Aging process of PEDOT:PSS dispersion and robust recovery of aged PEDOT:PSS as a hole transport layer for organic solar cells

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Abstract

Conducting p-type polymer of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been widely used for organic optoelectronics, particularly as a hole transport layer for organic solar cells. While the aged PEDOT:PSS dispersion impacts device performance, the aging of PEDOT:PSS dispersion have not been well investigated. Moreover, the recovery process of aged (two-year-old) PEDOT:PSS dispersion has not been demonstrated yet. Herein, it is found that aqueous PEDOT:PSS dispersion undergoes extensive phase separation during the aging process, resulting in both nanoscale and macroscale hydrophobic PEDOT-rich agglomerates. When the aged PEDOT:PSS thin film is integrated into P3HT:PCBM organic solar cells, the PEDOT-rich agglomerates trap the photogenerated holes at the PEDOT:PSS/P3HT interface, resulting in poor extraction

efficiency in organic solar cells. To recover a hole transport functionality from aged PEDOT:PSS, three different solvents such as isopropyl alcohol (C_3H_7OH), ethanol (C_2H_5OH) and methanol (CH_3OH) are investigated. Among them, it is found that isopropyl alcohol (IPA) yielded very uniform PEDOT:PSS thin film layer. This is because hydrophobic functional groups of IPA solvent facilitated the preferential solvation of phase separated hydrophobic PEDOT-rich agglomerates. However, when non-optimal concentration of IPA solvents was added into the aged PEDOT:PSS dispersion, the size of PEDOT-rich agglomerates was adversely enlarged. When organic solar cells were fabricated using more than a two-year-old PEDOT:PSS that was treated with IPA solvent, the resulting device performance of organic solar cells was fully recovered and became comparable or better than that of organic solar cells fabricated with fresh PEDOT:PSS.

1. Introduction

Conducting p-type polymer of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been widely used for many applications in optoelectronic, electronic, electrical, and electrochemical devices due to its high transparency, electrical conductivity, chemical stability, and low-cost fabrication process [1-3]. Typically, to increase solubility of PEDOT:PSS in water, excess amount of PSS is required and commercial PEDOT:PSS dispersion has the PEDOT to PSS ratio ranging from 1:2.5 to 1:20[4]. In this case, the negatively charged, hydrophilic PSS allows positively charged, hydrophobic PEDOT to be dispersed in an aqueous solution [5-7]. As a result, the conformation of PEDOT:PSS in water forms a colloidal gel particle which has a core-shell structure, i.e. the hydrophobic PEDOT core region is surrounded by a hydrophilic PSS shell [5,8,9]. Currently, only a few studies reported the aging of PEDOT:PSS that mainly addressed the aging of PEDOT:PSS thin films. In addition, a clear understanding of the aging mechanism of aqueous PEDOT:PSS

dispersion has not been systematically studied. For instance, very thin PEDOT:PSS thin films processed from an aqueous PEDOT:PSS dispersion were prepared and then tested for the aging including a thermal treatment at different temperatures and times [10,11]. Vitoratos, *et al.* reported an interesting finding of the thermally aged PEDOT:PSS thin films in which an excess of PSS existing at the surface of fresh PEDOT:PSS was partially removed after the thermal aging process [10]. Critically, the aging of PEDOT:PSS thin films led to irreversible morphological and compositional deformation of PEDOT:PSS that subsequently influenced optical, electrical and structural properties of PEDOT:PSS. Jin et al, reported that the organic solar cells processed with aged PEDOT:PSS thin film typically led to S-shaped J-V curve due to an increased sheet resistance and a poor contact between photoactive layers and thermally aged PEDOT:PSS [12].

