

High Performance Flexible Transparent Electrode via One-Step Multifunctional Treatment for Ag Nanonetwork Composites Semi-Embedded in Low-Temperature-Processed Substrate for Highly Performed Organic Photovoltaics

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For ideal flexible transparent electrodes, the features of good electrical/optical properties, low surface roughness, efficient charge transportation, robust electrical stability under simultaneously continuous operation bias, and mechanical bending are critical. Herein, a flexible transparent electrode fulfilling all these features is demonstrated by silver (Ag) nanonetwork composites semi-embedded in low-temperature-processed colorless polyimide (cPI), which shows a figure of merit over 1000 ($5.4 \Omega \text{ sq}^{-1}$ sheet resistance and $>94\%$ diffused transmission at 550 nm wavelength), extremely smooth topography ($<1 \text{ nm}$ root-mean-square roughness and $<3 \text{ nm}$ peak-to-valley roughness), remarkable bending stability under continuous operation bias, and increased work function favoring the band alignment with typical charge transport layers for efficient devices. These characteristics are attributed to one-step multifunctional chemical treatment on the composite of Ag nanowires and an example polymer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). The strategic one-step process simultaneously offers selective welding at nanowires cross junctions to form an Ag nanonetwork, and removing polyvinylpyrrolidone surfactant from Ag nanowires and PSS from PEDOT:PSS. The flexible electrode also favors the residue-free cPI transfer for applications. Flexible organic solar cells (OSCs) made from the electrode achieve an averaged power conversion efficiency of 14.46% (best, 15.12%), which is the best flexible OSCs reported so far.

1. Introduction

While flexible electronics have become emerging technologies for various applications such as solar cells, displays, thin-film transistors, sensors, and power generating window,^[1–15] flexible transparent electrodes need to fulfill the requirements of high transparency, good conductivity, efficient charge transportation to adjacent layers, and robust electrical stability under simultaneously continuous operation bias and mechanical bending. Among various flexible electrodes such as graphene,^[16,17] carbon nanotube,^[18] metallic nanowire,^[19–21] conductive polymer^[22] and their combination,^[23–25] silver nanowire (AgNW)-based electrode is one of the attractive candidates.^[26–29] However, the electrodes of directly dispersed Ag nanowires on solid substrates typically show rough surface, which will deteriorate other film formations on it and cause the penetration of nanowires into adjacent films in a device structure and thus cause short-circuit in devices.^[27,30] Recently, relatively smooth morphology has been made by integrating the nanowires in polymer

substrate matrix, but still with sharp peak-to-valley roughness of about 25 nm mainly due to the adhesion issue between the solid substrate and polymer liquid, which could cause current leakage in devices.^[31,32] Besides, the full coverage of Ag nanowires by insulating polymer substrate matrix will degrade their charge transportation between the Ag nanowires and adjacent charge transport layer (CTL) and thus hinder their device applications.^[33]

To address these issues, precoating of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) before deposition of the nanowires was applied to maintain electrical conduction pathways exposed to the top surface after transferring from the supporting solid substrate.^[34] However, there are concerns that the scattered individual nanowires without physical welding and the presence of insulating surfactants such as polyvinylpyrrolidone (PVP) on the nanowires will affect charge

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 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aenm.201903919>.

DOI: 10.1002/aenm.201903919

transportation and thus device performances.^[35,36] Besides, the unconnected nanowires could be fatal to mechanical durability due to more heat production.^[37] In addition, because of the strong adhesion strength between the pre-coating PEDOT:PSS and the supporting rigid substrate, relatively sharp peak-to-valley roughness of about 26 nm on a flexible electrode surface had been observed after peeling off from the supporting solid substrate. This will increase current leakage.^[34] Consequently, it is highly desirable to realize the strategy development of simultaneously welding metal nanowire junctions and removing surfactants while their surface roughness topography in a flexible electrode can become very smooth for suppressing energy loss in the nanowires based flexible transparent electrode.

Regarding the flexible substrates, colorless polyimide (cPI) has been a promising flexible substrate candidate due to its high optical transparency, thermal stability, and compatibility with new generations of flexible transparent electrodes favoring the cast-in-situ fabrication process.^[38–41] Nevertheless, a high imidization reaction temperature of 200 °C or more in processing fabrication of cPI will negatively modify and even damage silver-based nanomaterials. Meanwhile, the electrical properties of conductive polymers degrade at the process temperatures above 200 °C.^[42,43] Overall, there is a strong demand of low-temperature process of cPI substrate particularly for those thermally sensitive electrode materials (preferably <200 °C) with high degrees of imidization for enhancing device fabrication reliability.

In this study, we demonstrate an approach to form a flexible transparent electrode with features of excellent conductivity, high transparency, very smooth surface topography, robust electrical stability applied with simultaneously continuous operation bias and mechanical bending, efficient charge transportation, and very good device fabrication reliability based on the composite Ag nanonetwork with an example conductive polymer of PEDOT:PSS semi-embedded in low-temperature-processed cPI substrate. The flexible transparent electrode with the outperformed characteristics is realized through a new one-step multifunctional chemical treatment of the Ag nanowire composites together with the low imidization processing temperature (<200 °C) based highly transparent cPI substrate (>91% diffused transmission). Interestingly, through our

approach, we achieve that 1) intrinsic resistances in the composite electrode are substantially reduced; 2) the surface roughness of flexible composite electrode is overall very smoothed after its completely peeling off from the supporting rigid substrate; and 3) the electrical reliability of the flexible electrode under continuous operation bias and mechanical bending at the same time is greatly reinforced as compared to their corresponding sample without the proposed chemical treatment. To the best of our knowledge, the demonstration of such electrical stability is reported for the first time. By using our flexible electrodes, organic solar cells (OSCs) have been fabricated and achieved the highest power conversion efficiency (PCE) value of averaged 14.46% (best 15.12%) among the reported indium tin oxide (ITO) free flexible OSC devices so far. Consequently, the strategic design of fabricating flexible composite electrode in low-temperature-processed cPI substrate realized in this work can not only contribute to reducing energy loss in typical Ag nanowires based electrodes but also advancing the emerging flexible electronics.

