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COMMUNICATION

Solution polarity modulated electrochromic devices with tunable colored states

Junjie Chen, [a] Wanli Li, [a] Ke Li, [a] He Zhang, *, [b, c] and Su Ding [*, a]

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Electrochromic devices (ECDs) hold great promise for applications in displays and smart military camouflage. However, achieving different electrochromic colored states with compatible integration into a monolithic device remains a significant challenge. In this study, we realized effective color modulation of ECDs by tuning the solvent composition, leveraging the the effects of solvent polarity. The resulting ECDs exhibited tunable absorption peaks and color switching behaviors across various solvent systems. The ECDs achieved a high optical contrast of 74%, while maintaining a coloration efficiency of 41.6 cm²/C.

Electrochromic devices (ECDs) attract significant attention for their reversible changes in optical properties induced by a small applied electric field[1-4], which exbibits potential applications in displays[5-7], smart military camouflage[8,9], and other advanced technologies[10, 11]. These applications place a strong demand on the realization of different colors at customized regions[12, 13]. However, despite extensive efforts, achieving different electrochromic colored states with compatible integration into a monolithic device remains challenging.

For instance, inorganic EC materials typically display monotonous colors, as illustrated by tungsten trioxide (WO_3), which mainly presents a single shade of blue with varying brightness under different applied voltages[14]. Physical structures such as Fabry-Pérot nanocavity, optical crystal were exploited for imparting colorful presentation ability for EC materials with monotonous colored states[15]. However, it is difficult to achieve them within a monolithic ECD due to the differing requirements (such as the thickness of the EC layer) across various colored regions. Viologen-based ECDs, derived from 1,1′-substituted-4,4′-bipyridinium salts, can display various colors by adjusting molecular structures, including substituent types and chain lengths[16, 17]. Moreover, their all-in-one device configuration enables the simultaneous integration of different viologen derivatives within a single device. However, the distinct redox properties of viologens with varying molecular structures often result in potential mismatches when operated under the same applied voltage.

Despite accounting for over 90 wt % of the functional components in all-in-one viologen-based ECDs, the influence of solvents on the colored states has received little attention. In principle, solvent properties such as polarity can play a critical role in shaping the UV-visible absorption spectra and tuning the displayed colors[18]. Here, we report a ECD system modulated by solvent composition. Distinct colors, including blue and purple, can be customized by adjusting the solvent polarity parameters. Notably, different color states can be achieved using the same viologen, allowing for identical fabrication processes and operating voltages. This approach enables the successful demonstration of distinct colors in different regions within a single device. Furthermore, the simple processing techniques employed for these ECDs support the patterning of device arrays, highlighting their potential for the development of next-generation display electronics.

The ECDs is fabricated by sealing the electrochromic solution containing ethyl viologen (EV) in different solvents and $Zn(CF_3SO_3)_2$ between the two indium tin oxide (ITO) glasses (**Fig. S1**). **Fig. 1a** illustrates the reversible switching process between the bleached state (top) and the colored state (bottom) of the ECDs, along with the corresponding chemical structural changes of the EV molecules at different redox states. Specifically, the application or removal of an external voltage induces a reversible redox reaction in the EV molecules, driving the transition of the device between the bleached and colored states. The color of viologen-based ECDs can be adjusted by the selection of solvents with different polarities. In our study, water and ethanol were selected as representative high- and low-polarity solvents, respectively, and solvent systems with varying polarities were prepared by adjusting their mixing ratios. Indeed, the decrease of solvent polarity in ECDs realizes the

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[a] *School of Intelligent Manufacturing, Jiangnan University, Wuxi 214122, P.R. China.*
[b] *Department of Mechanical Engineering, The University of Hong Kong, Hong Kong SAR 999077, China.*
[c] *Advanced Biomedical Instrumentation Centre Limited, Hong Kong SAR 999077, China.*
†Email: hitzhanghe@outlook.com (He Zhang), dingsu@jiangnan.edu.cn (Su Ding).

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evident red shift in the UV-Vis absorption peaks of under the same-colored voltage (~1.4 V), confirming the color tuneability by solvent composition (**Fig. 1b**). Correspondingly, the distinct color change from purple to blue can be clearly distinguished by the naked eye, as exemplified by the colors of the letters "J," "N," and "U" (**Fig. 1c**). Furthermore, the patterning of ECDs was achieved through spatially selective printing of electrochromic solutions using customized masks, enabling the fabrication of complex patterns for display electronics, such as an "umbrella," "glass," and "airplane". The color of viologen-based ECDs can be adjusted by the selection of solvents with different polarities.