Currently experimental results reported in the literatures are based on thin films prepared from fresh PEDOT:PSS dispersion. However, it is recommended from commercial vendors that the best and reliable experimental results from aqueous PEDOT:PSS dispersion can be achieved within six to nine months from the date of purchase even though it is claimed that a commercially available PEDOT:PSS dispersion remains stable for 9~12 months from the date of production in sealed original containers when stored at temperatures between 5 and 10°C [13]. This indicates that aqueous PEDOT:PSS dispersion is vulnerable to aging with time and the optimal use of PEDOT:PSS is only limited to a certain period from the date of purchase. However, until now there is no report regarding properties of aged PEDOT:PSS, its impact on device performance, and particularly a method to prolong the use beyond the shelf time of aqueous PEDOT:PSS dispersion.

In this work, fresh PEDOT:PSS and aged PEDOT:PSS dispersion that was left on shelf for more than two years are investigated to elucidate the aging mechanism of aqueous PEDOT:PSS dispersion. We also explore the recovery from aged PEDOT:PSS dispersion to

fresh-like PEDOT:PSS dispersion. Particularly, an aqueous PEDOT:PSS dispersion, obtained by addition of solvents to aged PEDOT:PSS dispersion was investigated to gain a deeper understanding of the fundamental property of the solvent-modified PEDOT:PSS. Currently, many studies used a variety of solvents for an enhancement in the conductivity of PEDOT:PSS. For instance, the conductivity of PEDOT:PSS thinfilms were enhanced by the addition of solvents like sorbitol, ethanol, isopropyl alcohol (IPA), acetonitrile(ACN), acetone, or tetrahydrofuran (THF), and others to the aqueous dispersion [6,7,14-17]. One possible explanation of enhanced conductivity in PEDOT:PSS is related to a rearrangement of PEDOT-rich clusters or the preferential solvation of PEDOT:PSS with solvents [10,14,15]. The recovery process of aged PEDOT:PSS dispersion using solvents such as isopropyl alcohol (IPA), ethanol, and methanol was explored and correlated to morphological and compositional variations of PEDOT:PSS. The aging mechanisms of aqueous PEDOT:PSS are best explained by the phase separation, resulted in nanoscale and microscale PEDOT-rich agglomerates that were observed by transmission electron microscope (TEM) and energy-dispersive X-ray spectroscopy (EDS) measurement. We also show the optimal concentration of IPA solvents is critical in preferentially solvating phase-separated, hydrophobic PEDOT-rich agglomerates in aged PEDOT:PSS dispersion. In addition, fresh and aged PEDOT:PSS thin films were integrated as a hole transport layer in organic solar cells and the role of aged and recovered PEDOT:PSS thin films on organic solar cells has been identified.

2. Experimental

PEDOT:PSS dispersion has been stored in a sealed original container in the laboratory at room temperature that has a humidity of less than 50 %. For the first year, the opening of the original container of PEDOT:PSS was minimized by allocating some portion of PEDOT:PSS

dispersion for materials characterization and device fabrication. And then the PEDOT:PSS dispersion was completely sealed and left on the shelf for another year. The fresh PEDOT:PSS layer was the one processed within six month from the date of purchase while aged PEDOT:PSS layer was processed using a two-year old PEDOT:PSS dispersion. The fresh PEDOT:PSS (CleviosP VP AI 4083) was mixed with isopropyl alcohol (IPA, Aldrich 99.7%), ethanol (Aldrich 99.5%) and methanol (Aldrich 99.8%) while IPA solvent was mixed with a two-year- old PEDOT:PSS with different volume ratios of PEDOT:PSS to IPA, ranging from 1:0 to 1:9. The PEDOT:PSS films were prepared by spin coating (3000 rpm for 3 minutes) on pre-cleaned glass substrates and then annealed at 100 °C for 15 minutes. The high-resolution microscopic images of the PEDOT:PSS thin film layers were taken using HiROX (KH-7700 High Resolution Digital-Video) microscopy system. The transmittance of the PEDOT:PSS films were measured by UV-Vis spectra (Perkin Elmer Lambda 45) with a slit width of 1 nm and a scanning speed of 480 nm/min. For sheet resistance (R_{sh}) measurements, the PEDOT:PSS thin films were prepared by spin coating on pre-cleaned glass substrates and then annealed at 100 °C for 15 min. The sheet resistance of films were measured by a four point probe technique using Keithley 2400 as a source measurement unit. For each sample, two identical films were prepared and measured. The average values of R_{sh} were calculated. To investigate morphologies and chemical compositions of PEDOT:PSS, high-resolution field emission transmission electron microscope (HR-TEM) (JEM-2100F JEOL) and energy-dispersive X-ray spectroscopy (EDS) (INCAx-sight Oxford Instruments) were used. TEM samples were prepared by dropping 5 μ L solvent treated PEDOT:PSS on the micro-grid (Lacey Formvar/Carbon, 300 Mesh Copper Grids, Ted Pella). And then samples dried at 100 °C for 15 minutes. For time-correlated single photon counting (TCSPC) measurements, the samples were prepared by spin coating solvent treated PEDOT:PSS (3000 rpm for 3 minutes) on pre-cleaned glass substrates, then annealed at 100 °C for 15 minutes.

