

# High-performance embedded nickel grid electrodes for fast-response and bendable all-solid PEDOT: PSS electrochromic devices

Cheng Chen<sup>a</sup>, Yan-Hua Liu<sup>a,\*\*</sup>, Ming Zhu<sup>a</sup>, Shi-Qing Zhao<sup>a</sup>, Wen-Wen Xu<sup>a</sup>, Linsen Chen<sup>a</sup>, Wenbin Huang<sup>a,b,\*</sup>

<sup>a</sup> School of Optoelectronic Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, 215006, China

<sup>b</sup> State Key Lab of Applied Optics, Changchun Institute of Applied Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin, 130033, China

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## ABSTRACT

Electrochromic devices are emerging as a futuristic technology for flexible electronics with the practical application values in energy-saving, displaying and military camouflage, however, the limitations in the optical, electrical and mechanical properties of the existing transparent conducting electrodes (TCEs) appear as a major obstacle for realizing high performance flexible electrochromic devices. In this work, we have proposed and demonstrated a fast-response and bendable polymer poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT: PSS) electrochromic device based on the embedded nickel (Ni) grid electrode. The Ni grid electrode, fabricated through patterned electroplating, has low sheet resistance ( $\sim 1.3 \Omega/\text{sq}$ ), high transparency ( $\sim 80\%$ ), excellent mechanical reliability and long-term chemical stability, exhibiting a figure of merit of 1250, surpassing the most existing TCEs. In addition, we have proposed a compact electrochromic architecture with the electrochromic PEDOT: PSS layer and solid polymer electrolyte being sandwiched between two embedded Ni grid electrodes. The device shows a short coloration and bleaching time ( $\sim 1 \text{ s}$  for 90% optical contrast), a high coloration efficiency ( $325 \text{ cm}^2/\text{C}$ ) and excellent mechanical reliability (optical contrast retention  $\sim 80\%$  after 1000 bending circles), paving a way for high performance flexible electronics.

## 1. Introduction

Electrochromic devices (ECDs), exhibiting a reversible color change when the material is oxidized or reduced, need low power consumption for operation due to low potential requirements and the optical memory effect [1]. They have been employed in diverse practical applications including smart windows, ant glare mirrors, and information displays, where modulation of optical absorbance, transmittance or scattering by means of an external voltage is desirable [2,3]. Early studies focused on inorganic electrochromism such as transition metal oxides [4], which suffered from compatibility, processing, and performance problems. Recently, EC research has focused heavily on conjugated polymer films [5] which offer the benefits of good processability, volume production capability, vivid color performance, high coloration efficiency and fast switching time, broadening the applicability in devices such as large area displays, signs, and optical filters [6]. Among them, PEDOT:PSS has

attracted special attentions due to the reasons including ease of preparation by oxidative chemical or electrochemical polymerization, well-defined polymer backbone structure with little defects, high electrochemical stability and high optical contrast between the doped and undoped states [7–9].

A common PEDOT:PSS ECD consisted of a thin PEDOT:PSS layer, an ion conducting layer and a polymer electrolyte layer being sandwiched between two TCE layers [10]. A number of efforts are being devoted to improving the working properties such as the switching speed, mechanical flexibility and bendability, by optimizing the materials, the working architecture and the TCEs. It is shown that subsecond switching with a transmittance contrast approaching 70% could be achieved by increasing the size of the alkylenedioxy ring or varying the substitutions at the PEDOT:PSS ring [11–15]. The EC performance improvement may also be done by the blending of the PEDOT:PSS electrochemical material with another conjugated polymer through electrochemical

\* Corresponding author. School of Optoelectronic Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, 215006, China.

\*\* Corresponding author.

E-mail addresses: [yhliu@suda.edu.cn](mailto:yhliu@suda.edu.cn) (Y.-H. Liu), [wbhuang@suda.edu.cn](mailto:wbhuang@suda.edu.cn) (W. Huang).

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polymerization [16] or with inorganic nanoparticles [17,18], albeit with little success probably due to the incompatibility among different materials. On the other hand, the ion conductivity of the solid polymer electrolyte could be improved via the addition of low molecular weight organic solvents or ionic liquid [19,20], and a fast bleaching time between 0.7 s and 3.8 s was demonstrated by varying the material system including the salt, the plasticizer and the polymer host [21–23]. As for the working structure, a simple device architecture consists of two conductive and electrochromic PEDOT:PSS polymer layers and one electrolyte layer is demonstrated to provide easy fabrication and good flexibility, which shows slow bleaching and coloring time of 20 s and 16 s, respectively [24]. Ionic self-assembled multilayers of alternating conjugated polymers are shown to provide ultra-fast coloration time around 100 ms, probably due to the ultra-fast ionic motion in such thin binary EC layers with high diffusion coefficients [25,26]. However, common indium doped tin oxide (ITO), with high sheet resistance, low mechanical stability and conformal deposition difficulty, has been widely used as the electrode material in these devices, exhibiting difficulties in realizing portable, stretchable, and flexible devices for numerous flexible electronic applications.

