Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1021/ed800045r">http://dx.doi.org/10.1021/ed800045r</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>Version</td>
<td>Author’s final manuscript</td>
</tr>
<tr>
<td>Accessed</td>
<td>Wed Mar 16 02:06:43 EDT 2016</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/70081">http://hdl.handle.net/1721.1/70081</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Article is made available in accordance with the publisher’s policy and may be subject to US copyright law. Please refer to the publisher’s site for terms of use.</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td></td>
</tr>
</tbody>
</table>
Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film

Daniel J. Schmidt, Eric M. Pridgen, Paula T. Hammond, J. Christopher Love*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 USA

*To whom correspondence should be addressed. Email: clove@mit.edu

Final Manuscript Published as:

Abstract:
This paper summarizes an experiment on thin film fabrication with layer-by-layer (LbL) assembly that is appropriate for undergraduate laboratory courses. The purpose of this experiment is to teach students about self-assembly in the context of thin films, and to expose students to the concepts of functional polymeric coatings. Students dip coat both microscope slides and conductive glass with films containing polyaniline (PANI), a conducting polymer, and sulfonated polystyrene (SPS). Assembly of the film is characterized by visual inspection, UV/Vis spectroscopy, and conductance measurements with a handheld multimeter. Green-colored films with measurable conductance are apparent after two PANi layers. Subsequently, the students observe the pH-dependent optical properties of the films, and also determine the electrochromic performance of the films using spectroelectrochemistry. The feasibility of this experiment has been tested by inclusion into an undergraduate-level polymer science laboratory with third and fourth year students at the Massachusetts Institute of Technology.

Keywords: Upper-Division Undergraduate, Laboratory Instruction, Polymer Chemistry, Analytical Chemistry, Chemical Engineering, Hand-On Learning / Manipulatives, Conductivity, Electrochemistry, Materials Science, Oxidation/Reduction, Oxidation State, pH, Solid State Chemistry, Surface Science, UV-Vis Spectroscopy

Introduction

This paper describes an experiment that demonstrates both the process for fabricating thin films of polymers using layer-by-layer (LbL) assembly, and some of the properties of the resulting films. Many strategies exist for coating a substrate with a thin film including physical vapor deposition, chemical vapor deposition, electrodeposition, and spin coating, among others. Most of these techniques require complex and expensive equipment. In contrast, LbL assembly is a simple yet powerful technique, and is therefore particularly suitable to implement in an undergraduate lab. While a number of papers have been published in this journal on the
fabrication and analysis of various thin films (1-12), the utility of LbL assembly for teaching concepts related to self-assembly and polymeric thin films has not been reported. The experiments outlined here were designed for and carried out in an upper-level undergraduate laboratory course in polymer science at the Massachusetts Institute of Technology. Through this exciting and visually appealing experiment, students gain exposure to the growing area of functional polymeric coatings.

Layer-by-layer assembly, first reported by Decher (13,14), is a method for fabricating thin films of polymers by the sequential adsorption of two or more polymers with complementary functional groups. Typically, positively and negatively charged species are used (Figure 1), but LbL assembly can also be accomplished by hydrogen bonding, covalent bonding, as well as other specific interactions. Besides natural and synthetic polymers, a number of other species including metallic and inorganic nanoparticles, micelles, and even small molecules can be included in LbL films. Assembly can be carried out by dip coating, spin coating, or spray coating to coat conformally virtually any substrate of any shape or size (15,16). In this paper, we employ dip coating since this process can be easily accomplished by hand. LbL assembly is extremely simple and versatile, making it possible to control thickness, morphology, and functionality of thin films with excellent precision.
POLYCATION  

POLYANION  

POLYELECTROLYTE MULTILAYER FILM
Figure 1: Schematic representation of the layer-by-layer assembly of a polycation and a polyanion to form a polyelectrolyte multilayer thin film.

Conducting polymers are one class of functional materials that can be incorporated into LbL assemblies. Discovered in 1970, conducting polymers remain an area of interest as responsive materials (17-19). These polymers usually possess a conjugated backbone and must be “doped” through partial oxidation or reduction of the polymer backbone to generate a delocalized π-electron network with free charge carriers. Conducting polymers can possess an interesting combination of properties: the conductivity of metals along with the processability of polymers (18). This combination makes them useful for biological and chemical sensors, displays, batteries, antistatic coatings, and artificial muscles (20,21). The experiments described here use polyaniline (PANi), a conducting polymer, and sulfonated polystyrene (SPS) to assemble LbL films (Figure 2). The assembly and conductivity of this system was first reported by Cheung et al. (22) and further characterized by Ram et al. (23). Since then, LbL films containing PANi and other electroactive polymers have been used as optical pH sensors (24) and electrochromic displays (25).