2. Results and Discussion

2.1. Formation of the Electrode of Ag Nanonetwork Composite Semi-Embedded in cPI

The new one-step multifunctional chemical treatment process on Ag nanowires composite with PEDOT:PSS is shown in **Figure 1**. The process was carried out entirely in the solution at room temperature. Starting with the ultraviolet ozone (UVO) treatment, forming of PEDOT:PSS (e.g., by spin-coating) with a thickness of about 20 nm, and coating of Ag nanowires with different averaged diameters of 30, 60, and 100 nm have been sequentially prepared on the rigid supporting substrate (e.g., glass, quartz, etc.). It should be noted that the composite electrode of Ag nanowires with PEDOT:PSS is resistive and the figure of merit (FoM) is only about 100^[44] due to unsoldered Ag nanowires at the cross junctions, surfactants PVP on Ag nanowires, and PSS from PEDOT:PSS. FoM is a well-known parameter and very useful to evaluate the electrical/optical performance of a transparent electrode, which is

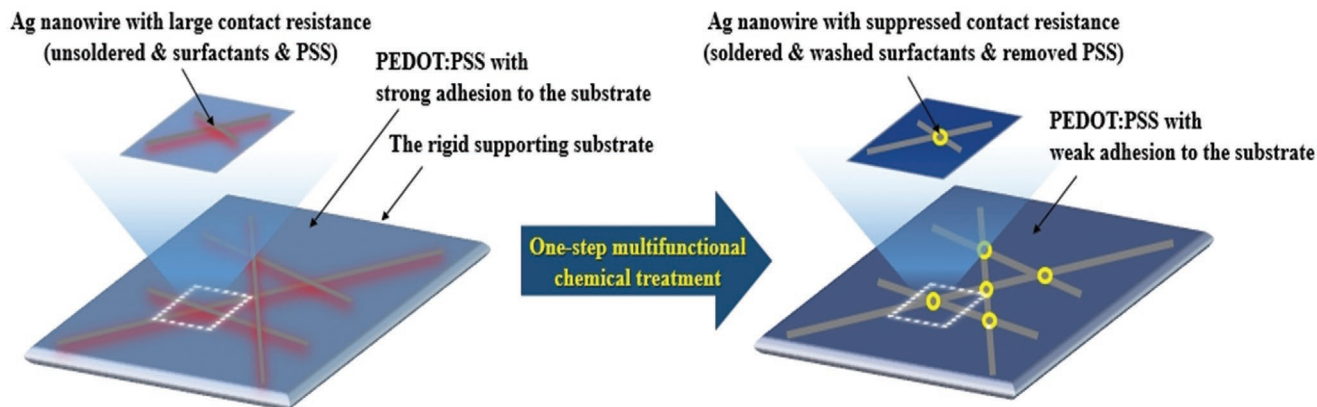


Figure 1. The new one-step multifunctional chemical treatment process for the flexible transparent electrode, composed of Ag nanonetwork with PEDOT:PSS.

Table 1. A summary of the sheet resistance of composite Ag nanowires (30, 60, and 100 nm of the diameters on average) with PEDOT:PSS regarding before/after the one-step multifunctional chemical modification.

Ag nanowires diameters on average	Ag nanowires composite (before the modification)	Ag nanonetwork composite (after the modification)
30 nm	181	5.4
60 nm	268	6.5
100 nm	352	7.2

defined as the ratio of the electrical conductivity to the optical conductivity.^[45]

Here, we propose a one-step multifunctional chemical treatment for addressing all the resistive components within the composite electrode of Ag nanowires with PEDOT:PSS. For achieving the dedicated purpose, different chemicals are strategically selected and prepared into a solution. Silver nitrate and ascorbic acid are, respectively, chosen as the silver salt and the reducing agent for soldering Ag nanowires only at the cross junctions but not other places via the capillary force. Acetic acid is selected for the unique contributions that its mixture solution with silver nitrate and ascorbic acid offers: 1) the controllable redox reaction between the silver salt and the reducing agent in the mixed solution before soldering Ag nanowires at the cross junctions,^[46] 2) elimination of an insulating surfactant such as PVP on Ag nanowires, and 3) removal of resistive PSS from PEDOT:PSS. As shown in **Table 1**, the sheet resistance of all the Ag nanowire composite electrodes with different diameters dramatically decreased after the chemical treatment. The detailed functions of the acetic acid in the chemical mixture solution are explained in Figure S1 (Supporting Information). Additionally, the one-step treatment released the adhesive strength between the precoated PEDOT:PSS and the rigid supporting substrate, which contributes to the complete detachment of the composite electrode semi-embedded in cPI without any residue left on the rigid substrate (and thus achieve very smooth electrode surface and good work function) as will be discussed later. Hereafter, Ag nanowires with 30 nm averaged diameter serve as representative case for further characteristic understanding.

Figure 2a shows the scanning electron microscope (SEM) top-view image of the treated composite electrode, clearly exhibiting Ag nanonetwork with no clear damage through the evolution from disconnected Ag nanowires. However, for the untreated electrode as shown in **Figure 2b**, the Ag nanowires are not only disconnected, but also some of them are broken by the rapid heat accumulation due to the nonuniform heat distribution over the untreated electrode. Regarding eliminating the PVP surfactant, it is confirmed by transmission electron microscopy (TEM) that no PVP surfactant at the Ag nanowire surface after the one-step treatment is found in **Figure 2c** while about 3-nm-thick insulating surfactant firmly remains on the untreated Ag nanowire surface as shown in **Figure 2d**. The surfactant elimination can be attributed to acetic acid in the chemical mixture solution which washes and etches the surfactant on Ag nanowire surface promoted by the enhanced electron density between PVP and Ag nanowires due to the charge transfer from PVP to Ag nanowires.^[47–49] In order to

clarify the effects of PVP removal by acetic acid, chemical treatments with ethanol liquid (used for the solvent of the one-step chemical treatment), ascorbic acid solution of 1×10^{-3} M in ethanol, and acetic acid liquid were carried out on Ag nanowires electrode. It was found that only the sheet resistance of Ag nanowires electrode treated by acetic acid has been decreased from 65 to $55 \Omega \text{ sq}^{-1}$ as shown in Table S1 (Supporting Information), which means that the surfactants on the Ag nanowires had been removed after the acetic acid treatment as verified by SEM images of **Figure S2** (Supporting Information). To further characterize it, the transmission spectroscopy and X-ray photoelectron spectroscopy (XPS) were adopted and results are as shown in **Figures S3 and S4** (Supporting Information), respectively. The diffused optical transmission of Ag nanowires on glass substrate exhibits two sharp surface plasmon resonances (SPR) at the wavelengths 351 and 375 nm before the acetic acid treatment. The SPRs shifted to 351 and 345 nm, respectively, after the acetic acid treatment can be explained by the PVP surfactant removal and thus the change of dielectric environment around silver nanowires.^[50] For the XPS results, Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks after the acetic acid treatment shifted toward higher binding energies of 368 and 374 eV, respectively, which is close to the pure silver peak according to the literature.^[51] Meanwhile, **Figure 2e,f** shows atomic force microscope (AFM) phase images of the composite electrode, exhibiting a contrast between a PEDOT part and a PSS part. With the one-step treatment, the sharp contrast disappeared as shown in **Figure 2e**, indicating that most PSS was removed from the composite electrode surface. However, the PSS remained on the untreated samples as shown in **Figure 2f**. In addition, the removal of PSS from the composite electrode has been confirmed by XPS spectra as shown in **Figure S5** (Supporting Information) which is consistent with the previously reported work.^[52] Consequently, our results confirm that the one-step approach can effectively form the Ag nanonetwork composite with removal of PVP and PSS offering higher conductivity without degrading the transmission properties.