The desire for the exploitation of ECDs for flexible electronics drives intense research interest for high performance electrodes, which should simultaneously possess high optical transparency, high electrical conductivity, good chemical resistance, excellent thermal stability and long-term mechanical durability. To this regard, several attempts have been carried out, for example, the conjugated polymer PEDOT:PSS was directly employed as the flexible transparent electrode for ECDs, and a slow switching time to reach 90% of the optical contrast around 10 s is demonstrated, probably due to the low conductivity of the organic material [24,27]. A stretchable electrochromic PEDOT:PSS device was demonstrated using wrinkled graphene as the transparent electrode. The switching time for the device was around 5 s and retained the switching contrast at 15% uniaxial strain conditions, however, a high voltage of 15 V is required due to the high sheet resistance [28]. The Ag nanowire network with intrinsically good conductivity and mechanical compliance has been successfully transferred onto the polyethylene terephthalate (PET) substrates and adopted as the conductive layer to demonstrate large-area and flexible PEDOT:PSS ECDs with a comparatively fast response time around 4 s [29]. However, the Ag nanowire is electrochemically unstable and prone to oxidation, and additional processing procedures such as UV or thermal sintering and overcoating a protective layer are often required [30,31]. Recently, the metal grid with advantages of high transparency, conductivity and flexibility, is emerging as the high performance TCE to build flexible ECDs, where the grid pattern works as a highly conducting path for electrons and a polymer conducting layer was used to solve the blooming effect caused by the uneven electric-field in the metal grid. Silver metal grids from flexographic printing and confined filling of nanoparticles [32,33] and gold metal grids from patterned etching [34] were successfully utilized to construct flexible PEDOT ECDs, showing a fast switching time around 1 s. However, the metal grid has low durability as a result of the metal decomposition during doping and undoping of PEDOT, and has to be protected by an additional passivation layer such as the graphene oxide [35] to prevent metal oxidation and corrosion, exhibiting fabrication complexity and long-term performance issues. As a result, novel metal grids with volume manufacturing, good optical transmittance, excellent conducting properties and high stability are in urgent demand for building fast-response and flexible ECDs.

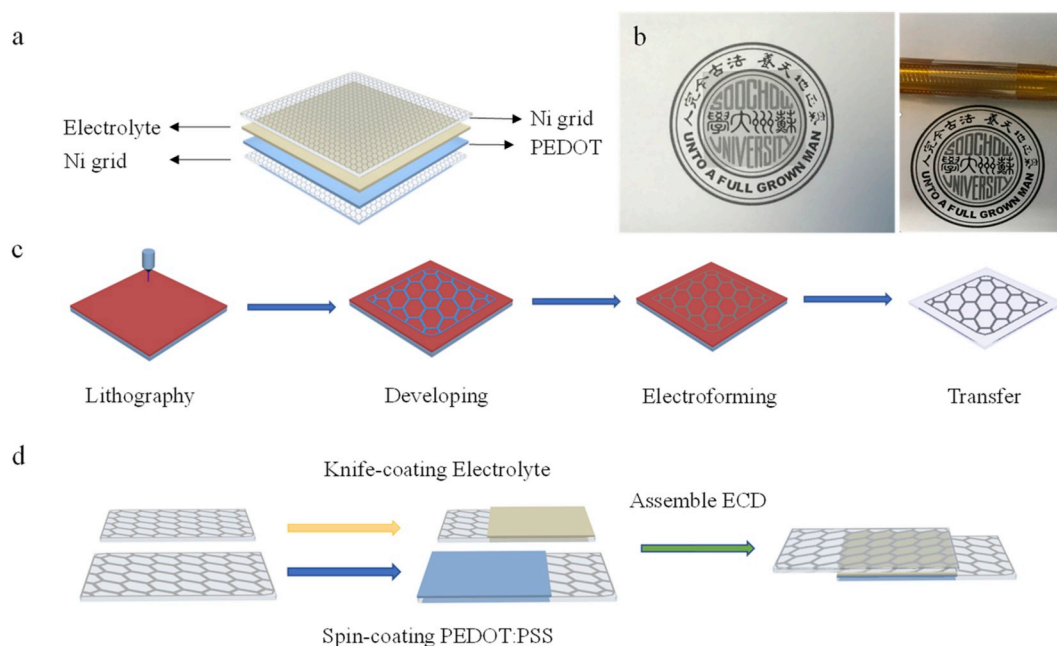
In this work, we have proposed and demonstrated the potential of the embedded Ni grid electrode for the construction of fast-response and bendable PEDOT:PSS electrochromic device in a very simplified architecture. The embedded Ni grid electrode was obtained via the confined electroplating process with volume production capacity and shows electrical properties comparable to bulk metals while preserving excellent mechanical reliability. The chemically stable Ni grid electrode also exhibits a very high optical transmittance, implying an extremely high

