

# Simultaneous *in situ* electrochemical, surface plasmon optical, and atomic force microscopy measurements: Investigation of conjugated polymer electropolymerization

Akira Baba

*Department of Chemistry, University of Houston, 136 Fleming Building, Houston, Texas 77204-5003*

Wolfgang Knoll

*Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany*

Rigoberto Advincula<sup>a)</sup>

*Department of Chemistry, University of Houston, 136 Fleming Building, Houston, Texas 77204-5003*

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We report the simultaneous *in situ* electrochemical, optical, and surface morphological studies of conjugated polymer ultrathin film formation using a novel combined electrochemical instrumentation–surface plasmon resonance spectroscopy–atomic force microscopy. The initial stages of the electropolymerization of poly(3,4-ethylenedioxythiophene) films on flat gold electrode/substrates were observed in all three experiments simultaneously. In addition to the electrochemical information obtained, the surface plasmon optical technique showed the deposition of the film, and provided electrochromic behavior of the deposited film. Simultaneously, atomic force microscopy gave surface morphological properties and domain growth of the film. The complementarity of the information obtained from the combined techniques is useful for the investigation of polymer growth mechanism between cyclic voltammetry and potentiostatic deposition methods. © 2006 American Institute of Physics. [DOI: 10.1063/1.2204587]

## INTRODUCTION

Optical techniques such as surface plasmon resonance spectroscopy (SPS), waveguide spectroscopy, or ellipsometry are well-established methods for the characterization of surfaces, interfaces, and thin films.<sup>1</sup> SPS, in particular, uses evanescent waves to probe thin films. This technique allows for the determination of optical constants and the thickness of layered systems. The combination of SPS with electrochemical measurements has been demonstrated as a powerful analytical technique for the simultaneous characterization and manipulation of electrode/electrolyte interfaces.<sup>2</sup> In electrochemical-SPS (EC-SPS) measurements, the gold substrate that carries the optical surface mode is also used as the working electrode in the electrochemical experiments.<sup>3</sup> One advantage of using the EC-SPS technique is that the electrochemical and optical properties are simultaneously obtained on surfaces and ultrathin films at the nanometer scale. Our group and other groups have been applying the EC-SPS technique for the characterization of conducting polymer thin films.<sup>4–8</sup> This involved the *in situ* monitoring of the film swelling/contraction and of electrochromic properties during electropolymerization or during the anion doping/dedoping process of deposited conducting polymers.<sup>9</sup> Simultaneous optical and surface morphological measurements such as combinations of a scanning near field optical microscope (SNOM)–scanning tunneling microscope<sup>10</sup> (STM), or

ellipsometry–atomic force microscopy (AFM),<sup>11</sup> have also been shown to be powerful tools for the study of organic ultrathin films, biological samples, and others. Previous work on combining the AFM and SPS has been reported by Shakesheff *et al.*<sup>12</sup> and Chen *et al.*<sup>13</sup> They showed the simultaneous surface plasmon resonance (SPR) optical measurement at a fixed angle and surface morphological information by AFM for probing polymer film properties and biodegradation studies.

The conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is a promising candidate for a variety of applications such as biosensors,<sup>14</sup> hole-injection layer in organic light emitting diodes,<sup>15</sup> electrochromic devices,<sup>16</sup> and others.<sup>17</sup> Many of these applications make use of the fact that the conductivity or color of the film can be controlled by its redox state. Upon oxidation (doping), thin PEDOT films become positively charged, with their conductive state having a transparent skyblue color. In the insulating state, it assumes a deep dark blue color upon reduction (dedoping). Several chromic states have been observed at various degrees of doping but these have never been fully understood. Thus, due to their complex properties, it is very intriguing to obtain more information in a single experiment. Because PEDOT films change its optical, electrical, and morphological properties upon various redox states, one needs to combine complementary techniques *in situ*.

