

# Electrochemical Properties of Self-Assembled Monolayers of Polyaniline: Effects of the Thiol Substituent and Reduced Dimensionality

Burak Ulgut,<sup>†</sup> Yu Zhao,<sup>†</sup> Jacob E. Grose,<sup>§</sup> Daniel C. Ralph,<sup>§</sup> and Héctor D. Abruña<sup>\*,†</sup>

*Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853*

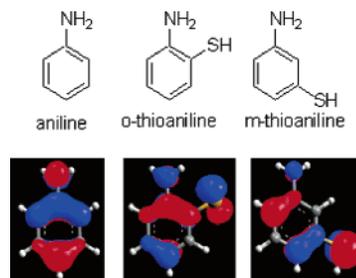
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Self-assembled monolayers and bulk films of thioanilines, polymerized on gold and platinum surfaces, have been characterized and compared to bulk polyaniline (PANI) films. In a previous study [Kuwabata; et al. *Langmuir* **1999**, *15*, 6807–6812], only one redox couple was observed in the cyclic voltammetric profile of a polymerized monolayer of thioaniline on gold, in contrast to the known profiles of bulk PANI, which exhibit two couples. We observe two couples in both a polymerized thioaniline monolayer and a bulk polythioaniline (S-PANI) film, but the 200 mV window between the couples (the width of the region of high conductivity) in the S-PANI films is much smaller than the 600 mV window in bulk PANI. We ascribe this difference to the presence of the thiol substituent. The windows of high conductivity of the polymerized thioaniline monolayer and the bulk S-PANI film are the same within the limits of our experiment, implying that the difference in the dimensionality of the films (a 2D monolayer vs 3D bulk films) has a limited effect on the films' voltammetric profiles.

## Introduction

Conducting polymers have been the subject of intensive research because they are synthetic materials that can achieve high conductivities upon doping. For example, films of stretch-oriented, doped polyacetylene<sup>1</sup> have conductivities approaching those of conventional metals. However, even though its peak conductivity can be extremely high (10<sup>5</sup> S/cm), polyacetylene suffers from severe atmospheric instability, and thus, it is not suitable for device applications. Under ambient conditions and for a variety of different conducting polymers, conductivities on the order of 10<sup>2</sup> S/cm can be routinely achieved.<sup>1</sup> Furthermore, the conductance of thin films can be easily and reversibly switched from low to high, both electrochemically in electrolyte solutions<sup>2</sup> and in the solid state using a field effect transistor (FET) geometry.<sup>3</sup> Of the more stable conducting polymers, polyaniline (PANI) is well suited to electrochemical applications since its conductivity can be switched from low to high to low within the electrochemical potential window of aqueous electrolytes and because films of PANI can be readily prepared from aqueous electrolytes. For these and other reasons, PANI is currently being employed in a number of devices including batteries, antistatic coatings, electromagnetic shields, and others.<sup>4</sup>

Given the recent trend toward device miniaturization, it would be both interesting and important to study and characterize PANI films in reduced dimensions/scales. Attempts at making and characterizing PANI in reduced dimensions have focused on using self-assembled monolayers made out of thiol derivatives of aniline (see Figure 1).<sup>5–9</sup> Monolayers derived from aniline



**Figure 1.** Schematics of aniline and thiolated aniline derivatives and their corresponding HOMO contours.

thiol isomers have yielded films whose cyclic voltammetric response exhibits only one peak around +0.4 V vs Ag/AgCl (with an occasional shoulder on the cathodic side),<sup>5,9</sup> whereas bulk PANI films exhibit two redox peaks around +0.1 and +0.7 V vs Ag/AgCl. One can envision two possible explanations for this discrepancy: either the thiol substituent alters the redox properties of the thioaniline monomer and polymer as compared to those of aniline and PANI or the redox properties are affected by the change in dimensionality (3-D bulk PANI films vs 2-D polythioaniline (S-PANI) monolayers). We sought to determine the validity of these explanations by making bulk films of S-PANI and comparing the resulting voltammetry with that of standard PANI. Because of the quantitative differences in the cyclic voltammograms, we wanted to verify that S-PANI and PANI have qualitatively similar redox properties. To this end, we analyzed the impedance behavior of the resulting films and investigated the electrochemistry of the analogous compound anisidine.