Figure 2: Molecular structures of polyaniline (acid-doped, conducting emeraldine salt form) (left) and sulfonated polystyrene (right).

PANi can exist in four different oxidation states termed leucoemeraldine, emeraldine salt, emeraldine base, and pernigraniline (in order of increasing oxidation state). The different oxidation states possess four different colors (clear, green, blue, and purple). Only the emeraldine salt is conducting and charged, and is the form used to assemble LbL films. PANi can be switched between oxidation states by acid/base chemistry (which changes the electronic energy levels) or by electrochemistry (which injects or removes electrons from the polymer backbone) (18). Given the visual appeal and versatile functions of PANi films, other undergraduate-level experiments investigating electropolymerized PANi thin films have been described (5,10-12).

In the experiment described in this paper, students prepare (PANi/SPS)_n films by hand (where n is the number of deposited bilayers). They monitor the assembly of the films by visual inspection, UV/Vis spectroscopy, and conductance measurements. The pH-dependent optical properties of the films are observed, and the electrochromic properties of the films are demonstrated using a potentiostat to modify the oxidation state of PANi in the films. Students executing this experiment are exposed to a versatile technique for preparing thin films by self-assembly. An instructor can place LbL assembly in context with other methods for producing polymeric thin films, and provide examples demonstrating the prevalence and many functions of
coatings in everyday life. Furthermore, an instructor can use LbL assembly as a model system to discuss the thermodynamics of self-assembly.

**Experimental Methods and Results**

*Module #1: Fabrication and characterization of (PANi/SPS)$_n$ thin films*

The first module of this experiment involves the assembly and characterization of (PANi/SPS)$_n$ layer-by-layer films by dip coating. The instructor should prepare the substrates and the PANi and SPS solutions beforehand (see Supplemental Materials). For this module, the students prepare films with 2, 4, 6, and 8 bilayers on microscope slides cut into 1 cm x 2 cm pieces. The students rinse the provided glass microscope pieces and conductive glass with ethanol followed by deionized water. Each slide is immersed in the PANi solution for 3 min., and then rinsed in three separate rinse baths with agitation. Next, the slides are immersed in the SPS solution for 3 min. and rinsed in three separate rinse baths with agitation. This cycle is repeated to prepare films comprising the specified number of bilayers. Once deposition of each film is complete, the films are dried under a stream of nitrogen gas.
A green-colored film is apparent after two bilayers. As additional bilayers are deposited the students will notice that the color intensity of the film increases proportionately (Figure 3). The incremental increase in color can be quantified using a UV/Vis spectrometer. For the most accurate absorbance measurement, the PANi in the films should be deprotonated to the blue emeraldine base form by immersion in a 0.1 M NaOH solution for 10 seconds. The height of the absorbance peak at ~620 nm should increase linearly with the number of deposited bilayers (Figure 4). This measurement indicates that the assembly process occurs in a stepwise fashion, and that an equivalent amount of PANi is adsorbed at each step. Furthermore, students observe here that the color of the films is sensitive to pH. The students are required to consider how they would characterize these films as potential pH sensors, and what properties an ideal pH sensor would possess.

a)

b)
Besides being colored, PANi is also a conducting polymer. Students can measure the conductivity of their (PANi/SPS)\textsubscript{n} films using a handheld multimeter. First, the PANi in the films must be protonated to the emeraldine salt by immersion of the films in 1 M HCl for 30 sec., and then drying with nitrogen. Next, two pieces of conducting copper tape can be affixed to a film to measure its in-plane conductance (Figure 5a). The conductivity may then be estimated by dividing the conductance by the distance between the pieces of copper tape. Pieces of tape with equal areas, and good adhesion between the tape and film, are necessary to compare the conductivity of films with different numbers of layers quantitatively. The conductivity of (PANi/SPS)\textsubscript{n} films should increase linearly to a limiting value for films with fewer than 10 bilayers (22). Students observed a non-linear induction period for films with 2 bilayers or less, likely due to a lack of a completely interconnected PANi network; a linear trend in the conductivity was observed for films comprising 4 to 8 bilayers (Figure 5b).
b)
Module #2: Electrochromic properties of (PANi/SPS)$_n$ films

The second module of this experiment demonstrates the electrochromic properties of (PANi/SPS)$_n$ layer-by-layer films. As reported by Sherman et al. for an electropolymerized PANi film, electrochromism may be observed using a simple one- or two-battery electrochemical cell (10). This strategy may be employed for the (PANi/SPS)$_n$ LbL films prepared here as well. One modification we suggest is to use a potentiostat if available to control the applied voltage precisely and to give the ability to sweep the voltage.

