Energy & Environmental Science

PAPER

Highly conductive PEDOT:PSS electrode by simple film treatment with methanol for ITO-free polymer solar cells

Desalegn Alemu,[abc] Hung-Yu Wei,[d] Kuo-Chuan Ho[d] and Chih-Wei Chu*[be]

We proposed a simple yet robust film treatment method with methanol having only one hydroxyl group to enhance the conductivity of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) by four orders of magnitude. Different methods of film treatment: immersing PEDOT:PSS film in the methanol solution; dropping methanol on the film; and a combination of these are employed and the results are compared. The conductivity of PEDOT:PSS films was enhanced from 0.3 S cm^{-1} to 1362 S cm^{-1} after film treatment with methanol. Other alcohols like ethanol and propanol were also used to treat the PEDOT:PSS film and showed inferior conductivity enhancement compared to methanol. The conductivity enhancement was greatly affected by the hydrophilicity and dielectric constant of the alcohols used. The mechanism of conductivity enhancement was investigated through various characterization techniques including FTIR, XPS and AFM. Removal of the insulator PSS from the film, and morphology and conformational changes are the mechanisms for the conductivity enhancement. The treated films also showed high transmittance and low sheet resistance desirable for a standalone electrode. ITO-free polymer solar cells were fabricated using PEDOT:PSS electrodes treated with methanol and showed almost equal performance to ITO electrodes.

a Nanoscience and Technology Program, Taiwan International Graduate Program, Academia Sinica, Taipei 115, Taiwan

b Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan. E-mail: gchu@gate.sinica.edu.tw; Fax: +886-2-27896680; Tel: +886-2-27898000 ext. 70

c Department of Engineering and Systems Science, National Tsing Hua University, Hsinchu 30013, Taiwan

d Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

e Department of Photonics, National Chiao Tung University, Hsinchu 300, Taiwan

1. Introduction

Polymer solar cells (PSCs) are attractive for next generation green energy sources because of their promising potential for roll-to-roll and large area processing, flexibility and cheap cost of manufacture.[1–3] The recently reported high power conversion efficiencies approaching 10% signal that their commercialization will be soon.[4–6] The next challenge is to realize the high speed manufacturing of cells and modules with long lifetimes. The electrodes are the bottleneck for the roll-to-roll high speed processing of PSCs. At least one of the electrodes in solar cells needs to be transparent in order to allow light to be harvested by the

Broader context

Polymer solar cells are considered as next generation renewable energy sources since they can produce low cost electricity owing to their roll-to-roll processability on flexible substrates. ITO, which is a currently used transparent electrode, is not ideal because of its high cost due to its limited availability and other technical drawbacks. Poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) is envisioned as quite promising; however, pristine PEDOT:PSS has a very low conductivity for use as an electrode. We propose a simple and easy way to scale up the film treatment method with cheap and less environmentally hazardous methanol to enhance the conductivity of PEDOT:PSS. By employing simple treatment of immersing the PEDOT:PSS film in methanol, dropping a small amount methanol on the film or a combination of these, we were able to tremendously enhance the conductivity from 0.3 S cm^{-1} to 1362 S cm^{-1}. Methanol treated films have sheet resistance as low as 25 Ω □$^{-1}$ while maintaining 85% transmittance. ITO-free polymer solar cells with standalone PEDOT:PSS anodes showed equal performance to their ITO counterpart. These results indicate that PEDOT:PSS films with high conductivity, transmittance and flexibility are highly promising to replace ITO for low cost and flexible polymer solar cells.

active layer. Currently tin doped indium oxide (ITO) coated on rigid glass is used as the standard transparent electrode. However, ITO's price is skyrocketing due to its limited availability, in addition it is mechanically brittle and has poor adhesion on organic and polymeric materials.[7,8] This will not only increase the cost of the solar cells but also affect roll-to-roll fabrication on flexible substrates. Additionally, ITO has some inherent problems such as the release of oxygen and indium into the organic layer, poor transparency in blue region, and complete crystallization of ITO films, which requires high temperature processing.[9] All these drawbacks of ITO make it a non-ideal transparent electrode for PSCs and the search for an alternative transparent electrode is inevitable.[10]

This motivated researchers to investigate different materials including metal nanowires,[11–13] carbon nanotubes,[14–18] graphene[19–21] and conducting polymers[22–27] as replacements for ITO. In particular, the conductive polymer poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS) is quite promising as a next-generation transparent electrode material owing to its enormous advantages over other conducting polymers. PEDOT:PSS films have high transparency in the visible range, high mechanical flexibility, excellent thermal stability and can be fabricated through conventional solution processing. However, pristine PEDOT:PSS suffers from a very low conductivity of less than 1 S cm^{-1} when used as a standalone electrode. The PSS which is used as the counter ion and charge compensator and template for polymerization of PEDOT, making it easily dispersible in water, is an insulator and the main reason for the low conductivity of the commercial PEDOT:PSS.[28,29]

Increasingly intensive work is going on by several people to significantly enhance the conductivity of PEDOT:PSS by more than three orders of magnitude to replace ITO. Po *et. al.* have reviewed the work on the conductivity enhancement of PEDOT:PSS including the methods of treatment and the treatment chemicals used.[30] The methods used include vapor phase polymerization of PEDOT,[31] addition of organic compounds such as ethylene glycol (EG), dimethyl sulphoxide (DMSO), dimethyl sulphate, sorbitol, mannitol, ionic liquid, anionic surfactant, *etc.* in to the PEDOT:PSS aqueous solution[27,32–38] and treatment of PEDOT:PSS films with polar organic compounds, salt, acid, zwitterions or cosolvents.[39–43] It has been said that the origin and mechanism of conductivity improvement differs widely and is considered controversial.[25,44,45] It rather is, the mechanism of conductivity enhancement depends on the treatment chemicals, their properties and the method of treatment employed. Morphology changes with phase separated PEDOT and PSS leading to larger grain sizes and lower intergrain hoping,[32,46] screening effects by polar solvents,[47] washing away of the excess insulator PSS from the film surface,[48] conformational changes by reorientation of PEDOT:PSS chains leading to better connection between the conducting PEDOT chains,[45,49] and even some doping effects are among the mechanisms proposed by different researchers.[36,43] Generally, polar solvents which are secondary dopants added in the PEDOT:PSS aqueous solution bring about morphology changes showing greater grain size and better connected PEDOT chains; whereas film treatments lead to both morphology change and removal of excess PSS from film surface. That is why mostly methods employing film treatment or

both film treatment and additives in the solution show better conductivity than the additives in the PEDOT:PSS aqueous solution.[43,48]

Earlier reports showed that polar organic additives should have two or more polar groups to give appreciable conductivity improvement.[45] Xia and Ouyang used cosolvents like methanol and ethanol with water to improve the conductivity by three orders of magnitude by film treatment while they reported that methanol alone didn't show a great improvement.[49] Here we show a simple film treatment of highly conductive PH 1000 PEDOT:PSS films with cheap and less environmentally hazardous methanol giving four orders of magnitude conductivity enhancement. The PEDOT:PSS films were treated either by immersing in methanol solution or dropping a small amount of methanol on the film or a combination the two methods. The high dielectric constant and highly hydrophilic methanol induce a screening effect between PEDOT and PSS and hence the hydrophilic –OH groups of methanol dissolve and remove the hydrophilic and insulator PSS from the film and the conductivity was significantly enhanced from 0.3 S cm^{-1} to 1362 S cm^{-1} after film treatment. ITO-free PSCs were fabricated with methanol treated PEDOT:PSS films as standalone transparent electrodes and demonstrate almost equal performance to devices with ITO electrodes.