In the following study, the experimental setup and a theoretical description of surface plasmon resonance spectroscopy is presented. Subsequently, we demonstrated a novel

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: radvincula@uh.edu

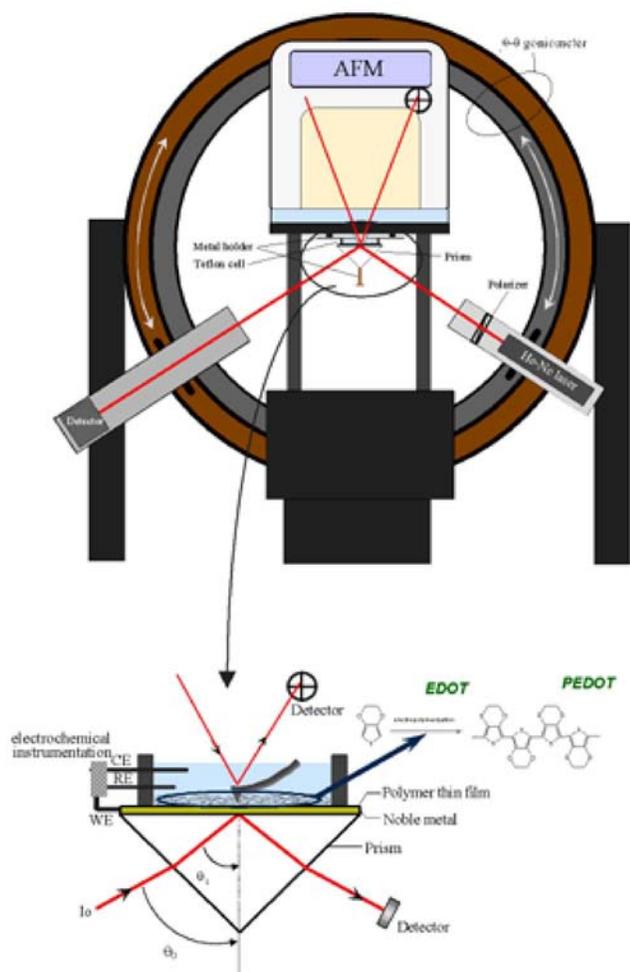


FIG. 1. (Color online) A schematic diagram of the combined electrochemical-SPR-AFM instrumentation.

combined electrochemical–surface plasmon resonance spectroscopy–atomic force microscope (EC-SPS-AFM), which provides simultaneous and *in situ* optical, electrochemical, and surface morphological information of electrochemically deposited ultrathin PEDOT films. With independent and separate measurements using electrochemistry, SPS, and AFM, it is possible to obtain three types of data, but the results are collected under basically different conditions. Especially in surface science studies at the nanometer scale, very careful measurements are required in order to interpret the data and to obtain quantitative results. Our newly developed technique leads to “real time” dynamic and simultaneous acquisition of the dielectric (optical), surface morphological, and current data of depositing PEDOT thin film at the electrode/electrolyte interface.

## EXPERIMENTAL SETUP

A schematic diagram of the combined electrochemical-SPR-AFM instrumentation is shown in Fig. 1. An attenuated total reflection (ATR) setup (Optrel GbR, Germany) using a wide circle  $\theta$ - $\theta$  goniometer was utilized for the excitation of surface plasmons in the Kretschmann configuration. In order to remove vibration, the system was set on a Sigma optical table. The AFM head (Pico-SPM, Molecular Imaging, Phoe-

