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Conductivity Enhancement of PEDOT:PSS Films via Phosphoric Acid Treatment for Flexible All-Plastic Solar Cells

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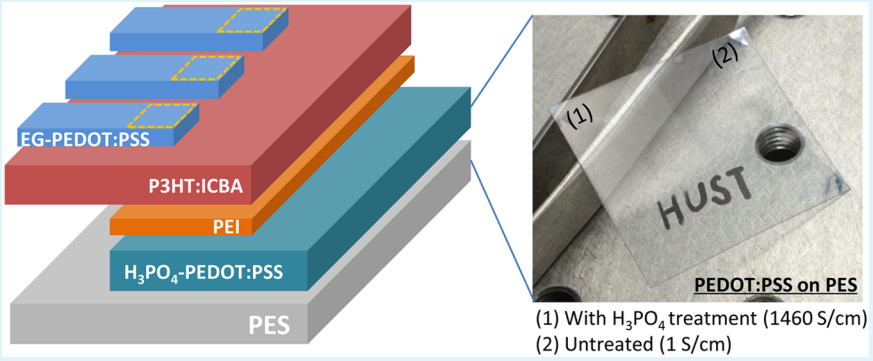

(1) With H_3PO_4 treatment (1460 S/cm)
(2) Untreated (1 S/cm)

ABSTRACT: Highly conductive polymer films on plastic substrates are desirable for the application of flexible electronics. Here, we report the conductivity of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) can be enhanced to 1460 S/cm via phosphoric acid (H_3PO_4) treatment. The conductivity enhancement is associated with the partial removal of PSS from the film. The H_3PO_4 treatment is compatible with plastic substrates, while sulfuric acid (H_2SO_4) can easily damage the plastic substrate. With the flexible electrode of poly(ether sulfone) (PES)/H_3PO_4-treated PEDOT:PSS, we have demonstrated flexible all-plastic solar cells (PES/H_3PO_4-treated PEDOT:PSS/PEI/P3HT:ICBA/EG-PEDOT:PSS). The cells exhibit an open-circuit voltage of 0.84 V, a fill factor of 0.60, and a power conversion efficiency of 3.3% under 100 mW/cm^2 white light illumination.

KEYWORDS: *PEDOT:PSS, phosphoric acid treatment, conductivity, flexible electrode, all-plastic solar cells*

1. INTRODUCTION

Organic solar cells have been attracting great attention due to their advantage of easy fabrication, light weight, and excellent mechanical flexibility.[1−5] Most of organic solar cells reported in the literature are fabricated on indium tin oxide (ITO) glass substrates and with vacuum-deposited metals used as the top electrodes. However, the problems that ITO possesses high mechanically brittleness and high price limit its application to the flexible organic solar cells.[6−8] Conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has advantages of easy film-processing, high transparency, and tunable conductivity (10^{-4} to 10^3 S/cm). So, it has been widely studied and considered as a promising transparent conductive electrode for replacing ITO.[9−18]

To act as an efficient transparent electrode, the conductivity of the PEDOT:PSS films needs to be maximized. Organic polar solvents such as dimethyl sulfoxide (DMSO) or ethylene glycol (EG) have been widely employed to enhance the conductivity of the PEDOT:PSS films because of the simplicity of this method. With the addition of about 5 wt % DMSO or EG into the PEDOT:PSS formulation (PH1000, Heraeus), the conductivity of the films prepared by simply spin coating the formulation can reach about 600 S/cm.[19−23] Besides, post-treatment on the PEDOT:PSS films via organic polar solvents,[12,14,16,24] surfactant[15,25] or acids[13,26,27] could also significantly enhance the conductivity of PEDOT:PSS. With the post treatment, the conductivity of PEDOT:PSS could reach above 1000 S/cm. The Ouyang group[13] and the Lee group[27] have reported that the conductivity of PEDOT:PSS could reach about 3000 S/cm via post treatment with sulfuric acid (H_2SO_4). However, the treatment using such strong H_2SO_4 is very hash. It could damage most underlayers including flexible plastic substrates. Therefore, there are few reports of this treatment employed in flexible optoelectronic devices. Recently, the Lee group[28] reported flexible organic devices using H_2SO_4-treated PEDOT:PSS films (hereinafter referred to as H_2SO_4−PEDOT:PSS) as the electrodes using transfer printing technique, where the H_2SO_4 treatment was applied to the PEDOT:PSS films on glass substrates and then the treated PEDOT:PSS films were transferred onto plastic substrates or organic layers. The transfer printing technique requires precise control of the adhesion at the interfaces of