figure of merit of 1250, surpassing the present TCEs used in ECDs. The revealed device shows high performance in terms of the switching time, the optical contrast, the coloration efficiency and the cyclical operation stability. In addition, the unique embedded grid structures have good mechanical properties without the issue of delamination, resulting in ECDs with high bendability for future flexible electronics.

## 2. Experimental details

In order to optimize the fabrication process and improve the device mechanical reliability, we have proposed and adopted a simplified working structure as shown in Fig. 1(a). The electrochromic device is consisted of the PEDOT:PSS layer and the polymer electrolyte layer being sandwiched between two Ni grid electrodes. The highly conductive and flexible Ni grid electrodes work as the reliable metal motif for efficient electron collection and transmission. As for the thin PEDOT:PSS layer, it not only undergoes reversible oxidative and reduced reactions with the double injection and extraction of ions and electrons for color manipulation, but also homogenizes the electric-field distribution across the film for uniform coloration. We have further adopted the polymer electrolyte containing tetra-n-butylammonium hexafluorophosphate (TBAPF6) for both effective ion transportation and counterbalancing the ion concentration during coloration processes. The embedded Ni grid electrode is fabricated by a scalable fabrication process (Fig. 1(c)). Firstly, microstructures of periodic hexagons (with a line width of 6.5  $\mu\text{m}$  and a side length of 58  $\mu\text{m}$ ) were patterned by the laser direct write technique into the photoresist (6  $\mu\text{m}$ ) on an ITO glass substrate, which leaves the trenches at the exposed regions after development. Then the sample was placed in a plating station (China Electronics Technology Group Corporation, DDT-3), where the Ni plating solution was composed of 4 g  $\text{Ni}(\text{SO}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$ , 0.6 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.3 g  $\text{HBO}_3$  and 150 mL distilled water in an unchanged pH environment of 4.0. Ni was electrodeposited at the conductive regions in the photoresist trenches at a constant cathode current density of 0.5  $\text{A}/\text{cm}^2$ , where the Ni grid electrode thickness can be controlled by the electrodeposition time, thereby adjusting the electrical properties without affecting the optical transmittance. After electrodeposition, the photoresist was removed which leaves the bare Ni grid electrode on the ITO glass. Then the UV-curable resin was drop-casted onto the substrate, followed by fixing a PET substrate (thickness 25  $\mu\text{m}$ ) onto the UV resin through a roll-to-roll process. Finally, the resin was cured under UV light (1000  $\text{mW}/\text{cm}^2$ , Led Lamplic) for 15 s and the PET was peeled off from the ITO substrate with the Ni grid embedded in the cured resin on it. The optical transmittance and mechanical flexibility properties of the resulted Ni grid electrode was initially verified in the images, where the clearly visible logo “Soochow University” beneath the electrode indicate its high optical transmittance (Fig. 1(b)). Fig. 1(b) further shows another example of the electrode film being conformably attached to a ball pen, further demonstrating its flexible mechanical behaviors and good optical transmittance properties.

The ECD was assembled using the procedure in Fig. 1(d). The Ni grid embedded in the PET substrate was treated with oxygen plasma for 15 s to improve the interface compatibility for further film deposition. By comparing the resistance of the electrode before and after treatment with oxygen plasma, it is found that the sheet resistance of the embedded PET/Ni grid electrode hardly changes, indicating the high stability of the Ni grid electrode. The purified PEDOT:PSS solution (Heraeus) was mixed with 7 wt% ethylene glycol and 0.25 wt% surfactant (Triton-X 100, Shanghai Aladdin Biochem) and was spin-coated onto one grid electrode at 3000 rpm for 60 s and annealed at 100  $^\circ\text{C}$  for 20 min in ambient air conditions. As for the fabrication of the polymer electrolyte, the electrolyte solution which consists of the polymer host PMMA, the salt TBAPF6 (Alfa Aesar), the plasticizer propylene carbonate (Shanghai Aladdin Biochem) and the solvent acetonitrile (Shanghai Aladdin Biochem) in weight ratios of 6: 2: 9: 20 was mechanically stirred at 45  $^\circ\text{C}$  for 4 h, and was blade-coated onto the

