The effect of ethylene glycol post-treatment on the electrical conductivity of PEDOT: PSS thin films

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Abstract. The application of organic conducting polymers such as poly (3,4-ethylene dioxythiophene): poly (4-styrene sulfonate) (PEDOT: PSS) is vastly expanding for the development of advanced and flexible organic electronic devices, such as solar cells, light-emitting diodes, and organic electrochemical transistors (OECTs). Also, PEDOT: PSS can perfectly replace high-cost Indium tin oxide (ITO) thin films. In this study, PEDOT: PSS was synthesized via the chemical oxidative polymerization method. The film formation was carried out through a feasible drop-casting method onto a cleaned glass substrate. To further enhance the conductivity of pristine PEDOT: PSS, the PEDOT: PSS thin films were post-treated with different concentrations (3, 5, and 7% v/v) of ethylene glycol (EG). Based on the electrochemical impedance spectroscopy (EIS) analysis, it was revealed that the post-treated sample had a higher conductivity value compared to the untreated sample ($2.48 \times 10^{-4}$ S/cm), with the highest recorded conductivity value of $2.67 \times 10^{-3}$ S/cm at 5% v/v of EG. This result corresponds to the previous study, which highlighted that the optimum concentration of EG is 5% v/v to achieve the optimum conductivity value for thin film application. Furthermore, the structural properties of the thin films were characterized using Fourier transform infrared (FTIR) spectroscopy to confirm the presence of PEDOT: PSS and EG in the samples.

1 Introduction

Conducting polymers (CPs) are conjugated polymers with superior electrical conductivity comparable to metals due to the presence of alternating single and double covalent bonds at the polymer backbone that transport charges regardless of their intrinsic conductivity and charge transport characteristics [1], [2]. As a result, CPs exhibit conductor, semiconductor, superconductor, and magnetic properties. In addition, due to the $\pi$-conjugated backbone, CPs are recognized for their distinctive electrical, electrochemical, and optical properties akin to metals and inorganic semiconductors, as well as their ease of synthesis and processing versatility [3]. Some of the common CPs are poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT: PSS) [4]–[6], polyaniline (PANI) [7], [8], polypyrrole (PPy) [9], [10].

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and polyacetylene (PA) [10]. Among these CPs, polythiophene derivatives, such as PEDOT, have become one of the most extensively studied organic conducting materials for film-forming applications due to their excellent film-forming ability, transparency, thermal and environmental stability. Also, the intrinsic conductivity properties of PEDOT are useful for applications such as wearable electronics, solar cells, smart sensors, and organic light-emitting diodes (LEDs) [11].

However, a pristine PEDOT: PSS shows a poor conductivity value of less than 1 S/cm, hindering a more comprehensive potential application [12], [13]. Hence, it is crucial for the electrical conductivity enhancement of PEDOT: PSS to serve the specific conductivity value required for each application field. A few methods to be considered for conductivity enhancement include the doping process [14], physical approaches, and chemical approaches [15]. This work selected a chemical approach via solvent post-treatment of the PEDOT: PSS films using ethylene glycol, an organic solvent. The post-treatment process of pristine PEDOT: PSS films has been regarded as an effective way to improve conductivity ever since 2012 [13]. Previously, [16] reported that the conductivity of PEDOT: PSS thin films was increased from 0.84 S/cm to 1210 S/cm by an immersion treatment technique employing a solution comprising 67% ethylene glycol (EG) and 33% hexafluoro-isopropyl (HFIP) alcohol by volume. Moreover, it was proven by a study conducted by [17], where the EG-treated CNT/PEDOT: PSS nanocomposite films demonstrated an improved electrical conductivity of up to 780 S/cm. The phenomenon of enhanced conductivity occurred due to the partial removal of insulating PSS chains. Thus, the conducting PEDOT chains becomes more connected and transformed from a de-doping (benzoid structure) to a doping (quinoid structure) conformation state [17].