## Experimental Section

**Reagents.** *o*-Thioaniline (Aldrich, 99%), *m*-thioaniline (Aldrich 96%), and aniline (Aldrich, 99%) were distilled under reduced pressure and kept under nitrogen at ~4 °C. Anisidine (Aldrich 99%)

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\* To whom correspondence should be addressed. E-mail: hda1@cornell.edu.

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<sup>§</sup> Laboratory of Atomic and Solid State Physics.

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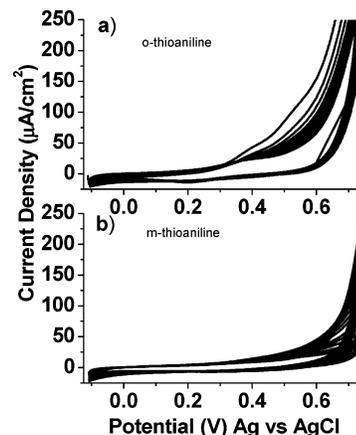
and redistilled perchloric acid (Alfa Aesar 70%) were used as received. Millipore water (18 M $\Omega$ ·cm Millipore Milli-Q) was used to make all aqueous solutions. The monolayers were prepared from aqueous 0.1 M *o*-thioaniline monomers in 1 M perchloric acid by immersion of an electrochemically cleaned gold electrode for 30 min. The perchloric acid in the solution keeps the thiol group of the molecules protonated, slowing down disulfide formation, in addition to making the molecule more soluble (since the amino group is also kept protonated). Bulk PANI, poly(*o*-thioaniline), and poly(anisidine) films were made from 1 mM solutions of the corresponding monomer in aqueous 1 M perchloric acid solution by cycling the potential between 0 and +0.9 V vs Ag/AgCl.

**Instrumentation.** All electrochemical measurements were performed using an Ensmann EI-400 potentiostat driven by an EG&G PARC Model 175 universal programmer. Data were collected through an AD/DA converter card using in-house software. For capacitance measurements, an EG&G Princeton Applied Research Model 5209 lock-in amplifier was used and the internal reference from the lock-in amplifier was used to modulate the signal output of the function generator. We monitored the 90° out-of-phase (quadrature) current response to an applied small-amplitude (2 mV) sine wave at relatively low frequencies (<1 kHz) on top of the triangular waveform necessary for cyclic voltammetry. The current signal out of the potentiostat was fed into the lock-in amplifier directly to measure the capacitive response and to the computer through a low-pass filter to record the cyclic voltammogram. The outputs of the lock-in amplifier, as well as the cyclic voltammetric current, were recorded as a function of the applied potential. The impedance experiments had to be done on platinum electrodes since gold electrodes themselves show changes in capacitance (similar to the S-PANI) due to the rearrangement of crystal faces, as previously reported.<sup>10</sup> A Ag/AgCl (saturated NaCl) reference electrode was employed for all measurements. Both gold and platinum electrodes were sonicated in a 1:1:1 water/ethanol/acetone mixture for 10 min and polished with 1  $\mu$ m diamond paste prior to electrochemical cleaning. The electrochemical cleaning procedure involved holding the electrode potential at around +2.0 V for 30 s followed by holding the potential at around -0.5 V for 30 s and cycling at 10 V/s between hydrogen evolution and oxygen evolution regions until the voltammetry showed the characteristic profile of a clean polycrystalline gold or platinum electrode. The electroactive area was calculated by integrating the charge under hydrogen adsorption and oxide reduction peaks for platinum and gold electrodes, respectively. The theoretical modeling was done using ArgusLab 4.0.<sup>11</sup> All the geometries were optimized using the AM1<sup>12</sup> method, and the orbital energies and shapes were calculated using the INDO<sup>13</sup> method.

