

Letter

Phthalate-based Electrochromic Device Using a Cellulose Substrate Enabling a Form of Reflective Representation As Designed

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Abstract: We fabricated an electrochromic device with a cellulose substrate impregnated with a dimethyl terephthalate-based electrochromic solution. By cutting the cellulose substrate into a shape of an alphabetical letter, we succeeded in displaying an electrochromic letter. The simple fabrication and the biodegradable cellulose substrate potentially contribute to the sustainability-oriented development.

Key words: Electrochromism, Electrochromic display, Cellulose substrate, Dimethyl terephthalate, Display device

Introduction

Electrochromism is a reversible color change phenomenon triggered by electrochemical redox. Reflective display devices based on an electrochromic (EC) reaction are in commercial use as rearview mirrors in cars and window glass in airplanes. This is because of their low driving voltage and continuous variability in transmission and memory. In recent years, new functionalities of EC devices have been demonstrated, such as energy storage,¹⁾ tactile sensing,²⁾ and reversible handwriting functions.³⁾ In addition to conventional EC devices that change color when voltage is applied to them, promising candidates for next-generation devices are in development.^{4,5)} For routine use, electrolyte leakage must be prevented; this is generally done by mixing a polymer material into the electrolyte to form a gel electrolyte. For example, EC devices have been realized by using poly (methyl methacrylate) (PMMA),⁶⁻⁸⁾ polyvinyl butyral (PVB),⁹⁻¹¹⁾ and poly (vinylidene fluoride) (PVDF).^{12,13)} However, these polymers are non-biodegradable, warranting biodegradable polymers to achieve sustainability.

Cellulose, which is a natural polymer derived from plants, is a biodegradable material but with excellent coating properties and processability. It is used as a substrate for various electronic devices such as organic transistors,¹⁴⁾ light-emitting electrochemical cells,¹⁵⁾ and powder electroluminescent devices.¹⁶⁻¹⁸⁾ Dioxythiophene-based EC devices can be realized by forming poly (3,4-ethylenedioxythiophene) :poly (styrenesulfonate) (PEDOT:PSS) electrodes on a cellulose substrate.¹⁹⁾ Recently, Su et al. reported the fabrication of a nanocomposite film combined with biodegradable cellulose nanocrystals and molecular viologens (as EC materials), leading to the construction of a flexible and environmentally friendly EC device.²⁰⁾ However, the procedure of fabricating cellulose nanocrystals is complicated by the requirement of a hydrolysis with strong acids such as sulfuric acid.

We report the fabrication of a biodegradable composite EC film via a simple process. We constructed a new EC device by sandwiching a commercialized cellulose substrate impregnated with the EC electrolyte solution between a pair of indium tin oxide (ITO) transparent electrodes. As the EC material, a phthalate derivative²¹⁾ was employed because it clearly obtains the peak of the redox wave in a two-electrode device²²⁾ and has a good switching stability.²³⁾ Finally, we evaluated its photoelectrochemical properties.

Experimental Method

We prepared the electrolyte solution by dissolving 200 mmol/L of tetrabutylammonium perchlorate (T0836, Tokyo Chemical Industry Co., Ltd.) in dimethyl sulfoxide (10378-00, Kanto chemical Co., Inc.). We fabricated the two-electrode device by placing a cellulose substrate (Kimwipe S-200, Nippon paper Creca Co., Ltd.) with dimensions of approximately 1 cm × 1 cm between a pair of ITO electrodes (1005, Geomatec Co., Ltd.) and adding 0.05 g of the electrolyte solution. We used double-sided tape to maintain an inter-electrode distance of 0.5 mm. We prepared the EC electrolyte solution by dissolving 10 mmol/L of dimethyl terephthalate (DMT) (T0015, Tokyo Chemical Industry Co., Ltd.) and 20 mmol/L of ferrocene (D0444, Tokyo Chemical Industry Co., Ltd.) in the electrolyte solution and similarly fabricated the EC device. We performed cyclic voltammetry (CV) measurements on both devices with a potentiostat (ECstat-301WL, EC Frontier Co., Ltd.) at a sweep rate of 100 mV/s. We measured the transmittance spectra of the EC device using a spectrometer (SEC2020, ALS Co., Ltd.) before and after the application of a direct current voltage. With the EC device placed between the spectrometer and the light source, we set the transmittance to 100% when the light source was turned on and 0% when the light source was turned off. Using the same instruments, we measured the changes in the current and transmittance at a

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wavelength of 500 nm when a coloring voltage (+2.65 V for 25 s) and a bleaching voltage (−1.0 V for 5 s) were alternately and repeatedly applied to the device. In addition, before fabricating the EC device, we cut cellulose substrates to form the letters *O*, *I*, *T*, and *A*. We then fabricated the devices as above, observing the appearance of the devices before and after the application of coloring and bleaching voltages.

