Effect of Chemical Treatment on Conducting Polymer for Flexible Smart Window Application

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Abstract. Conductive polymer poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is one of the most attractive materials for transparent conductive electrodes, energy storage and electrochromic devices for smart window application. In this work, we investigated the effect of various chemical treatment on flexible transparent PEDOT:PSS electrode. The optoelectronics properties, electrochemical supercapacitor performance, and electrochromic behavior was determined. Based on the findings, the benzenesulfonic acid (BSA) shows high optical transmittance of 95% and high conductivity with sheet resistance of 97 Ω, which demonstrate an areal capacitance of 0.58 mF/cm² higher than the previous report. In addition, flexible transparent electrode shows excellent mechanical properties when folded for 9000 cycles at bending radius of 1 mm. In addition, when potential applied into all solid-state flexible PEDOT:PSS, the transmittance change of 22% at 630 nm showed promising electrode for electrochromic devices.

1. Introduction

Flexible and transparent energy storage devices, such as thin-film supercapacitors (SCs) are currently potential to be excellent candidates for smart window application when integrated with electrochromic device [1]. In addition, SC shows promising prospect owing to its low cost, fast charging time, high power density and long cycle life compared to batteries technologies [2]. More interestingly, it is suitable for smart window application when integrated with electrochromic device, which exhibit reversible colour changes upon application of a driving potential for energy saving application such as, displays, self-dimming rear mirrors for automobiles, and so on [3]. Most transparent conductive electrode materials available in the market is based on indium tin oxide (ITO), however, due to its brittleness, high vacuum processing and high cost, thus hinder the development in flexible TCEs [4]. In order to replace ITO, conductive polymer of poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) are an attractive electrode materials for flexible, transparent, solution-processed, cost-effective, potential as pseudocapacitors and electrochromic [5].

Herein, we investigate the effect of various chemical treatment on the performance of electrochemical supercapacitor and electrochromic device performance. The PEDOT:PSS electrodes in this work were used as both current collector and active electrodes. Flexible polycarbonate (PC) was used as a substrate to
deposit thin layer of PEDOT:PSS layer via spin-coating process due to its high temperature resistance [6]. Based on the finding, we found that benzenesulfonic acid treated PEDOT:PSS demonstrate excellent optoelectronics and electrochemical properties. In addition, it shows good mechanical stability and high transmittance changes under low potential.

2. Materials and Methods
Firstly, the flexible PC substrates was cleaned in isopropanol solution under mild ultrasonic cleaning for 15 min and dried in oven at 100 °C for 10 min. Subsequently, the substrate was transferred to UV-ozone chamber for surface treatment for 10 min. PEDOT:PSS PH1000 (Heraeus, Clevious) solution was filtered with 0.22 µm prior to spin-coated on the PC substrates at 2000 rpm for 30 s, followed by annealing at 130 °C for 5 min in air. After the substrate was cooled down, various chemical treatment such as ethylene glycol (EG), benzenesulfonic acid (BSA), methanesulfonic acid (MSA) and p-toluenesulfonic acid (PTSA) solution were spin casted at 5000 rpm for 20 s. Afterwards, the substrate was annealed at 120 °C for 5 min on hotplate to remove the excess of the acid solution. To assemble the all solid-state electrochromic device, two identical flexible PEDOT:PSS was sandwich together with PVA/H$_2$PO$_4$ electrolyte. Figure 1 shows the schematic illustration of fabrication process of flexible supercapacitor and electrochromic device. The optical and electrical properties were investigated using UV-Vis spectrophotometer Lambda 950 and non-contact resistance measurement (EC-80P, Napson, Co.) In order to evaluate the electrochemical performance, three-electrode system consist of Ag/AgCl as reference electrode, Pt wire as counter electrode and PEDOT:PSS treated film as working electrode measured in 1 M of H$_2$SO$_4$ solution using Iviumcompactstat (Ivium). The optical transmittance changes for electrochromic device was measured using Lambda 950 integrated with driven potential by Ivium.

![Figure 1](image.png)

**Figure 1.** Schematic illustration of fabrication process of flexible transparent electrode for smart window application under various treatment of EG, MSA, BSA and PTSA on PEDOT:PSS layer. Inset shows the field emission scanning electron microscope (FESEM) images of PEDOT:PSS before and after BSA-treated PEDOT:PSS films. Inset shows the top FESEM images of uniform film of pristine and BSA-treated PEDOT:PSS.
3. Results and Discussion

Figure 2a depicts the optical transmittance of PEDOT:PSS film with thickness of 30 nm coated on flexible PC substrates. The transmittance of modified PEDOT:PSS is approximately 95% (at 550 nm), which is relatively transparent in visible region. Inset Figure 2b shows the sheet resistance (Rs) of modified PEDOT:PSS film of 193, 97, 118, and 115 Ω for EG, BSA, MSA and PTSA treatment, respectively. These results suggest that acid treatment of BSA resulting in removal excess amount of PSS [7]. However, when exposed the films on ambient air for 300 h at humidity of 70%, it shows that the Rs of EG-treated sample increase by 72%, meanwhile acid treated shows only 48% of Rs increment. Accordingly, BSA-treated PEDOT:PSS shows higher conductivity, stability and high transmittance, thus indicates excellent optoelectronics properties. Therefore, only EG and BSA-treated PEDOT:PSS electrode was used to investigate the electrochemical performance.