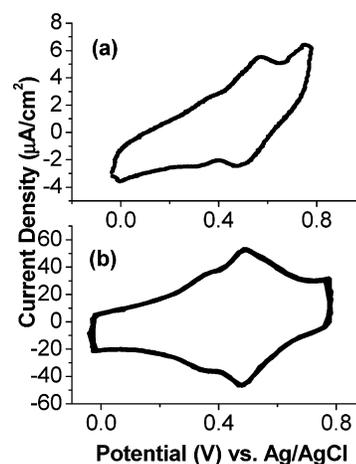
## Results and Discussion

The cyclic voltammetric response of an adsorbed monolayer of an equimolar mixture of *o*-thioaniline and *m*-thioaniline on a polycrystalline Au disk electrode is in accordance with the report by Kuwabata et al.<sup>9</sup> They attribute the redox couple around +0.45 V to PANI-like behavior even though it is only a single couple whereas PANI exhibits two redox couples around +0.2 and +0.8 V vs Ag/AgCl, respectively. To our knowledge, this discrepancy remains largely unexplained.

We found that bulk electropolymerization of *m*-thioaniline was considerably more difficult than that of *o*-thioaniline, as shown in Figure 2. While there is an oxidation current for both monomers, there was no apparent film formation for the *m*-thioaniline monomer. This can be rationalized by considering that the cation radical formed upon oxidation of the monomer



**Figure 2.** Cyclic voltammetry experiments for film growth for *o*-thioaniline (a) and *m*-thioaniline (b). Sweep rate is 100 mV/s in both cases.



**Figure 3.** Steady-state cyclic voltammogram in 0.1 M HClO<sub>4</sub> of a Au electrode modified with an *o*-thioaniline monolayer at 100 mV/s (a) and 2 V/s (b).

has to attack the 3, 4, or 5 positions of an unoxidized monomer to initiate the free-radical polymerization. In the case of the *m*-thioaniline, the HOMO has no significant amplitude on the 5 position and the 4 position is sterically hindered due to the thiol group, whereas for *o*-thioaniline, both the 4 and the 5 positions have significant HOMO amplitude and neither is sterically hindered (see Figure 1). Therefore, the cation radical formed upon electrooxidation has a higher probability of successfully attacking the ortho isomer than the meta isomer to yield the polymer. Arguably, the S-PANI monolayer derived from a mixture of the two monomers will mostly consist of poly-*o*-thioaniline since the meta isomer polymerizes much more slowly. Moreover, it is known that when making self-assembled monolayers out of two different molecules, the resulting monolayer can often consist of phase-segregated domains of each component (even in the case of molecules as similar as different chain-length alkanethiols<sup>14</sup>). The steady-state voltammetric response of a gold electrode modified with an electropolymerized monolayer of *o*-thioaniline is presented in Figure 3. The profile is qualitatively similar to that of the mixed monolayer (ortho and meta) except for a small additional shoulder at about +0.3 V for the *o*-thioaniline monolayer case. On the basis of these observations and the similarity of the response, all further studies were carried out with pure *o*-thioaniline as opposed to

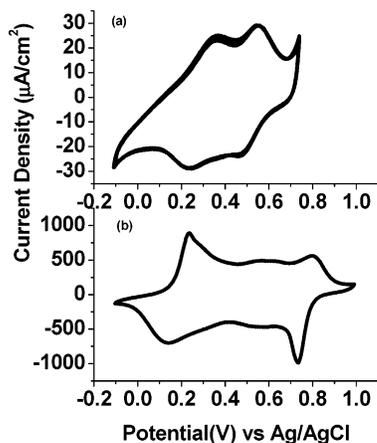
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**Figure 4.** Comparison of polythioaniline (a) and polyaniline (b) bulk films on platinum electrodes. The sweep rate is 100 mV/s in both cases.

the equimolar mixture of *o*-thioaniline and *m*-thioaniline used in previous studies.<sup>9</sup>

We should mention that the previous study by Kuwabata et al.<sup>9</sup> was performed on Au(111) surfaces whereas the current study is performed on polycrystalline gold. The fact that monolayers derived from a single compound (as opposed to two in the aforementioned study) could be polymerized in the current study might be related to the grain boundaries associated with the polycrystallinity of the electrodes.

