Flexible and Tailorable Alkylviologen/Cellulose Nanocrystals Composite Films for Sustainable Applications in Electrochromic Devices


The new, sustainable, and pro-environmental electrochromic devices (ECDs) have attracted tremendous attention due to the current issues regarding energy sources consumption and environmental pollution. A free-standing composite film, consisting of cellulose nanocrystals (CNCs) as a biological matrix, viologen, and KCl, was prepared by a casting method. Such a composite film is flexible and can be tailored into various shapes for patterned applications. The viologen/KCl/CNCs film was sandwiched between two indium-tin oxide (ITO) glasses to construct viologen-based ECDs. The performance of the viologen-based ECDs did not depend on the organic solvent. ECDs based on four kinds of viologens with different substituent groups exhibited distinct coloration response. Besides the nature of the substituent groups attached to the bipyridine rings, the presence of CNCs is a crucial factor that affects the electrochromic performance of ECDs. The dimethyl-substituted viologen ECD has a fast response time (10 s for bleaching and 7.3 s for coloring). And for the dibenzyl-substituted viologen, a low voltage of −2.2 V can drive the coloration of its ECDs. The diethyl-substituted viologen ECD exhibits 30% transmittance variation and good coloring/bleaching stability. The ability to be tailored and degradability of the composite film provides a feasible strategy for the sustainability of electrochromic displays.

1. Introduction

Electrochromic (EC) materials belong to stimuli-responsive reversible coloration-change materials and represent a highly demanded type of intelligent system useful for a wide variety of applications such as displays, electronic paper, smart windows and antiglare rearview mirrors.[1–8] Among EC materials, viologens (a class of 1,1'-disubstituted-4,4'-bipyridinium salts) exhibit cathodic EC behavior and perform highly stable redox activity, low driving voltages for visual changes and high optical contrast.[9] Depending on the nature of the substituents groups attached to the bipyridine rings, the corresponding viologen species show distinct colors due to a reversible electron-transfer process.[10] Therefore, alkylviologen is expected to be applied in electrochromic devices (ECDs) to realize multicolored changes.

Due to the risk of electrolyte leakage and the difficulty of manufacturing and handling, solid-state or semi-solid (i.e., gel) electrolyte based ECDs gradually replace the liquid-state based ECDs.[11–13] However, solid polymer electrolyte in solid-state ECDs has low ionic conductivity, poor contact at electrode/electrolyte interface and its preparation process need organic solvent.[14] Hence, it is still a challenge to simplify the architecture of viologen-based environmentally friendly solid-state ECDs and also obtain excellent EC performance.

Recently, there has been a growing interest to apply nanocellulose and cellulose derivatives in ECDs in virtue of sustainability, pro-environment, good mechanical property and film-forming property.[15–16] Cellulose is the most abundant biopolymer resource on the planet and it can be obtained from plant, algae, fungi, bacterial and so on.[29–33] Nonetheless, cellulose is insoluble in most common solvents which restricts its processing. Therefore, cellulose is usually disintegrated into nanostructured cellulose for further application.[24–28] As one kind of several nanocellulose, cellulose nanocrystals (CNCs) exhibit distinct properties, including high mechanical strength, aqueous dispersion stability, low thermal expansion coefficient, degradability and biocompatibility.[29,30] More importantly, CNCs have outstanding film-formation character and optical transparency.[31–33] These properties combined with their low cost, light weight, and flexibility, make CNCs promising candidates for fabrication of environment-friendly composite coatings and energy devices.[14–30] Stoenescu et al. prepared a composite film of tungsten oxide and CNCs by a sol-gel method and the uniform film showed good EC performance.[31] Zhang et al. used nanocellulose to successfully improve the film forming property of polyaniline (PANI) and as-prepared nanocellulose-based PANI composites film with core-shell structure showed high contrast ratio and coloration efficiency in ECDs.[32] These pioneer works inspire us to construct uniform CNCs/viologen composite films and make use of them to design a novel viologen-based ECDs. To the best of our knowledge, this is the first time to report the preparation of CNCs/viologen composite-based ECDs with an organic solvent-free process.
In this work, a series of composite films, consisting of CNCs, alklyviologens and KCl, were prepared by volatilizing their mixed aqueous solutions in polystyrene (PS) petri-dish. Three components play respective roles in the integrated films, in which CNCs serves as film-forming agent, viologen serves as EC molecule and KCl serves as electrolyte. Such an integrated film has many advantages: (i) aqueous film-forming system is environmentally benign; (ii) nanocomposite films are flexible to be cut into different shaped pieces for the practical ECDs and especially for flexible devices; (iii) such integrated film can be easily assembled between two transparent electrodes in a sandwich architecture to assess its EC behavior, moreover, this film can also be detached from ECDs for reutilization; (iv) the CNCs-based composite film is degradable; (v) viologens with different substituent groups can offer the ECDs distinct colors. Taking full account of some factors, including environment-friendliness, recycling, easily handling, tailored character and flexibility, the as-prepared viologen/CNCs composite film is expected to be widely used in designable and multicolored ECDs.