nix, AZ) was mounted on an XYZ- $\theta$  adjustable stage. An equilateral triangular LaSFN9 prism (Hellma Optik GmbH) was used with its base optically coupled to a LaSFN9 glass substrate using refractive index matching fluid. An evaporated-Au ( $\sim 45$  nm)/LaSFN9 glass substrate/LaSFN9 prism was clamped against the Teflon cell using a metal prism holder with an O ring providing a liquid-tight seal. The size of the LaSFN9 glass slide was  $38 \times 26$  mm<sup>2</sup> and the thickness  $\sim 1.5$  mm. The volume of the Teflon cell was 0.5 ml. The holder was then magnetically attached to the electrochemical-AFM system. Surface plasmons are excited at the Au-electrolyte interface, upon total internal reflection of a polarized laser light beam. A He-Ne laser with a wavelength of  $\lambda = 632.8$  nm (2 mW power) irradiated from the bottom side was used in all measurements. The Au/glass substrates used for the excitation of surface plasmons served as a working electrode in the electrochemical measurements, with a Pt counter and a Ag reference electrode. The exposed electrode area was 2.0 cm<sup>2</sup>. The electrochemical experiments were controlled using a Picostat instrument (Molecular Imaging, Phoenix, AZ). In the AFM measurements, the sample surface was scanned with a sharp tip situated on the probe cantilever, while a potential was applied to the samples. Contact mode AFM images with a top down  $6 \mu\text{m}$  size scanner can be recorded, while SPR angular or kinetic measurements are measured at various applied potentials simultaneously. The monomer 0.01M 3,4-ethylenedioxythiophene (EDOT) (Aldrich) was used as received. An acetonitrile solution was prepared containing tetrabutylammonium hexafluorophosphate (0.1M) as the supporting electrolyte.

## Theoretical considerations of surface plasmon resonance properties for the electropolymerization of PEDOT

Unlike conventional adsorption/deposition processes such as the self-assembly of monolayers or the layer-by-layer deposition of ultrathin organic films, kinetic processes during electropolymerization are complicated. This is especially true for electropolymerization by potential cycles, in which the dielectric properties of the depositing material changes due to the doping/dedoping effects simultaneously occurring with film growth and swelling. In this case, the ATR-based surface plasmon spectroscopy is ideal since it allows for the investigation of film properties in the region of the interfacial evanescent optical fields (ca. 150 nm). Furthermore, the surface plasmon strongly depends on the real and the imaginary part of the complex dielectric constants ( $\epsilon' + i\epsilon''$ ) as well as film thickness  $d$  of the interfacial layer architecture.

Based on a previous study of PEDOT film electropolymerization, the reflectivity mainly depends on the thickness.<sup>18</sup> This means that the dielectric constant at a fixed potential can be assumed to be almost constant. Shown in Fig. 2(a) (black line) is a simulated reflectivity change as a function of thickness using a Fresnel algorithm calculation assuming a constant dielectric function. The first decrease in the reflectivity indicates that the real part of the dielectric constant of deposited PEDOT in the doped state is lower than that of the solvent (acetonitrile). The following increase of the reflectivity is then due to an increase of the SPR mini-

