Sequential Solution Polymerization of Poly(3,4-ethylenedioxythiophene) Using V_2O_5 as Oxidant for Flexible Touch Sensors

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Rui Chen,1 Kuan Sun,1* Qi Zhang,1 Yongli Zhou,1 Meng Li,1 Yuyang Sun,2 Zhou Wu,2 Yuyang Wu,3 Xinlu Li,3 Jialie Xi,4 Chi Ma,4 Yiyang Zhang 4 and Jianyong Ouyang5**

1MOE Key Laboratory of Low-grade Energy Utilization Technologies and Systems, School of Energy & Power Engineering, Chongqing University, Chongqing 400044, China.
2MOE Key Laboratory of Dependable Service Computing in Cyber Physical Society, School of Automation, Chongqing University, Chongqing 400044, China.
3School of Materials Science and Engineering, Chongqing University, Chongqing 400044, China.
4Chengdu Mobius Technology, Sichuan 610015, China.
5Department of Materials Science and Engineering, National University of Singapore, Singapore 117574, Singapore.
*Correspondence: kuan.sun@cqu.edu.cn
**Correspondence: mseoj@nus.edu.sg

SUMMARY

Various in-situ synthesis methods have been developed for the polymerization of 3,4-ethylenedioxythiophene (EDOT) monomers, such as electropolymerization (EP), oxidative chemical vapor deposition (OCVD) and vapor phase polymerization (VPP). Additional to these existing techniques, here a novel and facile method is introduced to fabricate highly conductive poly(3,4-ethylenedioxythiophene) (PEDOT) films in-situ by solution means. The process contains sequential deposition of oxidants and monomers. V$_2$O$_5$ is introduced as the oxidant in this synthetic route. Excess reactants and by-products can be completely removed from the PEDOT film by MeOH-rinsing. The obtained PEDOT films possess good crystallinity and high doping level, with carrier concentration three orders of magnitude higher than the commercial product (PH1000, Heraeus GmbH). The electrical conductivity of the as-cast PEDOT film reaches up to 1420 S/cm. In addition, this method is fully compatible with large-scale printing techniques. A 15 cm × 12 cm PEDOT film is printed on polyethylene terephthalate (PET) substrate by bar coating. These PEDOT conducting films enable the realization of flexible touch sensors, which demonstrate superior flexibility and sensitivity. The low-cost and highly efficient synthetic method shows great potential for large-scale production of PEDOT films that have wide applications in electromagnetic shielding, antistatic coating, sensor, etc.
INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conjugated polymer with many attractive properties, such as good conductivity, high optical transparency in visible range, excellent flexibility and good chemical stability. These properties render it a key component for transparent electrodes, electrochromic devices, electromagnetic shielding, etc.\textsuperscript{12,49,51,61,66} In-situ polymerization of 3,4-ethylenedioxythiophene (EDOT) monomers is an approach to obtain PEDOT films. There are generally three methods, namely electro-polymerization (EP),\textsuperscript{53} oxidative chemical vapor deposition (OCVD) and vapor phase polymerization (VPP).\textsuperscript{1,13} In an EP process, EDOT monomer is dissolved in electrolyte and then polymerized on an electrode under electrical bias.\textsuperscript{47,52} A conductive substrate is required in such a process, thus limiting the application of this method. In the OCVD process, monomer and oxidant are delivered in vapor phase at the same time, making it possible to synthesize, deposit and dope the conjugated polymer in a single step.\textsuperscript{1,29} In contrast, VPP needs two steps: (1) forming an oxidant layer on the substrate by solution means, e.g. spin-coating, dip-coating, blade coating, etc.; (2) exposing the oxidant-covered substrate to monomer vapor.\textsuperscript{5} In recent years, VPP method has gained popularity in EDOT polymerization. Kim et al. first polymerized PEDOT film via VPP; they used FeCl\textsubscript{3}\textbullet6H\textsubscript{2}O as oxidant and the obtained PEDOT film exhibited a low conductivity of 1 S/cm at the thickness ranging from 20 to 100 nm.\textsuperscript{24} Then Winther-Jensen et al. changed the oxidant to iron (III) p-toluenesulfonate, the conductivity exceeded 1000 S/cm with the addition of pyridine.\textsuperscript{59} After that, different weak bases such as pyridine, imidazole, and glycol-based block copolymers such as PEG-PPG-PEG and PEG-ran-PPG was added to the oxidant solution to adjust the polymerization rate and to inhibit side reactions, leading to highly conductive PEDOT films.\textsuperscript{5,13,14,26,8,44,67} Notably Sung et al. obtained single-crystalline PEDOT nanowires in nanoscale channels of a mold covered with FeCl\textsubscript{3}, the average conductivity reached 7629 S/cm, and the highest value was up to 8797 S/cm.\textsuperscript{10} Although extremely high conductivity of PEDOT is demonstrated, the
deposition rate and film homogeneity still cannot meet the industrial requirement. Therefore, a faster and more controllable polymerization technique is highly desirable.

