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Metal salt modified PEDOT:PSS as anode buffer layer and its effect on power conversion efficiency of organic solar cells

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Abstract:

The effects of metal chlorides such as LiCl, NaCl, CdCl₂ and CuCl₂ on optical transmittance, electrical conductivity as well as morphology of PEDOT:PSS films have been investigated. Transmittance spectra of spun PEDOT:PSS layers were improved by more than 6% to a maximum of 94% in LiCl doped PEDOT:PSS film. The surface of the PEDOT:PSS films has exhibited higher roughness associated with an increase in the electrical conductivity after doping with metal salts. The improvement in the physical properties of PEDOT:PSS as the hole transport layer proved to be key factors towards enhancing the P3HT:PCBM bulk heterojunction (BHJ) solar cells. These improvements include significantly improved power conversion efficiency with values as high as 6.82% associated with high fill factor (61%) and larger short circuit current density ($\sim 18 \text{ mA}\cdot\text{cm}^{-2}$).

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1. Introduction:

Organic solar cells (OSCs) have received significant attention during the last few decades due to their low cost processing which is compatible with flexible substrates, high throughput and thus requires less capital investment [1]. OSCs are mainly based on bulk heterojunctions (BHJ) of conjugated polymers such as poly (3-hexylthiophene) (P3HT) and fullerenes such as (6,6)-phenyl-C61 butyric acid methyl ester (PCBM). Power conversion efficiencies (PCE) in the region of 5% have been achieved [2] and PCE of 10% or larger [3] is projected for the foreseeable future, which makes OSCs a viable replacement of the well-established silicon SCs. OSCs are diverse and versatile, and can offer wide range of properties including tailored band gap and thus varied range of light harvesting efficiency covering a broad range of the solar spectrum. It could be argued that OSCs based on BHJ comprising P3HT and PCBM are considered as the most investigated devices [4]. The nature of contacts on both sides of the active layer is considered as an essential feature to determine the device performance, and therefore their PCE. Poly (3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate), abbreviated as PEDOT:PSS has been widely known as one of the most promising conductive polymers employed as a hole transporting layer, due to its simple processing, high transparency and high stability. It is considered as a favorable material to replace inorganic materials to deposit on flexible substrates for plastic electronics applications such as memories, sensors, OLEDs and flexible PV devices [5]. PEDOT:PSS dispersed in water can easily form a transparent film with high conductivity by spin coating, thus producing a low sheet resistance film [6]. The optimised combination of conductivity and surface morphology is essential for numerous applications of PEDOT:PSS thin films; these could be influenced by a variety of factors during the drying process including the fraction of solid content, particle size, proportion of PSS and the solution viscosity which could lead to different morphological and electrical properties [7]. The photovoltaic (PV) device performance is mainly defined by the PCE which depends on several parameters such as light harvesting properties of the active layer, generation of excitons, exciton diffusion and separation, transportation and collection by the cell electrodes [8]. However, the modification of both contacts has been demonstrated to play significant role in the enhancement of charge collection (electrons and holes), which could largely improve the device PCE [9]. To date, several treatments were carried out to modify the properties of the PEDOT:PSS layer, which included the use of different organic solvents. Among those solvents are ethanol, dimethylsulfoxide, acetonitrile, and tetra-hydrofuran which have resulted in a considerable

improvement of PEDOT:PSS layer conductivity [10]. Through an alternative approach, Ouyang has studied the effect of various salts on PEDOT:PSS conductivity and it was shown that the conductivity enhanced by employing metal salts as dopants within the aqueous PEDOT:PSS solution. This was ascribed to the binding of the metal ions to the PSS anions of PEDOT:PSS layer [11]. Furthermore, PEDOT:PSS treatment with hexafluoroacetone (HFA) were shown to reduce the sheet resistance from $7 \text{ M}\Omega/\square$ to $40 \text{ k}\Omega/\square$ [12]. For the work presented here, the effect of metal salts, both in powder form and as aqueous solutions on the PEDOT:PSS films' properties such as conductivity, transmittance and morphology were investigated. The modified PEDOT:PSS layers were adopted as anode buffer layer to study their effects on P3HT:PCBM OSCs performance and thus on device PCE. To the best of the authors' knowledge this is the first attempt to apply salt-modified PEDOT:PSS layers to P3HT:PCBM-based OSCs.

