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Article

Flexible, Highly Transparent, and Conductive Poly(3,4-ethylenedioxythiophene)-Polypropylene Composite Films of Nanofibrillar Morphology

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A novel chemical strategy for fabricating flexible, transparent, and conductive poly(3,4-ethylenedioxythiophene) (PEDOT) films with a nanofibrillar morphology by in situ deposition on commercial plastic substrates has been developed. The key points of the strategy include (1) preimplanting surface sulfate groups (SO_4^-) onto the substrate surface by a confined photocatalytic oxidation (CPO) technique, which was critical both for improving the adhesion of the PEDOT with the substrate via static interactions and for inducing polymerization of EDOT onto the substrate surface, and (2) deliberately controlling the nanofibrillar network morphology by means of the reaction recipe and parameters, which was critical for balancing conductivity and transparency. On the basis of this design, with BOPP as a model substrate, PEDOT−BOPP composite films approximately 20 nm in thickness with a transparency as high as 90% and a conductivity of 300 S/cm were obtained. Moreover, XPS data demonstrated that the SO_4^- implanted on the substrate surface constituted the primary dopant of the deposited PEDOT, and peeling tests with 3M Scotch adhesive tape proved that the adhesion between the substrate and PEDOT was drastically enhanced. Combined with a photomask, a PEDOT micropattern on the polymer substrate could also be fabricated.

Introduction

Polymer electronics is considered a promising technology because of the lightweight, high flexibility, and solution-processable properties of these materials.[1a] Electronic devices based on polymers as the active material, such as polymer light-emitting diodes (PLEDs)[1−4] and photovoltaic cells (PVs),[5−10] exhibit excellent performance. Indium tin oxide (ITO) is a transparent inorganic anode material for these devices, presently employed as an industrial standard. However, it is not an ideal choice for flexible devices because of its inherent brittleness and susceptibility to conductivity changes after bending.[11,12] Therefore, one of the key goals that needs to be achieved in this field is the fabrication of high-performance, fully plastic electronic devices. However, it remains a great challenge to develop novel organic electrode materials with conductivities and stabilities comparable to those of existing inorganic materials. Furthermore, for optoelectronic devices, at least one of the electrodes needs to be

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transparent. It is thus rational to design organic-based electrodes with both high transparency and high conductivity for plastic optoelectronics.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is widely used as an organic electrode material for its elevated conductivity, good stability, and high transparency in the oxidized state.[13−15] Like many inherent conductive polymers, PEDOT is not easily processed into thin films via solution or melt because of its rigid conjugated bond conformation. Consequently, it is difficult to coat onto polymer substrates. Until now, numerous efforts to overcome this limitation have been made. Bayer AG has for instance developed an aqueous dispersion of a PEDOT−PSS complex with good film forming properties by using a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS), during polymerization in water.[14,16]

Increasing conductivity is the key to opening the envelope for extensive application of the PEDOT−PSS complex. Researchers have observed that the conductivity of PEDOT−PSS films can be enhanced by more than 1 order of magnitude by the addition of polyalcohols (alcohols with more than two OH groups on each molecule) or high-dielectric solvents, such as dimethyl sulfoxide (DMSO) and *N*,*N*′-dimethylformamide (DMF), to the PEDOT−PSS dispersion.[17−24] Recently, H. C. Starck Clevios GmbH announced that the conductivity milestone of 1000 S/cm had been achieved using the optimized PEDOT−PSS conductive polymer called Clevios.

In situ deposition, which can be used to produce films with thicknesses ranging from 100 to 200 nm, is also an effective means of preparing PEDOT-coated organic electrodes. Films of polyaniline and polypyrrole prepared with this technique have been shown to be applicable for electronic devices, such as liquid crystal displays[25] and capacitors.[26] However, according to the literature, only a limited number of research studies have explored such in situ deposited films of PEDOT.[27]

Moreover, the adhesion between polymer substrates and a deposited PEDOT film is not strong enough because of the low surface energy of most polymer substrates. Numerous strategies for improving this property exist, for instance, plasma treatment and surface graft polymerization. Confined photocatalytic oxidation (CPO) is a facile method invented in our laboratory,[28] with which sulfate anion groups (SO_4^-) can be introduced onto various polymer substrate surfaces, including polyolefins, polyesters, nylons, and rubbers. In this way, a variety of micro/nanosized and micropatterned structures of TiO_2,[29] ZnO,[30] and biochips have been formed in situ on polymeric substrate surfaces.[31]

It is well-known that oxidized PEDOT is positively charged and needs to be doped with anions. It is thus expected that SO_4^- groups, introduced onto the substrate by CPO, could improve both the adhesion of the PEDOT with the substrate through static interactions and the conductivity of the composite via dopation.

Another challenge in the preparation of PEDOT-based organic electrodes is finding a balance between the requirements for high transparency and high conductivity. The transmittance of conducting polymer films is expected to follow Beer's law. Thinner films are more transparent, but this might be at the expense of higher sheet resistances, leading to the electronic performance becoming worse. An ideal approach to circumventing this problem would be to design or build a PEDOT network of nanowires or nanorods onto the polymer substrates. There are several methods for preparing such PEDOT nanostructures, including surfactant-mediated interfacial polymerization,[32] reverse microemulsion systems,[33,34] a self-assembly micellar soft-template approach,[35] V_2O_5 seed polymerization,[36] interfacial polymerization crystallization,[37] and electrochemical polymerization.[38] To the best of our knowledge, there have been no reports regarding the building of such nanostructures on organic polymer substrates.