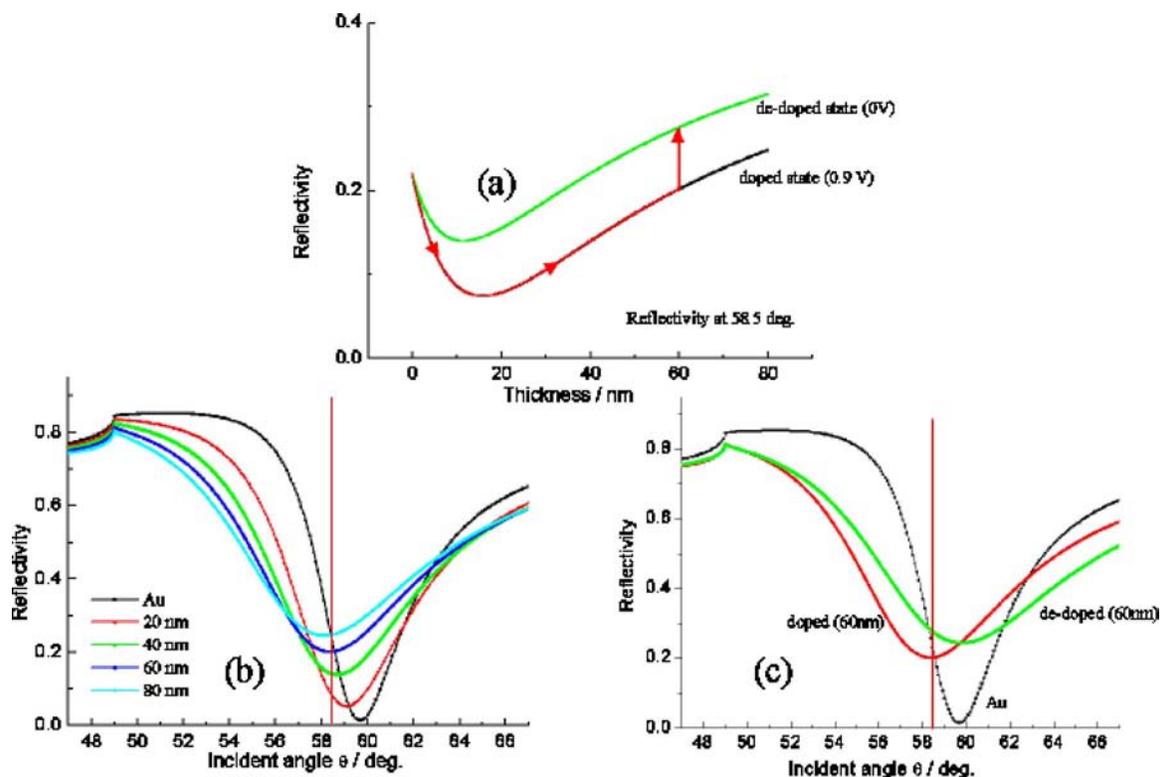


FIG. 2. (Color online) Simulated reflectivity change during electropolymerization of PEDOT as a function of thickness (a); simulated reflectivity curves after electropolymerization (b),(c).

mum value as seen in Fig. 2(b), indicating that the PEDOT film in the doped state has a small imaginary part contribution to the dielectric constant.

On the other hand, the kinetic properties during electropolymerization by potential cycles (cyclic voltammetry) depend on both the thickness and the dielectric constant of the film. The conjugated polymer film grows at a particular potential, and then doping by anions happens simultaneously. At a certain stage, the anion is excluded from the film if the applied potential changes towards lower potentials. It should be noted that this doping/dedoping effect largely depends on the polymer material. Furthermore, film swelling/shrinking usually occurs during the doping/dedoping process due to a change in solvent miscibility. This results in a complex mechanism for the electropolymerization and film growth of conjugated polymers. Figure 2(c) shows an example for SPR curves at a doped and dedoped states, assuming the dielectric constants taken from our previous study. The shift towards a higher angle of the SPS curve seen in this calculation is due to dedoping. For the kinetic scans taken during electropolymerization by potential cycles, the simulated reflectivity change is shown in Fig. 2(a) (red line) as a function of thickness.

## RESULTS AND DISCUSSION

### Electropolymerization by potential cycling (CV)

Figure 3(a) shows simultaneous traces of the potential ramp (top), the amount of charge (second trace from the bottom), the AFM image (second figure from top), and the SPS data (bottom) for the Au electrode. The measurements

were taken as a function of time during the electropolymerization of EDOT by a potential cycle from 0 to 1.2 V (from 0 to 96 s on the time scale) at a scan rate of 25 mV/s in 0.1M TBAPF<sub>6</sub> acetonitrile solution. Figure 3(b) shows the rms roughness (top), the amount of charge  $Q$  (middle), and the SPS data (bottom) as a function of the applied potential. A decrease of the reflectivity in the SPS corresponds to the start of the EDOT oxidation as seen in the CV. In this simultaneous *in situ* study, large signal changes were observed in all of the three measurements. The slow decrease in the SPS optical signal was observed prominently in the anodic scan at about 0.95 V and corresponded to the oxidation current of the EDOT monomer to form the polymer PEDOT. The SPS curve then decreased steeply in the anodic scan at 1.05 V. Then it increased at 1.18 V in the cathodic scan followed by a gentle increase at 0.88 V. In the AFM image and rms roughness evaluation, very slight changes were observed until 1.15 V in the anodic scan, which was followed by clear surface morphological changes. The average rms roughness was evaluated for voltage steps of  $\Delta E=0.3$  V ( $\sim 350$  nm in the image). A clear morphological change was prominently observed at around 1.15–1.2 V (46–48 s in time scale) in both the anodic and the cathodic scan, and the average roughness reached to about 5.5 nm. Then the surface morphology smoothed again slightly.

