact of a gold-coated optical fiber, the deposited gold layer was connected to a copper wire with silver epoxy (Epoxy Technology, Billerica, MA) and cured in an oven at 80 °C for 3 h.

(c) Electrical Insulation and Exposure of Tip Ends. For electrochemical studies, the gold coating has to be insulated, except for the end of the tip, to produce a ring electrode around the fiber. The tips were insulated with anodic electrophoretic paint (Glassophor ZQ 84-3225, BASF, Münster, Germany). Anodic paint consists of poly(acrylic acid) (PAAH) with an excess of base to make it water soluble by deprotonation of the acidic groups. The tip insulation procedure with anodic paint is similar to the methods described elsewhere[35−37] except for minor changes in some experimental conditions, such as the dilution factor, applied potential, and curing temperature. Anodic paint was diluted by volume 15 times with water. Gold-coated pulled optical fibers were dipped into the diluted anodic paint solution and a +2.2 V dc potential was applied between the optical fiber and a Pt coil (∼1-cm diameter) until the current dropped to a small steady-state value (after ∼30 s). The optical fiber was placed in the center of the Pt coil during the application of the dc potential. The anodic current flow produces a local pH decrease at the electrode surface, induced by water oxidation, and generates water-insoluble PAAH that deposits onto the gold electrode surface.[37] Heat curing of this insulating film was achieved by heating at 150 °C for 3 min. The insulating layer shrinks during heating so that the sharp end of the tip is exposed, while the wall of the tip is completely insulated.[37] To provide an electrode with center area exposed, the ends of tips were held upward (perpendicular to the plane of the floor) during curing. A second insulation was carried out with a more dilute anodic paint solution (30 times) for 2 s followed by the same curing to ensure any pinholes formed in the first curing were sealed. Tips with less than 1-μm outer radii were prepared consistently by this procedure with a yield of ∼50% for the curing process.

Electrochemical Experiments. For electrochemical experiments, a three-electrode system was used. The working electrode was the prepared tip, the counter electrode was a Pt wire, and the reference electrode was Ag/AgCl. A CH Instruments (Austin, TX) model 900 SECM and a home-built SECM were used for all electrochemical measurements.

Scanning Electrochemical Optical Microscopy (SECM/OM). The instrumentation for SECM/OM is similar to the SECM setup previously used,[42−44] with the addition of optical components. The program to control the SECM/OM setup was written in LabVIEW (National Instruments, Austin, TX). The probe tip was held perpendicular to the substrate surface and moved in *x*, *y*, and *z* directions with inchworm motors (Burleigh Instruments) as well as a 40-μm piezoelectric pusher (Burleigh) for fine resolution in the *z* direction. For SECM/OM experiments, a given potential that was sufficient to reduce $Ru(NH_3)_6^{3+}$ was applied to the tip, and the tip was also coupled to a laser. Ar ion laser light (Coherent, Innova 90) at 514 nm was coupled to the other end of a probe tip and used as a light source. The light transmitted through the substrate was detected with a PMT (model R4220P, Hammatsu), placed directly under the substrate, and the current generated was measured with a Keithley 6517 electrometer. The tip faradaic current and transmitted light intensity were measured simultaneously while the tip was moved in the *x*, *y*, or *z* direction above the substrate. All experiments were performed in a darkbox to avoid interference of ambient light. A block diagram of the experimental setup for SECM/OM is shown in Figure 2.

