The thin and flexible triple-layered electrochromic device based on the multifunctional hydrogel

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Abstract. Electrochromic devices (ECDs) are widely used in smart color changing windows, automotive anti-glabre rear-view mirrors and electronic wearable devices owing to their controllable for colouration, reduced energy consumption and modulated incident light. Traditional ECDs composed of complicated configurations, commonly five layers of structure, extremely increased the complexity of structure and fabrication process, especially cut down the performance of the device. In this paper, the introduction of hydrogel (The transmittance in the visible light spectrum reached up to 95%), both acted as the conductive layer and the dielectric layer, simplified the structure of the device to a triple-layered one. Flexible electronic products require good flexibility of conductive materials, so we introduced flexible Indium tin oxide (ITO) as the transparent conductive substrate, which have excellent bending properties, the sheet resistance increased only from 12.6 $\Omega$ sq to 31.4 $\Omega$ sq, after 2500 bending cycles. The assembled ECD has a slight transmittance attenuation ($\Delta T_e/\Delta T_0=7\%$) after 1500 bending cycles. Importantly, the device showing excellent cycling performance, has just 2% attenuation of transmittance at wavelength of 640 nm, after 1000 cycles ($\Delta T$ changes from 32% to 30%), which also has a fast coloration and bleaching time, respectively 3 and 4.7 seconds. Compared with five layered structure, three layered ECDs show prominent advantages, accelerating the development of simple structure electrochromic applications in the future.

1. Introduction
In recent years, with the aggravation of resource consumption and environmental pollution, more and more attention has been directed towards the exploitation of new energy and the reduction of energy consumption. Through the world, a large amount of energy is consumed by buildings every year [1], including air conditioning and indoor lighting, etc., electrochromic windows can artificially change the incident light transmittance, so influence the heat entering the room, thereby reduce the electrical consumption of air conditioning and indoor lighting [2-3]. It will be of great significance to develop a high-performance electrochromic window. ECDs are widely used in displays [4-5], smart windows [6-9], sensors [10], electronic tags [11], anti-glare rearview mirrors and adaptive camouflages [12-15]. Electrochromic materials largely determined the ECDs performance. Currently, tungsten trioxide is a kind of relatively mature electrochromic material for smart windows, which has a high resistance and a long response time (15s-50s) as an inorganic semiconductor material, but its contrast ratio can reach a
very high level ($\Delta T$ over 70%) [16-18]. Commonly used organic electrochromic materials include polyaniline, polypyrrole, polythiophene, etc. [19-23], they tend to have a very fast response speed, which is easily destroyed by ultraviolet light, causing the shorter cycle life. Polythiophenes are wildly used in EC materials for their advantages of easy electrochemical synthesis, processability, and aesthetically pleased color changes between redox states [24-25]. 3,4-ethylenedioxythiophene (EDOT) as an electron-donating heterocyclic unit shows brilliant electrons transfer after the polyreaction, optimizing the absorption of polymer. Yassin et al. [26] reported the preparation of terminal electropolymerizable EDOT-thiophene groups and the corresponding polymers showed excellent conductivity and good optical properties at medium voltages. PEDOT: PSS is widely used in ECDs for its excellent electrical conductivity and chemical stability [27-28].

Electrochromic devices continuously develop towards low power, light weight, transparency, and deformability. The flexibility of ECDs mainly depends on the materials of conductive substrates and electrolytes. Silver nanowire is used as the conductive substrate, in which the conductivity for high transmittance is lower and it’s easily suffered with oxidation of air, at the transmittance of 80%-90% among visible light spectrum, sheet resistance of silver nanowires is about 30 - 500 $\Omega$/sq [29-30]. Using carbon nanotubes and graphene for conductive bases, have a sheet resistance about 100-1000 $\Omega$/sq, at the transmittance of 80% - 90% [31]. For the reason of the inherent brittleness of carbon materials, the substrate is easy to crack after bending and causing the reducing of electrical conductivity [32]. Because the conductive material evenly distributed in the surface, the flexible ITO have relatively lower sheet resistance about 12.6 $\Omega$/sq. Using a PET substrate ensures that the ECD has good flexibility and transparency, although the sheet resistance increases to 31.4 $\Omega$/sq after bending 2500 times, which has a lower sheet resistance than the carbon nanotube or graphene conductive substrates at the same transmittance [33]. Liquid electrolytes are widely used in electrochromic devices because of their good ion mobility [34]. However, liquid electrolytes have problems of hard to packaging and possible dissolving of electrochromic materials. Solid electrolytes are easier to encapsulate in devices, but ion mobility is much lower for solid electrolytes [35]. The gel electrolyte has good ion mobility, and also solves the problem of packaging difficulty. The gel electrolyte has good transmittance (~95%) and good deformability, which will be beneficial for fabrication of flexible electrochromic devices [36]. Traditional five-layered ECDs having excellent capacitive property can maintain the colored states for a long time after electric power-off, while the complicated construction increased the making complexity. Myoung et. al. reported the single-layered EC gel to achieve multiple colored displays. Missing the symmetrical capacitance structure causing the difficulty of keeping the display state for a long time [37]. The triple-layered ECD based on hydrogel possesses capacitive property maintaining the continuous working state and simple construction reducing the structural complexity.

