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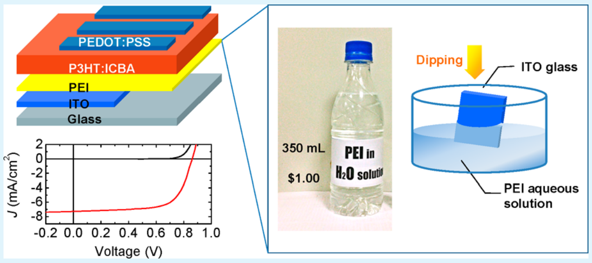
Polyethylenimine Aqueous Solution: A Low-Cost and Environmentally Friendly Formulation to Produce Low-Work-Function Electrodes for Efficient Easy-to-Fabricate Organic Solar Cells

Xue Min, Fangyuan Jiang, Fei Qin, Zaifang Li, Jinhui Tong, Sixing Xiong, Wei Meng, and Yinhua Zhou*

Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China



ABSTRACT: Polyethylenimine (PEI) has been widely used to produce low-work-function electrodes. Generally, PEI modification is prepared by spin coating from 2-methoxyethanol solution. In this work, we explore the method for PEI modification on indium tin oxide (ITO) by dipping the ITO sample into PEI aqueous solution for organic solar cells. The PEI prepared in this method could reduce the work function of ITO as effectively as PEI prepared by spin coating from 2-methoxyethanol solution. H_2O as the processing solvent is more environmentally friendly and much cheaper compared to the 2-methoxyethanol solvent. The dipping method is also compatible with large-area samples. With low-work-function ITO treated by the dipping method, solar cells with a simple structure of glass/ITO/PEI(dipping)/P3HT:ICBA/PEDOT:PSS(vacuum-free processing) display a high open-circuit voltage of 0.86 ± 0.01, a high fill factor of 66 ± 2%, and power conversion efficiency of 4.4 ± 0.3% under 100 mW/cm^2 illumination.

KEYWORDS: *PEI aqueous solution, low work function, dipping, organic solar cells*

INTRODUCTION

Organic optoelectronic devices hold great economic potential due to their low cost, light weight, and ease of fabrication.[1−5] A low-work-function electrode is required in organic optoelectronic devices to either inject electrons into or to collect electrons from a given organic semiconductor. Previously, we demonstrated that polyethylenimine (PEI) is able to substantially reduce the work function of conductors such as metals, metal oxides, conducting polymers, and graphene.[6] Later, it was widely used to produce low-work-function electrodes for semiconducting optoelectronics devices, such as organic (or perovskite) solar cells,[7−14] organic (or inorganic) light emitting diodes,[15−20] organic photodetectors,[21,22] and organic (or inorganic) field effect transistors.[23−27]

Generally, 2-methoxyethanol (MEA) has been used as the solvent to process the PEI and the modification layer is typically prepared by spin coating method. Since the PEI is an insulator material, the layer of PEI has to typically be less than 10 nm as a modification layer in electronic devices. With the spin coating method, the concentration of PEI solution in MEA solvent is generally less than 0.4% to obtain such a thin layer of PEI. In the dilute PEI solution, the solvent of MEA is the major part. With the spin coating method, a large quantity of MEA is needed. However, 2-methoxyethanol has been reported to be toxic to bone marrow and testicles,[28−31] which is very serious. Furthermore, the price of MEA is quite high. For example, a 100 mL bottle of anhydrous MEA from Sigma-Aldrich is $60.60.[32] Though the price is lower when a large quantity of MEA is sold at once, the cost of the MEA solvent still much higher (over 100 times) than that of the active substance of PEI because only a small amount of PEI is needed in such a low concentration. Therefore, it is important to find an environmentally friendly and cheap solvent to replace the MEA solvent, but the solvent has to work as effectively as the MEA.