RESULTS AND DISCUSSION

Shape of Pulled Optical Fibers: Pulling Parameters and Their Effect on Gold Coating. As previously reported,[41] the tapered end shape of a tip was a function of four pulling parameters: (a) the heating power specifying the output power of the laser, (b) the pulling velocity, (c) the time delay between reaching the specified pulling velocity and the initiation of the pull, and (d) the pulling power. A good gold coating that has a small aperture at the end of the tip but blocks the light from coming out of pinholes on the sides of the tip was obtained when the optical fiber was pulled with the specified pulling parameters

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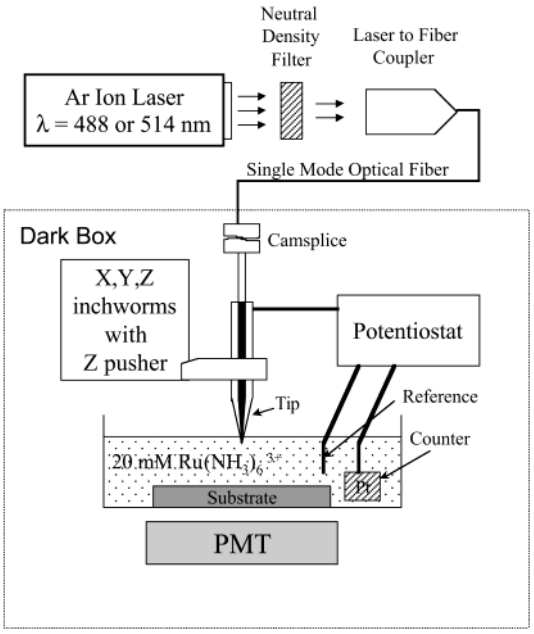

Figure 2. Block diagram of experimental setup for scanning electrochemical and optical microscopy (SECM/OM).

described in the Experimental Section. Average pulling time was ~0.17 s.

Characterization of Tips. Optical Microscopy. The insulation method modified from Shulte et al.[37] allowed the simple removal of insulator at the end of the tip by curing rather than polishing. The gold-coated optical fiber and insulating sheath were readily distinguishable by observation with an optical microscope (Figure 1b and c). The brighter band of the tip image is the result of reflection from the gold, and the outer layer is the insulating film. A uniform metal coating on an optical fiber was also confirmed by coupling a laser to the tip. As shown in Figure 1c, with a tip with a good Au coating, the laser light came out from only the aperture at the end of the fiber but not from the sides. The estimated entire tip size including the insulating sheath by optical microscopy with a high magnification was used to determine the geometry, especially the thickness ratio of a gold ring and an insulating sheath, and to compare the actual size of the tip as determined in the electrochemical experiments.

Electrochemical Approach Curves at Air/Solution Interface. The purpose of the preparation of this kind of tip is to use it as a simultaneous electrochemical and optical probe. Thus, the prepared tips were tested by both electrochemical and optical techniques to verify the utility of the tips as successful scanning electrochemical/optical probes.

First, to check for complete electrical insulation on the sides of the prepared tip but with an open end of the tip, electrochemical approach curves were obtained at an air/solution interface, where the solution contained 20 mM $Ru(NH_3)_6Cl_3$ and 0.1 M KCl in water. The potential, (−0.4 V vs Ag/AgCl) sufficient to reduce $Ru(NH_3)_6^{3+}$, was applied to the tip and the tip current was monitored as the tip was moved from air into the 20 mM $Ru(NH_3)_6Cl_3$ aqueous solution. In Figure 3, representative air/solution approach curves are shown for a tip insulated with anodic paint. A well-insulated tip showed approach curves such as those in Figure 3a, while a poorly insulated tip produced Figure 3b. To compare two tips of the same size in terms of a travel distance,