In this work, the five-layered electrochromic device is changed into a three-layered one by introducing a hydrogel, which reduces the complexity of the device and the manufacturing process. Meanwhile the performance of the device is greatly improved, the introduction of the hydrogel solves the problem that the liquid electrolyte is difficult to encapsulate and the solid electrolyte has low ion mobility. Using of flexible ITO as a conductive substrate allows the ECDs to be applied in wearable electronic products, which greatly expands the field of application.

2. Experimental

2.1. Synthesis of PMMA hydrogel
2.3 g AAM (acrylamide, biological reagent with 98% purity) was added into 15ml deionized water and magnetically stirred for 30 minutes. Then 4.3 g LiClO$_4$ (lithium perchlorate, biological reagent with 98% purity) was added and stirred on the magnetic stirrer for 30 minutes. Then 8.2 mg AP (ammonium persulfate, biological reagent with 98% purity) was added and stirred until completely dissolved. Then 7.8 mg MBAA (methylene double acrylamide, biological reagent with 98% purity) was added and stirred until completely dissolved, the mixture solution was put into the vacuum drying oven for 2 hours,
removed the oxygen inside the solution, 3 mg TEMED (tetramethyl ethylenediamine) was added and stirred for 5 minutes.

2.2. Preparation of the PEDOT: PSS layer
Flexible ITO was firstly cut into 3 x 4 cm size, and cleaned with ethanol and deionized water respectively, then the processed ITO was cleaned by plasma cleaning machine with oxygen for 2 minutes to improve surface hydrophilicity, after that PEDOT: PSS was evenly coated on the surface of cutting flexible ITO rotating at 3000 rpm for 40 s, finally dry on the hot plate 120 °C for 20 minutes, and repeating the above procedure for three times.

2.3. Preparation of the ECD
Prepared hydrogel was coated on the surfaces of flexible ITO which be coated with PEODT: PSS with a dropper, curing on the hot plate in 60 °C for 30 minutes, finally, an electrochromic device is obtained.

3. Results and discussion
Materials with different valences often correspond to different colors, and the materials are used to make the ECDs, which have a multi-layered structure and has different functions. The applied voltage controls the oxidation-reduction reaction of the electrochromic material, thereby controlling the coloration and bleaching process of the device. As shown in Figure 1a, the three-layer ECD consists of an ITO conductive layer, the PEDOT: PSS electrochromic layer, and the hydrogel layer. The ITO is connected to the negative electrode of the electrical power supply, the gel layer is connected to the positive electrode, and the electron is obtained on the negative electrode. In the PEDOT: PSS electrochromic layer, the reduction reaction occurs, and the cation moves toward the negative electrode, and injected in the PEDOT: PSS electrochromic layer. The PEDOT: PSS layer simultaneously obtains electron and metal lithium ions, and accompanied with color-changing, where the color changes from a transparent state to deep blue. The chemical reaction formula is described as follow: PEDOT^{m+}/(PSS^{m-})+ne^-+nLi^+ → PEDOT^{m-n}/(PSS^{m-})Lin^+