Results And Discussion

To reveal the electrochemical behavior of DMT in cellulose substrates, we measured the CV of the two-electrode device at a sweep rate of 100 mV/s (Fig. 1). In the device without EC materials, we observed no clear electrochemical response over the applied voltage range of 0–2.65 V. This suggests that the cellulose substrates are not electrochemically active. On the other hand, in the device with EC materials, we observed a current peak at approximately 2.3 V. This signal is consistent with the report of Y. Watanabe²²⁾ et al., suggesting that EC reaction of DMT occurred even in the cellulose substrates.

Next, to demonstrate the EC reaction of DMT, we measured the transmission spectra of the EC device before and after voltage application (Fig. 2 (a)). Prior to voltage application, the visible light transmittance of the device was approximately 100%. In contrast, under the application of +2.3 V, the transmittance of the device decreased to 10–20% at wavelengths of approximately 500–550 nm, and the appearance of the device changed from translucent to magenta due to the redox reaction of DMT (Fig. 2 (b)). The magenta coloration was uneven because of the rough texture of the cellulose substrate. When we applied −1.0 V to the device, the appearance changed back to translucent. This change in transmittance is consistent with a previous report²³⁾ that described the effect of counter electrode reaction materials in DMT-based EC devices. From these results, we found that the EC reaction of DMT can be accomplished in cellulose substrates.

Next, we measured the changes in current and transmittance at a wavelength of 500 nm when the applied voltage was switched be-

tween +2.65 V for 25 s and −1.0 V for 5 s (Fig. 3). We did this to evaluate the response time and switching stability of the EC device. When we applied the coloring voltage of +2.65 V to the device, we obtained the current response because of the Faraday reaction. Applying a bleaching voltage of −1.0 V to the device, we observed the current response corresponding to the reversal of polarity. With this current behavior, the visible light transmittance decreased from approximately 97% to 25% upon application of the coloring voltage. When applying a bleaching voltage, the transmittance returned to the initial state of approximately 97%. The coloring and bleaching times, defined as the time required for a 90% change in transmittance, were approximately 3.8 and 14 s, respectively. The cycle was

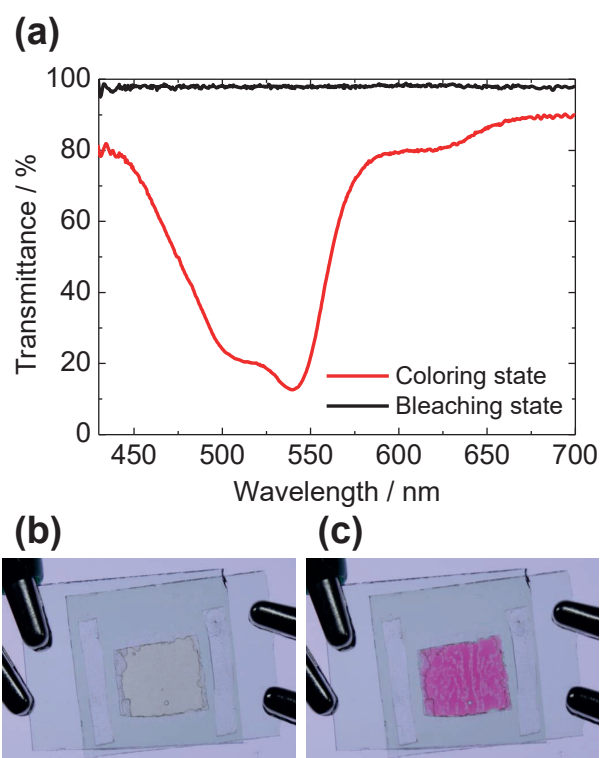


Fig. 2. (a) Change in transmittance spectra of the EC device using the cellulose substrate in the bleaching (black line) and coloring states (red line). Photographs of the device in the (b) bleaching and (c) coloring states.

