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Electrochemical Polymerization of Thiophene Derivatives attached to Lead Sulfide Nanoparticle

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Project Abstract:

Polythiophene has proven to be an excellent conductive polymer, and has been thoroughly researched over the past decade. Because of its conjugated backbone, it has gained popularity in photovoltaic cells as both n and p-type materials. Thiophene based derivatives: 3-(5-bromopentyl)thiophene, 5-(3'-thienyl)pentanoic acid (53TPA), 5-(3'-thienyl)-1-mercaptopentane (53T1MP), and both 53TPA and 53T1MP capped PbS nanoparticles were electrochemically polymerized with varying ratios of 2,2'-bithiophene onto an ITO working electrode. Resulting polymer films were characterized with cyclic voltammetry, and insoluble and soluble films were characterized using FTIR and NMR respectively.

The student-authored final report **MUST** include each of the following (check boxes to verify inclusion of each component):

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Introduction

The electrochemical polymerization of Thiophene has been thoroughly researched for its conduction properties, and many applications in organic solar cells. Because of polythiophene's conjugated pi system, it acts as an electron transport system, although polythiophene can dramatically change its application to either an n or p type semiconducting materials through doping. The focus of this research was to generate a method for successfully depositing a polythiophene film onto an ITO glass substrate through electrochemical polymerization, and studying the electrochemistry of both the film and monomers. Thiophene based derivatives such as: 3-(5-bromopentyl)thiophene, 5-(3'-thienyl)pentanoic acid (53TPA), 5-(3'-thienyl)-1-mercaptopentane (53T1MP), and both 53TPA and 53T1MP capped PbS nanoparticles will be electrochemically polymerized and characterized once a polythiophene film has been successfully made.

Figure 1 gives a general mechanism for the polymerization of Thiophene. The kinetics of the mechanism is still under investigation, but it is accepted that the reaction proceeds as either a radical – monomer or radical – radical coupling.¹⁻³