Several things can be pointed out based on these observations. Clearly, the combination of CV, SPS, and AFM provided interesting findings on the relationship between the oxidation current, the polymer deposition, and the electrochromic properties in the initial electrogrowth stage. The signal changes seen in CV and SPS are almost coincident, while

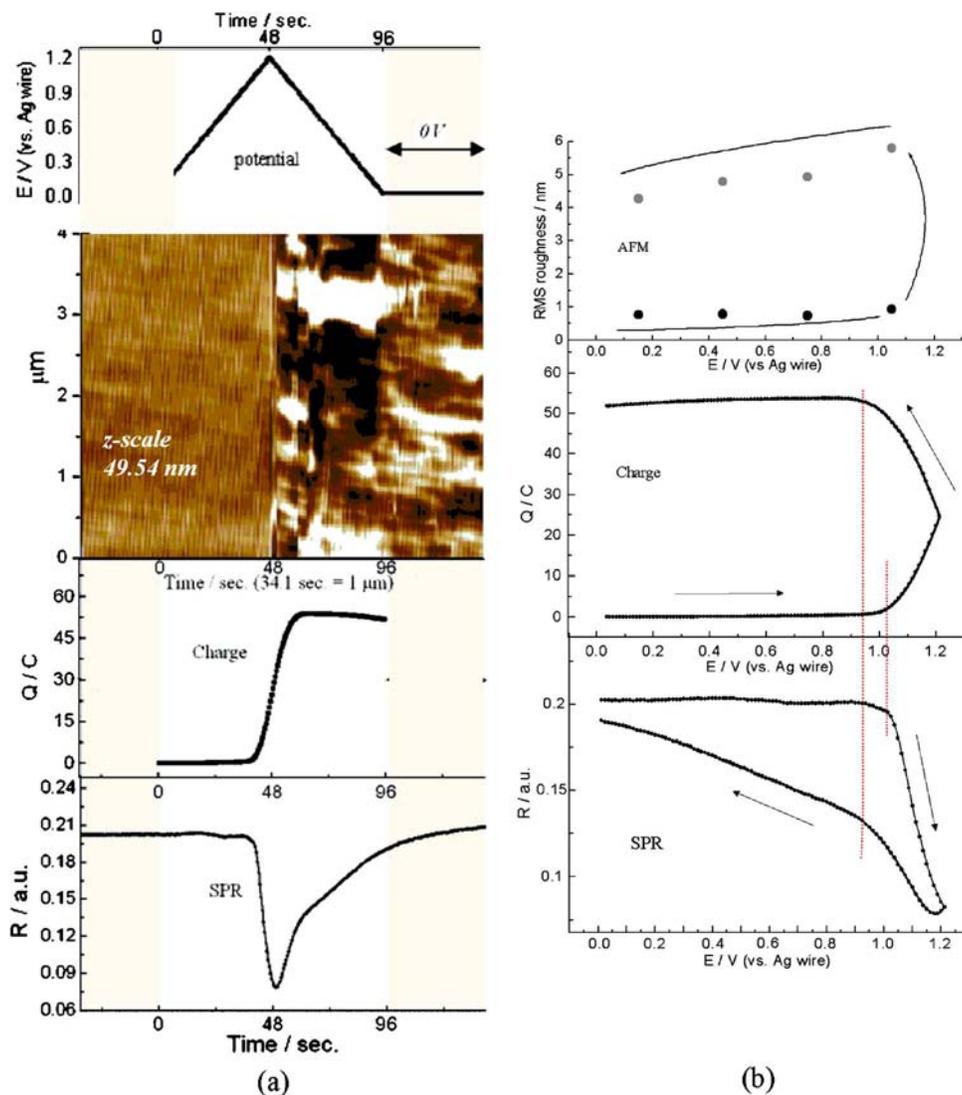


FIG. 3. (Color online) Simultaneous traces of the potential ramp (top), the AFM image (second figure from top), the amount of charge (second trace from the bottom), and the SPS data (bottom) for the Au electrode as a function of time during the electropolymerization of EDOT by a potential cycle from 0 to 1.2 V (from 0 to 96 s on the time scale) at a scan rate of 25 mV/s in 0.1M TBAPF<sub>6</sub> acetonitrile solution. (a) rms roughness (top), amount of charge  $Q$  (middle), and SPS (bottom) as a function of potential (b).