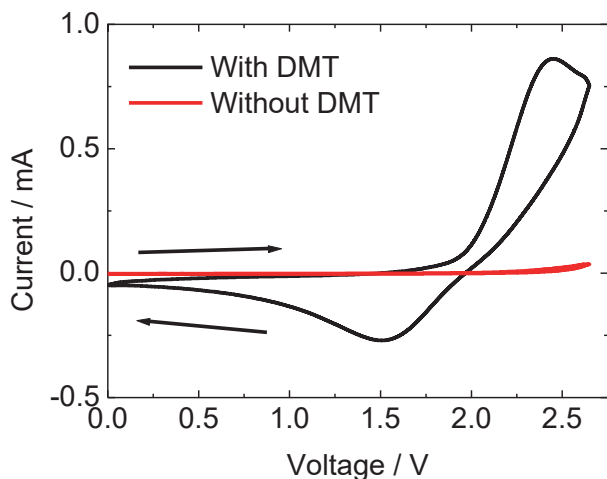


Fig. 1. CV of the two-electrode device with a sandwiched cellulose substrate containing electrolyte solution with and without DMT.

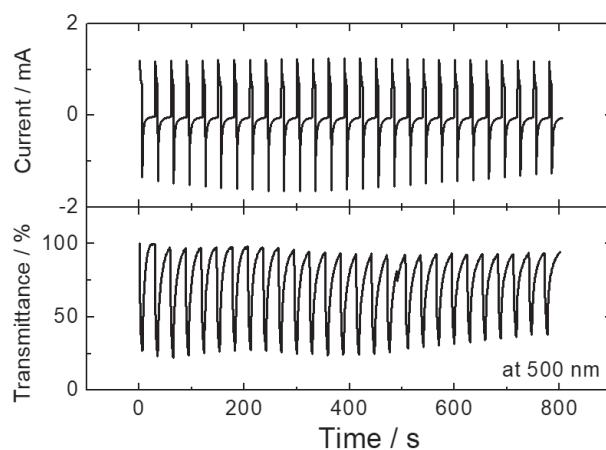


Fig. 3. Changes in current (top) and transmittance (bottom) of the device at a wavelength of 500 nm using the cellulose substrate during the application of +2.65 V for 5 s and −1.0 V for 25 s.

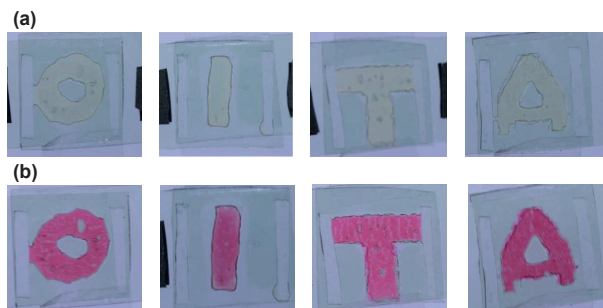


Fig. 4. Photographs of the device using the cellulose substrate, which was cut into letters prior to fabrication of the device, in the (a) bleaching and (b) coloring states.

repeated approximately 30 times. The performance of EC devices is determined by various factors such as material concentration, device structure, and driving voltage conditions, and thus it is difficult to compare with previous reports. It is considered that the performance is not significantly decreased by the introduction of cellulose substrate because this response time is the same order of magnitude in the three-electrode system.²⁴⁾

Lastly, before fabricating the device, we cut the cellulose substrates into the letters *O*, *I*, *T*, and *A*, and each letter containing the EC solution was sandwiched between a pair of ITO electrodes, as seen in Fig. 4. Prior to application of the coloring voltage, the letters were translucent; they changed color to magenta after the coloring voltage was applied. When we applied a bleaching voltage to the device, the original translucent state returned. This indicates that by cutting the substrate prior to device fabrication, it is possible to realize a display device showing intended forms of color change. This eliminated the need to etch the electrode, reducing the complexity of device fabrication.

Conclusion

In this letter, we fabricated composite EC films consisting of a biodegradable cellulose substrate and an EC material via a simple process. The device demonstrated the EC reaction of phthalate derivatives. By cutting the cellulose substrate before device fabrication, we successfully demonstrated reflective representation in a designed form without etching the ITO electrode. We expect this new biodegradable display device, which was constructed via a simple process, to be suitable for use in sustainable display devices.

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