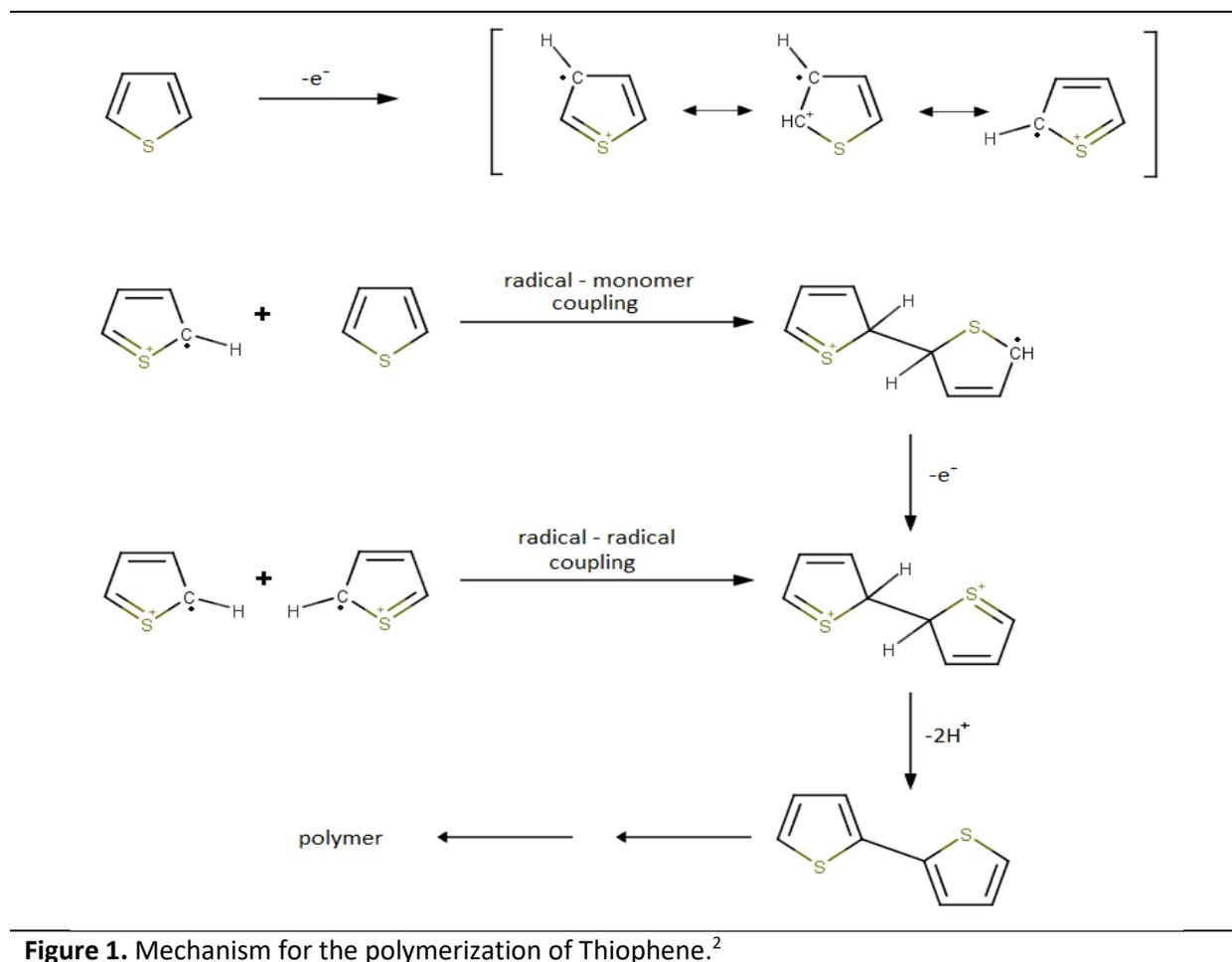


Figure 1. Mechanism for the polymerization of Thiophene.²

Methods

Setup and classification of Thiophene using CV

The Electrochemical setup consisted of a three-electrode cell, where the reference, counter, and working electrode were Ag/AgCl, platinum wire, and a gold or ITO on glass respectively (Figure 7B). Acetonitrile was distilled and stored over molecular sieves before electrochemistry was performed. A solution of 0.1 M Lithium perchlorate (purchased from sigma-Aldrich) and 0.2 M thiophene or 0.1 M 2,2'-bithiophene, in acetonitrile was prepared. ITO substrates were sonicated in an acetone bath for 15 minutes and dried prior to use. Cyclic voltammetry was performed on both thiophene and 2,2'-bithiophene solutions from -0.2 V to 2 V and -0.2 to 1.5 V respectively, with a scan rate of 100 mV/s. A solution of 0.1 M lithium perchlorate and 0.5 M thiophene in acetonitrile was used for the polymerization of thiophene onto an ITO glass substrate. Cyclic potential sweep technique from -0.2 to 1.8 V at a scan rate of 100 mV/s was used to control the polymerization

Cleaning ITO on glass

Recovered ITO on glass from polymerization will be coated with thiophene, and can be recycled.

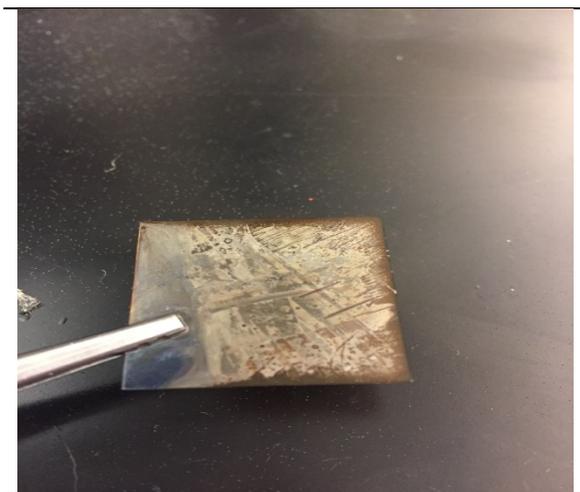


Figure 2. Picture of thiophene film after electrochemical polymerization.