the surface morphology changed lagged. At the initial stage of the current, a small change in the SPS data (ca. 0.95–1.0 V) could be due to the nucleation of oligomers or chains of polymer that become insoluble and, hence, are deposited onto the Au surface. At this stage though, almost no surface morphological change is seen in the AFM image. Then abruptly, a change in surface roughness is observed at around 1.15 V as the SPR curve decreases steeply. Both pronounced changes in the SPS data and the AFM image are indicative of the rapid deposition of insoluble PEDOT as a film on the Au electrode surface. In the cathodic scan, the SPS curve increases gently from  $-0.85$  V. This variation is not due to changes of the thickness of deposited film but is mainly due to changes of the (optical) dielectric constant of the film, i.e., its electrochromism due to dedoping. The rms value in the region of dedoping after the growth of the film slightly decreased as seen in Fig. 3, indicating that the surface morphology of the electropolymerized PEDOT film becomes slightly smoother by dedoping. Although one needs to do further analysis, this indicates already the sensitivity of *in situ* EC-SPS-AFM even for morphological changes that occur during the dedoping of anions. After cycling the potential, the potential was kept at 0 V. The increase of the SPS

curve after electropolymerization should be due to a gradual dedoping of ions from the deposited film, indicating that the film achieves a more neutral state. Again, the surface morphology at 0 V is almost constant. A clear change before and after electropolymerization is seen in the angular surface plasmon resonance curve and the AFM images shown in Fig. 4. This coincides with the increase of the reflectivity as explained in the kinetic measurements. The modulation seen at around  $69^\circ$  might be due to an interference effect between the Au surface and AFM cantilever tip. Since this modulation does not disturb the surface plasmon resonance minimum angle, the analysis is not further pursued in this article though. The surface morphological change after electropolymerization is clearly seen in the entire surface of the  $5 \times 5 \mu\text{m}^2$  image as well as in the change of the SPS curve. In the electropolymerization of EDOT by cycling the potential, change in surface roughness was clearly observed at around 0.9–1.2 V.

#### Electropolymerization at constant potentials (potentiostatic)

Simultaneous observation during electropolymerization at constant potential was also tested. The difference in the

