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Enhanced PEDOT: PSS films by acetonitrile co-solvents and their application on polymer solar cells

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The application of Acetonitrile (ACN) on Polymer Solar Cells (PSCs) was investigated in this paper. The conductivity of PEDOT: PSS was significantly enhanced compared with that of untreated samples. The PEDOT: PSS was mixed with freshly-prepared co-solvents of ACN and De-Ionized water. Meanwhile, the Power Conversion Efficiency (PCE) of PSCs was improved by a freshly-prepared co-solvent treatment. The PCE of co-solvent treated devices achieved 1.27% while the untreated one was only 0.3%. However, expired co-solvents were found to be negative to PSCs because of ACN hydrolysis. The PCE of PSCs based on hydrolyzed co-solvents was lower than 0.01%. It was found that the H^+ and NH_4^+ ions generated from ACN aggregates the PEDOT: PSS and roughs the surface of PEDOT: PSS thin films. Meanwhile, Indium ions was dissolved and transported to the PEODT: PSS surface by the acetic acid could be another possibility of the performance decrease. Although the conductivity dramatically increased to 230S cm^{-1}, the series resistance simultaneously increased over $1.5\times10^3\ \Omega\cdot cm^2$, leads to a great loss of current output. Because of that, charges could not be transported to the electrodes since they are recombined at the PEDOT: PSS surface.

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Keywords: Polymer Solar Cells, PEDOT: PSS, Doping, Hydrolysis

1. Introduction

Organic devices such as Polymer Solar Cells (PSCs) [1, 2] and Organic Light-Emitting Diodes(OLEDs) [3, 4] have been attracting increasing attention due to their use in various applications [1-6]. At least one transparent electrode [5, 6] is required in such devices in order to harvest or emit light. In general, Indium Tin Oxide (ITO) [6] is the most common material as the transparent electrode of optoelectronic devices [1-4]. However, ITO has problems with brittleness [7] that affects its application in flexible devices and poor adhesion [8] to organic materials. As a result, p-type poly (3, 4-ethylenedioxythiophene): poly (styrene-sulfonate) (PEDOT: PSS) [9.10] is used between the Indium Tin Oxide (ITO) anode and the BHJ blend. One reason [9] for this is that PEDOT: PSS has a higher work function (5.0eV) compared to ITO (4.7eV) which can improve the injection efficiency of holes and block electrons. PEDOT: PSS also provides a better contact interface [10] between the active blend and the electrode, which decreases the ohm resistance and recombination probability. Moreover, PEDOT: PSS film has high transparency [11], high flexibility, [12] and better thermal stability [13]. However, the low conductivity [14] (initially below 1 S/cm) is the main problem of PEDOT: PSS, which limits its application.

It is a high possibility that the conductivity of PEDOT: PSS can be enhanced by doping anions [14] since PEDOT is originally stretched by coulomb interaction with PSS, as Fig. 1 shows. Adding a polar organic compound has been reported as a possible method, such as ethylene glycol ordimethyl sulfoxide (DMSO) [15, 16] and glycerol [17, 18]. Ouyang and his research team [19] found that the co-solvent treatment for PEDPT: PSS can improve conductivity, while neither pure water nor pure organic solvent contributes to the improvement of conductivity. A probable hypothesis [20] for this improvement in conductivity is that agglomerations can be minimized by polar organic compounds. Also relative low boiling points [14] of organic compounds are another reason for a better interface. Acetonitrile (ACN), a kind of polar molecules, is a potential dopant because of its stable and soluble properties. Meanwhile, the boiling point of ACN is only 80°C which is an ideal solvent for PEDOT: PSS. However, the application of ACN on PSCs has rarely been reported [19] and worth in-depth investigation, such as the best volume fractions and the effect of ACN hydrolysis on co-solvent.