To realize the robust flexible transparent electrode, the substrate material shall be carefully selected for embedding Ag nanowires, particularly that the processing temperature shall not be over 190 °C. **Table 2** shows a sheet resistance progress of Ag nanowires/nanonetwork after annealing with different temperatures for 30 min. It was found that the scattered Ag nanowires on a glass substrate started to break when the annealing temperature is beyond 190 °C, which is consistent with the broken Ag nanowires in the SEM image of **Figure 2b**. Meanwhile, the sheet resistance of Ag nanonetwork on a glass substrate is slightly fluctuated after both 180 and 190 °C annealing as stated in **Table 2**. However, the amount of broken Ag nanowires dramatically increased when the temperature was increased by only 10 °C and the resistance significantly increased. Although thermal stability of the Ag nanowires slightly improved in the case of the Ag nanowires composite with PEDOT:PSS, the degradation of PEDOT:PSS started from 200 °C^[48] and the Ag nanowires composite with PEDOT:PSS can only withstand 20 min annealing at 210 °C as previously reported.^[53] Consequently, low-temperature-processed cPI (<200 °C) is critical for the composite of Ag nanonetwork and PEDOT:PSS as the effective flexible transparent electrode.

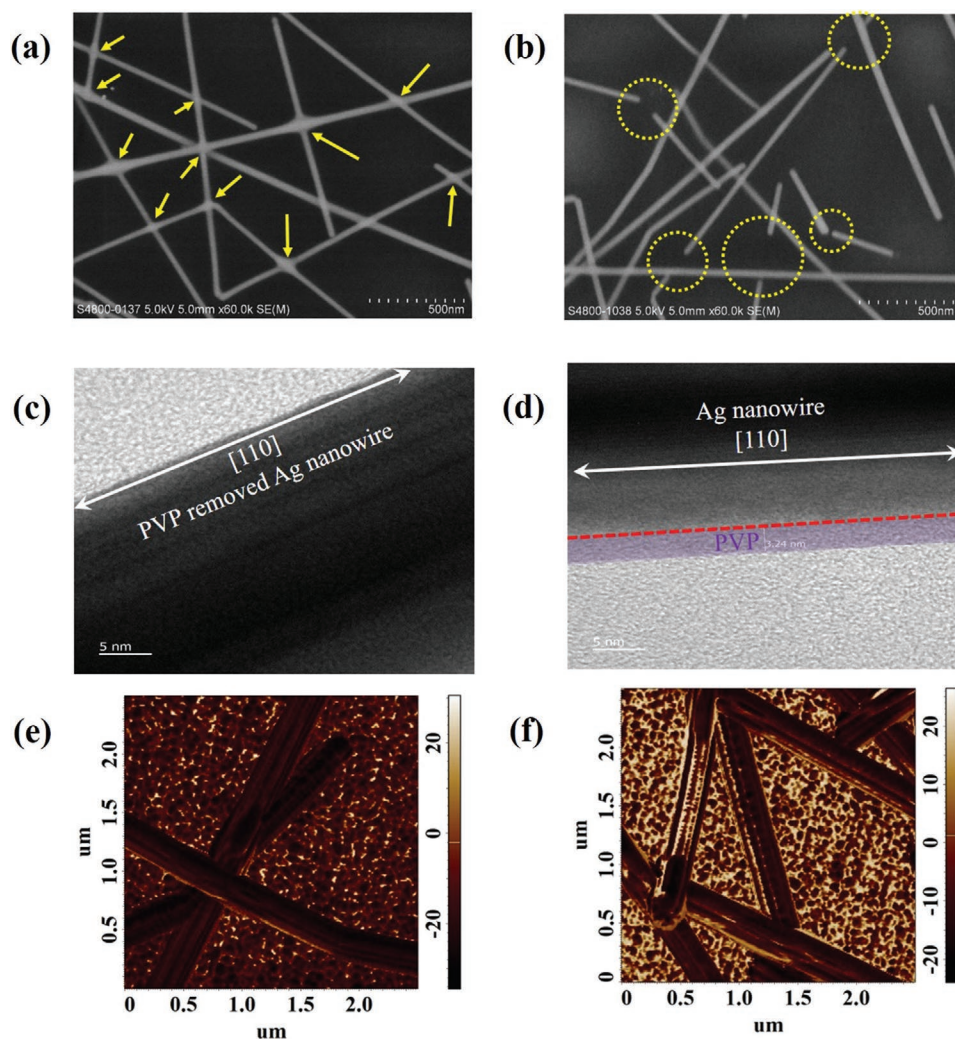


Figure 2. a,b) SEM images of the Ag nanonetwork/Ag nanowires at the surface of the composite electrode semi-embedded in cPI with/without the chemical modification, respectively. c,d) The TEM images of an Ag nanowire with and without the one-step modification showing no PVP and PVP surfactant, respectively. e,f) The measured AFM phase profiles of the surface of the composite electrode with/without the chemical modification, respectively.

In this study, we select 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with multi-bulky pendant trifluoromethyl groups to prepare a viscous precursor (poly(amic acid) (PAA)) for achieving cPI at relatively low temperature.

Incorporating trifluoromethyl groups onto polyimide chains can disturb the interactions and chain packing, which has been considered as an effective means to realize soluble and transparent PI.^[54] Moreover, the high electronegativity and low electric polarity of these fluorine atoms can provide many

Table 2. A summary of the sheet resistance of Ag nanowires coated on a glass substrate and the sheet resistance of Ag nanonetwork on a glass substrate after annealing at different temperatures for 30 min.

Ag nanowire diameter 30 nm on average	Annealing temperature	Before the annealing [$\Omega \text{ sq}^{-1}$]	After the annealing for 30 min [$\Omega \text{ sq}^{-1}$]
Ag nanowires/glass	180 °C	75.2	60.16
Ag nanowires/glass	190 °C	76.6	114.6
Ag nanowires/glass	200 °C	74.5	5436.0
Ag nanonetwork/glass ^{a)}	180 °C	74.4	74.0
Ag nanonetwork/glass ^{a)}	190 °C	72.2	73.0

^{a)}After the one-step multifunctional treatment.

important features for the cPI, such as low refractive index, low moisture absorption, and high thermal resistance, to serve as an attractive substrate for flexible transparent electrodes. We believe that TFDB-6FDA-based cPI has not been applied in transparent electrodes yet. The as-prepared viscous PAA precursor was coated on the composite electrode and followed by imidization reaction under gradually heating process (80, 100, 150, and 190 °C for 1 h, respectively). After cooling down, a high-quality transparent electrode can be perfectly peeled off in water thanks to the moisture-induced adhesion degradation and strong interaction between the composite electrode layer and in situ formed cPI. The detail cPI synthesis process is described in Figure S6 (Supporting Information) and the formation of cPI has been verified by Fourier transform infrared (FTIR) spectroscopy as shown in Figure S7 (Supporting Information). The FTIR results show that the formation of cPI is not completed at annealing temperature below 190 °C because there are very clear FTIR peaks at 3252 and 1595 cm^{-1} of N–H and C=O, respectively, from the precursor of cPI. As a result, the imidization process temperature at 190 °C is the lowest temperature for forming the Ag nanonetwork composite semi-embedded in cPI as the flexible transparent electrode. The cPI processed at 190 °C with a thickness of 20 μm is highly transparent and show very good chemical resistances against different solvents as shown in Figures S8 and S9 (Supporting Information), respectively. Consequently, with the careful selection and the sequential temperature annealing process of appropriate polyimide, the low-temperature-processed cPI is realized to be integrated with Ag nanonetwork composites as efficient flexible transparent electrode.