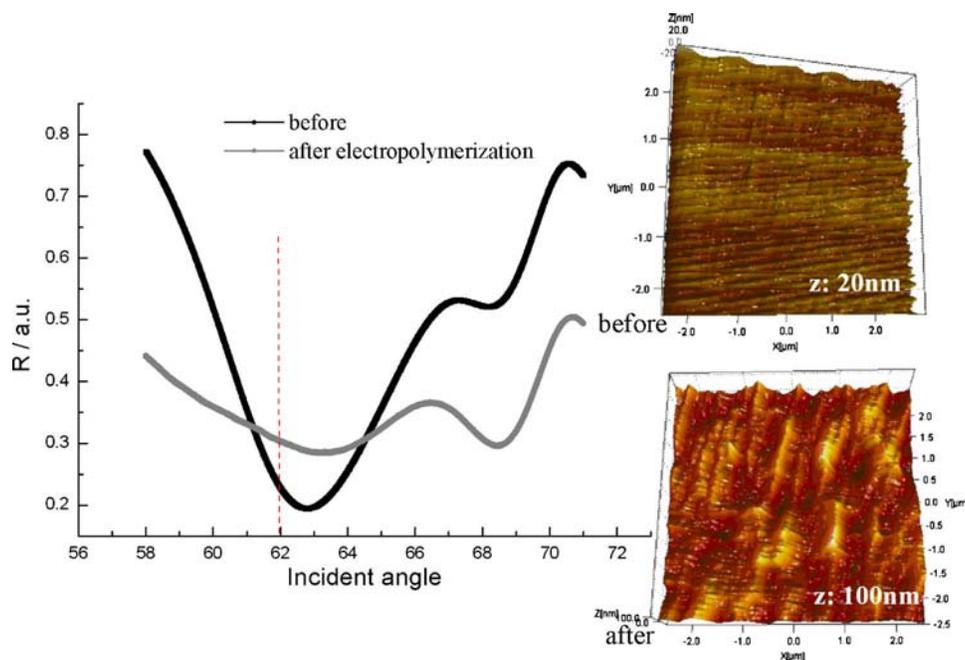


FIG. 4. (Color online) Angular surface plasmon resonance curves and AFM images before and after electropolymerization of PEDOT.

initial stages of film growth was also investigated using the EC-SPS-AFM system by potentiostatic electropolymerization as shown in Fig. 5. In this experiment, a potential of 0 V was applied for 22 s, then 0.9 V from 22 to 88 s, and 1.0 V from 88 to 170 s. Figure 5 shows the potential (top), the AFM morphology (second figure from a top), the amount of charge (second figure from a bottom), and the SPS reflectivity curve (bottom). At 0 V, all three signals showed no change. Then, the SPS curve decreased and the amount of charge increased once a potential of 0.9 V was applied. When 1.0 V was applied, the SPS signal decreased further and the amount of charge increased more steeply, indicating that the speed of electrodeposition and oxidation of EDOT was accelerated. In order to evaluate this observation quantitatively, the theoretical fitting to experimental SPS curves was done for the prism/Au/PEDOT/acetonitrile system using Fresnel calculations as shown in Fig. 1. As can be seen, the theoretical fitting showed good agreement with the experimental result. In this calculation, the dielectric constant of the PEDOT film was assumed to be constant  $\epsilon=(1.88+0.1)$ , which was estimated from previous studies<sup>18,19</sup> and this experiment. The fitting was tried as a factor of the deposition rate. The calculated curve was also shown in Fig. 5 (three dashed curves in the SPS reflectivity). As shown in this fit, the deposition rate can be divided into three parts, i.e., two parts in the initial deposition at 0.9 V and one part in the subsequent deposition at 1.0 V. This calculation indicated that the PEDOT film initially grows on the gold electrode until it reaches a thickness of  $d=1.3$  nm (for 1 s) at a deposition rate of 1.3 nm/s and then slows down to 0.07 nm/s. It is an interesting observation in that initially the film formation occurs rapidly but that the subsequent growth proceeds more gradually. If 1.0 V was applied continuously, the deposition rate increased to 0.3 nm/s. However, if the potential of 0.9 V was applied, the average roughness observed by the AFM increased very slightly, indicating that the deposited film was rather smooth. This result agrees well with the cal-

culated thickness of  $d=5.3$  nm at the end of the period while the potential of 0.9 V was applied. Once the deposition rate was increased at 1.0 V, a certain increase of the surface roughness of the PEDOT film was also observed. The electrodeposition at constant potential shows that there is no obvious border for the surface morphological change in the AFM image unlike the cyclic voltammetry experiment as shown in Fig. 3. In this case, the potentiostatic method seemed to require an “induction period” which would have required the buildup of charge that eventually resulted in the nucleation of both polymerization and gradual deposition to the surface. In general, cyclic voltammetry electrodeposition of polymer films has been found to be more reproducible and homogeneous.<sup>20</sup> For example, previous AFM studies differentiating polypyrrole deposition have shown different morphologies especially at the early stages of deposition. The nucleation mechanism can be very different for the two processes, involving differentiation between two versus three-dimensional or slow versus rapid nucleation and growth mechanisms.<sup>21</sup> For potentiostatic methods, typical chronoamperograms show a constant current when initially applied, which then abruptly decreases (sharply) followed by a gradual rise. In this case, this is related to a nucleation process involving two stages. The slow initial stage is related to the nucleation on the bare sections of the electrode surface involving a double layer charging effect. The second stage involves rapid deposition of the polymer corresponding to autocatalytic growth. The magnitude of the current change and the slope reveal much about the polymer growth mechanism under various conditions.<sup>22,23</sup> For cyclic voltammetry methods, the formation of oxidized radical cation species (for anodic polymerization) results in *simultaneous polymerization and deposition* once the appropriate peak oxidation potential ( $E_p$ ) is reached. Subsequent cycles result in lowering this oxidation potential due to the formation of more conjugated monomeric species and the possible appearance of new oxidation and reduction peaks.<sup>24</sup> The rapid nucleation