Considering the popularly used, high-work-function layer of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) in organic optoelectronic devices for improving hole collection (or injection), it is processed from aqueous solution. Water is more environmentally friendly and low cost comparing with other organic solvents. Here, we use deionized water as the processing solvent instead of the MEA to reduce the work function of electrode. The PEI (branched, Figure 1a) can dissolve in H_2O very well. The use of water as the processing solvent can significantly reduce the cost of PEI solution. The formulation of aqueous PEI solution could lower the work function of indium tin oxide (ITO) as effectively as the PEI in MEA solvent. Besides the replacement of solvent, we use a dipping method instead of spin coating to prepare the PEI modification. The use of a dipping method saves PEI solution and is compatible with large-area samples. The dipping method does not need expensive precision instruments. It is simpler and fast-processing. The treatment of ITO with dipping method could significantly reduce the work function of ITO. With the low-work-function ITO treated with dipping method, solar cells with a simple structure of glass/ITO/PEI(dipping)/ poly(3-hexylthiophene) (P3HT):indene-C60 bis-adduct (ICBA)/ PEDOT:PSS (vacuum-free processing) display a high open-circuit voltage (V_{OC}) of 0.86 ± 0.01, a high fill factor (FF) of 66

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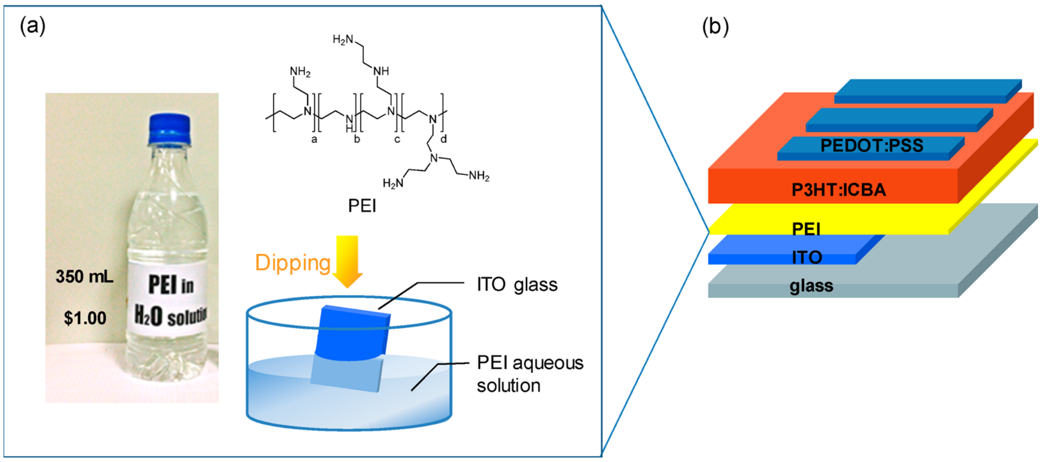

Figure 1. (a, clockwise from left) The low-cost formulation of PEI dissolved in deionized water for low-work-function tuning; chemical structure of branched PEI; the modification process of ITO by dipping the sample into the aqueous solution. (b) Device structure of organic solar cells with ITO treated with PEI by dipping the ITO substrate into the PEI aqueous solution as illustrated in panel a.

± 2%, and power conversion efficiency of 4.4 ± 0.3% under 100 mW/cm^2 illumination.

EXPERIMENTAL SECTION

Work Function Measurement of Electrodes. ITO glass substrates (CSG Holding Co. Ltd.) with a sheet resistance of 10 ohm/sq were cleaned in sequential ultrasonic baths of detergent in deionized water, deionized water, acetone, and isopropyl alcohol (IPA). The deionized water was from Milli-Q Integral Water Purification System (Millipore). Nitrogen was used to dry the ITO glass substrates after the last bath. Before preparing the PEI modified layer, the ITO glass substrates were treated by air plasma for 50 s.

Different PEI modification were prepared on top of ITO glass substrates by spin coating (5000 rpm for 1 min) from (1) 0.4 wt % MEA solution (denoted as s-MEA), (2) 0.4 wt % IPA solution (denoted as s-IPA), or (3) 0.4 wt % deionized solution (denoted as s-H_2O, and (4) by dipping method (denoted as d-H_2O). For the dipping method, in detail, the ITO glass substrate was fully immersed in 0.4 wt % PEI aqueous solution for 30 s and then rinsed in deionized water for about 3 s. All four types of ITO/PEI substrates were immediately thermal annealed at 100 °C for 10 min in air. As a reference, a bare ITO glass substrate was also prepared with air plasma treatment and thermal annealing under the same conditions. Surface tension of the PEI in MEA, IPA, and H_2O solutions was measured using pendant drop method using a interfacial tension meter (JC2000X, Shanghai Zhongchen Digital Technology Co., Ltd.).

Work function (contact potential difference) of ITO/PEI and ITO was conducted on a Kelvin probe system (KP020, KP Technology) in air. Three different locations were measured for each type of sample.

Solar Cell Fabrication and Characterization. To verify whether ITO/PEI(d-H_2O) and ITO/PEI(s-H_2O) could work as well as ITO/PEI(s-MEA) for electron collection, we fabricated organic solar cells with a simple structure of glass/ITO/PEI/P3HT:ICBA/PEDOT:PSS (Figure 1) with vacuum-free processing.

ITO glass substrates were patterned using acid etching. The ITO cleaning procedure and the preparation of PEI modification on the ITO were same as those for preparing the samples for work function measurement. The active layer of P3HT:ICBA (Lumtec) (1:1, w/w) was prepared by spin coating from a 1,2-dichlorobenzene (Sigma-Aldrich) solution with a total concentration of 40 mg/mL at a speed of 800 rpm for 40 s in a N_2-filled glovebox. The sample was immediately thermal annealed at 150 °C for 15 min on a hot plate after spin coating without the step of solvent annealing. The thickness was about 180 nm. The PEDOT:PSS top electrode was prepared by transfer lamination technique as described before.[33] In brief, a piece of polydimethylsioxane (PDMS) transfer medium was adhered on a clean glass substrate and was then exposed to oxygen plasma for 50 s to tune its surface hydrophilic. PH1000 with 5 wt % ethylene glycol and 0.5 wt % surfactant (superwet-304, SurfyChem) was spin-coated onto the PDMS at 1000 rpm for 60 s and dried in air for 9 min without thermal annealing. During drying, the PDMS with PEDOT:PSS was cut into 2 mm-wide finger electrodes. Before transferring the electrodes, samples of ITO/PEI/P3HT:ICBA were in oxygen plasma for 5 s. Then the PDMS with PEDOT:PSS was transferred onto the receiving surface of active layer facing down with PEDOT:PSS contacting the active layer and then the top PDMS was slowly peeled off, and PEDOT:PSS was left on the active layer. Ag paint (Letsilber 200, Ted Pella) was applied onto PEDOT:PSS and ITO for electrical contact during the measurement. The overall devices were thermal annealed at 150 °C for 5 min in N_2-filled glovebox to finish the device fabrication. The effective device area ranging from 4 to 10 mm^2 was determined precisely under an optical microscope (DM4000 M, Leica). Current density−voltage ($J-V$) characteristics were measured inside a N_2-filled glovebox by using a source meter (2400, Keithley Instruments) controlled by a LabVIEW program in the dark and under white light illumination (100 mW cm^{-2}).

RESULTS AND DISCUSSION

Figure 1 shows the chemical structure of PEI (branched). The branched PEI is liquid or gel at room temperature, depending on the molecular weight. The PEI used in the work is a gel with a molecular weight of 25 000 Da. The branched PEI can be dissolved very well in water at room temperature. Linear PEI is solid at room temperature, which is insoluble in water (at room temperature). The branched PEI's good solubility in water indicates the possibility that the PEI modification can be done using water as the processing solvent instead of the commonly used MEA which has been mentioned is toxic to bone marrow and testicles and is costly. With water as the processing solvent, a 350 mL of PEI aqueous solution (0.4 wt %) needs 1.4 g PEI (shown in Figure 1), which costs about \$0.8. Considering the cost of deionized water, which is daily used for substrates cleaning, is negligible, we calculate the 350 mL of PEI aqueous solution approximately costs about \$1. It is very attractive for mass production. More importantly, water is more environmentally friendly compared with other organic solvents.

Figure 2 shows the work function of ITO/PEI electrodes where PEI modification is prepared from different PEI solutions (MEA, IPA, and water solutions) and by different fabrication methods (spin coating and dipping). Compared to the bare ITO, all the ITO/PEI samples show similar work

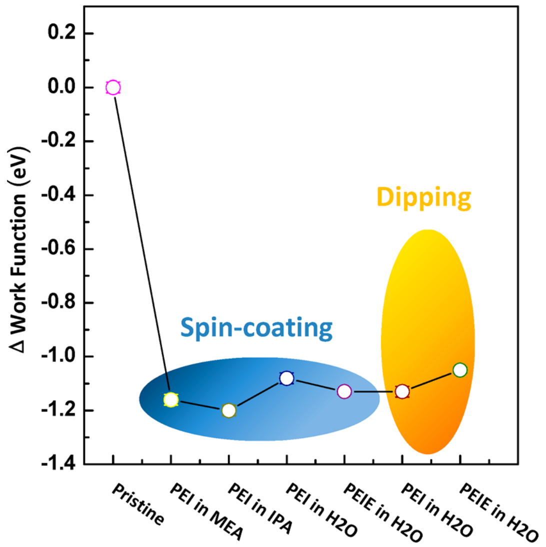

Figure 2. Work function change relative to bare ITO of ITO/PEI and ITO/PEIE samples where PEI and PEIE is prepared by spin coating from MEA, IPA, and H_2O and by dipping ITO substrates into the aqueous solution to be modified.