For this module, the students prepare one (PANi/SPS)$_8$ film on an ITO-coated glass slide. Next, with the help of the instructor, a three-electrode cell is prepared with a reference electrode (saturated calomel (SCE) or Ag/AgCl), a Pt wire counter electrode, and the (PANi/SPS)$_8$ film on ITO-glass as the working electrode. The electrolyte is an aqueous solution of 0.05 M $\text{H}_2\text{SO}_4$ with 0.1 M KCl. The potential at the working electrode is controlled with an EG&G Princeton Applied Sciences 263A potentiostat/galvanostat.
After an introduction to the potentiostat, the students can evaluate the electrochromic response of the films by a cyclic voltammetry experiment where the potential is swept between -0.2 V and +0.9 V with respect to the SCE reference electrode at a scan rate of 50 mV/s. This protocol allows visualization of three to four of the PANi oxidation states (Figure 6a).\footnote{1} Students also carried out spectroelectrochemistry wherein an electrochemical cell was set up directly in a UV/Vis cuvette for simultaneously monitoring absorbance while changing the applied voltage. The absorbance at 620 nm of a (PANi/SPS)$_8$ film changed over time when square wave potentials of -0.2V and 0.9 V were applied (Figure 6b). From these data, students determined the contrast and response time of the electrochromic film. Contrast is defined as the change in percent transmittance between two states; the response time is the time required to achieve 90% of the maximum contrast. Students are asked to think practically about these values in terms of the suitability of these films for displays, electrochromic windows, or other applications.

a)

\begin{center}
\includegraphics[width=\textwidth]{chart.png}
\end{center}

b)
Figure 6: (a) A cyclic voltammogram and photos showing the electrochromism of a (PANi/SPS)$_8$ film on ITO-glass. The colors of three PANi oxidation states, leucoemeraldine, emeraldine salt, and pernigraniline, are apparent in the photographs from right to left. (b) Model student data showing spectroelectrochemistry of (PANi/SPS)$_8$ subject to square waves at -0.2 V and 0.9 V (with respect to a Ag/AgCl reference electrode).

Summary
With the prevalence of polymeric coatings in many common products, it is important for students in the areas of chemistry, chemical engineering, materials science, and related fields to be familiar with the various techniques used to make these thin films. Through the experiments described here, students are able to explore an emerging method for preparing and characterizing a visible polymeric coating used as an electrochromic material. This experiment has been successfully integrated into an undergraduate polymer laboratory course; it is simple to execute and does not require expensive or sophisticated equipment. The results obtained by students were repeatable and consistent with those reported here. Students found this experiment interesting and exciting, given its visual appeal and its connection to cutting edge research; multiple students inquired about pursuing undergraduate research on layer-by-layer assembly.

Hazards
The students should wear nitrile or latex gloves and goggles to avoid contact with the chemicals. The PANi solution contains 10% N,N-dimethylacetamide, which is flammable and toxic. The acidic polymer solutions, rinse baths, and electrolyte solution are mildly corrosive. The students should be careful when handling the glass microscope pieces because of sharp edges. Students should also avoid looking directly at the UV light source of the UV/Vis spectrometer. Lastly, if a saturated calomel electrode is used, care should be taken when handling this electrode since it contains mercury.

**Acknowledgments**

This work was supported primarily by the MRSEC Program of the National Science Foundation under award number DMR-0819762. PTH is a Bayer Chair Professor. JCL is a Texaco-Mangelsdorf Career Development Professor. The authors also thank the Massachusetts Institute of Technology and the Department of Chemical Engineering for support and maintenance of the undergraduate teaching laboratory.

**Supplemental Materials**

Notes for instructors and a student handout with additional introductory information, step-by-step experimental procedures, and post-lab questions are available in this issue of *JCE Online*.