The P3HT:PCBM photoactive layer was spin coated (≈ 130 nm) on the top of PEDOT:PSS in the glove box. In addition, the solvent treated PEDOT:PSS was integrated into P3HT:PCBM organic solar cells. First, the aged PEDOT:PSS (CleviosP VP AI 4083, two- year-old) was mixed with IPA with different volume ratios. Then PEDOT:PSS thin films were prepared by spin coating (3000 rpm for 3 minutes) on pre-cleaned indium tin oxide (ITO) coated glass substrates, followed by annealing at 100°C for 15 minutes. The photoactive layer is P3HT:PCBM where P3HT (Rieke Metals, Inc, $\text{RR} \geq 97\%$) and PCBM (Nano-C, 99.9%) were blended together with a weight ratio (1:0.8) in 1,2 dichlorobenzene (DCB, Alfa Aesar, 99 %) in a nitrogen filled glove box (O_2 and $\text{H}_2\text{O} < 0.1$ ppm). The devices were completed by depositing aluminium electrode ($\text{Al} \approx 100$ nm) and the resulting device active area was 10 mm^2 . After Al deposition, the ITO/PEDOT:PSS:IPA/P3HT:PCBM/Al devices were subjected to post annealing in glove box at 150°C for 10 minutes. We also fabricated the devices with the same condition but using the fresh PEDOT:PSS. The current density–voltage (J-V) characterization of the organic solar cells was measured under simulated AM 1.5G illumination (100 mW/cm^2).

3. Results and discussion

3.1. Transmission electron measurement and energy dispersive X-ray of PEDOT:PSS

The effect of the addition of solvents on aqueous PEDOT:PSS dispersions. Isopropyl alcohol (IPA) was added to fresh and aged (two-year-old) PEDOT:PSS dispersion and then PEDOT:PSS thin films were characterized. Fig. 1 shows transmission electron microscope (TEM) measurement for three PEDOT:PSS films; untreated fresh PEDOT:PSS (Fig. 1a and b), untreated aged PEDOT:PSS (Fig. 1c and d), and aged PEDOT:PSS treated with IPA at a volume ratio of 1:4 (Fig. 1e and f). TEM images showed clearly different morphologies, revealing different distributions of mixed dark agglomerates and bright film layer. Untreated,

