



Spectroscopic And Structural Studies Of PEDOT:PSS With DMSO

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Abstract

PEDOT:PSS is a conductive polymer has optical transparency in its conducting state, high stability, moderate band gap and low redox potential. PEDOT:PSS was spin coated on the glass substrate with different spin speed, starting by injecting a constant volume of PEDOT:PSS solution at the centre of the spin coater and letting the volume spread on the surface via spinning action for 30sec. PEDOT:PSS is the conventional hole transport layer, because it provides a reproducible work function can be cast to give a smooth interface and hinders oxidation at the emissive interface. Spectral analysis like FTIR, UV-Vis analysis, Band gap energy, Raman analysis were investigated. SEM studies were undergone to investigate the structural nature of the sample.

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Introduction

Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) is used as an anode buffer layers for both OLEDs and solar cells. The main advantage of this material such as high work function, high stability, high conductivity, good film forming properties and high transparency. PEDOT:PSS enhances good interaction with ITO substrates(5), because of easy film formation, low surface roughness and low cost. Instead of ITO layer we can use PEDOT:PSS layer for both bottom and top electrodes in solar cells and OLED device fabrication. PEDOT:PSS is doped with dimethyl sulfoxide (DMSO). In order to provide good electrical conductivity(5,7). Among the various conducting polymers, PEDOT (poly(3, 4-ethylenedioxythiophene)) has attracted considerable interest due to its electrical and optical properties(4,5,8). Generally, PEDOT/PSS is not only precipitated from solution during storage, caused by aggregating particles slowly, but also difficult to be redispersed from the aggregated solids because PEDOT:PSS is not soluble but dispersible in water. The PEDOT:PSS composite is one of the most promising organic based electrode materials owing to its inherent advantages over other conducting polymers such as high transparency in the visible region, long term stability and

solution processability. PEDOT:PSS has been used extensively as an interfacial layer to improve hole injection in many organic devices(6). However, the use of PEDOT:PSS as an electrode material has been restricted because commercially available PEDOT:PSS, which is typically used as a buffer layer in organic electronics has a low conductivity. The pristine PEDOT:PSS thin films exhibit excellent transparency (T>90% for 400-800nm). PEDOT:PSS was originally developed as an antistatic coating for photographic films, PEDOT:PSS is successfully used for the fabrication of coated photographic film per year exceeds 108 m². Additionally, it is used for packaging microelectronics components. Other applications include electrode material in solid-state capacitors, substrates for electrodeless metal deposition in printed circuit boards and electrode material in organic electroluminescent lamps. Due to the high work function of PEDOT, it is also a good material for making anodes in light emitting devices(13). Electrical conductivity of PDDA/PEDOT:PSS multilayer films was around 0.31 S cm⁻¹, optical reflectometry was observed(14). PEDOT:PSS is a good alternative electrode for solar cell fabrication(17). Thin film solar cells based on polymer materials have low cost, readily available energy. PEDOT:PSS have good optical transparency in the visible range, it has the ability to transfer holes to the anode and blocking electrons, high work function i.e., 4.8-5.2 eV. The addition of 5% of DMSO increases the conductivity up to 470 S/cm. With the addition of DMSO, there will be an increase in film roughness, it causes reduction of the contact surface between grains leading to a superior charge transport within the layer.

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The addition of DMSO resulted in the reduction of content at the surface of the pedot grain, weakening the barrier effect with the improvement of conductivity. DMSO and patterned anodes was made with PDMS masking and brush painting technique. Conductivity increase of 400 s/cm reported (18). Schottky solar cells, post annealing. The effect of annealing and PEDOT:PSS based Schottky solar cells were investigated to improve the performance of this device. (20) Seebeck coefficient is also found (16). Direct conversion between thermal energy and electrical energy can be noted. Chemical structures of the films are analysed by FTIR and UV-Vis spectra. (16)