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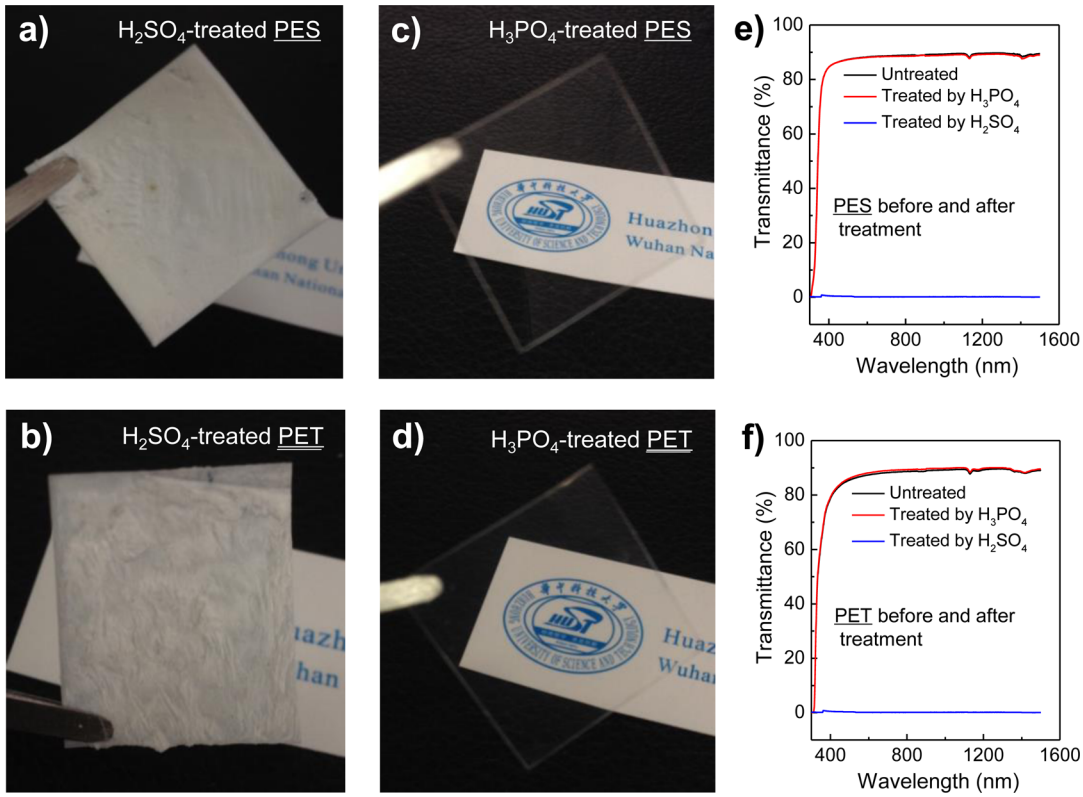

Figure 1. Pictures of plastic substrates treated by H_2SO_4 or H_3PO_4: (a) PES substrate after immersed into H_2SO_4 at room temperature; (b) PET substrate after immersed into H_2SO_4 at at room temperature; (c) PES substrate after immersed into H_3PO_4 at 150 °C; (d) PET substrate after immersed into H_3PO_4 at 150 °C or H_2SO_4 at room temperature. Transmittance: (e) PES substrate before and after immersed into H_3PO_4 at 150 °C or H_2SO_4 at room temperature; (f) PET substrate before and after immersed into H_3PO_4 at 150 °C.

glass/PEDOT:PSS, PEDOT:PSS/transfer medium and PEDOT:PSS/target surface. The technique is rather complicated and the yield of large-area (1 × 1 in.) uniform films via the transfer is low.