The thiophene covered ITO on glass (Figure 2) was placed within a 0.05 M solution of NaOH in DiH₂O, and sonicated for ~30 minutes. Upon completion, rinse the surface with distilled water (use gloves when handling the ITO on glass, any oil on the surface will have an effect on polymerization). A second cleaning

method must be used to remove any small particles or oils on the surface of the ITO, before polymerization. A series of solutions used for a sonicating bath: deionized water, acetone, aqueous ethanol, and 2-propanol can be used to clean the ITO even further.⁴ The ITO is then dried with N₂, and can be used in electrochemical polymerization.

Results

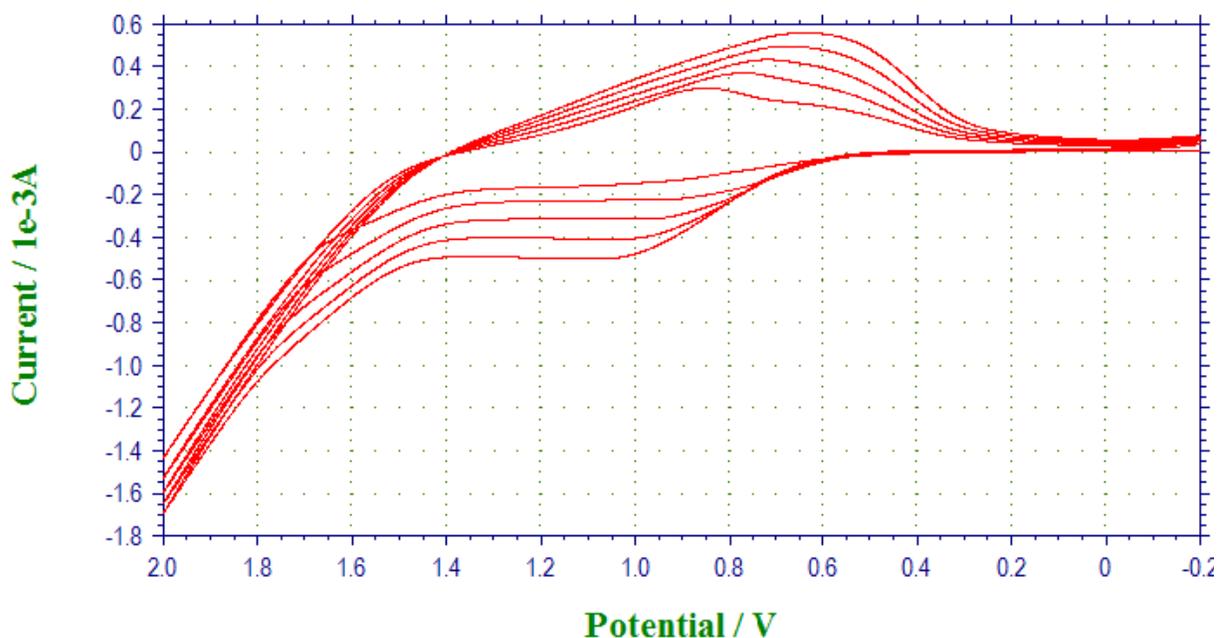


Figure 3. Multisweep CV of a 0.2 M thiophene in acetonitrile solution from -0.2 to 2.0 V.
Sensitivity(A/V) 1e-3