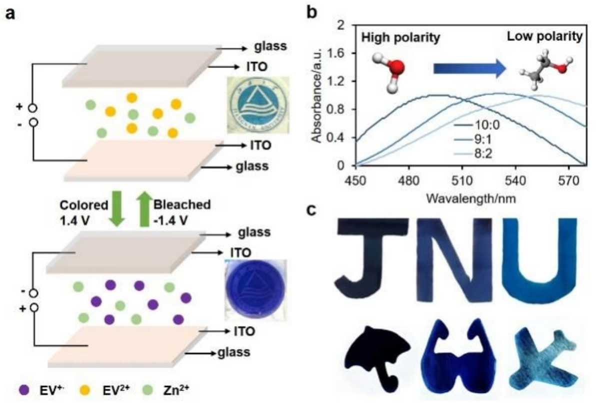

Fig. 1 Design and structure of ECD fabricated by ethyl viologen (EV)-based electrochromic solution with different solvents. (a) Schematic illustration of structure and electrochromic process of an ECD. (b) The absorbance curves of ECDs fabricated with solvents of different polarities (water to ethanol from 10:0 to 8:2) at the voltage of (~ 1.4 V). (c) Photographs of ECDs fabricated with solvents of different polarities (with water to ethanol ratio of 9:1, 7:3, and 5:5) at the voltage of (~ 1.4 V).

Fig. 2a shows the colors of the prepared ECDs under different applied voltages (0 V, 1 V, 1.2 V, 1.3 V, and 1.4 V) and various solvent ratios (water and ethanol). As the applied voltage is gradually increased, all the ECDs undergo a transition from a nearly bleached state to a colored state, highlighting the color modulation process induced by the electric field. Taking the ECD with water as the solvent as an example, the more pronounced darkening of the absorption peak with increasing voltage further confirms the coloring process (**Fig. 2b**). Moreover, the round-trip color changes within the voltage window from 0 V to 1.4 V demonstrate excellent electrochemical reversibility (**Fig. S2**).

In addition to conventional voltage-induced color changes, we noted that solvent polarity also plays a crucial role in determining the color states of the ECDs. As the water-to-ethanol ratio decreases, the solvent polarity diminishes, leading to a color transition of the device from purple to blue (**Fig. 2c**). The color change was also reflected in the UV-Vis absorption spectra. The changes in the absorption peak shape in **Fig.2c** mainly arise from the combined effects of solvent polarity, solvation, and molecular aggregation of the reduced ethyl viologen species (Et-Vi^{+}•). High-polarity solvents stabilize the radical cation and broaden the absorption bands, while low-polarity solvents promote π–π stacking and dimer formation, leading to narrower or distorted peaks[19,20]. Specifically, the absorption peak of the ECD with pure water as the solvent appeared at 480 nm, whereas for the ECD with a 1:9 water/ethanol ratio, the peak shifted to 566 nm. The distinct absorption peak shape in pure water arises from viologen aggregation into dimers or polymers (radical cations), causing peak splitting, broadening, or red-shifting in the highly polar environment, whereas lower-polarity water-alcohol mixtures stabilize monomeric viologen, yielding sharper peaks; this systematic shift from monomers to aggregates with increasing water proportion drives the observed spectral changes[21,22]. As the water/ethanol ratio decreased, the absorption peak exhibited a pronounced red shift, confirming the modulation of the ECDs' color states by solvent polarity.

On the other hand, it is observed that as the ethanol content increases, the colored state becomes progressively lighter, indicating a gradual weakening of the electrochromic response. This may be attributed to the poor solubility of $Zn(CF_3SO_3)_2$ in ethanol which consequently hampers the electrochemical redox process. This hypothesis is supported by the observation that the current density peak corresponding to the redox process of the ECDs decreases as the solvent polarity decreases (**Fig. 2d**).