Here, we report the conductivity enhancement of PEDOT:PSS films through a treatment with phosphoric acid (H_3PO_4). The H_3PO_4 is gentler, or less corrosive, than the H_2SO_4. The plastic substrates, such as PES, could stay in the H_3PO_4 without damage at a high temperature up to 150 °C. With the H_3PO_4-treated PEDOT:PSS films (hereinafter referred to as H_3PO_4−PEDOT:PSS) employed as the transparent electrodes on plastic substrates, we demonstrate flexible all-plastic solar cells with the device structure of PES/H_3PO_4−PEDOT:PSS/PEI/P3HT:ICBA/EG-PEDOT:PSS. The cells exhibit good performance with an open-circuit voltage (V_{OC}) of 0.84 V, a fill factor (FF) of 0.60 and a power conversion efficiency (PCE) of 3.3% under 100 mW/cm^2 white light illumination.

2. EXPERIMENTAL SECTION

2.1. Preparation and Characterization of PEDOT:PSS Films. PEDOT:PSS aqueous solution (Clevios PH1000) was purchased from Heraeus. The concentration of PEDOT:PSS was 1.3% by weight, and the weight ratio of PSS to PEDOT was 2.5 in the solution. To compare with the H_2SO_4 treatment, we prepared PEDOT:PSS films on the clean glass substrates by spin coating the PEDOT:PSS aqueous solution at the speed of 1000 rpm for 60s in air. Prior to film fabrication, the glass substrates were precleaned with detergent, deionized (DI) water, acetone, and isopropyl alcohol, sequentially. Then, the PEDOT:PSS films were dried at 120 °C on a hot plate for 15 min immediately. After that, the H_3PO_4 treatment was performed by dipping the films into H_3PO_4 (Sinopharm Chemical Reagent Co, Ltd., 85%) at different temperatures (25−160 °C) for 3 min while the H_2SO_4 (98 wt %, Aladdin Reagent Co., Ltd.) treatment was conducted at 25, 40, 60, 80, and 100 °C. Then, the samples were taken out of the acid solutions, cooled to room temperature, and rinsed with deionized water three times. Finally, they were dried at 120 °C for 5 min. The sheet resistance was measured by a four-point probe (RTS-8) and the film thickness measurement was performed using a surface profiler (Veeco Dektak 150). Then, the conductivity was calculated based on the sheet resistance and the film thickness. The transmittance (T) and reflectance (R) of these films were characterized by a UV−vis−NIR Spectrophotometer (UV-3600, Shimadzu). Baseline correction was performed on air for the transmittance. Atomic force microscopy (AFM) images of the PEDOT:PSS films before and after H_3PO_4 treatment were taken using a Veeco NanoScope IV MultiMode in the tapping mode.