2. Experimental

2.1. Preparation and characterization of PEDOT:PSS films

PEDOT:PSS aqueous solution (Clevios PH1000) was purchased from Heraeus with a PEDOT:PSS concentration of 1.3% by weight and the weight ratio of PSS to PEDOT was 2.5. Glass substrates of area $1.5 \times 1.5 \text{ cm}^2$ were cleaned with a sonicator successively in detergent water and twice with deionized water for 15 min each and then dried in an oven. PEDOT:PSS filtered through a 0.45 μm syringe filter was spin coated at 3000 rpm for 60 s on glass substrates which were treated with UV/ozone for 15 min prior to spin coating. The films were annealed on a hot plate in the ambient atmosphere at 130 °C for 20 min and film treatment was performed by immersing (hereafter referred as the 'dip' method) the annealed films in methanol or other alcohols for 10 min. Then the films were again dried at 140 °C for 5 min. The other film treatment was done by dropping (hereafter referred as the 'drop' method) 120 μL of methanol on the film at 130 °C before annealing; and annealing continued for 20 min. A combination of the two treatment methods was also done one after the other. Thicker PEDOT:PSS films were prepared by multiple spin coating; and annealing and film treatment were conducted after each layer.

Film thickness was measured using a Veeco Dektak 150 alpha step surface profiler. Conductivities were measured using the van der Pauw four-point probe technique with Hall effect measurement system (Ecopia, HMS 5000). Transmission and absorption spectra of the films were measured using Jacobs V-670 UV-Vis-NIR spectrophotometer. The values of transmittances reported in this paper are at the wavelength of 550 nm and include the absorption of the glass substrate. X-Ray photoelectron spectroscopy (XPS) was done using a PHI 5000 VersaProbe equipped with an Al Kα X-ray source (1486.6 eV). The attenuated total

reflectance Fourier transform infrared (ATR-FTIR) measurements were conducted with a Vertex-70 (Bruker SN-101050) by dropping methanol solution collected after film treatment on the IR cell. Vecco di Innova was used in the taping mode to take the atomic force microscopy (AFM) images of polymer films. The SEM images were obtained using FEI Noval 200 scanning electron microscope.

2.2. Fabrication and characterization of PSCs

PSCs were fabricated using both ITO-free highly conductive PEDOT:PSS films treated with methanol and ITO anodes on glass. A relatively well studied and stabilized donor:acceptor blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), were used as the active layer. The PSC devices were fabricated by a spin coating blend solution of P3HT:PCBM, prepared by dissolving 20 mg mL^{-1} of each component in 1,2-dichlorobenzene at 70 °C for 3 h, at 600 rpm for 60 s in a nitrogen filled glove box on the PEDOT:PSS modified with methanol and an ITO surface. Less conductive PEDOT:PSS (Clevios P VP 4083) was spin coated on an ITO surface as a buffer layer prior to the active layer deposition. The active layer was then dried in covered Petri glass dishes, and subsequently the films were annealed on the top of the hotplate at 130 °C for 30 min. The devices were completed by thermal deposition of 30 and 60 nm thick calcium and aluminum respectively, at a pressure below 10^{-6} Torr through a shadow mask.

The photovoltaic performance of the devices was measured inside a glove box filled with N_2 under simulated AM 1.5G illumination (100 W cm^{-2}) using a xenon lamp based solar simulator (Thermal Oriel 1000 W). The light intensity was calibrated by a mono-silicon photodiode with KG-5 color filter (Hamamatsu, Inc.). Devices were illuminated under a mask and the active area of the device was controlled to be 0.1 cm^2. The external quantum efficiency (EQE) spectra were obtained under short-circuit conditions. Devices were encapsulated before they were taken out for EQE measurement. The light source was a 450 W Xe lamp (Oriel Instruments, Model 6123NS). The light output from the monochromator (Oriel Instruments, Model 74100) was focused on the photovoltaic cell being tested.

3. Results and discussion

3.1. Conductivity and opto-electronics properties of treated PEDOT:PSS films

Many reports show that adding polyols in the aqueous solution of PEDOT:PSS or film treatment with them can significantly enhance its conductivity. Xia and Ouyang[49] showed conductivity enhancement by film treatment with cosolvents, including water and alcohol, and proposed the mechanism as preferential solvation of the hydrophilic PSS by the hydrophilic water and hydrophobic PEDOT by hydrophobic solvents. Cosolvents were not showing appreciable conductivity enhancement when used to treat the film as single solvents. Recently, the same authors[50] showed conductivity enhancement by three orders of magnitude using methanol alone for the less conductive PEDOT:PSS which is used as a buffer layer for ITO electrodes. However, they reported that methanol didn't show a conductivity difference

for the highly conductive PEDOT:PSS films and they claimed it may be due to the lesser amount of PSS present in the high conductivity PEDOT:PSS formulation. Motivated by why this is happening, we tried film treatment of highly conductive PH 1000 PEDOT:PSS by immersing in methanol and other alcohols. We got a strikingly high conductivity which is among the highest reported. Fig. 1a shows the conductivities along with the error bars of pristine PEDOT:PSS and after film treatment with different alcohols by the dip method for 10 min.

The average conductivity drastically changed from 0.3 S cm^{-1} for the untreated to 1015 S cm^{-1} after immersing it in methanol. This conductivity is far higher than the conductivities obtained after single treatment using well studied additives like EG and DMSO reported elsewhere.[44,48] The film thickness also decreased from 60 nm to 50 nm for methanol and to 53–55 nm for ethanol,
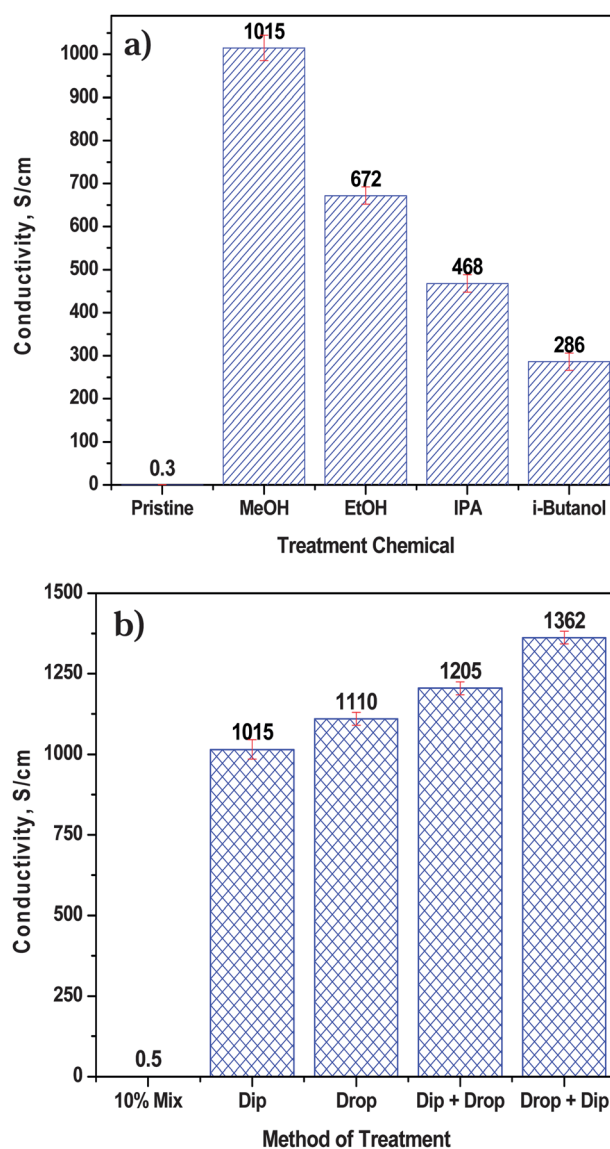