**Note**

1. The leucoemeraldine (clear), emeraldine salt (green), and pernigraniline (purple) oxidation states will all be visibly apparent. The emeraldine base (blue) form may be visible at 0.5-0.6 V (versus SCE) between the green and purple colored states.

**Literature Cited**

Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film

Aim:
To assemble layer-by-layer polymer thin films of polyaniline and polystyrene sulfonate, to follow film assembly visually, with UV/Vis spectroscopy, and with conductivity measurements, and to characterize the electrochromic response of these films.

Materials:
Polyaniline (PANi) solution in water/dimethylacetamide (10 mM) – pH 2.5
Polystyrene sulfonate (SPS) solution in water (10 mM) + 0.5 M NaCl – pH 2.5
Deionized water – pH 2.5
0.1 M Sodium hydroxide (NaOH)
1.0 M Hydrochloric acid (HCl)
Glass slides (1 cm x 2 cm) (Total of 4)
ITO-coated glass cuvette slide (Delta Technologies)
Binder clips (Total of 5)
Plastic troughs (Total of 2)
Forceps

Equipment:
Multimeter (Fluke 189 True RMS multimeter)
UV/Vis spectrometer (Stellarnet EPP2000C with SL1 light source)
Potentiostat (EG&G Princeton Applied Research 263A)

Brief Background:
Layer-by-layer assembly:
Coatings are widely used to modify the surface properties (e.g. adhesion, corrosion resistance, wettability, etc.) of a variety of materials. We encounter coatings in everyday life with examples including non-stick Teflon coatings on pots and pans, anti-reflective coatings on eyeglass lenses, anti-corrosive coatings on razors, and stain-repellant coatings on fabrics, among many others. One emerging technique for assembling thin film coatings is layer-by-layer (LbL) assembly, which was introduced by Decher at the University of Mainz, Germany in the early 1990s (1,2).
Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film

It is a simple and versatile technique for constructing polymer multilayer thin films through the sequential adsorption of materials with complementary functional groups. Polyelectrolyte films are built up by alternately exposing a charged substrate to polycation and polyanion solutions with intermediate rinse steps (Figure 1). The driving forces for multilayer formation are the pairwise electrostatic interaction between oppositely charged polyelectrolytes as well as the entropic gain from expelling small counterions during assembly. When the charged substrate is immersed in a solution of oppositely charged polymer, the polymer diffuses and adsorbs onto the surface. The adsorbed polymer overcompensates for the charge on the substrate and thereby reverses the surface charge (3). The rinse step removes any weakly adsorbed material, and then the substrate is again immersed in a solution of oppositely charged polymer. This process is simply repeated a desired number of times and is amenable to dip coating as well as spin coating and spray coating.

LbL assembly is a particularly robust and repeatable technique, which yields precise control over thickness, morphology, and functionality of thin films. Thickness and morphology can be fine-tuned on the nanometer scale by altering the number of layers as well as the pH and ionic strength of the solutions. Researchers have also been able to incorporate a number of functional materials (e.g. conjugated polymers, small molecules, inorganic nanoparticles, proteins, nucleic acids) into LbL films to achieve materials with chemical, electric, electrochemical, and optical activity. Some of the many applications of LbL films include chemical and biological sensing, electrochromic devices, selective membranes, catalytically active films, electro- and photoluminescent films, solid state electrolytes, and drug delivery devices. LbL assembly is also a scalable process; it is easily automated and can been achieved through roll-to-roll processing. Lastly, LbL assembly is relatively cheap and environmentally friendly, as solutions are water based and only low polymer concentrations are needed (~10^{-2} M).

A number of authors have reviewed the fundamentals and applications of LbL assembly (4-9).

**Polystyrene sulfonate (SPS) and Poly(aniline) (PANi):**
Polystyrene sulfonate (SPS) (Figure 2) is the polyanion, and poly(aniline) (PANi) (Table 1) is the polycation used in this experiment. SPS is used as a dispersant for calcium carbonate and metal
oxides, as an ion exchange material in columns and membranes, as a suspending aid for particulates, and in water treatment (Sigma Aldrich).