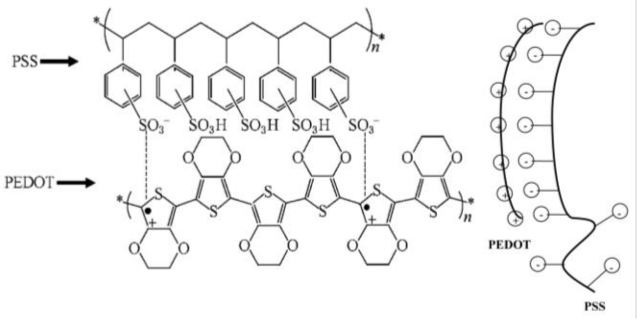


Fig. 1. Structure of PEDOT: PSS. The solubility of PEDOT is enhanced when it interact with PSS, however, if the degree of polymerization is different, the longer one would aggregate itself as shown in the figure

2. Experiment

2.1. Co-solvent treatment of PEDOT: PSS

Freshly-prepared PEDOT: PSS (Sigma-Aldrich, high-conductivity grade) was strictly controlled such as the purity (1.1% in H_2O), the hydrogen ion concentration (pH) (3.42±0.1 in room temperature). PEDOT: PSS was stirred into the co-solvent of ACN and De-Ionized (DI) water for 2 hours with different ACN volume fractions (0%, 5%, 10%, 15%, and 20%). Additionally, there was a co-solvent sample with an ACN volume fraction of 20% stirred for 720h to completely hydrolyze the ACN (The Hydrolyzed samples).

2.2. Fabrication

PSCs (Fig. 2) in this paper were prepared on glass substrates coated with patterned ITO (10Ω/□). These were pre-cleaned by an ultrasonic treatment in acetone, isopropyl ethanol, and DI water. PEDOT: PSS was spin-coated on the ITO substrate by 15μm filter. The samples were subsequently annealed in a nitrogen environment at 130 °C for 10 min to remove excess water. All further steps of processing were carried out in an inert nitrogen glove box. P3HT (Sigma-Aldrich) and PCBM (Sigma-Aldrich) in a 1:1 weight ratio were used to prepare a solution of 10 mg/ml in chlorobenzene. The solution was stirred inside the glove box at room temperature. The active layer was spin-coated at 1500 rpm for 60s to give a 130 nm thick layer. The samples were subsequently heated at 135 °C for 10 min to achieve optimal interfaces. Finally, 20 nm of Calcium (Ca) and 100 nm of Aluminum (Al) were thermally deposited using a metal mask to fabricate an active area of 15.92mm^2. During the evaporation, the rate was 1 Å/s without breaking the vacuum seal (6×10^{-4} Pa). It should be mentioned that the temperature during evaporation fluctuated though the current and voltage was stable, this is the reason of the relative low performance. However, we mainly focus on detailed properties change by ACN and investigate its mechanism, and on the other hand, the Performance of PSCs were guaranteed because at least 12 samples were measured for each type.