function reduction between 1.1 and 1.2 eV (Table 1). Though these PEI solutions have different surface tensions, 29.2, 25.1, and 64 mN/m for MEA, IPA, and H2O respectively, the work function reduction is very similar. The difference of work function reduction of 0.12 eV might be considered negligible considering the substrate-to-substrate variation of preparation and measurement. These values are comparable to the previous results.[6] This means, in term of work function tuning, that water or IPA as the processing solvent can work as effectively as the MEA. The PEI treatment by dipping method in water solution is also as effective as treatment by spin coating method from PEI solutions. Besides PEI modification, ITO/PEIE samples were also prepared where PEIE modification was prepared by spin coating from or dipping the substrates into its aqueous solution. As shown in Table 1, the work function reduction by PEIE from its aqueous solution is comparable to that by PEI.

To further validate if the ITO with PEI treatment from aqueous solution and dipping method could efficiently collect electrons from the photoactive layer, organic solar cells with the structure of glass/ITO/PEI/P3HT:ICBA/PEDOT:PSS have been fabricated. Figure 3 shows the current density−voltage (J−V) characteristics of the organic solar cells. The devices treated with PEI aqueous solution exhibit excellent performance. Averaged over 12 devices, the solar cells with ITO/PEI(s-H_2O) where PEI is prepared by spin coating from aqueous solution display V_{OC} = 0.86 ± 0.01 V, short-circuit current density (J_{SC}) = 7.8 ± 0.7 mA/cm^2, FF = 65 ± 2% and PCE = 4.4 ± 0.4% under 100 mW/cm^2 illumination (Table 2). Averaged over 10 devices, the solar cells with ITO/PEI(d-H_2O) where PEI is prepared by dipping method display V_{OC} = 0.86 ± 0.01 V, J_{SC} = 7.7 ± 0.6 mA/cm^2, FF = 66 ± 2% and PCE = 4.4 ± 0.3% (Table 2). The device performance is very similar to that of solar cells with ITO/PEI(s-MEA) where PEI is prepared from by spin coating from the MEA solution, which display V_{OC} = 0.86 ± 0.01 V, J_{SC} = 8.6 ± 0.5 mA/cm^2, FF = 61 ± 3% and PCE = 4.2 ± 0.4% averaged over 11 devices. Though there might be minor difference of work function of ITO after treatment with different solutions and methods, the V_{OC} of the cells are almost the same. This is because when the WF of the electrode approaches the limit of the bandgap (ionization energy or electron affinity), a substantial charge transfer can occur between the electrode and the semiconductor, leading to interfacial dipoles and pinning of the Fermi level at an energy.[10,34] For comparison, solar cells with bare ITO electrodes are also fabricated. The J−V characteristics in the dark shows poor rectification because the work function of ITO is not low enough. The cells also exhibit poor performance with low V_{OC} = 0.29 ± 0.04 V and PCE = 0.55 ± 0.30% under illumination. These results show that ITO treated with PEI aqueous solution and dipping method could collect electrons from the active layer very efficiently. The efficiency of the cells with ITO/PEI is lower than some reported P3HT:ICBA-based solar cells.[35,36] This could be mainly attributed to our solar cells in semitransparent structure that uses transparent PEDOT:PSS as the top electrode instead of metals. The absence of metal electrode as the light reflector results in lower J_{SC}, leading to lower power conversion efficiency.[6,37] It should also be noted that efficiency of polymer solar cells is strongly dependent on the polymer properties (e.g., regioregularity or molecular weight) that vary in different batches of polymers.[38,39] In some reports, P3HT:ICBA-based solar cells display lower power conversion efficiency about 4%.[40,41]

It should be noted that, during this set of experiments, we constantly observed that the V_{OC} values of the solar cells were strongly influenced by the post-treatment on the active layer. The P3HT:ICBA layer is prepared by spin coating from 1,2-dichlorobenzene solution (total concentration is 40 mg/mL) at 800 rpm for 40 s. The film is still wet after spin coating. Direct thermal annealing (150 °C for 15 min) on the wet film leads to a V_{OC} of 0.86 ± 0.01 V (Table 2). When the wet film is first solvent annealed (slow drying, about 30 min) and then thermally annealed, the V_{OC} is 0.82 ± 0.01 V. The solvent annealing on the wet active layer treatment leads to the V_{OC} reduction by about 0.04 V. It might be related with the morphology change or P3HT chain stacking change due to the solvent annealing.[42,43] But the physics behind it needs to be further studied.