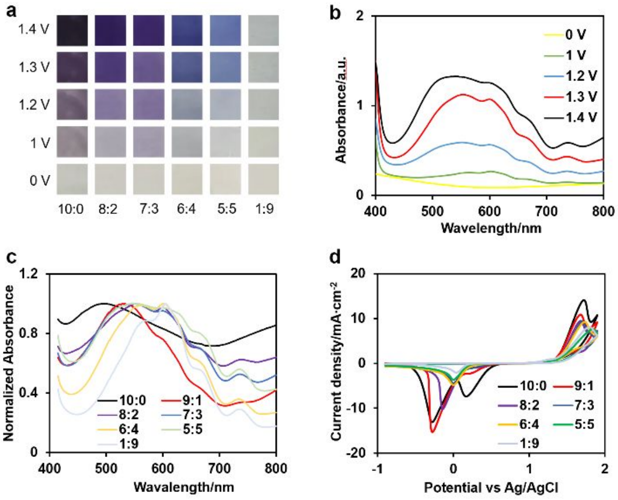

Fig. 2 Electrochromic properties of ECDs with different water/ethanol ratios in electrochromic solution. (a) Colors of ECDs in water/ethanol solvent with various ratios under different voltages. (b) Absorbance curves of ECDs under different voltages. (c) Normalized absorbance spectra and (d) CV curves of the ECDs in water/ethanol solvent with various ratios.

To further validate this mechanism, we conducted cyclic voltammetry (CV) measurements of EV in solvents of varying polarities by adjusting the water–alcohol ratio. The results revealed that the reduction peak potential shifted positively with increasing polarity. This is attributed to polar and electrostatic interactions in highly polar solvents, which

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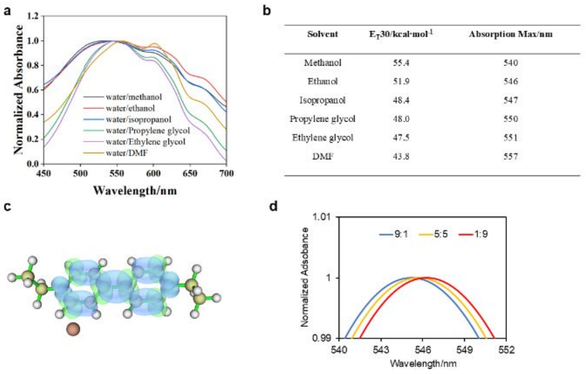
stabilize the positively charged viologen intermediates formed during reduction, thereby lowering the energy barrier and facilitating the redox process. In contrast, lower polarity solvents reduce solvation strength and intermediate stability, resulting in more negative reduction potentials (**Fig. S4**)[23-25].

To further investigate the role of solvent polarity, ethanol in the ECDs was replaced with methanol, isopropanol, propylene glycol, ethylene glycol or N, N-dimethylformamide (DMF) with different polarity, and the properties of the resulting ECDs were examined (**Fig. S4**). When methanol was used as a co-solvent with water, the absorption peak shifted from 517 nm to 561 nm as the water/methanol ratio decreased from 10:0 to 6:4 (**Fig. S5a**). A similar trend was found when isopropanol, propylene glycol, ethylene glycol and DMF were used as co-solvents, the absorption peaks of the ECDs also exhibited notable red shifts as the water content decreased from 10:0 to 5:5, (**Fig. S5**). These results indicate that as the proportion of water (a high-polarity solvent) decreases, the absorption peak shifts significantly toward longer wavelengths, consistent with the trend observed in water/ethanol systems. The optical absorption spectra of ECDs prepared in mixed solvents of isopropanol, ethanol, methanol, propylene glycol, ethylene glycol and DMF at identical water/organic ratios are presented in **Fig. 3a**. Notably, the absorption peaks are shifted from 540 nm to 557 nm depending on the choice of co-solvent (**Fig. 3b**). This red shift correlates well with the solvent polarity parameters, with lower solvent polarity leading to a more pronounced shift toward longer wavelengths. These results confirm that solvent polarity directly influences the displayed colors.



Solvent	E_T30/kcal·mol^{-1}	Absorption Max/nm
Methanol	55.4	540
Ethanol	51.9	546
Isopropanol	48.4	547
Propylene glycol	48.0	550
Ethylene glycol	47.5	551
DMF	43.8	557

Fig. 3 Mechanism analysis. (a) Normalized absorbance spectra of the ECDs in various solvent. (b) Table of the physical parameters and the absorption peak of various solvents. (c) Molecule structure of the excited state of EV diiodide. (d) Simulated absorbance curves of ECDs in water/ethanol solvent with different ratios.

To understand the mechanism of color modulation of ECDs by changing the polarity of solvent, a simulation was conducted to evaluate the function of solvent polarity. The molecular structure of the exited state for EV diiodide is computationally optimized as shown in **Fig. 3c**. Similar to the results observed in the experiments, a slight blue shift in the absorption peak was observed as the solvent polarity increased with the addition of more polar water (**Fig. 3d**). This is because the ground state of viologen exhibits higher polarity than the excited state. Consequently, the ground state is stabilized more in high-polarity solvents, requiring additional energy for redox reactions to proceed. As a result, the absorption peak undergoes a blue shift. This is reported as negative solvatochromism. The combination of this negative solvatochromism phenomenon with electrochromic processes enables simultaneous control of color modulation through both solvent and voltage.