2.2. Fabrication and Characterization of the All-Plastic Solar Cells. The flexible all-plastic solar cells were fabricated on PES substrates with the following device configuration: PES/H_3PO_4−PEDOT:PSS/PEI/P3HT/ICBA/EG-PEDOT:PSS (Figure 4a). First, PES substrates were adhered onto polydimethylsiloxane (PDMS) films that attached onto glass substrates. PDMS films was prepared by mixing Dow Corning Sylgard 184, with a ratio of base to cross-linker of 10:1 by weight and cured on a hot plate at 75 °C for 40 min in air. The bottom electrode of H_3PO_4−PEDOT:PSS was prepared and patterned through surface energy tuning via plasma treatment, as previously described,[29] and then immersed into H_3PO_4 for 3 min at 100 °C. Next, the substrates were transferred to the N_2-filled glovebox. PEI (Sigma-Aldrich) was spin coated onto the H_3PO_4−PEDOT:PSS at 5000 rpm for 1 min and annealed at 100 °C for 10 min to reduce the work function.[30] The active layer was prepared by spin coating poly(3-hexylthiophene):indene-C60 bis-adduct (P3HT:ICBA, 1:1, weight ratio) with a total concentration of 40 mg/mL at 700 rpm for 40 s and annealed at 150 °C for 10 min. The thickness of

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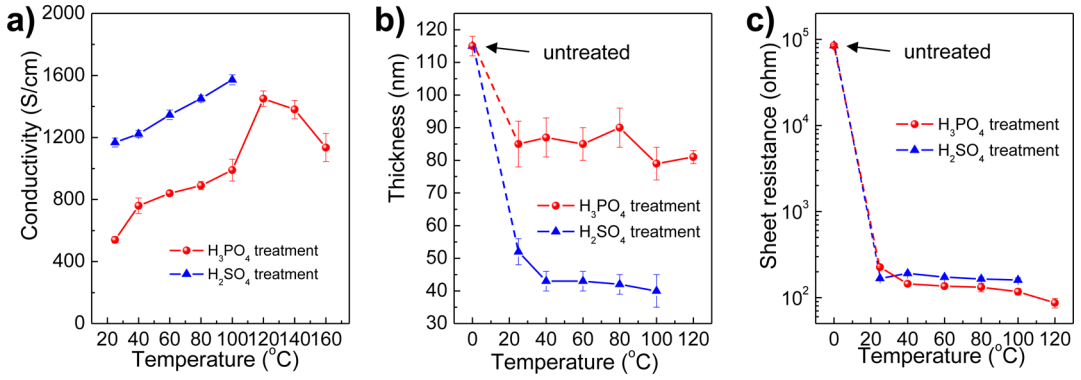

Figure 2. (a) Conductivity, (b) thickness, and (c) sheet resistance of PEDOT:PSS films treated by H_3PO_4 and H_2SO_4 at different temperature on glass substrates.