This article thus presents a novel and very successful strategy for fabricating a transparent and conductive composite PEDOT film, according to Scheme 1. The approach includes (1) implanting SO_4^- groups onto the substrate surface [here, biaxially oriented polypropylene (BOPP) was chosen as a model substrate because of its good transparency and mechanical properties], (2) in situ depositing the PEDOT onto the treated substrate surface by using iron(III) chloride ($FeCl_3$) as the oxidant and an

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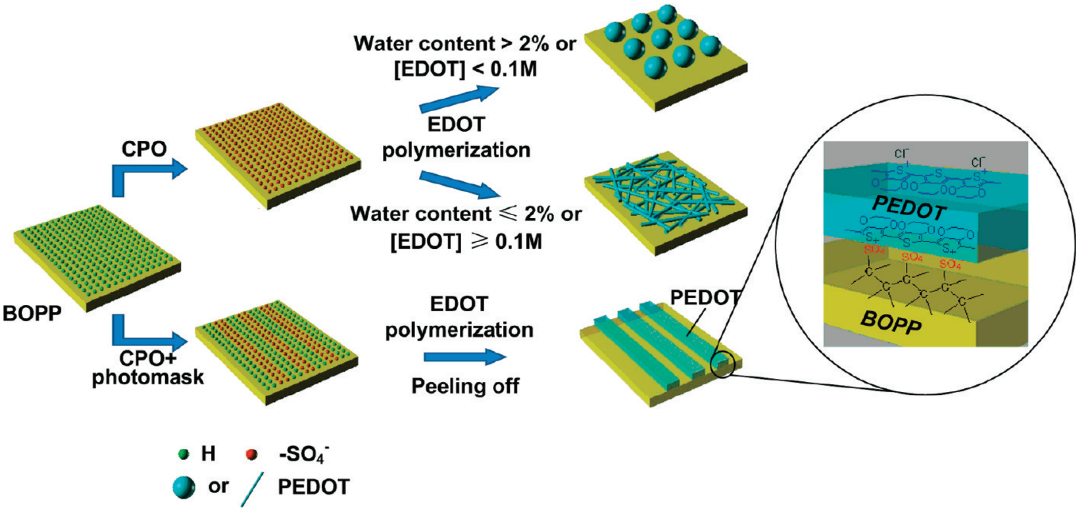
Scheme 1. Illustration of the Fabrication Method for PEDOT Nanostructures on the Surface of BOPP



acetonitrile/water mixture as the solvent and controlling the morphology by adjusting the concentrations of both water and the EDOT monomer as well as the reaction time (this resulted in a significantly enhanced adhesion strength and the formation of the desired fibrillar network morphology without the aid of a template), and (3) micropatterning the PEDOT onto the polymer substrate with the help of a photomask.

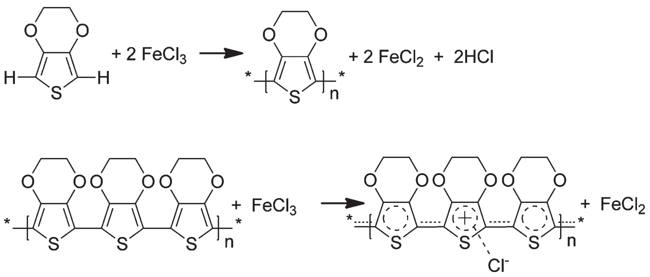
Experimental Section

Materials and Reagents. 3,4-Ethylenedioxythiophene (EDOT, Sigma Aldrich, ≥98.0%) was distilled under vacuum prior to use. Acetonitrile (AN, Beijing Chemical Reagents Co., ≥99.0%) was dehydrated by a 4 Å zeolite for 24 h and then redistilled by using P_2O_5 as a dryer. BOPP was a commercial product 19 μm in thickness, cut into 1 cm × 3 cm slides, and was extracted with acetone for 24 h. All the other reagents, including ammonium persulfate (APS, Beijing Chemical Reagents Co., ≥98.0%) and anhydrous iron(III) chloride ($FeCl_3$, ≥98.0%, Alfa Aesar), were used as received. The water used was tridistilled with a conductivity of < 0.09 μS/cm^2.

Implanting of SO_4^- Groups by Confined Photocatalytic Oxidation (CPO). As described in detail elsewhere,[28] a thin layer of an APS aqueous solution (30 wt %) was sandwiched between two BOPP films, and this structure was UV irradiated (UV intensity of 9000 μW/cm^2 and irradiation time of 120 s). For the wettability pattern process, a strip photomask with channels of 50 μm was used. The samples were further employed for PEDOT deposition without delay.

Deposition of PEDOT. The synthesis procedure was based on the report of McDiarmid.[27] Typically, 0.1 M EDOT and 0.2 M $FeCl_3$ solutions in a component solvent of AN and H_2O (water content of 1%) were prepared separately. The BOPP substrates (pristine and treated with CPO) were placed in a 250 mL beaker filled with a 100 mL EDOT solution. At room temperature, a 100 mL $FeCl_3$ solution was added rapidly. To prevent the hydrolysis of $FeCl_3$, 5 drops of concentrated HCl (37%) was added to the reaction solution. The clear solution became darker in < 10 s as the oxidative polymerization began (Scheme 2). After a certain time, the substrates were removed and rinsed with deionized water and methanol to remove the residual reactants and unbound oligomer. Subsequently, the composite films were dried in air at room temperature. The reactions were also conducted at varying percentages of water, ranging from 0 to 5%, and at EDOT monomer concentrations between 0.2 and 0.02 M.

