In Situ Investigations on the Electrochemical Polymerization and Properties of Polyaniline Thin Films by Surface Plasmon Optical Techniques

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The combination of in situ surface plasmon resonance spectroscopy (SPS) and surface plasmon field-enhanced light scattering (SPLS) with an electrochemical method was used to *simultaneously* investigate the optical and electrochemical properties of polyaniline films on a planar gold electrode. First, the electropolymerization process of aniline and then the doping–dedoping process of the resulting polyaniline film were investigated using SPS and SPLS. The electropolymerization of aniline was achieved by applying a cycling potential known from cyclic voltammetry. Potential cycling resulted in distinct oscillations sensitively monitored with both techniques. Information was obtained on the change of the dielectric constant of the film and of the film thickness, corresponding to morphology transitions of the polyaniline film. The time-differential SPS kinetic reflectivity curve was correlated with cyclic voltammetry. SPLS was also applied in a reversed attenuated total reflection configuration to obtain more correlation with the electrochemical behavior and optical properties of the polyaniline film. Thus, this combination of experimental approaches allows for the simultaneous elucidation of optical and electrochemical properties of an ultrathin conducting polymer film.

1. Introduction

The evaluation of film formation and the electrochemical properties of conducting polymers are very important. Understanding their properties on an electrode surface is of great interest for a variety of device applications including, for example, battery electrodes,¹ electrochromic displays,² light-emitting devices,^{3,4} etc. Several techniques, for example, using the quartz crystal microbalance (QCM),^{5,6} FTIR,⁷ electron spin resonance (ESR),⁸ or scannning probe microscopy (SPM),⁹ have been used in combination with cyclic voltammetry for the in situ investigation of electrochemical processes in polyaniline film.

Surface plasmon resonance spectroscopy (SPS) has been shown to be a technique of high sensitivity for characterizing ultrathin films at the nanometer thickness scale.¹⁰ Recently, the combination of the SPS with electrochemical techniques for the simultaneous characterization and manipulation of an electrode/ electrolyte interfaces has been demonstrated.^{11,12} The roughness of adjacent layers on metal surfaces has also been evaluated by monitoring the light scattered from metal surfaces and was shown to also be enhanced by surface plasmons.¹³ We have attempted to combine the techniques of in situ electrochemical SPS and in situ electrochemical surface plasmon field-enhanced light scattering (SPLS) to investigate the electrochemical process of polyaniline film formation and its properties on a flat gold electrode surface.

In this study, electropolymerization of aniline was investigated by applying potential sweeps during cyclic voltammetry experiments, while simultaneously monitoring the film formation by SPS and SPLS. The SPLS in the reversed attenuated total reflection (R-ATR) setup¹⁴ was also applied to probe the electropolymerization process. By simultaneous investigations with SPS, the refractive index or film thickness changes or both of polyaniline during electropolymerization can be monitored in situ. Thus, the incident light enhanced by surface plasmons and scattered off the substrate/electrode interface allows for the investigation of changes in morphology of the polyaniline films simultaneous with potential cycling.

2. Experimental Details

Figure 1a shows the Kretschmann configuration¹⁵ for the excitation of plasmon surface polaritons (or simply surface plasmons)¹⁶ in the attenuated total reflection (ATR) mode. If a p-polarized laser beam is reflected at the (internal) incident angle, θ_i , from the base of a prism of refractive index n_p above $\theta_{\rm c}$, a strong nonradiative electromagnetic wave is excited at the resonant angle. This surface plasmon propagates at the metal/ electrolyte interface, with the coupling angle being given by the energy- and momentum-matching conditions between photons and surface plasmons. A detailed theory for surface plasmons in the ATR format has been described previously.¹⁷ As the energy of the incident light is transferred toward excitation of the surface plasmon, a decrease of the reflectivity in the ATR scan is observed as shown in Figure 2. The resonance character of this excitation gives rise to an enhancement of the electric field at the interface by more than an order of magnitude, which is the origin of the remarkable sensitivity enhancements, for example, in scattered light,¹⁸ fluorescence,^{19,20} or Raman spectroscopies^{21,22} when working with surface plasmon light.