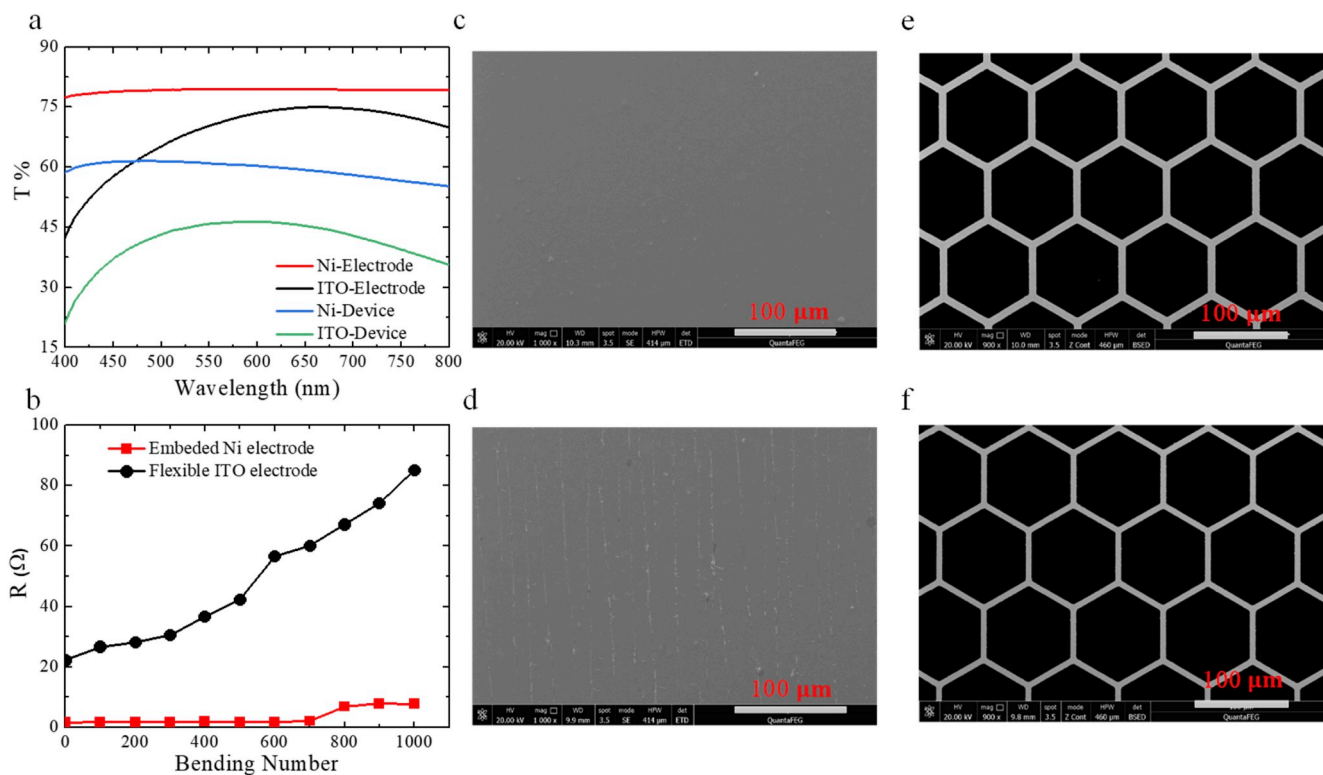


**Fig. 1.** (a) Illustration of the simplified ECD with the PEDOT: PSS film and the polymer electrolyte layer being sandwiched between two embedded Ni TCs. (b) Images demonstrating the excellent transparency and flexibility of the embedded Ni TCs. (c) Illustration of the scalable fabrication process for the embedded Ni transparent electrode including the photolithography, developing, electroplating and grid transferring steps. (d) Illustration of the device fabrication process including the coating of the electrochromic layer and the polymer electrolyte on opposite TCs and device assembling.

second PET substrate with the embedded Ni electrode for four times to yield an electrolyte thickness of 200  $\mu\text{m}$ . The two electrodes with corresponding PEDOT: PSS layer and electrolyte layer were laminated together using a sealing machine and stored in ambient conditions for 5 h to evaporate the residue solvent. For a direct performance

comparison, same electrochromic devices were constructed on commercially available PET ITO electrodes.