Fig. 1 Conductivities of PEDOT:PSS films: (a) treated with different chemicals by the dip method. (b) Treated with methanol by different methods of treatment. [10% mix – done by mixing 10% methanol in the aqueous solution of PEDOT:PSS.]

isopropyl alcohol (IPA) and i-butanol after film treatment. Physical properties of treatment chemicals used are presented in Table 1. As it can be clearly seen from Fig. 1a and Table 1, conductivity decreased with decreasing dielectric constants and polarities of the alcohols used. Owing to this, the average conductivities were 1015, 672, 468 and 286 S cm^{-1} after film treatment of PEDOT:PSS with methanol, ethanol, IPA and i-butanol respectively by the dip method. It is a well established fact that polar solvents with higher dielectric constants induce a stronger screening effect between counter ions and charge carriers, which again reduces the Coulomb interaction between positively charged PEDOT and negatively charged PSS dopants.[47] It is also worth noting that treatment times 1, 3, 5 and 10 min gave almost similar conductivities. Methanol treatment not only enhanced the conductivity by four orders of magnitude, but also with short treatment times.

Conductivity values by different methods of treatment with methanol are shown in Fig. 1b. Dropping 120 µL of methanol on the PEDOT:PSS film at 130 °C prior to annealing gave average conductivity of 1110 S cm^{-1}. We also observed that the conductivity of the films treated by the drop method is more reproducible than those treated by the dip method. When the drop treatment is done after annealing, the conductivity is less than the one done before annealing. Before annealing, the polymer chains are free to segregate as little water is still in the film and hence methanol can easily penetrate better and dissolve the hydrophilic PSS facilitated by the heat energy supplied. Serrated white lines/structures are clearly seen on the film surface by eye, which are similar to the white patches reported by Xia and Ouyang.[41,49] Interestingly, the serrated lines were fully washed away when the same film was treated by immersing in methanol, again enhancing the conductivity to 1362 S cm^{-1}. Fig. 2 shows the SEM images of PEDOT:PSS films before treatment and after treatment by different methods. The darker lines of the SEM images seen in Fig. 2c and d are segregated PSS chains which are easily washed by immersing in methanol. When the treatment order was immersion followed by the dropping methanol on the film (dip + drop), the conductivity is only 1205 S cm^{-1}. In the latter case, the excess PSS is already removed from the film surface during immersion, and treatment by dropping will bring about little impact as methanol can't fully penetrate the dry film. Mixing even 10% of methanol with an aqueous solution of PEDOT:PSS hardly improved the conductivity, which is in agreement with the previous reports. The low dielectric constant of methanol, which is present in small amounts in the PEDOT:PSS solution, is unable to bring about a screening effect compared to the high-boiling-point and high-dielectric-constant solvents like DMSO and EG. Moreover, in the mixing method methanol will evaporate quickly, due to its low boiling point, prior to giving the screening effect between PEDOT and PSS
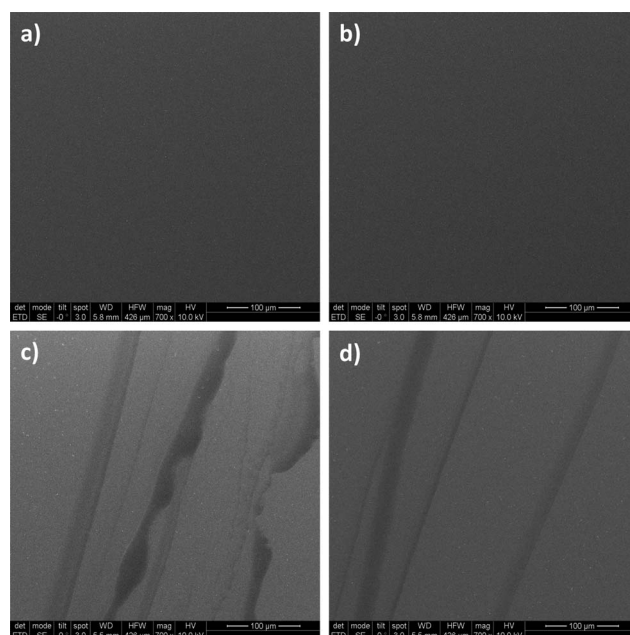

Fig. 2 SEM images of PEDOT:PSS films: (a) pristine; (b) treated by the dip method; (c) and (d) treated by the drop method with methanol.

charges required for the necessary morphology change. On the other hand, when methanol is used for film treatment, it is available in large quantities and will induce the necessary changes in the film before its evaporation.

The bulk concentration of PEDOT:PSS films increased from an order of 17 to the order of 21 after film treatment. The relationship between conductivity, mobility and bulk concentration is given by:[51]

$$\sigma = e\mu N \tag{1}$$

where σ is the conductivity, e is elementary charge and N is bulk concentration. The bulk concentration for semi metals is in the order of 17 to 21 and that of metals is more than order of 22. This indicates that methanol treatment of PEDOT:PSS gave it more metallic property.

Fig. 3a show the transmittance of ITO and one and three layers of PEDOT:PSS films on glass treated by dip method with methanol. Films before and after treatment have same transmittance value, showing that the treatment method didn't impair its transmittance. Interestingly, a one layer PEDOT:PSS film which is about 50 nm thick has more than 90% transmittance, and this is a little higher than the transmittance of ITO especially in the blue and green regions. Fig. 3b gives the variation of sheet resistance and transmittance with film thickness.

Table 1 Physical properties of solvents used for film treatments[60]