The ECDs fabricated using an electrochromic solution with a water/ethanol ratio of 7:3 were selected as a representative example to evaluate their electrochromic performance (**Fig. 4**). In the unbiased state, the device exhibited high transparency with a transmittance of 79%. Upon applying a voltage to induce coloration, the transmittance significantly dropped to 5%, resulting in a high optical contrast of 74% (**Fig. 4a**). The response time and recovery time during the switching process were further investigated. As shown in **Fig. 4b**, at a wavelength of 550 nm, the coloration and bleaching times were measured to be approximately 15 s and 25 s, respectively. Minor variations in switching times were observed at other wavelengths (500 nm and 600 nm) and when using methanol or isopropanol as co-solvents (**Figs. S6 and S7**). The cycling stability of the ECDs and the attenuation degree of ΔT were evaluated through repeated coloration and bleaching cycles, as shown in **Fig. 4c**. The device underwent 1000 consecutive coloration/bleaching cycles. During this process, the optical contrast (ΔT) showed only a slight attenuation, decreasing from 74% to 72.4%, indicating excellent cycling durability and stability (**Fig. S8**).

Additionally, **Fig. 4d** presents the relationship between optical density change (ΔOD) and charge density (Q) at a given wavelength. The coloration efficiency (CE), which is a key metric for evaluating the energy efficiency of ECDs, was determined from the linear region of the ΔOD and Q plot. ΔOD increased rapidly with Q before gradually reaching saturation, and linear fitting yielded a CE of approximately 41.6 cm²/C. Overall, these results demonstrate that the ECDs prepared in this study possess excellent cycling durability, high reversibility, strong optical modulation per unit charge, and outstanding operational stability. We compared the properties of our ECD and other devices as shown in **Tab. S1**. Our device exhibits a high optical contrast and density. While other electrochromic devices demonstrated color-switching and bleaching responses at specific wavelengths. In contrast, our device achieved absorption peaks across a certain wavelength range from 540 nm to 557 nm by modulating solvent polarity, showing advantages in displays.

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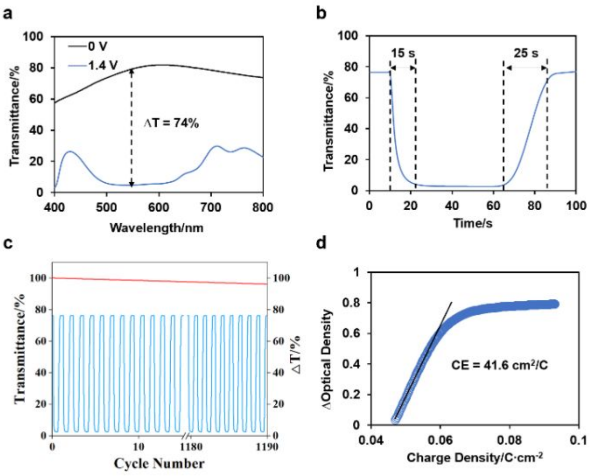

Fig. 4 Electrochromic properties of ECDs fabricated with a water/ethanol ratio of 7:3. (a) Transmittance curves in bleached and colored states. (b) Response and recovery duration for the coloration and bleaching process at 550 nm. (c) Cycle performance between 0 V and 1.4 V to record in situ changes of transmittance at 550 nm. (d) Changes in optical density respect to the injected charge density.

In summary, we have demonstrated effective color regulation in ECDs by tuning the solvent polarity, which enables a wide range of color presentations for display applications. The as-prepared ECDs exhibit a reversible color transition from purple to blue accompanied by an 86-nm bathochromic shift (480 to 566 nm) as the solvent polarity decreases through systematic variation of the water/ethanol ratio (10:0 to 1:9). The tunable electrochromic behavior and absorption shift are also demonstrated in various solvent systems with different polarity parameters. In addition, the ECD with water/ethanol solvent achieved a high optical contrast of 74% in a rapid response, while maintaining a coloration efficiency of approximately 41.6 cm²/C and stable performance during prolonged cycling tests. Further optimization of solvent compositions, printing techniques, and other fabrication parameters could open up diverse opportunities for the development of next-generation display electronics.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Acknowledgement

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Data availability Statement

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials