

Article

Electrochromic Polymers: From Electrodeposition to Hybrid Solid Devices

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Abstract: This paper reports on the linear colorimetric and electrochromic (EC) characteristics of electrodeposited polyaniline (PANI) films. This paper also investigates the infrared EC properties of acid-doped PANI films. The electrochemical polymerization method was employed to create a porous and thin PANI film layer onto PET-ITO substrates. This layer was capped with WO_3 film to create a gel electrolyte sandwich structure that demonstrates the compatibility of PANI films with cathodic WO_3 films in full devices. The electrodeposition of the film was fabricated by applying different voltages and time, with the optimal film quality achieved with the 1.7 V voltage and a 20 min deposition period. The surface morphology, optical performance, electrochemical behavior, and molecular structure evolution are comprehensively studied in this work. The linear colorimetric behaviors and the corresponding significant changes in the structure in Raman spectra build direct strong quantitative relations in EC polymers. The well-defined oxidation and reduction peaks observed in the cyclic voltammetry indicate the ion-diffusion dominant process in the electrochromism of PANI. Significant transitions between the benzene and quinone phases in the Raman spectra are found in the bleached and colored states of polymers. This study enhances the understanding of PANI film structure and electrochemical and associated optical properties, providing more insights into the dual-function EC charge storage polymers and other energy-related functional materials.

Keywords: electrochromic; polymers; thin solid films; devices



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1. Introduction

Electrically conducting organic polymers and transition metal oxides are the subject of extensive research for use in capacitive and electrochromic (EC) devices [1–3]. Polyaniline (PANI) stands out as a highly conducting polymer with exceptional electrical properties, easy synthesis, and extraordinary chemical stability, and it also exhibits strong environmental resilience and distinct color changes corresponding to different redox states. Unlike inorganic materials, e.g., transition metal oxides, that suffer from poor processability and a tendency to crack under recurrent bending, organic polymers like PANI can withstand bending throughout the life of a device. As the performance of the electrochemical systems is negatively impacted by degradation in mechanical properties, their use in devices that undergo flexing (bending/stretching) is restricted. The conducting polymer PANI continues to be one of the most promising organic polymers for flexible applications [4]. PANI has several benefits compared to other conducting polymers and inorganic materials. Electrodeposited PANI films have shown promise as potential candidates for the creation of EC and color-changing devices [5]. PANI has gained attention due to its applications in diverse fields, including EC devices, electrochemical sensors and biosensors, supercapacitors, solar cells, and rechargeable batteries [6–8]. PANI film characteristics can be fine-tuned by altering deposition parameters, such as applied potential and duration time. This enables tailoring of the properties of PANI films to satisfy specific requirements of the target application. The investigation of the film's basic optical and EC behaviors by modifying its properties paves the way for diverse technological applications.

Amongst the many properties of PANI, it has the ability to change optical properties and color. The primary cause of the colorimetric changes in electrodeposited polyaniline films is their capacity to undergo reversible redox reactions, which result in changes to the electronic structure of PANI and concurrently its optical absorption [9,10]. It is well known that PANI has three main stable oxidation states: the entirely reduced leucoemeraldine (LB) form, which has a translucent yellow color, the 50% oxidized emeraldine salt (ES) form, which has a green color, and the fully oxidized pernigraniline (PS) form [6–8]. ES is the only oxidation state of polyaniline that displays electrical conductivity. However, protonation/deprotonation with an acid/base can convert emeraldine base (EB) into ES and vice versa [11]. Applying the appropriate potential allows for precise control and reversal of the color changes. PANI exhibits remarkable infrared (IR)-blocking properties, particularly in its leucoemeraldine state, which makes it an excellent choice for applications requiring concealment from IR detection [12]. The development of thermal management, surveillance, and stealth technology is considerably aided by this trait. PANI's capacity to inhibit IR detection, which is essential for camouflage, evasion, and protection purposes, benefits industries like the military and security sectors [13]. Use of ANI-based materials may be a practical way to reduce heat signatures and guarantee undetectability by IR imaging equipment. Despite intensive work on the integration of advanced nanostructures and complex compositions obtained by doping for a broadened response range in optical spectra for PANI films; however, few studies have been performed on the linear colorimetric properties of the polymer itself in the dynamic EC process and the optical properties as a function of the structural evolution. It is of great importance to build the quantitative relations between colorimetric behaviors and the intrinsic molecular structural changes that take place in EC polymers.