2.2. Morphology, Optical/Electrical, and Reliability Characterizations of the Flexible Ag Nanonetwork Composite Electrode

Figure 3a,b shows 45° tilted SEM images at the surface of the composite electrodes semi-embedded in cPI with and without the one-step treatment, respectively. The treated flexible electrode after peeling off from a rigid supporting substrate displays very smooth surface topography as shown in Figure 3a while the untreated one shows very rough surface morphology. These different surface roughness can be ascribed to different adhesion forces between the precoated PEDOT:PSS and the rigid supporting substrate. Because of the sulfonate functional group of PSS in the precoating PEDOT:PSS,^[55] the strong adhesion force of PEDOT:PSS to the substrate will hinder their entire transferring to cPI substrate. Interestingly, our strategically introduced acetic acid in the chemical mixture solution can strongly bond with the PSS by hydrogen bonding, which removes PSS from PEDOT:PSS.^[56] Consequently, the composite electrode can be completely detached from the rigid supporting substrate. As shown in AFM images of Figure 3c,d, root-mean-square (RMS) roughness of the untreated flexible electrode semi-embedded in cPI is about 3 nm. However, their overall surface roughness has highly fluctuated, evidenced by many about 25 nm sharp peaks of Ag nanowires as shown in Figure 3d. Remarkably, through our chemical treatment, the composite electrode semi-embedded in cPI with the fluctuated surface characteristics has been greatly reduced to <1 nm

of RMS roughness and very smooth <3 nm of peak-to-valley roughness, exhibiting complete transfer of the composite electrode to cPI substrate.

Figure 4a shows the optical properties of the composite electrode. The negligible optical loss of the sample after the one-step treatment can be explained by the selective welding at the cross junctions of Ag nanowires under the capillary force and high diffused transmission >94% at 550 nm wavelength as shown in Figure 4a. Meanwhile, the sheet resistance has been significantly decreased from 181 to 5.4 Ωsq^{-1} . Consequently, our transparent electrode semi-embedded in cPI flexible substrate shows a comparable diffused transmission of 84.4% in visible light wavelength region to commercial ITO/glass substrate and encouragingly with the lower sheet resistance as shown in Figure 4b. The photograph in Figure 4c represents the treated flexible composite electrode semi-embedded in cPI and a comparison to glass/ITO. The FoM of our flexible transparent electrode with/without one-step multifunctional chemical treatment are depicted in Figure 4d. The results show that after the treatment, both the transparency and FoM improve significantly. It should be noted that the untreated Ag nanowires cannot achieve FoM of 1000. Remarkably, our flexible transparent electrode in cPI shows the highest FoM value of over 1000 among the reported Ag nanowires based transparent electrode so far. Table 3 shows a summary of sheet resistance, transmittance, and FoM value of our electrode and the previously reported transparent electrodes using Ag nanowires and their composite with other conductive materials.^[30,39,57–62] The work function (WF) of the pristine (untreated) composite electrode semi-embedded in cPI has been increased from 4.825 to 4.985 eV as shown in Table 4. This phenomenon could be explained by two reasons. The one is mainly due to the lack of PEDOT:PSS at the surface of the composite electrode semi-embedded in cPI as the residues remain on the rigid supporting substrate when they are peeled off. The other one could be caused by the flatten roughness.^[63]

It is important to note that the flexible devices will be subjected to external electrical bias and simultaneously under repeated mechanical bending in the practical application. More specifically, our flexible transparent electrode is subjected to continuous operation bias under 20 V for 3000 s and the simultaneously bending test with a bending radius of 1 mm for 1000 cycles. The current change of the flexible electrodes with and without the one-step treatment is shown in Figure 5a,b. For the untreated flexible transparent electrode, the gradual decrease of the current can be ascribed to the effects of mechanical bending and continuous operation bias generating mechanical strain and joule heat, both of which will deteriorate the unsoldered contacts of Ag nanowires in the untreated flexible electrode. However, in the treated flexible electrode as shown in Figure 5a, less current variation has been observed for the periodic current variation. The remaining variation could be explained by natural extension during the electrode bending, which will slightly increase the resistance of the electrode, while the rapid recovering to the original current value caused no obvious damage against the soldered contact under the simultaneously mechanical bending and electrical heating. In addition, the comparison between the treated and untreated transparent electrodes are investigated by individually applying continuous