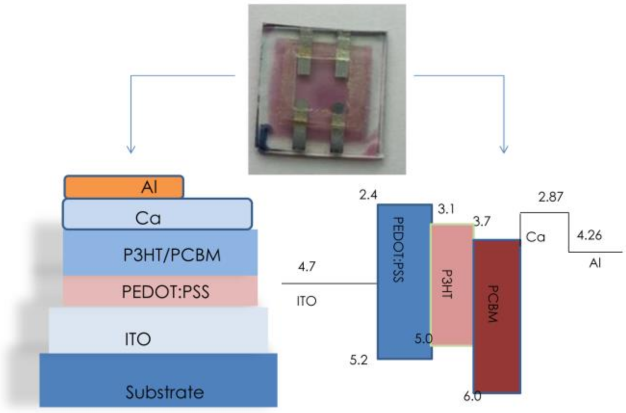


Fig. 2. Schematic representations of the PSCs

2.3. Characterization

After Samples were fabricated, the Current Density-Voltage (*J*-*V*) measurements of all OPVs were conducted on a computer-controlled Keithley 2400 Source Measure Unit. Device characterizations were carried out inside of the glove box under illumination of air mass 1.5 global (AM1.5G 100mW/cm^2) by using a xenon-lamp-based solar simulator (from SAN-EI ELECTRIC Co., LTD.). The transmittance, absorbance, surface quality, conductivity and pH were measured using a Spectrometer (EDINBURGH INSTRUMENT FLS920P), a UV-Vis spectrophotometer (HITACHI UV3900), an atomic force microscopy (AFM, Agilent 4200), a four-point-probe (Keithley 4200-SCS), and a pH meter (METTLER-TOLEDO SevenEasy pH), respectively.

3. Results and discussion

To investigate the feasibility of PEDOT: PSS thin film as a transparent layer [11], transmittance and absorbance measurements were carried out. PEDOT: PSS was spin-coated on quartz substrates and measured by spectrophotometers. The results are shown in Fig. 3. The samples exhibited relative high transparency (>78%) in the overall visible range of 400-800nm. However, the PEDOT: PSS dissolved in pure water (100% DI water) showed a higher transmittance around 400nm and stronger absorption after 800nm. As a result, the BHJ would absorb more ultraviolet photons, which would decrease the stability of PSCs. Additionally, the interfacial diffusion can be sped up after infrared photon absorption, indicating a low performance level of PSCs based on the untreated pure water (100% DI water) PEDOT:PSS solution. On the other hand, co-solvents have a limited impact on reflection of PEDOT: PSS films, there was only a 1% difference between the samples.

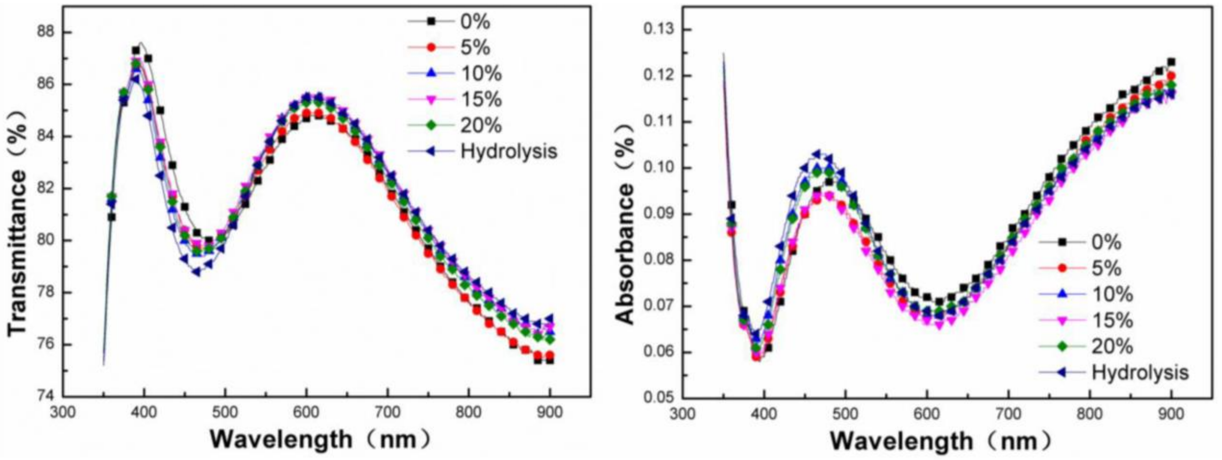


Fig. 3. Optical transmission and absorbance spectrums of PEDOT: PSS layers as a function of the volume fraction