Figure 3a and b shows the voltammetric profiles of the same polymerized *o*-thioaniline monolayer at 100 mV/s and 2 V/s, respectively. We should mention that the monolayer was polymerized by sweeping the potential to +0.9 V before the data shown were taken. Since in cyclic voltammetry faster sweep rates favor Faradaic processes of surface confined species (relative to species freely diffusing in solution), by employing relatively faster sweep rates (up to 2 V/s), we were able to observe two distinct redox transitions (as opposed to only one at 100 mV/s) in the voltammetric profiles for the monolayer (Figure 3b). However, further increases in the sweep rate resulted in a smearing of the peaks due to kinetic limitations.

In bulk film voltammograms, the two peaks are more easily observable due to larger Faradaic currents at sweep rates which are sufficiently slow to be compatible with PANI or S-PANI switching kinetics. This will give rise to high signal-to-noise ratios, leading to enhanced resolution of the peaks. Therefore, we will defer a comparison of the profiles of the polymerized *o*-thioaniline monolayer and bulk PANI film and first examine the voltammetry of bulk S-PANI films.

We have prepared electropolymerized bulk films of *o*-thioaniline on both Au and Pt electrodes. Film growth appears to be favored on Pt electrodes relative to Au electrodes, although both voltammograms clearly display two redox peaks at approximately the same potentials. We believe that growth is more difficult on gold because thioaniline monomers are likely self-assembling on the gold surface, which renders the amino group on the monomer less accessible. On Pt, the interactions would be anticipated to be weaker so that the cation radicals would be accessible for attack from either side. This would, in turn, give rise to thicker films, which would have correspondingly larger Faradaic currents and allow better resolution of the peaks as mentioned above.

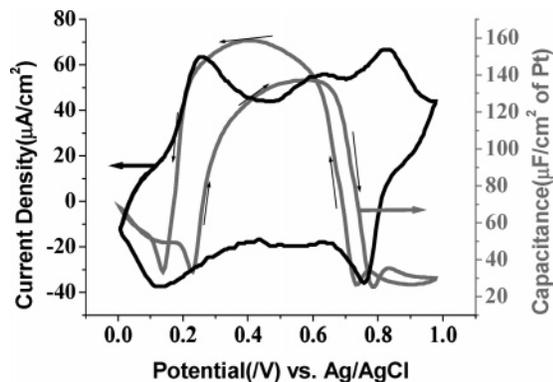
A comparison of the voltammetry of bulk films of PANI and S-PANI on polycrystalline Pt is shown in Figure 4. Both films were grown by electropolymerization out of the appropriate monomer solution. After electropolymerization, the electrodes

were removed from the solution and the films were rinsed with deionized water before the voltammetric measurements were carried out. The films were insoluble and electroactive in the acid solution without any monomer. This leads us to believe that the films made are polymers of thioaniline. The voltammetric behavior shown was obtained in the absence of any monomer in solution (0.1 M HClO<sub>4</sub>). Since the S-PANI film overoxidizes at more negative potentials than PANI, we kept the switching potential lower than that of PANI. While the voltammetric profiles are now qualitatively similar (both have two redox waves), the redox potentials are strikingly different. Whereas PANI has two transitions around +0.2 and +0.8 V, S-PANI shows the corresponding transitions around +0.3 and +0.5 V, respectively. The ca. 600 mV window of conductivity of bulk films of PANI drops down to ca. 200 mV for bulk films of S-PANI. The reason for this difference can only be attributed to the presence of the thiol in S-PANI. However, the presence of the thiol could impact the redox properties of the film via two distinct mechanisms: it could change the electronic structure of the monomer or it could change the binding configuration (i.e., 3 position to amino group vs 4 position to amino group) of the polymer, which, in turn, would change the electronic structure of the resulting film. It is not clear which mechanism is dominant. However, it is clear that there is a drastic quantitative difference between the electronic structures of S-PANI and PANI, even though qualitatively they are similar. The window of conductivity gets narrower when the thiol group is added onto the aniline monomer.