fresh PEDOT:PSS in Fig. 1a and b have a number of small black agglomerates with grain sizes of less than 100 nm. However, the untreated, aged PEDOT:PSS in Fig. 1c is characterized by a high density of dark agglomerates. Higher magnification TEM image of aged PEDOT:PSS in Fig. 1d revealed mixed black agglomerates from tens of nanometers to several hundred nanometers. By contrasting fresh and aged TEM images, two key findings are revealed. First, the smaller agglomerates in fresh PEDOT:PSS became enlarged during the aging process of PEDOT: PSS. Second, a large number of small black agglomerates of aged PEDOT:PSS in the range of 30-80 nm also appeared and were randomly distributed to cover the entire surface area. Overall the extensive aging process of PEDOT:PSS resulted in formation of various agglomerates of PEDOT:PSS. When the aged PEDOT:PSS was treated with IPA, remarkably improved morphologies were observed in the TEM images in which a number of smaller agglomerates presented in aged PEDOT:PSS disappeared. Also, the larger agglomerates were substantially reduced to smaller agglomerates.

To find out the chemical compositions of black agglomerates an energy-dispersive X-ray spectroscopy (EDS) measurement was performed. Fig. 2 shows the analysis of EDS of the black agglomerate and white domain for the relative atomic concentrations, revealing higher oxygen and sulfur atomic concentrations in black agglomerate. Na was also detected that stems from the fabrication process of EDOT in which $\text{Na}_2\text{S}_2\text{O}_8$ oxidizing agents is typically used for polymerization of EDOT [18]. It is theoretically calculated that relative sulfur atomic concentration in PEDOT is higher than in PSS [18]. Therefore, the relatively higher concentration of sulfur atomic concentration in black agglomerate indicates that agglomerates can be ascribed to PEDOT-rich clusters which is consistent with observation reported by Hsiao, *et al*[19] Inferred from TEM and EDS measurements, the aging process of an aqueous PEDOT:PSS dispersion led to the extensive phase separation of PEDOT:PSS, leading to PEDOT-rich agglomerates.

3.2. Effect of various solvents on morphologies of PEDOT:PSS

To understand the effect of solvents on morphologies of PEDOT:PSS, three different solvents of IPA ($\text{C}_3\text{H}_7\text{OH}$), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and methanol (CH_3OH) were used. In this case, all of solvents were applied to fresh PEDOT:PSS dispersion. Fig. 3. shows TEM images of PEDOT:PSS treated with IPA (Fig. 3a and d), ethanol (Fig. 3b and e) and methanol (Fig. 3c and f) that were obtained before and after filtration using a $0.45\ \mu\text{m}$ filter, respectively. It is clear that a density of PEDOT-rich agglomerates are different with the solvent treatment of fresh PEDOT:PSS. It should be noted that fresh PEDOT:PSS thin film presented a number of isolated PEDOT-rich agglomerates that has nanoscale size of less than 100 nm, indicated in Fig. 1a and b. When IPA was added to fresh PEDOT:PSS dispersion, uniform PEDOT:PSS morphologies were observed while methanol and ethanol treated PEDOT:PSS thin films still showed a number of PEDOT-rich agglomerates. An interesting observation is that even though filtration was performed nanoscale PEDOT-rich domains still exist for ethanol and methanol treated PEDOT:PSS as shown in Fig. 3e and f, respectively. Particularly, when compared with TEM images of fresh PEDOT:PSS (Fig. 1a and b), nanoscale PEDOT-rich domains of ethanol and methanol treated PEDOT:PSS became enlarged. These results indicate that IPA solvent led to a greater degree of solvation of hydrophobic PEDOT-rich agglomerates while methanol-treated PEDOT:PSS led to poor solvation of PEDOT-rich agglomerates. The solvation of PEDOT-rich agglomerates in an aqueous PEDOT:PSS with solvents can be explained in terms of chemical structures of solvents. Organic solvents consist of two different hydrophobic and hydrophilic functional groups. One end of the molecules of solvents has hydrophobic character while the other end contains an OH group that is hydrophilic. As the hydrocarbon chain becomes longer, the hydrophobic character of the molecule increases, and the solvation of hydrophobic PEDOT-rich agglomerates in

PEDOT:PSS dispersion gradually increases. Among three solvents, IPA has the longest hydrocarbon chains that promote solvation of PEDOT-rich agglomerates. Therefore, it can be concluded that the improved morphologies of IPA treated PEDOT:PSS compared to other solvents of methanol and ethanol are due to larger portion of hydrophobic functional group of IPA which will promote the solvation of phase separated PEDOT-rich agglomerates as shown in Fig. 3a and d. It should be noted that methanol ($\epsilon=32.6$, polarity=76.2) and ethanol ($\epsilon=22.4$, polarity =65.4) have higher dielectric constants and relative polarities than IPA ($\epsilon=18.3$, polarity =54.6) [15] has. It is well known that organic solvents with higher dielectric constant and polarity will reduce the Coulomb interaction between positively charged PEDOT and negatively charged PSS, leading to phase separation [15]. Therefore, the use of higher dielectric or strong hydrophilic organic solvents such as methanol and ethanol will not preferentially solvate PEDOT-rich agglomerates but rather promote the phase separation of PEDOT:PSS by solvating hydrophilic, insulating PSS. As a result, hydrophobic PEDOT-rich domains will be enlarged, as confirmed from TEM images in Fig. 3e and f. However, another aspect of use of methanol and ethanol was known to enhance conductivity of PEDOT:PSS by reorienting the phase-separated, conductive PEDOT polymer chains from a coiled structure to linear or extended coil structure [15,18].

3.3. Aging and recovery mechanisms of PEDOT:PSS

The aging and recovery mechanisms of aqueous PEDOT:PSS dispersion were developed and illustrated in Fig. 4. As stated earlier, fresh PEDOT:PSS will have a complex configuration in which a low molecular weight (MW), hydrophobic PEDOT is linked to a high MW, hydrophilic PSS chains by tight ionic bonds [5,8,9]. Typically, a commercial PEDOT:PSS dispersion is designed with high weight ratio of PSS to PEDOT in an aqueous PEDOT:PSS solution to increase hydrophilic characteristic. Based on TEM and EDS measurements, the

aging of PEDOT:PSS causes extensive phase separation, resulting in PEDOT-rich agglomerates. Since PSS is hydrophilic and dissolved in water, PEDOT-rich agglomerates will typically remain in an aqueous dispersion. Fig.4a shows the high-resolution of microscopic image of a fresh PEDOT:PSS thin film which has good wetting property. However, the aged PEDOT:PSS thin film layer shows relatively poor wetting that indicates very strong hydrophobic PEDOT characteristic. This confirms radical phase separation of aged PEDOT:PSS. Therefore, it is concluded that the aging process of PEDOT:PSS underwent phase separation process, leading to PEDOT-rich agglomerates while hydrophilic PSS was dissolved in the solution. Our observation is consistent with a study reported for thermally aged PEDOT:PSS thin film in which the PSS shell layer becomes thinner during the thermal aging process. When IPA was added to the aged PEDOT:PSS with a volume ratio of 1:1.5, uniform coverage and better wetting of PEDOT:PSS was obtained in Fig. 4c, inferring that the addition of IPA enhanced solvation of PEDOT agglomerates. However, large black agglomerates were still observed. The further addition of IPA volume ratios of 1:2~1:4 substantially reduced size of agglomerates as shown in Fig. 4d. This is due to preferential solvation of PEDOT-rich agglomerates with IPA solvent. However, when IPA volume ratio was increased to 1:9, a number of agglomerates were increased again, as shown in Fig. 4e. This might result from the enhanced interaction between hydrophobic groups of IPA organic solvent that surrounded PEDOT-rich agglomerates. To further confirm the increased density of agglomerates, we also perform transmittance measurement of PEDOT:PSS layers that will indirectly provide the degree of distribution of agglomerates. Indeed Fig.5 shows the transmittance of PEDOT:PSS layers in which PEDOT:PSS treated with IPA with a volume ratio of 1:4 have increased transmittance while the smaller and larger IPA volume ratio than 1:4 decreased transmittance, indicating an increase in density of agglomerates of PEDOT:PSS. This result indicates the optimal volume ratio of IPA should be

around 1:4 to have very strong preferential solvation of phase-separated PEDOT-rich agglomerates.

3.4. Effect of solvents on organic solar cells

To investigate the effect of solvent treated PEDOT:PSS on photovoltaic performance of organic solar cells, P3HT:PCBM solar cells were fabricated with standard structures. The P3HT:PCBM organic solar cells fabricated with aged PEDOT:PSS showed the typical S-shaped J-V characteristic as shown in Fig. 6a. When the aged PEDOT:PSS dispersion was treated using IPA with a volume ratio of 1:1.5, the S-shaped J-V characteristics disappeared due to improved fill factor. With further addition of IPA to a volume ratio of 1:4, the device performance is fully recovered with increased short circuit current density (J_{SC}), fill factor (FF) and open circuit voltage (V_{OC}) and became comparable to that of organic solar cell fabricated with fresh PEDOT:PSS. However, when IPA volume ratio is increased to 1:9, the V_{OC} is decreased while maintaining the J_{SC} .

To further understand the underlying effect of solvent treated PEDOT:PSS on device performance, photocurrent-effective voltage J_{ph} - V_{eff} was analyzed [20-22]. In this case, the photocurrent (J_{ph}) was extracted by subtracting the dark current density from the current density measured under the illumination. The effective voltage of V_{eff} is determined from V_0 - V where V_0 is defined by the voltage at which the $J_{ph} = 0$, and V is the applied voltage. When the effective voltage is a larger value, a very strong electric field is typically formed inside photoactive layer so that the photocurrent will be dominated by the field dependent dissociation of e-h pairs. Indeed, at a large effective voltage ($V_{eff} = \sim 1V$), all of organic solar cells in Fig. 6b showed the saturated J_{ph} values, suggesting that most of photo-generated excitons are dissociated into free charge carriers that are subsequently collected at the electrodes. However, a lower effective voltage ($V_{eff} < 0.4V$) will form a flat energy band

structure so that the recombination process will dominate due to the poor carrier extraction and/or low exciton separation efficiencies. As expected, the organic solar cells fabricated with aged PEDOT:PSS showed the lowest J_{ph} at the low effective voltage, suggesting lower exciton dissociation efficiency and/or charge collection efficiency [23]. However, the modification of aged PEDOT:PSS with IPA improved the J_{ph} in which the J_{ph} of organic solar cell fabricated with PEDOT:PSS with a volume ratio of 1:4 became comparable to that of organic solar cell fabricated with fresh PEDOT:PSS. This result indicates the IPA treatment of aged PEDOT:PSS is a simple and robust method to fully recover the functionality of PEDOT:PSS as hole transport layer in organic solar cells. Another interesting observation is that the further modification of IPA with a volume ratio of 1:9 lowered the J_{ph} that can be attributed to reduced exciton dissociation rate or lower extraction efficiency that should be determined. To identify exciton dissociation rates of organic solar cells, time-correlated single photon counting (TCSPC) measurement was performed for P3HT:PCBM photoactive layer fabricated with fresh PEDOT:PSS, untreated aged PEDOT:PSS, and IPA treated aged PEDOT:PSS. As shown in Fig.6c, organic solar cells fabricated with three different PEDOT:PSS showed nearly identical lifetime of exciton, indicating dissociation rates of organic solar cells will be not much different. As well known, the exciton dissociation rate is closely related to bulk heterojunction morphologies [24,25] in which donor and acceptor molecules are interconnected to provide the large interfacial chemical potential for the exciton dissociation [26]. Thus the TCSPC results infer that morphologies of P3HT:PCBM for all solar cells have similar characteristics even though beneath PEDOT:PSS thin film layers as a hole transport layer are differently prepared with different IPA volume ratios. Therefore, the account of exciton generation/dissociation in bulk heterojunction as a possible explanation of different J_{ph} values for organic solar cells can be excluded. Instead, the extraction efficiency of free charge carriers into electrodes could be more responsible for the