Scheme 2. Oxidative Polymerization of EDOT to PEDOT and Subsequent Doping of PEDOT with $FeCl_3$



Fabrication of PEDOT Patterns. The PEDOT pattern was formed as follows. A piece of 3M Scotch adhesive tape was placed on the film deposited with PEDOT, gently pressed to create a homogeneous contact between the adhesive tape and the film, and then quickly peeled off.

Characterization. The UV−vis absorption spectra were recorded using a GBC Cintra 20 spectrophotometer. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet Nexus 670 spectrometer with 8 cm^{-1} resolution, and a variable-angle attenuated total reflectance (ATR) accessory (PIKE ATRMax II) was utilized with ZnSe (n = 2.43) as the internal reflection element wafer. X-ray photoelectron spectra (XPS) were recorded on an ESCA Lab 22i-XL instrument (VG Scientific) using K-Alα as the excitation source. Scanning electron microscopy (SEM) was performed on a JEOL JSM 6700F instrument. Atomic force microscopy (AFM) was conducted on a Nano Scope III (DI), and 256 × 256 pixel images were obtained under ambient conditions in contact mode. Microscopic observations were made with a Nikon (Tokyo, Japan) TE2000-s system. The resistivity of the deposited PEDOT layer was measured with a Keithley 2400 constant current source and a Keithley 6571A digital voltmeter with a four-point probe.

Results and Discussion

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy. Figure 1 shows the FTIR spectra of the deposited PEDOT film under conditions of

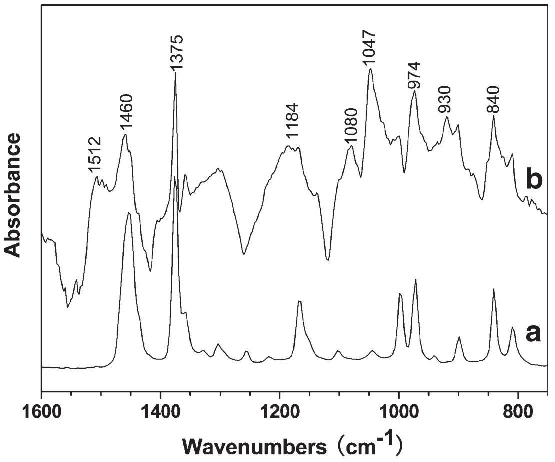


Figure 1. ATR-FTIR spectra of (a) BOPP and (b) PEDOT films deposited on BOPP (surface treated with CPO for 10 min). Reaction conditions: 1% water content, 0.1 M EDOT, and 0.2 M $FeCl_3$ at ambient temperature.

1% water in the solvent, 0.1 M EDOT, and 0.2 M $FeCl_3$ at room temperature. The following discussion is based on these conditions unless stated otherwise. Figure 1a represents a typical IR spectrum of pristine BOPP (with a strong absorption of C−H deformation vibration at 1458 and 1375 cm^{-1}). The FTIR spectrum of the deposited PEDOT is displayed in Figure 1b. The vibrations at 1512 and 1375 cm^{-1} corresponded to the C=C and C−C stretching in the thiophene ring; the bands at 840 and 930 cm^{-1} were ascribed to vibration modes of the C−S bond in the thiophene ring, and the peaks at 1184, 1080, and 1047 cm^{-1} were attributed to the vibration modes of the ethylenedioxy group in the PEDOT molecule.[39,40] All the FTIR results indicated that PEDOT had been successfully deposited on the modified BOPP film.

X-ray Photoelectron Spectroscopy (XPS). Panels a and b of Figure 2 show XPS survey scans of PEDOT deposited on CPO-treated BOPP films as a function of time. C, O, and S are the characteristic elements of the PEDOT polymer, while Cl represents the dopant ions. The quantitative analysis from the XPS survey scan of PEDOT deposited after 30 min (Figure 2b) demonstrates that the atomic C (71−72%):O (19−20%):S (8−9%):Cl (1−2%) ratio displayed a good fit with the theoretical atomic ratio of PEDOT [i.e., C (65%):O (22%):S (10%):Cl (2−3%)].[41] A somewhat elevated composition was observed for C, which most likely arose from the substrate and environmental carbon contamination.

The contents of Fe and Cl in the PEDOT films deposited at various times were quite different. The film deposited for 1 min (Figure 2a) displayed a higher content (3−4%) of Fe and hardly any Cl as compared to that of the film deposited for 30 min (Figure 2b). Previous work has shown that sulfate anion groups (SO_4^-) can be implanted on substrate surfaces with the CPO process.[28] When an $FeCl_3$ solution is introduced into the reactant mixture, Fe(III) is rapidly combined with SO_4^-. The fastened Fe(III) oxidizes the EDOT monomer, transforming it into a cation radical which can subsequently be captured by SO_4^-. Thus, at the beginning of the PEDOT deposition, the dopant of PEDOT on the CPO-treated surface is SO_4^-, and Cl^- is removed by rinsing. After 30 min, no Fe is detected at the surface, indicating that reaction byproducts from the $FeCl_3$ oxidizer are completely removed by the rinsing step. Jones and co-workers suggested that the possible dopants of bulk PEDOT were $FeCl_4^-$ or simple Cl^- ions with $FeCl_3$ as the oxidizer.[42] From the XPS spectrum, the possibility of $FeCl_4^-$ dopants could be clearly excluded. It could therefore be concluded that the surface consisted of only PEDOT chains doped solely with Cl^-. The absence of detectable iron ions in the PEDOT films constitutes an advantage for certain applications, e.g., when used as the cathode materials of capacitors or wires connecting the components on the board.