PANi is a unique material in that it is a conducting polymer. It is used as an additive in polymer blends and liquid dispersions for electromagnetic shielding and charge dissipation (i.e. anti-static materials) (Sigma Aldrich). Further, it is used in electrodes, batteries and sensors, and is being researched for use in electroactive inks, paints, coatings, and adhesives, electrochromic “smart” windows, electrically conductive transparent films, and conductive high performance fibers (10-14). PANi can exist in four different oxidation states (Table 1). The oxidation states possess different colors: clear, green, blue, and purple, in order of increasing oxidation state. One can switch between these states either electrochemically or by changing the solution pH (i.e. level of acid-doping) (15). Only the emeraldine salt form is charged (and conducting), so we use this form for LbL assembly and for subsequent conductivity measurements.

Table 1. The four oxidation states of polyaniline.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Color</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leucoemeraldine</td>
<td><img src="image" alt="Structure" /></td>
<td>Clear</td>
<td>Fully reduced Insulating</td>
</tr>
<tr>
<td>Emeraldine salt</td>
<td><img src="image" alt="Structure" /></td>
<td>Green</td>
<td>Partially oxidized Conducting</td>
</tr>
<tr>
<td>Emeraldine base</td>
<td><img src="image" alt="Structure" /></td>
<td>Blue</td>
<td>Partially oxidized Insulating</td>
</tr>
<tr>
<td>Pernigraniline</td>
<td><img src="image" alt="Structure" /></td>
<td>Purple</td>
<td>Fully oxidized Insulating</td>
</tr>
</tbody>
</table>

Precautions:

Wear nitrile gloves. Follow general precautions. The experiment may be carried out on the benchtop. Polyaniline and polystyrene sulfonate are themselves non-toxic, but all of the aqueous solutions are acidic (pH 2.5) and thus mildly corrosive; the polyaniline solution contains 10% N,N-Dimethylacetamide, which is toxic and flammable. Avoid contact with the skin. Be careful when handling the glass microscope slides since they may have sharp edges. Do not look directly into the light source of the UV/Vis spectrometer.
Layer-by-Layer Assembly of a pH-Responsive and Electrochromic Thin Film

Procedure:
Module 1: Layer-by-layer film assembly

1. Pour ~80 mL of PANi solution into one compartment of a plastic trough.
2. Pour ~80 mL of SPS solution into one compartment of a second plastic trough.
3. Fill the rest of the compartments with pH 2.5 rinse water.

4. Secure four glass slides and one ITO-glass slide with binder clips.
5. Rinse slides with ethanol and then DI water.
6. String four of the binder clips with microscope slides onto a threaded rod or stirring rod as shown in the picture below.
7. Immerse slides in PANi solution for 3 minutes.
8. Rinse slides thoroughly in the polycation rinse baths.
9. Immerse slides in SPS solution for 3 minutes.
10. Rinse slides thoroughly in the polyanion rinse baths.
11. Repeat steps 7-10 above for the desired number of bilayers. You will need films of 2, 4, 6, and 8 bilayers on glass and a film of 8 bilayers on the ITO-glass.
12. After each film is complete, dry under a stream of nitrogen gas.
13. Place the 2, 4, 6, and 8 bilayers films on a white piece of paper and observe the color intensity of each film.
14. Next, immerse each film in a 0.1 M NaOH solution for 10 seconds to deprotonate the PANi, converting it to the emeraldine base form. Remove from the solution and dry with nitrogen. Use the UV/Vis spectrometer to record absorbance at 620 nm for the 2, 4, 6, and 8 bilayer films.
15. Now immerse each of the films in 1 M HCl for ~30 seconds each to re-dope the PANi to the emeraldine salt form. Dry the films thoroughly with nitrogen.
16. Use a multimeter to measure the conductance of each of your films (and a plain glass slide). To ensure good electrical contact with the film, cut pieces of conductive copper tape of identical areas and affix two pieces of tape to each film an equal distance apart as shown in the picture below. Measure the distance between the pieces of tape to convert conductance to conductivity.
Module 2: Electrochromism of (PANi/SPS)$_8$ films

1. With the help of the instructor, set up a three-electrode electrochemical cell with the following, as shown in the picture below.
   - Electrolyte: 0.05 M H$_2$SO$_4$, 0.1 M KCl in water
   - Reference Electrode (RE): Saturated calomel electrode (SCE)
   - Counter Electrode (CE): Pt coil
   - Working Electrode (WE): (PANi/SPS)$_8$ film on ITO-glass

