

Properties of Poly(3,4-ethylenedioxythiophene) Ultrathin Films Detected by in Situ Electrochemical-Surface Plasmon Field-Enhanced Photoluminescence Spectroscopy

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In this paper, we describe, for the first time, the combination of surface plasmon resonance spectroscopy (SPS) and surface plasmon enhanced photoluminescence spectroscopy (SPPL) with electrochemical techniques for the detection of photoluminescence in poly(3,4-ethylenedioxythiophene) (PEDOT) ultrathin films. The EC-SPS/SPPL technique allows for the recording of the weak photoluminescence from an ultrathin PEDOT film in its neutral state. A distinct photoluminescence switching was observed during the potential dependent doping/dedoping process. The EC-SPS/SPPL characterization results are consistent with the observed PEDOT bulk electrochromic properties obtained from UV–vis–NIR spectra. This suggests that the described combination method is capable of electrochemically controlling and optically detecting the very weak photoluminescence of ultrathin films.

Introduction

The combination of surface plasmon resonance spectroscopy (SPS) with electrochemical measurements has been demonstrated as a powerful technique for the simultaneous characterization and manipulation of electrode/electrolyte interfaces.^{1–3} In electrochemical-SPS (EC-SPS) measurements, the gold substrate that carries the optical surface mode, simultaneously is used as the working electrode in electrochemical experiments. One of the advantages in using the EC-SPS technique is that the electrochemical and optical properties are simultaneously obtained on surfaces and ultrathin films at the nanometer scale. Recently, the EC-SPS technique has been applied for the characterization of conducting polymer thin films.^{4–10} This involved the in situ monitoring of the film swelling/contraction and of electrochromic properties during electropolymerization or during the anion doping/dedoping of deposited conducting polymers. This technique has also been applied in biosensor development, e.g., by integration of redox enzymes with conducting polymers as a bioelectrocatalytic layer.¹¹ Other combination methods have also been reported for the characterization of conducting polymers, e.g., using surface plasmon enhanced light scattering (SPLS) and the quartz crystal microbalance (QCM) technique. Recently, a first attempt to combine QCM/SPS¹² with electrochemical measurements was reported by Bailey et al.¹³ It was shown that the thickness and the dielectric constant of polypyrrole during and after electropolymerization can be evaluated simultaneously by this method. Attempts to combine SPS/SPLS with the electropolymerization of conducting polymers have recently been described by our group.^{5,6} We first investigated the electrochemical preparation of polyaniline using the EC-SPS/SPLS technique and obtained information on morphological transitions in the film as it was related to the electrochemical and dielectric properties of the film.

In this paper, we report the combination of SPS and surface plasmon enhanced photoluminescence spectroscopy (SPPL) with electrochemistry for the detection of photoluminescence from poly(3,4-ethylenedioxythiophene) (PEDOT) films. First, the optoelectrochemical properties of the doped PEDOT films at

constant potential and during potential cycling were investigated in the UV–vis–NIR region. Then various modes of EC-SPS/SPPL, e.g., the constant potential mode, cyclic voltammetry, or chronoamperometry were experimentally tested and the results analyzed in terms of the photoluminescence properties. Three independent signals were monitored at different potentials applied. To our knowledge, photoluminescence from an ultrathin PEDOT film has not been previously reported because its neutral state is very unstable and it is difficult to exclude residual doping. This residual charge carrier might largely be responsible for the quenching of luminescence in PEDOT films. However, by using the EC-SPS/SPPL measurement, we were able to detect and manipulate the photoluminescence properties. This can have important applications in the field of sensor development, optical switching devices, and microelectrooptical systems.

Experimental Section

Materials. 3,4-Ethylenedioxythiophene (EDOT) and tetrabutylammonium hexafluorophosphate were purchased from Aldrich and used as received.

Electrochemical Measurement. Electrochemical experiments were performed in a conventional three-electrode cell with the Au/LaSFN9 glass substrate as the working electrode, a platinum wire as counter electrode, and an Ag/Ag⁺ nonaqueous reference electrode in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. All potentials reported in this paper were relative to this electrode. A potentiostat (Princeton Applied Research 263A, EG&G) was used for the cyclic voltammetry experiments. Optoelectrochemical spectroscopy was carried out on an UV–vis–NIR spectrometer (Perkin-Elmer, Lambda 9).