The XPS S2p core level high-resolution XPS spectra of PEDOT deposited onto the pristine and CPO-treated BOPP for 1 min provided additional information indicating that SO_4^- was the predominant dopant on the treated surface (Figure 2c,d). Sulfur atoms have a spectral characteristic of a spin−split doublet, S2p1/2 and S2p3/2, which has an energy splitting of 1.18 eV, an intensity ratio of 1:2, and an equivalent fwhm and shape.[41,43] For all samples, subpeaks with binding energies of 164 and 165.18 eV could be seen, which was attributed to the sulfur atom in PEDOT. The subpeaks with higher binding energies of 168.5 and 169.68 eV in the spectrum of the PEDOT film deposited on CPO-treated BOPP for 1 min were associated with SO_4^-.

Morphology. Figure 3 shows SEM images of the deposited PEDOT films on pristine and CPO-treated BOPP in the AN/H_2O component solvent with 1% water for various times. Upon comparison of panels a and b of Figure 3, it can be observed that more PEDOT was deposited on the CPO-treated surface at an early stage, which was in accordance with the XPS result. The SEM images in Figure 3b−f revealed the growth process of the deposited PEDOT on the CPO-treated BOPP surface at reaction times of 1, 1.5, 2, 5, and 10 min, respectively. At first, the deposited PEDOT could be seen merely as sparse dots with a diameter of < 20 nm. With the extension of the reaction time, the deposited PEDOT grew longer and exhibited nanofibrillar morphology with fibril dimensions of 100 nm (length) and 20 nm (width). When the reaction time was prolonged to more than 5 min, these deposited PEDOT nanofibrils started to overlap each other, thus forming a dense and continuous network of nanofibrils that were ~200 nm in length and 30−40 nm in diameter. This result differs from that of deposited films

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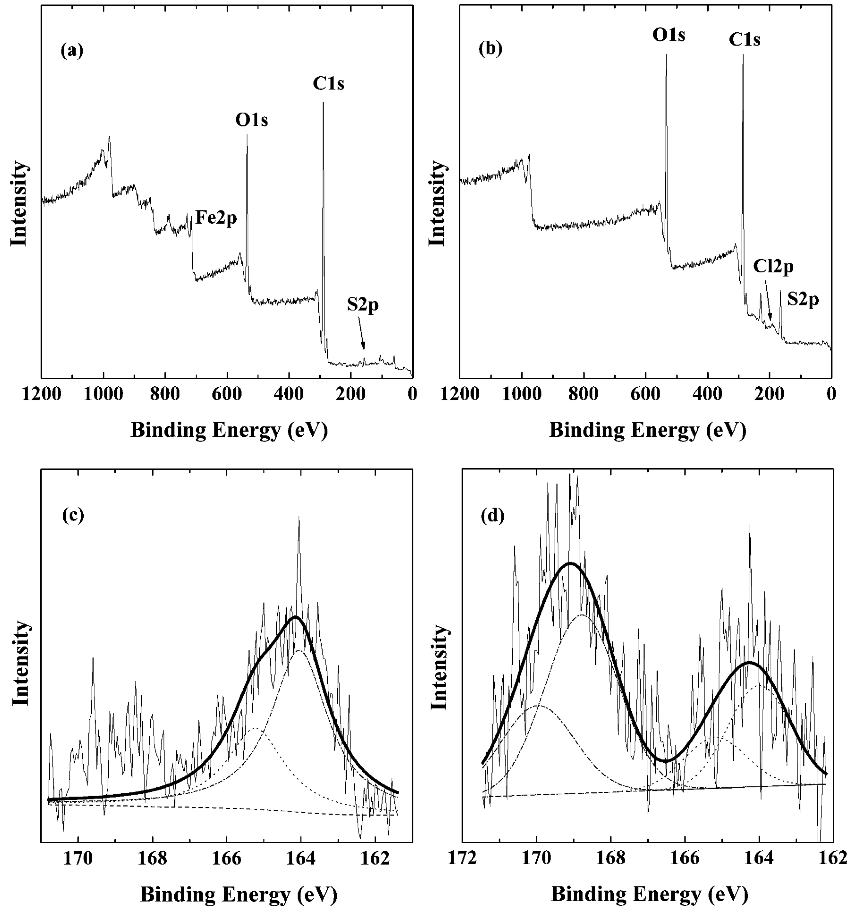

Figure 2. XPS survey scans of PEDOT deposited on CPO-treated BOPP for (a) 1 and (b) 30 min. S2p core level spectra of PEDOT deposited on (c) pristine BOPP for 1 min and (d) treated BOPP for 1 min. Reaction conditions: 1% water content, 0.1 M EDOT, and 0.2 M FeCl$_3$ at ambient temperature.

of polypyrrole described in the literature, which exhibited a granular or "cauliflower" morphology.[44]