2. Sample Preparation

2.1. Preparation of PEDOT: PSS Thin Films

All samples were treated for two minutes in oxygen plasma prior to the film deposition. This resulted in good hydrophilic surfaces on which the aqueous solution of PEDOT: PSS was spin-cast. Samples with high conductivity were prepared by using PEDOT: PSS (1.3 wt% of dispersion in H₂O) conductive grade was procured from Sigma Aldrich. To achieve different film thicknesses, the parameter of the spinner was kept at 2000-2500 rpm at 30 secs. PEDOT:PSS different samples of various layers like 7, 9, 11, 13, 15 layers were cast on top

of each other, the films are not uniform anymore. Since the water of the thin film evaporates quickly, the films dry easily within minutes. For the multi-layered samples, the time between two subsequent deposition steps was typically five minutes. Finally, to remove the water solvent completely, the samples were heated to approximately 90°C for two hours in a vacuum oven. To avoid the absorption of humidity, the samples were then stored in a desiccator under a constant dry nitrogen flow.

2.2. Annealed PEDOT: PSS thin films

From the above samples the 9 layer sample was taken for annealing, the film was kept in muffle furnace at 150°C for 2 hrs and the samples were then stored in a desiccator under a constant dry nitrogen flow.

2.3. Preparation of PEDOT: PSS Doped With DMSO

5ml of PEDOT: PSS doped with 50 µl of DMSO was taken in a beaker, and then ultrasonicated for 10 minutes. It is then spin coated in a glass substrate for film formation. The coated film is heated at 100°C and then it is placed in a desiccator under a constant nitrogen atmosphere.

3. Result and Discussion

3.1. Structural Properties

3.1.1. SEM Analysis

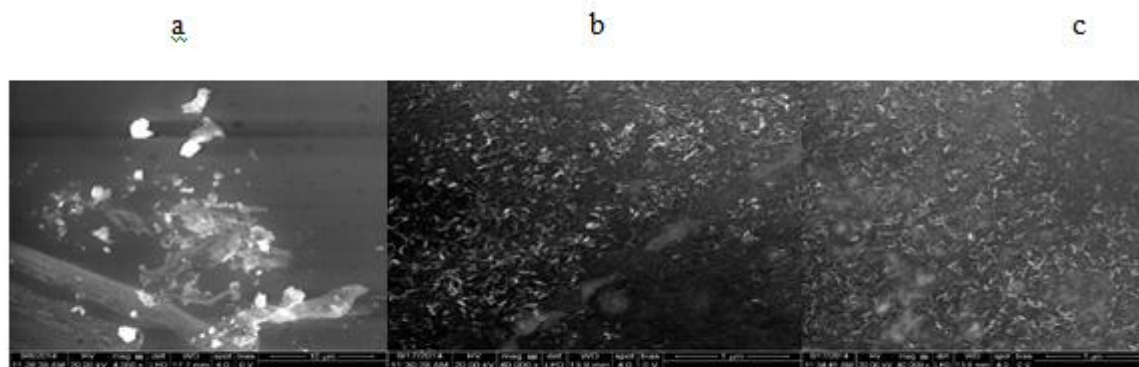


fig a) Pure Pedot:Pss

b&c) pedot:pss doped with DMSO

fig a) Pure Pedot:Pss

b&c) pedot:pss doped with DMSO

SEM image pure Pedot:Pss sample shows small nanoparticles, while the sample doped with DMSO shows nanowire-like formation. It gives that the addition of DMSO will make a change and have good properties in the formation of nanoparticles. In the SEM analysis, because of the addition of DMSO in the PEDOT:PSS sample, it shows nanofiber-like structure.

3.2. Optical properties

3.2.1. UV Analysis

All polymer solar cells showed an optical transmittance of 10-55% in the range of 400-800 nm (18). Maximum transparency of 51% at 550 nm. Due to the mechanical flexibility, light weight and cost-effective productions through solution-based manufacturing process, polymer solar cells are fabricated nowadays (19).