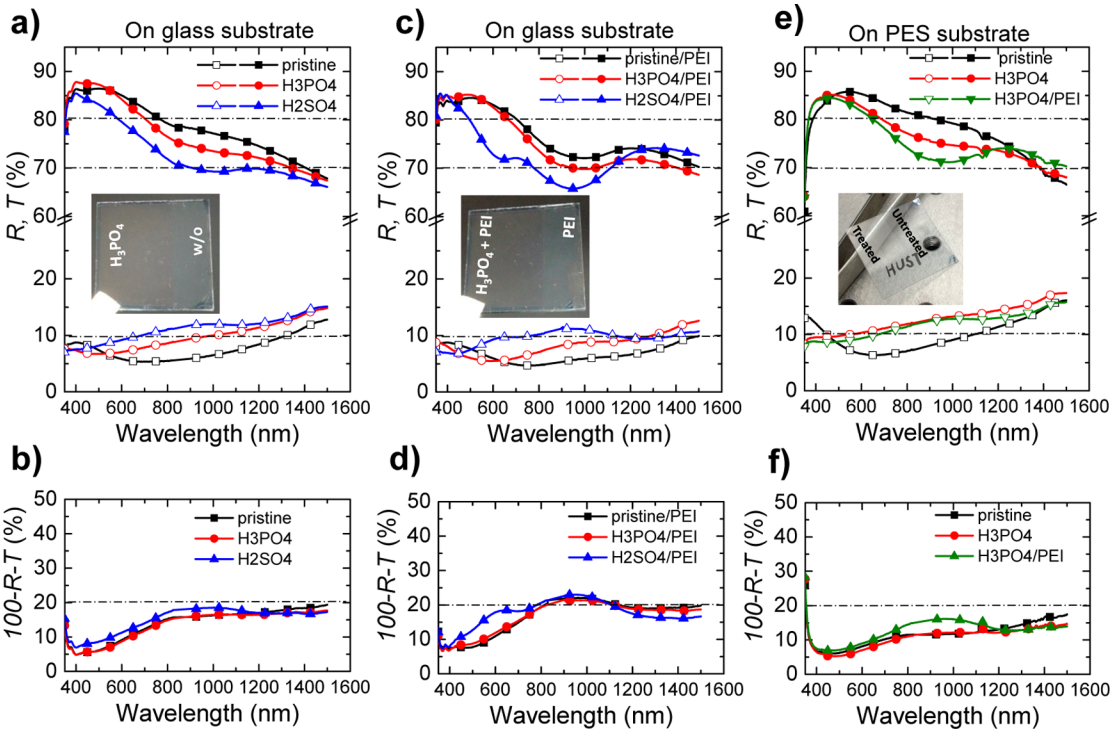

Figure 3. (a and b) Transmittance (T), reflectance (R) and absorption ($A = 100 - R - T$) of pristine, H_3PO_4-treated and H_2SO_4-treated PEDOT:PSS films on glass substrates; (c and d) T, R, and A of the three types of films after PEI modification on glass substrates; and (e and f) T, R and A of pristine, H_3PO_4-treated PEDOT:PSS and PEI-modified H_3PO_4-treated PEDOT:PSS films on PES substrates.

P3HT:ICBA is about 200 nm. Finally, the PEDOT:PSS PH1000 with 5 wt % EG (Sigma-Aldrich) and 0.1 wt % surfactant polyethylene glycol 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol ether (PEG-TmDD, TOYNOL Superwet-340, Tianjin SurfyChem T&D Co., Ltd.) which is used as the top electrode (denoted as EG-PEDOT:PSS) was prepared by transfer lamination technique, as previously described.[31,32] Silver paint was applied onto H_3PO_4–PEDOT:PSS and EG-PEDOT:PSS for electrical contact during the measurement. The cells were annealed in a N_2-filled glovebox at 150 °C for 5 min to dry the PEDOT:PSS top electrode. Current density–voltage (J–V) characteristics were measured inside a N_2-filled glovebox by using a sourcemeter (2400, Keithley Instruments) controlled by a LabVIEW program in the dark and under white light illumination (100 mW/cm^2).

3. RESULTS AND DISCUSSION

Figure 1a,b shows pictures of poly(ether sulfone) (PES) and polyethylene terephthalate (PET) substrates after immersion in concentrated H_2SO_4 at room temperature for 3 min. The PES and PET substrates are damaged by the concentrated H_2SO_4, while they stay highly transparent and clear after the H_3PO_4 treatment at 150 °C (Figure 1c,d). Concentrated H_2SO_4 has a strong oxidizing property and a powerful dehydrating property. It has been used as the reaction reagent for sulfonation of PES.[33] As shown in Figure 1e,f, the PET and PES substrates become not transparent after the concentrated H_2SO_4 treatment. On the contrary, the H_3PO_4 does not have oxidizing or a dehydrating property. The transmittance of the PES and PET substrates is almost unchanged after the H_3PO_4 treatment. Therefore, the H_3PO_4 treatment of PEDOT:PSS films for conductivity enhancement is compatible with the flexible substrates.