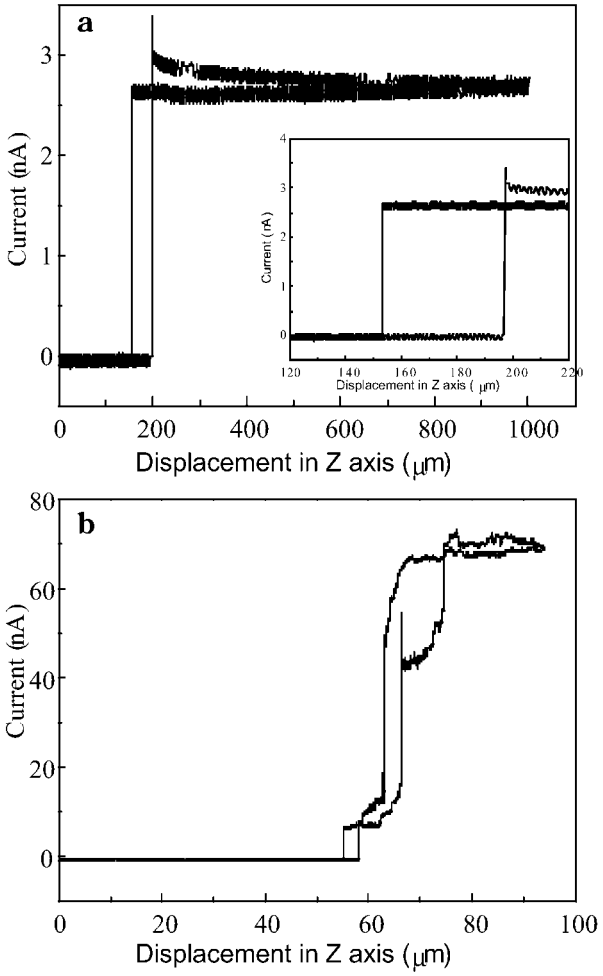

Figure 3. Electrochemical approach curves of the tips with (a) good insulation and (b) poor insulation at the air/20 m M $Ru(NH_3)_6^{3+}$ aqueous solution interface with a tip potential at −0.4 V vs Ag/AgCl. The solution contained 0.1 M KCl as a supporting electrolyte. The speed of the tip approach was 1 μm/s. Inset in (a) is the magnified approach curve of (a).

the magnified figure for 100-μm travel distance is also presented. For a well-insulated tip, when the tip first enters the solution, the current sharply rises in a typical ultramicroelectrode transient and then attains the steady-state current and maintains a constant value as more of the tip is immersed into the solution. This observation indicates a tip that is completely insulated over a length of at least ~800 μm from the end of the tip while only the very end of the tip is uncovered. In the reverse scan, the withdrawal of the tip from solution to air, a corresponding response was observed except the ~40-μm gap produced by the surface tension of the solution that allows a small amount of solution to be held on the tip as it crosses the air/solution interface. On the other hand, a poorly insulated tip (Figure 3b) showed leaks along the sides as more of the tip was immersed into the solution. The current rises when the tip first enters, indicating leaks near the tip. At the moment when the end of the tip touched the solution interface, an abrupt current rise occurs and the tip current increases stepwise as more of the tip is dipped into the solution, indicating pinholes in the insulating film. The integrity of the tip insulation could be confirmed simply by these electrochemical approach experiments at the air/solution interface.

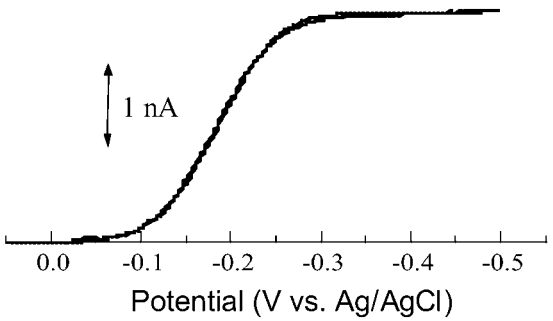

Figure 4. Cyclic voltammograms obtained using anodic paint insulated/cured tips. Solution contained 20 mM $Ru(NH_3)_6^{3+}$ and 0.1 M KCl in water. Scan rate, 50 mV/s.