observed J_{ph} values of organic solar cells. Previous studies indicated that poor performance of organic solar cells fabricated with a thermally aged PEDOT:PSS layer was attributed to poor contact between PEDOT:PSS and photoactive layer or increased contact resistance [12]. To verify this point, sheet resistance (R_{sh}) was measured on various PEDOT:PSS layer spin-coated on glass slides and improved conductivity was observed for IPA solvent treated PEDOT:PSS. Particularly, R_{sh} value of aged PEDOT:PSS was two times larger than that of fresh PEDOT:PSS as shown in Fig.6d. When IPA volume ratio was applied more than 2, R_{sh} of IPA treated, aged PEDOT:PSS layers presented the slightly lower R_{sh} than that of fresh PEDOT:PSS. It should be noted that even though R_{sh} of solvent treated, aged PEDOT:PSS have similar or lower R_{sh} values compared with fresh PEDOT:PSS, the observed J_{ph} of organic solar cells are much different as shown in Fig.6b. Therefore, poor contact or poor R_{sh} does not explain the observed J_{ph} values that can be more related to different interfaces between the PEDOT:PSS and photoactive active layer, leading to different interfacial recombination rates. Typically, PEDOT:PSS will have an excess PSS layer in which PSS-rich PEDOT:PSS will have a workfunction around 5.2 eV or higher values [7,17]. In this case, work-function of PEDOT:PSS will be aligned with the highest occupied molecular orbit (HOMO) of P3HT. However, as demonstrated in our TEM measurement, aged PEDOT:PSS will have PEDOT-rich agglomerates that will typically have a lower workfunction. Recently, Vitoratos, *et al.* [10] reported that thermally aged PEDOT:PSS layer deformed to PEDOT-rich PEDOT:PSS that had a work function of 3.7 eV, much lower than a typical work function of fresh PEDOT:PSS. In addition, Narders, *et al.* reported the reduction of work function of PEDOT:PSS to 4.8-4.9 eV after a removal of the PSS-rich surface with sorbitol treatment [17]. Combining these key information, Fig.7 illustrates the possible recombination mechanisms of organic solar cells with aged and fresh PEDOT:PSS layer. Since it is expected that PEDOT-rich agglomerates will have the lower work function, the energy barrier (Φ_b) for

holes will be formed at the PEDOT:PSS/P3HT interface. As a consequence, a poor extraction of photo-generated holes will increase an interfacial recombination due to an increased interfacial barrier. Particularly, the observed S-shaped J-V characteristics of organic solar cells fabricated with aged PEDOT:PSS in Fig.6a can be explained by a high interfacial recombination rate at PEDOT:PSS/P3HT layer. This observation is consistent with the finding reported by Yang, *et al.*[27], indicating the S-shaped kinks in organic solar cells are attributed to an interfacial energy barrier between metal and photoactive layer, resulting in the drastic bimolecular recombination. On the contrary, fresh or aged PEDOT:PSS treated with optimal amount of solvent showed a few PEDOT-rich agglomerates that have work functions well aligned energy band structures with organic photoactive layers. As a result, photo-generated holes can be effectively extracted through PEDOT:PSS layer while the lower work function of aged PEDOT:PSS will trap photo-generated holes, thereby increasing recombination rate at the ITO/PEDOT:PSS interface.