2. Experimental methods

2.1. Preparation of PEDOT:PSS solution with metal salts

PEDOT:PSS (conductive grade-483095 Aldrich) were mixed with different metal salts (Sigma Aldrich); these are CuCl_2 (99.99%), CdCl_2 (99.99%), NaCl (99.99%) and LiCl (99.99%) used as powders and as aqueous solutions. 1 mg of the metal salts was added separately as powders to 1ml of PEDOT:PSS solution; the final solutions were sonicated for 30 min to ensure good dispersion and complete solubility of the salts. In a separate method, aqueous solutions of each metal salt with the concentration of $1 \text{ mg}\cdot\text{ml}^{-1}$ were prepared in deionised (DI) water. The solutions were sonicated for 30 min before mixing with PEDOT:PSS solution with a volume ratio of 0.1:1ml. Further sonication for 30 min was carried out for efficient dispersion after mixing the PEDOT:PSS with the aqueous salts solutions. Additional samples of LiCl and CdCl_2 in DI water were used in the concentrations of $5 \text{ mg}\cdot\text{ml}^{-1}$ and $10 \text{ mg}\cdot\text{ml}^{-1}$ in order to examine the role of dopant concentration on the electrical and optical properties of PEDOT:PSS.

2.2. Organic solar cells preparations

ITO-coated glass slides (sigma Aldrich; sheet resistance $8\text{-}10 \text{ }\Omega/\square$) were cleaned using DI water, acetone and 2-propanol for 10 min each in ultrasonic bath, respectively, and then blown dry in N_2 gas. PEDOT:PSS (pure and doped) were spin coated on ITO slides at a spin speed of 2000 rpm for 30 sec and annealed on a hot plate at 150°C for 10 min in ambient air. P3HT:PCBM (in 1:1 ratio) active layer ($14 \text{ mg}\cdot\text{ml}^{-1}$) were dissolved in co-solvents of chloroform and

chlorobenzene (CB:CF) with the ratio 1:1. The active layers were spin coated inside a nitrogen-filled glove box followed by annealing inside the glove box at 120 °C for 10 min. Film thickness of 95 nm was obtained as determined by spectroscopic ellipsometry. A top contact of aluminum (Al) was evaporated with a thickness of about 100 nm, at the deposition rate of 0.1-0.2 nm/sec as was monitored by a quartz crystal thickness monitor. All the devices were subjected to further heat treatment inside the glove box at 120°C for 10 min and left to cool down for 30 min before measurements were carried out.

2.3. Measurements

A UV-visible spectrophotometer (Varian 50-scan UV-visible) in the range of 190-1100 nm was used to study the transmittance spectra of PEDOT:PSS layers which were spin coated onto cleaned glass substrates. The active layer and PEDOT:PSS layer thicknesses were determined using M2000 (J.A. Woollam Co., Inc.) spectroscopic ellipsometry operating in the wavelength range 370-1000 nm. Morphology of PEDOT:PSS layers were examined using a Nanoscope IIIa multimode atomic force microscope (AFM). DC electrical characteristics in the form of current density-voltage (J-V) dependence and electrical conductivity of PEDOT:PSS layers as well as completed OSC devices were studied using a 4200 Keithley semiconductor characterisation system and the photo current was generated under AM 1.5 solar simulator source of 100mW.cm⁻². The fill factor (FF) and the overall light to-electrical energy conversion efficiency (PCE) of the solar cell were calculated according to the following equations [13]:

$$\text{PCE (\%)} = \frac{J_{\text{max}}V_{\text{max}}}{P_{\text{in}}} \quad (1)$$

$$\text{FF} = \frac{J_{\text{max}}V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}} \quad (2)$$

where J_{sc} is the short-circuit current density (mA.cm⁻²), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power and J_{max} (mA.cm⁻²) and V_{max} (V) are the current density and voltage at the point of maximum output power in the J-V curves, respectively. Furthermore, the electrical conductivity was determined using interdigitated platinum electrodes (IDEs) purchased from DropSens (Spain). The IDE can be used to measure the surface conductivity (σ) of the samples from the following relationship [14]

$$\sigma = [I / V] [n / W t L] \quad (3)$$

where, t is the thickness of the film, W is the distance between the fingers (6.67mm), n is the number of fingers (500), and (L) is the distance between electrodes (5 μ m).

2. Results

2.1. Transmittance spectra

Fig. 1 shows transmittance spectra of metal salts treated PEDOT:PSS films as well as those of films prepared from as purchased PEDOT:PSS. Modified PEDOT:PSS films doped with metal salts have exhibited higher transmittance as compared to pure PEDOT:PSS films. Conversely, aqueous solution-treated PEDOT:PSS films showed a higher transmittance than those treated with metal salt powders. In both cases, metal chloride treated PEDOT:PSS layers are found to be useful for solar cells specifically for materials employed as a windows layer. The maximum transmittance of pure PEDOT:PSS film was in the range 88 -91% within the wavelength range (400–650 nm), while transmittance of powder salts treated-PEDOT:PSS films has increased up to 93%. Aqueous solution (1mg.ml⁻¹) of metal salts treated PEDOT:PSS films have however exhibited further increase in transmittance, reaching 94%. The PEDOT:PSS films treated with LiCl and CdCl₂ were shown to demonstrate maximum transmittance in both cases of treatment, in powder and in aqueous solutions. Moreover, an increase in the aqueous solution concentration of LiCl and CdCl₂ has led to further improvement in transmittance.