In this study, a thin layer of PANI was synthesized successfully using the electrochemical polymerization procedure on a flexible substrate. The quantitative linear colorimetric, optical, and structural evolution and EC properties of electrodeposited PANI film have been comprehensively investigated at various potentials. The Raman spectra elucidate the mechanisms behind the observed color changes in response to external stimuli. The synthesized film was studied using a variety of characterization methods to elaborate the electrochromism and color-changing mechanism, including scanning electron microscopy (SEM), colorimetric studies, UV-vis spectroscopy, Raman spectroscopy, and cyclic voltammetry. These methods contribute to a thorough understanding of the PANI films' properties by offering insights into the surface morphology, electrochemical behavior, and molecular structure evolution of the film. The IR-blocking qualities of PANI films are also studied, emphasizing their significance as a useful material for applications that demand concealment from IR detection such as in military applications. The results of this study advance the fundamental understanding of EC PANI at different oxidation/reduction states and open the door for the creation of advanced hybrid EC devices interfaced with inorganic EC materials.

2. Experimental Method

Materials: Polyethylene terephthalate/indium tin oxide (PET/ITO) was purchased from Sigma Aldrich and served as the optically transparent electrodes. Aniline ($C_6H_5NH_2$), sulfuric acid (H_2SO_4), and anhydrous ethyl alcohol (C_2H_5OH) were obtained from Thermo Fisher.

PANI Electrodeposition: The ITO-coated PET substrates were ultrasonically cleaned in the acetone solution for 5 min and then in anhydrous ethanol for 3 min. Finally, the substrates were sonicated in deionized water for 5 min. The substrates were air-dried at room temperature. A three-electrode electrochemical cell was used to electrodeposit PANI thin films onto ITO-coated PET substrates. The bath solution contained 642.6 mL of H_2O , 18.655 mL of H_2SO_4 (6 mol/L), 38.7942 mL of aniline (ANI: $C_6H_5NH_2$), and 32.03046 g of sulfosalicylic acid (SSA). In this configuration, a platinum sheet was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The electrodeposition process was carried out using different potentials of 1.2 V, 1.5 V, 1.7 V, and

2 V, while the duration of polymerization was set at 10, 15, 20, and 30 min. It was found that it is challenging for the nucleation and forming of the films at lower voltages, with the appearance of no films being deposited or very minimal being formed, in which case, the extension of duration cannot improve the film quality. When the voltage is too high, the deposited films are in a very dark green state and cannot exhibit significant bleaching behaviors, wherein the decrease in duration does not make a big change. After conducting the deposition at different conditions, we optimized the electrodeposition parameters eventually at 1.7 V and 20 min.

PANI Characterization: All the EC studies and electrochemical tests were conducted in 0.5 M H₂SO₄ electrolyte. The optical transmission and absorbance spectra of EC films were recorded ex situ using a Biochrom Ultrospec 2000 UVeNIR spectrophotometer at colored/bleached states at various voltages. The duration was 20 s for each constant voltage to obtain a fully colored/bleached state in the chronoamperometry method. After the immersion and drying steps and before optical characterizations, we took pictures of the films over a white background quickly at the same positions and with the same parameters using a Canon camera (4.3 V; PC 1743; No. 492172002247; N118; Canon Inc. Japan). Quantitative CIE1976 L*x*y* colorimetric measurements were performed using a MiniScan EZ spectrophotometer from HunterLab. The electrochemical cyclic voltammetry (CV) measurements were carried out in a three-electrode cell of conventional design, using an electrochemical workstation (Metrohm, PGSTAT30 potentiostat). The working electrode was a commercial PET/ITO on which thin solid films of PANI were previously deposited. The counter and reference electrodes were platinum wire and Ag/AgCl, respectively. The potentials reported in this work are referenced against Ag/AgCl. We used 0.5 M H₂SO₄ as the electrolyte in these experiments. In the CV scans, an optimal potential window is applied to where the redox peaks are fully completed. Meanwhile, the sweep rate remains constant at 100 mV/s. Raman spectroscopy was recorded at room temperature with a Jobin-Yvon Labram HR micro analytical spectrometer using a 633 nm laser filtered to give ~1.5 mW at the sample surface. The spectra were generated with 1800 grooves/mm grating across the 0.8 m length of the spectrograph, giving a resolution estimated to be less than 0.5 cm⁻¹ for a slit width of 150 μm and a confocal hole of 300 μm. Consistent with the optical characterizations, the duration 20 s is used for each constant voltage applied to obtain a fully colored/bleached state prior to the ex situ Raman measurements.