2. Results and Discussion

2.1. Properties of Viologen/KCl/CNCs Solution

It is well-known that CNCs obtained by strong sulfuric acid hydrolysis possess negative charges. As for the selected viologen molecules, such as MV$^{2+}$, it is positively charged. The mixing of CNCs and MV$^{2+}$ lead to the aggregation and instability of the system because of electrostatic interaction. To obtain a stable mixture, KCl electrolyte was added to screen some charges and also be used for electrolyte for the following experiment. Therefore, MV$^{+}$ was premixed with KCl and then added into CNCs suspension to keep the final solution well dispersed. The zeta potentials data from Table S1 proves the good physical stability of these mixtures. Parts of viologen molecules bind on the surface of CNCs, which cause the particle size become bigger (see the data in Table S1).

Herein, two main factors should be considered. One is the concentration of CNCs, and the other is the structure of viologen molecules. Firstly, with a concentration of CNCs increasing from 15 mg/mL to 38 mg/mL, the three-component system (MV$^{2+}$/KCl/CNCs) kept stable as showed in Figure 1a. In general, a high-concentrated CNCs solution benefits the formation of intact free-standing film. So the substance of 38 mg/mL CNCs was selected to prepare the composite film in the following descriptions. Figure 1b showed the photos of pure CNCs and mixed solution containing different viologen molecules, which can keep stable state at least for two weeks. In addition, the BV$^{2+}$/KCl/CNCs mixed solution emerged yellow because of the nature color of BV$^{2+}$ molecules.

2.2. Electrochemical Behavior of Viologen/KCl/CNCs Aqueous Solution

The electrochemical behavior of viologens can be investigated by cyclic voltammogram (CV). Figure 2a showed a typical CV curve of MV$^{2+}$ in a 0.1 M KCl aqueous solution (red curve) including two coupled redox peaks for MV$^{2+}$. The first redox couple at $-0.71$ V ($I_{pa}$) and $-0.47$ V ($I_{pc}$) is correlated with the redox reaction between the colorless di-cationic species (MV$^{2+}$) and blue radical-cation (MV$^{+}$), respectively. The visible purple color is the result of color mixing of the blue MV$^{+}$ and red methyl viologen radical cation dimer in aqueous electrolyte solution. The second coupled redox peak at $-1.05$ V ($I_{pa}$) and $-0.74$ V ($I_{pc}$) is assigned to the electron-transfer reaction between the MV$^{+}$ and di-reduced species (MV$^{0}$). When CNCs was introduced into MV$^{2+}$ solution, a subtle change happens in its CV curve. As shown in Figure 2a black curve, MV$^{2+}$ still displays two coupled redox peaks but their potentials are different. Two reduction peaks shifted to negative potential, while the oxidation peaks shifted to positive potential. Such a change of peak potential is supposed to be related to the rate of charge transfer. And the enlargement of the coupled reduction/oxidation potential separation demonstrates that the reversibility of redox process (fast exchange of electrons with the surface of the electrode) of MV$^{2+}$ becomes a little worse. This phenomenon is attributed to the interaction of CNCs with viologen. However, such an interaction only has a limited influence in the electrochemical activity. For example, although the concentration of CNCs in mixed solution is increasing, the redox behavior of MV$^{2+}$ is almost not affected, as shown in Figure S2a. In addition, the relationship between scan rate and peak current was also studied in Figure S2b. With the increase of the scan rate, the peak currents increases accordingly and the peak potentials shift to more negative potentials.
of scan rate, all cathodic peak current and anodic peak current enhanced and the potential difference between cathodic peak and anodic peak changed from 68 mV to 190 mV. Scan rates in the range of 10–200 mV s^{-1} gave a straight line for the plot of peaks current (cathodic and anodic) verse the square root of the scan rate, as depicted in the inset of Figure S2b. It can be inferred that the electrochemical process was controlled by semi-infinite diffusion behavior and quasi-reversible from the linear relation.\cite{41,42}