2.2. Surface morphology

Fig.2 shows AFM images obtained for treated and untreated PEDOT:PSS films. The pure film has exhibited smooth surface with rms=1.25nm while rougher morphologies were markedly clear in the metal salts-treated films; LiCl (10mg.ml⁻¹ aqueous solution) doped PEDOT:PSS has exhibited more rough surface with rms=3.38nm. Generally speaking the brighter regions observed in the AFM images could be associated with the PEDOT whereas the darker regions are related to the less conductive PSS regions [15]. This increase in the surface roughness may be ascribed to the increase in grain size after metal chloride treatment. It has recently been shown that surface roughness and grain size of inorganic CdS layer has increased as a result of CdCl₂ treatment [16]. At the same time, the group VII element (Cl) has also acted as a p-type dopant when it produces complexes with un-known native defects within the inorganic layer [16]. It can be assumed here that Cl⁻ ions play a similar role when organic layers of PEDOT:PSS are treated with metal chlorides. The PSS could be removed by the metal ions (cations) leaving the Cl

(anion) to act as a dopant impurity to improve the PEDOT conductivity and enhance its surface roughness as shown in Fig.3 (a) and (b). It therefore appears that this treatment improves the light harvesting by the active layer as well as decreasing the contact resistance of the interfacial layer, hence increasing the short circuit current density (J_{sc}).

2.3. Electrical conductivity

Fig.4 illustrates the variation in electrical conductivity of the PEDOT:PSS layer as a result of treatment with different metal chlorides (Fig. 4a), as well as the effect of concentration of the chloride aqueous solutions (Fig. 4b). A maximum conductivity of 0.41 S.cm^{-1} was obtained for the LiCl treated film when the metal salt was added in powder form while a conductivity of 0.43 S.cm^{-1} was obtained using aqueous solution. Further treatment was carried out to examine the effect of CdCl_2 and LiCl concentrations on PEDOT:PSS conductivity, using concentrations of 5mg.ml^{-1} and 10mg.ml^{-1} metal salt solutions. Fig.4(b) shows the increase in films' conductivity with increased concentration of the aqueous solution added to the PEDOT:PSS. The LiCl treated film (10mg.ml^{-1}) shows higher conductivity of 0.485 S.cm^{-1} while the CdCl_2 treated (10mg.ml^{-1}) films exhibited slightly lower conductivity of 0.48 S.cm^{-1} . Once again, this could be ascribed to the removal of PSS chains from the PEDOT:PSS films by the cations, as illustrated in Fig.3(b). This could be further understood as the result of dissociation of the metal salts where the higher dissociation contributes higher ions concentration which significantly reduces the coulombic attraction between the PEDOT and PSS chains, thus more loss of PSS chains from the PEDOT:PSS film via the salt treatment [17]. It has been established that conduction in PEDOT:PSS films is due to charge transport across the PEDOT chains via hopping, and that it remains unchanged after impurities addition [11].

2.4. Series resistance determination

The series resistance (R_s) is an effective parameter which influences the solar cell behavior. Fig.5 shows the dark J-V curves for the pure PEDOT:PSS based device and devices with CdCl_2 and LiCl treated PEDOT:PSS based devices with different concentrations. Shen and co-authors have argued that dark I-V characteristics is an efficient method to determine the R_s using the following equation [18]:

$$I = I_L - I_0 \left[e^{q(v-IR_s)/nkT} - 1 \right] - \frac{v-IR_s}{R_{sh}} \quad (4)$$

where I_L is the light current, I_0 is the saturation current, n is the ideality factor, kT/q is the thermal energy, R_s is the series resistance, and R_{sh} is the shunt resistance. Typically, under dark conditions the photocurrent is zero and therefore it could be presumed that R_{sh} is large enough to ignore the last term in Eq.4. Therefore, the dark I-V characteristics can be described as follows:

$$I = I_0 [e^{q(V-IR_s)/nkT} - 1] \quad (5)$$

Re-arranging Eq. 5 the following relation is obtained:

$$V = \frac{nkT}{q} \ln \left(\frac{I}{I_0} + 1 \right) + IR_s \quad (6)$$

Therefore, at higher applied voltage when $I \gg I_0$, Eq. 6 becomes:

$$I \frac{dV}{dI} = IR_s + \frac{nkT}{q} \quad (7)$$

Using Eq. 7, R_s could be extracted from the slope at the high current region of $I(dV/dI)$ vs. I plot as shown in Fig. 6 for the pure PEDOT:PSS based device as an example. The lowest R_s was exhibited by OSC devices with LiCl treated PEDOT:PSS with the value of $R_s=52.3\Omega$ compared to devices employing pure PEDOT:PSS layer which revealed $R_s=111.2\Omega$ (results are summarised in table 3). This improvement in R_s could be a key factor among others towards achieving efficient electrode properties and therefore better device performance.