![Figure 1. The structure schematic diagram and optical properties of the three-layer ECD. (a) the coloration progress of the ECD; (b) the bleaching progress of the ECD; (c) the transmittance of the components in the ECD at wavelength spectrum of 400 - 800 nm; (d) Physical photos of the components in the device.](image-url)
The ITO conductive layer is connected to the positive pole of the power supply, and the hydrogel layer is connected to the negative pole of the power supply. PEDOT: PSS electrochromic layer loses electrons due to oxidation reaction when it is connected to the positive pole. Metal cations on the surface of the PEDOT: PSS layer move towards the negative pole under the force of the electric field. Electrons and lithium ions are simultaneously extracted from the PEDOT: PSS, caused the color changing from dark blue to transparent state, the chemical reaction happens from right to left in the formula, as shown in Figure 1b. Thus, under the alternating applied voltage, the electrochromic device shows the corresponding change of coloration and bleaching state, and realizing the modulation of visible light transmittance in smart windows. Electrochromic windows require high transmittance of devices to ensure sufficient visible light transmission in the transparent state, so the higher the transmittance of each layer of electrochromic devices, the property will be better. As shown in Figure 1c, hydrogel with a transmittance up to 95% have little loss of visible light, so they have great advantages for ECDs. At the same time, the main components of the hydrogel are water, a kind of weak electrolyte to a certain extent, which can increase the electrical conductivity of electrolyte layer. As shown in Figure 1 d (iii), hydrogel has good electrical conductivity, under an external electrical power connection, the LED bulb could be light. Especially, hydrogel is highly flexible, which can be bend and stretched dramatically, ensuring that be used in flexible transparent ECDs. As the conductive substrate of flexible ECDs, flexible ITO plays the role of supporting the whole device. Its transmittance at the wavelength of 640 nm is 75%, and the transmittance of assembled electrochromic devices at the wavelength of 640 nm is 52%. This is because the PEDOT: PSS electrochromic layer has a color residue after film formation, resulting in a decrease in the transmittance of the device.

Figure 2. The electrochromic properties of the three layered flexible ECD. (a) at wavelength spectrum of 400 -800 nm, the transmittance of the device under applied voltages of 0 V, -0.5 V, -1 V, -1.5 V, -2 V, respectively; (b) the physical photos of the ECD under different voltages; (c) the respond time of the ECD; (d) Optical modulation curve of the ECD under applied voltages.
The ECD has different contrast changes for different applied voltages. As the voltage increases, the contrast gradually increases. As shown in Figure 2a, the transmittance of the ECD at voltage of 0 V, -0.5 V, -1 V, -1.5 V, -2 V were given. At a voltage of -0.5 V, the transmittance of the ECD at the wavelength of 640 nm is 18.3%, at a voltage of -2 V, the contrast at a wavelength of 640 nm is 37.2%. As shown in Figure 2b, the corresponding physical photos at 0 V, -0.5 V, -1 V, and -2 V are given. We can see that there is maximum contrast at -2 V. As shown in Figure 2c, under the applied voltages of 2 V and -2 V, the cycle curve of the ECD is obtained. From one of the cycle curves, we can see that the ECD has a fast response speed and the coloration time is 3 s, the bleaching time is 4.7 s, in which the fast response speed can satisfy the use of some e-readers and smart windows, but still cannot meet the requirements of display such as computer or mobile phones. As shown in Figure 2d, the cycle within 120 s shows that the ECD has stable electrochromic performance, without obvious transmittance attenuation, and a contrast ratio of 35%. The stable cycle performance ensures that the ECD has a longer service life.

Figure 3. The bending performance of the three layered flexible ECD. (a) at wavelength spectrum of 400 - 800 nm, the transmittance of the ECD after bending from 0 to 1500 times; (b) at wavelength of 640 nm, the optical modulation of the ECD with the increase of the bending times; (c) the function curve between of the contract and the bending times; (d) the photos of the flexible ECD in colored and bleached state; (e) cyclic voltammograms of the ECD at a scan rate of 100 mVs⁻¹ in the potential range of 0 – 1.5 V vs. Ag/AgCl. (f) the optical performance of the ECD in initial and leave for 24 h.