To investigate the influence of the reaction conditions on the morphology of the deposited PEDOT films, the volume percentage of water in the component solvent and the EDOT monomer concentration were adjusted. Figure 4 shows SEM images of deposited PEDOT on CPO-treated BOPP surfaces in a water/AN mixture with a varying water content (V%). When pure acetonitrile was used as the solvent (Figure 4a), there was hardly any polymer deposited on the substrate surface, and the existing deposition exhibited a nanoisland with an irregular shape. When the water content was increased to 0.5 and 1% (panels b and c, respectively, of Figure 4), the continuous network of fibrils appeared, with almost the same length and width. The fibril network obtained in a 0.5% water/AN mixture was somewhat denser than that in a 1% water/AN mixture. Furthermore, in a water/AN mixture with 2% water (Figure 4d), the fibril morphology remained the same, but the density became smaller and the length shorter. The dimensions were as follows: ∼100 nm in length and ∼30−40 nm in width. When the water percentage was increased to 3 and 5% (panels e and f, respectively, of Figure 4), the deposited PEDOT films presented a granular morphology with diameters in the range of 70−100 nm, like those of polyaniline or polypyrrole films obtained by in situ deposition.

A similar change in morphology was also observed when the reactant concentration was varied, as presented in Figure 5. At higher EDOT monomer concentrations, i.e., 0.2 and 0.1 M (shown in panels a and b, respectively, of Figure 5), the deposited PEDOT films took on a nanofibril network structure, with a fibril length of 200 nm and width of 30−70 nm. Further, a granular morphology appeared when the EDOT monomer concentration was 0.05 and 0.025 M (cf. Figure 5c,d).

It could thus be concluded from the SEM images that the kinetics of the polymerization reaction played a significant role in determining the morphology of the deposited PEDOT. Huang and Kaner reported that during the chemical polymerization of aniline in water, nanofibers represent the initial product formed, and it was only the secondary growth process that resulted in the formation of particles.[45] Thus, the key to achieving a deposited PEDOT film with an entirely fibrillar morphology may lie in the choice of appropriate reaction conditions to suppress the overgrowth of PEDOT after the initial nanofibrillar formation stage. Because the EDOT monomer demonstrates a lower oxidation potential in organic solvents, such as acetonitrile, the polymerization

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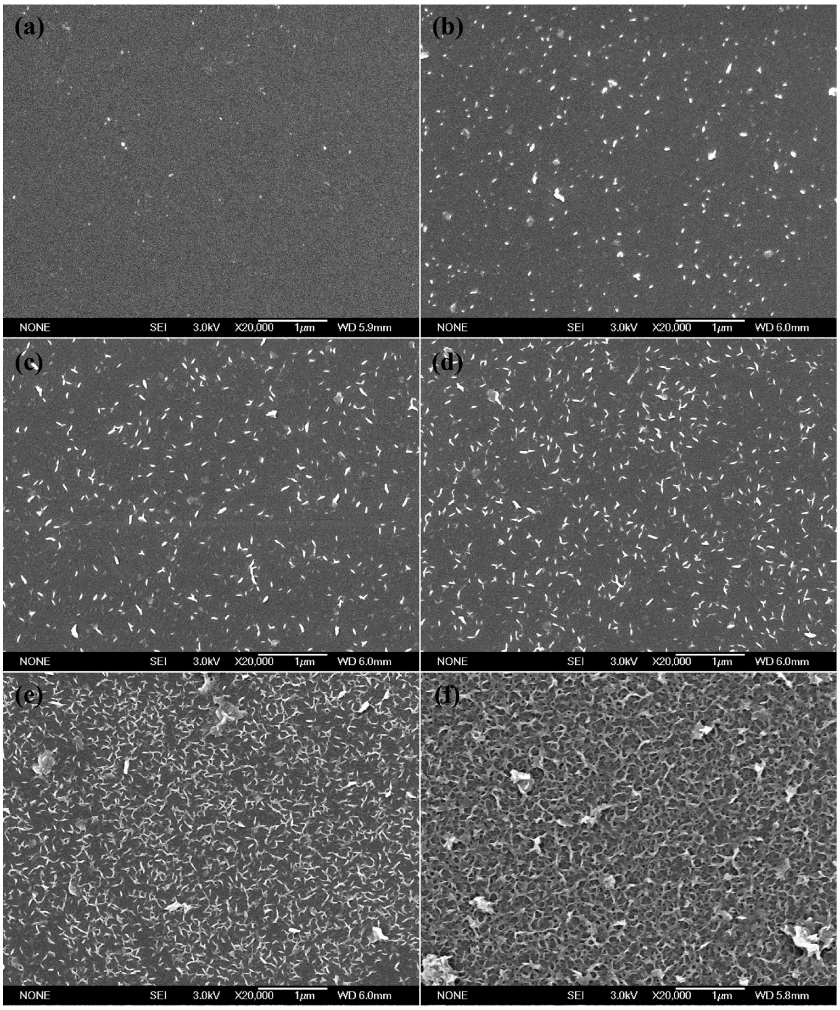

Figure 3. SEM images of deposited PEDOT on different surfaces after varying reaction times. (a) Deposition on pristine BOPP, after reaction for 1 min. (b−f) Deposition on CPO-treated BOPP, after reaction for 1, 1.5, 2, 5, and 10 min, respectively. All reactions were conducted in an AN/H_2O component solvent with 1% water, 0.1 M EDOT, and 0.2 M $FeCl_3$ at ambient temperature.

can proceed faster than in aqueous solution. When the percentage of water in the component solvent is low (between 0.5 and 2%) or the reactant concentration is high (from 0.1 to 0.2 M EDOT monomer with a water content of 1%), iron(III) ions induce the formation of nanofibrils by rapidly polymerizing the EDOT monomer in their vicinity, and subsequently, the monomers and oxidant are consumed in a short amount of time. As a consequence, secondary growth of PEDOT is limited due to a lack of available reactants, and a PEDOT film with a nanofibrillar morphology is formed on the BOPP surface.