In most of the redox reaction of EDOT polymerization, Fe(III) acts as the electron acceptor. But common oxidants like FeCl₃ and Fe(III) tosylate can crystallize easily, resulting in structural defects in the polymerized film.¹³,¹⁸ Vanadium pentoxide (V₂O₅) is known for its strong oxidizing property and high activity towards EDOT monomer.¹⁵,¹⁹ Zhang et al. synthesized PEDOT nanofibers using V₂O₅ as the oxidants at room temperature in a single step, and the conductivity was 15 S/cm, higher than that of pristine PEDOT-PSS film.⁵⁵ V₂O₅ could change the morphology of PEDOT chains from granular to nanofibrillar for better electrical connectivity. Guo et al. synthesized layered V₂O₅/PEDOT nanowires in large scale by stirring the aqueous mixture of V₂O₅ powder and EDOT at room temperature.¹⁶ V₂O₅ acted as both oxidant and template for EDOT polymerization. Therefore, V₂O₅ could be a good candidate for the polymerization of EDOT due to its dual-function of oxidizing and seeding template.

In this work, a novel and facile method is introduced to fabricate highly conductive PEDOT films in-situ by solution means in high throughput. As showed in Scheme 1, the process involves sequential deposition of a methanesulfonic acid (MSA) solution of V₂O₅ and 2,6-di-tert-butylpyridine (DTBP) as well as an acetonitrile (MeCN) solution of EDOT monomers.³⁴ The whole process can be completed within a minute. The electrical conductivity of the PEDOT film can reach 1420 S/cm, with an average value around 1333 S/cm. Compared to the widely-used commercial poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, PH1000, Heraeus GmbH), the sequential solution polymerized (SSP) PEDOT film has better crystallinity and higher doping level. Characterizations suggest the SSP PEDOT films has a comparable charge carrier mobility as PH1000, but three orders of magnitude higher carrier concentrations than PH1000. In addition, this process is compatible with large-scale printing techniques. A large area (15 cm × 12 cm) PEDOT film is deposited successfully on polyethylene terephthalate (PET) film, and a low sheet resistance of 81 Ω/sq was obtained. The flexible SSP PEDOT film was applied to capacitive touch sensor, which showed favorable touch function and still work well after folding it with a bending radius less than 1 mm. This new polymerization route paves the way to scalable deposition of conductive and homogeneous PEDOT films on flexible substrate.
RESULTS AND DISCUSSION