In this study, the conductive films were fabricated via a drop-casting method. It is a cost-effective and simple technique that provides a flexible, transparent, and conductive film with good quality [18]. PEDOT: PSS was the conductive agent, synthesized via a chemical oxidative polymerization method to impart conductivity to the films. For conductivity enhancement purposes, the PEDOT: PSS films were then immersed in ethylene glycol as a post-treatment process and subsequently underwent thermal annealing. Electrochemical impedance spectroscopy (EIS) and Fourier-transform infrared spectroscopy (FTIR) characterized the fabricated thin films to investigate their electrical conductivity and chemical structure.

2 Experimental

2.1 Materials

3,4-ethylendioxythiophene monomer solution (EDOT, 97%), poly (4-styrenesulfonic acid) solution (PSS), low molecular weight chitosan (CS), and ethylene glycol (EG, 99%) were purchased from Sigma-Aldrich. In contrast, ammonium persulfate (APS) was purchased from Merck chemicals. Glass substrates were purchased from a local shop. All reagents were analytical reagent grade and were not further purified.
2.2 Synthesis of PEDOT: PSS solution

The PEDOT: PSS colloidal sample was synthesized by mixing 0.0500 g of EDOT, 0.1250 g of PSS and 7.45 mL of distilled water. The solution was then magnetic stirred for an hour at room temperature. This step was followed by adding 0.1000 g of APS as an oxidant to promote the polymerization process by stirring for another 2 hours until the colour of the solution changed from light green to dark blue.

2.3 Fabrication of drop cast PEDOT: PSS onto CS thin films

2.3.1 Preparation of CS solution

A low molecular weight chitosan powder of 0.9 g was dissolved in 0.25 mL of acetic acid and 0.75 mL of distilled water. Next, the solution was stirred for 15 minutes to obtain a good homogeneity. Then, the chitosan solution was transferred into a centrifugal tube and centrifuged for 5 minutes at the speed of 5000 rpm.

2.3.2 Drop-casting of PEDOT: PSS onto CS thin films

The glass substrates were primarily cleaned by acetone immersion for 30 minutes, followed by rinsing with deionized water and leaving them dry in the oven. Next, 1.6 mL of prepared CS solution was dropped using a syringe and evenly spread onto the glass substrate/microscope slide (75 × 50 mm), cut into three parts. Subsequently, about ten drops of the PEDOT: PSS solution was added onto the CS layer. An annealing process was done by inserting them in the oven for an hour at 80 °C for drying purposes. Once the drying process was completed, the thin film was peeled off from the glass substrate successfully.

2.4 Ethylene glycol post-treatment

Firstly, ethylene glycol (EG) solution was prepared into three concentrations of 3, 5, and 7% v/v. The PEDOT: PSS thin films were immersed in the prepared EG solution for post-treatment purposes. Subsequently, the treated films were annealed in the oven at 80 °C for 30 minutes.

2.5 Materials characterization

2.5.1 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (HIOKI 3520 LCR Hi-Tester) was employed to determine the conductivity of the sample (Fig. 1). At room temperature, the frequency range employed was 100 Hz to 1000 kHz. To clip the untreated and treated PEDOT: PSS thin films, two stainless steel disc electrodes with a diameter of 2.0 cm were utilized. For each operating frequency, the impedance was measured, and the conductivity value was calculated. The complex impedance, Z, for each measured sample were plotted using Nyquist plotting (-Im (Z) versus Re (Z)). Additionally, each sample was measured three times consecutively to obtain an average conductivity value. We can derive the electrical conductivity, σ, by obtaining the thickness of the films, geometry of the sample and the bulk resistance under test from the following expression [19]–[21]:

$$\sigma = \frac{d \cdot R}{A}$$

Where:
- \( \sigma \) is the electrical conductivity (S/cm)
- \( d \) is the thickness of the film (cm)
- \( R \) is the bulk resistance (Ω)
- \( A \) is the area of the electrode (cm²)
\[ \sigma = \frac{t}{Rb \cdot A} \]

Where \( t \) is the thickness of the thin film, \( Rb \) is the bulk resistance measured from the interception between the end of a semicircle and commence off a spike, and \( A \) is the cross-sectional contact area of the electrode with the film.