![Figure 2](image)

Figure 2. (a) Optical transmittance, (b) sheet resistance (Rs) as function of aging time in ambient humidity of 50%, (c) Electrochemical characteristics and (d) areal capacitance against scan rate (80 – 10,000 mV/s) for EG and BSA treated transparent electrode.

In order to investigate the electrochemical performance of modified PEDOT:PSS electrode, cyclic-voltammetry measurement was carried out. Figure 2c shows the CV curves of PEDOT:PSS electrodes treated with EG and BSA as comparison at a scan rate of 80 mV/s which represent the quasi-rectangular CV shape. Notably, the current density of BSA treated sample was increased, which is in accordance with increase of conductivity. The areal capacitance of treated PEDOT:PSS was extracted at various scan rate from 80 to 10,000 mV/s as shown in Figure 2d calculated based on Equation 1, where C/A is a real
capacitance, $A$ is active area, $\Delta V$ represent potential window, $v$ is scan rate, $j$ is current density and $v_1$ and $v_2$ represent the initial and final vertex voltage [8].

$$C/A = \frac{1}{\Delta V} \int_{v_1}^{v_2} j dV$$  \hspace{1cm} (1)

While $C/A$ value is highly dependent on scan rate, based on the Eq.2, the scan rate independent or so called intrinsic areal capacitance ($C_A$) by extrapolating the fitted curves and simultaneously the time constant of supercapacitor can be determine [8].

$$C/A = C_A \left[ 1 - \frac{\nu \tau}{\Delta V} (1 - e^{-\frac{\Delta V}{\nu \tau}}) \right]$$  \hspace{1cm} (2)

where, $\tau$ is time constant. Accordingly, the $C_A$ of EG and BSA treated PEDOT:PSS are 0.43 and 0.58 mF/cm$^2$. The time constant was obtained and summary in Table 1. As expected, the low time constant of 58 ms for BSA treated sample, implies that rapid electron transport through the PEDOT:PSS electrodes compared to EG treated sample. This finding suggests that high conductivity of BSA treated PEDOT:PSS could improves the pseudocapacitance.

**Table 1.** Summary of optoelectronics and electrochemical properties of EG and BSA treated PEDOT:PSS electrode.

| Chemical Treatment       | Rs  ($\Omega \cdot \square$) | $C_A$ (mF/cm$^2$) | $\tau$ (ms) |
|--------------------------|------------------------------|------------------|-------------|
| Ethylene glycol (EG)     | 180                          | 0.43             | 118.70      |
| Benzenesulfonic acid (BSA)| 97                           | 0.58             | 58.54       |

The mechanical stability of BSA-treated PEDOT:PSS electrode was determined by folding test for 9,000 cycles at bending radius of 1 mm. Figure 3a depicts the capacitance retention of flexible BSA treated PEDOT:PSS electrode calculated based on $C/A$ divided by $C/A_{initial}$ (before bending condition). It can be clearly seen that after 9,000 bending cycles, the capacitance can retain up to 90%, thus implies excellent mechanical stability of flexible PEDOT:PSS. For electrochromic study, the solid-state device was assembled based on two identical flexible BSA treated PEDOT:PSS electrode as shown in Figure 3b. At 0V, the sample is transparent and when applied potential at 1.8 V, the corresponded color gradually changesto deep blue. In order to observe the detail of transmittance (@630 nm) changes upon applied voltage, the sample was modulated by on and off at each 20 s for total 200 s (4 cycles). The 0.6 V shows 5% of transmittance modulation, while 1.8 V shows higher transmittance change of about 22%. This results suggests that BSA treated PEDOT:PSS shows excellent electrochromic behavior.
Figure 3. (a) Capacitance retention at different bending cycles, (b) Photograph image of assembled two symmetrical flexible transparent electrode for without and applied 1.8 V, (c) Transmittance changes under different applied potential of 0.6 V and 1.8 V for 200 s.

4. Conclusion
In summary, we have successfully demonstrated the chemical treatment on flexible PEDOT:PSS substrate for electrochemical supercapacitor and electrochromic devices. The high optical transmittance and conductivity of 95 % and 97 Ω/ cm, respectively when treated the PEDOT:PSS with benzenesulfonic acid (BSA) which could be due to the removal of PSS. Accordingly, excellent areal capacitance of 0.58 mF/cm² was achieved after BSA treatment and shows rapid electron transfer through the electrode compared to ethylene glycol (EG). In addition, the flexible PEDOT:PSS electrode shows excellent mechanical stability and good transmittance changes when applied potential. The findings show that our flexible PEDOT:PSS electrode is promising for electrochromic and supercapacitor devices.

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