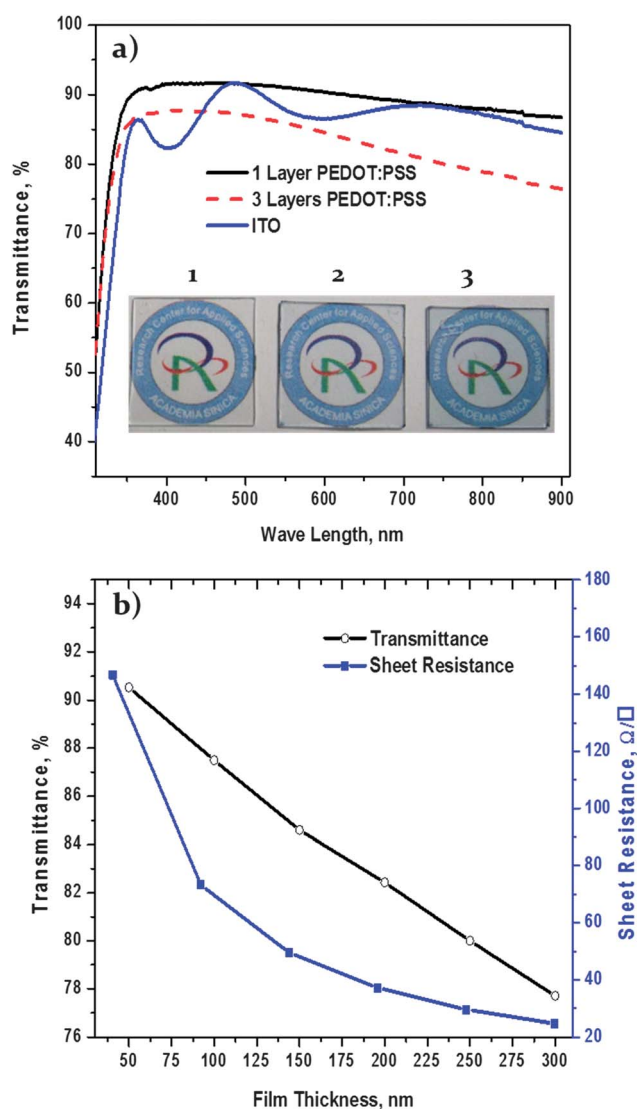| Chemical	Boiling pt./°C	Dielectric constant	Absolute viscosity	Polarity (water = 100)
MeOH	64	32.6	0.6	76.2
EtOH	78	22.4	1.08	65.4
IPA	82	18.3	2.0	54.6
i-Butanol	108	17.7	3.96	55.2

Fig. 3 (a) Transmittance of ITO and 1-layer (50 nm thick) and 3-layers (150 nm thick) PEDOT:PSS films treated with methanol by the dip method. (b) Variation of transmittance and sheet resistance with film thickness for PEDOT:PSS treated with methanol by the dip + drop method. Inset compares the transmittances of bare glass (1), 1 layer PEDOT:PSS coated glass (2) and ITO coated glass (3).

The sheet resistance of the single layer films is 197, 164 and 147 $\Omega\ \square^{-1}$ after treatment by dip, drop and a combination of both, respectively. The sheet resistance can go well below 25 $\Omega\ \square^{-1}$ with multiple layers while still maintaining more than 78% (~85% without the glass substrate) transmittance. Two layers of PEDOT:PSS film treated by methanol fulfil the minimum optical and electrical requirements for transparent electrodes, which are transmittance higher than 90% and sheet resistance less than 100 $\Omega\ \square^{-1}$, ensuring that PEDOT:PSS films are promising replacements for ITO electrodes. For transparent electrodes, the relationship between the transmittance and sheet resistance is given by:[52]

$$T = \left(1 + \frac{Z_0}{2R_s}\frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2} \quad (2)$$

where T is the transmittance, R_s is the sheet resistance, $Z_0 = 377$ Ω is the impedance of free space, σ_{op} and σ_{dc} are the optical and dc conductivities respectively. T and R_s are controlled by $\sigma_{dc}\sigma_{op}^{-1}$ and the minimum industry standard is $\sigma_{dc}\sigma_{op}^{-1} > 35$. All methanol treated films show $\sigma_{dc}\sigma_{op}^{-1} > 58$, and even higher for large thickness films.

3.2. Mechanism of conductivity enhancement

There have been various mechanisms proposed by many researchers for conductivity enhancement of PEDOT:PSS. We utilized various chemical and physical characterization methods to investigate the mechanism of conductivity enhancement of PEDOT:PSS by simple film treatment with methanol. The 10 nm thickness loss after film treatment with methanol (from 60 nm to 50 nm) gives a clue that PSS is removed from the film surface as the hydrophobic PEDOT is insoluble in highly hydrophilic methanol. Fig. 4 shows the UV absorption spectra of the films before and after methanol treatment. The two absorption bands originate from the aromatic rings of PSS.[24,48] The bands fall well after methanol treatment and indicate that there is a decrease in the amount of PSS in the film after methanol treatment.

Further confirmation for the removal of PSS from the film was conducted using ATR-FTIR. The methanol solution after film treatment by the dip method was evaporated to increase the concentration of the washed away PSS; ATR-FTIR measurements were conducted by dropping this methanol solution on the IR cell. The IR spectra of the methanol solution taken after methanol evaporation is given in Fig. 5, and represents a characteristic spectra of PSSH.[53] The absorbance peaks 1165, 1125, 1035 and 1005 cm^{-1} correspond to the stretching vibration of $-SO_3^-$ group of the PSS. We also compared the PSSH spectra with the commercial poly(sodium 4-styrenesulfonate) (PSSNa) taken from the solid pellet, and they have the same spectra. This confirms that PSS is washed away from the film with methanol treatment and without any chemical modification too. To the best of our knowledge, this is the first quantitative confirmation using IR for the removal of PSS from the PEDOT:PSS film after
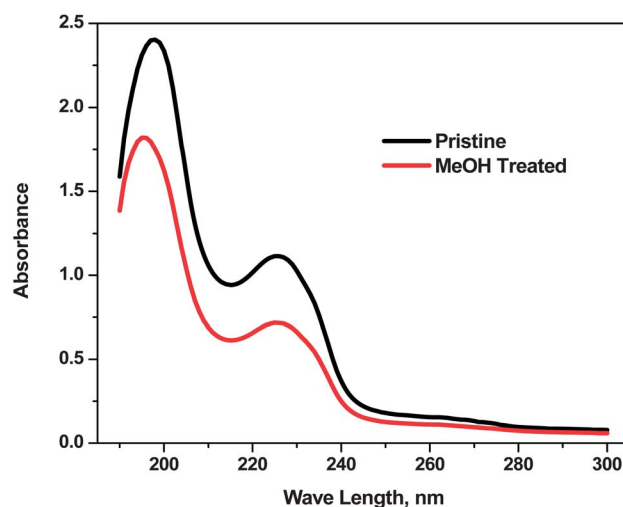

Fig. 4 UV absorption spectra of PEDOT:PSS films before and after methanol treatment by the dip method.
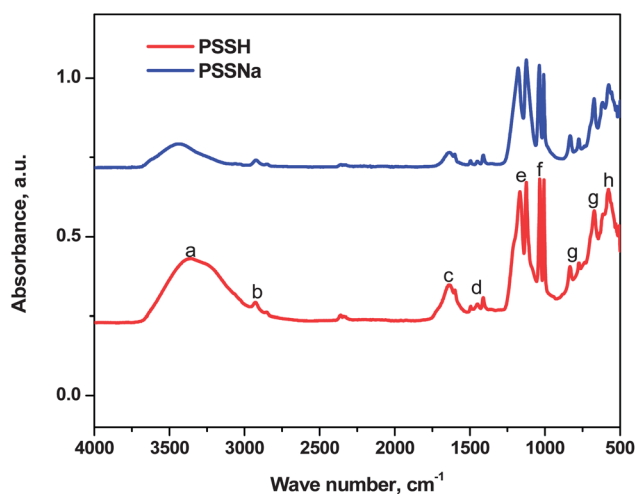
Fig. 5 ATR-FTIR spectra of the methanol solution after PEDOT:PSS film treatment (PSSH) and commercial poly(sodium 4-styrenesulfonate) (PSSNa). (a) 3700–2965 cm^{-1}: stretching vibration of O–H; (b) 2925 cm^{-1}: alkyl C–H stretching vibration; (c) 1640 cm^{-1}: O–H bending vibrations; (d) 1600, 1495, 1450 and 1410 cm^{-1}: aromatic –C≡C– stretching vibrations; (e) 1165 and 1125 cm^{-1}: –SO$_3^-$ asymmetric stretching vibrations; (f) 1035 and 1005 cm^{-1}: –SO$_3^-$ symmetric stretching vibrations; (g) 833, 776 and 670 cm^{-1}: ≡C–H out of plane deformation vibrations h. 615 cm^{-1}: ring in-plane deformation vibrations.[53]

Fig. 6 S (2p) XPS spectra of untreated and methanol treated PEDOT:PSS films.

film treatment. Methanol with a reasonably high dielectric constant induces a screening effect between the positively charged PEDOT chains and negatively charged PSS chains, thus reducing the Coulombic interaction between them, as is the case for high boiling point secondary dopants.[47] This will lead to a phase separation on the nanometer scale characterized by segregation of the excess PSS. The highly polar hydrophilic methanol can also easily dissolve the phase separated hydrophilic PSS and facilitate its removal from the film.