On the other hand, with reaction conditions including a high percentage of water ($>3\%$) or a low reactant concentration (<0.05 M EDOT with a water content of 1%), the polymerization of EDOT proceeded very slowly, and the consumed reactant could be compensated by diffusion. Consequently, secondary growth occurred, resulting in the formation of PEDOT films with a granular morphology. As for the deposition in acetonitrile without addition of water, there was no deposit on the BOPP surface, which may be attributed to the excessively rapid polymerization of EDOT. The precipitation was formed before the initial adsorption of PEDOT cation radicals on the BOPP surface.

Thickness and Transmittance. The evolution of the thickness with the time of deposition is shown in Figure 6a. At the early stage of the PEDOT deposition, the thickness did not change significantly with time. This was due to the deposited PEDOT not having completely covered the substrate surfaces. After 5 min, the thickness started increasing rapidly and reached a stable level after 30 min. Figure 6b shows the results of light transmission of a conductive polymer layer at various deposition times, measured by subtracting the spectrum of substrate film (BOPP) from the spectrum of PEDOT deposited on the BOPP film in the range of 350−800 nm. The 20 nm thick PEDOT films displayed very high transmittances, up to 90%. According to Lambert−Beer's law, the absorption intensity is proportional to the thickness of the layer. Consequently, the thicker PEDOT deposited layers increased the absorption, and their transmittances were lower than 80%, as shown.

Conductivity. Table 1 lists the conductivities of the deposited PEDOT films under varying reaction conditions. With a water content of 1%, the measured conductivity values of the deposited PEDOT films increased dramatically as the reaction time increased from 1 to 30 min.

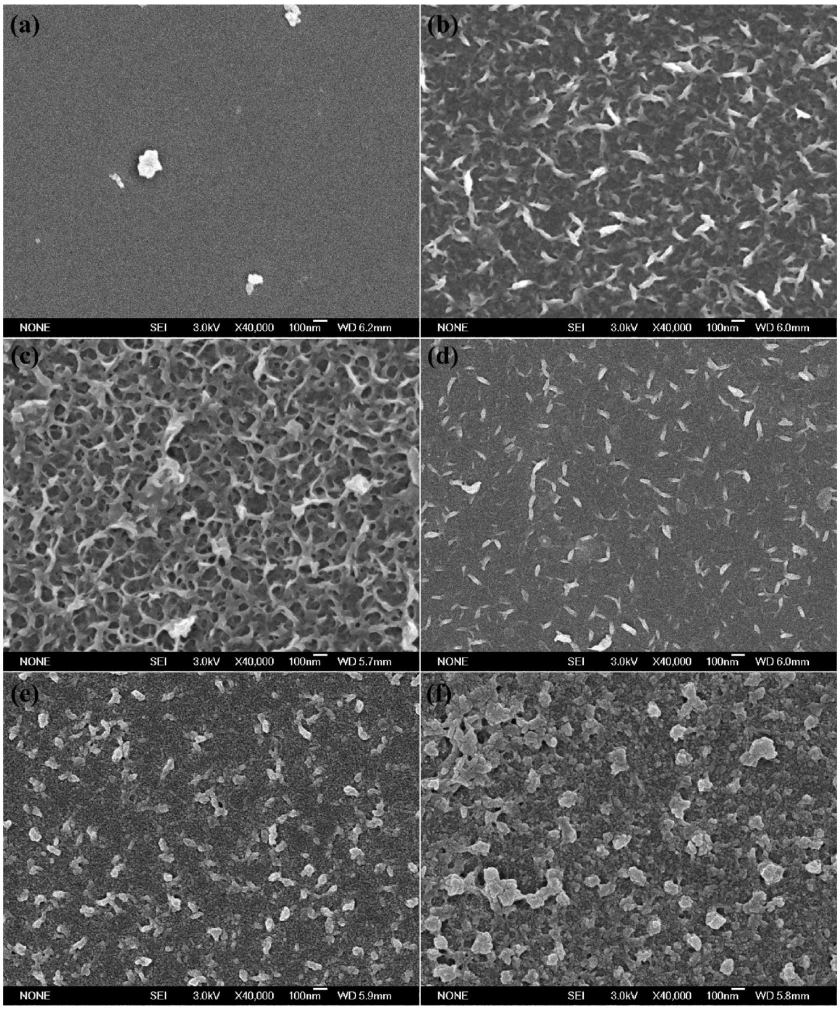

Figure 4. SEM images of deposited PEDOT on CPO-treated BOPP surfaces in the water/AN component solvent with varying water contents, maintaining the reactant concentrations as 0.1 M EDOT and 0.2 M $FeCl_3$. The reaction time was changed as follows: (a) no water, 5 min; (b) 0.5% water, 5 min; (c) 1% water, 10 min; (d) 2% water, 20 min; (e) 3% water, 4 h; (f) 5% water, 12 h.