If the formation of a thin dielectric coating is observed in situ, for example, during the electropolymerization process of conducting polymers at the metal electrode/electrolyte interface, kinetic information can be obtained. This includes film deposi-

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Figure 1. Experimental ATR (a) and R-ATR (b) setup for the excitation of surface plasmons in the Kretschmann geometry combined with electrochemical instrumentation.

tion and diffusional transport of mass adjacent to the interface by cycling potentials. The experiment often involves monitoring the reflected intensity at a fixed angle of observation, θ_{obs} (see Figure 1).⁷

The experimental setup for monitoring surface-plasmonenhanced scattered light is also shown in Figure 1a. The intensity ratio of the surface-plasmon-enhanced light scattering, dI_s/I_0 , at θ_s per solid angle, $d\Omega$, can be given by

$$\frac{\mathrm{d}I_{\mathrm{s}}(\theta)}{I_{\mathrm{o}}\,\mathrm{d}\Omega} = \left(\frac{\omega}{c}\right)^{4} \frac{4\sqrt{\epsilon_{\mathrm{p}}}}{\cos\theta_{\mathrm{i}}} |F|^{2} |s(\Delta k)|^{2} \tag{1}$$

where ϵ_p and ϵ_e are the dielectric constants of the prism and the electrolyte solution, respectively, and I_0 is the incident laser intensity. *F* is a function of Fresnel's reflection and transmission coefficients and also depends on θ_i and θ_s .²³ If we assume a Gaussian distribution as the correlation function that describes the inhomogeneity at the interface, the roughness function $|s(\Delta k)|$ can be obtained from the Fourier transform of a Gaussian distribution and is given by

$$|s(\Delta k)|^{2} = \frac{\sigma^{2}\delta^{2}}{4\pi} \exp\left[-\frac{\sigma^{2}(\Delta k)^{2}}{4}\right]$$
(2)

with σ being the transverse correlation length and δ being the



Figure 2. Calculated reflectivity and light intensity, $dI_s/(I_0 \, d\Omega)$ scattered off the solution interface at $\theta_s = 0^\circ$ for several roughness parameters, , $\sigma(nm)/\delta(nm)$: 0 nm/0 nm (line 1); 50 nm/1 nm (line 2); 100 nm/1 nm (line 3). The film parameters used for the calculation were as follows: film, d = 10 nm, $\epsilon = 2.25 + i0$; electrolyte, $\epsilon = 1.75 + i0$.

surface corrugation depth. It has been shown that eq 1 can also be applied for surface inhomogeneities of ultrathin polymer coatings.²⁴ In our experiments, $dI_s/(I_0 d\Omega)$ is measured as a function of incident angle θ_0 at a fixed scattering angle $\theta_s = 0$ or at a fixed angle of observation θ_{obs} and $\theta_s = 0$ for in situ investigation during the electropolymerization process of a conducting polymer at the planar electrode/electrolyte interface.

Figure 2 also shows spectra of surface-plasmon-enhanced light scattered off the polymer/electrolyte interface. This assumes different roughness parameters as a function of the incident angle θ_0 but at a fixed scattering angle $\theta_s = 0$ and laser wavelength of $\lambda = 633$ nm (He–Ne). In this spectral range, the dielectric function of Au allows for a field enhancement of about a factor of 20. The evanescent character of this enhanced optical field has an exponential decay into the polymer/electrolyte solution with a characteristic length scale of ca. 200 nm.

Figure 2 shows that the peak intensity of the light scattering is at a slightly lower incident angle than the minimum in reflectivity. The angle of the peak intensity corresponds to the resonance angle of the surface plasmon. The reason for this angle difference is related to the resonance character of the surface plasmon excitation. Because we are observing in reflection a coherent superposition of partial waves directly reflected from the metal/prism interface and (a fraction of) the surface mode reradiated via the prism, the minimum in the total reflection is given by the destructive interference of two partial waves differing in phase by 180°. This is reached just above the angle of maximum surface plasmon intensity. If we are to measure at an incident angle slightly lower than the peak intensity of the scattered light for the on-line monitoring measurement, we expect the reflectivity to increase and the scattered light to decrease with increase of the film thickness or the dielectric constant or both. However, for much thicker films, the inhomogeneity at the polymer/electrolyte interface is not expected to change much with further film thickness increase.