Figure 2a shows the electrical conductivity of PEDOT:PSS films after H_3PO_4 treatment at different temperature. The pristine PEDOT:PSS PH1000 film has a conductivity of 1 S/cm. After H_3PO_4 treatment, the conductivity is significantly

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enhanced. The conductivity increases as the treatment temperature goes higher. When the treatment temperature is 120 °C, the conductivity of the PEDOT:PSS films reach maximum of 1460 S/cm. The H_3PO_4 treatment leads to the conductivity of PEDOT:PSS films slightly lower than that of H_2SO_4-treated PEDOT:PSS films. It should be noted the electrical conductivity (σ) is derived from the sheet resistance (R_{sq}) and the film thickness (t) with the following equation:

$$\sigma = \frac{1}{R_{sq} \times t} \quad (1)$$

Figure 2b shows the thickness of PEDOT:PSS films as a function of the temperature of H_3PO_4 or H_2SO_4 treatment. The thickness of the pristine PEDOT:PSS film is about 115 nm. The thickness is significantly reduced to about 40−50 nm after H_2SO_4 treatment. The thickness reduction is ascribed to the removal of PSSH from the PEDOT:PSS film during the H_2SO_4 treatment.[13,27] The small values of the thickness of PEDOT:PSS films yield high values of conductivity according to eq 1. For the H_3PO_4 treatment, the thickness of PEDOT:PSS film is also reduced but the reduction is much less pronounced with a value of about 85 nm. The yielded thickness of PEDOT:PSS after H_3PO_4 treatment is about twice of the thickness after H_2SO_4 treatment. Considering that if the sheet resistance is similar for the both treatments, the calculated conductivity of the H_3PO_4−PEDOT:PSS will be half of that of the H_2SO_4−PEDOT:PSS films. Figure 2c shows the sheet resistance of H_3PO_4−PEDOT:PSS films is similar to or slightly smaller than that of H_2SO_4−PEDOT:PSS films. The calculated higher conductivity in Figure 2a is ascribed to the more pronounced thickness reduction for the H_3PO_4−PEDOT:PSS films. The sheet resistance of H_3PO_4−PEDOT:PSS films on PES substrates have also been fabricated and measured to be about 120 Ω/sq which is slightly higher than that of the films on glass substrates.

As an effective conductive transparent electrode, the sheet resistance and the transmittance are two main parameters for evaluation. Figure 3a shows that the transmittance of pristine, H_3PO_4− and H_2SO_4−PEDOT:PSS films on glass substrates. It can be seen that both H_3PO_4 treatment and H_2SO_4 treatment reduce the transmittance (T) but the H_3PO_4 treatment reduces the T less. The reduction of the T induced by H_3PO_4 treatment and H_2SO_4 treatment is mainly associated with the increase of the reflectance (R), because the acids treatment removes the PSSH inside the film and thus makes it more metallic with higher reflectance. The inset picture in Figure 3a demonstrates that the H_3PO_4−PEDOT:PSS (left) is more reflective and metallic than the untreated one (right). Figure 3b show the absorption ($A = 1 - T - R$) of the three different PEDOT:PSS films are similar, which indicates the amount of PEDOT moiety stays in the film and contributes to the absorption. Figure 3c,d show the T, R, and A of the pristine, H_3PO_4−PEDOT:PSS and H_2SO_4−PEDOT:PSS films after PEI coating to produce low work function for electron collection in organic solar cells. Comparing with the samples without PEI coating, the coating leads to the lower T which is attributed to the increase of A after the PEI coating even though the R is slightly reduced. PEI is a reduction reagent for PEDOT:PSS so that increases the A of the PEDOT:PSS films.[34] Like the PEDOT:PSS films without PEI coating, the H_2SO_4−PEDOT:PSS films exhibit lower T than H_3PO_4−PEDOT:PSS films because of the higher R. Furthermore, a absorption band centered at 600 nm appears after PEI coating which is associated with transformation of positively charged PEDOT to neutral PEDOT,[24] which also leads to the reduction of transmittance (Figure 3c) and electrical conductivity. The transmittances of these films on PES substrates were also characterized. As shown in Figure 3e,f, the films exhibit similar transmittance to that of films on glass substrates.

Figure 4 shows the atomic force microscopy (AFM) images of the PEDOT:PSS films before and after H_3PO_4 treatment.