The surface morphology of the Ni grid electrode was carried out with the field emission scanning electron microscopy (SEM) (JEOL, JSM-5400, USA). The electrical properties of the electroplated Ni grid



**Fig. 2.** (a) Optical transmittance of the embedded PET/Ni grid electrode, the PET/ITO electrode and the resulted devices fabricated from them at the bleaching state. (b) Electric resistance as a function of the bending number for the embedded PET/Ni grid electrode and the PET/ITO electrode. The SEM images of the ITO surface on the PET (c) before and (d) after a bending number of 1000. The SEM images of the Ni grid (e) before and (f) after a bending number of 1000.

electrodes were measured by a four-point probe (CMT SR2000, A. I. T.). Electrochromic properties were measured on a UV-VIS spectrophotometer (SPECORD 210 PLUS, Analytikjena) under the aid of the electrochemical workstation (CHI 760E, Shanghai CH Instrument).

### 3. Results and discussions

In order to ensure the color contrast of the ECD between the coloring and bleaching states, the optical transmittance superiority of the conducting electrode is very important. The simple four-layered working structure could decrease optical loss to a great extent and has much better mechanical stability under repeatedly bending circles when compared with the common five-layered one due to the conformal and robust contact among the three functional layers, thereby ensuring satisfying optical and mechanical performance. The transmittance spectra in the visible spectrum for the Ni grid electrode, the PET/ITO and the resulted ECDs are shown in Fig. 2(a). The embedded Ni grid electrode exhibits a high optical transmittance ( $\sim 80\%$ ) in the whole visible spectrum and it should also be noted that the main optical loss was caused by the reflection and absorption of the PET substrate, considering the Ni grid network only takes 4% of the whole PET/Ni grid electrode area. For comparison, the PET/ITO shows a significant decrease in transmittance, probably due to absorption of the thick ITO layer for effective electron conducting and the incompatibility between the inorganic ITO and the organic PET substrate for conformal deposition. As for the ECDs constructed from the two electrodes, they exhibit a decrease of the transmittance from 5% to 20% compared to their corresponding electrode, depending on the absorption band of the PEDOT: PSS in the reduced state. As the ionic mobility depends on the electric field between electrodes, it is desirable to use electrodes with high conductivity to achieve a fast response time and color modulation. The sheet resistance of the embedded Ni grid electrode is  $1.33 \Omega/\text{sq}$  while that of the PET/ITO is  $13.2 \Omega/\text{sq}$ , indicating a much higher figure of merit of 1250, obviously much more advantageous for fabricating high performance ECDs. In addition, the electric resistance as a function of bending cycles for the embedded PET/Ni grid electrode and the PET/ITO film in Fig. 2(b) implies that the conducting properties of former one is quite stable over a bending number of 1000 at bending radius of 0.5 cm, further demonstrating the suitability of the embedded grid electrode for flexible ECDs. The abrupt difference of the two electrodes in the bending performance would be further explained in terms of the surface morphology (Fig. 2(c), (d), (e) and (f)). It is clear that cracks appeared on the ITO surface at a number of bending cycles while the honeycomb patterned Ni grid shows no degradation in morphological appearance, due to the ultra-thin and ultra-fine characteristics of these metal wires and the embedded nature of the metal grid, giving rise to ultra-high mechanical robustness for flexible electrochromic devices.

The excellent performance of the embedded Ni electrode in both optical and electrical characteristics is beneficial for the realization of the high-performance flexible ECD. However, the grid nature of the embedded Ni electrode would lead to a non-uniform electric-field distribution which makes the coloring and bleaching procedures in the electrochromic layer near the metal grids faster, while in our device, the electrochromic material PEDOT: PSS is conductive which is beneficial for uniform device coloration. For those electrochromic materials which are nonconductive, we can use composite electrodes, such as spin-coating silver wires on the Ni grid electrode, to obtain a uniform electric-field distribution for coloration, in which the blank areas of the Ni grid electrode could be nicely bridged together. In addition, the four-layered working structure with the polymer electrolyte for both ion storage and ion transportation not only simplifies the fabrication procedure, but also ensures satisfying properties with regard to mechanical reliability and optical contrast. When a negative (positive) voltage is applied between the two electrodes, an electric-field is formed, which will drive the charge in (out) of the PEDOT: PSS film. This flow of charge across the electrolyte triggers an electrochemical redox reaction in the PEDOT: PSS