Likewise, the other three viologens mixed solution systems were measured as presented in Figure S3. The addition of CNCs did not affect the electrochemical behavior of viologen strongly by evaluating the corresponding peak current and potential. However, the electrochemical behavior of viologen specie is dependent on its structure, especially the structure of substituent group. By comparing four viologen molecules, it was found that the cathodic peak potential gradually shifted to positive value in sequence of MV^{2+}, EV^{2+}, HV^{2+} as shown in Figure 2b. It is worth mentioning that the four viologen molecules show different colors at their radical-cation states. Such a difference provide us some inspiration for preparing variously colored electrochromic materials by a choice of viologen molecule with different substituent groups.\cite{43}

2.3. Structure and Morphology of Viologen/KCl/CNCs Films

Figure 3a presents a SEM image of surface morphology of pure CNCs film. The rod-like structure of CNCs is visible and lots of holes between CNCs nanorods are obvious. By comparison, the composite films emerged more network morphology and the size of rod structure became bigger (as shown in Figure 3b). It can be regarded because of the attachment of viologen molecules on the surface of CNCs rods due to some interactions. Such a structure makes ion diffusion easier and benefits the enhancement of electrochemical behavior of viologens.\cite{38} Besides, the stratified structure of composite film and many cavities can be clearly seen in Figure 3c and the corresponding EDX mapping of the nitrogen element in Figure 3d demonstrated the uniform distribution of MV^{2+} in composite film.

Figure 2. (a) CV curves of MV^{2+} and MV^{2+}/CNCs in KCl aqueous solution using ITO as working electrode. The inset is a photo of MV^{2+} solution taken at a potential of −0.8 V; (b) CV curves of four viologens/CNCs in KCl aqueous solution. Note: the scan rate is 0.1 V s^{-1}; the concentration of CNCs, viologen, KCl respectively are 38 mg/ml, 0.01 M, 0.1 M.

To verify the interaction between CNCs and viologen, FTIR spectra of CNCs, MV^{2+} and MV^{2+}/KCl/CNCs composite film were measured and presented in Fig. S4. The skeletal vibration of pyridine ring in 1506 cm^{-1}, 1560 cm^{-1}, 1636 cm^{-1} can be seen in MV^{2+} and MV^{2+}/KCl/CNCs composite film. Besides, the S–O vibration of CNCs in 887 cm^{-1} caused slightly red shift for the composite film. From the above results, we speculated that the nitrogen divalent ion of MV^{2+} absorbs on the surface of CNCs nanorod through the electrostatic interaction with the sulfate half-ester groups.