The amount of PSS removed from the PEDOT:PSS film was estimated using XPS measurements of the films before and after film treatment with methanol (Fig. 6). The S (2p) peaks observed at the binding energy of 167.8 eV correspond to the sulfur signal from PSS and at the 164.2 eV and 163.4 eV correspond to the sulfur signal from PEDOT both before and after treatment.[54] The ratios of PSS to PEDOT were calculated using the integral area ratio of the peaks assigned to PEDOT and PSS. The ratio of PSS to PEDOT decreased from 1 : 2.71 before film treatment to 1 : 1.76 after film treatment leading to 35% reduction of PSS from the film surface. The PSS to PEDOT ratio of 1 : 2.71 for the pristine film agrees well with the already accepted idea that the film surface contains more PSS than the bulk.[44] The removal of the insulator hygroscopic PSS from film surface will not only increase the conductivity of the film but also improve its long term stability, as PSS is the prime reason for the degradation of organic solar cells.[48] The conductivity stability of the PEDOT:PSS films was assessed by keeping them in ambient atmosphere at room temperature and humidity higher than 75%. As expected, methanol treated films can maintain up to 80% of the original conductivity while the pristine film maintains only 35% after sixteen days [Fig. 7]. For comparison, another sample was made by mixing 6% EG in the aqueous solution of
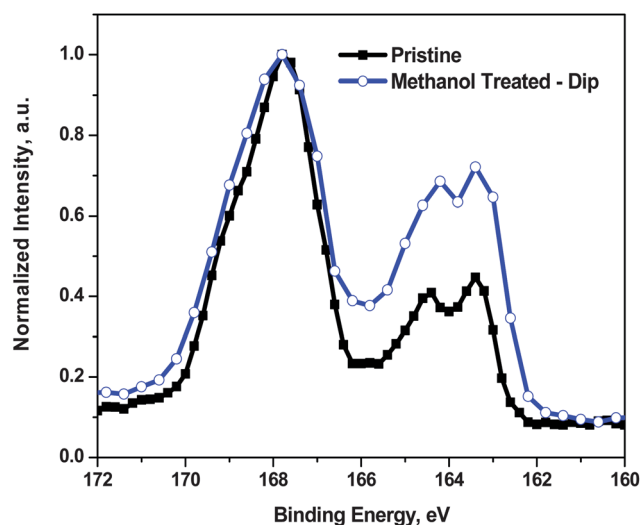
PEDOT:PSS, as reported elsewhere,[48] and maintained only about 60% of its conductivity.

To gain further information for the mechanism of conductivity enhancement and to investigate the possible changes in the morphology and correlation between morphology and conductivity, AFM images were taken and are presented in Fig. 8. The phase image shows disconnected PEDOT chains with weak phase separation between PEDOT and PSS for the pristine samples, whereas there is a good phase separation between PEDOT and PSS chains with more interconnected conductive PEDOT chains after film treatment. It also suggests that the conformation of PEDOT will be changed from a coiled to a linear/extended-coil structure owing to the removal of PSS from the film surface. The height image shows that both the pristine and treated films are reasonably smooth with an rms roughness of 0.7 nm and 1.44 nm for the pristine and methanol treated films, respectively. PEDOT chains were seen to be more aggregated, and increased in size after film treatment.
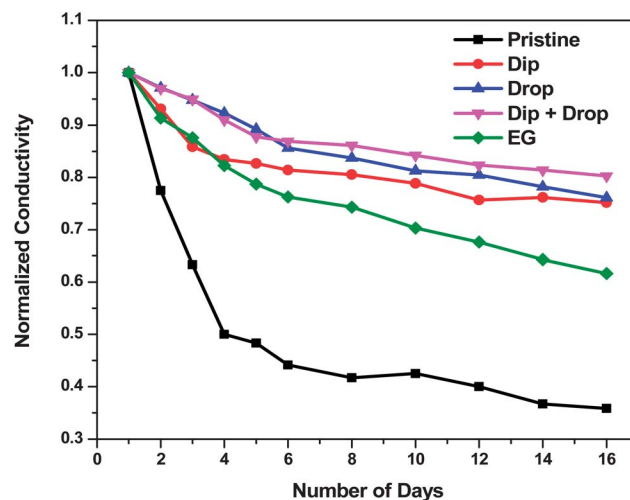

Fig. 7 Conductivity stabilities of PEDOT:PSS films in the ambient atmosphere treated by different methods with methanol and EG [EG – mixing 6% EG in aqueous solution of PEDOT:PSS].
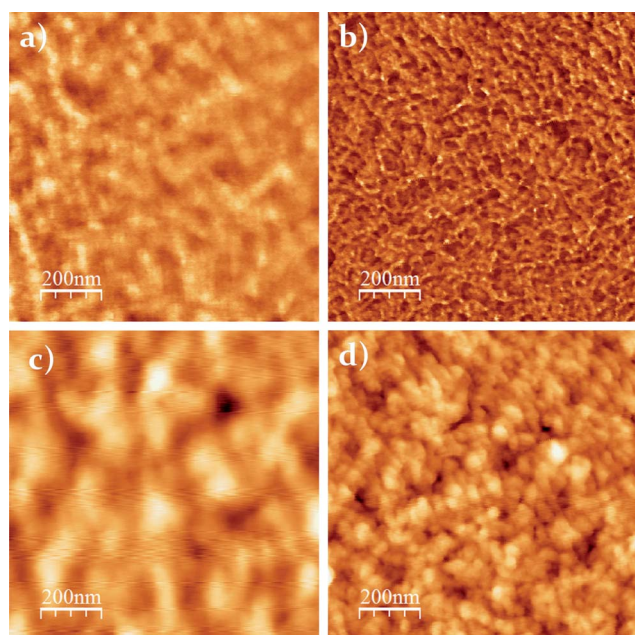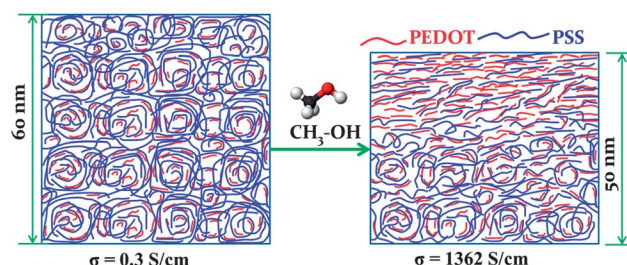
Fig. 8 AFM images of PEDOT:PSS films before (a and c) and after film treatment with methanol by the dip method (b and d). (a and b) are phase images while (c and d) are topography images. All the images are 1 μm × 1 μm.