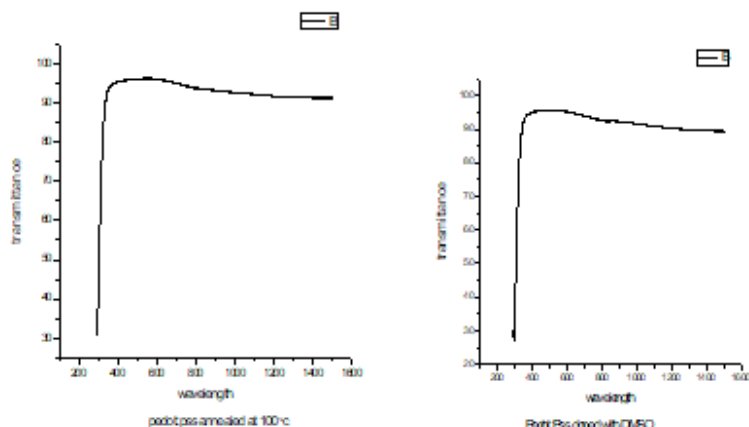


fig d) Pure Pedot:Pss

figd shows that the absorpton peak from 350nm-1500nm in the pure Pedot:pss sample.fig.e. Shows that the absorpton peak nearly from 350nm, with the addition of dopant to the pure sample the absorption range remain constant.

3.2.2. Band Gap Determination

Determination of absorption coefficient (α) of the film in this region was found by using the expression given below

$$\alpha = \ln(1/T)/t \text{-----(1)}$$

Where T is the normalised transmittance and t is the film thickness. With the help of the calculated absorption coefficient values, we can found out the optical band gap energy of pedot:pss thin film and doped thin film.

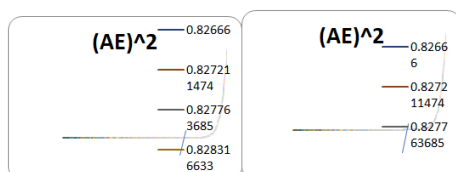


fig. f Pure Pedot:Pss

fig. g. pedot:pss doped with DMSO

bThe above graph shows the plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient and $h\nu$ is the energy of the incident photon. Considering the direct transition between the conduction and valence band, the energy band gap (E_g) can be determined by the formula below

$$\alpha h\nu = k(h\nu - E_g)^{1/2} \text{-----(2)}$$

Where k is the constant. Band gap energy can be calculated by drawing a straight line to the curve. The optical E_g is nearly 3.8eV in both pure sample and with the dopant.

3.3. FTIR analysis

In this study FTIR is used to interpret the observed frequencies of the major peaks in the spectra, to discuss the impact of spectral resolution on the identification of the unknown samples. The PEDOT: PSS films, the

fig e) pedot:pss doped with DMSO

vibration at 1325 and 1515 cm^{-1} are caused by the c-c and c=c stretching of the quinoidal structure and the ring stretching of the thiophene ring of PEDOT chains. Band at about 835 cm^{-1} is related to c-s bond vibration in the thiophene ring. C-H deformation vibration appears at 1030 cm^{-1} . the absorption peak at 910 cm^{-1} can be assigned to the C-H deformation vibration in the $-\text{CH}=\text{CH}-$ group. Uv-vis has increasing absorption peak after 500nm(16)

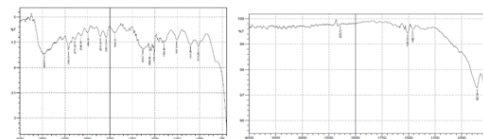


fig. h Pure Pedot:Pss

fig. i. pedot:pss doped with DMSO

The fig.h & i illustrates the spectral ranges of pure and doped Pedot:Pss with DMSO. In fig.f it gives the spectrum range from 1014-3516 m. The peak 2920.23m indicates O-H stretching carboxylic bond, 2214 indicates C triple bond N stretch nitriles bond, 1255 shows C-N stretch aromatic amines-O stretch alcohols-carboxylicacids, esthers, ethers. In fig.e. 1510m peak shows N-O asymmetric stretch nitro compounds, 958m shows C-H bending occurs.