Electrochemical-SPS/SPPL. Figure 1 shows the attenuated total reflection (ATR) setup used for the excitation of surface plasmons in the Kretschmann configuration combined with an electrochemical cell. Details of the principle for surface plasmon resonance have been well documented.¹⁴ Details in surface plasmon field-enhanced fluorescence spectroscopy have been also described.¹⁵ A LaSFN9 prism ($n = 1.85$ at 594 nm) was

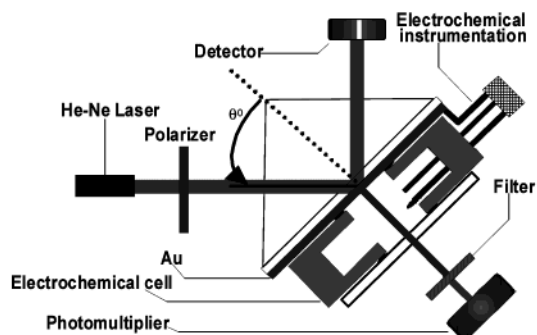


Figure 1. ATR setup for the excitation of surface plasmons in the Kretschmann configuration combined with elements for the photoluminescence detection and the electrochemical instrumentation.

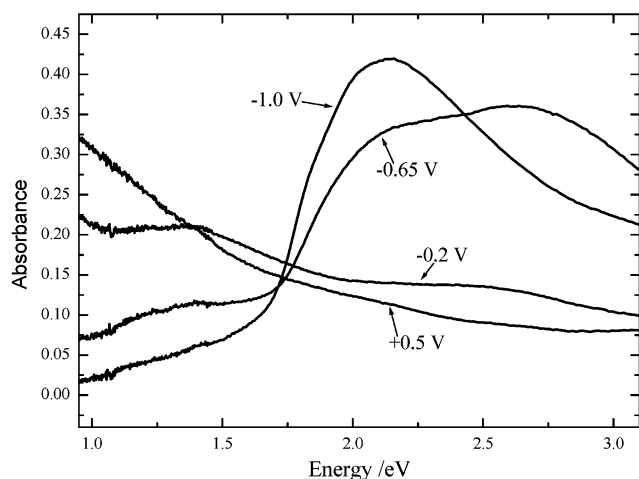


Figure 2. UV-vis-NIR spectra of a PEDOT film on ITO glass at different potentials applied (as indicated).

used as the coupling element in this Kretschmann configuration. The Au/LaSFN9 glass substrate was clamped against the Teflon cell, with an O-ring providing a liquid-tight seal. The Teflon cell was then mounted to the 2-axis goniometer for investigations by SPR. Surface plasmons were excited at the metal-dielectric interface, upon total internal reflection of polarized light from a He-Ne laser. The yellow line ($\lambda = 594$ nm) of the laser was used in EC-SPS/SPPL measurements and the red laser line ($\lambda = 632.8$ nm) was used in EC-SPS/SPLS measurements. The optical/electrochemical processes at the gold substrate were detected by monitoring the reflectivity as a function of the incident angle θ . Surface plasmon enhanced photoluminescence from the deposited film was detected by a photomultiplier after passing through a low wavelength cutoff filter ($\lambda = 610$ nm).

Results and Discussion

Optoelectrochemical Spectroscopy. To study the electrochromic properties of PEDOT films, UV-vis-NIR spectra were taken at various applied constant potentials. The obtained UV-vis-NIR spectra at several potentials are shown in Figure 2. The PEDOT film was electropolymerized on an ITO electrode from an EDOT monomer solution for 90 s at 0.9 V (vs Ag/Ag⁺). The film thickness was obtained by surface contact profilometry and was determined to be ca. ~ 200 nm. As the applied potential decreased, the absorption in the visible due to the π - π^* transition increased. In the dedoped (neutral) state, the electronic band gap (E_g) was determined to be ca. 1.7 eV from the onset of the π - π^* transition. The average transition energy from the valence band to the conduction band was determined from λ_{\max}

