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In-situ synthesis of transparent conductive PEDOT coating on PET foil by liquid phase depositional polymerization of EDOT

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ABSTRACT

To prepare FTCF, PET film was dipped in $Fe(OTs)_3$ *n*-butanol solution for $Fe(OTs)_3$ adsorption and suspended in EDOT cyclohexane solution for EDOT depositional polymerization. The adsorbed $Fe(OTs)_3$ were determined with idometry and the synthesized PEDOT coating were characterised with FTIR and UV–vis spectroscopes. The sheet resistance and transmittance of synthesized PEDOT/PET films were measured with four-point probe and spectrophotometer. The effect of $Fe(OTs)_3$ drying time and polymerization time on sheet resistance and transmittance were investigated. From 80 mmol/L of $Fe(OTs)_3$ solution, PET film could adsorb $Fe(OTs)_3$ at a magnitude of 1.7 mmol/m^2. As PET with adsorbed $Fe(OTs)_3$ was suspended in EDOT solution, EDOT monomers deposited to PET surface and joined one another to form positive charged PEDOT molecules continually, resulting in transparent and conductive PEDOT coating on PET film. After dipped in 80 mmol/L $Fe(OTs)_3$ solution, dried at temperature 40 °C and suspended in 80 mmol/L EDOT solution for 15 h, PEDOT coating with thickness about 100 nm and conductivity 530 S/cm generated; flexible PEDOT/PET films with transmittance above 80% and sheet resistance below 200 Ω/area were produced.

1. Introduction

Flexible transparent conductive film (FTCF) is a crucial raw material for touch screens, flexible display panels, electronic papers, smart windows and many other optoelectronic devices. Currently, most FTCFs commercially available are transparent polymeric films with indium tin oxide (ITO) coating. The transmittance are above 80% and the sheet resistance are about hundred Ω/area. Because ITO coating is mechanical brittle, these FTCFs have poor fatigue lifetime [1]. Furthermore, indium is a rare metal; the supply of ITO is scare and the price has been increasing since the end of last century due to the extensive application of touch screens. Many scientists have devoted to developing transparent conductors for FTCF, including oxide semiconductor [2,3] and silver nanowire [4,5].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an intrinsically conducting polymer. It can exhibit not only prominent electrical conductivity but also excellent optical transparency and high environmental stability. PEDOT has been considered another candidate to replace ITO and fabricate FTCF at low cost. However, PEDOT is neither fusible nor soluble. It is difficult to process virgin PEDOT powders into thin films. The researchers of Bayer aimed at the processing problem in 1990s. They polymerized EDOT monomers in poly(styrene sulfuric acid) (PSS) solution and produced an aqueous dispersion of PEDOT/PSS complexes, branded Baytron P. This dispersion can convert to thin coating and provides a solution to the processing problem of PEDOT. However, this coating contains nonconductive PSS component; the planar PEDOT molecules may be distorted during drying. It exhibits lower electrical conductivity, though the conductivity can be improved by adding polar solvents and annealing at elevated temperature [6,7]. Also, the PSS component absorbs moisture strongly and causes corrosion in device assemblies [8,9]. This brings about reliability problem to devices. Although the PEDOT/PSS dispersion has demonstrated the applications of PEDOT for electrode materials in various optoelectronic devices, it has rarely been used in commercial products.

Many researchers attempt to convert EDOT monomer to PEDOT coating on transparent polymeric films to solve the processing problem of PEDOT [10]. Of the exploited methods, vapor phase polymerization (VPP) has attracted much attention because it gives PEDOT with high conductivity [11]. Kim et al. exposed poly (ethylenephthalate) (PET) film with ferric tosylate ($Fe(OTs)_3$) coating to EDOT vapors in closed chamber [12], in which gaseous EDOT molecules deposed on PET film and joined one another to

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form long PEDOT chains. By this way, they synthesized 100 nm thick PEDOT coating on PET and produced PEDOT/PET film with transmittance above 80% and sheet resistance about 150 Ω/area. Madl et al. [13] spin-coated $Fe(OTs)_3$ and pyridine solution on poly (ethylenenaphthalate) (PEN) film and exposed the film to EDOT vapor in vacuum chamber. They prepared PEDOT/PEN films with transmittance above 94% and electrical conductivity about 600 S/cm.

But VPP has a few inherent drawbacks. Firstly, the dimension of processed films is restricted by VPP chamber. It is a challenging task to maintain the homogeneity of EDOT vapors in large vacuum chamber. Secondly, VPP is very sensitive to humidity in VPP chamber [14]. Moisture does benefit deprotonation of cationic EDOT dimers so as to construct conjugative PEDOT molecules. However, high humidity will stimulate the hydration and crystallization of ferric oxidants. This may lead to pinholes in final PEDOT film [15]. Thirdly, the C=C double bonds in EDOT monomer is able to participate in acidity driven addition polymerization, which leads to non-conjugated chain elements. Solid $FeCl_3$ or $Fe(OTs)_3$ oxidants are acidic enough to catalyze the addition polymerization of EDOT [16]. To depress the acidity driven side reaction, volatile organic bases [10,16] or polymeric surfactants [14,17] have to be incorporated into oxidant solutions before coating. In VPP, only chamber humidity, oxidant formula and reaction conditions are controlled tightly, high quality PEDOT coating could be obtained.