2.5. Photovoltaic measurements

Using measured $J(V)$ characteristics under illumination, the PV properties of PEDOT:PSS/P3HT:PCBM/Al OSCs were determined with PEDOT:PSS layers treated with different metal chlorides. Fig.7 shows J-V curves of the investigated OSCs with different salts treated-PEDOT:PSS. Devices with untreated PEDOT:PSS layer have exhibited lower PV performance with $V_{oc}=0.62V$, $J_{sc}=11.9 \text{ mA.cm}^{-1}$, $FF=53\%$ and PCE of 3.92%. These are in line with values frequently reported in the literature [19]. However, devices with powder metal salt treated PEDOT:PSS layers have demonstrated significant improvement in all PV parameters as revealed in Fig. 7(a), and the results are summarised in Table 1. The highest PCE of 5.6% and short circuit current density $J_{sc}=16.1 \text{ mA.cm}^{-1}$ were achieved when LiCl_2 powder was added to PEDOT:PSS; FF and V_{oc} however, remained unchanged for all metal salts. When the same metal salt was added to PEDOT:PSS in aqueous form as in Fig. 7(b), the device PCE and short circuit

current density have reached values of about 6% and 17.4 mA.cm⁻¹, respectively, in the case of LiCl added with the concentration of 1mg.ml⁻¹. Once again, V_{oc} and FF remained more or less unchanged for all metal salts studied in this work. Table 2 provides a summary of the electrical properties of ITO/PEDOT:PSS/P3HT:PCBM/Al OSCs when metal chlorides were used in aqueous form. The substantial increase in J_{sc} could be ascribed to the improved electrical conductivity of PEDOT:PSS layers as a result of metal salt treatment while enhanced PCE could be associated with the increased films' transmittance and surface roughness. Values of V_{oc} remained unchanged since its value is mainly determined by the difference between the donor's higher occupied molecular orbital (HOMO_d) and the lower unoccupied molecular orbital of the acceptor (LUMO_a) [20]. Furthermore, the metal salt treatment of PEDOT:PSS layers seems to solve the wetting problem between the active layer, which is hydrophobic and the hydrophilic PEDOT:PSS [21]. Such film processing method would be more favored for the fabrication of inverted OSC structure. Electrical properties of the OSCs were further improved when the concentration of CdCl₂ and LiCl in aqueous solution increased to 5 and 10mg.ml⁻¹ as demonstrated in Fig. 7(c). Moreover, the estimation of J_{max} and V_{max} values is illustrated in Fig 7(c). Fig. 7(d) shows the variation of output power as a function of applied voltage.

A summary of the electrical parameters of the ITO/PEDOT:PSS/P3HT:PCBM/Al OSCs treated with these solutions is given in Table 3. PCE as high as 6.82% associated with FF=61%, J_{sc}≈18 mA.cm⁻² and V_{oc}=0.62 V have been recorded for LiCl treated devices using a higher concentration of 10mg.ml⁻¹. Treatment of PEDOT:PSS with metal salts of concentrations higher than 10mg.ml⁻¹ has not shown any further improvement in device performance. The above reported efficiency of 6.82% is found to be repeatable and on comparing this value with PCE values obtained for other metal salts treatment (see Table 3 and data summarised in Fig. 7) it can be confirmed that these results are very reliable. The optimization of electrode treatment [22-25] as well as active layer thickness [26,27], are found to be key processing conditions to achieve good device performance. In a recent review [11] conductivity enhancement of PEDOT:PSS thin films for use in polymer light-emitting diodes and polymer solar cells has been discussed and conductivity increase of up to 1000 S.cm⁻¹ was reported depending on the type of additives. Recently modification of electron transport layer in P3HT:PCBM-based OSC has revealed 3 times improvement in the cells' PCE as compared to untreated electrodes [28]. In the present work improvement of the hole transport layer via doping of PEDOT:PSS with metal salts,

preferably in solution form, has been shown to play crucial role in improving OSCs performance as well as device stability.