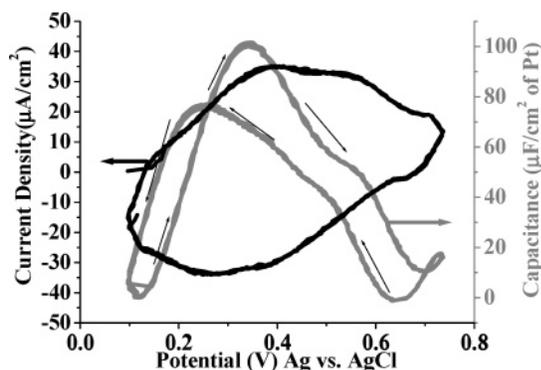
It has been previously reported that the oxidation of aniline can give rise to the formation of phenazine via a coupling-type mechanism. The analogous reaction with thioaniline to yield phenothiazine is, in our view, most unlikely. In the case of monolayers, formation would be precluded by the fact that the sulfur atom is bonded to the gold surface. In the case of bulk film derived from the thioanilines, we believe that the formation of phenothiazines is unlikely in the current work for two reasons. First, the mechanisms proposed for the formation of phenazines involves deprotonation of the thiol and the amino group, which will be slowed in 1 M HClO<sub>4</sub>, in which we make our films. Second, geometrically there is only one orientation that the molecules could transform into the phenothiazine molecule. Moreover, it should be mentioned that the coupling of thioanilines, would not give rise to phenothiazines but rather to a "mercapto amino phenothiazine". Given the above, we believe that formation of phenothiazine-like products is most unlikely, and thus, we will not consider this possibility further.

Since there is a significant difference in the redox potentials of bulk films prepared from thioaniline and bulk PANI films, we wanted to ensure that polymerizing thioaniline isomers leads to films with similar electronic properties (i.e., three different electronic states—insulating, conducting, insulating). To address this question, we have carried out ac impedance studies of films derived from thioaniline isomers and compared them to those of standard PANI. The response for PANI, shown on Figure 5, is in good agreement with the previously published data of Santiago et al.<sup>15</sup> The impedance measurements were carried out at relatively fast sweep rates (compared to standard ac voltammetric measurements) since only at those sweeps were the peaks resolved (for the previously mentioned reasons). The capacitance is higher when the film is in the conducting state and lower when the film is in either insulating state. This behavior stems from the fact that increasing the number of charge carriers

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**Figure 5.** Capacitance profile of PANI at 1 kHz. The capacitance is high when the film is in its conducting state and low otherwise. The sweep rate is 100 mV/s. The capacitance values were divided by the electroactive area of the underlying platinum electrode.

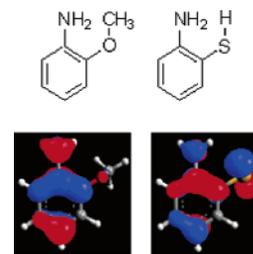


**Figure 6.** Capacitance behavior of poly-*o*-thioaniline. The sweep rate is 100 mV/s. The capacitance values were divided by the electroactive area of the underlying platinum electrode.

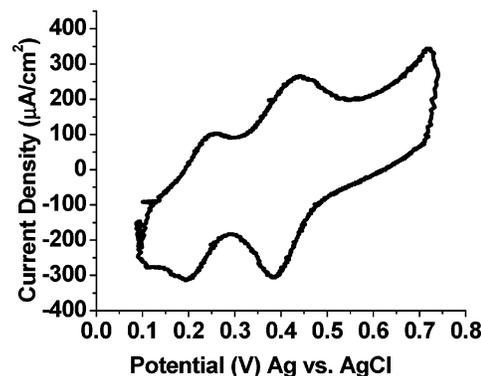
in the conducting polymer film increases the polarizability, in turn increasing the dielectric constant. The capacitance behavior of S-PANI was measured in a similar fashion (Figure 6). We observe that the capacitance behavior of S-PANI is similar to PANI, in that it rises when the film switches from low dielectric constant to high dielectric constant and it falls back when the film switches back to the low-dielectric-constant state. As explained above, capacitance behavior is strongly correlated with the changes in the polarizability, hence the conductivity of the film. The fact that the capacitance behaviors are qualitatively the same (i.e., low–high–low as a function of applied potential) supports our contention that the films formed by oxidizing *o*-thioaniline are electronically analogous to PANI.