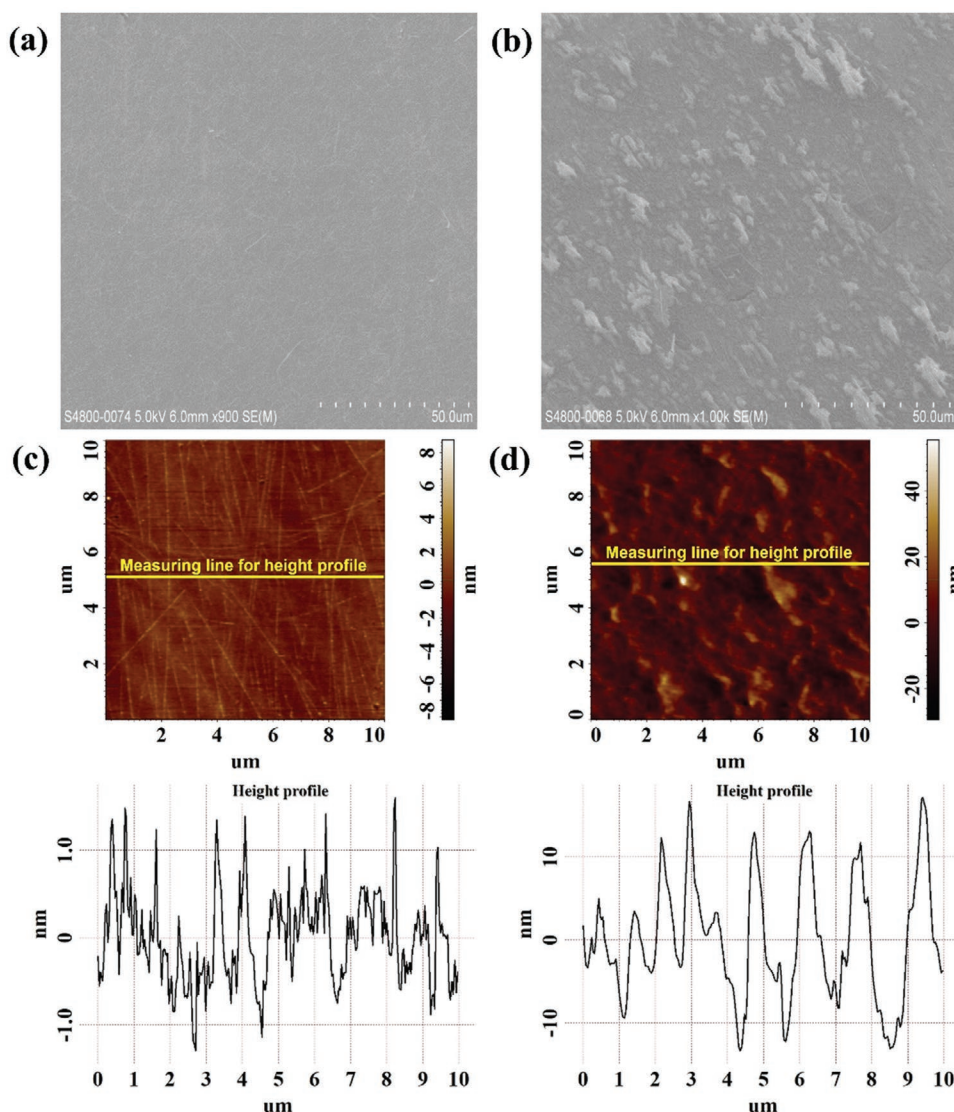


Figure 3. a,b) The 45° tilted SEM images. c,d) The measured AFM height profiles at the surface of the composite electrode semi-embedded in cPI flexible substrate according to with/without the chemical modification, respectively.

mechanical bending or operation bias, and the improved stability of the treated electrode has been clearly indicated in Figure S10 (Supporting Information), which further proves the reliability of the proposed flexible electrode. We have also investigated the air exposure stability of the Ag nanowires composite electrode semi-embedded in cPI with and without the one-step multifunction treatment. We find that the air exposure stability of the treated composite electrode has been enhanced by about 12% as shown in Figure S11 (Supporting Information). In addition, the thermal annealing stability test has been examined and no obvious variation of sheet resistance of the treated composite electrode has been confirmed as shown in Figure S12 (Supporting Information). Consequently, the composite electrode semi-embedded in cPI with the fluctuated surface characteristics has been greatly reduced to <1 nm of RMS roughness and very smooth <3 nm of peak-to-valley roughness, exhibiting complete transfer of the composite electrode to cPI substrate.

Remarkably, our flexible transparent electrode in cPI shows the good work function favoring the band alignment, greatly reinforced electrical stability, and highest FoM value of over 1000 among the reported Ag nanowires based transparent electrode so far.

2.3. High-Performance Bulk Heterojunction OSC Devices

To further evaluate our flexible electrode, OSC devices made of three different sorts of bulk heterojunction active layer are fabricated based on our flexible transparent electrodes as a bottom electrode. The optimized photovoltaic parameters of the three different bulk heterojunction OSC devices on a new flexible electrode are summarized in Table 5. Figure 6a shows the $J-V$ curves with the best PCE under the AM 1.5G illuminated state of the flexible OSC devices with P3HT:PC₆₁BM,

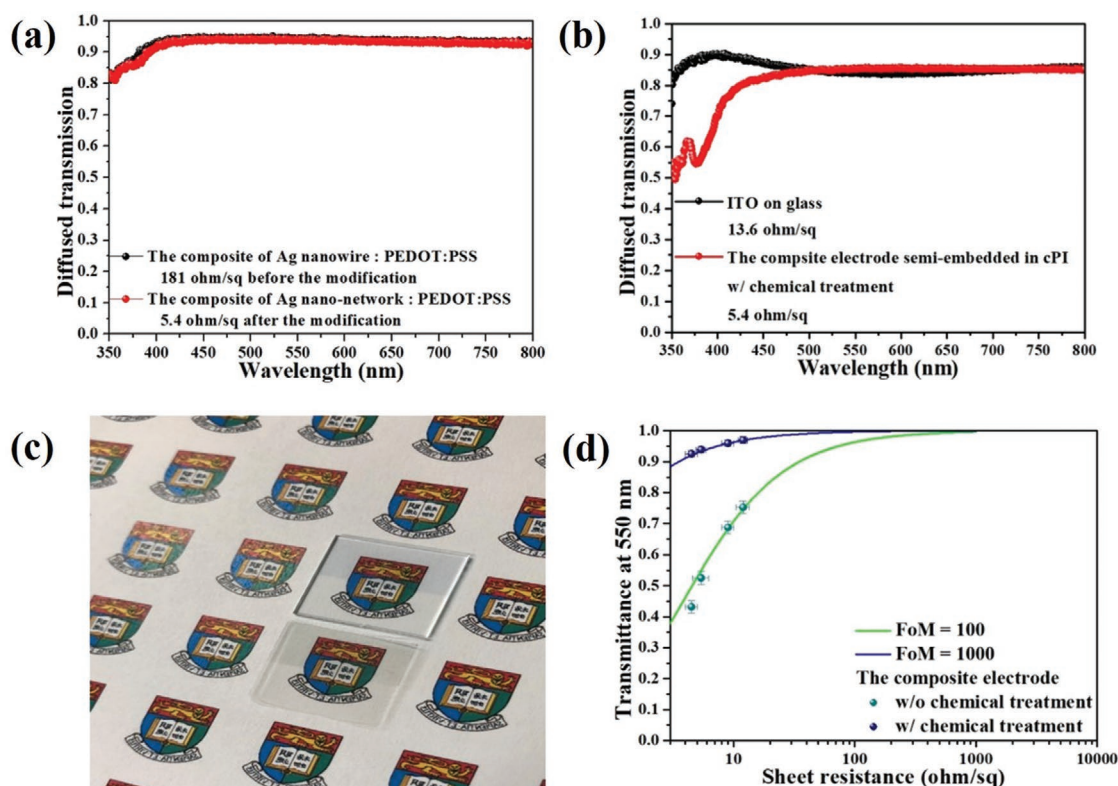


Figure 4. a) Diffused transmission of the composite electrode with/without the chemical treatment, respectively. b) A comparison of diffused transmission of the composite electrode semi-embedded in cPI and ITO/glass. Their corresponding sheet resistances of these samples are stated in the figures. c) Photography of the flexible transparent electrode semi-embedded in cPI substrate and ITO/glass as a comparison (Top sample is the ITO/glass and the bottom one is the new electrode semi-embedded in cPI). d) FoM at values 100 and 1000 of the composite electrode semi-embedded in cPI without and with the chemical treatment, respectively.