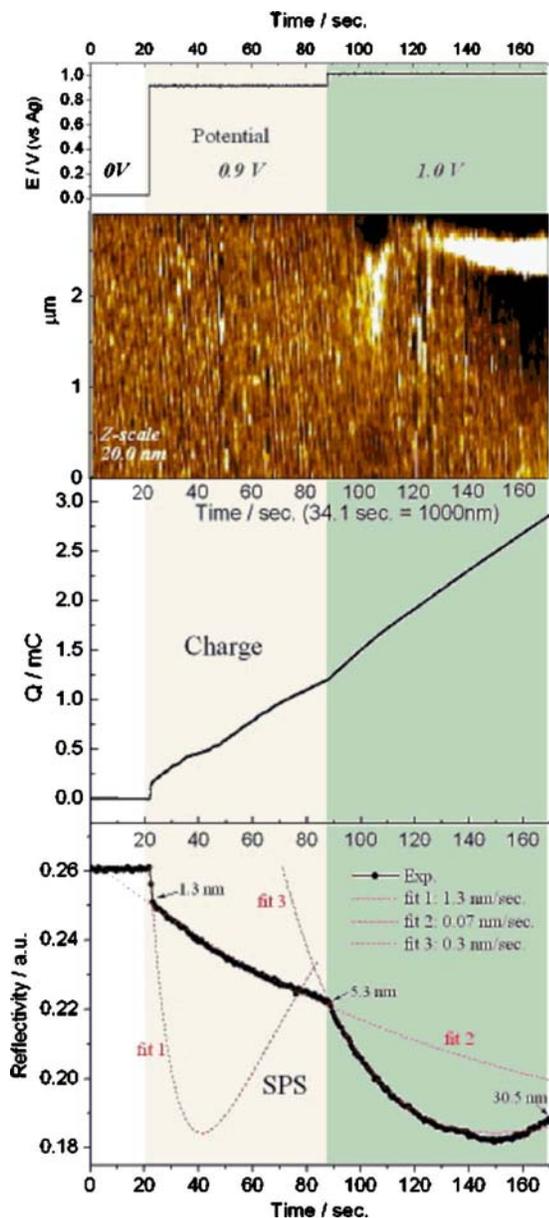


FIG. 5. (Color online) Simultaneous observation of EC-SPS-AFM during electropolymerization at constant potentials. Potential (top), AFM morphology (second figure from top), amount of charge (second trace from the bottom), and the SPS reflectivity curve (bottom). The three dashed curves in SPS reflectivity show the theoretical fitting to experimental SPS curves.

and deposition results in a very abrupt change in morphology or appearance of a polymer, as observed (Fig. 3). It should be noted that both processes could be dramatically influenced by solvent, concentration, temperature, monomer, etc., conditions since these are essentially polymerization processes that results in precipitation and adsorption of polymers towards an interface.

The combined EC-SPR-AFM allowed a very important observation and differentiation of these two common methods for depositing electropolymerized films.

## CONCLUSION

In summary, we have demonstrated the novel combination of electrochemical measurements, SPS, and AFM by

investigating the initial stages of the electropolymerization process of EDOT onto a flat Au electrode surface. The difference of the electropolymerization mechanisms between potentiostatic and cyclic voltammetry was clearly observed. Using Fresnel calculations, the deposition rate of the PEDOT film was estimated, and simultaneously the morphological change was monitored in the AFM images. The complementarity of the information obtained from these three experiments showed the oxidation (polymer growth in solution), deposition rate onto substrate, thickness, surface morphology, and electrochromism of deposited film can be correlated at the same time. The combination of all three techniques holds particular promise for the investigation of electrochromic electropolymerized films and other electrochemically addressable materials.

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