2. Using the potentiostat software, set up a cyclic voltammetry experiment sweeping the voltage from -0.2 V to 0.9 V at a scan rate of 50 mV/s.
3. Observe the color changes of the film at different applied voltages.
4. Now set up the electrochemical cell inside a UV/Vis cuvette, as shown below, this time using a smaller Ag/AgCl reference electrode and a smaller Pt coil, making sure that the light beam is not impeded by the RE or CE.
5. Using the SpectraWiz software for the UV/Vis spectrometer, set up an “Episodic Data Capture” experiment to record the absorbance at 620 nm over time. Concurrently, using the potentiostat software, apply square waves of -0.2 V and 0.9 V for 10 seconds each.
Questions:

1. **Film assembly**: Did you see an increase in color intensity of your (PANi/SPS)_n films with number of layers? Describe your results.

2. **Film assembly**: From your UV/Vis spectroscopy data, plot the absorbance at 620 nm versus the number of deposited bilayers. Does your plot appear linear? What are the implications of a linear or non-linear trend?

3. **Film assembly**: Tabulate your conductance values for your (PANi/SPS)_n films for n = 0, 2, 4, 6, 8. Do you see a trend and is it as expected?

4. **pH sensitivity**: Were you able to re-dope the blue colored (PANi/SPS)_n films and see the color revert to green? What does this imply about the use of these films as potential pH sensors?

5. **pH sensitivity**: What properties would an ideal pH sensor possess?

6. **Electrochromism**: What is the approximate contrast (percent change in transmittance) for the films in the clear state versus the blue/purple state?

7. **Electrochromism**: What is the approximate response time for a (PANi/SPS)_n film defined as the time required to undergo a 90% change in absorbance between the clear state and the blue/purple state? What applications do you envision for electrochromic coatings in general, and would you deem your (PANi/SPS) films practical for these applications?

8. **General LbL assembly**: How do you think changing the ionic strength of the dipping solutions will change film thickness?

Literature Cited

NOTES FOR INSTRUCTORS

PREPARATION OF POLYMER SOLUTIONS

1. **Polyaniline solution:** The PANi solution should be made according to the method from Cheung et al. (16). PANi should be dissolved in N,N-dimethylacetamide at a concentration of 20 mg/mL and stirred vigorously overnight. The solution should then be filtered to remove undissolved solids, and then diluted into deionized water (at a ratio of 1:9 v/v) that has been previously adjusted to pH 3.0 using HCl. The resulting aqueous solution of PANi should then adjusted to pH 2.5 with HCl and then filtered again to remove any undissolved solids. Note that the PANi solution has a finite lifetime as it is prone to precipitation. It can be used for up to 1-2 weeks. If the pH is adjusted below 2.5, the polymer will precipitate out of solution; the pH adjustment should therefore be done gradually. Filtration must be carried out using a filter material compatible with the N,N-dimethylacetamide. We used disposable Nalgene filter units with 0.45 µm Nylon filter membranes (VWR Product #28199-349).

2. **Polystyrene sulfonate solution:** The SPS solution should be made by dissolving SPS in deionized water at a concentration of 10 mM (based on the repeat unit (MW 206.2 g/mol) along with 0.5 M NaCl, and stirred overnight. The polymer should dissolve almost immediately; no filtration is required. The pH of this solution should then be adjusted to pH 2.5 with HCl. This solution can be used for many years. Storage in a refrigerator will prevent growth of bacteria.

3. **Rinse water:** The water for rinsing the (PANi/SPS)$_n$ films between polymer solutions should be deionized water that is adjusted to pH 2.5 with HCl.

PREPARATION OF SUBSTRATES

1. **Glass microscope slides:** Glass microscope slides (VWR precleaned) should be cut by the instructor (using a diamond-tipped glass cutter) into multiple 1.0 cm x 2.0 cm pieces. In our case,
this size was appropriate for our UV/Vis cuvette holder. Depending on the specific UV/Vis spectrometer used, another size or even uncut microscope slides could be used.

2. **ITO-coated glass slides:** ITO-coated glass cuvette slides were purchased from Delta Technologies (Product #CD-50IN-CUV). These slides are unpolished float glass coated on both sides with ITO to give a sheet resistance of 8-12 Ω/square. Another equivalent transparent conducting oxide-coated substrate could also be used. It is most convenient to use slides coated on both sides. Otherwise, the film would have to be removed from the uncoated side for spectroelectrochemical characterization.

3. **Substrate cleaning:** Both substrates can be cleaned by a quick rinse with ethanol followed by a rinse with deionized water.