Polymerization of PEDOT Film Via Sequential Solution Deposition

Scheme 1 shows the SSP process to deposit the PEDOT film. Firstly, a MSA solution of V$_2$O$_5$ and DTBP is spin coated on glass substrate. Then a MeCN solution of EDOT is dropped onto the spinning oxidant covered substrate. The whole process can be completed within a minute. Finally, the film is rinsed in MeOH to remove residuals and dried to form a solid film. The first precursor solution contains V$_2$O$_5$, MSA and DTBP. Among them, V$_2$O$_5$ acts as the oxidant and seeding template for EDOT. MSA is employed to dissolve V$_2$O$_5$ and to drive the polymerization of EDOT. To avoid uncontrollable polymerization and side reactions, a weak base (DTBP) is added to serve as proton scavenger; meanwhile it can also increase the viscosity of the precursor solution. Thus DTBP is able to adjust the polymerization rate and improve the film quality. The monomer solution consists of EDOT and MeCN solvent. EDOT is water insoluble, the type of solvent has a significant impact on the reaction rate and ultimate properties of the polymerized films. A polar organic solvent, MeCN, is chosen to improve the reaction activity of EDOT due to its high polarity and low donor number. The yellowish oxidant-covered substrate turns into light blue, which is the color of PEDOT, immediately when the monomer solution is dropped onto the surface,

![Scheme 1. Polymerization of PEDOT Film via Sequential Solution Deposition.](image)
To confirm the EDOT monomers are polymerized into PEDOT, Fourier Transform infrared spectroscopy (FTIR) is employed to compare the functional groups of SSP PEDOT, EDOT monomers and PH1000. As shown in Figure 1a, the absorption bands around 1364 cm\(^{-1}\) and 1481 cm\(^{-1}\) in EDOT spectrum can be assigned to C-C and C=C bonds.\(^{2,3,4,5}\) They are shifted to 1385 cm\(^{-1}\) and 1400 cm\(^{-1}\) in SSP PEDOT and PH1000, implying the conjugated structure is altered. In addition, the absorption band around 746 cm\(^{-1}\), 889 cm\(^{-1}\) and 1182 cm\(^{-1}\) for =C-H in-plane and out-of-plane vibrations are found in the EDOT spectrum. But they are absent in SSP PEDOT and PH1000, suggesting the successful polymerization due to formation of α-α coupling.\(^{2,11,15}\) Furthermore, a characteristic peak for –SO\(_3\)\(^-\) group is observed in SSP PEDOT, implying that MSA might exist in PEDOT film to act as counter ions, similar to the role of PSS in PEDOT:PSS. Besides all these changes, a few peaks related to the monomer structure can also be found in SSP PEDOT. For example, the absorption bands for C-O-C stretching in ethylenedioxy group appeared on the spectra at 1051 cm\(^{-1}\).\(^{7}\) The vibration modes of C-S bond in the thiophene ring can be observed at 676 cm\(^{-1}\).\(^{5}\) These matched peaks indicate the monomer unit of SSP PEDOT is still EDOT.

**Figure 2. Structural characterization of SSP PEDOT**

(a) FTIR spectra of EDOT, PH1000 and SSP PEDOT.
(b) Raman spectra of PH1000 and SSP PEDOT.
(c) Benzoid or quinoid structure in a PEDOT chain.
Figure 1b presents the Raman spectra of SSP PEDOT and PH1000 in a wavenumber range of 400-2000 cm\(^{-1}\). The spectrum of SSP PEDOT matches well with the PH1000 spectrum, indicating they are nearly identical polymers. More specifically, the peaks at 438 cm\(^{-1}\), 575 cm\(^{-1}\) and 988 cm\(^{-1}\) are associated with the deformation of oxyethylene ring.\(^4\)\(^8\) The peaks at 696 cm\(^{-1}\), 853 cm\(^{-1}\) and 1103 cm\(^{-1}\) are in connection with symmetric C-S-C and C-O-C stretching.\(^4\)\(^8\) The bands at 1262 cm\(^{-1}\), 1364 cm\(^{-1}\) and 1427 cm\(^{-1}\) (1441 cm\(^{-1}\) in PH1000) are corresponding to the C\(_\alpha\)-C\(_\alpha\), C\(_\beta\)-C\(_\beta\) and symmetric C\(_\alpha\)=C\(_\beta\) stretching vibrations, respectively (see Figure 1c for assignment of C\(_\alpha\) and C\(_\beta\)).\(^1\)\(^9\) These characteristic resonance peaks reflect the structure of a PEDOT chain.\(^4\)\(^8\)\(^4\)\(^8\) The FTIR and Raman spectra together suggest the PEDOT is synthesized successfully by the sequential solution polymerization method.