PTB7-Th:PC₇₁BM, and PM6:Y6 as the bulk heterojunction active layers and the composite electrode with and without the one-step treatment. The OSCs with P3HT:PC₆₁BM and PTB7-Th:PC₇₁BM as the active layers and the treated flexible electrodes exhibit averaged J_{SC} of 8.95 and 16.27 mA cm⁻², V_{OC} of 0.60 and 0.78 V, FF of 0.62 and 0.66, and PCE of 3.33% and 8.38%, respectively, achieving PCE improvement of 15.9% and 8.95% as compared to the corresponding untreated control

samples. The high-performance OSC on the treated flexible electrode has achieved averaged J_{SC} of 25.62 mA cm⁻², V_{OC} of 0.83 V, FF of 0.68, and averaged PCE of 14.46% (best PCE of 15.12%), achieving PCE improvement of 11.8% as compared to the untreated samples. To the best of our knowledge, that is the highest performance among the ITO-free flexible OSC devices so far. The improved J_{SC} and FF values are the major reasons for the PCE improvement, which can be ascribed to the synergic

effect of the suppressed contact resistance of Ag nanowires, the reduced surface roughness without PSS resistive components, and the increased work function of the treated composite electrode. All of these effects will contribute to the efficient charge transportation between the treated composite electrode and the hole transport layer (HTL). As shown in the J - V curve under the dark state of Figure 6b, the OSC device on the dark state of Figure 6b, the OSC device on the treated composite electrode shows the lower current density over the reverse electrical bias than the untreated control device while it exhibits the higher current density over the forward electrical bias after the 1 V. The phenomena under the reverse and forward electrical bias are also contributed by the reduced surface roughness and the suppressed contact

Table 3. Sheet resistance, transmittance, and FoM value of the previously reported works using Ag nanowires and/or their composite with other conductive materials and the new electrode semi-embedded in cPI substrate demonstrated in this work.

Electrode structure	Sheet resistance [Ω sq ⁻¹]	Transmittance at 550 nm [%]	FoM value	Refs.
AgNW:PEDOT:PSS	7.7	93	662.5	[35]
AgNW:PEDOT:PSS:ITO	41.4	95	175.3	[45]
AgNW:IZO:PEDOT:PSS	5.9	86	407.9	[58]
Ag Nanonetwork	19	98	977.2	[59]
AgNW:SnO ₂ ·xH ₂ O	12	92	369.0	[60]
AgNW:MXene	26	92	162.5	[61]
AgNW:cellulose nanofibers	56	90	62.2	[62]
Ag nanonetwork	2.5	85.5	933.0	[63]
Ag nanonetwork:PEDOT:PSS	5.4	94	1110.9	This work

Table 4. A summary of one-step multifunctional chemical modification effect on the work function of the flexible composite electrode embedded in cPI substrate, respectively.

The flexible composite electrode semi-embedded in cPI	Work function [eV]
With the one-step modification	4.985
Without the one-step modification	4.825

resistances, respectively, for achieving the low leakage current and electrical barrier for charge transfer in the device. The incident photon-to-electron conversion efficiency (IPCE) spectra and integrated J_{SC} of the OSC devices fabricated with PM6:Y6 active layer have been obtained as shown in Figure 6c, which is consistent with the previously reported work except for the region between 350 and 400 nm of wavelengths due to the absorption of cPI as evidenced in Figure S8 (Supporting Information).^[64]

The effective carrier extraction properties have been demonstrated by the transient photocurrent (TPC) spectrum and impedance spectroscopy (IS). As shown in the TPC spectrum of Figure 6d, the charge extraction time of the OSC device fabricated on the treated composite electrode decreases from 1.106 to 0.961 μ s, indicating the fast charge extraction from the active layer. The extraction characterization in the IS measurement as shown in Figure 6e shows the one obvious semicircle, expressing a bulk recombination channel (R_{bulk}).^[65,66] The IS spectrum is fitted by the equivalent circuit shown in the inset of Figure 6e, and the R_{bulk} of 257 Ω was extracted for the untreated device. Interestingly, the R_{bulk} decreases to 198 Ω with the one-step multifunctional chemical treatment when using the same equivalent circuit model, presenting the abrupt reduction of the semicircle radius as shown in Figure 6e. With these results, the enhanced charge extraction properties have been experimentally confirmed, which can explain the J_{SC} and FF for boosting the PCE of the OSC devices on the treated flexible composite electrode as shown in Figure 6a. Meanwhile, the relatively higher V_{OC} values from the treated OSC devices than the untreated samples are obtained. It could be due to the increased WF of the treated electrode as listed in Table 4. The treated OSC devices exhibit very good performance similar to

the rigid ITO/glass-based devices as indicated by the J - V curves and the summarized photovoltaic parameters in Figure S13 and Table S2 (Supporting Information). Figure 6f shows mechanical bending stability of the treated flexible OSC devices with 1 mm bending radius. The decreased PCE is due to the reduction of J_{SC} , V_{OC} , and FF with bending cycles. The mechanical bending test was carried out in the glovebox filled with nitrogen environment and the video for short demonstration of the mechanical bending test of the OSC device conducted in ambient environment is provided in the Supporting Information.

3. Conclusion

The outperformed flexible transparent electrode, composed of Ag nanonetwork and an example polymer of PEDOT:PSS semi-embedded in low-temperature-processed cPI, featured with optimal electrical/optical properties, extremely smooth surface topography, robust electrical stability loaded with simultaneously continuous operation bias and mechanical bending, and efficient charge transportation with adjacent layer has been demonstrated. Particularly, a new one-step multifunctional chemical treatment is proposed to achieve the electrode through simultaneously realizing selective welding at cross junctions of the nanowires, eliminating surfactant of PVP from Ag nanowires, and removing PSS from PEDOT:PSS. The treated flexible transparent electrode shows the FoM value over 1000 ($5.4 \Omega \text{ sq}^{-1}$ of sheet resistance with the corresponding >94% of diffused transmission at wavelengths at 550 nm). The electrical stability is also dramatically improved as compared to the untreated sample verified by bending test under continuous operation bias. Interestingly, the one-step treatment also contributes offering extremely smooth topography (<1 nm of RMS roughness and <3 nm of peak-to-valley roughness) and the increased work function for the efficient charge transfer with the adjacent transporting layer. Based on these outstanding features of the treated flexible electrode, the OSC devices have been fabricated with three different kinds of bulk heterojunction active layer. Among them, the treated OSC device with PM6:Y6 has achieved the averaged PCE of 14.46% (with best PCE of 15.12%), which is the best performance among

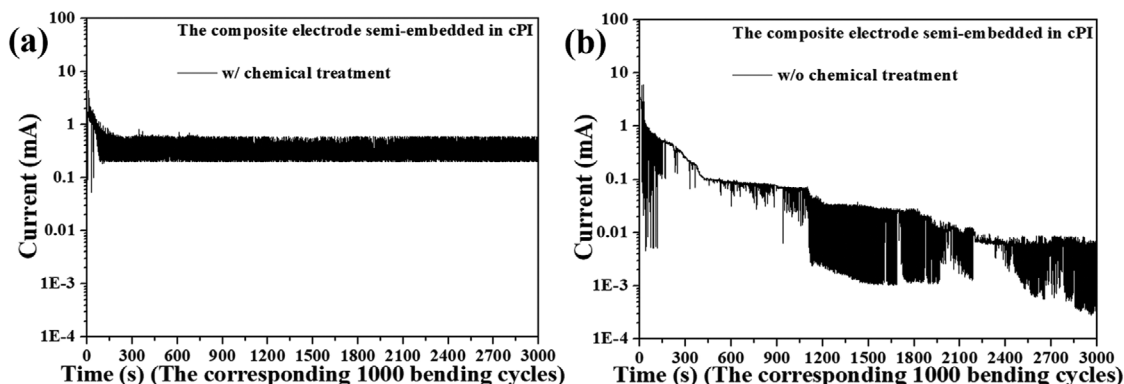


Figure 5. a,b) The variation of the current density of the flexible electrode plotted with both continuous external electrical bias and the number of mechanical bending cycles with and without the one-step multifunctional chemical treatment, respectively. 3000 s means the corresponding 1000 bending cycles.