Fig. 1. Electrochemical impedance spectroscopy set-up, which connects the electrodes with thin film during EIS measurement.

2.5.2 Fourier Transform Infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy was utilized to determine the chemical composition and present functional groups in the thin film samples. Infrared spectra were obtained using the Spectrum RX 1 FTIR instrument (Perkin Elmer) with a wavenumber range of 400 to 4000 cm\(^{-1}\) by accumulating 32 scans at a resolution of 8 cm\(^{-1}\).

3 Results and Discussions

3.1 Synthesis of PEDOT: PSS

In this work, the conductive PEDOT: PSS was synthesized via a chemical oxidative polymerization method which binds a strong electrostatic association between the PEDOT- and PSS- chains [22], [23]. Briefly, chemical polymerization begins with the oxidation of an EDOT monomer in the presence of an oxidant (dopant ions) or catalyst [24]. The EDOT monomer was first added to an aqueous solution of PSSH and vigorously agitated to obtain good homogeneity [25]. The polymerization was performed immediately with the addition of both ammonium persulfate ((NH\(_4\))\(_2\)S\(_2\)O\(_8\)) and iron (III) chloride (FeCl\(_3\)) oxidants which produced a complex. The addition of ammonium persulfate solution (APS) acts as an oxidant that changes the reaction mixture from greenish to a dark blue solution that indicating a complete polymerization process of EDOT has taken place (Fig. 2). Fig. 3 depicts the process of PEDOT: PSS film formation.
Fig. 2. Images of the steps in PEDOT: PSS synthesis via chemical oxidative polymerization, (a) mixture of EDOT monomer in aqueous PSSH solution, (b) first cycle of colour changes in the reaction mixture as APS was added (yellowish greenish), and (c) the second cycle of the colour changes from greenish to dark blue solution, indicates a complete polymerization process of EDOT monomer.

Fig. 3. Film formation of PEDOT: PSS. (a) Drops of CS layer as a base and PEDOT: PSS as conducting agent cast onto a glass substrate, and (b) PEDOT: PSS thin film formation after thermal annealing.

3.2 Electrical conductivity of the films

Fig. 4 illustrates the conductivity of films under different conditions. Based on the EIS analysis, it was proven that a solvent post-treatment process successfully enhances electrical conductivity. The untreated PEDOT: PSS films had the lowest conductivity value of $2.48 \times 10^{-4}$ S/cm due to the absence of the EG post-treatment process, which might result in the domination of the benzoid (coil) structure in the PEDOT: PSS matrix. The conductivity of the PEDOT: PSS thin film increases to $8.93 \times 10^{-4}$ S/cm when being treated with 3% v/v of EG. There was a gradual increase in conductivity value by one magnitude ($2.67 \times 10^{-3}$ S/cm) as the PEDOT: PSS film was exposed to 5% v/v of EG and slightly dropped to $2.56 \times 10^{-3}$ S/cm at 7% v/v of EG. The highest conductivity value was recorded at 5% v/v, which suggests the optimum concentration of EG to obtain a steady increase in electrical conductivity for PEDOT: PSS thin films is at 5% v/v.
According to [26], there are a few underlying mechanisms for conductivity enhancement via EG incorporation into the PEDOT: PSS systems. First, the EG induction removes excess insulating PSS from PEDOT: PSS films which subsequently improves the concentration of charge carriers (Nc). Also, the inclusion of EG induces the PSS chain to restructure while the PEDOT chain assemblies and forms a higher-ordered layer structure. As a result, the number of polarons and bipolarons where PEDOT chain stores charges increased, leading to the transition of quinoid- and benzoid-dominated structures. An electrical current can be propagated along the polymer chain by both polarons and bipolarons. Moreover, the bipolarons in conducting polymers can travel two times faster than polarons, explaining the increased electrical conductivity of EG-treated PEDOT: PSS samples.