**FILM ASSEMBLY**

1. Hand dipping can be carried out with beakers or any convenient vessel such as the plastic troughs used here.

2. It is easiest to string the binder clips holding the substrates onto a rod (e.g. stirring rod or threaded rod) such that all or most of the films can be moved from bath to bath at one time.

3. The three minute dip time in the polymer solutions could be shortened if necessary, but this may give slightly thinner films.

4. If the PANi solution contains solid particulates, then likely patchy, non-uniform films will likely result. Filtering the PANi is crucial to improve film uniformity.
ELECTROCHROMISM

1. *Demonstration of electrochromism:* Before carrying out spectroelectrochemistry measurements, it is instructive for the students to visually observe their (PANi/SPS)$_n$ films on ITO-glass changing color in response to an applied voltage. The instructor could set up one electrochemical cell, placing white paper in the background for best visualization of the color states.

2. *Spectroelectrochemistry:* Any UV/Vis spectrometer that can record absorbance or transmittance at one or more wavelengths over time could be used for this exercise. For the most accurate determination of response time, a data acquisition rate faster than ~200 ms is preferred. When configuring the software, set integration time to the smallest (fastest) value and number of scans to average to 1 or the smallest value. These parameters will maximize the data acquisition rate to best capture the kinetics of the color change.

HAZARDS

The students should wear nitrile or latex gloves and goggles to avoid contact with the chemicals. The PANi solution contains 10% N,N-dimethylacetamide, which is flammable and toxic. The acidic polymer solutions, rinse baths, and electrolyte solution are mildly corrosive. The students should be careful when handling the glass microscope pieces because of sharp edges. Students should also avoid looking directly at the UV light source of the UV/Vis spectrometer. Lastly, if a saturated calomel electrode is used, care should be taken when handling this electrode since it contains mercury.
INSTRUMENTATION
1. Digital multimeter (e.g. Fluke 189 True RMS multimeter)
2. UV-Vis spectrometer (e.g. StellarNet EPP2000C with SL1 lightsource)
3. Potentiostat (e.g. EG&G Princeton Applied Sciences 263A potentiostat/galvanostat)
4. Stir plate

LABORATORY SUPPLIES:
(Prices as of November, 2008)

<table>
<thead>
<tr>
<th>Product</th>
<th>CAS #</th>
<th>Supplier</th>
<th>Price</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline, emeraldine base, MW 100K</td>
<td>25233-30-1</td>
<td>Sigma Aldrich</td>
<td>$138.50</td>
<td>5 g</td>
</tr>
<tr>
<td>Poly(sodium 4-styrenesulfonate), MW 70K</td>
<td>25704-18-1</td>
<td>Sigma Aldrich</td>
<td>$31.30</td>
<td>100 g</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>7447-40-7</td>
<td>Sigma Aldrich</td>
<td>$40.30</td>
<td>500 g</td>
</tr>
<tr>
<td>N,N-Dimethylacetamide</td>
<td>127-19-5</td>
<td>Sigma Aldrich</td>
<td>$52.10</td>
<td>1 L</td>
</tr>
<tr>
<td>Ethanol</td>
<td>64-17-5</td>
<td>Sigma Aldrich</td>
<td>$76.40</td>
<td>1 L</td>
</tr>
<tr>
<td>Hydrochloric acid, 1.0 M solution</td>
<td>7647-01-0</td>
<td>VWR</td>
<td>$37.36</td>
<td>1 L</td>
</tr>
<tr>
<td>Sodium hydroxide, 0.1 M solution</td>
<td>1310-73-2</td>
<td>VWR</td>
<td>$27.50</td>
<td>1 L</td>
</tr>
<tr>
<td>Sulfuric acid, 0.05 M</td>
<td>7664-93-9</td>
<td>VWR</td>
<td>$17.53</td>
<td>1 L</td>
</tr>
<tr>
<td>Microscope slides</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Plastic dipping troughs</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Forceps</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stirring rods</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stir bar</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glass bottles or flasks</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glass cutter</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nylon filters, 0.45 µm</td>
<td>-</td>
<td>VWR</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ITO-glass cuvette slides</td>
<td>-</td>
<td>Delta Technologies</td>
<td>$62.00</td>
<td>Pack of 25</td>
</tr>
<tr>
<td>Binder clips</td>
<td>-</td>
<td>Office supply store</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>