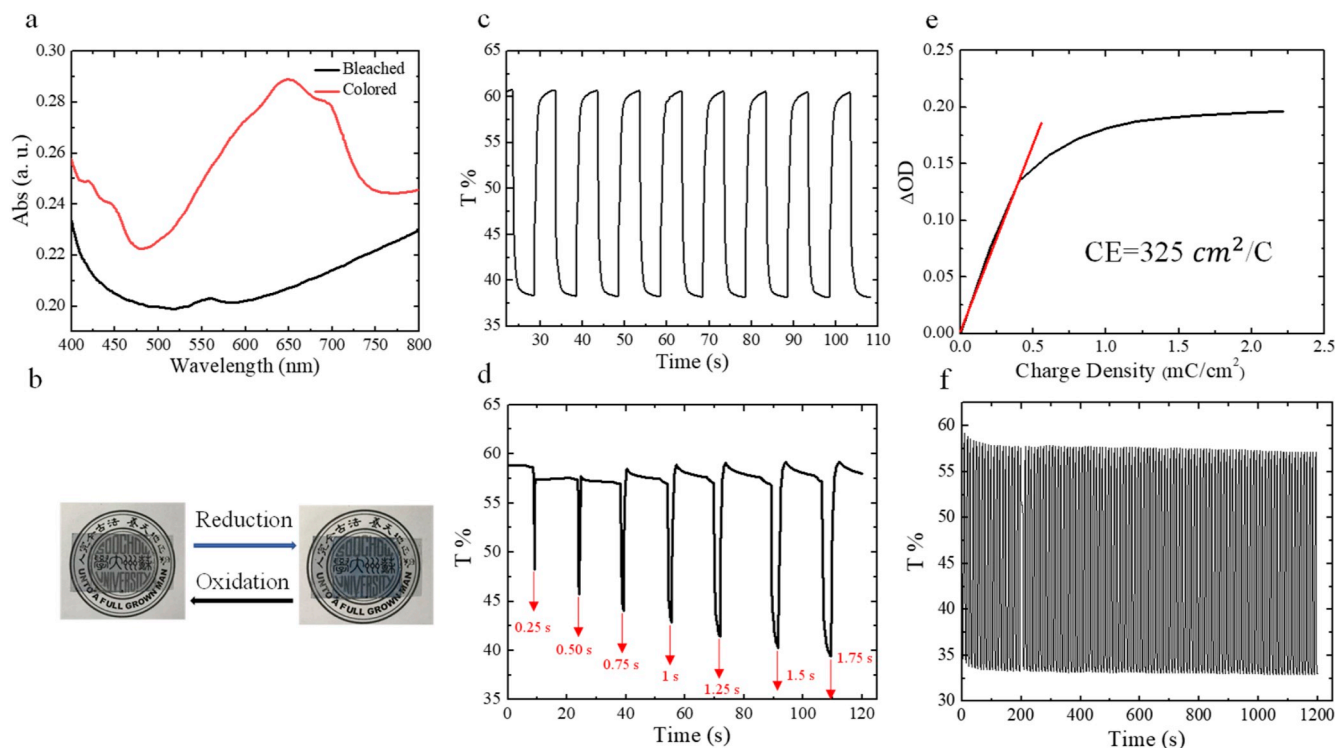
film enabling its electrochromic behavior and bringing about alternate color changes in accordance with the applied voltage. The reduced PEDOT: PSS form exhibits strong absorption in the visible spectrum that peaks around 650 nm (Fig. 3(a)), which is related with the  $\pi-\pi^*$  transition, leading to a deep blue color (Fig. 3(b)). As for the oxidative PEDOT: PSS form, it exhibits strongly attenuated absorption in the visible range (Fig. 3(a)) because of the depletion of low-energy  $\pi-\pi^*$  absorption bands, in addition, the absorption increases slightly as it goes toward the long wavelength end, resulting in a pale blue appearance (Fig. 3(b)).

We then investigated the switching behaviors of the device under alternate bleaching and coloring voltages of 3.5 V and  $-2.5$  V at 644 nm in accordance with the maximum absorption change in Fig. 3(a) to quantify the electrochromic performance (Fig. 3(c)). The device shows an absolute transmittance change of 22%, comparable with that on the ITO substrate (Supplementary Information Fig. S1), and could be further improved by optimization of the working parameters and material compositions. The fast response behavior of the device was further investigated by its optical transmittance response to the constant coloring ( $-2.5$  V) and bleaching (3.5 V) voltages with varying durations (Fig. 3(d)). As expected, the attainable optical contrast increases with the elongation in coloration duration, and it exhibits a very fast increase in the initial stage ( $\sim 10\%$  contrast for 0.25 s and  $\sim 15\%$  optical contrast for 1 s), and then the speed of the transmittance change slows down. The coloration or bleaching response depends on the carrier diffusion of ions or electrons under the applied electric-field. With the advance in the coloration, the build-in electric-field would balance the external electric-field, leading to decreased carrier diffusion under attenuated effective electric-field. Anyway, the device shows a very fast coloring and bleaching time, where it undergoes a 90% of the maximum optical contrast with a coloring time of 1 s and a bleaching time of 1 s, which is superior to the present PEDOT: PSS ECDs based on the aforementioned TCEs [27–29]. The embedded Ni grid fabricated via the electroplating process has comparable electrical properties to bulk metals and its highly conducting characteristic ensures a fast diffusion of charge carriers in and out of the electrochromic layer, thereby yielding a reliable device with fast response.