Table 5. A summary of the optimized photovoltaic parameters of OSC devices with the chemically treated and untreated flexible transparent electrodes measured under solar simulator AM 1.5G illumination.

Anode		J_{sc}	V_{oc}	FF	PCE
P3HT:PC ₆₁ BM as bulk heterojunction active layer					
Untreated cPI/AgNW:conductive polymer	Avg.	−8.48	0.59	0.56	2.80
	Max.	−8.96	0.60	0.57	3.06
Treated cPI/AgNW:conductive polymer	Avg.	−8.95	0.60	0.62	3.33
	Max.	−9.46	0.61	0.67	3.87
PTB7-Th:PC ₇₁ BM as bulk heterojunction active layer					
Untreated cPI/AgNW:conductive polymer	Avg.	−15.73	0.77	0.63	7.63
	Max.	−16.13	0.78	0.64	8.05
Treated cPI/AgNW:conductive polymer	Avg.	−16.27	0.78	0.66	8.38
	Max.	−16.55	0.79	0.68	8.89
PM6:Y6 as bulk heterojunction active layer					
Untreated cPI/AgNW:conductive polymer	Avg.	−24.32	0.82	0.64	12.76
	Max.	−24.83	0.81	0.66	13.27
Treated cPI/AgNW:conductive polymer	Avg.	−25.62	0.83	0.68	14.46
	Max.	−26.03	0.83	0.70	15.12

ITO-free flexible OSCs so far. Consequently, the new one-step approach for outperforming flexible composite electrode semi-embedded in cPI demonstrated in this work contributes not only providing a new strategy of developing highly qualified flexible electrode with robust durability but also advancing the developing of emerging flexible electronics.

4. Experimental Section

Flexible Composite Electrode Composite Semi-Embedded in cPI Flexible Substrate: Ag nanowires used in this work were with diameters of 30, 60, and 100 nm and lengths of 100–300 μm . They were synthesized according to a previous work^[46] PEDOT:PSS was used as the conductive polymer. As for the preparation of the chemical mixture solution used in the multifunctional chemical treatment, silver nitrate, ascorbic acid, and acetic acid were mixed together. First, a certain amount of acetic acid was added into silver nitrate solution (0.1×10^{-3} M) dissolved in ethanol, followed by the addition of ascorbic acid (1×10^{-3} M) dissolved in ethanol. The synthesis of PAA of the 6FDA-TFDB structure was followed by the previously reported work^[54] to be fully contributed to 1:1 copolymerization by mildly stirring ended up a viscous precursor (poly(amic acid) (PAA)) for 6 h, which is a precursor of cPI flexible substrate. Rigid supporting substrates (e.g., glass, quartz, etc.) were cleaned using sequential ultrasonication in deionized water, acetone, and ethanol for 15 min, respectively. The cleaned substrates were then treated by UVO, followed by spin-coating the alternating conducting polymers at 8000 rpm for 40 s (about 20 nm thickness). The resultant film was annealed at 120 °C for 10 min. Then, Ag nanowires were spin-coated with well-optimized between its transparency and conductivity via varying thickness, concentration, drop-casting volume, and spin-coating rate. As for the multifunctional chemical treatment on the composite electrode, firstly, wetting the surface of as-prepared composite Ag nanowires with conductive polymer with the prepared chemical mixture solution. Subsequently, the chemical solution can be removed from the composite electrode by methods such as spin-coating or blowing-off by nitrogen gun while the reactive nanodroplets trapped on the nanoscale at the junction under the capillary force. Then, selectively patterning

can be enabled by simply using 3M tape due to the weak adhesion force between the composite electrode and the supporting substrate. The residue solvent of the resultant film was removed by 80 °C annealing for 5 min. On this selectively patterned composite film, the precursor PAA viscous solution of the cPI was added and adjusted in order to fulfill the optimal requirement of flexibility and bending reliability (about 20 μm thickness). Then, the low imidization processing temperature from 80 °C up to 190 °C gradually was carried out from 80, 100, 150, and 190 °C for 1 h each step. After slowly cooling down to room temperature, the flexible composite electrode in cPI was peeled off by soaking in water, which is assisted by the moisture-induced adhesion degradation and strong interaction between the composite electrode layer and in situ formed cPI.

Fabrication of Organic Solar Cell Devices: P3HT:PC₆₁BM, PTB7-Th:PC₇₁BM, and PM6:Y6 were purchased from Solarmer Materials Inc. 1-Chloronaphthalene (CN) and 1,8-di-iodooctane (DIO) were purchased from Acros Organics and Dieckmann, respectively. Polydimethylsiloxane (PDMS) was used as an adhesive film so that the peeled flexible composite electrode in cPI flexible substrate were stuck to glass/PDMS as supporting adhesive substrate. All of the organic solar cell devices with three different bulk heterojunction

active layers were made as conventional device structure composed of anode/PEDOT:PSS Al 4083/the three active layers/ZnO nanoparticles/Al(evaporated) as cathode. ITO-coated glass substrates as comparison were cleaned using sequential ultrasonication in deionized water, acetone, and ethanol for 15 min, respectively. Glass/ITO was treated by UVO. PEDOT:PSS (Clevios P VP Al 4083, Heraeus) as HTL were deposited on both the flexible electrode substrate and ITO/glass by spin-coating at 4000 rpm for 40 s, followed by drying at 120 °C for 20 min. Three different kinds of organic bulk heterojunction active layers with P3HT:PC₆₁BM (1:1, 20 mg mL^{−1} in dichlorobenzene (DCB)), PTB7-Th:PC₇₁BM (1:1.5, 25 mg mL^{−1} in chlorobenzene (CB), with additives of 3 wt% of DIO), and PM6:Y6 (1:1.2, 15 mg mL^{−1} in chloroform (CF), with additives of 0.5 wt% of CN) prepared, respectively. After transferring samples into the nitrogen-filled glovebox, these three organic active layers were formed on PEDOT:PSS, followed by post-treatment of 1 h slow growth and 130 °C annealing for 10 min. for the P3HT:PC₆₁BM film, anhydrous ethanol washing at 4000 rpm for the PTB7-Th:PC₇₁BM film, and annealing 110 °C for 10 min for the PM6:Y6 film. ZnO nanoparticles as ETL were synthesized and dispersed in *n*-butanol according to the previous reports^[67] and ZnO deposited onto the active layer by spin-coating at 3000 rpm for 40 s with no post-treatment. Finally, Al electrode with a thickness of 120 nm was thermally evaporated on top of the device under a base pressure of 10^{-4} Pa.