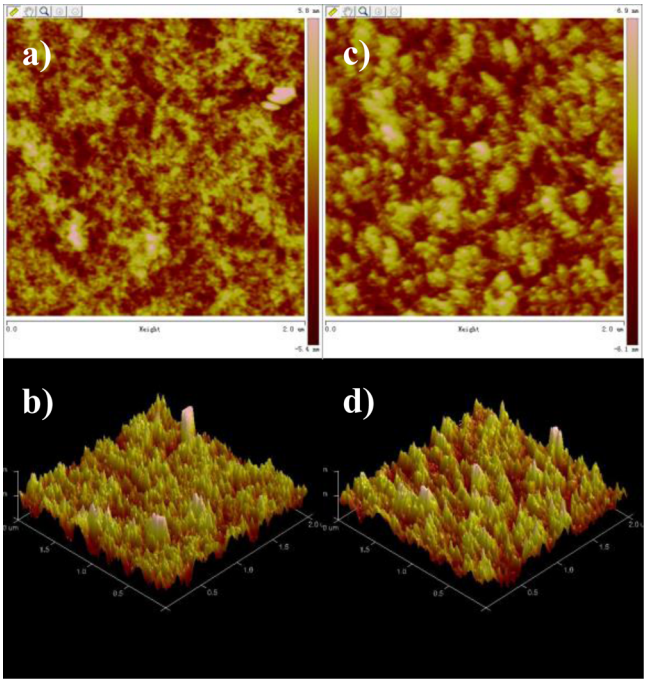

Figure 4. (a) and (b) AFM images of the pristine PEDOT:PSS film; (c) and (d) AFM images of H_3PO_4 treatment PH1000 film. (a) and (c) are 2D height images, and (b) and (d) are 3D images. The image area is 2 × 2 μm.

The PEDOT:PSS film after H_3PO_4 treatment displays a surface roughness with a root-mean-square (RMS) value of 1.87 nm, which is slightly rougher than the untreated PEDOT:PSS film with a RMS surface roughness of 1.6 nm. The rougher surface is associated with the removal of PSSH.[35]

Considering the two key parameters of a transparent conductive electrode: sheet resistance and transmittance, the H_3PO_4 treatment is superior to the H_2SO_4 treatment, because the H_3PO_4-treated PEDOT:PSS films exhibit higher transmittance and even lower sheet resistance than the H_2SO_4-treated films. Based on the flexible, conductive, and transparent H_3PO_4−PEDOT:PSS electrode, we demonstrate all-plastic solar cells with a device structure of PES/H_3PO_4−PEDOT:PSS/PEI/P3HT:ICBA/EG-PEDOT:PSS (Figure 5a). The solar cell structure is all-plastic, and the devices are fabricated by fully solution-processing. The inset is a fabricated all-plastic solar cell with H_3PO_4−PEDOT:PSS as the bottom electrode on a PES substrate. Figure 5b shows the picture of the device, from which we can know that it exhibit excellent flexibility. The J−V characteristics of cells in the dark and under 100 mW/cm^2 illumination are shown in Figure 5c. The cells exhibit large rectification in the dark and good performance under illumination of V_{OC} = 0.84 V, short-circuit current (J_{SC}) = 6.6 mA/cm^2, FF = 0.60, and PCE = 3.3%. Reference devices