3. Conclusion

PEDOT:PSS layers doped with different metal salts (LiCl, NaCl, CdCl₂ and CuCl₂) were employed as hole transport layers in P3HT:PCBM based OSCs. The effects of metal salts added as powders or as solutions on the electrical, optical as well as morphological properties of PEDOT:PSS layers were investigated. PEDOT:PSS films doped with LiCl salt in solution form with the concentration 10mg.ml⁻¹ have exhibited the highest electrical conductivity as well as highest transmittance intensities. The metal salt doping has resulted in a more rough surface morphology of PEDOT:PSS layers compared to pristine PEDOT:PSS films. Furthermore, in doped films the series resistance has exhibited much lower values of about 52.3Ω. These improvements in PEDOT:PSS layer structural, optical and electrical properties are thought to be the main reasons for the enhancement of P3HT:PCBM based solar cells performance, with PCE as high as 6.82% , FF=61% and J_{sc}~18 mA.cm⁻² in the case of PEDOT:PSS doped with LiCl (10mg.ml⁻¹ aqueous solution) device.

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Figure captions

Fig. 1 The transmittance spectra of PEDOT:PSS films: (a) on treatment with powder salts of NaCl, CuCl₂, CdCl₂ and LiCl; (b) on treatment with aqueous solution of NaCl, CuCl₂, CdCl₂ and LiCl in DI water with the concentration 1 mg.ml⁻¹; (c) on treatment with aqueous solutions of LiCl and CdCl₂ with the concentrations 5 mg.ml⁻¹ and 10 mg.ml⁻¹

Fig. 2 AFM images for pure (a) and LiCl aqueous solution treated PEDOT:PSS layers (b,c and d) of concentrations 1 mg.ml⁻¹, 5 mg.ml⁻¹ and 10 mg.ml⁻¹ respectively

Fig. 3 (a) The cross-section of the P3HT:PCBM solar cell after modifying PEDOT:PSS layer and the scattering of the incident light within the active layer due to PEDOT:PSS surface roughness. (b) The PEDOT:PSS after chlorine salts treatment and the dissociation of the metal ions and the Cl⁻ within the PEDOT:PSS

Fig. 4 (a) The conductivity of PEDOT:PSS variation with salts treatment. (b) Dependence of conductivity on LiCl and CdCl₂ solution concentration

Fig. 5 Dark J-V characteristics for P3HT:PCBM solar cell based on PEDOT:PSS treatment with LiCl and CdCl₂ aqueous solutions of different concentrations (1, 5, 10 mg.ml⁻¹)

Fig.6 I(dV/dI) vs. I characteristics of P3HT:PCBM solar cell based on pure PEDOT:PSS

Fig. 7 J-V characteristics for P3HT:PCBM solar cell based on PEDOT:PSS treatment with several salts as powder (a), as aqueous solution (b), subjected to further treatment with different CdCl₂ and LiCl concentrations (c) and output power plotted as a function of voltage for pure PEDOT:PSS and LiCl (10mg.ml⁻¹) aqueous solution-treated PEDOT:PSS based devices (d)

Table (1): OSC parameters of devices having PEDOT:PSS layer treated with powder salts (NaCl, CuCl₂, CdCl₂ and LiCl)

POWDER	pure	CuCl ₂	NaCl	CdCl ₂	LiCl
V _{oc} (V)	0.62	0.62	0.6	0.62	0.59
J _{sc} (mA.cm ⁻²)	11.9	13.37	12.92	14.8	16.1
FF %	53	59	59	59	59
PCE %	3.92	5	4.6	5.4	5.6

Table (2): Photovoltaic parameters of devices with PEDOT:PSS layer treated with aqueous solutions of NaCl, CuCl₂, CdCl₂ and LiCl with the concentration of 1mg/ml

SOLUTION	pure	CuCl ₂	NaCl	CdCl ₂	LiCl
V _{oc} (V)	0.62	0.63	0.61	0.62	0.6
J _{sc} (mA.cm ⁻²)	11.9	15.4	13	16.77	17.37
FF %	53	57	59	59	58
PCE %	3.92	5.52	4.7	6.1	6

Table (3) Photovoltaic parameters of devices with PEDOT:PSS layer treated with different concentrations of aqueous solution of CdCl₂ and LiCl

SOLUTION	Pure	CdCl ₂ (1mg/ml)	CdCl ₂ (5mg/ml)	CdCl ₂ (10mg/ml)	LiCl (1mg/ml)	LiCl (5mg/ml)	LiCl (10mg/ml)
V _{oc} (V)	0.62	0.62	0.62	0.62	0.6	0.62	0.62
J _{sc} (mA.cm ⁻²)	11.9	16.77	17.23	17.8	17.37	17.3	17.97
FF %	53	59	62	61	58	63	61
PCE %	3.92	6.07	6.65	6.72	6	6.77	6.82
R _s (Ω)	111.2	86.86	62.5	53.2	59.5	56.2	52.3