In our experiments, a LaSFN9 prism was used. The Au film, ca. 50 nm thick, evaporated onto BK7 glass slides with a 1–2 nm thick chromium adhesion layer was used as the working electrode. The Au/Cr/glass substrates were clamped against the Teflon cuvette with an O-ring providing a liquid-tight seal. The cuvette was then mounted on a two-axis goniometer for angular-reflectivity scans by SPS. Details of this setup have been described previously.²⁵ Surface plasmons are excited at the metal-dielectric interface upon total internal reflection of a



Figure 3. Simultaneous observation of SPS kinetic curves and SPLS kinetic curves with cyclic voltammmograms during the potential cycling in 0.5 M H_2SO_4 solution at a scan rate of 20 mV s⁻¹: top, cyclic voltammmogram (solid line); middle, SPS kinetic curve (dashed line); bottom, SPLS kinetic curve (dotted line).

polarized He–Ne laser light ($\lambda = 632.8$ nm). The electropolymerization processes on the gold surface were detected in situ by monitoring reflectivity changes as a function of time at a fixed incident angle, θ_0 .

The reversed attenuated total reflection (R-ATR) setup for the excitation of surface plasmons is shown in Figure 1b. In this case, the incident He–Ne laser irradiates the sample from the other side of the prism. Surface plasmons can be excited by the roughness at the Au/electrolyte interface and reradiated via the prism at an angle corresponding to their dispersion behavior.

Electrochemical experiments were performed with a conventional three-electrode cell and the Au/Cr/glass substrate as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl (3 M NaCl) reference electrode. A potentiostat (Princeton Applied Research 263A, EG&G) was used for the cyclic voltammetry experiments. Electropolymerization of aniline at the gold surface was achieved by applying potential cycles at a sweep rate of 20 mV/s from -0.2 to 1.0 V.

3. Discussion and Results

3.1. Simultaneous SPS and SPLS Cyclic Voltammetry with Au in H₂SO₄. At first, the optical and electrochemical characteristics of a bare Au surface were investigated simultaneously with SPS and SPLS as reference for the electropolymerization experiments. Figure 3 shows the simultaneous trace of the cyclic voltammogram (top), the SPS (middle), and the SPLS (bottom) data for the Au electrode surface in 0.5 M H₂SO₄ solution. In the double layer region, the SPS showed an increase in reflectivity with potential in the anodic scan and a decrease with potential in the cathodic scan. This behavior has been previously reported by other groups²⁶⁻²⁸ and is primarily attributed to local dielectric changes at the interfacial region between the subphase and the Au surface. On the other hand, the SPLS curve (bottom figure) showed a decrease in intensity with the potential in the anodic scan and an increase in the cathodic scan. This is also primarily attributed to local dielectric changes. These electrochemical SPS/SPLS observations are mainly attributed to the absorption and desorption of sulfate ions and change of the electron density in the vicinity of the gold surface. These phenomena are consistent with the theoretical calculations.

The increase observed with the cyclic voltammogram corresponds to the formation of a partial oxide layer on top of the Au surface, as observed at the region above 0.86 V, Figure 3 (top). From theoretical calculations, the reflectivity in the SPS is expected to increase gradually if the gold oxide film is grown on the exposed surface of gold.²³ Note that the reflectivity in the SPS will also increase if the thickness of the Au film is decreased. An increase on the SPLS curve was observed above 0.86 V. From the theoretical calculations as shown in Figure 2, the SPLS curve should decrease continuously in the cathodic scan if the surface roughness is *constant*. Therefore, the increase on the SPLS curve within the oxidation of Au indicates an increase in surface roughness compared with a bare Au surface. This phenomena was observed above 0.86 V for the partial oxidation of the Au. The normal reduction peak, which should be seen if the potential cycling is done with a higher positive potential, was not observed. This is attributed to an inhomogeneous oxidation of the gold surface. The small reduction peak at 0.77 V (cathodic scan) should correspond to the shoulder of the reduction peak for a gold oxide layer. These observations were confirmed by other groups employing simultaneous optical reflectivity and QCM measurements.29

3.2. Electropolymerization of Polyaniline Film at Various Stages or Cycles. *3.2.1. Simultaneous Observations of SPS and SPLS during Electropolymerization of Aniline in* H_2SO_4 *Solution by Potential Cycling.* Figure 4a–c show the cyclic voltammograms (top), SPS (middle), and SPLS (bottom) with the first, second, and fifth electropolymerization cycles. These were obtained at a concentration of 0.1 M aniline in 0.5 M H₂SO₄ with repeated potential cycling between -0.2 and 1.0 V at a scan rate of 20 mV s⁻¹.