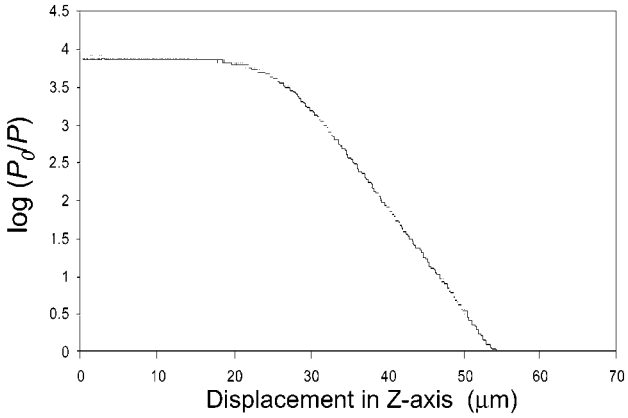

Figure 5. Optical approach curve toward 75 mM Chromotrope 2R aqueous solution/nitrobenzene interface. The wavelength of Ar ion laser was 514 nm (P_0 IS the measured PMT current without dye, and P IS the measured PMT current with dye). The tip was insulated with anodic paint.

Steady-State Cyclic Voltammetry. To verify the ability of the prepared tip to serve as an ultramicroelectrode, cyclic voltammetry was carried out in a 20 mM $Ru(NH_3)_6^{3+}$/0.1 M KCl aqueous solution. The cyclic voltammograms obtained with the prepared tips is shown in Figure 4. Typically, a sigmoidal cyclic voltammogram of a good-quality microelectrode was obtained with a tip insulated with anodic paint.

The stability of the steady-state tip current is very important for SECM. Stable and consistent tip currents lasted over ~3 h in aqueous solution. The measured diffusion-limited steady-state tip currents showed values of between 1 and 5 nA depending not only on insulation, but also on the procedure for gold deposition onto the optical fibers.

Recently, we reported a good strategy for determining the geometry and size of a similar ring-shaped electrode to the tip used here.[45] The diffusion-limited steady-state current is one piece of essential data, which allows determination of tip geometry and size. It was especially important to initially estimate the tip size from optical microscopic images of the tip shown in Figure 1.

Optical Approach Curves. Another procedure for tip characterization involved optical approach experiments performed at a water/nitrobenzene interface. In this experiment, the light emission from the tip is monitored with a photomultiplier as it passes through a solution containing a dye. A liquid/liquid interface was employed instead of liquid/solid interface to protect the tip from any damage that could result from the tip touching a solid surface during the approach. A schematic diagram of the experimental setup is given in the Supporting Information. The upper phase was water containing 75 mM Chromotrope 2R (Aldrich), a dye with a high molar absorptivity at 514 nm that is soluble only in the aqueous phase. The optical approach curve obtained for a tip insulated with anodic paint is shown in Figure 5. The measured absorbance exhibited an excellent linear response with displacement in the z direction until the end of the tip touched the water/nitrobenzene interface. The plateau region at a long distance between the tip and liquid/liquid interface occurs where most of the light source is absorbed by the dye solution. Moving the tip in the z direction toward the interface reduces the light path length of the effective spectrophotometric "cell" bounded by the bottom of the tip and the water/nitrobenzene interface. The optical molar absorptivity of Chromotrope 2R at 514 nm can be obtained from the slope of the optical approach curve based on Beer−Lambert law shown in eq 1, where

$$A = \log(P_0/P) = \epsilon bc \qquad (1)$$

A is absorbance, P_0 is the light intensity in the case of no light absorption through the solution, P is the measured light intensity, ϵ is the molar absorptivity, b is the light path length, and c is the concentration of the absorbing species in solution.

The value of P_0 can be measured in pure water without Chromotrope 2R. In Figure 5, $\log(P_0/P)$ is plotted as a function of b; therefore, the slope of the line in Figure 5 is ϵc. Thus, the absorption coefficient (ϵ) for a certain concentration could be extracted from the optical approach curves. The molar absorptivity obtained (ϵ) was ~17 500 M^{-1} cm^{-1} for a 75 mM Chromotrope 2R aqueous solution. The value of ϵ was a function of the concentration of dye. For example, ϵ was 22 000 M^{-1} cm^{-1} (at 514 nm) at a concentration of 2.25 mM.