4. Conclusions

In summary, we investigated the aging of aqueous PEDOT:PSS dispersion which underwent the extensive phase separation of PEDOT:PSS. The consequence of phase separation of PEDOT:PSS is the PEDOT-rich agglomerates while hydrophilic PSS layer might be dissolved in water. Particularly, when the aged PEDOT:PSS was spin casted onto glass slide, a high density of nanoscale and macroscale PEDOT-rich agglomerates were observed. To restore the aged PEDOT:PSS dispersion, organic solvents such as IPA, ethanol, and methanol were investigated. Among them, IPA solvent preferentially promoted solvation of PEDOT-rich agglomerates in an aqueous PEDOT:PSS due to a larger portion of hydrophobic functional group of IPA solvent, producing uniform PEDOT:PSS layer. When PEDOT:PSS layer is integrated into organic solar cells as a hole transport layer, PEDOT-rich agglomerates

adversely formed an interfacial energy barrier between PEDOT:PSS and photoactive layer. As a consequence, the formation of large interfacial energy barrier near the anode electrode enhanced an interfacial recombination rate in organic solar cells that explains the S-shaped J-V curves of organic solar cells fabricated with aged PEDOT:PSS. However, the optimal treatment of IPA led to uniform PEDOT:PSS and the device performance of organic solar cells fabricated with aged PEDOT:PSS was comparable to organic solar cells fabricated with fresh PEDOT:PSS. This result indicates that organic solvents treatment for PEDOT:PSS will produce the reliable device performance using the aged PEDOT:PSS.

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Figure captions

Figure 1. Low and high magnification TEM images of (a) and (b) of fresh PEDOT:PSS, (c) and (d) of aged PEDOT:PSS without IPA treatment, and (e) and (f) of aged PEDOT:PSS with IPA a volume ratio of 1:4.

Figure 2. EDS spectra of PEDOT:PSS of black agglomerate and white domain showing various atomic concentrations. Black agglomerate has higher sulfur atomic concentration, indicating that black agglomerate is PEDOT-rich domain.

Figure 3. TEM images of fresh PEDOT:PSS treated with (a) IPA (C_3H_7OH), (b) ethanol (C_2H_5OH), and (c) methanol (CH_3OH) without filtration. After 0.45 μm filtration, TEM images are shown with (d) IPA (C_3H_7OH), (e) ethanol (C_2H_5OH), and (f) methanol (CH_3OH) that did not reduce a density of black domains. Among three solvents, IPA has longest hydrocarbon chain which promoted the solvation of hydrophobic PEDOT-rich agglomerates in PEDOT:PSS dispersion.

Figure 4. Recovery mechanism illustrating the solvation of PEDOT-rich agglomerate with different IPA volume ratios. (a) PEDOT:PSS core-shell structures of fresh PEDOT:PSS, (b) formation of PEDOT-rich agglomerates due to extensive aging or phase separation of PEDOT:PSS, (c) solvation of PEDOT-rich agglomerates with IPA volume ratio of 1:1.5, (d)

optimal solvation of PEDOT-rich agglomerate with IPA volume ratio of 1:2-1:4, and (d) enlarged PEDOT-rich agglomerates due to the enhanced interaction between hydroxyl group of organic solvents that surrounded PEDOT-rich agglomerates.

Figure 5. Transmittance measurement of aged PEDOT:PSS with different IPA volume ratios.

When the aged PEDOT:PSS is not treated with IPA, the transmittance showed the lowest value while a highest transmittance was achieved with IPA volume ratio of 1:4.

Figure 6. J-V characteristics of P3HT:PCBM solar cells fabricated with different PEDOT:PSS, (b) photocurrent density as a function of effective voltage (V_{eff}), (c) lifetime of P3HT:PCBM with different PEDOT:PSS and (d) the sheet resistance of various PEDOT:PSS thin film layers measured by four point probe.

Figure 7. Proposed energy band alignment of P3HT:PCBM and PEDOT:PSS. The PEDOT-rich agglomerate will have a lower work function of PEDOT:PSS which will form the energy barrier at the PEDOT:PSS and P3HT interface while fresh or organic solvent treated PEDOT:PSS will have energy band structure well aligned with P3HT.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Recovery of aged PEDOT:PSS illustrating the preferential solvation of PEDOT-rich (black) agglomerates with IPA solvent.