Developing a Novel Image Analytical Method for Studying the Electrochromic Properties of Metallo-Supramolecular Polymer-Based Electrochromic Devices

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ABSTRACT

This study introduces a novel image analytical method which integrated advanced imaging techniques with quantitative analysis, providing a comprehensive understanding of the electrochromic behavior and performance of MSP-based solid state ECDs. Results illustrate the effectiveness of this method in capturing real-time color changes, contrast, and uniformity of the electrochromic response.

1 Introduction

Electrochromic devices (ECDs) have emerged as transformative technologies with applications ranging from smart windows and displays to energy-saving systems and adaptive camouflage. These devices incorporate materials that change color upon the application of an electric voltage, offering dynamic control over their optical properties. Traditional materials which are used for ECDs such as metal oxides and organic compounds; among those metallo-supramolecular polymers (MSPs) have gained significant interest due to their inherent structural versatility and tunable optical properties.

MSPs consist of metal ions coordinated with organic ligands, forming a network with unique electronic and structural characteristics. These materials offer several advantages, including tunable redox properties, mechanical flexibility, and ease of processability. The electrochromic properties of MSP-based ECDs are affected by factors such as the nature of the metal ions, the polymer matrix, and the supramolecular interactions. Therefore, understanding and optimizing these properties are crucial for the development of high-performance ECDs.

Despite the potential of MSPs in ECDs, a significant challenge remains in the analytical methods used to study their electrochromic properties. Traditional methods for evaluating electrochromic properties often depend on spectrophotometric techniques that provide limited spatial resolution and are unable to capture the full dynamic range of electrochromic changes. To address these limitations, we have developed a novel image analytical method that leverages high-resolution imaging and quantitative analysis to study the color changing behavior of MSP-based solid-state ECDs in a detailed and non-destructive manner. Moreover, this approach offered a valuable user-friendly software tool for researchers and engineers in the field of smart materials and devices.

2 Experiment

2.1 Fabrication of metallo-supramolecular polymer thin film

The thin film of Fe (II)- based metallo-supramolecular polymer (polyFe) was prepared on the ITO (indium tin oxide) glass substrate by a spray-coating method from a methanol solution of Fe polymer (3 mg/ml).

2.2 Preparation of solid-state electrochromic devices (ECDs)

Solid-state electrochromic devices (ECDs) composed of using the thin films of Fe(II) based metallo-supramolecular polymer (polyFe) (an electrochromic active layer) and Nickel hexacyanoferrate (NiHCF) (an ion storage layer), both of which were fabricated by a spray coating method on the ITO substrates and served as working (WE) and counter (CE) electrodes, respectively (Fig. 1a). The transparent gel electrolyte thin film was prepared by mixing PMMA, propylene carbonate (PC), and LiClO4 salt in an 8/46/46 (w/w) ratio. The WE and CE were placed in a sandwich model that was separated by the transparent gel film, followed by annealing at 95 ºC and 40% relative humidity.

3 Results and Discussions

A methanol solution of Fe polymer is purple which exhibited an absorption maximum at ~580 nm for MLCT (metal-to-ligand charge transfer transition) in the UV-visible spectrum. At a very low potential at 1.2 V, the ECD showed a bleaching and coloring state.

In the image data analytical method, After the fabrication of ECD, we took movies of the device during the cyclic test to record the color-changing phenomena at each cycle using a digital microscope equipped with a

lens. After that, the Python OpenCV library was used to extract images from the movies. From the images region of interest (ROI) was selected which were then converted into grayscale images. From grayscale images, pixels were extracted which were merged into segments by averaging nearby pixel values. Every 25 pixels (5×5) were merged into one segment. Finally, these segments were used to plot the time vs. contrast graph to observe the color-changing pattern for each transition of the device from color to colorless state.

For a transition from color to a colorless state 150 grayscale images showed that the device changed its color within less than 2 seconds for the 1st cycle at 1.2 V. From the time vs. contrast graph, we observed the color-changing trend of the device. The lines in the graph which are the intensity of pixel values, were very sharp initially and after these became curvature with time during the transition period. As these intensities of pixel values represented each distinct position in the image, we investigated that the device took a short time to change its color at the periphery region compared to the central region which required more time (Figure 1b). Moreover, by analyzing the graphs for higher cycles we noticed that the response time of the device became slower with successive cycles and for 1000th the device was not able to show a complete colorless state within the same time framework.

The examination of pixel distribution histograms unveiled changes in pixel intensity distribution, shedding light on the overall color-changing trends and potential failure modes. At the 1000th cycle, the pixel distribution broadened, indicating increased heterogeneity in the electrode surface. For higher cycles, a loss of uniformity in the color transition process was observed in the visualized pixel distribution analysis. Meanwhile, exploring pixel values versus distance from the center revealed a symmetrical pattern for the 1st cycle, with pixels progressively transitioning from higher to lower grayscale values toward the center, and uneven bleaching for the 1000th cycle. These results offer insightful information on the electrochromic behavior of ECDs, emphasizing the need for spatially resolved studies in comprehending EC transition processes and device performance.

4 Conclusions

We successfully developed a novel image analytical method to investigate the electrochromic properties of polyFe-based solid-state ECDs. The method's ability to provide real-time, quantitative analysis of electrochromic behavior has significant advantages for material characterization and device optimization. Future research will focus on improving the method for higher resolution and applying it to a wide range of electrochromic materials.

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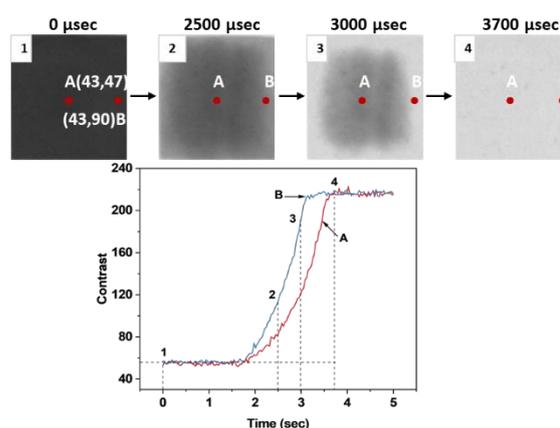
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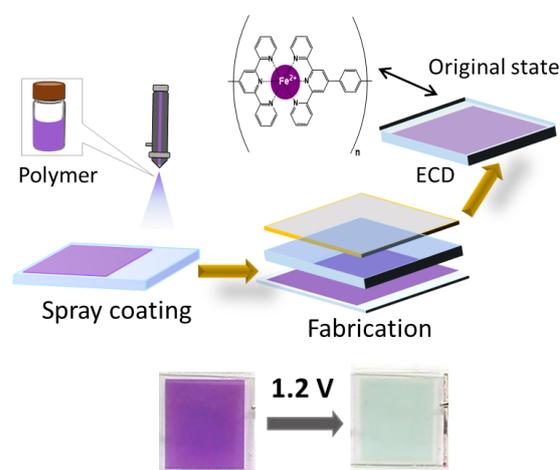
(b)

Fig. 1 (a) preparation and color-changing properties of ECD. (b) time vs. contrast graph with transition to a colorless state in grayscale images.