An increase in reflectivity with the SPS (Figure 4a, middle) and a decrease of the SPLS (Figure 4a, bottom) correspond to the start of aniline oxidation as seen with the cyclic voltammogram (Figure 4a, CV). This was observed prominently in the anodic scan of the first cycle at about 0.8 V and is indicative of the oxidation of the aniline monomer to form polyaniline. From the SPS curve in the anodic scan of the first cycle, the slope can be divided into two regions, 0.8–0.9 and 0.9–1.0 V. This corresponds to two separate phenomena: (1) the oxidation of aniline monomer started at the vicinity of the Au surface at 0.8 V. The SPS curve increased because the growing polyaniline film has a higher dielectric constant than aniline monomer. (2) The growing polyaniline deposits and becomes insoluble to the H₂SO₄ solution at 0.9 V, that is, essentially precipitates out because of increasing chain length (polyaniline is insoluble in H₂SO₄ solution). In this manner, the polyaniline was deposited onto the Au substrate at the region where the SPS curve was steeper, that is, between 0.8 and 0.9 V. These phenomena are consistent with previous results using in situ EQCM as reported by Park et al.⁶ They observed a time delay in polyaniline deposition with the oxidation peak of the cyclic voltammogram.

For the cathodic scan of the first cycle, the SPS curve (middle) continued to increase up to 0.88 V then decreased until 0.52 V and then subsequently increased again up to 0 V. From the cyclic voltammogram, the first region corresponds to reduction of deposited polyaniline. The reduction of deposited polyaniline can decrease the SPS curve either because of a change in the dielectric constant or because of a change in the film thickness.³⁰



Figure 4. Simultaneous observation of SPS kinetic curves and SPLS kinetic curves with cyclic voltammmograms during the electropolymerization of 0.1 M aniline in 0.5 M H₂SO₄ solution using repeated potential cycling between -0.2 and 1.0 V at a scan rate of 20 mV s⁻¹: (a) first cycle; (b) second cycle; (c) fifth cycle.

The reflectivity in the SPS is high after anion dedoping. If the change of the SPS curve in this region is mainly due to the film thickness, the SPS curve should continuously decrease because of film contraction by anion dedoping or expulsion of water molecule into the solution or both. We believe that in this case the SPS curve behavior is mainly due to the increase of the imaginary part of the dielectric constant (refractive index). We have observed similar phenomena on our investigations with the layer-by-layer polyaniline/sulfonate polyaniline film by using another surface plasmon technique.³⁰ This reduction region of the SPS curve consistently decreased during second and fifth redox processes in cathodic scans (Figure 4b,c), followed by an increase during anion dedoping. This phenomenon is discussed later.

From Figure 4a, the SPLS curve decreased during monomer oxidation and deposition onto the Au surface. As shown in the experimental section, the factors affecting the SPLS behavior include the dielectric constant, film thickness, and roughness (internal morphology of film or solution) within the evanescent field. If the change of the SPLS curve is due to a change of dielectric constant or film thickness, the change should be consistent with the SPS property, that is, the SPLS curve should decrease with increase of the SPS. However, if the change is dependent on the surface roughness/internal morphology, the change of the SPLS curve should show a different property compared with the SPS curve.