Absorption spectra obtained using a spectrophotometer (Milton Roy Spectronic 3000 Array) and a thin-layer cell (Starna Cells, optical path length, 10 μm) supported the strong dependency of ϵ on the concentration of dye. Spectra at different dye concentrations are shown in Figure 6. Aggregation (e.g., stacking) of dye molecules is a well-known phenomenon and can account for the different absorption spectra at different concentrations. At least two isosbestic points are observed in this dye's absorption spectra at various concentrations (points A and B in Figure 6). These isosbestic points are strong evidence that more than one absorbing species is present and is a function of the concentration. The fairly flat structure of the dye (See inset of Figure 6) is consistent with aggregation. It was also possible to extract an ϵ value at a selected wavelength from these absorption spectra. The ϵ value obtained was 24 500 M^{-1} cm^{-1} at 514 nm at a concentration of 2.25 mM. The reason that this value does not agree exactly with the one obtained from the optical approach curve (22 000 M^{-1} cm^{-1}) can possibly be explained by the difference in bandwidth of light sources used in each experiment. The monochromator of the spectrophotometer does not produce an exact single wavelength. To our knowledge, these are the first experiments to utilize a pulled optical fiber-based system to do spectrophotometric experiments.

SECM Approach Curves. The steady-state tip current was measured as a function of the tip−substrate distance for Pt and

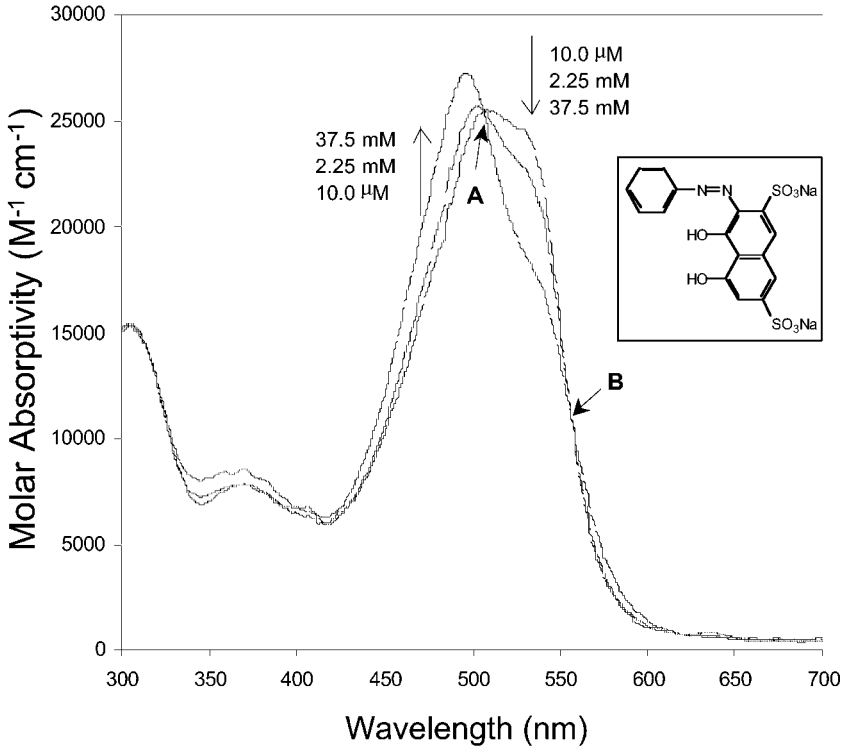

Figure 6. Absorption spectra of Chromotrope 2R as a function of concentration. Inset shows the structure of Chromtrope 2R.

glass substrates. To obtain SECM approach curves, the tip potential was held at − 0.4 V versus Ag/AgCl, which is sufficient to reduce $Ru(NH_3)_6^{3+}$, the electroactive species in solution. Approach of the tip was terminated before the tip hit the substrate surface to protect the tip from damage, which can occur even with light touching. In this experiment, the tip movement was stopped when there was a 10−30% change in the tip current compared to the steady-state tip current $i_{T,\infty}$, (for the tip located very far from the substrate surface).