To be a reliable formulation for lowering work function, it has to be physically and chemically stable over time. We tested the stability of PEI aqueous solution (0.4 wt %) by testing the solar cell performance with ITO/PEI where PEI was kept in air (capped in a bottle). We found that solar cells with ITO modified by PEI solution stored in air for two months

Table 1. Work Function Change Relative to Bare ITO of ITO/PEI and ITO/PEIE Samples[a]

	spin-coating				dipping	
ITO/PEI or ITO/PEIE	PEI in MEA solution	PEI in IPA solution	PEI in H_2O solution	PEIE in H_2O solution	PEI in H_2O solution	PEIE in H_2O solution
ΔWF (eV)	−1.16 ± 0.02	−1.20 ± 0.02	−1.08 ± 0.02	−1.13 ± 0.01	−1.13 ± 0.02	−1.05 ± 0.01

[a] PEI (or PEIE) modification is prepared by spin coating from MEA, IPA, or H_2O and by dipping ITO substrates into the aqueous solution to be modified.

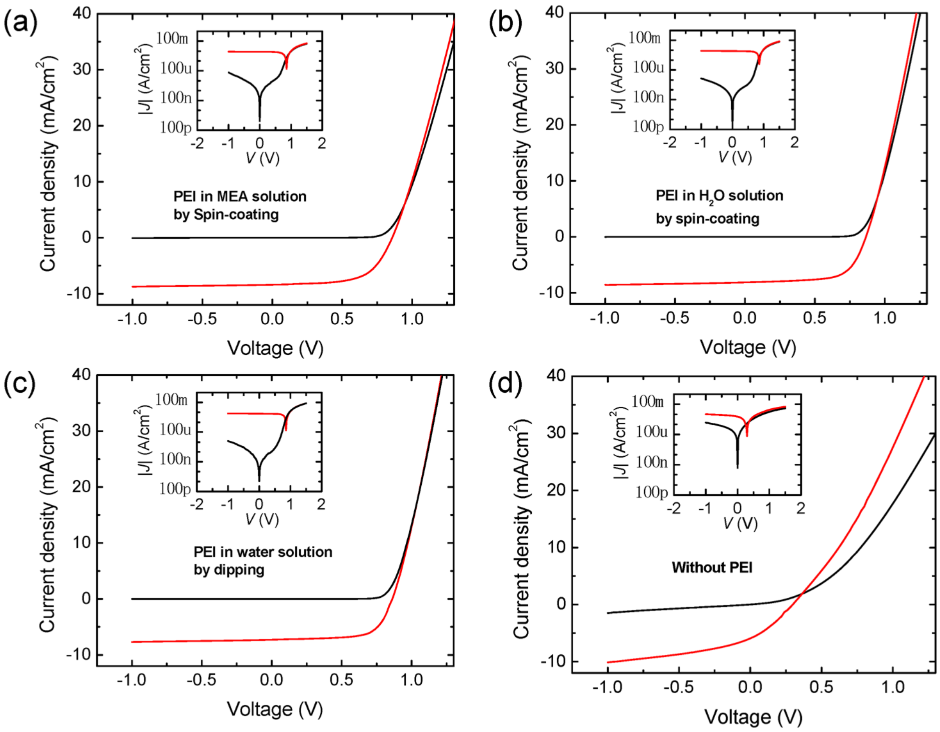

Figure 3. Current density−voltage (J−V) characteristics in the dark and under white light illumination (100 mW/cm^2) of organic solar cells (glass/ITO/PEI/P3HT:ICBA/PEDOT:PSS) where PEI is prepared from different solution and by different methods: (a) PEI is from MEA solution by spin coating, (b) PEI is from water solution by spin coating, and (c) PEI is prepared by dipping ITO into the aqueous solution; (d) reference device without PEI modification; (insets) J−V characteristics in semilog scale.