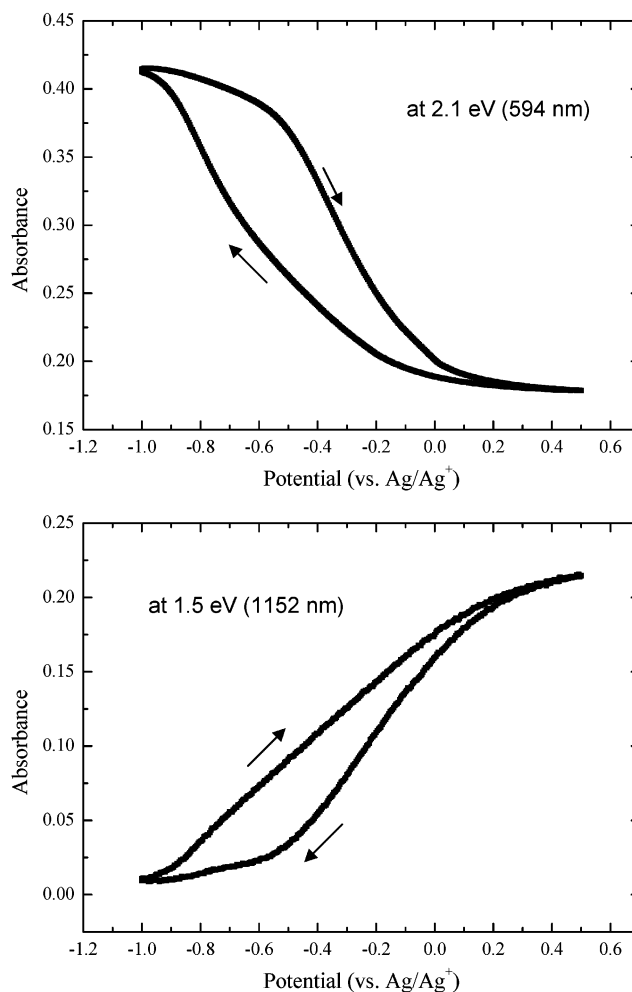


Figure 3. Absorbance change at two different wavelengths ($\lambda = 594$ and 1152 nm, corresponding to 2.1 and 1.5 eV, respectively) during potential cycling between -1.0 and $+0.5$ V at a scan rate of 20 mV/s.

to be 2.1 eV. The absorbance in the NIR region due to the intraband transition decreased with decreasing potential. The weak peak at 1.4 eV seen at -0.2 and -0.65 V is interpreted as being a transition to a polaronic state in the forbidden band. It was observed that the thin PEDOT film was dedoped at -1.0 V. Similar values for a PEDOT film have been previously reported by other groups.¹⁶ At an applied potential of -0.65 V, it is expected that one deals with two electronic states, i.e., PEDOT being partially in a neutral state and partially in a polaronic state with an enlarged energy band gap, so that two π - π^* transition peaks at 2.1 eV and at 2.75 eV are observed.

The absorbance change of the PEDOT film was monitored at 2.1 eV ($\lambda = 594$ nm) and at 1.5 eV ($\lambda = 1152$ nm), respectively, while the potential was cycled from -1.0 to $+0.5$ V at a scan rate of 20 mV/s. The results are shown in Figure 3. At 2.1 eV, the PEDOT film became more transparent with increased potential, i.e., p-doping, and the absorption increased upon dedoping. On the other hand, at 1.5 eV, the absorption of PEDOT film increased upon p-doping but became more transparent upon dedoping (reverse behavior). In both cases, hysteresis was observed at similar scan rates. This hysteresis behavior is typical for this type of conjugated polymer and should be related to the doping-dedoping mechanism: the oxidation (doping) of conjugated polymers corresponds to the emission of electrons from the valence band and the reduction (dedoping) corresponds to the injection of electrons to the polaron or bipolaron states. This difference in the mechanism

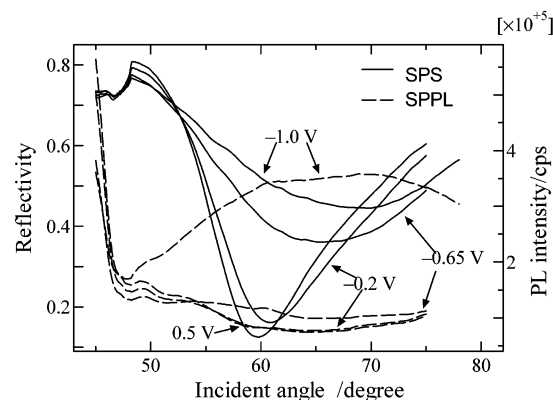


Figure 4. Angular SPS and SPPL curves of a PEDOT film: solid curve: SPS; dotted curve: SPPL.

might be responsible for different potentials at the same electronic state seen in the anodic scan and in cathodic scan, respectively.^{17–21} Further studies are underway to understand this phenomenon.