In this present system, the decrease in the SPLS trace during first cycle monomer oxidation and deposition onto the Au surface (anodic scan) is symmetrically consistent with the SPS curve behavior (compare the SPS and SPLS anodic scans of Figure 4a). However, the cathodic scan is very different especially at the region between -0.2 and 0.88 V, which corresponds to the reduction of deposited polyaniline. In the

first cycle anodic scan, the surface plasmon is still sensitive to the immediate Au surface and the solution. With the deposition of the polyaniline film, the dielectric constants and morphology (roughness) of the deposited polymer create a new interface profile. This will indicate a new layer model incorporating a deposited dielectric polymer film between the Au surface and the solution subphase. The result is a change in the scattered light intensity curve with the evanescent field (Figure 2). Therefore, we believe that the SPLS change in this region at the cathodic scan is primarily dependent on the change in surface roughness or internal film morphology of the deposited polymer (or oligomers) dielectric at the Au surface. The differences in the evanescent field effects with film deposition are shown schematically in Figure 5a. Notice that the evanescent field gradient is continuously changing with increasing thickness of the deposited film.

In the second cycle anodic scan (Figure 4b, middle), the SPS reflectivity curve decreased during insertion of the anion into the deposited polyaniline and increased at the oxidation peak and monomer oxidation in the anodic scan. Moreover, with the cathodic scan, a decrease of the curve during the second reduction peak and an increase during the dedoping of the anion were observed. In the experiment using electro-QCM by Orata et al., an increase in the film mass by the doping of the ion has been reported.^{5,6}

As previously reported, the first redox process (ca. 0.22 V in the anodic scan and 0.05 V in the cathodic scan) corresponds to anion transport, that is, anion doping and dedoping,³¹ on the electrodeposited polyaniline film. The electrodeposition of polyaniline on the Au electrode proceeds via a radical cation mechanism. The second redox process (ca. 0.5 and 0.45 V) corresponds to proton transport, that is, protons in the polyaniline film are expelled into the electrolyte solution and inserted into

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Figure 5. Schematic representation of the relation between the evanescent field and the deposited polyaniline film.

the polyaniline film.^{31,32} Others have reported the possibility of side reactions such as decomposition of the polymer.^{2,33,34}

In our SPS measurement, SPS reflectivity is observed to decrease by doping with the ion. On the other hand, the SPLS showed only a decrease in the anodic scan (Figure 4b, bottom). To understand these phenomena better, the SPS and SPLS curves in the anodic scan can be divided into three regions, -0.2 to 0.25, 0.25 to 0.55, and 0.55 to 1.0 V. The SPS and SPLS were constant from -0.2 to 0.25 V. This region contains information on the surface roughness and internal morphology of the previously deposited polyaniline. One of the possible explanations for this constant behavior is that although anion doping causes surface roughness^{35,36} this was always compensated by dedoping from the last cycle so that the SPS and SPLS values remained constant. This is reasonable because an equilibrium in the flux of ions during the immediate doping and dedoping cycles is expected. The fact that both the SPS and SPLS are constant indicates that no gross changes are observed with the thickness, dielectric constant, and roughness on the films. This behavior is also consistently observed with the fifth cycle.

It is therefore thought that the changes of the SPS and SPLS curve in the regions 0.25 to 0.55 and 0.55 to 1.0 V should correspond to the changes of the internal morphology or dielectric constant of the deposited polyaniline and the continuous oxidation of the aniline monomer/deposition of polyaniline, respectively. These effects are again observed to be consistent with the fifth cycle, that is, thicker film than the evanescent field.

From the anodic scan (Figure 4b), the insertion of the ions, 0.25 to 0.55 V, results in a decrease in the SPS (middle) followed by an increase from 0.55 to 1.0 V during monomer oxidation and polymerization. The SPLS (bottom), on the other hand, showed a continued decrease in this region followed by a change in slope at 0.6 V. This decrease, as mentioned earlier, mirrors the change in the SPS indicating primarily a change in thickness with the continuous oxidation of the monomer and deposition of the polymer. For the cathodic scan, the SPS curve decreased and increased during anion doping and dedoping, respectively. This again corresponds to the change of the

dielectric constant of the deposited polyaniline film, as discussed with the first potential cycle. On the other hand, the SPLS curve decreased during anion doping followed by a gentle slope and subsequently an increase during dedoping. Again, if the dielectric constant is the main cause for the change of the SPLS curve, the SPLS curve should mirror an increase with decrease of the SPS curve, especially at the doping region. Because this is not the case, the change is again attributed to an increase in the roughness of the film to the subphase vicinity, sensitively monitored during the doping–dedoping stage. Note that the change on the SPLS curve is due to a different process from the change on the SPS curve as shown in the experimental section.