The *J-V* characteristics of the PSCs (Fig. 4) were measured under simulated AM1.5G solar irradiation (See Table 1). Although the PCE is not high, we mainly focus on detailed properties change by ACN and investigate the mechanism. The values of untreated PSCs were measured by open-circuit voltage (V_{oc}), the short-circuit photocurrent (J_{sc}) and the fill factor (FF) of, respectively, 500.2mV, 2.87 mA cm^{-2} and 0.2123. These yielded a solar-to-electric PCE slightly over 0.3% (Table 1). Meanwhile, the conductivity of PEDOT: PSS films were carried out by a four-point-probe system. The conductivity as low as 0.289S/cm of untreated PEDOT: PSS reveals that the resistance limits the transportation of charges. After the ACN was doped into the PEDOT: PSS solution, the conductivity of PEDOT: PSS thin films was significantly improved from 0.289 S/cm to 7.985 S/cm. The J_{sc} and FF showed similar increasing tendencies after the ACN doping. J_{sc} and FF rose by 100% compared to untreated PCSs. The performance improvements mainly attributed to improvements of PEDOT: PSS layer since the stretch of PEDOT chains by polar organic compounds is the only change during this experiment. Because of the improvement, the PCE increased up to 1.27 % (20% ACN-80%DI water). However, it seemed that the co-solvent could not be used after the hydrolysis of ACN. Though the conductivity of PEDOT: PSS thin films have dramatically increased to nearly 230S/cm, the J_{sc} sharply decreased from 2.87mA/cm^2 to 0.03mA/cm^2. As a result, the PCE of the hydrolyzed samples was only 1% compared to the untreated samples.

Table 1. The performance of PSCs based on different PEDOT:PSS films

Volume fractions	V_{oc}(V)	J_{sc}(A/cm^2)	FF (%)	PCE (%)	Conductivity(S/cm)	R_S(Ω • cm^2)
0%	0.5002	2.87×10^{-3}	21.23060	0.30425	0.289	205.8595
5%	0.4840	5.13×10^{-3}	26.98122	0.66992	2.281	35.51817
10%	0.5454	5.81×10^{-3}	33.86715	1.07225	3.453	54.00306
15%	0.5454	5.99×10^{-3}	35.05568	1.14525	5.679	57.15369
20%	0.5152	5.70×10^{-3}	43.24476	1.27050	7.985	32.90595
Hydrolysis (20%)	0.4848	0.03×10^{-3}	23.71577	0.00388	229.839	15506.56218

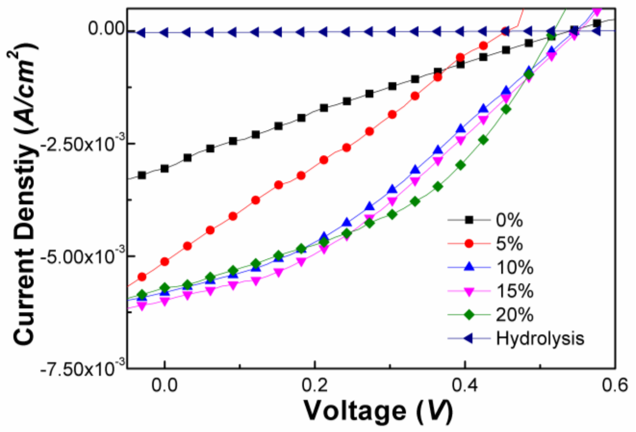


Fig. 4. J−V curves of the devices based on different PEDOT: PSS thin films. Samples were measured under simulated AM1.5G solar radiation

In attempting to clarify the current decrease of hydrolyzed samples, the PEDOT: PSS thin films were further characterized with a tapping-mode AFM. As shown in Fig. 5, freshly-prepared samples were smooth and showed a declining tendency of roughness. The differences in roughness (Ra) are (a) 3.68nm (untreated), (b) 3.27nm (5% ACN-95% DI-water), (c) 3.07nm (10% ACN-90% DI water), (d) 2.64nm (15% ACN-85% DI water), and (e) 2.30nm (20% ACN-80% DI water), respectively. After the polar organic solvent was applied, PSS chains stretched the PEDOT chains instead of aggregating. The decrease of aggregation [21] provided better transportation for holes which is consistent with the improvement of conductivity. Although the conductivity of hydrolyzed samples was the highest among the measurements, these films exhibited a roughest surface. The Ra of the hydrolyzed samples achieved 7.71nm, over 100% higher than that of untreated samples. Contrasted with untreated samples in Fig. 5, the vertical distance of the hydrolyzed surface is 78.36 nm (11.09 nm only for untreated samples), the Thickness of PEDOT:PSS layer is only 30 nm as we mentioned before (see in Experiment), the high vertical distance reveals hydrolysis has an impact on the morphology and some heavy particles were transported to the surface.