An additional aspect likely present when studying the polymerization of thioanilines (and not present in PANI) relates to the oxidation of the thiols to disulfides and re-reduction back to thiols. To address this issue, we have studied the electrochemical behavior of *o*-methoxyaniline (anisidine) and the PANI analogue made when it is oxidized to the cation radical. Electronically, methoxy and thiol substitutions result in similar shapes and energies of frontier orbitals (Figure 7), yet the methoxy substitution precludes any reaction similar to that of thiols mentioned above. The voltammetry (steady-state) of the resulting film is shown in Figure 8 where the two-peak structure is still evident although the peaks are shifted in potential. This is a clear indication that neither of the peaks in bulk films of S-PANI are caused by the thiol–disulfide couple.

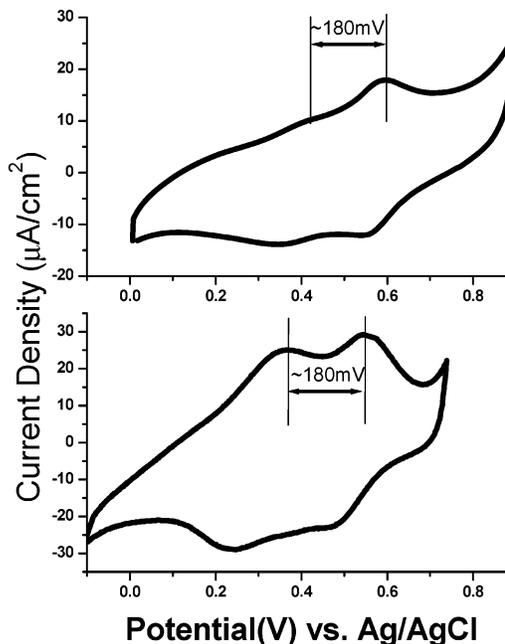
A comparison of the voltammetric profile of a S-PANI monolayer with that of a bulk film of S-PANI will illustrate the effects of dimensionality on the films' redox chemistry.



**Figure 7.** Schematics of methoxyaniline, *o*-thioaniline, and the HOMOs of the molecules.



**Figure 8.** Steady-state voltammetry of poly(methoxy-aniline) at 100 mV/s.



**Figure 9.** Comparison of steady-state voltammetric profiles of a monolayer and a bulk film of S-PANI at 100 mV/s.

As shown in Figure 9, the width of the windows of conductivity of the S-PANI monolayer and the bulk S-PANI film at 100 mV/s are the same within the resolution of our experiment. There is a slight difference between the actual peak positions of the couples which arise as a result of different kinetic overpotentials or a slight shift in the reference electrode. We make the comparison on the basis of the peak potentials and not the electrochemical standard reduction potentials because the latter is difficult to calculate due to the fact that the overpotential will be different when sweeping from an insulating to a conducting state than it will be when sweeping from a conducting to an insulating state.

### **Conclusion**

Bulk PANI, S-PANI films, and S-PANI monolayers have been made and characterized. At relatively high coverages, the S-PANI monolayer was found to have two distinct redox peaks in contrast to previous studies which found only one.<sup>5,9</sup> A comparison of bulk S-PANI and PANI reveals that the thiol group affects the electronic structure of the resulting film, giving rise to a narrowing of the conductivity window from 600 to ca. 200 mV. The comparison of the voltammetric profiles of a S-PANI monolayer and bulk S-PANI film does not reveal any significant difference

in the widths of the conducting regions. Therefore, the reduction in dimension from a bulk 3D film to a 2D monolayer film does not appear to affect the width of the conductivity window within the resolution of our experiment.

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