In the fifth cycle (Figure 4c), the change of the SPS (middle) due to monomer oxidation of aniline and polymerization was smaller compared with those of the first and second cycles. The dip position of the SPS is almost the same as that in the second scan. The thickness of deposited polyaniline film is now much thicker than the main evanescent field so that the changes of the SPS curve due to the oxidation of aniline monomer and deposition of polymer are not as sensitively measured with respect to thickness. Thus, the change of the SPS curve becomes mainly dependent on the dielectric constant of the deposited polyaniline. The SPLS (bottom) observation supports this explanation. If the deposited film is thick, as shown in Figure 5e, the factors affecting the SPLS curve become mainly dependent on the change of the internal morphology and dielectric constant of the polyaniline and not the roughness (immediately to the subphase). Therefore, the oxidation of aniline monomer and the deposition of the polyaniline film, which is further from the main evanescent field, do not cause changes in the SPLS so that the region above 0.6 V was almost constant.

These correlations suggest that the SPS and SPLS behavior observed during the electrochemical process reflects changes on the dielectric constant, thickness, internal morphology, and roughness of the polymer film and its deposition. The anion doping-dedoping process produces the surface roughness,^{35–37} changing at different stages of the cycle. We believe that the domain after dedoping by the anion roughened the morphology and that doping of the anion compensates for this domain. The fact that thickness changes occurred with subsequent cycles because of polymer deposition resulted in changes in sensitivity due to the evanescent field effects. This suggests that specific correlations between the cyclic voltammogram peaks and the SPS and SPLS curves should be more exact at the first few cycles or with thinner deposited layers.

3.2.2. Electropolymerization Process of Aniline in Several Electrolytes. To further probe the effect of changes on the deposited polyaniline film with doping and dedoping, we measured the rate of this process based on several types of supporting ion (electrolyte) used for the electropolymerization. The electrolytes varied mainly in size or molecular mass and slightly with charge density, for example, H₂SO₄, HClO₄, and HCl. The differences in the electropolymerization process of polyaniline could be observed clearly in the time differential curve of the reflectivity, dR/dt. Figure 6 shows this kinetic reflectivity curve (dR/dt) as a function of potential cycling between -0.2 and 1.0 V in 0.5 M H₂SO₄, HClO₄, and HCl solution at a scan rate of 20 mV s⁻¹, together with the cyclic voltammogram of the fifth cycle. Peaks corresponding to the anion doping-dedoping (first redox process in CV) were observed in each figure. It is clearly seen that the dR/dt curves are decreased by anion doping and increased by anion dedoping.



Figure 6. The time-differential SPR kinetic curve (dR/dt) as a function of potential cycling between -0.2 and 1.0 V at a scan rate of 20 mV s⁻¹ and the cyclic voltammogram of the fifth cycle in 0.5 M H₂SO₄, HClO₄, and HCl solutions.

The dR/dt curves have a delay compared with the oxidation peaks of the polyaniline film during the doping process but change earlier than the CV peak during the dedoping process. This comparison indicates that the discrepancy between CV and SPS (dR/dt) increases in the order of $H_2SO_4 < HClO_4 < HCl$. This means that the change of the dielectric constant during the doping and dedoping of the polyaniline film upon electropolymerization is faster in H₂SO₄ than in HCl. Okamoto et al. observed a similar effect in the impedance change of polyaniline films electropolymerized in HClO₄ and HCl.³⁷ A possible explanation for this is the effect of the size of dopant anion. In the case of the electropolymerization in HCl solution, the dopant anion is smaller; therefore, the deposited film is not made as porous with subsequent cycles so that the change of the dielectric constant was slower with the anion hardly able to penetrate. This is not unfounded because the formation of a porous film is affected by the transport properties of the electrolyte both during and after film formation. Hence, a more porous film is expected with H₂SO₄ as a supporting electrolyte, consistent with the observations by Okamoto. The extent of ion incorporation with changes in the film dielectric constant is not presently determined.