Fig. 4. Electrical conductivity of PEDOT: PSS thin films at different concentrations of ethylene glycol.

3.3 FTIR analysis

In order to confirm the presence of different functional groups in the thin films, FTIR analysis was performed. Fig. 5 shows the FTIR spectrum of untreated PEDOT: PSS and PEDOT: PSS treated with EG. Table 1 reported the FTIR characteristic bands and assignment of EG-treated PEDOT: PSS, which are comparable to the PEDOT: PSS. According to the FTIR data, there is a broad slope at the peak between ~3300-3400 cm\(^{-1}\) for both samples, indicating the stretching of the O-H bond present in both PEDOT: PSS and EG. Next, the FTIR band at ~1624 cm\(^{-1}\) is related to the C=C bond for PEDOT and PSS phenyl side groups. Also, it is worth mentioning that the C=C stretching of quinoid EDOT is blue-shifted from ~1624 to ~1644 cm\(^{-1}\) when treated with 5% v/v of EG. The dislocation of the effective π-electron probably causes the structure to go into a linear conformation [27]. In addition, [26] discovered that the increased intensity of the band between ~1624 to ~1644 cm\(^{-1}\) upon EG treatment reveals the quinoid-dominated structures of the PEDOT chain, which increase the number of polarons or bipolarons and hence increase Nc.
Moreover, the absorption band at ~1553 cm\(^{-1}\) represents C=C stretching in the PEDOT thiophene ring. The C-C stretching of PEDOT: PSS can be detected at ~1413 cm\(^{-1}\) absorption band. The absorption band at ~1085 cm\(^{-1}\) indicates the S-O stretching of the sulfonate group in PSS. Based on the FTIR analysis, the quinoid (linear) conformational structure provides better charge mobility and dominates the highly conductive PEDOT: PSS films.

![FTIR spectra of PEDOT: PSS and PEDOT: PSS/EG.](image)

**Fig. 5.** FTIR spectra of PEDOT: PSS and PEDOT: PSS/EG.

### Table 1. FTIR bands classification of PEDOT: PSS and treated PEDOT: PSS

| Wavenumber (cm\(^{-1}\)) | Absorption bands                      |
|--------------------------|---------------------------------------|
| ~3300-3400               | O-H stretch                            |
| ~1624-1644               | C=C stretching of PEDOT and PSS (phenyl side groups) |
| ~1553                    | C=C stretch                            |
| ~1413                    | C-C stretch                            |
| ~1085                    | S-O stretch                            |

### 4 Conclusion

In this study, the PEDOT: PSS films were post-treated with different concentrations of EG (3, 5, and 7% v/v) to enhance their conductivity properties. Based on the EIS analysis, we have drawn into a conclusion that the post-treatment process with 5% v/v of EG (2.67 \(\times\) 10\(^{-3}\) S/cm) exhibited superior conductivity compared to both untreated (2.48 \(\times\) 10\(^{-4}\) S/cm) and post-treated PEDOT: PSS films with 3% v/v (8.93 \(\times\) 10\(^{-4}\) S/cm) and 7% v/v (2.56 \(\times\) 10\(^{-3}\) S/cm) of EG. Hence, it was concluded that 5% v/v of EG was the optimum concentration to obtain a high conductivity value of PEDOT: PSS thin films. Furthermore, the FTIR analysis showed O-H, C=C, C-C, and S-O bands in the structure of untreated and EG-treated PEDOT: PSS thin films. Also, it unveiled a slight shift from 1624 to 1644 cm\(^{-1}\) for the peak C=C stretching.
in quinoid PEDOT when treated with 5% v/v of EG. In the near future, the morphological studies of the films can be explored to associate the effect of the post-treatment process with the surface of the thin films, along with the conductivity enhancement.

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