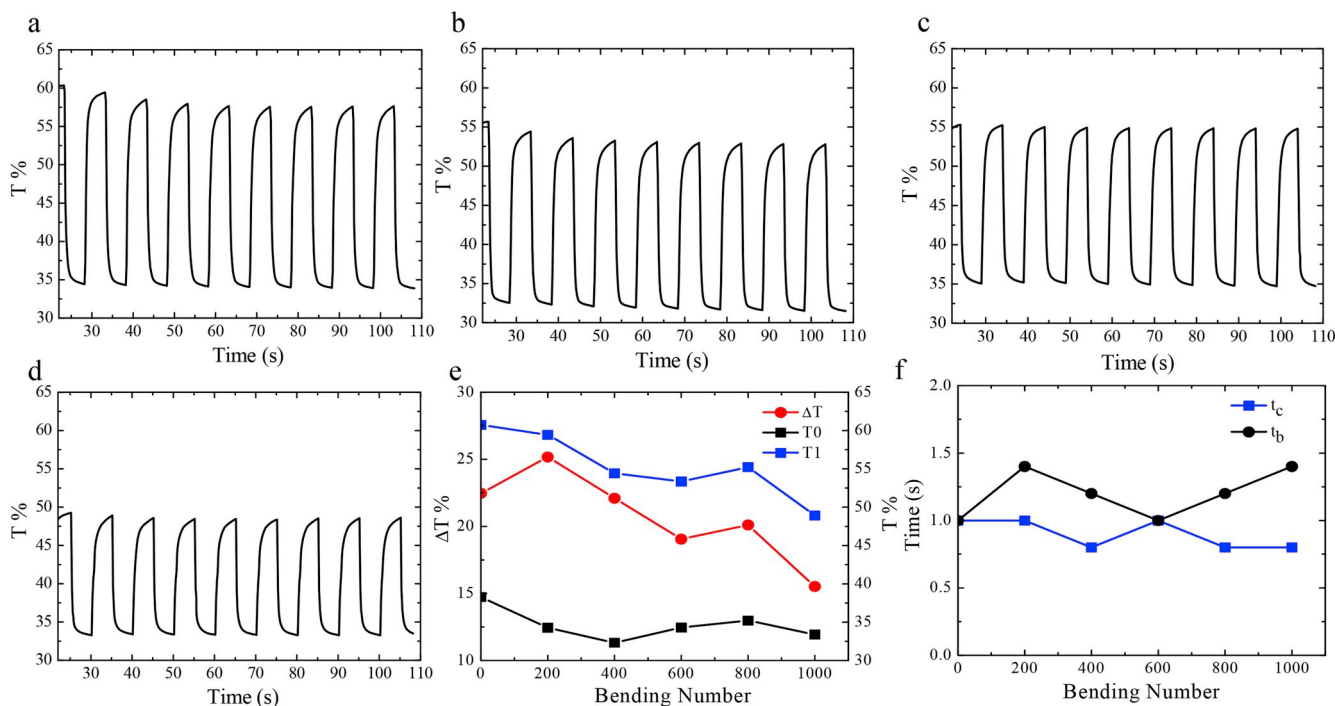
Coloration efficiency (CE), is one of the important performance evaluation parameters for the electrochromic device, defined as the change in optical density (OD) per unit of charge inserted into the electrochromic material at a certain wavelength, quantifying the efficiency of the device in coloration. The experimentally measured dependence of the optical density change on the inserted charge was shown in Fig. 3(e) and the slope of the linear fitting curve to the experimental data yields a CE of  $325 \text{ cm}^2/\text{C}$ , which is almost twice as high as that on the ITO electrode (Supplementary Information Fig. S1), which could be attributed to the excellent electrical conductivity and optical transmittance properties of the electroplated Ni grid electrodes. Common Ag grid electrodes suffer from metal decomposition during the repeated redox reactions for cyclical coloration and bleaching, which exhibits the issue of performance deterioration in long-term operation. In order to verify the chemical and environmental reliability of the embedded Ni grid electrode for electrochromism, the switching behaviors of the device with a cycling number of 200 were investigated (Fig. 3(f)). The device shows stable performance in terms of the optical transmittance contrast and the response time. With a further increase in operation cycles, the device performance is slightly reduced, due to the material decomposition during the repeated redox reactions, while still exhibiting an optical contrast retention of 90% after 500 operation cycles (Supplementary Information Fig. S1).