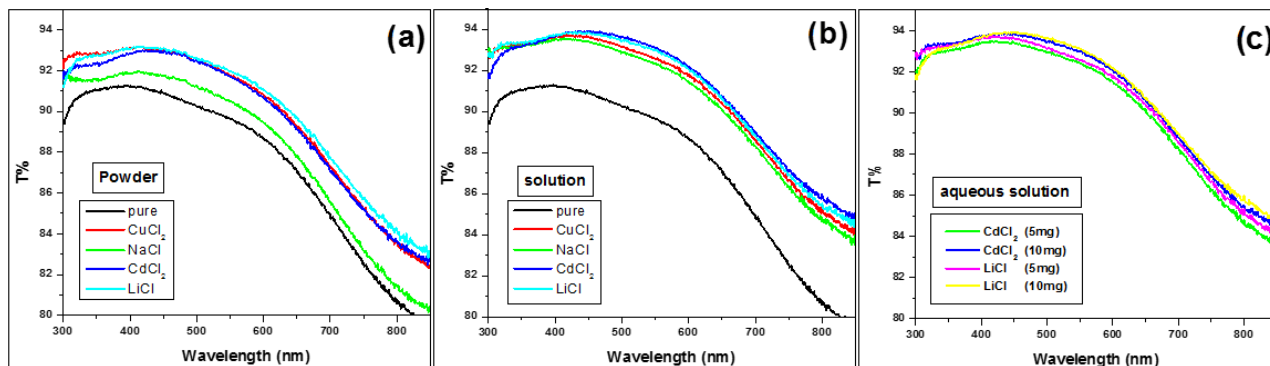


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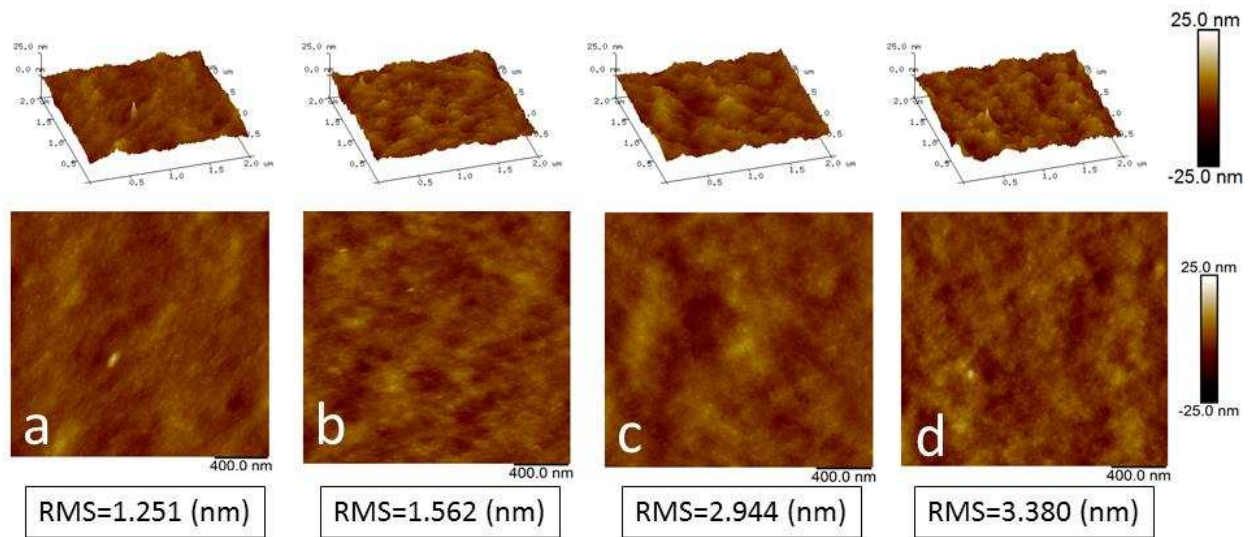