**Compositional Analysis of SSP PEDOT Film**

The as-cast film usually contains undesirable excess EDOT monomers, oxidants and the reduced oxidants, which could physically incorporate in the polymer matrix and influence the film properties.\(^4\)\(^8\) So rinsing the as-cast film is necessary. In FTIR spectra, the =C-H deformation vibrations were absent from SSP PEDOT, showing the excess EDOT monomers can be removed by MeOH-rinsing. A more detailed compositional analysis is carried out with X-ray photoelectron spectroscopy (XPS). As presented in Figure 2a, V\(_2\)O\(_5\) exhibits three typical peaks in the binding energy between 515 eV and 535 eV. The peak centered at 530 eV comes from the O\(_{1s}\) core level.\(^8\)\(^4\)\(^0\)\(^5\)\(^4\) The other two peaks positioned at 517 eV and 524 eV are from the V\(_{2p_{3/2}}\) and V\(_{2p_{1/2}}\) orbitals, respectively.\(^1\)\(^9\) Interestingly, the V\(_{2p}\) signals are completely disappeared in SSP PEDOT, which means no oxidant residue is left in the PEDOT film. An observable change has happened to the O\(_{1s}\) peak. The band
around 533 eV can be attributed to the C-O bond in PEDOT, while the peak at 531 eV can be assigned to S=O in the counter ions. A conclusion can be draw from the XPS and FTIR analysis that the MeOH rinsed film contains only PEDOT and its counter ions without residual reactants or oxidants.

To figure out the concentration of counter ions in the SSP PEDOT film, XPS fine scan on S2p was carried out and compared with PH1000 (Figure 2b and 2c). The S2p electrons associated with each moiety possess different binding energies due to their different chemical environments. For example, the doublet peaks between 162 eV and 166 eV are related to the sulfur atoms in the PEDOT, while the band from 166 eV to 172 eV are coming from the sulfonate groups in the counter ions, i.e. MSA or PSS. The area ratio of the two bands could be used to estimate the relative molar ratio of PEDOT and counter ions in the film. For the sample of PH1000, the relative molar ratio of PEDOT to PSS is close to 1:2, which is consistent with the weight ratio of 1:2.5 provided by Heraeus. The small PEDOT/PSS ratio indicates a large number of insulating PSS exist in the PH1000 film. In great contrast, the ratio between PEDOT and MSA in SSP PEDOT film is much higher, up to 2.2:1. This result demonstrates that PEDOT is the dominant component in the SSP PEDOT film.

**Electrical Properties of SSP PEDOT Film**

The electrical properties of PH1000 and synthesized PEDOT were summarized and listed in Table 1. The electrical conductivity of synthesized PEDOT film can reach 1420 S/cm, with an average value around 1333 S/cm, while the conductivity of PH1000 is lower than 0.5 S/cm. Since the conductivity (σ) is related to carrier concentration (ρ) and carrier mobility (μ), \( σ = qρμ \) (q is the unit charge, \( 1.6×10^{-19} \) C), Hall effec measurement is carried out to pinpoint the change in \( ρ \) or \( μ \) or both. The average Hall mobility of SSP PEDOT and PH1000 is 2.41 cm²/Vs and 2.70 cm²/Vs, which are quite comparable. However, the carrier concentration of SSP PEDOT (2.62 \( 10^{18} \) cm⁻³) is three orders of magnitude higher than that of PH1000 (2.60 \( 10^{18} \) cm⁻³). So the high conductivity of SSP PEDOT is mainly due to the high carrier concentration.

| Sample | Sheet resistance* | Conductivity* | Carrier concentration* | Carrier mobility* |
|--------|-----------------|---------------|------------------------|------------------|
| PH1000 | \( (303±24)×10^3 \) | 0.43±0.04    | \( (2.60±0.84)×10^{18} \) | 2.41±0.93       |
Doping Level of SSP PEDOT Film