Device Assembly: For the electrolyte employed in the device, a mixture of polyurethane acrylate (PUA)-based UV curing adhesive and 1 M LiClO₄ propylene carbonate (PC) ionic liquid with a specific ratio of 2:1 was prepared in advance. The EC device was composed of WO₃ as a cathodic electrode, a LiClO₄-PC gel polymer as an electrolyte, and PANI as an anodic electrode. A hollow frame of two EC single layers on glass was prepared for the perfusion of the electrolyte mixture. Epoxy adhesive was used as a sealer to avoid liquid leakage. After the perfusion, the frame full of the electrolyte mixture was exposed to two parallel UV light sources (8 W, Philips, Poland) for 20 min to ensure complete curing. The 10 cm × 10 cm device fabrication was followed by EC optical characterization with UV-Vis spectroscopy, at -1.9 V and +1.9 V for bleaching and coloration with duration of 40 s, respectively.

3. Results and Discussion

3.1. Morphology

The SEM images (Figure 1) show the initial electrodeposited PANI films on conductive PET/ITO substrate. Based on the cross-section in Figure 1, it can be concluded that PANI crystal's nucleate and grow randomly on the surface. In our experiments, the thickness of the electrodeposited films was about 800 nm. According to the top-view image, the film morphology is very porous, seaweed-network-like, and composed of many suspended rods. The loose and porous features of the polymers are expected to be favorable for the efficient ion transport for the doping and reversible de-doping in the dynamic coloration/bleaching cycles.

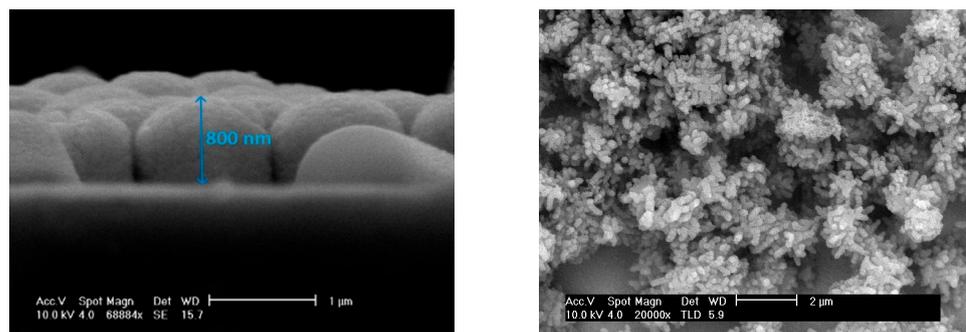


Figure 1. SEM images of the cross-section (left) and top view (right) of as-electrodeposited PANI films.