3.2.3. R-ATR Measurement during Electropolymerization of Aniline in the HCl Solution by Potential Cycling. To further probe the effect of doping and dedoping with film roughness, we applied reversed attenuated total reflection (R-ATR) measurements during electropolymerization. Figure 7a shows the angular dependence of the measured reflectivity and of the light intensity scattered off the substrate/gold/electrolyte interface in



Figure 7. An angular reflectivity curve ((a) ATR) and scattered light intensities ((a) ATR and (b) R-ATR) of substrate/gold/solution system, that is, before the electropolymerization.

the ATR set up before the electropolymerization, and Figure 7b shows the scattered light intensity from the electrolyte/gold/ substrate system in the R-ATR set up. The emitted peak angle of the scattered light in the R-ATR set up is almost coincident with the peak incident angle of the scattered light in the ATR set up. Therefore, we believe that the surface plasmon can be excited in the R-ATR set up. The efficiency of this coupling should be sensitive to the roughness at the electrolyte/gold interface.

The SPS kinetic reflectivity property and the kinetic scattered light intensity during electropolymerization were measured at a slightly lower angle than the resonance minimum (Figure 7). This implies that the scattered light intensity in the kinetic measurement should decrease if the film thickness becomes thicker during the electropolymerization. Figure 8 shows the simultaneous observation of the SPR kinetic reflectivity curve and the kinetic scattered light intensity curve during the electropolymerization of 0.1 M aniline in 0.5 M HCl solution at a scan rate of 20 mV s⁻¹. The kinetic reflectivity curve of the scattered light in the R-ATR experiment was also increased by anion dedoping and decreased by anion doping, in the same way as in the case of the ATR setup.

However, the intensity of the light scattering at the fifth cycle in the R-ATR measurements continued to decrease during the oxidation of aniline monomer/deposition of polyaniline, whereas that in the ATR does not. It should be noted that, in the case of the R-ATR configuration, the direction of incident light follows a path through the electrolyte solution and on to the polyaniline/ gold interface (Figure 1b). This means that for a thicker film, such as that in the fifth cycle, the factors affecting light scattering behavior still include the dielectric constant, film thickness, and surface roughness and internal morphology. On the other hand, the light scattering in an ATR measurement will have less sensitivity to film thickness and surface roughness of deposited polyaniline. The evanescent field decreases considerably (exponentially) from the gold surface to the deposited polyaniline film at this thickness as discussed in the section 3.2.1 and shown



Figure 8. Observations of SPR kinetic reflectivity curves and SPLS kinetic curves during the electropolymerization of 0.1 M aniline in 0.5 M HCl solution at a scan rate of 20 mV s⁻¹: (a) potential ramp vs time; (b) a reflectivity kinetic curve as a function of potential cycling (solid line) and scattered light (dotted) (ATR); (c) scattered light (R-ATR).

schematically in Figure 5. Therefore, this differences in the light scattering behavior between the R-ATR and the ATR configuration is consistent with the SPS and SPLS results with potential cycling as previously discussed.

4. Conclusions

Our studies have demonstrated the possibilities of performing a combined in situ surface plasmon resonance spectroscopy (SPS), surface-plasmon-enhanced light scattering (SPLS), and cyclic voltammetry for the investigation of the electrochemical processes of conducting polymers on flat electrode substrates. The potential cycling resulted in a sensitive oscillation of the SPS and the SPLS curve. The time-differential SPS curve could be correlated with the cyclic voltammogram. The scattered light enhanced by the surface plasmon is very sensitive to changes in the morphology of the deposited polyaniline film during electropolymerization. The changes of the dielectric constant and the morphology of the polyaniline film are due to redox processes and are easily detected by this method. The transitions of film deposition result in changes to dielectric constants at the interface and to the internal morphology or surface roughness. Furthermore, comparison of the light scattering between the ATR configuration and the R-ATR configuration clarified the changes to these parameters. These parameters could be simultaneously observed on the deposited polyaniline with potential cycling. Thus, these results indicate that the simultaneous observation of SPS kinetic reflectivity curves and the SPLS with the cyclic voltammogram will allow for the

elucidation of the electrochemical properties and the morphology of conducting polymers during the electropolymerization. We intend to investigate further the stages of morphology change on the electropolymerization process by in situ atomic force microscopy (AFM) imaging combined with electrochemistry.

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