The carrier concentration has a direct correlation with the doping level of PEDOT chains. To learn about the oxidative state of SSP PEDOT, ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectra of SSP PEDOT and PH1000 films were recorded. According to literatures, the absorption band around 600 nm is attributed to $\pi \rightarrow \pi^*$ transition of the thiophene rings at neutral state; it will shift to 800 nm and 1200 nm after being oxidized to polaron and bipolaron state, respectively. The UV-Vis-NIR spectra of synthesized PEDOT and PH1000 normalized with film thickness are displayed in Figure 3a. From 400 to 1200 nm, the normalized absorption spectrum of SSP PEDOT exhibits a stronger intensity than that of PH1000, implying the carrier concentration in all three states is higher than that of PH1000. SSP PEDOT shows a strong absorption band at 900 nm, suggesting polaron state is dominant in SSP PEDOT.

To quantify the doping level, the main Raman peaks of SSP PEDOT and PH1000 are deconvoluted and compared (Figure 3b and 3c). The most notable peak at 1427 cm$^{-1}$ in Figure 3b and at 1441 cm$^{-1}$ in Figure 3c is corresponding to the symmetric C=C stretching vibration in the thiophene rings of PEDOT. This peak is a combination of two bands, one of which at a smaller Raman shift is due to the vibration of the benzoid (neutral) structure, and the other one at a slightly higher Raman shift is related to the quinoid (oxidized) structure.
So the area ratio of the two peaks (oxidized/neutral) reflects the doping level of PEDOT chains. Following this calculation, the SSP PEDOT has a doping level close to 0.35 while that of PH1000 film is only 0.20. The doping level in SSP PEDOT is 75% higher than in PH1000. This explains why SSP PEDOT possesses higher carrier concentration.

The Molecular Packing of SSP PEDOT

The molecular packing in nano- and micro-scale is of importance to the carrier transport. Atomic force microscopy (AFM) is employed to compare the surface morphology of the SPP PEDOT film with the PH1000 film. As shown in Figure 4a, the average grain size of the PH1000 is small, and the surface of film is smooth with a root-mean-square roughness (Rq) of 1.44 nm. In contrast, a much larger domain size and rougher surface are observed in Figure 4b, with a Rq of 11.28 nm. It was reported that rinsing the as-cast PEDOT films could cause a collapse and volume contraction of the film due to removal of residuals. Due to that, SSP PEDOT displays a more aggregated yet slightly rougher surface.
Figure 4c shows the particle size distribution of the SSP PEDOT and PH1000 dispersed in DI water by ultrasonication for 3 min. The average particle size of the SSP PEDOT is 348.65 μm, which is much higher than that of the PH1000 (1.84 μm). The average particle size is an indicator for the molecular size of the polymers, as well as inter-chain interactions. Therefore, a larger average particle size is expected to provide better charge transport due to longer conjugation length and easier charge hopping between adjacent backbones.

To further confirm the inter-chain interaction plays a role in the aggregation, X-ray diffraction (XRD) patterns of SSP PEDOT and pristine PH1000 film are recorded (Figure 4d). Both of the spectra showed a broad peak in the range of 15-35°. The diffused scattering peak centered at 23° could be attributed to the horizontal inter-chain planar ring-stacking of the PEDOT, indicating that the polymer are completely amorphous without any crystallinity. Compared to the PH1000 film, two sharp diffraction peaks located at 24.7° and 50.56° appeared in the diffraction pattern of the SSP PEDOT. These two peaks resemble the first and second order diffraction peaks, corresponding to a d-spacing of 3.6 Å. This typical d-spacing value signifies the PEDOT chains in SSP PEDOT have a well ordered π-π stacking. The XRD results confirm that SSP PEDOT exhibits a high crystallinity that is beneficial for charge transport.