Table 2. Photovoltaic Performance of Organic Solar Cells with ITO Electrodes Treated with Different PEI Solution and Different Treatment Methods

device with ITO/PEI (device yield)		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PEI in H_2O	spin coating (12/13)	0.86 ± 0.01	7.8 ± 0.7	65 ± 2	4.4 ± 0.4
	dipping (10/12)	0.86 ± 0.01	7.7 ± 0.6	66 ± 2	4.4 ± 0.3
PEI in MEA	spin-coating (11/12)	0.86 ± 0.01	8.0 ± 0.5	61 ± 3	4.2 ± 0.4
bare ITO	without PEI (4/4)	0.29 ± 0.04	5.8 ± 1.8	31 ± 2	0.55 ± 0.30

Table 3. Photovoltaic Performance of Organic Solar Cells with ITO Electrodes Treated with Different PEI Solution Stored in Air for Different Time to Test the Stability of PEI Solution in Air

device with ITO/PEI (device yield)		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PEI in H_2O (2 months)	spin coating (4/4)	0.85 ± 0.01	8.0. ± 0.3	62 ± 3	4.2 ± 0.2
	dipping (6/8)	0.86 ± 0.01	7.9 ± 0.3	63 ± 1	4.3 ± 0.1
PEI in MEA (1 month)	spin-coating (8/10)	0.86 ± 0.01	7.8 ± 0.4	63 ± 2	4.2 ± 0.2
PEI in IPA (0.5 month)	spin-coating (4/4)	0.85 ± 0.01	5.8 ± 0.3	48 ± 1	2.4 ± 0.1

performed similar to cells where ITO modified by newly prepared PEI solution via spin coating or dipping (Table 3). This means the formulation of PEI in water is stable over at least two months. As mentioned, the PEI is an insulator. The thickness control of the PEI layer is critical to the device performance. Concentration of the solution and the boiling temperature of the solvent generally determine the thickness. Water has relatively higher boiling temperature (100 °C) than typical alcohol solvents, such as methanol, ethanol, IPA, and so on. The evaporation speed of the water solvent can also be controlled by tuning the humidity of the environment (water is environmentally friendly). Thus, the concentration of PEI solution is easier to keep constant. We did try using IPA as the processing solvent. With the newly prepared PEI in IPA solution (0.4 wt %), solar cells with ITO/PEI where PEI was spin coated from the IPA solution performs similarly to those with PEI processed from MEA or H_2O. But when the PEI spin coated from the IPA solution that was prepared half a month ago, the solar cell performance dropped significantly (V_{OC} = 0.85 ± 0.01 V, J_{SC} = 5.8 ± 0.3 mA/cm^2, FF = 48 ± 1% and PCE = 2.4 ± 0.1%, averaged over four devices, Table 3) which is because the concentration of PEI in IPA increases and PEI modification layer become too thick. Once the half-a-month-old PEI in IPA solution was diluted, the solar cells performed very well again. For comparison, we also tested the air stability of PEI in MEA solution for solar cells. The cells with ITO modified by the MEA solution stored for about 1 month via spin coating performed similarly to the cells with ITO modified by the newly prepared MEA solution (Table 3), which is due to its high boiling temperature (124 °C). The high boiling temperature and the cost-effective, environmentally friendly properties of water help keep the concentration of PEI constant and improve the reliability of PEI modification.

■ CONCLUSION

We have demonstrated that the formulation of PEI in deionized water could effectively reduce the work function of electrodes. Compared with the commonly used solvent of 2-methoxyethanol, water as the processing solvent is more environmentally friendly and cost-effective. Dipping ITO into PEI aqueous solution could reduce the work function of ITO as effectively as by spin coating the formulation on top of the ITO. Organic solar cells with PEI modification by dipping method exhibit excellent performance, a high fill factor of 66 ± 2%, and power conversion efficiency of 4.4 ± 0.3%. The dipping method is simple, fast, and suitable for large-area treatment. The formulation of PEI aqueous solution is stable and reliable over time kept in air. It is well-know that aqueous solution of PEDOT:PSS is very popularly used as a high-work-function modulator to improve hole injection or collection. It could be expected that the low-cost, environmentally friendly, effective PEI aqueous solution will be as popular as PEDOT:PSS, but working in the other direction, as a low-work-function modulator to improve electron injection or collection.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: yh_zhou@hust.edu.cn.

Notes

The authors declare no competing financial interest.

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