Figure 7 shows SECM approach curves obtained with the SECM/OM tip at Pt and glass substrates. The steady-state tip current increased as the tip approached the conductive Pt substrate surface because of the regeneration of $Ru(NH_3)_6^{3+}$ at the Pt surface (Figure 7a). On the other hand, at a glass substrate, a negative feedback curve was obtained because of hindered diffusion of the electroactive species to the electrode (Figure 7b).

The SECM approach curves show a dependence on the geometry of the electrode for both insulating and conductive substrates.[27,43,44] As reported previously,[45] SECM approach curves for a ring electrode at a conducting substrate depend on the ratio of inner (a) to outer ring radii (b) rather than the outermost radius of insulating sheath (r_g) (see schematic tip diagram in Figure 1a). On the other hand, approach curves for an insulating substrate are relatively more sensitive to r_g. Thus, SECM approach curves for a ring microelectrode allowed one to extract information about the tip geometry, such as the thickness of the ring and radius of the insulating sheath, by comparing theoretical and experimental approach curves at both insulating and conductive substrates.

The obtained experimental approach curves fit the theoretical ones fairly well with a given a/b ratio and RG value (r_g/b). The geometry of prepared tips obtained using this technique are as follows. The a/b ratio and RG value were quite consistent as 0.85−0.95 and 1.5−3, respectively, while the gold ring thickness was 50−100 nm. With this procedure for tip preparation, an outer radius of a tip less than 1 μm could thus be attained. The average yield of good small tips (less than 1-μm outer gold ring radius), verified electrochemically and optically with the methods described above, was ∼35%.

Scanning Electrochemical Optical Imaging. The utility of this tip as an optical and electrochemical probe was demonstrated above. We finally show simultaneous optical and electrochemical imaging using this tip. For the imaging experiment, an IDA electrode possessing insulating as well as conductive zones was used as a sample substrate. Figure 8 shows the electrochemical and optical single line scans of an IDA electrode that were obtained simultaneously using tips (a = 0.62 μm, b = 0.7 μm, and r_g = 1.75 μm) prepared by this method. The IDA electrode has 30-μm gold bands spaced by 25-μm glass. To obtain these single line scans, the tip was approached toward the IDA substrate until an SECM feedback current was observed. Then, the tip movement in the z direction was stopped and scanning in the x direction was performed.

When the tip was located above a gold band, the electrochemical current increased and the optical signal, which was the transmitted light intensity, detected under the substrate, was almost zero. When the tip was positioned over the glass part, the opposite response was observed. Electrochemical and optical line scans correlated well with each other. The tip current increased over the gold by ∼33% and decreased over the glass by ∼10% compared to $i_{T,\infty}$ (∼2.8 nA) even though both the positive and negative feedback effects were slightly enhanced when the substrate was scanned from left to right. This could be the effect of a tilted substrate with the left side lower and the right higher.

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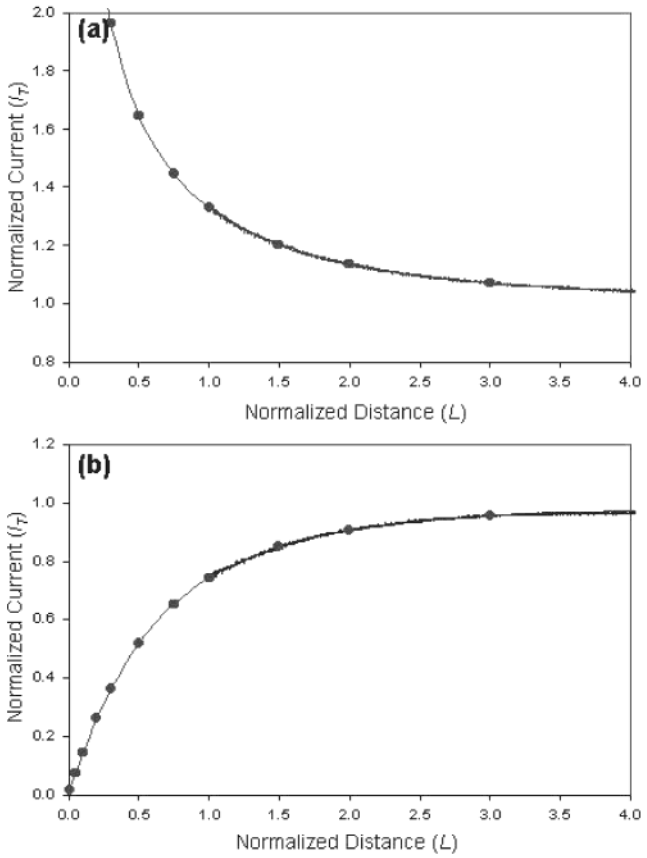