**Large-scale Polymerization and Realization of Flexible Touch Screen**

The synthetic route can be easily transferred to large-scale fabrication. Here we demonstrate printing of 15 cm × 12 cm PEDOT films on PET by bar coating. In brief, the oxidant solution is first bar coated on a PET substrate, which is quickly immersed in the monomer solution where PEDOT film forms in less than 1 s. The whole process is displayed in Supplementary Video 1. It is believed that this synthesis route can be further adaptable to other solution-based manufacturing techniques, such as doctor blading, screen printing, inkjet printing or roll-to-roll printing, etc. As shown in Figure 5, the obtained PEDOT film is homogeneous with a sheet resistance of 80.3 Ω sq⁻¹, which is low enough for many applications such as electromagnetic shielding, antistatic coatings and sensors.

Owing to the low sheet resistance and high flexibility, the SSP PEDOT film is used to fabricate capacitive touch sensors (see inset of Figure 5). When connected to a controller and a computer, the sensor allows human to input information by touching the surface.
Touch functions of the sensor are shown in Supplementary Video 2. We demonstrated writing the abbreviation of Chongqing University (CQU) on the touch sensor. We further showed that the flexible touch sensor could maintain its touch functions after bending back and forth, or even being folded at a bending radius less than 1 mm. The extremely high flexibility of the touch sensor will provide more interfaces for human-machine interactions.27,44,57 Besides the ultra-high flexibility, the touch sensors made from SSP PEDOT also exhibit high sensitivity. As demonstrated in Supplementary Video 3, the sensor is able to control the rotation of a motor or the brightness of a light bulb even it is beneath a piece of leather. Such a combination with leathers can lead to many new opportunities in control applications such as in smart homes and automobiles.

CONCLUSION

A low-cost and high-throughput synthetic route for PEDOT films is highly desirable due to the wide applications of the transparent and conducting polymer films. In this work, a novel and facial method is introduced to fabricate highly conductive PEDOT films in-situ by solution means. The process consists of sequential solution deposition of oxidants and monomers, and can be completed within a minute. The subsequent MeOH-rinsing can effectively remove excess EDOT monomers and oxidants in the synthesized PEDOT films. Characterization shows PEDOT is the dominant component in the film that is heavily doped by the MSA counter ions. The SSP PEDOT possesses good crystallinity, extremely high carrier concentration and good carrier mobility, all of which contribute to its high electrical conductivity that reaches 1420 S/cm. We further demonstrate that the synthesis method can be extended to large-scale printing techniques on flexible substrate. The printed films
exhibit a sheet resistance of 81 Ω sq−1, which is low enough for many applications. For demonstration, flexible capacitive touch sensors are made from the SSP PEDOT film. The sensors exhibit superior flexibility and ultra-high sensitivity. The results together suggest sequential solution polymerization is a scalable new method that is ideal for the industrial production of conjugated polymer films.

EXPERIMENTAL PROCEDURES

Materials
3,4-Ethlenedioxythiophene (EDOT, P1328908, 99%), 2,6-di-tert-butylypyridine (DTBP, P1216954, 98%) and methanesulfonic acid (MSA, P1306518, 99%) were obtained from Adamas Reagent. Acetonitrile (MeCN, 80988I, 99%), vanadium pentoxide (V2O5, 20150613, 99%), methanol (MeOH, 2016012901, 99.5%), Triton X-100 (P1128113, 98%), petroleum ether (P1190274, 99%) and dimethyl sulfoxide (DMSO, 2015060801, 99%) were purchased from Sinopharm Chemica. All reagents were used without further purification.

Sequential Solution Polymerize PEDOT on Glass by Spin-Coating
To obtain the oxidant precursor, 0.45 g V2O5 was added in 12 mL MSA, sealed in a volumetric flask, stirred for 24 hrs with a magnetic stirrer and then aged for a month. The oxidant solution was formed taking the supernatant and blended with DTBP at a volume ratio of 475:575. The monomer solution was a mixture of EDOT and acetonitrile at a volume ratio of 9:1. The oxidant solution was spin-cast at 3000 r.p.m. for 12 s onto a 15 mm × 15 mm glass substrate and then the monomer solution was sequentially spin-cast for another 12 s without stopping the rotation. The coated substrate was then rinsed in MeOH for 2 min and annealed on a hot plate at 110 °C for 10 min. Finally, a solid PEDOT film was obtained.