3.4.Raman Analysis

Raman spectroscopy helps to analysis the amount of energy lost with the help of the variation of wave length. Raman spectroscopy has been used for studying doping changes in the sample. Raman spectrum of Pedot:Pss was identified in (21).The Raman spectra of pedot:pss thin films revealed a significantly strong vibration Raman band centered at 1500 cm^{-1} contributed to the symmetric stretching mode of aromatic C=C band. Three important peaks are at 500 cm^{-1} , 1000 cm^{-1} and 1500 cm^{-1} are related to C-Cl, aromatic chain vibration respectively. The bands located at 845-900 cm^{-1} have oxylene ring deformation. The band SO_2 bending from

pss was found at 450 cm^{-1} while comparing with the results of dopant film there was a strong symmetric

stretching mode of aromatic C=C band at 1500 cm^{-1} .

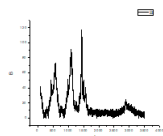


fig. j. Pure Pedot:Pss

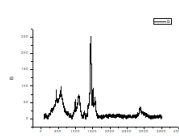


fig. k. pedot:pss doped with DMSO

Comparison tabular column for pure pedot:pss and doped with DMSO

<i>Raman</i>	<i>Region</i>	<i>Functional group(pedot:pss with DMSO)</i>	<i>Raman</i>	<i>Region</i>	<i>Functional group(pedot:pss)</i>
strong	$450\text{cm}-550\text{cm}^{-1}$	$\nu(\text{Si-O-Si})$	strong	500 cm^{-1}	$\nu(\text{C-Br})$
strong	$550-800\text{ cm}^{-1}$	$\nu(\text{C-Cl})$	strong	$550-800\text{ cm}^{-1}$	$\nu(\text{C-Cl}), \nu(\text{C-S})$ aliphatic
medium	970 cm^{-1}	$\nu(\text{C-O-C})$	strong	$1080 - 1100\text{ cm}^{-1}$	$\nu(\text{C-S})$ aromatic
strong	$1080 - 1100\text{ cm}^{-1}$	$\nu(\text{C-S})$ aromatic	weak	$1060 - 1150\text{ cm}^{-1}$	$\nu(\text{C-O-C})$ asym
weak	$1060 - 1150\text{ cm}^{-1}$	$\nu(\text{C-O-C})$ asym	Strong	$*1580, 1600\text{ cm}^{-1}$	$\nu(\text{CC})$ aromatic ring chain vibration
Strong	$*1580, 1600\text{ cm}^{-1}$	$\nu(\text{CC})$ aromatic ring chain vibrations	strong	$2800 - 3000\text{ cm}^{-1}$	$\nu(\text{C-H})$
strong	$2800 - 3000\text{ cm}^{-1}$	$\nu(\text{C-H})$	strong	$3000 - 3100\text{ cm}^{-1}$	$\nu(=\text{C-H})$

Conclusion:

In this present work the experiment is done for identifying the high transmission, absorbance and emission peak value of different layers of the samples for the fabrication of organic devices. The solution processability of organic semiconductors endow them great potential for realizing low cost, large area electronic devices by spin coating which is the key advantage of organic electronic devices such as OLEDs compared to traditional inorganic semiconductor based

electronic devices. To develop solution processed OLEDs, numerous efforts have been made on developing solution processed light emitting diodes and charge transport materials, resulting in variety of solution processed organic semiconductors, including polymers, dendrimers and small molecular semiconductors. polymer and dendrimer semiconductors are promising candidates for solution processed electronic devices due to their macromolecular nature.

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