3.2. Colorimetric Properties from CIE Studies

Chromaticity is the quantification of different colors [14]. CIE1976 $L^*x^*y^*$ color coordinates were used to evaluate the colors of PANI films as a function of applied potential. Herein, L^* represents the brightness with a range of 0 to 100; a^* stands for the degree of red against green, and b^* is yellow versus blue [15]. In the dynamic EC process, the CIE color coordinates were recorded in coloration, bleaching, and re-coloration at potentials 0, +0.5, +0.7, +0.9, +1.1, +1.3, +1.5, −0.5, −0.7, −0.9, −1.1, −1.3, −1.5, −1.9, +1.1, and +1.5 V (Figure 2). It was observed that the colorimetric coordinates (x, y) are confined to the linear formula $y = 1.18x + 0.00093$ with the linear coefficient $R^2 = 0.99$. The coloration and bleaching are accompanied by the linear decrease and increase in the chromaticity values, demonstrating excellent colorimetric linearity and reversibility of EC PANI films. In addition to the x and y coordinates, a third parameter of brightness is needed to define the colors [16]. It was found that the colorimetric luminance evolves with the potential. Upon coloration, the luminance significantly decreases and vice versa. During EC cycling, the relative luminance modulation of PANI is about 33%.

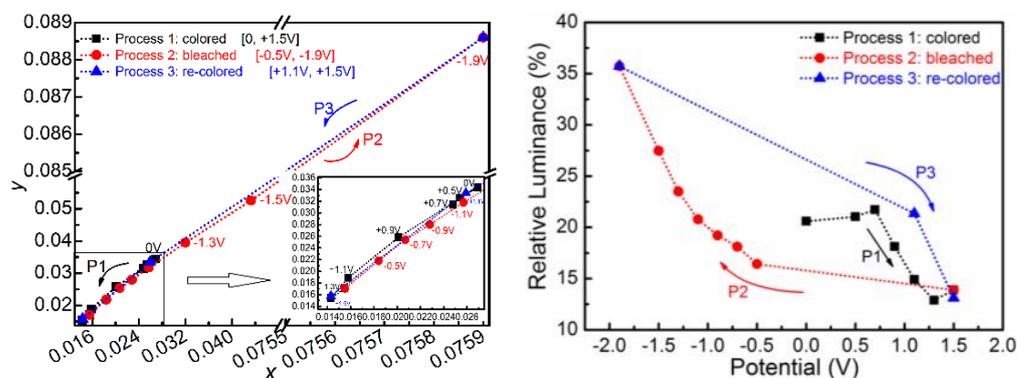


Figure 2. CIE 1931 xy chromaticity plots with linear correlation (left) and relative luminance (right) data vs. potential for EC PANI films. (“-” denotes a minus sign for the voltage applied).

3.3. Optical Modulation

The images in Figure 3 demonstrate the dynamic PANI film in various oxidation states, emphasizing its distinctive color-changing characteristics. The adaptability of the film enables it to maintain its color-changing properties under a variety of circumstances. It was observed that the PANI film changes between a variety of colors, including light green, green, and blue shades, as shown in the top image in Figure 3. When exposed to a -2 V potential, the PANI film reveals a characteristic light green color, demonstrating its rapid optical response. The color deepens and becomes a richer shade of green as the voltage rises. This progressive transition shows how sensitive the film is to various electrical stimulation. The film changes from green to a vivid blue color at a voltage of +2 V. This further demonstrates the PANI film’s adaptability since it can display a broad

variety of colors in response to various voltage levels. Overall, the pictures effectively demonstrate the PANI film's color-changing capabilities and vividly portray its dynamic nature. The EC PANI film is dynamic and visually appealing for a variety of applications arising from its wide range of colors and reversibility. Figure 3 also shows the electro-optical transmittance and absorbance spectra of a PANI film, providing valuable insights into its light interaction characteristics. Both the transmittance and absorbance graphs exhibit a pronounced modulation at the ~ 700 nm wavelength, indicating a strong interaction between light and the film. It clearly shows that the modulation intensity rises with voltage. In particular, the film obtains its maximum optical transmittance at a negative voltage of -1.5 V at the ~ 700 nm wavelength. At this highest transmittance level, the film only permits approximately 12% of the incoming light to pass through, suggesting that the PANI film absorbs most of the light and that its use would be better suited to situations requiring controlled light modulation rather than transmittance-based applications.