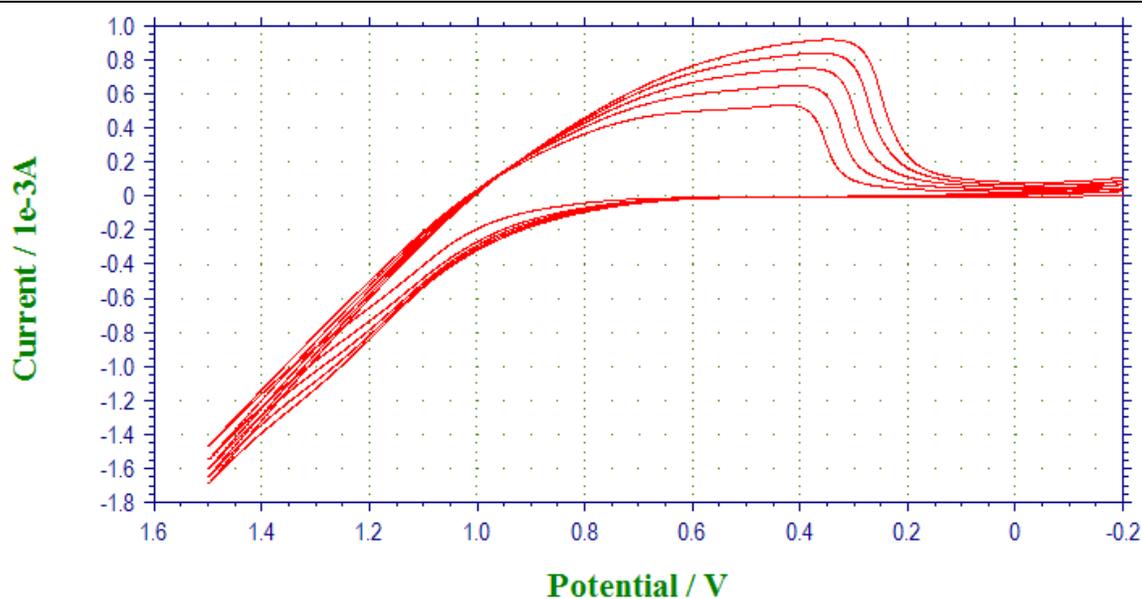


Figure 4. Multi-sweep CV of a 0.1 M 2,2'-bithiophene in acetonitrile solution from -0.2 to 1.5 V. Sensitivity(A/V): 1e-3

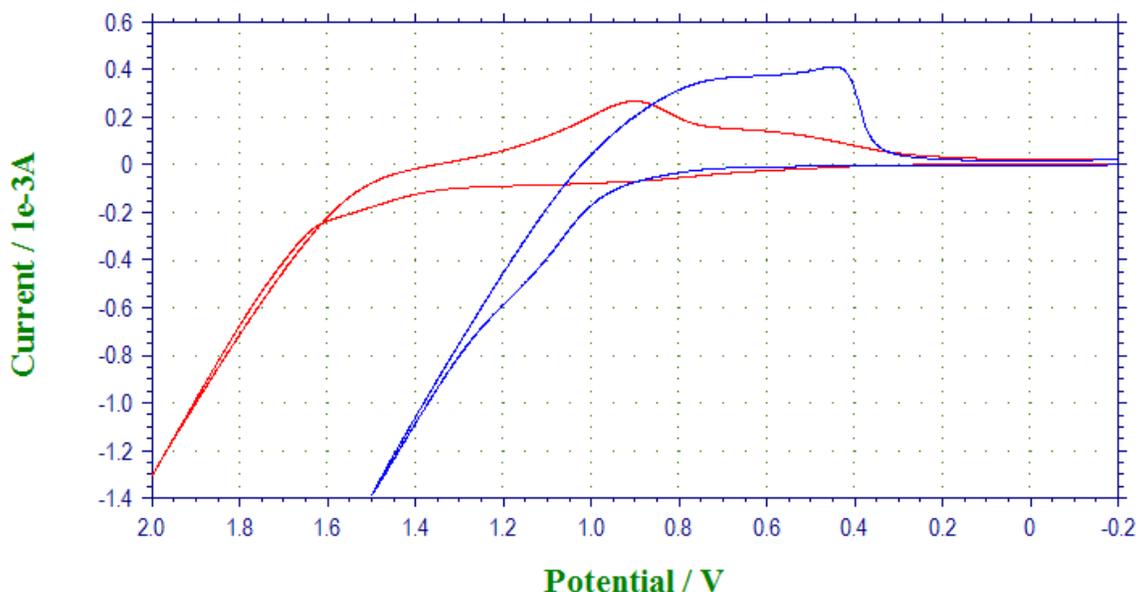


Figure 5. Overlaid first sweep plots of thiophene (red) and 2,2'-bithiophene (blue)

Cyclic voltammetry of thiophene and 2,2'-bithiophene

To further understand where polymerization occurs in thiophene and 2,2'-bithiophene, a CV was performed on each monomer in solution separately. The first sweep of both monomers was compared, and represented in figure 5. The anodic peak is nonexistent within the first sweep, and only shows up in the multi-sweep CV of thiophene (Figure 3). Because polymerization occurs earlier in 2,2'-bithiophene, the anodic peak is masked by the polymerization. Polymerization of thiophene and 2,2'-bithiophene occur at around 1.6 and 1.0 V respectively, which is shown by the large change in current once the sweep reaches these potentials.