Scheme 1 Schematic illustration of the mechanism of conductivity enhancement of PEDOT:PSS films by film treatment with methanol. The core–shell structure is changed to a linear/coiled structure. The removal of PSS leads to the thickness reduction of the film and also brings about bigger and better connected PEDOT chains.

hopping will be lowered and there will be better charge transfer among the PEDOT chains. The phase separated and re-oriented PEDOT chains will make the charge hopping easier and eventually there will be a tremendously enhanced conductivity.

3.3. ITO-free PSCs using PEDOT:PSS treated with methanol anodes

PSCs were fabricated using PEDOT:PSS treated with methanol by different methods as a standalone anode. The chemical structures of the active layer chemicals (P3HT and $PC_{61}BM$), device architecture, the current density (J)–voltage (V) curves and EQE of the PSCs with single layer (~50 nm) PEDOT:PSS anodes are shown in Fig. 9. PSCs using ITO anodes with a less-conductive PEDOT:PSS (Clevios P VP Al 4083) buffer layer were also fabricated as control devices. The power conversion efficiency (PCE), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and series resistance (R_S) and parallel resistance (R_{SH}) of the PSCs are given in Table 2. Generally, PEDOT:PSS anodes show an almost equal performance to the ITO anode owing to their high conductivity. The EQE values are in agreement with the J–V values of the devices. PEDOT:PSS anode treated with methanol by the drop method showed a J_{sc} 9.51 mA cm^{-1}, V_{oc} 0.58 V and PCE 3.71% with an FF of 67.33%. The PSC with the reference ITO electrode has a PCE of 3.77% with little higher FF and lower J_{sc}. Owing to their better transmittance, PSCs with the PEDOT:PSS electrodes have better J_{sc} than their ITO counterparts. Interestingly, all PEDOT:PSS electrodes showed the same V_{oc} value to their ITO counterpart, and their FF is higher than 66%. The PEDOT:PSS electrode treated only by the drop method shows a higher PCE, contributed by its higher J_{sc}, even though its conductivity is lower than the drop + dip method. For the film treated with only the drop method, a very thin PSS layer segregated by methanol is still on the film surface and it will act as a functional buffer layer, giving an electron blocking function to the device, which results in higher J_{sc} value. Additionally, the rough surface after drop treatment may serve as a center for the initial crystallization of the P3HT polymer which further leads to better alignment of the P3HT and PCBM domains.[57] It is also worth to note that PEDOT:PSS electrodes showed low R_S and high R_{SH} values comparable to the ITO electrode. Additionally, the preliminary stability of the devices was considered by keeping the devices in an N_2 filled glove box. Devices with PEDOT:PSS electrode

Film conductivity has a direct relation to the PEDOT particle size; as particles grow the total number of particle boundaries in a given volume or area can decrease. An increased particle size with decreased particle boundaries leading to few energy barriers will bring about conductivity enhancement.[46] Moreover, charge hopping among the polymer chains is believed to be the dominant conduction mechanism in conducting polymers.[55] The way charges are transported among the highly conducting PEDOT-rich grains will decide the overall conductivity of PEDOT:PSS films. Hence, the PEDOT-rich chains with a linear structure, larger grain size and lower intergrain hopping, resulting in thinner PSS barriers, can promote charge hopping leading to a higher conductivity.

Combining all the above-explained results, we proposed a model as in Scheme 1 to fully explain the mechanism of conductivity enhancement by methanol treatment. The current suggested model for the morphology of PEDOT:PSS solid films is that it consists of grains with a hydrophobic and highly conductive PEDOT-rich core and a hydrophilic insulating PSS-rich shell.[56] The highly hydrophilic methanol, with a high dielectric constant, will interact with the hydrophilic PSS and bring about a screening effect between the PEDOT and PSS chains. The screening effect and phase separation is dependent on both the dielectric constant and hydrophilicity of the treatment chemicals; that is why ethanol and IPA show lower conductivity than methanol. The screening effect will facilitate the phase separation between the PEDOT and PSS chains and hence the PSS will be dissolved by methanol. This intern will enable the reorientation of the PEDOT polymer chains from a coiled to linear or extended-coil structure which allows more inter-chain interaction between the conducting polymers. Thus, the energy barrier for inter-chain and inter domain charge

9668 | *Energy Environ. Sci.*, 2012, **5**, 9662–9671

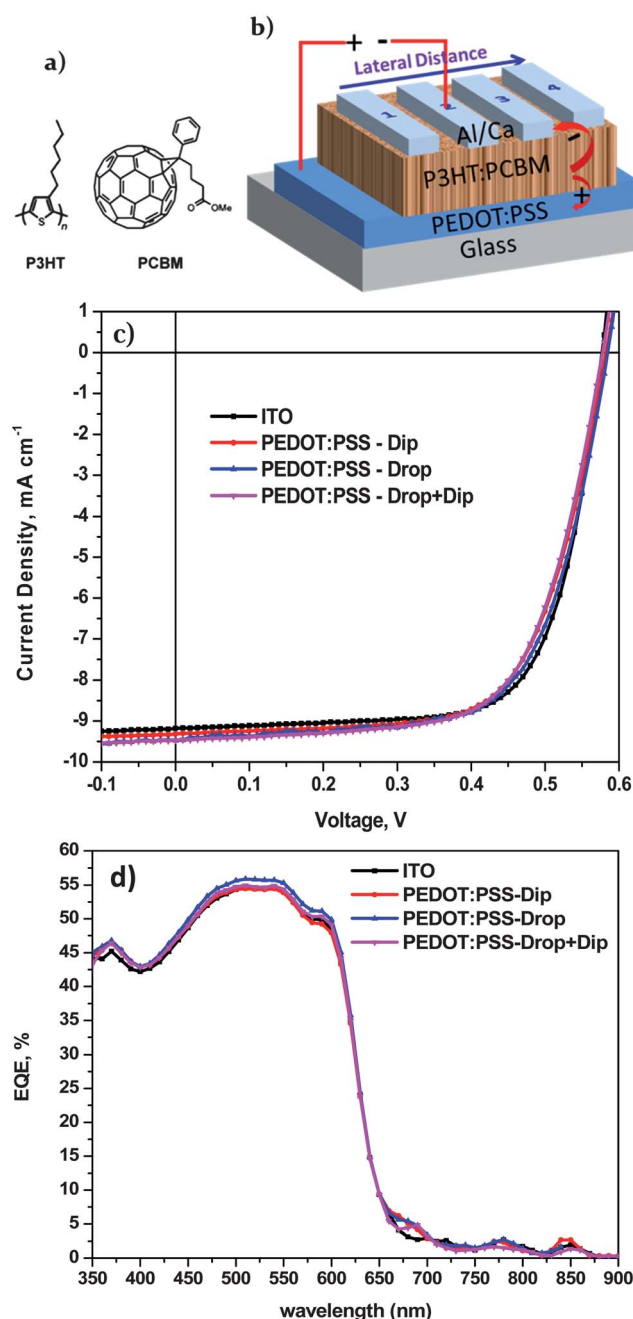This journal is © The Royal Society of Chemistry 2012

Fig. 9 (a) Chemical structures of the active layer chemicals. (b) Device architecture of the ITO-free PSC. (c) J–V curves of the PSCs with single layer PEDOT:PSS treated with methanol by different treatment methods and ITO anode electrodes. (d) EQE of the PSC devices with ITO and PEDOT:PSS anodes.