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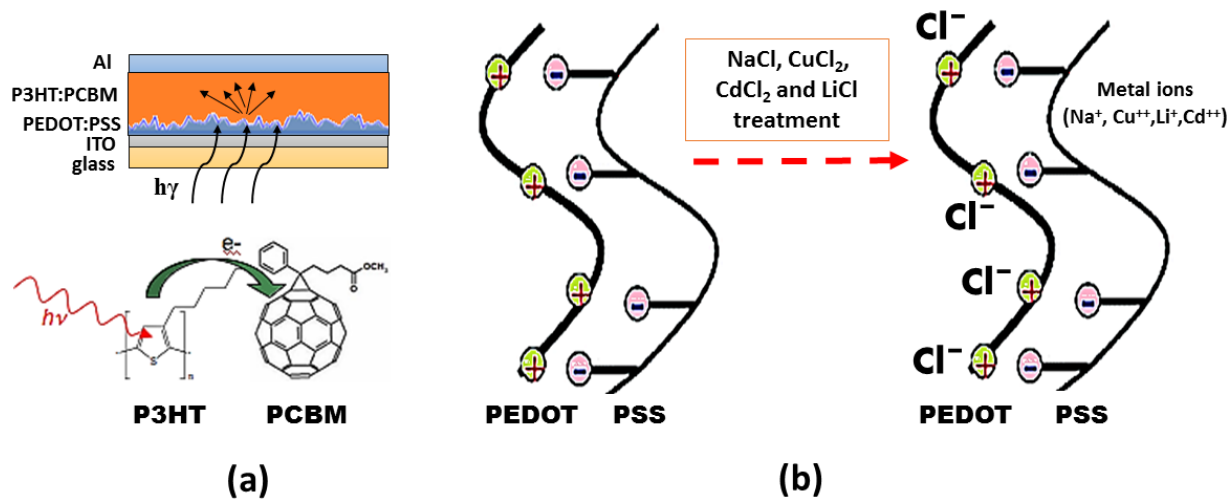


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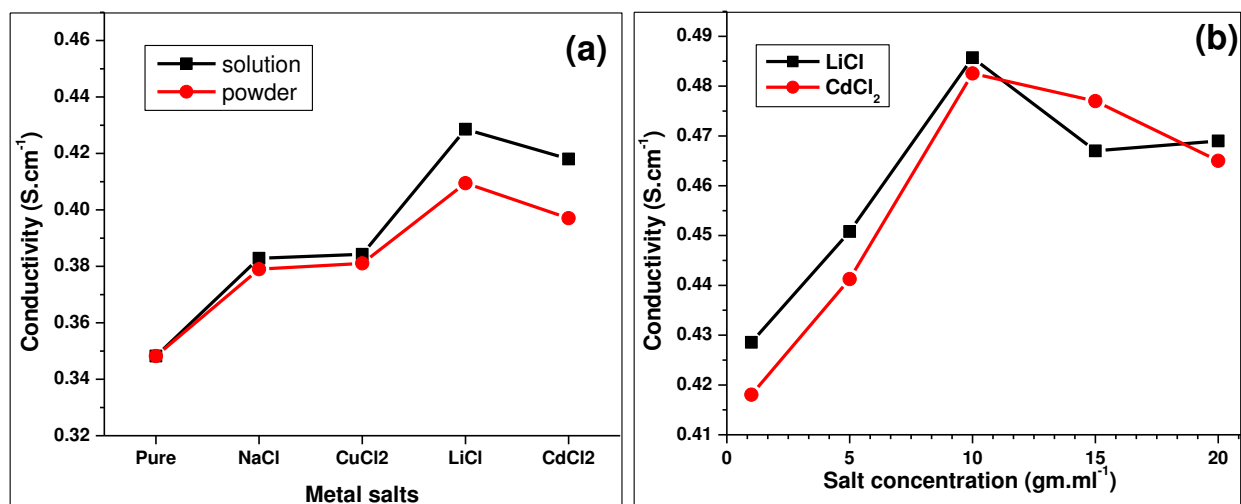


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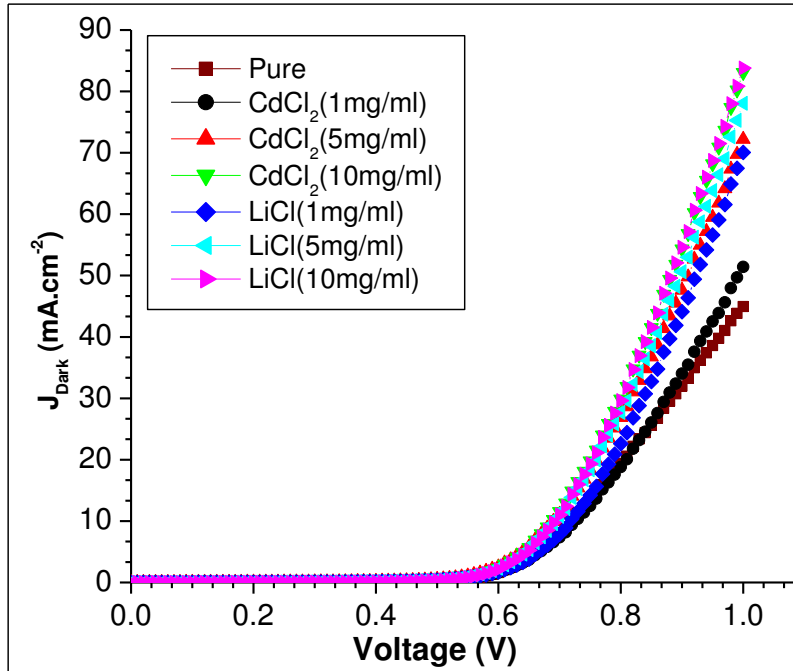