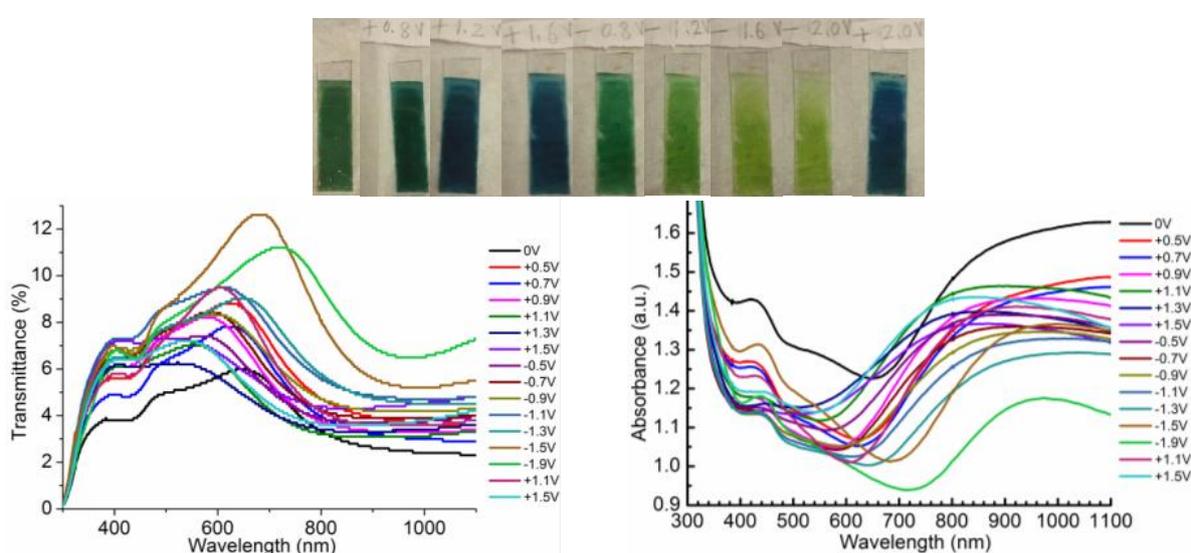


Figure 3. Transmittance (left) and absorbance (right) of PANI films as a function of voltage applied with digital photos of PANI film taken at various voltages. (“-” denotes a minus sign for the voltage applied).

PANI films have the unique property of blocking infrared (IR) radiation in EC processes. This characteristic has been demonstrated with an IR camera. In Figure 4, we show images of the same film in two distinct states: emeraldine base (EB) and leucoemeraldine (LE). Figure 4 depicts the films under an IR camera at different oxidation states. What is of particular interest is that the rightmost image shows a bleached PANI film (LE state). The leftmost image shows that the film appears completely black under an IR camera, meaning it has the lowest emittance. The low emittance implies that the film is effectively blocking IR radiation transmission, rendering the surface behind it invisible to the IR camera. The black image indicates that the surface behind the film is hidden from the camera. On the other hand, PANI films have a comparable color to the background when seen with an IR camera in the emerald base (EB) state. This implies that the EB state film does not obstruct IR radiation transmission, allowing the IR camera to measure heat radiated by the surface behind the film. In other words, the black image means that the surface behind the film is being concealed from the camera. The EB film has the same color as the background, meaning it is not blocking the IR camera from detecting the heat of the surface. Our multicolor polymers can appear invisible to heat-seeking technology, demonstrating much potential for stealth applications.

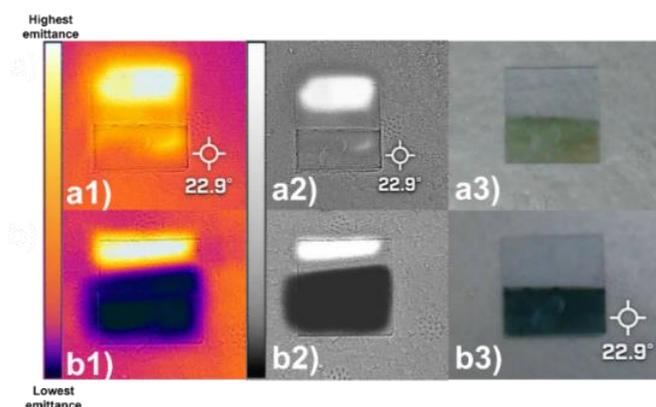


Figure 4. Images of PANI in bleached and colored states from infrared cameras: (a1–a3) tinted film at +1.6 V; (a1) IR Image; (a2) greyscale IR image; (a3) digital camera image; (b1–b3) tinted film at −1.7 V; (b1) IR image at −1.7 V; (b2) greyscale IR image; (b3) digital camera image.