XPS is also an effective tool to measure the elemental composition, which exists in the form of chemical state and electronic state. This information are dependent on the combination and interaction of the relative elements with other species. Hence, to further figure out the interaction between CNCs and viologen in composite films, as-prepared composite films were characterized by XPS. Figure 4a showed the XPS spectra of MV^{2+} and MV^{2+}/KCl/CNCs films in all the region. A peak around 400.0 eV is attributed to N 1s spectrum of MV^{2+} (black curve) and it also can be observed in MV^{2+}/KCl/CNCs films (red curve).
This result means the presence of MV$^{2+}$ in composite films. In addition, a peak of S$_{2p}$ at 169.0 eV is kept in MV$^{2+}$/KCl/CNCs films (as shown in inset of Figure 4a), which is originated from sulfonate groups in CNCs by sulfuric acid hydrolysis. In Figure 4b, the C 1s fitting spectrum of MV$^{2+}$ shows two peaks at 284.6 eV and 286.0 eV corresponding to C–C/C=O and C–O–H bonds. As for the pure CNCs, its C 1s fitting spectrum displayed three peaks at 284.8 eV, 286.4 eV and 288.1 eV, which are ascribed to C–C, C–O–H and C–O–C bonds, respectively.$^{[44]}$ The MV$^{2+}$/CNCs composite films exhibits three peaks similar to that of pure CNCs. Simultaneously, the N 1s spectra of MV$^{2+}$ and composite films are fitted in Figure 4c and Figure 4d. The N 1s spectrum of MV$^{2+}$ sample can be fitted with two peaks assigned to the viologen radical cation due to X-ray excitation (399.8 eV) and the positively charged nitrogen (401.4 eV).$^{[45]}$ As for the composite films, the two peaks presented a positive shift to some extent where the N$^+$ peak shows near 0.8 eV-shift. This is a direct and obvious interaction evidence of MV$^{2+}$ and CNCs by N active sites. Another attention should be paid to the relative intensity of radical cation N$^+$ to the positively charged nitrogen N$^+$. Under X-ray excitation, O free radical will be produced in CNCs.$^{[41]}$ Owing to the higher electronegativity of O than N, O free radical probably interacts with CH$_3$ so as to enhance the intensity of radical cation N$^+$ in composite films. Although the above results proved the existence of interaction between MV$^{2+}$ and CNCs, the accurate interaction types (electrostatic, hydrogen bonding, or van der Waals force) can’t be determined exactly.

2.4. Electrochromic Properties of Viologen/KCl/CNCs Composite Films

As mentioned in the experimental section, viologen-based electrochromic devices involving CNCs and KCl were investigated using a two-electrode configuration (Scheme 1b). In contrast to a conventional two-electrode mode with liquid system, our as-designed electrochromic device adopted a wetted and integrated three-components film as a sandwiched layer between two electrode slides.

**Figure 4.** X-ray photoelectron spectrogram of the samples (a), C 1s (b), and N 1s (c, d) for MV$^{2+}$ and MV$^{2+}$/CNCs film.

**Scheme 1.** (a) Preparation process of free-standing viologen/KCl/CNCs composite film and structures of the three components; (b) assembly process of the above three-components composite film-based ECD.
This construction can be regarded as semi-solid-state electrochromic devices. Figure 5a displays photographs of original MV\textsuperscript{2+}/KCl/CNCs film and its colored state in an assembled device using ITO glass substrates. The following characterizations displayed in Figure 5 correspond to such an ITO glass/film/ITO glass assembled device. The reversible color changes during CV scanning were carried out at a potential range of 0 V to −2.9 V. When a voltage was applied from 0 V to −2.9 V, the MV\textsuperscript{2+}/KCl/CNCs film was gradually colored to the final purple. The detected coloring process was shown in Figure S5. The absorbance spectrum of viologen-based device in visible region was characterized at an applied potential of 0 V and −2.9 V. As for the colored composite film, the maximum absorption wavelength is around 545 nm corresponding to the blue radical cations in equilibrium with their red dimers (Figure S5).

To examine the switching behavior and repeatability of viologen/KCl/CNCs based devices, transmittance spectra at wavelength of 545 nm were recorded during repetitive potential changes (Figure 5c). The applied voltage of 0 V (bleached state) and −2.9 V (colored state) were alternated with an interval of 15 s for the MV\textsuperscript{2+}-ECDs to monitor the changes of transmittance. After ten color/bleaching cycles, it is visible that the redox stability of electrochromic devices is good and average transmittance variation (ΔT %) is 8.94 %. When the concentration of CNCs was changed, the maximum absorption wavelength of the composite film remained at approximately 545 nm. And the applied voltage value for coloring process was not affected by the content of CNCs in composite film. However, the optical contrast of the MV\textsuperscript{2+}-ECDs is dependent on the content of CNCs. As shown in Figure 5d, the optical contrast increased with the increase of CNCs content. Therefore, a 38 mg/ml CNCs solution was used to prepare viologen/CNCs films to meet the requirement of ECDs with fast switching time.