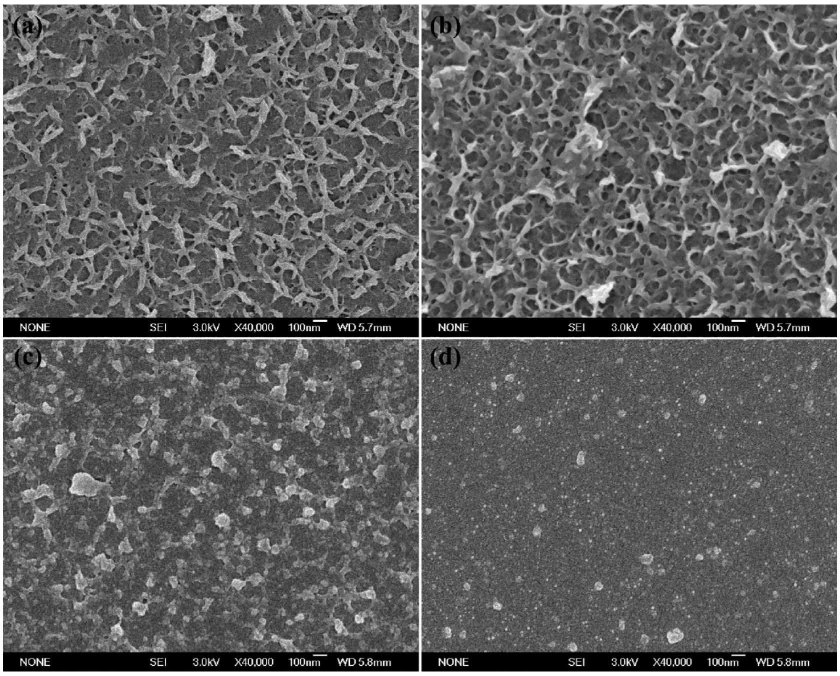

Figure 5. SEM images of deposited PEDOT on the CPO-treated BOPP surface with varying monomer and oxidant concentrations, maintaining the percentage of water as 1% in the solvent. The reaction time was varied as follows: (a) 0.2 M EDOT, 0.4 M $FeCl_3$, 10 min; (b) 0.1 M EDOT, 0.2 M $FeCl_3$, 10 min; (c) 0.05 M EDOT, 0.1 M $FeCl_3$, 60 min; (d) 0.025 M EDOT, 0.05 M $FeCl_3$, 4 h.

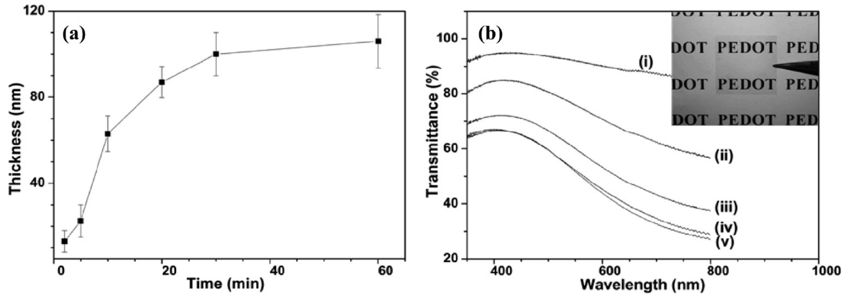

Figure 6. (a) Variation in the thickness of PEDOT as a function of deposition time. (b) Light transmission of conductive polymer layers at varying deposition times. Traces i−v represent deposition times of 5, 10, 20, 30, and 60 min, respectively. The inset in panel b shows the transparency of a PEDOT film deposited for 2 min. Reaction conditions: 1% water, 0.1 M EDOT, and 0.2 M $FeCl_3$ at ambient temperature.

Table 1. Conductivities (siemens per centimeter) of Deposited PEDOT Films under Several Reaction Conditions

	reaction conditions				
sample	water content (%)	[EDOT] (mol/L)	[$FeCl_3$] (mol/L)	reaction time	conductivity (S/cm)
1	1	0.1	0.2	1 min	0.000675
2	1	0.1	0.2	2 min	26.5
3	1	0.1	0.2	5 min	314
4	1	0.1	0.2	10 min	316
5	1	0.1	0.2	30 min	303
6	0.5	0.1	0.2	5 min	319
7	2	0.1	0.2	20 min	256
8	3	0.1	0.2	4 h	23.8
9	5	0.1	0.2	12 h	1.56
10	1	0.2	0.4	10 min	334
11	1	0.05	0.1	60 min	13.6
12	1	0.025	0.05	4 h	0.00278

The achieved conductivity ranged from a low of 6.75×10^{-4} S/cm (sample 1) to a high of more than 300 S/cm (samples 3−5). Thus, a PEDOT film with high transparency and conductivity could be readily fabricated with a reaction time of ~5 min, and the conductivity of the deposited PEDOT could also be controlled over a range spanning more than 5 orders of magnitude by simply mediating the reaction time.