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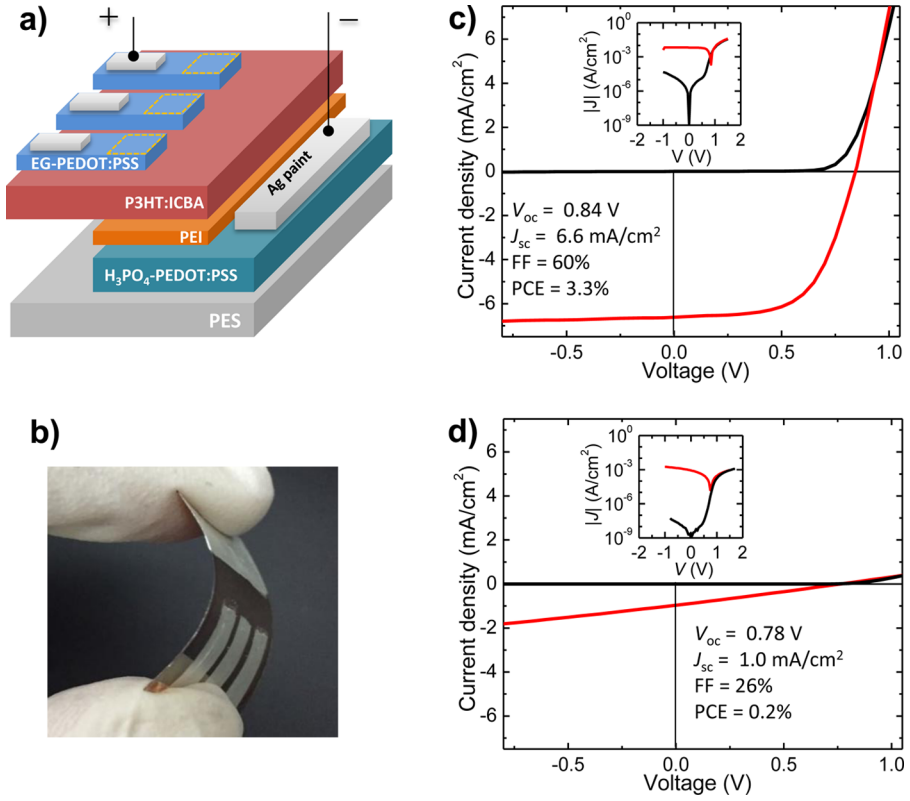

Figure 5. (a) Device structure of the flexible all-plastic solar cell; (b) picture of the flexible all-plastic solar cell; (c) $J-V$ characteristics of a representative solar cell in the dark and under 100 mW/cm^2 white light illumination in linear and semilog scale. (d) $J-V$ characteristics of the reference solar cell with untreated PEDOT:PSS as the bottom electrode.

without the H_3PO_4 treatment (PES/pristine PEDOT:PSS/PEI/P3HT:ICBA/EG-PEDOT:PSS) have been also fabricated. The $J-V$ characteristics of are shown in Figure 5d. The devices exhibit V_{OC} = 0.78 V, J_{SC} = 1.0 mA/cm^2, FF = 0.26, and PCE = 0.2%. The low performance is owing to the low conductivity (about 1 S/cm) of untreated PEDOT:PSS electrode. These show that the H_3PO_4−PEDOT:PSS could be used as an efficient transparent conductive electrode for flexible all-plastic solar cells.

4. CONCLUSIONS

We have reported H_3PO_4 treatment enhancing the conductivity of PEDOT:PSS on plastic substrates to build flexible transparent conductive electrode. The H_3PO_4−PEDOT:PSS films exhibit a high conductivity of 1460 S/cm. As a transparent conductive electrode, the H_3PO_4 treatment is superior to the H_2SO_4 treatment because the H_3PO_4−PEDOT:PSS films exhibit higher transmittance and even lower sheet resistance than the H_2SO_4-treated films. More importantly, the H_3PO_4 is compatible with flexible plastic substrates while H_2SO_4 treatment easily damages the plastic substrates. At the end, we demonstrate flexible all-plastic solar cell with the PEI-coated H_3PO_4−PEDOT:PSS films as the bottom electrodes for electron collection. The cells exhibit a V_{OC} of 0.84 V and a high FF of 60%. These demonstrated that H_3PO_4 treatment is an effective way to produce efficient polymer transparent conductive electrode for flexible electronics.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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