3.4. Raman Spectroscopy

From the Raman spectra of PANI film, two distinct stages, benzene and quinone, can be observed. These stages represent different molecular structures and oxidation states of the PANI polymer [9]. At about 1460 and 1600 cm^{-1} wavenumbers, significant transitions between the benzene and quinone phases can be seen in the Raman spectra of PANI (Figure 5). These transitions provide significant insight into the structural modifications and oxidation processes occurring within the polymer. The vibrational modes of the benzene rings within the polymer structure are represented by distinct Raman peaks in the benzene stage of PANI that peak at about 1460 cm^{-1} wavenumbers. These peaks indicate the presence of ring breathing modes and aromatic C–C stretching vibrations. The benzene phase is connected to the leucoemeraldine or reduced form of PANI, where the polymer takes on a more conjugated and planar structure, as evident in the significant change in the fully bleached state at −1.9 V. The oxidation of PANI leads to the formation of quinone-like structures within the polymer, which is related to the quinone stage. Quinoid rings and other functional groups containing oxygen are added to the PANI structure as a result of this oxidation, as shown in the colored state at +1.3 V. The characteristic peaks in the Raman spectra that are connected to the vibrations of the C=O and C=C bonds in the quinoid rings identify the quinone stage. The significant changes that occurred in the structure at +1.3 V and −1.9 V are consistent with the dramatic change in optical performance shown previously. What is noteworthy, arising from the internal structural change within the film driven by applied voltage, is that the optical IR emittance variation can reach 0.27, with 0.71 and 0.44 at −0.4 V and +1.5 V, respectively.

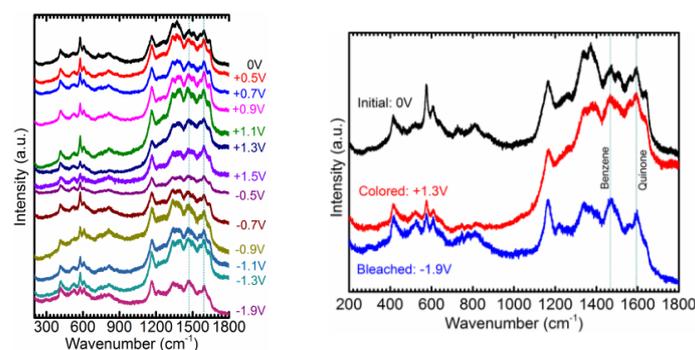


Figure 5. Raman spectra (left) of PANI films at various voltages and its enlargement (right). (“−” denotes a minus sign for the voltage applied).

3.5. Cyclic Voltammetry in EC Films

Figure 6 depicts a typical cyclic voltammogram for PANI films. Cyclic voltammetry is one of the electrochemical methods to characterize the oxidation and reduction electrochemical processes responsible for the color modulation in PANI films. This technique involves sweeping voltages over a potential window to determine the current through the electrochemical cell, with an EC polymer as the working electrode in this case. The resulting “duck-shaped” curve depicts peaks that represent the chemical reactions governing the continuous color change. The PANI’s oxidation level determines its color. When fully reduced, the resulting leucoemeraldine (LE) state is responsible for the pale yellow color. Likewise, the dark blue results from being fully oxidized in the emeraldine base (EB) state. Our setup involves a working electrode that attaches to the film, a platinum wire counter electrode, and a silver/silver chloride reference. The potentials in the curve from Figure 6 are relative to the reference electrode. The cyclic voltammetry is carried out between -1 and 1.5 V in a 0.5 M H_2SO_4 electrolyte. The protonated form of polyaniline has a light yellow color while it is in its reduced leucoemeraldine state, but as it undergoes additional electrochemical oxidations, it gradually changes color over a range of shades. The polymer’s color changes as the oxidation progresses, going from green to bluish green to greenish blue and then to deep blue, as shown in the images in Figure 6, which corresponds to its emeraldine and pernigraniline states. The color of electrodeposited PANI films varies intriguingly with applied voltage during the oxidation process. It shows pale-yellow color at a potential of -0.5 V, showing the reduced state. The color changes to a distinct shade of green as the voltage rises between 0 and 0.25 V, which is a result of the PANI’s continuing oxidation. A compelling light blue color is produced by increasing the potential even more, to a range of around 0.25 V to 1 V. At 1.5 V, the film finally develops a deep blue color, indicating that the oxidation process is almost complete. In other words, the transition between the leucoemeraldine and emeraldine salt forms of PANI is indicated by the oxidation peak at around 0.2 V and the reduction peak at around 0.7 V. The polymer experiences anion doping during oxidation, which causes it to change into the emeraldine salt state. This procedure enables the PANI film’s charge compensation. In contrast, de-doping happens during reduction, which restores the leucoemeraldine form by eliminating the previously added anion dopants.