As for different viologen-based ECDs, their transmittance variations were different. As shown in Figure S6, it is clear that the transmittance variation of EV\textsuperscript{2+}-based ECDs is near 30 % and the transmittance variation of HV\textsuperscript{2+}-based and BV\textsuperscript{2+}-based ECDs is lower than 4 %. Moreover, the stability of HV\textsuperscript{2+}-based and BV\textsuperscript{2+}-based ECDs is far worse than MV\textsuperscript{2+}-based and EV\textsuperscript{2+}-based ECDs. The specific reason is indistinct, but this result gave a hint that the substituent group plays a crucial role in performing electrochromic behavior of viologen/KCl/CNCs films. It is observable that EV\textsuperscript{2+}-based ECDs own the optimal electrochromic property in four viologen-based ECDs.

The electrochromic behaviors of the other three viologen species based composite films were investigated by UV-vis spectra. Because of the various substituted groups in pyridine ring, the speed of electron propagation is different. Hence, the applied voltage and the color change in four viologen films ECDs are different. The corresponding voltage are −2.2 V, −2.3 V, −2.5 V and −2.9 V for BV\textsuperscript{2+}-ECDs, HV\textsuperscript{2+}-ECDs, EV\textsuperscript{2+}-ECDs and MV\textsuperscript{2+}-ECDs, respectively. As shown in Figure 6a, the absorption wavelength observed for MV\textsuperscript{2+}/CNCs, EV\textsuperscript{2+}/CNCs, HV\textsuperscript{2+}/CNCs, BV\textsuperscript{2+}/CNCs film were 545 nm (black line), 538 nm (blue line), 556 nm (purple line), 450 nm (red line) respectively and these values were chosen as monochromatic wavelengths for studying EC properties. The inset in Figure 6a presented the corresponding colored composite film. The color is purple, dark purple, brown red and green in sequence of CH\textsubscript{3}-, C\textsubscript{2}H\textsubscript{5}-, C\textsubscript{7}H\textsubscript{15}- and C\textsubscript{7}H\textsubscript{7}- substitute group. Figure 6b showed the coincidence relation between the applied potential and different colored viologen films. It displayed a possible application in multicolored electrochromic glass and rainbow-like devices.

The coloration/bleaching time extracted for a 90 % transmittance change are calculated to be 7.3 s/10 s, 9.7 s/11.4 s, 15.85 s/12.29 s and 14.09 s/18.95 s for MV\textsuperscript{2+}-ECDs, EV\textsuperscript{2+}-ECDs, HV\textsuperscript{2+}-ECDs and BV\textsuperscript{2+}-ECDs, respectively. From Figure 7, it indicated that MV\textsuperscript{2+} based ECDs have faster response time compared to the other viologen-based ECDs and previous report.[45,46]

Such a result is attributed to the natural structure of different viologen molecules. Long alkyl chain and aromatic...
viologen (the structure is similar to ionic liquids which is served process in a certain humidity as well as the existence of CNCs filtered film (red line). In other words, the cast-film (black line) exhibits the higher elongation at break than pure as assembled on PET with ITO.

Figure 8. (a) Typical stress-strain curves of CNCs filtered film and MV\textsuperscript{2+}/KCl/CNCs composite film; (b) photograph of a bent MV\textsuperscript{2+}/KCl/CNCs device assembled on PET with ITO.

2.5. Processability and Flexibility of Viologen/KCl/CNCs Composite Films

In view of the practical application, resistance against bending and anti-leakage are critical parameters in flexible ECDs. First, we examined the mechanical property of MV\textsuperscript{2+}/CNCs composite film as showed in Figure 8a. Such a MV\textsuperscript{2+}/CNCs cast film showed in Figure S7). Good coloration/discoloration process can be observed. This result also reflected the processability of composite film and designability of electrochromic pattern.

3. Conclusions

Flexible viologen-based three-components composite films have been fabricated and exhibited obvious electrochromic behavior. Adjustment of CNCs amount and substituent group of viologen can realize the control of electrochromic property of as-prepared ECDs. More addition of CNCs in composite films could enhance the optical contrast of viologen-based ECDs. Methyl viologen-based ECDs performed the shorter response time, while benzyl viologen-based ECDs owned the smaller driving voltage. The as-prepared composite films can be randomly cut into certain shape and be peeled off from electrode surface for reutilization. Considering the degradability of CNCs, viologen molecules are expected to be released from composite film for renewal. Operation of the whole viologen-based ECDs only depended on a few drops of KCl rather than organic solvent. Therefore, this work benefits a development of sustainable and environment-friendly viologen-based ECDs for the application in smart windows and optical displays.