Figure 7. Comparison of the experimental and theoretical SECM approach curves at (a) gold and (b) glass substrates. Theoretical curves (dotted lines) for $a/b = 0.9$ and $r_g/b = 2.5$. Normalized experimental curves (solid lines) for aqueous solution containing 20 mM $Ru(NH_3)_6^{3+}$ and 0.1 M KCl using an anodic paint insulated/cured tip. Normalized distance (L) = d/b and normalized current (I_T) = $i_T/i_{T,\infty}$. a, b, and r_g were 0.62, 0.7, and 1.75 μm, respectively.

The approximate distance between the tip and substrate was extracted from the SECM approach curves at conductive and insulating substrates shown in Figure 7. The normalized distance (L) at 33% increase of $i_{T,\infty}$ for conductive substrate (See Figure 7a) was ~1.0 while L at 10% decrease of $i_{T,\infty}$ for insulating substrate (See Figure 7b) was ~2.1. Thus, the distance between the tip and the IDA substrate was approximately (calculated with the known value of b) as 0.7 and 1.47 μm over the gold and glass, respectively. Since the single line scan was obtained in the fixed-height mode, the observed difference of the tip separation from the gold and glass allows calculation of the thickness of the deposited gold layer of the IDA electrode as 0.77 μm.

Figure 9 shows the images of an IDA electrode acquired using the anodic paint insulated tip. This image was obtained by the tip moving in both the x and y directions when the tip separation from the substrate surface was ~1 μm. As with the single line scans, the bright part in the electrochemical imaging appeared dark in the optical imaging. Gold and glass parts were clearly distinguished, and one can recognize the structure of the IDA electrode sample. The widths of glass and gold band at cross section were obtained as ~27 and ~29 μm, respectively. These numbers match well with the known structure of the IDA electrode. The achieved spatial resolution using this tip was worse than that expected from the dimension of the tip. This is one disadvantage of imaging in the fixed-height mode.[46] Since the spatial resolution in SPM is controlled by not only the probe size but also the tip−substrate separation, it is necessary to maintain the tip in close proximity to the substrate to improve the resolution.