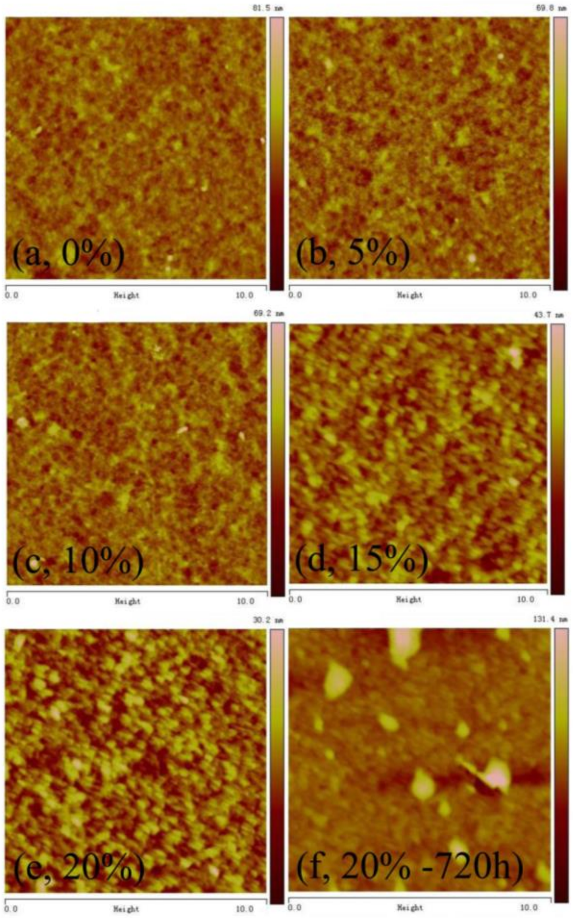
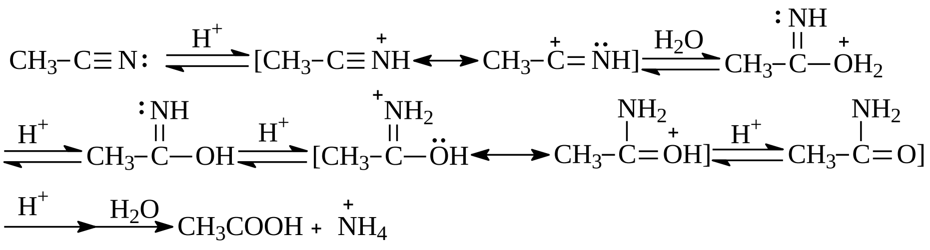


Fig. 5. AFM height images (10μm×10μm) of PEDOT：PSS thin films were dissolved in different volume fractions of ACN (a) 0%, (b) 5%, (c) 10%, (d) 15%, (e) 20%, (f) 20% (hydrolyzed for 720 hours). All the images have the same height scale