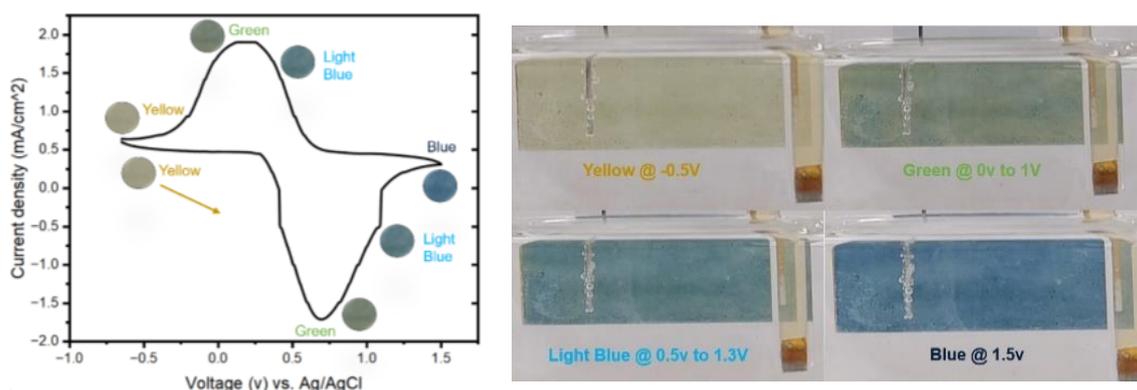


Figure 6. Cyclic voltammetry (left) and corresponding films’ dynamic colors (right) of the EC PANI, at scan rate of 100 mV/s. (“-” denotes a minus sign for the voltage applied.)

3.6. EC Device Based on PANI// WO_3

Motivated by the EC performance of PANI films, a laminated hybrid device assembly has been fabricated successfully by sandwiching the PANI polymers and cathodic EC WO_3 inorganic films with Li^+ -containing UV curing gel electrolyte. More details on the device fabrication can be referred to in previous work [17]. The complete device, with dimensions of 10 cm by 10 cm, was bleached and colored at -1.9 V and $+1.9$ V, respectively. The duration for each potential is 40 s to ensure the device is approaching its maximum colored/bleached

state. Its corresponding transmittance spectra and digital pictures are shown in Figure 7, which demonstrate the compatibility of PANI polymers with cathodic WO_3 films for hybrid all-solid device configurations, providing alternatives to smart window applications.



Figure 7. Transmittance spectra and corresponding digital photos of PANI/ WO_3 assembled device in bleached and colored states.

3.7. Circuit Design for EC Films

To provide the potential needed to drive the films to adjust the optical properties, an independent circuit allowing films to change tint through different visible color-modulated states has been designed. Figure 8 shows that the slider sensor and on/off button will work in unison to give the user complete control of the tint level. The signals provided to the user interface will then be distributed to the microcontroller. The microcontroller will draw power from the battery module to power its programming and output the corresponding signal that changes the opacity of the EC films. The user can use the interface to send signals to the microcontroller. After the microcontroller receives the signal, the battery is used to power the microcontroller and output the appropriate voltage to adjust the tint level on demand.