maintained up to 96% of the original efficiency after ten days while devices with an ITO electrode maintained only 87%. The highly acidic PSS buffer layer, which corrodes ITO, is the main reason for the fast degradation of the ITO device.[58]

The PCE of PSCs with 1 layer PEDOT:PSS decreased across the lateral distance (shown in the device architecture in Fig. 9b) due to the decrease in FF; which, in turn, is caused by the high sheet resistance of the thin layer of PEDOT:PSS electrodes. For example, the PCE and FF of PEDOT:PSS electrodes treated by the dip method fell from 3.57% and 66% for the first finger to 3.11% and 51% for the fourth finger, respectively, while the ITO performance remained almost the same. The power loss due to the high sheet resistance of the electrode is dependent on the area of the cell and is given by:[59]

$$P_{\text{loss}} = \frac{(jlw)^2 R_{\text{S}} w}{3l} \qquad (3)$$

where P_{loss} is the power loss, j is the J_{sc}, R_{S} is the sheet resistance of electrode, l and w are the length and width of the area, respectively, where current is collected at one of the edges with length l. The power losses of the methanol treated PEDOT:PSS electrodes across the lateral distance are in agreement with the above formula.

To circumvent the power loss with lateral distance we used PEDOT:PSS electrodes with multiple layers treated by the dip method. Fig. 10 shows the J–V curves of the devices and Table 3 presents the device performance values extracted from the curves. The lower J_{sc} value is due to the reduction in the transmittance of the electrodes with increasing thickness. The
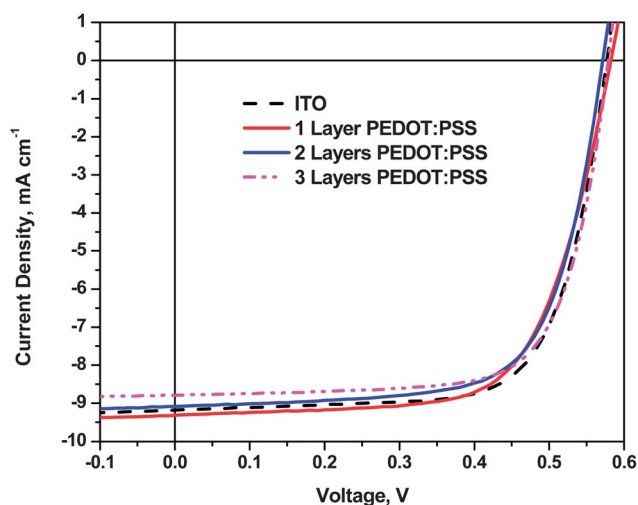

Fig. 10 J–V curves of different layers of PEDOT:PSS films treated by the dip method and ITO electrodes.

Table 2 Photovoltaic performances of PSCs with ITO and 1 layer PEDOT:PSS treated with methanol by different methods anodes extracted from the J–V curves

Anode	J_{sc}/mA cm^{-2}	V_{oc}/V	FF (%)	PCE (%)	R_{S}/Ω cm^2	R_{SH}/Ω cm^2
ITO	9.18	0.58	70.24	3.74	1.75	625
PEDOT:PSS – Dip	9.32	0.58	66.04	3.57	5.11	637
PEDOT:PSS – Drop	9.51	0.58	67.33	3.71	3.51	701
PEDOT:PSS – Drop + Dip	9.41	0.58	66.33	3.62	4.04	1042

This journal is © The Royal Society of Chemistry 2012

Energy Environ. Sci., 2012, **5**, 9662–9671 | 9669

Table 3 Photovoltaic performances of PSCs with ITO and different layers of PEDOT:PSS treated with methanol by dip method anodes extracted from the J–V curves

Anode	J_{sc}/mA cm^{-2}	V_{oc}/V	FF (%)	PCE (%)
ITO	9.18	0.58	70.24	3.74
1 Layer – PEDOT:PSS	9.32	0.58	66.04	3.57
2 Layers – PEDOT:PSS	9.02	0.58	68.62	3.59
3 Layers – PEDOT:PSS	8.81	0.58	69.08	3.53

reduction in J_{sc}, compensated by the increased FF, gave almost the same PCE for two and three layers of PEDOT:PSS. Moreover, there is only a small decrease in the FF across the lateral distance; from 68% to 60% for the first and fourth finger for two layers, and from 69% to 65% for three layers.

4. Conclusions

In conclusion, we have shown a simple yet robust treatment method for a PEDOT:PSS film using methanol, with only one hydroxyl group (which was considered not to enhance conductivity), to significantly enhance its conductivity. PEDOT:PSS film treatment by immersing the film in methanol, dropping small amount of methanol on the film or a combination of the two methods can enhance the conductivity while mixing methanol in aqueous PEDOT:PSS solution has hardly any effect on the conductivity. The conductivity was enhanced from 0.3 to 1362 S cm^{-1} while maintaining a transmittance higher than ITO and sheet resistance of 147 Ω □$^{-1}$ for a single layer of PEDOT:PSS film. By increasing the thickness of the film, we got a sheet resistance of about 25 Ω □$^{-1}$ while maintaining 85% transmittance. Moreover, our work clearly justifies that conductivity enhancement for PEDOT:PSS depends not only on the property of the chemical used but also on the method of treatment. Removal of insulator PSS from the film, morphology changes through phase segregation leading to larger domains and better connected conductor PEDOT, and conformation changes from a coiled to a linear/extended-coil structure are the main mechanisms for the high conductivity enhancement. ITO-free PSCs with standalone PEDOT:PSS anodes using P3HT:PCBM as the active layer showed a PCE of 3.71% while the ITO counterpart showed 3.77%. These results indicate that PEDOT:PSS films with high conductivity, transmittance and flexibility are highly promising to replace ITO for low cost and flexible PSCs.