Polymerization of Thiophene using CV

0.5 M and 0.1 M concentrations of Thiophene and LiCl_4 in acetonitrile were made. The working (ITO on glass), reference (Ag/AgCl), and counter (platinum wire) electrodes were connected to the green, white and red alligator clips on the potentiostat respectively. Polymerization of Thiophene occurs at potentials from 1.6 to 1.8 V, and setting a low scan rate (0.01 V), the polymerization can occur quickly and is recognized by the blue oxidative film (figure 7A). Figure 6 represents a CV of the polymerization of thiophene. Because polythiophene is building up onto the ITO on glass working electrode, there is a change in current measured, thus resulting in an outward expansion for each sweep. Polymerization for the first sweep (most inner sweep) occurs somewhere around 1.6 V and continuous to 1.8 V and then back to 1.6 V on the reverse sweep. It is even more noticeable on the last sweep, but polymerization occurs close to 1.4 V and ends on the reverse sweep at 1.6 V.

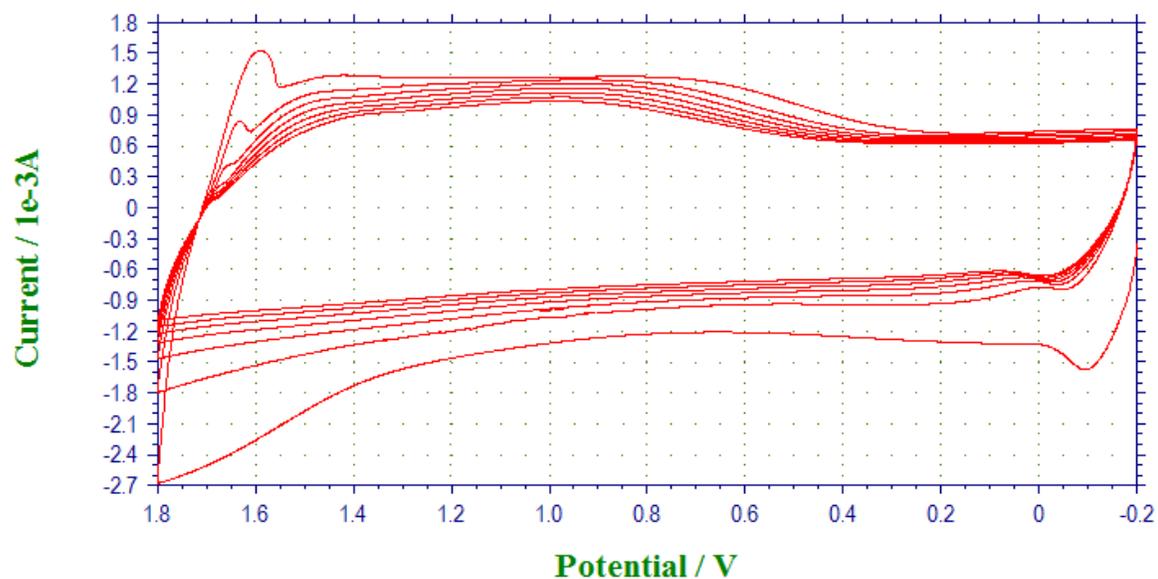


Figure 6. Multi-sweep CV of polymerization of 0.2 M Thiophene solution in acetonitrile from -0.2 to 1.8 V. Electrodes: (Working) ITO on glass, (reference) Ag/AgCl, (counter) Platinum wire.