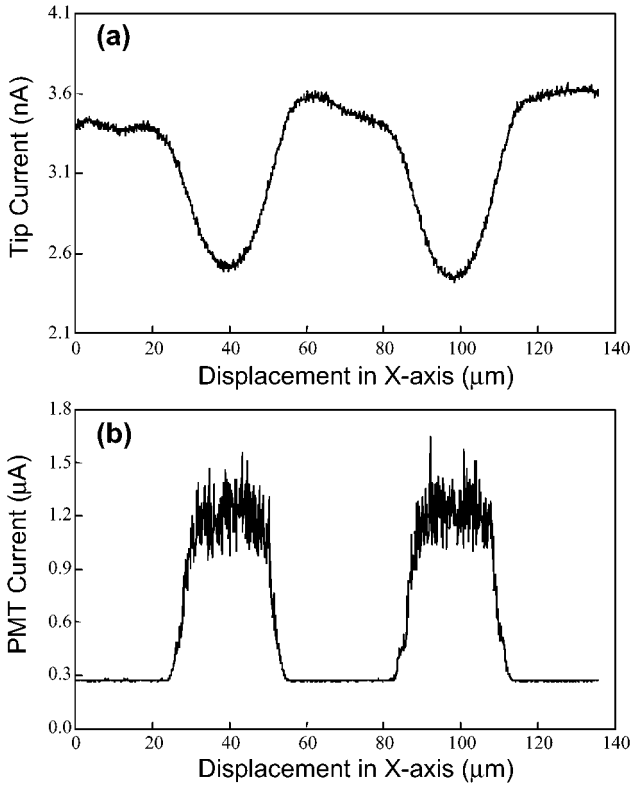

Figure 8. Simultaneous (a) electrochemical and (b) optical single line scans above an IDA electrode (30-μm gold bands spaced by 25-μm glass) in the fixed-height mode ($d \sim 0.7$ and 1.47 μm over the gold and the glass, respectively) using an anodic paint insulated/cured tip whose a, b, and r_g were 0.62, 0.7, and 1.75 μm, respectively.

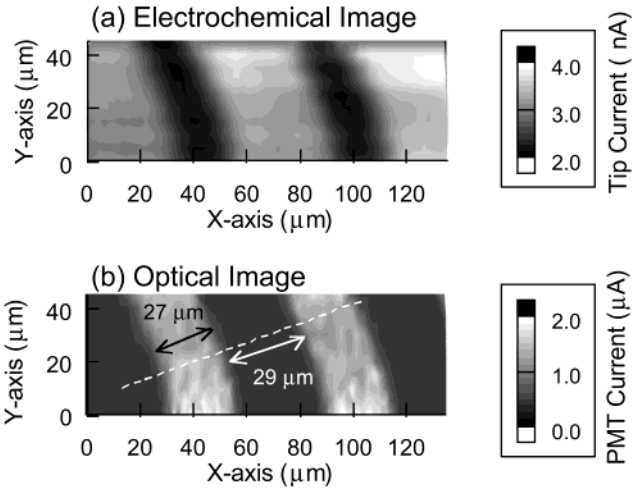

Figure 9. Simultaneously obtained (a) electrochemical and (b) optical images in the fixed-height mode ($d \sim 1$ μm over the gold layer) for an IDA electrode using an anodic paint insulated/cured tip whose a, b, and r_g were 0.62, 0.7, and 1.75 μm, respectively. Scan speed was 1 μm/s.

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CONCLUSIONS

A new probe for combined SECM/OM experiments has been demonstrated and both fabrication and characterization methods have been described. The tip preparation consists of heating−pulling optical fibers, gold deposition, electrical insulation with electrophoretic paint, and opening the end of the tip on curing. Reliable tips require an even gold coating, no leaks in the insulating layers, and a small exposed electrode area at only the very end of a tip. SECM tip approach at the air/solution interface is a useful and simple technique to verify the completeness of electrical insulation. In addition, cyclic voltammetry, optical and electrochemical approach experiments were performed to characterize this tip. These tips produced a stable steady-state current and distinct SECM approach curves for both conductive and insulating substrates. The geometry of tips determined using SECM curves[45] was a ring with different tip sizes depending on the specifics of tip preparation procedures.

Simultaneous electrochemical and optical images were obtained for an interdigitated array electrode at the micrometer scale. The SECM feedback current was successfully employed to determine the tip−substrate distance for SECM/OM imaging. From this result, the capability of the tip as both an optical and an electrochemical probe for imaging microstructures was confirmed though with a limited achievable resolution. SECM images with high lateral resolution topography have been reported using shear force feedback to approach a tip relatively close to a substrate.[46,47] We thus investigated obtaining improved resolution with a closer tip−substrate separation by introducing a tuning fork to the tip to detect the shear force. These results will be reported in a separate communication.[48]

With the characterization of tips using all of the techniques mentioned above, we conclude that anodic paint insulation and heat curing allows us to prepare reliable and small tips (less than 1 μm as an outer gold ring radius) for SECM/OM.

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SUPPORTING INFORMATION AVAILABLE

Schematics of experimental setup. This material is available free of charge via the Internet at http://pubs.acs.org.

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