Angular Scan Measurements of Electrochemical-Surface Plasmon Spectroscopy and Surface Plasmon Field Enhanced Photoluminescence (EC-SPS/SPPL). A most important question in this investigation is whether the photoluminescence can be detected from an ultrathin PEDOT film in the dedoped state. The He–Ne laser of 2.1 eV ($\lambda = 594$ nm), which corresponds to the average transition energy from the valence band to the conduction band obtained from UV–vis–NIR spectra, was chosen for the excitation of surface plasmons. The angular measurements were performed under equilibrium conditions with several potentials being held constant. The SPS and SPPL curves of a thin PEDOT film at four different potentials are shown in Figure 4. For these measurements, an ultrathin film was prepared intentionally to excite the photoluminescence with the evanescent field associated with the surface plasmon mode. The thickness of the film was about 25 nm as deduced from Fresnel fitting curves. From the spectra in Figure 4 one can see that the minimum angle of the reflectivity curve increased with increasing negative potential. The minimum angle of the SPR resonance curve for the ultrathin film increases upon decreasing the potential from +0.5 to -1 V, which indicates an increase of the real part, ϵ' , of the dielectric constant ($\epsilon' + i\epsilon''$) of the PEDOT film. Furthermore, the SPS reflectivity curves significantly broadened at negative potentials. In SPS measurements, curve broadening is either due to an increase of the imaginary part of the dielectric constant, ϵ'' , or to surface roughness. If this broadened curve would be due to surface roughness, the scattered light intensity enhanced by surface plasmon resonance⁵ should also increase. Because, in our light scattering measurements, an increase of the scattered light intensity was not observed at negative potentials, this result indicates that the electrodeposited thin PEDOT film has a smooth surface in which the surface roughness does not change with potential. Therefore, the broadening of the SP reflectivity curve is mostly due to an increase in the imaginary part, ϵ'' of the dielectric constant. This agrees with the observation that the absorption at 2.1 eV increased with negative potentials, i.e., upon dedoping as shown in Figure 2.

To observe photoluminescence from the conducting polymer film, we needed to use a laser with a higher photon energy than the electronic band gap energy, i.e., in the region that has a strong imaginary part of the dielectric constant. At the same time, the excitation of a surface plasmon is required to enhance the electromagnetic field at the Au/PEDOT/electrolyte interface.