A



B

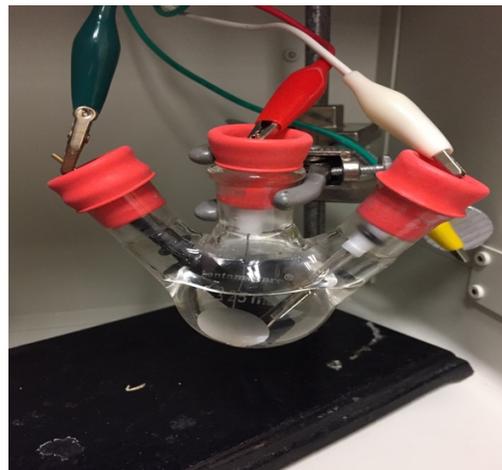


Figure 7. (A) Electrochemical setup and polymerization of Thiophene using CV from 1.6 to 1.8 V at a sweep rate of 0.01 V. (B) Three electrode cell consisting of gold working electrode, platinum wire counter electrode and Ag/AgCl reference electrode.

Polymerization of thiophene using chronoamperometry

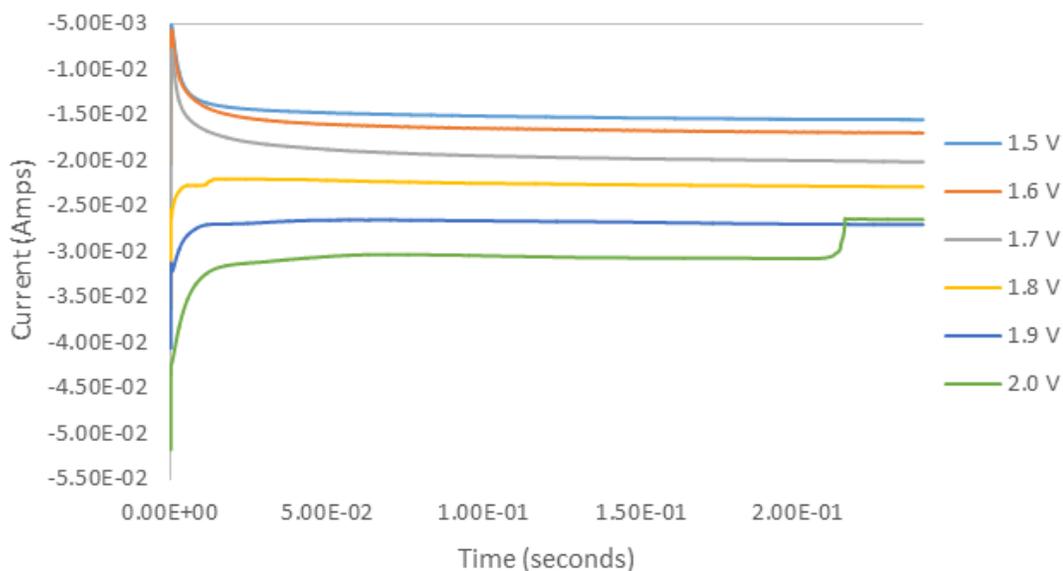


Figure 8. Chronoamperometry of different potentials held constant for 4 minutes.

To test new ways to grow films, different potentials were chosen and held constant. Figure 8 shows 6 different potentials. During the first several seconds of polymerization, there is a big change in current. It is theorized that current density is unstable initially, and takes time for the current to reach steady state. The decrease in current over time represents polymerization is occurring, because the buildup of polythiophene on the ITO glass substrate affects the resistance.

Conclusion

Thiophene films were successfully made through electrochemical polymerization using cyclic voltammetry and chronoamperometry. Polymerization was represented by the large drop in current close to 1.6 and 1.0 V for thiophene and 2,2'-bithiophene respectively. The chronoamperometry technique successfully polymerized thiophene onto the working electrode, which was represented by a decrease in current at steady state. Comparing these two techniques within this research, cyclic voltammetry made the most uniform films, and thus should be used for further investigation of film growth.

Future work

- Each new CV should have the same setup, and to maximize accurate results a constant distance of each electrode is important. To solve this problem, a rubber stopper with drilled holes can be made to keep the electrodes at an even and consistent distance from each other.
- CV can be performed on the nanoparticles and thiophene derivatives using the gold working electrode. Once consistently uniform films are made with thiophene, polymerization of thiophene derivatives films can be made.

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