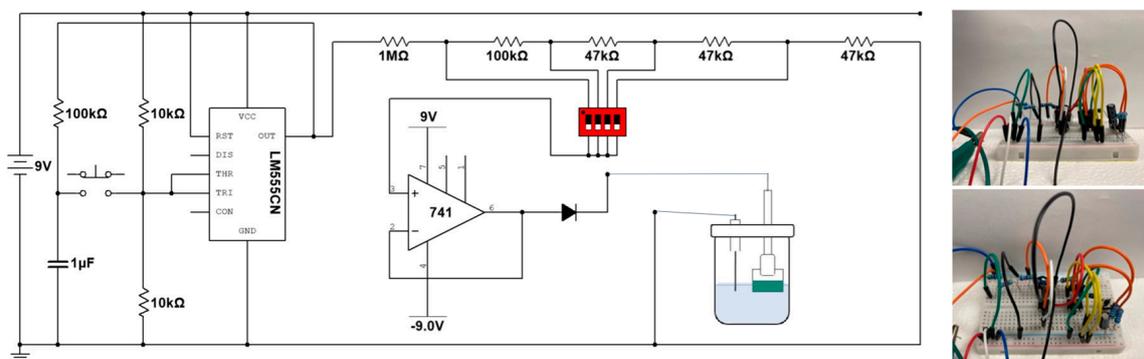


Figure 8. Electrical circuit design for modulating the optical properties of PANI.

A circuit that drives the color change on the EC films has been designed successfully. This circuit comprises essential electronic components and outputs discrete voltage levels corresponding to the film's colors. The voltages are set by having the user insert a pin into the appropriate slot. This method of changing voltages could be made more accessible by using a dipswitch or another method of switching inputs. Push buttons are much smaller and easy to integrate into a printed circuit board that could hold the rest of the circuitry. The timer output is placed in series with a sequence of resistors that divide the voltage into the values corresponding to the film's color changes. These outputs are placed into a dipswitch where users can select which voltage they want to apply. The output of the switch is then sent to an op-amp placed in a buffer configuration. The buffer is used to ensure that no current is lost through the voltage divider system. The effect is achieved because of the infinite impedance of the op-amp. Figure 8 shows the voltage that corresponds to each of

the switches. In the designed circuit, 1.74 V provides a blue tint; 1.02 V turns the film light blue; 679 mV gives a greenish yellow color, and 339 mV achieves a yellow color.

4. Conclusions

In conclusion, comprehensive investigations have been conducted on the electrodeposited PANI film's linear colorimetric and EC characteristics and solid-state devices. Successful fabrication of a complete laminated device employing PANI and WO₃ films enclosed in a gel electrolyte sandwich structure illustrates the compatibility of PANI films with cathodic WO₃ films for all-solid full-device applications. The well-defined oxidation and reduction peaks observed in the cyclic voltammetry test indicate the ion-diffusion dominant process in electrochromism. Significant transitions between the benzene and quinone phases in the Raman spectra are found in the bleached and colored states of PANI. A separate circuit has been developed that enables color changes in films via various visible color-modulated states. In a designed circuit, 1.74 V offers a blue tint, 1.02 V turns the film light blue, 679 mV produces a greenish yellow color, and 339 mV produces a yellow color. Through infrared camera testing, it was found that PANI films have a unique capacity to block infrared (IR) radiation during EC operations. With its ability to remain invisible to heat-seeking technologies, this versatile multicolored polymer holds great potential for satellite thermal management and military camouflage, opening the door for IR EC applications in the future.

Author Contributions: Conceptualization, D.D.; methodology, H.S.; software, D.D.; validation, H.S. and D.D.; formal analysis, D.D.; investigation, D.D.; resources, D.D.; data curation, D.D.; writing—original draft preparation, H.S.; writing—review and editing, H.S. and D.D.; visualization, D.D.; supervision, D.D.; project administration, D.D.; funding acquisition, D.D. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original raw data will be available upon request.

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