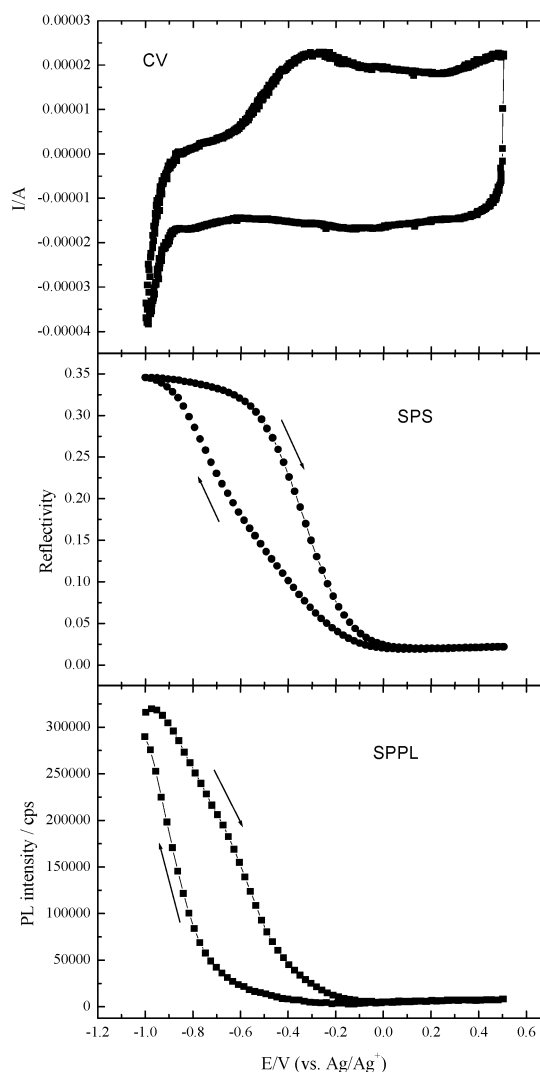


Figure 5. Simultaneous observation of SPS reflectivity and SPPL curves with the cyclic voltammogram of a PEDOT ultrathin film during potential cycling between -1.0 and $+0.5$ V at a scan rate of 20 mV/s.

However, a strong imaginary part of the dielectric constant dampens the excitation of a surface plasmon. An important point in this system is that the surface plasmon is still excited at the dedoped state (-1.0 V) which is only possible because we are dealing with an ultrathin film. Therefore, we can generate an evanescent optical field at the Au/PEDOT/electrolyte interface. The EC-SPPL measurements clearly show the different PL intensity properties at different potentials. Indeed, photoluminescence from PEDOT was observed in the dedoped state (-1.0 V), as shown in Figure 4. On the other hand, no significant PL intensity was observed at $+0.5$, -0.2 , and -0.65 V. As can be seen, the SPR curve is sharper in the more doped state, which means that the enhanced optical field for the Au/PEDOT/electrolyte system is stronger in the more doped state. However, the enhanced optical field at 2.1 eV is not expected to generate an appreciable π – π^* transition at $+0.5$, -0.2 , and -0.65 V, respectively, and the presence of increased charge carriers might quench the generated exciton. Consequently, no enhancement of luminescence was observed. One possible explanation for the finding that can detect the weak photoluminescence by the EC-SPS/SPPL technique is that the strongly enhanced optical field by the excitation of surface plasmons overcomes the dissipation of the photoluminescence (very low quantum efficiency) in the ultrathin PEDOT film. Another advantage for