Fig. 5 Dark J-V characteristics for P3HT:PCBM solar cell based on PEDOT:PSS treatment with LiCl and CdCl₂ aqueous solutions of different concentrations (1, 5, 10 mg.ml⁻¹)

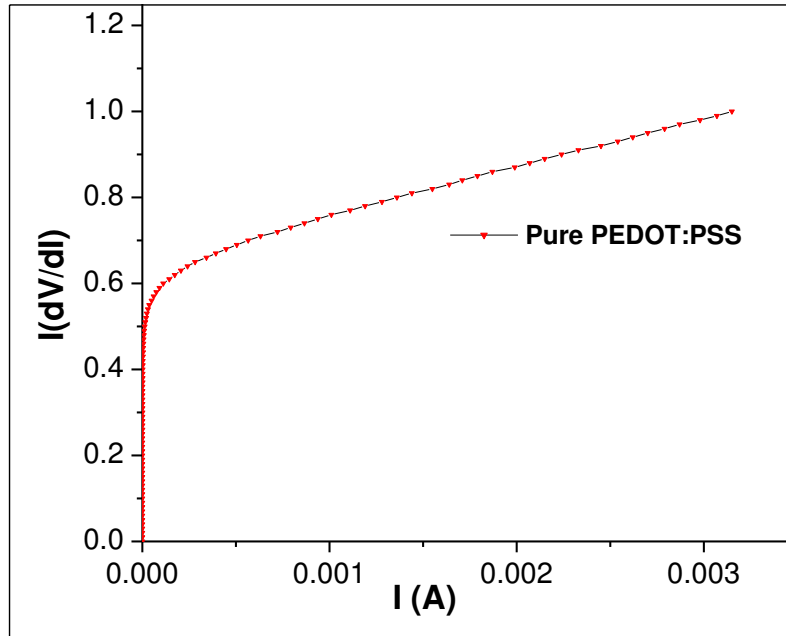


Fig.6 $I(dV/dI)$ vs. I characteristics of P3HT:PCBM solar cell based on pure PEDOT:PSS

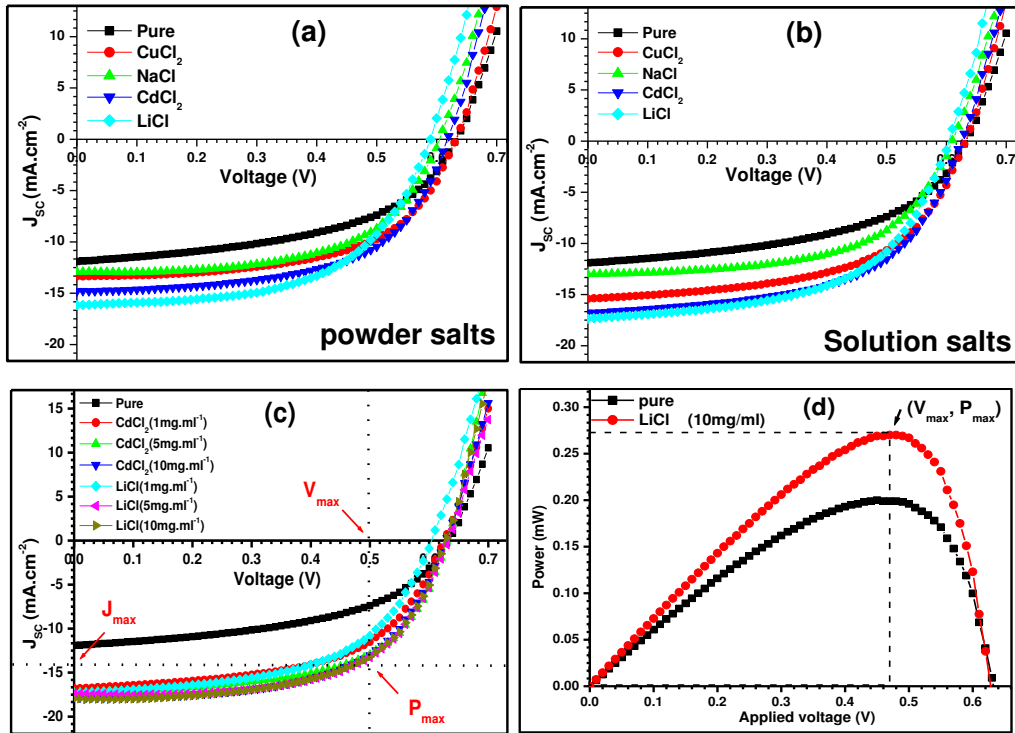


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