Characterization and Measurement: The surface topography of the flexible composite electrode in cPI was examined by SEM (Hitachi S-4800), TEM (Philips Tecnai G2 20 S-TWIN), tapping mode AFM (NT-MDT NTEGRA), respectively. XPS of Ag nanowires on ITO was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al K α X-ray source. The FTIR spectrum was recorded by using a Fourier transform infrared spectrometer (Bruker Tensor 27). The sheet resistances of the flexible electrode substrates were directly measured from a four-point probe approach, and diffused transmission spectra were obtained from a home-built optics system. The work functions of the flexible composite electrode in cPI and ITO/glass were measured by a SKP5050 scanning kelvin probe system (KP Technology Ltd.) with a resolution 1–3 meV. The thicknesses of PEDOT:PSS and cPI flexible substrate were measured from Alpha Step (KLA Tencor, D-500 stylus profilometer). The IPCE measurement of OSC devices was taken by

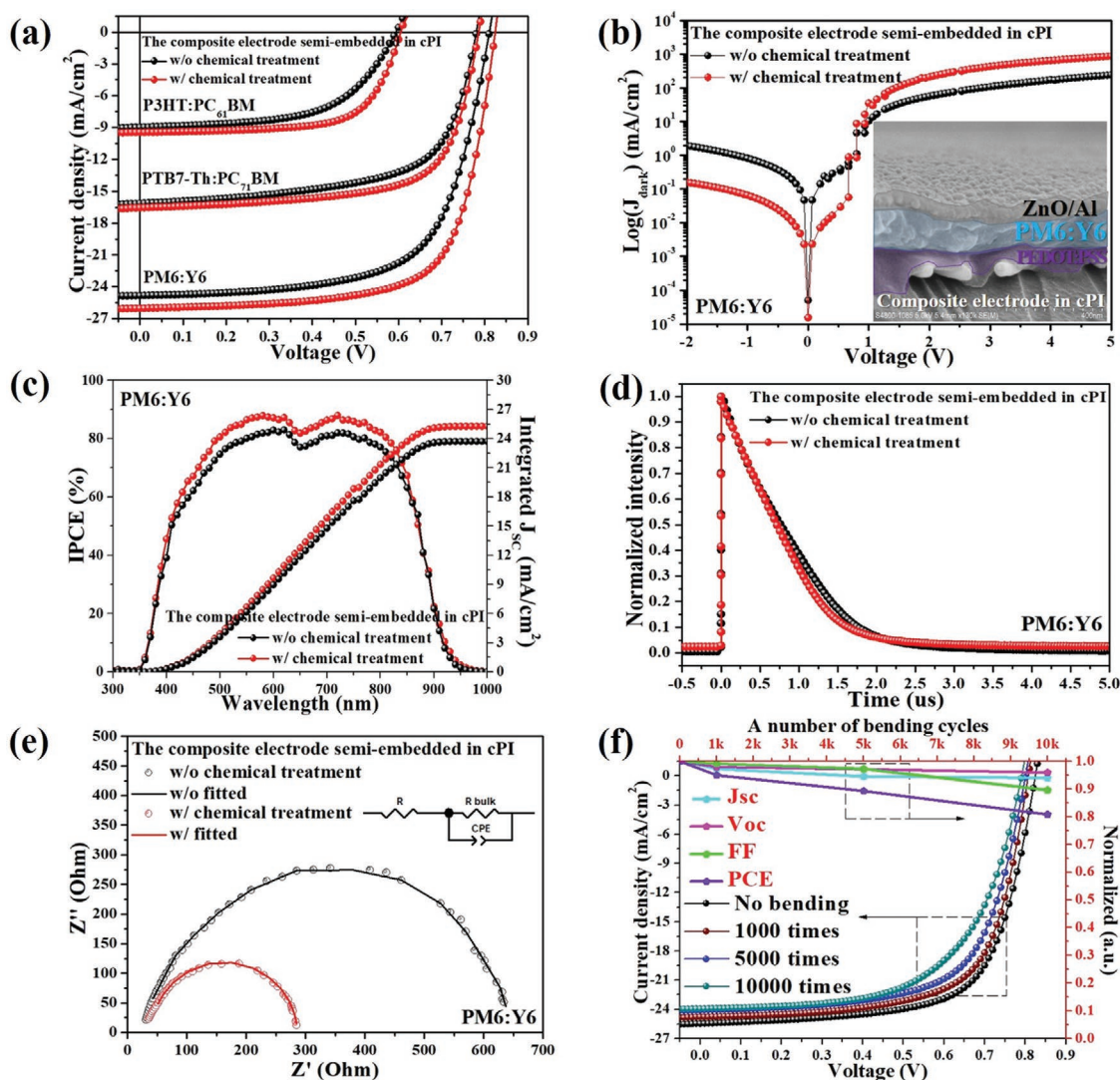


Figure 6. a) The J–V curve with the best PCE under the AM 1.5G illuminated state of the fabricated OSCs on the treated and untreated flexible electrode with P3HT:PC₆₁BM, PTB7-Th:PC₇₁BM, and PM6:Y6 as the active layers. b) J–V curve under dark state. The inset shows the SEM image of cross section of the flexible OSC device. c) IPCE spectra and integrated J_{sc}. d) Change in photocurrent as a function of time. e) Impedance spectrum of the fabricated OSC devices with PM6:Y6 active layer on the flexible electrode with/without the chemical modification, respectively. f) Mechanical bending stability of the treated flexible OSC device and measured J_{sc}, V_{oc}, FF, and PCE of the flexible OSC device after 10 000 times bending cycles with 1 mm bending radius (normalized to the initial value).

using a home-built IPCE measurement system with a Newport xenon lamp, a monochromator, a preamplifier, and a lock-in amplifier. The impedance spectroscopy results were measured by a computer-controlled potentiostat (Autolab PGSTAT320N) from 100 Hz to 1 MHz. A small voltage perturbation (20 mV rms) was applied. Measurements were carried out under 1 sun light intensity illumination at 0.8 V DC bias voltage. The measured data were fitted by Z-view to extract the resistance values. TPC measurements were conducted with a 532 nm 6 ps pulse width laser (130 μJ pulse⁻¹ at 100 Hz) and recorded by a 4 GHz Keysight MSO9404A digital oscilloscope. Lifetime values were extracted by using an exponential decay fitting. The current density–voltage (J–V) characteristics of each solar cell were measured by masking it under shadow mask with opening area of 0.0336 cm² and using Newport AM 1.5 G simulator under a light intensity of 100 mW cm⁻² calibrated with a standard silicon reference cell and the data were collected using a Keithley 2635 source.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by the University Grant Council (UGC) of the University of Hong Kong for the funding (Grant Nos. 201611159194 and 201811159147) and UGC Equipment fund, the General Research Fund (Grant Nos. 17204117, 17200518, and 17201819) from the Research Grants Council (RGC) of Hong Kong Special Administrative Region, and Environment and Conservation Fund (ECF Project 64/2018). The authors would like to acknowledge the useful discussion with Qian Kang, Bowei Xu, and Jianhui Hou from Institute of Chemistry, Chinese Academic of Sciences.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical treatment, flexible transparent electrodes, low-temperature substrates, organic solar cells, silver nanonetworks

Received: November 29, 2019

Revised: February 7, 2020

Published online:

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