The reason of increased roughness of hydrolyzed samples is that acetic acid generated and then increased the hydrogen ion concentration [22, 23] as ACN dissolved in DI water. Though PSS stretched the PEDOT chains, the interaction of H^+ and NH_4^+ ions aggregated PEDOT: PSS chains and roughed the surface. Additionally, the process can be accelerated as H^+ ions increase and NH_4^+ irons cannot be removed by annealing process. The process can be explained by the following function:



$$CH_3\text{–}C\equiv N: \overset{H^+}{\rightleftharpoons} [CH_3\text{–}C\equiv \overset{+}{N}H \longleftrightarrow CH_3\text{–}\overset{+}{C}=\ddot{N}H] \overset{H_2O}{\rightleftharpoons} CH_3\text{–}\overset{\overset{:NH}{\|}}{C}\text{—}\overset{+}{O}H_2$$
$$\overset{H^+}{\rightleftharpoons} CH_3\text{–}\overset{\overset{:NH}{\|}}{C}\text{—}OH \overset{H^+}{\rightleftharpoons} [CH_3\text{–}\overset{\overset{+}{N}H_2}{\|}{C}\text{—}\ddot{O}H \longleftrightarrow CH_3\text{–}\overset{\overset{NH_2}{|}}{C}=\overset{+}{O}H] \overset{H^+}{\rightleftharpoons} CH_3\text{–}\overset{\overset{NH_2}{|}}{C}=O]$$
$$\xrightarrow{H^+} \xrightarrow{H_2O} CH_3COOH + \overset{+}{N}H_4 \quad (1)$$

To clarify the hydrogen ion concentration, pH values were measured by a pH meter, the results are shown in table 2. During the measurements, the temperature was consistently set at 25°C. As the volume fraction increased, pH gradually decreased from 3.42 to 2.88 since the hydrogen ions in freshly-prepared solutions mainly come from the charge interaction between PEDOT: PSS and ACN. In contrast, the hydrogen ion concentration (NH_4^+ concentration is similar according to the chemical function) in hydrolyzed solutions increased to 0.014mol/L which is 37 times higher than that of the untreated solution. The ion concentration is also nearly 98% higher than freshly-prepared solutions (20%ACN-80%DI water, the same volume fraction).

Table 2. pH of different co-solvents each measurement was calibrated by Potassium dihydrogen phosphate (KH2PO4) buffer solution. The pH of the buffer solution is 6.72

Volume fractions	Temperature (℃)	pH
0	25.1	3.42
5	25.0	3.35
10	24.9	3.32
15	24.9	3.01
20	24.8	2.88
Hydrolysis (20%)	24.7	1.85

Meanwhile, the dramatic increase in conductivity of hydrolyzed samples indicates that heavy particles exist on the surface of PEDOT: PSS films. One possible reason for the presence of metal ions is that Indium atoms diffused [24, 25] from ITO substrates rise to the surface of the PEDOT: PSS films. To clarify this phenomenon, energy-dispersive X-ray spectroscopy (EDX) was carried out by Field Emission-Scanning Electron Microscopy (FE-SEM, Sirion 200 FEG) to detect the elements on the surface of PEDOT: PSS thin films. As shown in table 3, Carbon (C) atoms were the main elements detected in both samples since carbon is the backbone of PEDOT: PSS. Meanwhile, brittle samples were prepared in liquid nitrogen. As a result, powder from glass substrates composed of Sodium (Na), Calcium and Silicon Oxide (SiO_x), would adhere to the PEDOT: PSS surface. Those elements however are not of importance to this study. Indium cannot be found in freshly-prepared samples and the mass fraction of nitrogen on the PEDOT: PSS surface was only 1.58%. However, the mass fraction of In in the hydrolyzed samples was 24.06%, which proves the hypothesis of Indium diffusion. Moreover, the existence of nitrogen in the hydrolyzed samples was 240% higher than that of freshly-prepared solutions. This was caused by the generation of NH_4. These ions cannot be removed by the annealing process.