Acknowledgements

Notes and references

1 B. Azzopardi, C. J. M. Emmott, A. Urbina, F. C. Krebs, J. Mutale and J. Nelson, *Energy Environ. Sci.*, 2011, **4**, 3741–3753.
2 R. Søndergaard, M. Hösel, D. Angmo, T. T. Larsen-Olsen and F. C. Krebs, *Mater. Today*, 2012, **15**, 36–49.
3 N. Espinosa, M. Hosel, D. Angmo and F. C. Krebs, *Energy Environ. Sci.*, 2012, **5**, 5117–5132.
4 RF. Service, *Science*, 2011, **332**, 293.
5 G. Li, R. Zhu and Y. Yang, *Nat. Photonics*, 2012, **6**, 153–161.
6 L. Dou, J. You, J. Yang, C.-C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li and Y. Yang, *Nat. Photonics*, 2012, **6**, 180–185.
7 C. S. Tao, J. Jiang and M. Tao, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 3176–3180.
8 A. Chipman, *Nature*, 2007, **449**, 131.
9 J. Cui, A. Wang, N. L. Edleman, J. Ni, P. Lee, N. R. Armstrong and T. J. Marks, *Adv. Mater.*, 2001, **13**, 1476–1480.
10 C. J. M. Emmott, A. Urbina and J. Nelson, *Sol. Energy Mater. Sol. Cells*, 2012, **97**, 14–21.
11 M.-G. Kang, M.-S. Kim, J. Kim and L. J. Guo, *Adv. Mater.*, 2008, **20**, 4408–4413.
12 J.-Y. Lee, S. T. Connor, Y. Cui and P. Peumans, *Nano Lett.*, 2008, **8**, 689–692.
13 R. Zhu, C.-H. Chung, K. C. Cha, W. Yang, Y. B. Zheng, H. Zhou, T.-B. Song, C.-C. Chen, P. S. Weiss, G. Li and Y. Yang, *ACS Nano*, 2011, **5**, 9877–9882.
14 Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard and A. G. Rinzler, *Science*, 2004, **305**, 1273–1276.
15 M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson and R. H. Baughman, *Science*, 2005, **309**, 1215–1219.
16 G. Gruner, *J. Mater. Chem.*, 2006, **16**, 3533–3539.
17 S. B. Yang, B.-S. Kong, D.-H. Jung, Y.-K. Baek, C.-S. Han, S.-K. Oh and H.-T. Jung, *Nanoscale*, 2011, **3**, 1361–1373.
18 K.-H. Tu, S.-S. Li, W.-C. Li, D.-Y. Wang, J.-R. Yang and C.-W. Chen, *Energy Environ. Sci.*, 2011, **4**, 3521–3526.
19 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi and B. H. Hong, *Nature*, 2009, **457**, 706–710.
20 S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong and S. Iijima, *Nat. Nanotechnol.*, 2010, **5**, 574–578.
21 L. Gomez De Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson and C. Zhou, *ACS Nano*, 2010, **4**, 2865–2873.
22 G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477–479.
23 F. Zhang, M. Johansson, M. R. Andersson, J. C. Hummelen and O. Inganäs, *Adv. Mater.*, 2002, **14**, 662–665.
24 Y. Xia, K. Sun and J. Ouyang, *Energy Environ. Sci.*, 2012, **5**, 5325–5332.
25 J.-H. Huang, D. Kekuda, C.-W. Chu and K.-C. Ho, *J. Mater. Chem.*, 2009, **19**, 3704–3712.
26 Y.-S. Hsiao, W.-T. Whang, C.-P. Chen and Y.-C. Chen, *J. Mater. Chem.*, 2008, **18**, 5948–5955.
27 J. Ouyang, C. W. Chu, F. C. Chen, Q. Xu and Y. Yang, *Adv. Funct. Mater.*, 2005, **15**, 203–208.
28 L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481–494.
29 S. Kirchmeyer and K. Reuter, *J. Mater. Chem.*, 2005, **15**, 2077–2088.
30 R. Po, C. Carbonera, A. Bernardi, F. Tinti and N. Camaioni, *Sol. Energy Mater. Sol. Cells*, 2012, **100**, 97–114.
31 P. A. Levermore, L. Chen, X. Wang, R. Das and D. D. C. Bradley, *Adv. Mater.*, 2007, **19**, 2379–2385.
32 J. Huang, P. F. Miller, J. S. Wilson, A. J. de Mello, J. C. de Mello and D. D. C. Bradley, *Adv. Funct. Mater.*, 2005, **15**, 290–296.
33 A. M. Nardes, M. Kemerink, M. M. de Kok, E. Vinken, K. Maturova and R. A. J. Janssen, *Org. Electron.*, 2008, **9**, 727–734.
34 Y. Zhou, H. Cheun, S. Choi, J. W. J. Potscavage, C. Fuentes-Hernandez and B. Kippelen, *Appl. Phys. Lett.*, 2010, **97**, 153304.
35 Y. Zhou, F. Zhang, K. Tvingstedt, S. Barrau, F. Li, W. Tian and O. Inganas, *Appl. Phys. Lett.*, 2008, **92**, 233308.
36 M. Reyes-Reyes, I. Cruz-Cruz and R. López-Sandoval, *J. Phys. Chem. C*, 2010, **114**, 20220–20224.
37 C. Badre, L. Marquant, A. M. Alsayed and L. A. Hough, *Adv. Funct. Mater.*, 2012, **22**, 2723–2727.
38 C.-J. Ko, Y.-K. Lin, F.-C. Chen and C.-W. Chu, *Appl. Phys. Lett.*, 2007, **90**, 063509.
39 Y. J. Xia, H. M. Zhang and J. Y. Ouyang, *J. Mater. Chem.*, 2010, **20**, 9740–9747.

40 Y. Xia and J. Ouyang, *Org. Electron.*, 2010, **11**, 1129–1135.
41 Y. Xia and J. Ouyang, *ACS Appl. Mater. Interfaces*, 2010, **2**, 474–483.
42 Y. Xia and J. Ouyang, *Macromolecules*, 2009, **42**, 4141–4147.
43 Y. Xia, K. Sun and J. Ouyang, *Adv. Mater.*, 2012, **24**, 2436–2440.
44 S.-I. Na, G. Wang, S.-S. Kim, T.-W. Kim, S.-H. Oh, B.-K. Yu, T. Lee and D.-Y. Kim, *J. Mater. Chem.*, 2009, **19**, 9045–9053.
45 J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li and J. Shinar, *Polymer*, 2004, **45**, 8443–8450.
46 S.-I. Na, S.-S. Kim, J. Jo and D.-Y. Kim, *Adv. Mater.*, 2008, **20**, 4061–4067.
47 J. Y. Kim, J. H. Jung, D. E. Lee and J. Joo, *Synth. Met.*, 2002, **126**, 311–316.
48 Y. H. Kim, C. Sachse, M. L. Machala, C. May, L. Müller-Meskamp and K. Leo, *Adv. Funct. Mater.*, 2011, **21**, 1076–1081.
49 Y. Xia and J. Ouyang, *J. Mater. Chem.*, 2011, **21**, 4927–4936.
50 K. Sun, Y. Xia and J. Ouyang, *Sol. Energy Mater. Sol. Cells*, 2012, **97**, 89–96.
51 C. Kittle, *Introduction to Solid State Physics*, John Wiley & Sons, Inc., 2005.
52 V. Scardaci, R. Coull and J. N. Coleman, *Appl. Phys. Lett.*, 2010, **97**, 023114.
53 L. Li, R. Ma, N. Iyi, Y. Ebina, K. Takada and T. Sasaki, *Chem. Commun.*, 2006, 3125–3127.
54 X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, C. van Haesendonck, M. Van der Auweraer, W. R. Salaneck and M. Berggren, *Chem. Mater.*, 2006, **18**, 4354–4360.
55 A. Aleshin, R. Kiebooms, R. Menon and A. J. Heeger, *Synth. Met.*, 1997, **90**, 61–68.
56 U. Lang, E. Müller, N. Naujoks and J. Dual, *Adv. Funct. Mater.*, 2009, **19**, 1215–1220.
57 C. Gong, H. B. Yang, Q. L. Song, Z. S. Lu and C. M. Li, *Sol. Energy Mater. Sol. Cells*, 2012, **100**, 115–119.
58 M. P. de Jong, L. J. van Ijzendoorn and M. J. A. de Voigt, *Appl. Phys. Lett.*, 2000, **77**, 2255–2257.
59 M. W. Rowell, M. A. Topinka, M. D. McGehee, H.-J. Prall, G. Dennler, N. S. Sariciftci, L. Hu and G. Gruner, *Appl. Phys. Lett.*, 2006, **88**, 233506.
60 I. M. Smallwood, *Handbook of Organic Solvent Properties*, Halsted Press, New York, 1996.