For the samples with other water contents (samples 5−9), the conductivity changed more than 2 orders of magnitude. On the basis of the SEM images, it could be concluded that the samples with a nanofibrillar morphology presented conductivities as high as 250 S/cm, while those with a granular morphology displayed lower conductivities. A similar phenomenon was also observed when the reaction was conducted at different reactant concentrations. The conductivity of samples derived from an elevated concentration was much higher than the corresponding values derived from low concentrations. For the sample with 0.025 M EDOT, the conductivity even dropped to 0.002 S/cm because of the disconnected polymer particles. Besides the conjugation length and doping level, the electrical conductivity of the conjugate polymers also depended on the morphology. The nanofibrils of these PEDOT films overlapped more closely, which significantly enhanced the conductivity. Similar results have also been reported in the literature on conducting polymer films with a nanofiber morphology prepared by an electrochemical method. In this case, the electrical contact between the fibrils was improved.[46]

Table 2. Surface Resistances (KΩ/cm^2) of Deposited PEDOT Films as a Function of Deposition Time before and after Being Peeled by Adhesive Tape

sample	5 min[a]	10 min[a]	20 min[a]	30 min[a]
original BOPP	2.033	0.597	0.367	0.327
original BOPP after peeling	–[b]	–	–	–
treated BOPP	1.57	0.51	0.376	0.33
treated BOPP after peeling	2.367	0.767	0.633	0.567

[a] Deposition time. [b] Measurement beyond the detection limit.

Adhesion of Deposited PEDOT Films. To test the adhesion between the deposited PEDOT films and the substrates, the surface resistivity values of the deposited PEDOT films before and after peeling with 3M Scotch adhesive tape were measured and are listed in Table 2. Before the peeling, the resistivity values of each PEDOT film at the same reaction time were approximately equal and in the range of the conductor. After the adhesive tape had been peeled off, the resistivity of the PEDOT films on pristine BOPP exceeded the detecting limit of the meter (10^{12} Ω), signifying that the PEDOT became totally removed by the tape due to poor adhesion between the PEDOT and BOPP. However, the resistivity of PEDOT films on treated BOPP decreased slightly and remained in the range of the conductor. This suggests that the deposited PEDOT films were more robust on the CPO-treated surface than on pristine BOPP. According to the result of XPS, SO_4^- was the predominate dopant of deposited PEDOT on the CPO-treated substrate surfaces. The intensity of the electrostatic attraction between the materials was much higher than the peeling force of the adhesive tape. On the other hand, the adhesion between the pristine BOPP film and PEDOT originated from van der Waals forces, which are related to the surface free energy. The low-energy, hydrophobic surface of pristine BOPP was passive to adhesion.[47]

Because the BOPP film modified by the CPO technology was found to significantly improve the adhesion of the PEDOT with the substrate, this technology can be used to fabricate micropatterns of PEDOT associated with a photomask, using a procedure similar to the adhesive tape test. After removal of the film from the hydrophobic region by peeling off the adhesive tape, a

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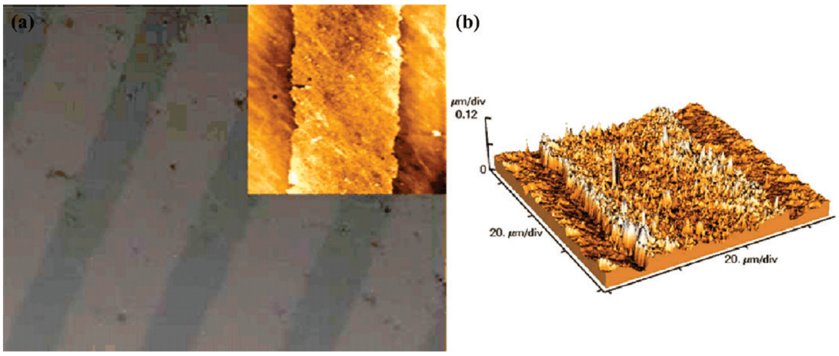

Figure 7. (a) Optical photo of the deposited PEDOT on the substrate after peeling with adhesive tape. The inset shows a detailed AFM image of the PEDOT strip. (b) Three-dimensional profile of the positive pattern. Reaction conditions: 1% water, 0.1 M EDOT, 0.2 M $FeCl_3$, and a reaction time of 20 min at ambient temperature.

positive pattern was left on the substrate (Figure 7a). The resulting PEDOT strip was 40−50 µm wide, which was close to the designed feature (50 µm) of the channels (Figure 7b). This PEDOT line pattern should have great potential for applications such as wires for connecting components on a circuit board.

Conclusions

This work describes the preparation of flexible, transparent, and conductive PEDOT films by an in situ deposition method on CPO-treated BOPP films. UV−vis, ATR-FTIR, SEM, and XPS were used to characterize the resulting films. The UV−vis transmittance showed that the PEDOT films that were 20 nm thick displayed very high transmittance values, up to 90%, and the deposited PEDOT film had a high conductivity of 300 S/cm. SEM images demonstrated that a fibril network of PEDOT had been deposited on the CPO-treated BOPP surface. Moreover, the influence of the reaction conditions on the morphology was investigated. When the water content in the component solvent was lower than 2% or the EDOT concentration was higher than 0.1 M, a polymer film with nanofibrillar morphology was achieved. On the other hand, with a water content of $>3\%$ or an EDOT concentration of <0.05 M, the morphology of the PEDOT film was granular. The kinetics of the polymerization reaction played a significant role in controlling the deposited PEDOT morphology. XPS data suggested that the SO_4^- implanted on the substrate surface by the CPO technology was the predominate dopant of the formed PEDOT. Furthermore, the PEDOT film formed on the pristine BOPP substrate could be removed by being peeled with adhesive tape, after which the conductivity vanished. However, the PEDOT film deposited on the modified BOPP films could not be removed by peeling and thus remained conducting, pointing at an enhanced adhesion between the deposited PEDOT and the CPO-treated substrate. On the basis of these results, a facile approach to fabricating positive patterns of PEDOT could be developed.

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