To overcome the drawbacks of vapor phase polymerization, the process of VPP has been modified in this laboratory. The depositional polymerization of EDOT was implemented in liquid phase. PI film with adsorbed $FeCl_3$ oxidant was suspended in EDOT solution to synthesize PEDOT coating in situ [18,19]. Wet chemistry is believed suitable for mass production and moisture control will become relatively easy. In EDOT solution, the adsorbed $FeCl_3$ diffused into the stagnant layer of the film and initiated chemical oxidative polymerization of EDOT. As the monomers in the stagnant layer converted to EDOT oligomers and attached to PI surface, the monomers in solution phase diffused into the stagnant layer continually and coupled with the oligomer one after another, thus, built up PEDOT coating on PI surface. The sheet resistance of insulating PI film could be reduced to 400 Ω/area [19].

In this article, the process of liquid phase depositional polymerization of EDOT was utilized to fabricate FTCF. Transparent PET film was used as substrate and $Fe(OTs)_3$ was selected as oxidant. The effects of processing conditions on the conductivity and transmittance of resultant PEDOT/PET films were investigated.

2. Materials and methods

2.1. Raw materials

PET film used in this work was Kolon KP 185 PET film. Oxidant ferric *p*-toluene-sulfonate was OX-DO55 (Fe(OTs)3, 55% in *n*-butanol) made by Shenzhen Capchem Technology. Monomer 3,4-ethylenedioxythiophene (EDOT, 99%) was purchased from Zhengzhou Alfachem. Cyclohexane and absolute ethanol were AR grade products of Tianjin Fuyu Chemistry. *n*-Butanol was AR grade product of Jiangsu Enox Chemistry. All other chemicals were AR grade and used as received without further purification

2.2. Adsorption of $Fe(OTs)_3$ oxidant

PET sheets with a dimension of 30 mm × 35 mm were immersed in toluene for surface cleaning and suspended in 80 mmol/L Fe $(OTs)_3$ *n*-butanol solution for $Fe(OTs)_3$ absorption. After immersed for 10 min, the PET sheet were taken out from the solution and dried in oven at temperature 40 °C for 3 min. The PET film was covered with a layer of $Fe(OTs)_3$ at content of 1.66 mmol/m^2 as determined by iodometry method.

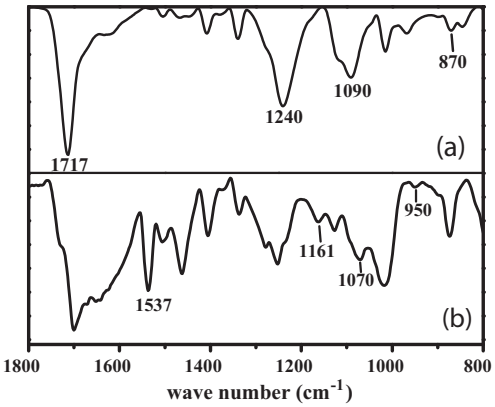

Fig. 1. ATR-FTIR spectra of PET film a): before and b): after PET with adsorbed Fe $(OTs)_3$ was immersed in EDOT cyclohexane solution.

2.3. Liquid phase depositional polymerization

After dried at 40 °C for 3 min, the PET sheet with adsorbed $Fe(OTs)_3$ were inserted in 80 mmol/L EDOT cyclohexane solution immediately. After suspended in the solution at ambient temperature for 20 h, the PET sheet were washed with 0.1 M H_2SO_4 solution, DI water and alcohol to remove any residual oxidants and un-reacted monomer. Finally, the PEDOT/PET sheets were dried in oven at 60 °C.

2.4. Characterization of PEDOT/PET film

The surface composition of PET films after liquid phase depositional polymerization was analyzed with BRUKER VECTOR 33 FTIR spectroscope in reflective mode. The UV–vis spectra of samples were examined with Yoke UV756CRT10008 UV–vis spectroscope. The transmittances at wavelength 550 nm were taken as the transmittance of the sample. The thicknesses of PEDOT coatings were determined with Acer View 34T α-step 500 Profiler. The sheet resistances of the samples were measured with Guangzhou Four Probe Tech RTS-8 4-point probes resistivity measurement system. The instrument was equipped with spring probe and the needles are spaced 1.0 mm apart. For each sample, five locations were measured and the average was reported.

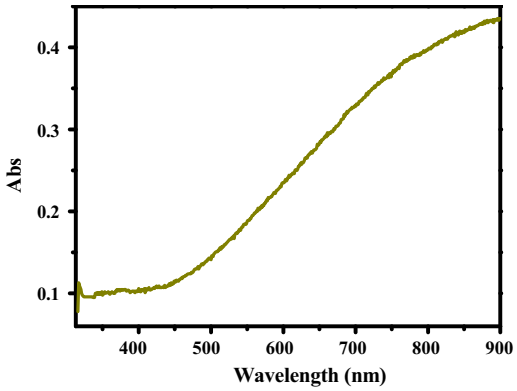

Fig. 2. UV–vis spectrum of PET film after PET with adsorbed $Fe(OTs)_3$ was immersed in EDOT cyclohexane solution.