The control sample was made by spin-coating PH1000 aqueous solution at 2000 r.p.m. on the 15 × 15 mm glass substrate and then dried at 110 °C for 10 min.

Sequential Solution Polymerize PEDOT on PET Film by Bar Coating
To reduce the viscosity of the oxidants solution, the MSA solution of V2O5 (supernatant) was diluted with MeOH and DMSO at a volume ratio of 5:4:1. Triton X-100 and Epoxy resin were added to tune the ink properties. Monomer solution was prepared by mixing chloroform with petroleum ether at 1:1 volume ratio, and then adding 10 vol% EDOT. The lower EDOT monomer concentration is helpful for decreasing the reaction rate and
obtaining long polymer chains of PEDOTs. Supplementary Video (1) showed the entire polymerization process. The oxidant solution was deposited on 15 cm × 12 cm PET films by bar coating. The coated film was immediately dipped into the monomer solution. The color of the film changed from yellow to blue within 1 s. Then the film was taken out and dipped in MeOH for 5 min. In the last step, the film was dried at 110 °C for 10 min. The capacitive touch sensors were fabricated by the laser patterning the SSP PEDOT film on PET, which was then covered by Optically Clear Adhesive. The sensors were bonded with a controller and connected with a computer for touch function demonstrations.

Characterization

Electrical conductivity was measured using the Van der Pauw four-point probe technique with a Keithley 2400 source meter. Carrier concentration and carrier mobility were measured by a Hall Effect measurement system (Phys Tech, RH 2035). Film thickness was obtained using a Bruker Dektak XT stylus profiler. Atomic force microscopic (AFM) images were acquired using a multifunctional scanning probe microscope (MicroNano D-5A) in tapping mode. X-ray diffraction (PANalytical X’Pert Powder) was carried out to study the crystallinity of the samples, the 2θ scans were from 10° to 60°. Fourier transform infrared (FTIR) spectroscopy was recorded by ThermoFisher Nicolet FT-IR spectrometer (Nicolet iN10) in the range of 400 cm⁻¹-2000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was acquired using x-ray photoelectron spectrometer (ESCALAB 250Xi). Raman spectra were carried out by a laser Raman spectrometer (LabRAM HR Evolution). Absorption spectra of the films were recorded using UV-VIS-NIR spectrophotometer (UV-3600). Dynamic light scattering (DLS) data were obtained by Mastersizer 2000. In the DLS experiment, SSP PEDOT films were scraped off from the substrates and dispersed in DI water. The commercial solution of PH1000 was directly diluted 100 times by DI water. Both of the dispersions were treated with ultrasonication (2000 W) for 3 minutes before the DLS measurement. The sheet resistance of the SSP PEDOT films on flexible PET substrate was measured by a four-probe meter (DMR-1C).

SUPPLEMENTAL INFORMATION

Supplemental Information includes three videos:
Video S1: Sequential Solution Polymerization (SSP) of PEDOT
Video S2, Touch Function of the SSP PEDOT Sensor
Video S3, Control of a Motor or a Light Bulb by the Touch Leather
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AUTHOR CONTRIBUTIONS

R.C. polymerized the PEDOT film and characterized the film properties using VDP, Hall Effect, FTIR, Raman, XPS, UV-VIS-NIR, AFM and XRD. Y.W. and X.L. performed DLS characterization and analysis. Q.Z. and Y.Z. scaled up the synthesis to print the large area PEDOT films. J.X., C.M. and Y.Z. fabricated the flexible touch screen sensors and touch leathers. Y.S. and Z.W. made the programme to use touch leathers to control motor and light bulb. K.S. and J.O. conceived the idea. R.C. and M.L. prepared the manuscript. K.S. and J.O. supervised the project and revised the manuscript. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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