Table 3. EDX analysis of PEDOT: PSS thin films. Before PEDOT: PSS thin films were spin-coated on to ITO substrates, PEDOT: PSS was dissolved into the co-solvent (20% ACN-80% DI water) which were stirred separately in two different samples

20%ACN Stirring Time: 2h		20%ACN Stirring Time: 720h	
Element	Mass Fraction (wt %)	Element	Mass Fraction (wt %)
C	27.66	C	21.27
N	01.58	N	05.37
O	36.27	O	31.52
Na	03.98	Na	02.32
Si	15.99	Si	13.35
Ca	02.46	Ca	02.12
S	12.07	In	24.06

The variation of series resistance is shown Fig. 6. It can be seen that the resistance of PSC were significantly improved once ACN was doped into PDEOD: PSS solvents. The R_S then was remained in stable around 40ohm while the ACN volume concentration increasing. Devices based on hydrolyzed, the R_S dramatically increased over $1.5\times10^3\ \Omega\cdot\mathrm{cm}^2$ that seems like an insulator instead of semiconductor devices. Interestingly, the FF and R_S behavior was perfectly coincident with the simulation work [26] of Ratner. We verified FF would drop in 30% to

40% if R_S was around 40ohm. On the other hand, current output would be blocked once R_S is over hundred ohms, eventually brings a low PCE behavior. Internal resistance of PSC was another important contributor in energy losses. By decreasing the series resistance, the FF and J_{sc} can be improved to higher level, which should receive more attention in future in-depth research as well. Tough FF is not ideal, it could be found that higher R_S blocks charge carriers, leading to a lower PCE.

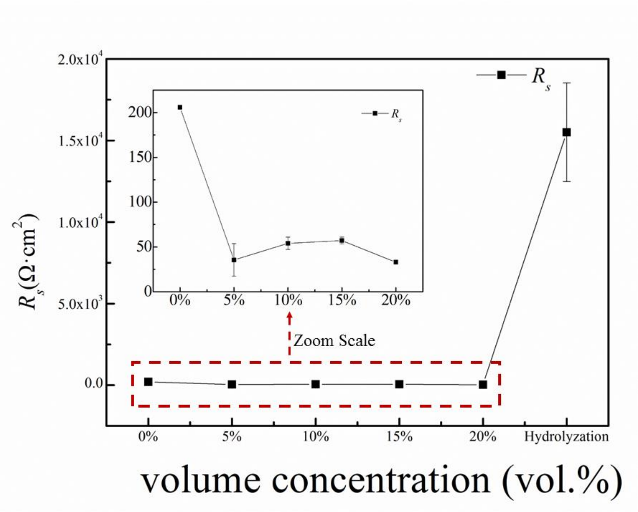


Fig. 6 Average sseries resistance (summarized 12 pieces) of PSCs based on different PEDOT: PSS thin films. The error bar was taken from the difference between the maximum resistance and average value.

4. Conclusion

Although the PCE remain in a relative low level, we demonstrated a valuable method to improve the conductivity of PEDOT: PSS by doping ACN. The conductivity of the PEDOT: PSS films was significantly increased from 0.29 S cm^{-1} to more than 7.9 S cm^{-1} when the PEDOT: PSS was mixed with the co-solvent of water and ACN. The enhanced conductivity was attributed to the extension of the PEDOT and PSS chains by the co-solvents. These induced the phase separations of PSSH chains from the PEDOT: PSS films. The co-solvent-treated PEDOT: PSS films were smooth which is suitable to combine with ITO as the transparent electrode for organic optoelectronic devices. PSCs with the co-solvent treated PEDOT: PSS films exhibited a higher photovoltaic performance. The variation of series resistance decreased one magnitude once ACN was doped. With the interface improving, the performance of co-solvent treated devices increased to 1.27% compared with original PCE of 0.3%. The main contribution of the PCE was the improvement of J_{sc} and FF because of both enhanced conductivity of PEDOT: PSS films and decreased series resistance of devices. On the other hand, the hydrolyzed samples expired if the pH value was less than 2. The existence of H^+ and NH_4^+ ions aggregated the PEDOT: PSS and roughed the surface. Moreover, In atoms can be diffused by acetic acid and transported to the surface of the PEDOT: PSS films. Though conductivity dramatically increased to 230S cm^{-1}, In ions increased the leakage current inside of samples, preventing the transport of charges to the electrodes.

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