The mechanical stability and reliability of the ECD is important in realizing flexible electronics as the futuristic technology for displaying. The organic nature of the electrochromic layer and the electrolyte layer, together with the ultra-thin nature of the embedded Ni grid electrode would be beneficial for the realization of flexible and bendable ECDs. The device with a size of  $2.5 \times 2.5 \text{ cm}^2$  was repeatedly bent to a radius of





**Fig. 3.** (a) Absorption spectra of the sample at bleached and colored states from 400 nm to 800 nm. (b) Photographs of the ECD at the oxidized state (transparent) and the reduced state (blue) under applied potentials of 3.5 V and  $-2.5$  V, respectively. (c) The switching characteristics of the ECD, where the coloring and bleaching voltage was  $-2.5$  V and 3.5 V, respectively. (d) The transmittance changes of the ECD at the wavelength of 644 nm as a function of the voltage duration, where the coloring and bleaching voltage was  $-2.5$  V and 3.5 V, respectively. (e) Optical density as a function of the charge density at 644 nm. (f) Switching behaviors of the device under cyclic operation, where the coloring voltage of  $-2.5$  V and the bleaching voltage of 3.5 V was alternately applied for 3 s. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 4.** Switching performance of the bendable electrochromic device. Switching behaviors of the device under a bending number of (a) 200, (b) 400, (c) 800 and (d) 1000. (e) Optical transmittance of the device at the bleaching and coloration states and the transmittance change as a function of the bending cycles. (f) Coloration and bleaching time of the device to reach 90% of the optical contrast as a function of the bending cycles.

0.5 cm and the electrochromic performance was measured after certain number of bending cycles (Fig. 4(a), (b), (c) and (d)). The transmittance of the device at the bleaching state stays almost the same while that at the colored state decreases from ~60% to ~55% after a bending cycles of 800 and further to ~50% at 1000 bending cycles (Fig. 4(e)), this is probably due to the material deterioration at the high bending stress or the slight dislocation of the electrochromic film from the electrolyte layer. As for the absolute transmittance contrast, it exhibited a decrease from ~22% to ~17%, indicating a contrast retention of ~80%, while the device on the ITO substrate exhibits a contrast retention of 20% after 600 bending cycles (Supplemental Information Fig. S1), and is comparable to the state-of-art flexible ECDs in publication [36]. The excellent mechanical properties of the embedded Ni grid electrode and the compact working architecture should be the dominant contributions to the mechanical reliability of the device. The switching performance at the bending state (See Supplemental Information Video 1) further demonstrates the mechanical flexibility of the device. As for the response time, the coloring time to reach 90% of the optical contrast increases slightly from ~1 s to ~1.5 s after 1000 bending cycles, while the corresponding bleaching time stays around 1 s (Fig. 4(f)), while the device based on the ITO substrate shows an abrupt degradation in switching performance after a number of bending cycles (Supplemental Information Fig. S1), due to the apparent difference in the mechanical reliability of the two electrodes, indicating the superiority of the Ni grid electrode for flexible electronics.

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.orgel.2019.105506>

#### 4. Conclusions

In summary, we have successfully fabricated a fast-response and bendable PEDOT: PSS ECD based on the embedded Ni grid electrode. The device has a very compact working structure with the electrochromic PEDOT: PSS layer and the polymer electrolyte being sandwiched between two embedded Ni grid electrodes. The PEDOT:PSS underwent reversible redox reactions in accordance with the injection and extraction of charge carriers under the aid of external bias and appeared repeatable coloration and bleaching states for efficient light modulation, in addition, the conducting polymer effectively distributed the electric-field across the film for simultaneous color control. The polymer electrolyte was for ion storage and transportation and a good lamination among the four layers. The embedded Ni grid electrode was developed through a novel patterned electroplating process which has electrical properties comparable to bulk metals and also high optical transmittance by controlling the metal grid width, thereby enabling efficient electron conduction without affecting the transmittance, implied by the coloration efficiency and absolute optical contrast. The Ni grid electrode further shows advantages of excellent mechanical and chemical reliability, yielding a fast-response and bendable electrochromic device with long-term stability.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.orgel.2019.105506>.

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