Experimental Section

Materials

Cotton pulps with polymerization degree (DP) of 700 were provided by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China), which were the initial material. Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 98 wt%) and NaOH with analytical grade were obtained from Zhengye Reagent Company (Qingdao, China). Viologens (1-1’-dimethyl-4, 4’-bipyridinium dichloride, 1-1’-diethyl-4, 4’-bipyridinium dibromide, 1-1’-dihexyl-4, 4’-bipyridinium dibromine, 1-1’- dibenzyl-4, 4’-bipyridinium dibromide, respectively) were purchased from Aladdin Industrial Corporation.

Preparation of CNCs Suspension

CNCs were prepared from cotton pulps by sulfuric acid hydrolysis as common mineral acid mentioned in majority literatures.\textsuperscript{45–46} The pulps were broken into flocculent by grinder machine (JYS-M01) and then immersed into 4 wt% aqueous NaOH solution for 24 h at room temperature. The above soaked pulps were sufficiently washed with deionized water until neutral pH and then entirely dried in a vacuum oven. Afterwards, pretreated pulps were hydrolyzed in a 64 wt% sulfuric acid solution at 50 °C for 45 min. The reaction was prevented by diluting with tenfold deionized water. Let the suspension stand for 2 h and then got rid of the supernatant liquid. The subnatant liquid was centrifuged with 8000 rpm for 10 min and washed repeatedly until the pH was close to 2. Finally, the ivory suspension was placed inside dialysis bags (8000–14000 molecular weight cutoff) and dialyzed against deionized water for a week to reach neutral. The final concentration of CNCs suspension was controlled at 38 mg/mL by condensing.

Preparation of CNCs Suspension
Other CNCs solutions with a concentration of 15 mg/mL, 20 mg/mL, 25 mg/mL and 30 mg/mL were prepared by a dilution of 38 mg/mL stock solution. The AFM image and TEM profile of CNCs suspension, which were presented as Figure S1, account for CNCs nanorod is about 200 nm long and with a diameter of 5–10 nm and has good dispersity in water.

**Electrochemical Characterization in Solution**

The three electrodes (an ITO glass as working electrode, a platinum wire as counter electrode, a Ag/AgCl as reference electrode) were inserted in the mixed solutions exhibited in Figure 1b. And the electrochemical process was measured by cyclic voltammogram (CV).

**Preparation of Viologen/KCl/CNCs Composite Films**

Viologen/KCl/CNCs composite films were prepared by following steps. To begin with, 0.5 mL KCl (0.1 M) was added dropwise into 5 mL viologen solution (0.01 M) by pipette. Then 5 mL CNCs suspension was mixed with the above viologen/KCl aqueous solution thoroughly with tiny vortex mixing apparatus for 10 minutes at ambient temperature. Afterwards, the mixture was cast into a PS Petri-dish with a diameter of 3.5 cm in 23°C and 40–60% relative humidity. The total evaporation time was about 5 days. The mass ratio of each component (viologen: CNCs: KCl) were 1 : 1 : 0.1.

**Fabrication of the Electrochromic Device**

The indium-tin oxide (ITO) glass substrate was used as the conducting substrate for the viologen/KCl/CNCs composite film. It was rinsed with acetone and ethanol in ultrasonic-bath successively, and cleaned with deionized water repeatedly to remove impurities from the surface and then dried at 50°C.[30] The ECDS were fabricated by putting the adhesive tape on one ITO glass to form a seal rectangular box, and then putting the composite film into sealing zone. A few drops of KCl were dripped on the film. Another corresponding ITO glass was laid on top of adhesive agent. The real active areas of the films were 0.8 x 1.2 cm. To obtain a flexible ECDS, a flexible substrate, polyethylene terephthalate (PET-ITO) was used. The preparation procedures of electrochromic device were depicted in Scheme 1b.[31]

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**Conflict of Interest**

The authors declare no conflict of interest.

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