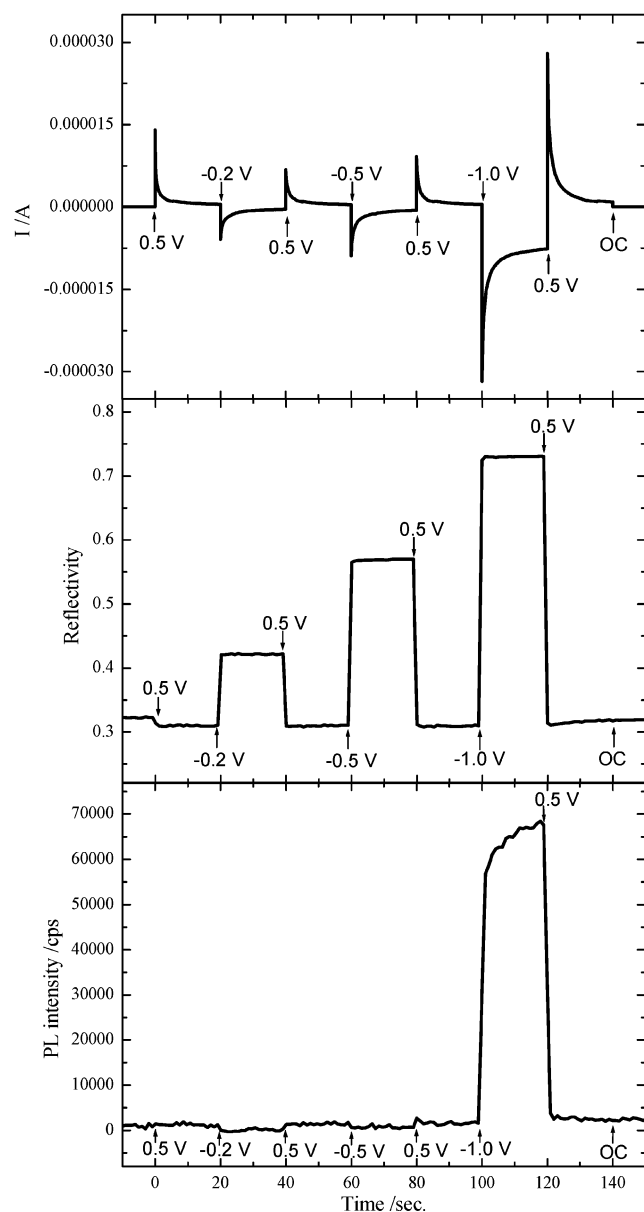


Figure 6. Chronoamperometric measurements of a PEDOT film switched sequentially between the doped state and the dedoped state (+0.5 \rightarrow -0.2 \rightarrow +0.5 \rightarrow -0.5 \rightarrow +0.5 \rightarrow -1.0 \rightarrow +0.5 V), respectively.

the use of EC-SPS/SPPL is that we can obtain a strong variation of the photoluminescence by changing the incident angle.

Potential Cycling Measurement of EC-SPS/SPPL. The SPPL intensity, the SPS reflectivity, and the current were measured simultaneously during potential cycles from -1.0 to +0.5 V at a scan rate of 20 mV/s. The 2.1 eV laser was used for this measurement. The reflectivity was monitored at an angle slightly lower than the minimum angle at 0.5 V. In this case, the reflectivity should increase if the real and imaginary parts of the dielectric constant increase. The result is shown in Figure 5. In the anodic scan, the reflectivity decreased slightly from -1.0 to -0.6 V, and then decreased steeply to -0.1 V. This value corresponds to the oxidation peak in the CV. The reflectivity change can be explained by the change of the dielectric constant due to the doping by the PF_6^- ion. The reflectivity reached a plateau above 0 V. This suggests that the dielectric constant of the thin PEDOT film is constant above that potential. In the cathodic scan, the onset of the reflectivity

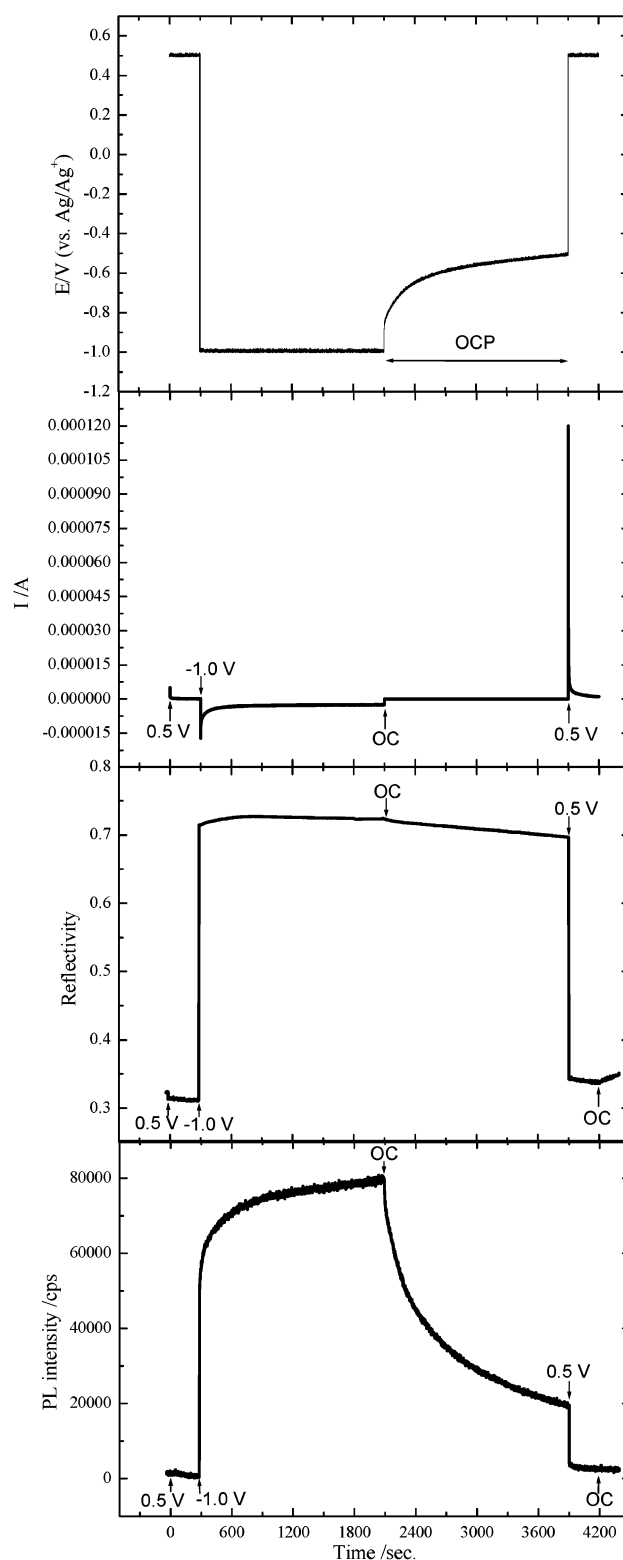


Figure 7. Simultaneous observation of potential, current, SPS reflectivity and SPPL at several potentials: +0.5 V, 5 min \rightarrow -1.0 V, 30 min \rightarrow open circuit, 30 min \rightarrow +0.5 V, 5 min.

change was seen at approximately -0.1 V. The trace of the reflectivity change was similar to the change of the absorption during the potential cycling. It is noted that the imaginary part of the dielectric constant corresponds to the extinction coefficient at the probe energy (wavelength). Because the change of the real part of the dielectric constant of the PEDOT film was

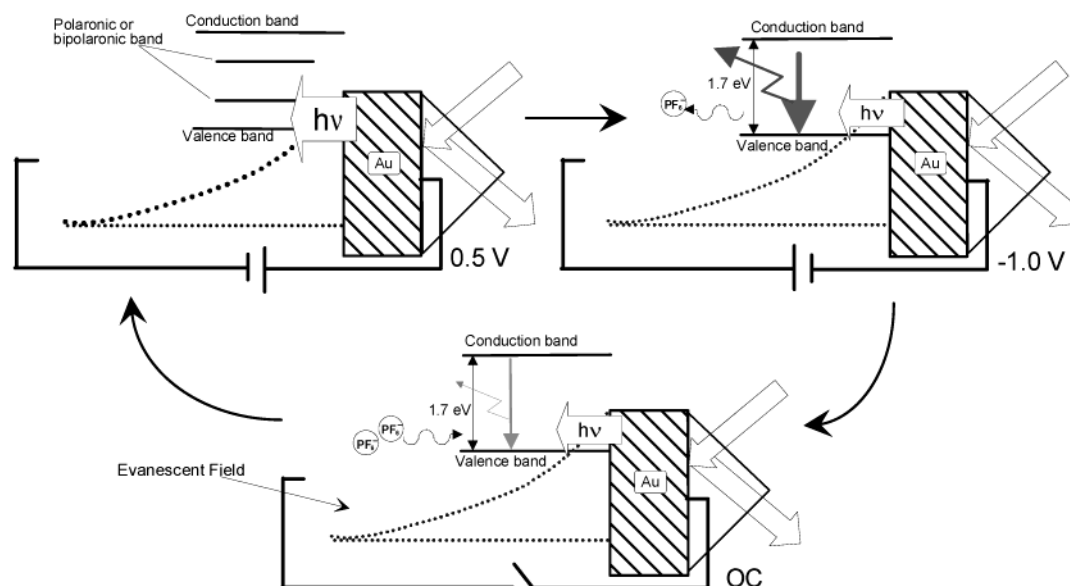


Figure 8. Schematic illustration of the mechanism for SPPL from an ultrathin PEDOT film under different potentials applied.

observed at different potentials as explained before (Figure 4), the observed changes should be due to both, the real and the imaginary part of the dielectric constant.

On the other hand, the PL intensity reached a plateau already at -0.2 V in the anodic scan and the onset of the PL in the cathodic scan was at ca. -0.7 V. Both values were more negative (more in the dedoped state) compared to the value of the reflectivity change. This difference might be due to the existence of partial polaron/bipolaron band, which affects no detection of PL but affects the change of the dielectric constant, compared to more doping level.

Chronoamperometric Measurement of EC-SPS/SPPL. To study the relation between the reflectivity and the photoluminescence, the chronoamperometric measurements using EC-SPS/SPPL were performed. The response of an ultrathin PEDOT film to a sequence of potential steps applied is shown in Figure 6. The potential was switched sequentially between the doped and the dedoped state, i.e., applied in the following sequence: $+0.5 \rightarrow -0.2 \rightarrow +0.5 \rightarrow -0.5 \rightarrow +0.5 \rightarrow -1.0 \rightarrow +0.5$ V. Each potential was applied for 20 s. Characteristic changes were observed in the SPS reflectivity and in the SPPL intensity. The reflectivity increased and decreased when the PEDOT film was dedoped and doped, respectively, whereas the increase of the SPPL signal was observed only while the potential was held at -1.0 V. This observation is quite interesting because it gives direct evidence of the differences between the SPS reflectivity and the SPPL emission. The phenomenon would be very useful in designing optical switching devices because one can obtain three independent signals by this technique. This switching property is in accordance with the result obtained from angular-reflectivity measurements. The reflectivity changed almost immediately if the potential step was applied, and reached a plateau characteristic for each potential applied. On the other hand, the SPPL intensity continued to increase gradually during the applied potential at -1.0 V. The change of the dielectric constant due to the dedoping should be a very fast process: the dielectric constant changed quickly and remained constant. One possible reason for the continued increased of the SPPL intensity is that during the applied potential at -1.0 V, the anion, which quenches the PL intensity in the PEDOT film moved to the electrolyte solution so that the PL intensity continued to increase at -1.0 V. Another possible explanation is that the injected

charge carriers (leading to recombination and photoemission) might contribute to the enhancement of the light emission process. In fact, a negative current was observed even after 20 s. Even in the dedoped state, an electronic current is expected to exist together with the ionic current.²² Note that the irradiated area for the excitation of surface plasmons is about 0.010 cm^2 whereas the electrode area is 0.785 cm^2 . Therefore, the observed current cannot be mainly assigned to the photocurrent.

To further probe this EC-SPPL property, we measured the potential, the current, the SPS reflectivity and the SPPL intensity simultaneously at several potentials, i.e., at $+0.5$ V, 5 min $\rightarrow -1.0$ V, 30 min \rightarrow open circuit, 30 min $\rightarrow +0.5$ V, 5 min, as shown in Figure 7. Here, again, the EC-SPPL intensity increased at an applied potential of -1.0 V. An interesting observation is that the SPPL decreased after the circuit was opened (OC). After 30 min of open circuit, the open circuit potential reached ca. -0.5 V. In this case (Figure 7), the reflectivity did not decrease significantly within 30 min of open circuit as compared to the reflectivity at -0.5 V applied, as shown in Figure 6. By taking all these simultaneous observations into consideration, one can come to the conclusion that this is attributed to the ionic charge carriers migrating to a new equilibrium state spontaneously because the dedoped state of the PEDOT film is not stable. However, the electrons were not emitted from the valence band because a potential was not applied, so that the dielectric constant did not significantly change. On the other hand, the PL intensity still continued to decrease even after 30 s of open circuit. This suggests that the migrating ionic charge carriers might quench the photoluminescence. When a potential of 0.5 V was applied to the PEDOT film after the 30 min at open circuit, a large current was observed and the SPPL and the reflectivity decreased significantly. This is further evidence that ionic charge carriers migrated into the PEDOT film under the open circuit conditions. A mechanistic model obtained from these observations is schematically shown in Figure 8.

Conclusions

We have used a combination of surface plasmon spectroscopy and surface plasmon enhanced photoluminescence spectroscopy with electrochemical control to monitor in situ the electrochro-

mic properties of and detect the photoluminescence from an ultrathin poly(3,4-ethylenedioxythiophene) film. The photoluminescence from PEDOT was detected when the polymer was dedoped under the influence of the corresponding applied potential. The photoluminescence intensity was controlled by the potential and was dependent on the angular position in an SPS reflectivity experiment. The SPS characterization of the PEDOT film is consistent with the PEDOT bulk electrochromic properties obtained from UV–vis–NIR spectra. A mechanistic model of the photoluminescence from PEDOT was obtained by taking into consideration the reflectivity and the SPPL data, which could be observed simultaneously by our system. Our results show that the EC-SPPL method is a sensitive tool in detecting weak photoluminescence from a conjugated polymer film and the setup allows for the electrochemical control of three independent signals. Applications to sensors and optoelectronic devices will be investigated.

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