The flexible ECDs have certain requirements for their bendability, and the performance will not be greatly attenuated after a certain number of bends. As shown in Figure 3a, the corresponding bleached state transmittance and the colored state transmittance after bending 500, 1000, and 1500 times in the visible spectrum range of 400-800 nm are shown. With the maximum contrast, as the number of bends increases, the transmittance of the colored state gradually increases, the transmittance of the bleached state is slightly attenuated, and the overall contrast is gradually reduced. As shown in Figure 3b, a transmittance modulation curve of an electrochromic device applying an applied voltage of plus or minus 2 V at a wavelength of 640 nm is given, and the device has the lowest color-state transmittance before bending, with the bending times increased, having the maximum transmittance of the colored state after bending 1500 times, with the smallest contrast. As shown in Figure 3c, the contrast before bending is 29.33%, the contrast is 25.13% after bending 1500 times, and the contrast is attenuated by 14.3%. As the number of bending increases, the main reason for the contrast decay of ECDs is because the electrical resistance of the flexible ITO conductive substrate gradually increases with the increase of
the number of bending times, resulting in poor electrical conductivity of the device as a whole, and the performance is degraded to some extent. Another important reason is that the discoloration material is separated from the flexible ITO due to the bending. Color changing process cannot occur, resulting in the decrease in overall contrast. Figure 3d shows the photos in coloration and transparent states of the device in bending. The electrochemical and electrochromic performances of the PEDOT: PSS film on the flexible ITO were evaluated in the three-electrode electrochemical cell. Figure 3e shows the typical CV curves of the PEDOT: PSS films on the flexible ITO measured at a scan rate of 100 mVs\(^{-1}\) in the potential region of 0 – 1.5 V (vs. Ag/AgCl). It shows that redox reactions and a reversible coloration–bleaching process can be achieved among this potential region. Because of the volatility of hydrogel mainly composed of water, the optical and electrochemical performances of the ECD will be affected. Figure 3f shows the optical modulation of the ECD at spectrum of 640 nm in initial state and leaving for 24 h, which indicated that the contrast of the ECD slightly decreased.

Figure 4. The cyclic property of the three layered flexible ECD. (a) the 1000 cycles of the ECD; (b) the function curve between the contract and the cycle number; (c) plot of the optical density as a function of the injected charge density. The coloration efficiency (\(\eta\)) was extracted from a fitted slope in the linear regime of the plot.

Cyclic stability is one of the important indicators to measure the performance of ECDs. The higher the number of cycles, the longer the service life of ECDs, which can be applied to actual smart windows and mobile display devices. As shown in Figure 4a, 1000 cycles of a three-layer ECD are given, with a voltage of 2 V and a negative 2 V. We can see that as the number of cycles is from 1 to 1000, there is no large change in the transmittance of the transparent state, and the transmittance of the colored state slightly increases. As shown in Figure 4b, in the 1-1000 cycles, the bleached state is changeless. The over-rate was attenuated from 44.12\% to 43.57\%, and the attenuation was 1.72\%. The color-state transmittance increased from 16.22\% to 17.62\%, an increase of 8.63\%. The overall contrast was attenuated from 27.9\% to 25.95\%, attenuating by almost 7\%. After 1000 cycles, the contrast of the
electrochromic device was attenuated by 7% indicating a better cycle stability. A high $\eta$ indicates that, at low charge injection, optical modulation is large. The $\eta$ can be estimated from a fitted slope in the linear regime of a $\Delta$OD versus $\Delta$Q plot. The $\eta$ of the triple-layered ECD was 38.92 cm$^2$/C, as shown in Figure 4c.

4. Conclusions
Compared to five-layered ECDs, a hydrogel-based three-layered ECD, where the hydrogel acts as a dielectric layer and a transparent conductive layer, greatly reduces device complexity and process flow. The hydrogel is between the liquid and the solid, which ensures that it has excellent conductivity of the liquid electrolyte and has the characteristics of easy packaging of the solid electrolyte, which makes the ECD has excellent electrical and chemical performance. By using flexible ITO as a conductive substrate, and a flexible ECD assembled with a hydrogel has good flexibility, the contrast change was attenuated from 29.33% to 25.13% after bending for 1500 times, and the attenuation was relatively small. Meanwhile, the ECD has good cycle stability. After 1000 cycles, the contrast decays from 27.9% to 25.95%, attenuating by almost 7%. In general, hydrogel-based ECDs with good bending properties, cycle stability and simple structure offer more possibilities for the development of electrochromism in the future.

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